





## NanoMed 2018 / SMS 2018 / EGF 2018

## Joint International Conferences

## 23 - 25 Oct, 2018 | Venice - Italy

# **Book of Abstracts**

Organizer



www.setcor.org

## NanoMed 2018 / EGF 2018 / SMS 2018 Joint Conferences Program

October 23, 2018		
NanoMed 2018 - Plenary session I		
Conference Room 1E		
Session's Chairs: Prof. Silvia Marchesan, University of Trieste, Italy Prof. Elena Vismara, Politecnico di Milano, Italy Prof. Patrizia Canton, Ca' Foscari University of Venice, Italy		
08:30 - 12:00	Registration	Registration Area
10:00 - 10:30	Coffee Break / Posters Session I	Coffee Break Area
10:30 - 11:00	Tapered optical probes and optrodes for optogenetics and neurophotonics. M.De Vittorio and F.Pisanello	<b>Prof. Massimo De Vittorio</b> , Italian Institute of Technology, <b>Italy</b>
11:00 - 11:30	Nanomedical Implications for Parkinsons Disease: Silver Nanoparticles Inhibits Catechol O-methyltransferase. A. Usman, K. Lobb, BI Pletschke, BS Wilhelmi and CG Whiteley	Prof. Chris Whiteley, Rhodes University, South Africa
11:30- 12:00	Nanocarbons shape matters. A journey towards biomaterials <b>S. Marchesan</b>	<b>Prof. Silvia Marchesan</b> , University of Trieste, <b>Italy</b>
12:00 - 14:00	Lunch Break	Restaurant

October 23, 2018			
NanoMed 2018 - Session I:			
Biona	anomaterials synthesis and characterization/ Nanomat	erials for Medicine	
	Conference Room 1E		
	Session's Chairs:		
	Prof Massimo De Vittorio, Italian Institute of Techno	ology, Italy	
	Prof. Chris Whiteley, Rhodes University, S. A	frica	
	Dr. Cleofe Palocci, University of Rome "La Sapien	iza", Italy	
	Dr. Ilaria Tonazzini, Erasmus Medical Center, Net	herlands	
14:00 - 14:15	The vault complex: production and studies on its usage as	Dr. Elisabetta Galbiati,	
	nano-vector	University of Milano-Bicocca,	
	E. Galbiati, M. Pozzi, M. Colombo, D. Prosperi and P. Tortora		
14:15 - 14:30	Litanium dioxide coating of porous silicon microparticles	Ms. Elena Chiste, University	
	towards nanomedicine applications	or verona, <b>italy</b>	
	Detavernier M Scarpa S Dusi and N Daldosso		
14:30 - 14:45	Structure and properties of composite TiO2+TiN diffusive	Mrs. Justvna Witkowska	
	surface lavers produced on NiTi shape memory allovs	Warsaw University of	
	J. Witkowska, A. Sowińska, E. Czarnowska, T.Płociński and	Technology, <b>Poland</b>	
	T. Wierzchoń		
14:45 - 15:00	Hybrid self-assembly of quantum dots and gold nanoparticles	Dr. Valérie Marchi, CNRS-	
	driven by protein pairing	Rennes University, France	
	M. Fernandez, L. Moreaud, A. Burel, A. Urvoas, M. Valerio-		
	Lepiniec, E. Dujardin, P. Minard, P. Even-Hernandez and V.		
15.00 - 15.15	Marchi Synthesis and characterization of SPIONs for smart	Me loana Matos Lisbon	
13.00 - 13.13	theranostics	University Portugal	
	J.C. Matos M.C. Goncalves I.C.J. Pereira and J.C.	onwersity, i ontugar	
	Waerenborgh		
15:15 - 15:30	Microfluidic technologies for biomaterials nanofabrication for	Dr. Cleofe Palocci,	
	drug delivery applications	University of Rome "La	
	C.Palocci, LChronopoulou and A. Di Nitto	Sapienza", <b>Italy</b>	

15:30 - 15:45	NIR Photo-triggered hybrid copper sulphide nanoparticles functionalized with thermo-responsive polymers for on- demand drug delivery <b>I. Ortiz de Solorzano</b> , T. Alejo, M. Abad, C. Bueno-Alejo, G. Mendoza, V. Andreu, S. Irusta, V. Sebastian and M. Arruebo	<b>Ms. Isabel Ortiz de Solorzano</b> , University of Zaragoza, <b>Spain</b>
15:45 - 16:00	Study of neuronal guidance dynamics in neurodevelopmental disorders models by nano-engineered platforms <b>I. Tonazzini</b> , C. Masciullo, G.M. Van Woerden, M. Cecchini and Y. Elgersma	Dr. Ilaria Tonazzini, Erasmus Medical Center, Netherlands / Nanoscience Istitute – CNR, Italy
16:00 - 16:30	Coffee Break / Posters Session I	Coffee Break Area
16:30 - 16:45	Biological characterization of osteoblast/osteoclast cell growth on polyamidoamine-coated bidimensional Buckypapers. <b>A. Paolini</b> , G. Battafarano, V. D'Oria, F. Mura, S. Sennato, V. Mussi, R. Risoluti, S. Materazzi, A. Del Fattore and A. Masotti.	<b>Dr. Alessandro Paolini</b> , Bambino Gesù Children's Hospital <b>, Italy</b>
16:45 - 17:00	Sorbtion and Desorbtion of Glycopeptide Antibiotics on the Surface of Nanocomposite PolyGraphene. <b>A.S. Botin</b> , V.N. Buravtsev, L.A. Baratova, A.V. Timofeeva, G.S. Katrukha, I.I. Han and T.S. Popova	Dr. Alexander Botin, Peoples' Friendship University of Russia- Moscow, <b>Russia</b>
17:00 - 17:15	Novel ultrashort self-assembling peptide bioinks for 3D culture of muscle myoblast cells <b>W. Arab</b> , S. Rauf, O. Al-Harbi and C.A. E. Hauser	<b>Ms. Wafaa Arab</b> , King Abdullah University of Science and Technologyl, <b>Saudi Arabia</b>
17:15 – 17:30	Incorporation of microgels in PLA monofilaments by wet spinning <b>G-P. Paar</b> , P. Reitzenstein, C. Molano-López, A. Pich, T. Gries, S. Jockenhoevel and A. Blaeser	Mr. Georg-Philipp Paar, RWTH Aachen University, Germany
17:30-17:45	Bacterial Cellulose Membrane with Functional Properties <b>A.S. Monteiro</b> , R.R. Domeneguetti, M.W. Chi Man, H.S. Barud, C.Carcel and S.J. L. Ribeiro	<b>Ms. Andreia Monteiro</b> , São Paulo State University, <b>Brazil</b>

October 23, 2018 EGF 2018 / SMS 2018 - Plenary session I		
Conference Room 1G		
Session's Chairs: Prof. Alberto Fina, Polytechnic University of Turin, Italy Prof. Luciana DI Gaspare, Roma Tre University, Italy		
08:30 - 12:00	Registration	Registration Area
10:00 - 10:30	Coffee Break / Posters Session I	Coffee Break Area
10:30 - 11:00	Towards future applications of graphene and other 2D materials - The Technology and Innovation Roadmap (TIR) of the Graphene Flagship <b>T. Reiss</b>	<b>Prof. Thomas Reiss</b> , Fraunhofer Institute for Systems and Innovation Research ISI, <b>Germany</b>
11:00 - 11:30	Germanene: graphene's little sister H.J.W. Zandvliet	Prof. Harold J.W. Zandvliet, University of Twente, Netherlands
11:30 - 12:00	Graphene Oxide Liquid Crystal and Relevant Functional Nanoscale Graphene Assembly <b>S.O. Kim</b>	Prof. Sang Ouk Kim, KAIST, Rep. of Korea
12:00 - 12:15	Reversible generation of large retractive tensile forces in isometric chemo-mechanical actuators composed of nanocomposite hydrogels and aqueous NaCl solutions <b>K. Haraguchi</b> , Y. Kimura and S. Shimizu	<b>Prof. Kazutoshi Haraguchi</b> , Nihon University, <b>Japan</b>
12:15- 12:30	<ul> <li>Biomimetic approaches targeting dairy fouling mitigation of stainless steel</li> <li>M. Jimenez, S. Zouaghi, M. Barry, S. Bellayer, S. Moradi, S.G. Hatzikiriakos, T. Dargent, V. Thomy, Y. Coffinier, C. André, M.A. Grunlan and G. Delaplace</li> </ul>	<b>Prof. Maude Jimenez</b> , University of Lille, <b>France</b>
12:00 - 14:00	Lunch Break	Restaurant

## October 23, 2018

EGF 2018 - Session I: Graphene synthesis, Growth, Functionalization and Characterization		
Conference Room 1G		
Session's Chairs:		
Prof. Harold J.W. Zandvliet, University of Twente, Netherlands		
Prof. Sang Ouk Kim, KAIST, Rep. of Korea		
	Prot. Andre Schirmeisen, Justus-Liebig-University,	, Germany
	Graphene vs. Heat Transfer: from thermally conductive	Prof. Alberto Fina,
14:00 - 14:30	nanomaterials to heat shealding under flame exposure	Polytechnic University Of
	A. Fina	Turin, <b>Italy</b>
	Coordination chemistry of metal-containing molecules with	Prof. Sungjin Park, Inha
14:30 - 15:00	graphene-based materials and their catalytic applications	University, Rep. of Korea
	S. Park	
45.00 45.00	Tunable Graphene-based Membranes	Prof. Rahul R.Nair,
15:00 - 15:30	K. Huang and <b>R.Nair</b>	Manchester University, UK
	Cristallization path of CVD graphene on Ge(001) substrate	Prof. luciana DI Gaspare,
	L. Di Gaspare, L. Persichetti, F. Fabbri, A. Sgarlata, M.	Roma Tre University. Italy
15:30 - 15:45	Eanfoni A Notargiacomo A M Scaparro V Miseikis C	······, ·····, ·····, ·····, ·····, ·····, ·····,
	Coletti and M. De Seta	
	Spontaneous deformations of carbon nanotubes: twisting and	Dr. Axel Pérez-Obiol. Kochi
15:45 - 16:00	shrinking	University of Technology
	A. Pérez-Obiol and V. Jakubský	Japan
16:00 - 16:30	Coffee Break / Posters Session I	Coffee Break Area
16.20 16.45	TAO-DFT and Its Applications to Carbon Nanomaterials	Prof. Jeng-Da Chai, Nat.
10.30 - 10.45	J-D. Chai	Taiwan University, <b>Taiwan</b>
	Multilayered graphene grafted copper wires	Dr. Lee-Woon Jang,
16:45 - 17:00	L-W. Jang, L. Zhang, M. Menghini, H. Cho, J.Y. Hwang, D.I.	Catholic University of
	Son, J-P. Locquet and J.W. Seo	Leuven, <b>Belgium</b>

17:00 - 17:15	Grafting of polymer chains onto graphite oxide sheets: Towards the design of functional composites A.Guimont, A. Dhahri, M. Hassen V Baouab and <b>E. Beyou</b>	<b>Prof. Emmanuel Beyou</b> , Lyon University, <b>France</b>
17:15 - 17:30	Towards Modified Graphene Oxide and Functional Derivatives for Industrial Applications <b>B. Gjoka</b> and R. Wendelbo	<b>Dr. Blerina Gjoka</b> , Abalonyx As, <b>Norway</b>
17:30 - 17:45	Synthesis of Multifunctional Graphene Based Nanocomposites for 3D Printing Applications <b>M. Soria Sánchez</b> and G. Tobías Rossell	Dr. Maria Soria Sanchez, Institute of Material Science of Barcelona- ICMAB (CSIC), Spain
17:45 - 18:00	Controlled pore tuning on freestanding graphene using focused ion beam and electron beam induced platinum deposition <b>T. Ashirov</b> , D. Aibek uulu, K. Celebi and A. Coskun	<b>Mr. Timur Ashirov</b> , University of Fribourg, <b>Switzerland</b>
18:00 - 18:15	Carbon atomic structures promoting twisted growth of second Graphene layer at magic angles 21.78o and 27.8o. <b>G. Gawlik</b> , Z. Kozioł, J. Jagielski and P. Ciepielewski	Dr. Grzegorz Gawlik, Institute of Electronic Materials Technology, Poland
18:15- 18:30	Advances in graphene preparation through chemical routes – detailed characterization and application <b>V. Skákalova</b> , M. Hulman, C. Hofer, V. Vretenár and P. Kotrusz	<b>Dr. Viera Skákalová</b> , University of Vienna, <b>Austria</b>
October 23, 2018 SMS 2018 - Session I: Novel Materials, Micro/Nanosystems, Composite and Eurotional Materials		
	Conference Room 5X	
	Session's Chairs:	
	Prof. Maude Jimenez, University of Lille, Fra	nce
	Dr. Giuseppe Forte, University of Catania, It	aly
Prof. Re	egina Paszkiewicz, Wrocław University of Science and	Technology, Poland
	Silicon-Carbon Films Synthesis by Figh-Frequency	wir. Alexander reminov,
14:00 - 14:15	Deposition <b>A.Temirov,</b> I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko	National University of Science and Technology, <b>Russia</b>
14:00 - 14:15 14:15 - 14:30	Deposition <b>A.Temirov,</b> I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning M. Fawzy, E. Elnabawy, A. Hassanain and <b>N. Shehata</b>	National University of Science and Technology, <b>Russia</b> <b>Dr. Nader Shehata</b> , Alexandria University, <b>Egypt</b>
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45	Deposition <b>A.Temirov,</b> I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning M. Fawzy, E. Elnabawy, A. Hassanain and <b>N. Shehata</b> Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application <b>A.Kurbanova</b> , G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova	NationalUniversityofScienceandTechnology,RussiaDr.NaderShehata,Dr.NaderShehata,AlexandriaUniversity, EgyptDr.AliyaKurbanova, University,KazakhstanUniversity,
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45 14:45 - 15:00	<ul> <li>Deposition</li> <li>A.Temirov, I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko</li> <li>Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning</li> <li>M. Fawzy, E. Elnabawy, A. Hassanain and N. Shehata</li> <li>Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application</li> <li>A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova</li> <li>Distributed control for a morphing wing with a macro fiber composite actuator</li> <li>F. Svoboda and M. Hromcik</li> </ul>	National University of Science and Technology, Russia Dr. Nader Shehata, Alexandria University, Egypt Dr. Aliya Kurbanova, Nazarbayev University, Kazakhstan Mr. Filip Svoboda, Czech Technical University in Prague,, Czech Republic
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45 14:45 - 15:00 15:00 - 15:15	<ul> <li>Deposition</li> <li>A.Temirov, I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko</li> <li>Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning</li> <li>M. Fawzy, E. Elnabawy, A. Hassanain and N. Shehata</li> <li>Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application</li> <li>A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova</li> <li>Distributed control for a morphing wing with a macro fiber composite actuator</li> <li>F. Svoboda and M. Hromcik</li> <li>Control of Vibration Suppression of Planar Structures Using Actuation by Clusters of Piezopatches</li> <li>J. Volech, Z. Šika, F. Svoboda, M. Hromčík, J. Zavřel and J. Karlíček</li> </ul>	National University of Science and Technology, Russia Dr. Nader Shehata, Alexandria University, Egypt Dr. Aliya Kurbanova, Nazarbayev University, Kazakhstan Mr. Filip Svoboda, Czech Technical University in Prague,, Czech Republic Mr. Jiri Volech, Czech Technical University in Prague, Czech Republic
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45 14:45 - 15:00 15:00 - 15:15 15:15 - 15:30	<ul> <li>Deposition</li> <li>A.Temirov, I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko</li> <li>Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning</li> <li>M. Fawzy, E. Elnabawy, A. Hassanain and N. Shehata</li> <li>Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application</li> <li>A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova</li> <li>Distributed control for a morphing wing with a macro fiber composite actuator</li> <li>F. Svoboda and M. Hromcik</li> <li>Control of Vibration Suppression of Planar Structures Using Actuation by Clusters of Piezopatches</li> <li>J. Volech, Z. Šika, F. Svoboda, M. Hromčík, J. Zavřel and J. Karlíček</li> <li>Self-stratifying fire retardant coatings</li> <li>C. Lemesle, A. Beaugendre, S. Bourbigot, S. Duquesne, A.S. Schuller, M. Casetta and M. Jimenez</li> </ul>	NationalUniversityofScienceandTechnology,RussiaDr.NaderShehata,Dr.AlexandriaUniversity, EgyptDr.AliyaKurbanova,NazarbayevUniversity,KazakhstanMr. FilipSvoboda,Mr.FilipSvoboda,TechnicalUniversityInPrague,,CzechRepublicMr.JiriVolech,CzechRepublicMs.CharlotteLemesle,University ofLille,France
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45 14:45 - 15:00 15:00 - 15:15 15:15 - 15:30 15:30 - 15:45	<ul> <li>Deposition</li> <li>A.Temirov, I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko</li> <li>Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning</li> <li>M. Fawzy, E. Elnabawy, A. Hassanain and N. Shehata</li> <li>Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application</li> <li>A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova</li> <li>Distributed control for a morphing wing with a macro fiber composite actuator</li> <li>F. Svoboda and M. Hromcik</li> <li>Control of Vibration Suppression of Planar Structures Using Actuation by Clusters of Piezopatches</li> <li>J. Volech, Z. Šika, F. Svoboda, M. Hromčík, J. Zavřel and J. Karlíček</li> <li>Self-stratifying fire retardant coatings</li> <li>C. Lemesle, A. Beaugendre, S. Bourbigot, S. Duquesne, A.S. Schuller, M. Casetta and M. Jimenez</li> <li>Water and Thermally-Induced Scratch Healing Metallo- Supramolecular Amphiphilic Polymer Conetworks</li> <li>C. Mugemana, P. Grysan, R. Dieden, D. Ruch, N. Bruns and P. Dubois</li> </ul>	NationalUniversityofScienceandTechnology,RussiaDr.NaderShehata,Dr.AlexandriaUniversity, EgyptDr.AliyaKurbanova,NazarbayevUniversity,KazakhstanMr.FilipMr.FilipSvoboda,CzechRepublicMr.JiriVolech,CzechRepublicMr.JiriVolech,CzechRepublicMs.CharlotteLemesle,University ofLille,FranceDr.ClémentMugemana,LuxembourgInstituteofScienceandTechnology,LuxembourgValueValue
14:00 - 14:15 14:15 - 14:30 14:30 - 14:45 14:45 - 15:00 15:00 - 15:15 15:15 - 15:30 15:30 - 15:45 15:45 - 16:00	<ul> <li>Deposition</li> <li>A.Temirov, I. Kubasov, R. Zhukov, D. Kiselev, M. Malinkovich and Y. Parkhomenko</li> <li>Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning</li> <li>M. Fawzy, E. Elnabawy, A. Hassanain and N. Shehata</li> <li>Spinel MgFe2O4 nanoparticles prepared by two way sol-gel method for photocatalytic application</li> <li>A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova</li> <li>Distributed control for a morphing wing with a macro fiber composite actuator</li> <li>F. Svoboda and M. Hromcik</li> <li>Control of Vibration Suppression of Planar Structures Using Actuation by Clusters of Piezopatches</li> <li>J. Volech, Z. Šika, F. Svoboda, M. Hromčík, J. Zavřel and J. Karlíček</li> <li>Self-stratifying fire retardant coatings</li> <li>C. Lemesle, A. Beaugendre, S. Bourbigot, S. Duquesne, A.S. Schuller, M. Casetta and M. Jimenez</li> <li>Water and Thermally-Induced Scratch Healing Metallo-Supramolecular Amphiphilic Polymer Conetworks</li> <li>C. Mugemana, P. Grysan, R. Dieden, D. Ruch, N. Bruns and P. Dubois</li> <li>Sensing fT magnetic fields by magnetoelectric metglas / bidomain y+140°-cut lithium niobate composite</li> <li>A.V. Turutin, J.V. Vidal, I.V. Kubasov, A.M. Kislyuk, M.D. Malinkovich, S.P. Kobeleva and N.A. Sobolev</li> </ul>	NationalUniversityofScienceandTechnology,RussiaDr.NaderShehata,Dr.AlexandriaUniversity, EgyptDr.AliyaKurbanova,NazarbayevUniversity,KazakhstanMr. FilipSvoboda,Mr.FilipSvoboda,CzechRepublicMr.JiriVolech,CzechRepublicMr.JiriVolech,CzechRepublicMs.CharlotteLemesle,University of Lille,FranceDr.ClémentMugemana,LuxembourgInstituteofScienceandTechnology,LuxembourgInstituteofScienceandTechnology,RussiaUniversityof

16:30 – 16:45	High Temperature Sensor For Detecting Low Frequency Vibrations <b>I. V. Kubasov</b> , A. M. Kislyuk, A. V. Turutin, A. A. Temirov, R. N Zhukov, A. S. Bykov, M. D. Malinkovich and Y. N. Parkhomenko1	<b>Mr. Ilya Kubasov</b> , National University of Science and Technology, <b>Russia</b>
16:45 - 17:00 17:00 - 17:15	Electrodepostion of biopolymer layers on fibrous matrices – pre-liminary results <b>E. Pabjanczyk-Wlazlo</b> , G. Szparaga and Z. Draczynski Anti-wetting Behavior of Mussel-inspired Materials Coated Anti-fouling Membrane <b>S.J. Choi</b> , S.S Kim, D.S. Hwang, A. Jang and S. Kang	Mrs. Ewelina Pabjańczyk- Wlazło, Lodz University of Technology, Poland Mr. Seungju Choi, Korea advanced institute of science and technology, Rep. of Korea
17:15 - 17:30	Synthesis of thermoelectric magnesium-silicide pastes for 3D printing and electrospinning <b>A.C. Marques</b> , D. Miglietta, A.C. Baptista, G. Gaspar, A. Gaspar, C. Bianquin R.C. da Silva, A. Gonçalves, F. Giorgis and I. Ferreira	Dr. Ana Marques, FCT- UNL, Portugal

October 24, 2018 NanoMed 2018 - Plenary session II: Nanotechnology in Therapy / Pharmaceutical Nanotechnology		
Conference Room 1E		
Session's Chairs: Prof. Valentina Cauda, Polytechnic University of Turin, Italy Dr. Davide Prosperi,University of Milano-Bicocca, Italy Dr. Fabrizia Cesca, Italian Institute of Technology- Genova, Italy		
09:00 - 09:30	Local and targeted delivery of nanomedicines for the treatment of glioblastoma <b>V.Preat</b> , C.Bastiancich, P.Ganipineni, EL. Bozzato, M.Zhao, J.Bianco and F.Danhier	<b>Prof. Veronique Preat</b> , University of Louvain, <b>Belgium</b>
09:30 - 10:00	Nanoparticle based approaches to induce long term immune tolerance to allografts F. Granucci	Prof. Francesca Granucci, University of Milano-Bicocca, Italy
10:00 - 10:30	Smart Hybrid nanocrystals as Trojan horses for effective theranostic applications <b>V. Cauda</b> , B. Dumontel, F. Susa, M. Canta, L. Racca, A. Ancona, N. Garino, T. Limongi, G. Canavese and M. Laurenti	<b>Prof. Valentina Cauda</b> , Polytechnic University of Turin, <b>Italy</b>
10:30 - 11:00	Coffee Break / Posters Session II	Coffee Break Area
11:00 - 11:30	Bioengineered colloidal nanoparticles for therapeutic applications <b>M. Colombo</b>	Prof. Miriam Colombo, University of Milano-Bicocca, Italy
11:30- 12:00	Bioelectronic Platform for Programmable Capture and Release of Circulating Tumor Cells P. Chen	Prof. Peilin Chen, Academia Sinica, Taiwan
12:00-12:15	Targeted vaccine delivery using functionalized gold nanocages characterized in small intestine orgnoid system <b>C. Yu</b> , T. Tong, Q. Wang and C. Miller	<b>Dr. Chenxu Yu</b> , Iowa State University, <b>USA</b>
12:30 - 14:00	Lunch Break	Restaurant

## October 24, 2018

NanoMed 2018 - Session II:		
Nanotechnology in Therapy / Pharmaceutical Nanotechnology		
Session's Chairs:		
Prof. Veronique Preat, University of Louvain, Belgium		
Prof. Miriam Colombo, University of Milano-Bicocca, Italy		
Prof. Sophia Hatziantoniou, University of Patras, Greece		
14:00 - 14:15	Glycosaminoglycan-Coated Superparamagnetic Iron Oxide Nanoparticles for Theranostic Applications <b>C. Bongio</b> , M. Mauri, G. Torri and E. Vismara	<b>Mrs. Chiara Bongio</b> , Politecnico di Milano, <b>Italy</b>
14:15 - 14:30	Conjugation with anti-transferrin receptor antibody increases PLGA nanoparticles uptake in Glioblastoma cells <b>M. J. Ramalho</b> , J. Lima, M. A. N. Coelho, J. A. Loureiro and M. C. Pereira	<b>Ms. Maria João Ramalho</b> , Porto University, <b>Portugal</b>
14:30 - 14:45	Targeted Multifunctional Theranostic Nanoparticle for Efficient Tumor Imaging and Therapy J. Lee and <b>W. I. Choi</b>	Dr. Won II Choi, Korea Institute of Ceramic Engineering and Technology (KICET), <b>Rep. of Korea</b>
14:45 - 15:00	New compounds for targeted photodynamic therapy of cancer <b>T. Michy</b> , C. Bernard, X. Jiang, JL. Coll, I. Texier, A. Hurbin, G. Royal and V. Josserand	Dr. Thierry Michy, University Grenoble Hospital, France
15:00- 15:15	<ul> <li>Application of hydroxyapatite as an innovative carrier for bacteriophages</li> <li>A. Fulgione, M. Iannaccone, M. Papaianni, F. Contaldi, C. Colletti, M. Lelli, N. Roveri and R. Capparelli</li> </ul>	<b>Dr. Andrea Fulgione,</b> University of Sannio, <b>Italy</b>

15:15 - 15:30	Pemetrexed-loaded nanoparticles targeted to malignant pleural mesothelioma cells: an in vitro study <b>L. Pandolfi</b> , E. Cova, S. Inghilleri, M. Morosini, V. Frangipane, S. Mrakic-Sposta, M. Colombo, P. Morbini, M. Monti, G. Stella,	<b>Dr. Laura Pandolfi</b> , Foundation IRCCS Polyclinic San Matteo, <b>Italy</b>
15:30 - 15:45	<ul> <li>Y. Pignochino, S. Benvenuti, D. Prosperi and F. Meloni.</li> <li>Preparation and characterization of Pistacia Lentiscus var.</li> <li>Chia essential oil-loaded poly(lactic acid) nanoparticles as novel wound healing agent</li> <li>I. Vrouvaki, E. Koutra, M. Kornaros, K. Avgoustakis, F. N. Lamari and S. Hatziantoniou</li> </ul>	Prof. Sophia Hatziantoniou,University of Patras, Greece
15:45 - 16:00	Graphene and the Brain: the Neurobiology of the Interaction between Graphene and Primary Neurons, Astrocytes and Microglia <b>F. Cesca</b> , M. Bramini and F. Benfenati	<b>Dr. Fabrizia Cesca</b> , Italian Institute of Technology, Genova, <b>Italy</b>
16:00 - 16:30	Coffee Break / Posters Session II	Coffee Break Area
16:30 - 16:45	A new lipopolyplex formulation with enhanced dendritic cell- targeting ability for mRNA/adjuvant vaccine delivery <b>S. Persano</b> and M.L. Guevara	<b>Dr. Stefano Persano</b> , University of Ottawa/CHEO Research Institute, <b>Canada</b>
16:45 - 17:00	Biophysical and biological contributions of polyamine-coated carbon nanotubes and bidimensional buckypapers in the delivery of miRNAs to human cells A. Celluzzi, A. Paolini, V. D'Oria, R. Risoluti, S. Materazzi, M. Pezzullo, S. Casciardi, S. Sennato, F. Bordi and <b>A. Masotti</b>	<b>Dr. Andrea Masotti</b> , Bambino Gesù Children's Hospital, IRCCS <b>, Italy</b>
17:00 - 17:15	Polyamine-coated carboxylated carbon nanotubes (CNTs- COOH) and nanohorns (NHs-COOH) in the delivery of miRNAs to human cells <b>A. Celluzzi</b> , A. Paolini, L. Lo Tufo, Z Abbaszadeh, R. Risoluti,2 S. Materazzi, D. Pozzi,G. Caracciolo and A. Masotti	<b>Dr. Antonella Celluzzi</b> , Bambino Gesù Children's Hospital, IRCCS <b>, Italy</b>
17:15 - 17:30	The effect of surface functionalization and pH on protein-gold nanoparticle interactions <b>B. Meesaragandla</b> , I. Garcia, L.M. Liz-Marzán and M. Delcea	Dr. Brahmaiah Meesaragandla, University of Greifswald, Germany

October 24, 2018 EGF 2018 / SMS 2018 - Joint Plenary Session		
Conference Room 1G		
Session's Chairs: Prof. Guenther Benstetter, Deggendorf Institute of Technology, Germany Prof. Luciana Di Gaspare, Roma Tre University, Italy		
09:30 - 10:00	Infrared and THz inter-subband optics of few-layer 2D materials <b>C. Yelgel</b>	<b>Dr. Celal Yelgel</b> National Graphene Institute, Univ. Of Manchester, <b>UK</b>
10:00 - 10:30	Smart Inspection Tools for Zero Defect Manufacturing Strategy <b>C. Cristalli</b>	<b>Dr. Cristina Cristalli</b> , Loccioni Research for Innovation, <b>Italy</b>
10:30 - 11:00	Coffee Break / Posters Session II	Coffee Break Area
11:00 - 11:30	Nanotechnology-based nanocoating and printed electronics in Smart Textiles A. B. Costa	Mr. António Braz Costa, CITEVE, Portuguese Technological Centre for Textile and Clothing Industries, Portugal
11:30 - 11:45	Smart carbon based textile reinforcement for sensing infiltration of water in concrete structures <b>G. Dittel</b> , Y. Goldfeld, G. Perry, T. Quadflieg and T. Gries	Mrs. Gözdem Dittel, RWTH Aachen University, Germany
12:00 - 14:00	Lunch Break	Restaurant

October 24, 2018 EGF 2018 / SMS 2018 - Joint Session II: Novel Materials / Graphene for Energy and Environment applications			
Conference Room 1G			
	Session's Chairs:		
Prof. Elena Voloshina, University of Shanghai, China Dr. Cristina Cristalli, Loccioni, Research for Innovation, Italy Dr. Pierre Legagneux, Thales R&T- Palaiseau, France			
14:00 - 14:30	Graphene Quantum Electromechanical Systems <b>C. Stampfer</b>	<b>Prof. Christoph Stampfer</b> , RWTH Aachen University, <b>Germany</b>	
14:30 - 15:00	Advances in Nanoscale Electrical and Thermal Characterization of Surfaces and Thin Films <b>G. Benstetter</b> , W. Lehermeier and C. Metzke	<b>Prof. Guenther Benstetter</b> , Deggendorf Institute of Technology, <b>Germany</b>	
15:00 - 15:15	Molecular dynamics study of thermo-responsive oligomer endgrafted onto graphene oxide and quartz: the effect of the surface coverage G. Forte and <b>G. Consiglio</b>	<b>Dr. Giuseppe Forte</b> , University of Catania, <b>Italy</b>	
15:15 - 15:30	Single Molecular Imaging of Fluorescent-Tagged Peptides Diffusing on a Surface of Boron Nitride <b>P. Li</b> , T. Seki, L. Sun and Y. Hayamizu	Ms. Peiying Li, Tokyo Insitute of Technology, Japan	
15:30 - 15:45	Nanographene oxide as an efficient photocatalyst in the degrdation of Rhodamine 6 B dye and solvent free oxidation of benzyl alcohol. D. Theresa, N. Nagaraju, H. Kathyayini and <b>S. Mathew</b>	<b>Dr. Shanty Mathew</b> , St. Joseph's College Research Center, <b>India.</b>	
15:45 - 16:00	Electrochemically Controlled Winding and Unwinding of HOPG Supported Carbon Nanoscroll <b>H. Tarábková</b> , Z. Zelinger and P. Janda	Dr. Hana Tarabkova, J. Heyrovský Institute, Czech Repblic	
16:00 - 16:30	Coffee Break / Posters Session II	Coffee Break Area	
16:30 - 16:45	Graphene devices for high frequency optoelectronic applications <b>P. Legagneux</b> , A. Montanaro, O. Bezencenet, B. Poupet, J. Cholet, M-B. Martin, M. Rosticher and B. Placais	<b>Dr. Pierre Legagneux</b> , Thales R&T - Palaiseau, <b>France</b>	

16:45 - 17:00	Photodetector based on CVD grown 2D materials in a van der Waals heterostructure <b>B Sompalle</b> , CD Liao, J Borme, V Saxena, F Cerqueira, S Sadewasser and P Alpuim	Mr. Balaji Sompalle, INL - International Iberian Nanotechnology Laboratory, Portugal
17:00 - 17:15	Electrochemical modulation of MoS2 photoluminescence behavior in various electrolyte aqueous solutions for potential biological sensing <b>T. Seki</b> , K. Yatsu and Y. Hayamizu	Mr. Takakazu Seki, Tokyo Institute of Technology, Japan
17:15 - 17:30	A fully organic battery made of electrospun fibers <b>A.C. Baptista</b> , I. Ropio, J.I. Martins, J.P. Borges and I. Ferreira	<b>Dr. Ana Baptista</b> , Faculty of Sciences and Technology (FCT NOVA), <b>Portugal</b>
17:30 - 17:45	Flexible Solid-State Supercapacitors Based on Tussock-Like Metal Oxide Nanowire Arrays <b>X. Cao</b> , J. Ø. Duus and Q. Chi	<b>Mr. Xianyi Cao</b> , Technical University of Denmark, <b>Denmark</b>
17:45 - 18:00	Cul-based thin films for planer, highly flexible and transparent p-n thermoelectric generators. <b>B.M.Morais Faustino</b> , J. Coroa, J. Faria, C. Bianchi, A. Marques and I. Ferreira	Dr. Miguel Morais Faustino, CENIMAT/ FCT UNL, Portugal
18:00- 18:15	Supraparticles-complex particles as smart objects for interactive materials and processes <b>K. Mandel</b>	<b>Dr. Karl Mandel</b> , Fraunhofer Institute for Silicate Research, <b>Germany</b>
18:15- 18:30	Graphene- based hybrids for solar thermal evaporation of saline water <b>N. Laidani</b> , F.Marchetti, H. Ullah, G. Gottardi, R. Bartali, M. Scarpa, E. Moser, S. Makhlouf, I. Mitiche and O. Lamrous	<b>Dr. Nadhira Laidani</b> , Bruno Kessler Foundation, <b>Italy</b>
18:30- 18:45	Graphene oxide/TiO2 heterojunction for efficient photocatalytic degradation of persistent aquatic pollutants <b>R. Zouzelka</b> , M. Remzova, L. Brabec and J. Rathousky	<b>Dr. Radek Zouzelka</b> , J. Heyrovsky Institute, <b>Czech Republic</b>

## October 24, 2018, 13:45 - 13:55

**Conference Group Photo** 

At the conference venue

All conference participants are requested to be present for the Conference Group Photo

October 24, 2018, 19:00 - 21:30 Conference Diner At the conference venue

All conference participants are invited to join

October 25, 2018		
NanoMed 2018 - Session III:		
Nanotechnology in Medical Diagnostics / Pharmaceutical Nanotechnology		
	Conference Room 1G	
	Session's Chairs:	
	Prof. Francesca Granucci, University of Milano-Bic	occa, Italy
	Prof. Paolo Ossi, Politecnico di Milano, Ital	у
09:00 - 09:15	Developing laser-synthesized optically-tuned SERS sensors for drug detection E. Fazio, S. Trusso, C. Zanchi, A. Lucotti, M. Santoro, S. Spadaro, F. Neri, M. Casazza, E. Ciusani, U. de Grazia, M. Tommasini and <b>P.M. Ossi</b>	Prof. Paolo Ossi, Politecnico di Milano, Italy
09:15 – 09:30	Plasmonic biosensors: a powerful tool in diagnostics <b>A. Minopoli</b> , B. Della Ventura, C. Schiattarella and R. Velotta	Mr. Antonio Minopoli, Napoli Federico II University, Italy
09:30 - 09:45	A novel optical biosensor for ochratoxin A based on aptamer- antibody sandwich assay and total internal reflection ellipsometry <b>A.G. Al-Rubaye</b> , A.Nabok,T. Smith , G. Catanante, J-L. Marty, E. Takacs and A. Szekacs	<b>Mr. Ali Al Rubaye</b> , Sheffield Hallam University, <b>UK</b>
09:45 - 10:00	Non-invasive monitoring of flap oxygenation using photoacoustic imaging M. Aribert, M. Henry, JL. Coll, G. Bettega and <b>V. Josserand</b>	<b>Dr. Veronique Josserand,</b> INSERM-Grenoble Alpes University, <b>France</b>
40.00 40.00		
10:00 - 10:30	Coffee Break	Coffee Break Area
10:00 - 10:30 10:30 - 10:45	Coffee Break Creating a sandwich assay of magnetic and gold nanoparticles for tau-protein quantification using ID-SERS Making Alzheimer's disease diagnosis reliable C Frank, V. Maurer, S. Wundrack, S.Schmidt, S. Zellmer, G. Garnweitner and R. Stosch	Coffee Break Area Dr. Claudia Frank, Federal Physical-Technical Institute, Germany
10:00 - 10:30 10:30 - 10:45 10:45 - 11:00	Coffee Break Creating a sandwich assay of magnetic and gold nanoparticles for tau-protein quantification using ID-SERS Making Alzheimer's disease diagnosis reliable <b>C Frank</b> , V. Maurer, S. Wundrack, S.Schmidt, S. Zellmer, G. Garnweitner and R. Stosch Functionalization of single-layer graphene transistors for immunoassays P. D. Cabral, E. Fernandes, M. F. Cerqueira, O. Bondarchuck, D. Y. Petrovykh, J. Borme and P. Alpuim	Coffee Break AreaDr. Claudia Frank, FederalPhysical-Technical Institute,GermanyMsPatríciaNanotechnology Laboratory,Portugal
10:00 - 10:30 10:30 - 10:45 10:45 - 11:00 11:00 - 11:15	Coffee Break Creating a sandwich assay of magnetic and gold nanoparticles for tau-protein quantification using ID-SERS Making Alzheimer's disease diagnosis reliable <b>C Frank</b> , V. Maurer, S. Wundrack, S.Schmidt, S. Zellmer, G. Garnweitner and R. Stosch Functionalization of single-layer graphene transistors for immunoassays P. D. Cabral, E. Fernandes, M. F. Cerqueira, O. Bondarchuck, D. Y. Petrovykh, J. Borme and P. Alpuim SI traceable quantification of hemoglobin using an ID-SERS active immunoassay <b>S. Schmidt</b> , C. Frank, S. Wundrack and R. Stosch	Coffee Break AreaDr. Claudia Frank, FederalPhysical-Technical Institute,GermanyMsPatríciaNanotechnology Laboratory,PortugalMrs.SarahSchmidt,FederalPhysical-TechnicalInstitute,Germany
10:00 - 10:30 10:30 - 10:45 10:45 - 11:00 11:00 - 11:15 11:15 - 11:30	Creating a sandwich assay of magnetic and gold nanoparticles for tau-protein quantification using ID-SERS Making Alzheimer's disease diagnosis reliable <b>C Frank</b> , V. Maurer, S. Wundrack, S.Schmidt, S. Zellmer, G. Garnweitner and R. Stosch Functionalization of single-layer graphene transistors for immunoassays P. D. Cabral, E. Fernandes, M. F. Cerqueira, O. Bondarchuck, D. Y. Petrovykh, J. Borme and P. Alpuim SI traceable quantification of hemoglobin using an ID-SERS active immunoassay <b>S. Schmidt</b> , C. Frank, S. Wundrack and R. Stosch Graphene Oxide acts as an imitative of Progesterone on sperm-oviduct interactions and sperm physiology <b>M.Ramal-Sanchez</b> , G.Tsikis, V. Labas, X. Druart, P. Mermillod, M.Saint-Dizier and N.Bernabò	Coffee Break AreaDr. Claudia Frank, FederalPhysical-Technical Institute,GermanyMsPatríciaNanotechnology Laboratory,PortugalMrs.SarahSchmidt,FederalPhysical-TechnicalInstitute,GermanyMrs.MarinaRamalSánchez,UniversityOfTeramo,Italy

October 25, 2018 EGF 2018 / SMS 2018 - Joint Session III.A: Energy applications		
Conference Room 5X		
	Session's Chairs:	
	Dr Hui-Lin Chang, Micron Technology, Manassas	VA, USA
Prof Yuhei Hayamizu, Tokyo Insisitute of Technolog, Japan		
09:00 - 09:30	Multifunctional graphene composites I. Kinloch	<b>Prof. Ian Kinloch,</b> University of Manchester, <b>UK</b>
09:30 – 10:00	An emerging material application in nanoelectronic devices and electrical performance <b>H-L Chang</b>	Dr Hui-Lin Chang, Micron Technology, Manassas VA, USA
10:00 - 10:30	Coffee Break	Coffee Break Area
	EGF 2018 / SMS 2018 - Session III. B: Biomedical ap	oplications
10:30 - 11:00	Self-assembled peptides on two-dimensional nanomaterials as a molecular scaffold for biosensing Y. Hayamizu	<b>Prof. Yuhei Hayamizu</b> , Tokyo Insisitute of Technolog, <b>Japan</b>
11:00 - 11:15	<ul> <li>Exploring the live matter interactions of bacteria and human cells with water exfoliated MoS2 nanosheets</li> <li>J. Kaur, M. Singh, C. Dell'Aversana, R. Benedetti, P. Giardina, M. Rossi, M. Valadan, A. Vergara, A. Cutarelli, A. Michela I. Montone, L. Altucci, F. Corrado, A. Nebbioso and C. Altucci</li> </ul>	<b>Mr. Manjot Singh</b> , University of Naples, Federico II, <b>Italy</b>
11:15 - 11:30	Observation of lactobacillus activity by MoS2 Sensor <b>S. Tezuka</b> , T. Seki, T. Ohnishi, and Y. Hayamizu	<b>Ms. Sayaka Tezuka</b> , Tokyo Institute of Technology, <b>Japan</b>
11:30 - 11:45	Fatigue life prediction of styrenic block copolymers for the application to prosthetic hearth valves <b>E. Biral</b> , J. Stasiak, M. Serrani and G. Moggridge	Ms Eugenia Biral, University of Cambridge, United Kingdom
11:45-12:00	Design of polymer coatings on Nitinol: towards cardiovascular applications <b>B. Arrotin</b> , J. Delhalle, P. Dubois, L. Mespouille and Z. Mekhalif	<b>Mr. Bastien Arrotin</b> , University of Namur, <b>Belgium</b>
12:00- 12:15	The influence of monovalent counterions and ionic strength on the structure and permeability of polyelectrolyte multilayers <b>M. Kolasinska-Sojka</b> , P. Skowron, M. Włodek, M. Szuwarzynski, P. Nowak and P. Warszynski	<b>Dr. Marta Kolasinska- Sojka</b> , Jerzy Haber Institute of Catalysis and Surface Chemistry, <b>Poland</b>

## October 23, 2018 NanoMed 2018 / EGF 2018 / SMS 2018 – Joint Posters Session I: Synthesis / characterization / properties

	Posters Hall	
Ν.	Title	Author, Affiliation, Country
1.	Ag+Cu Ion Implantation Fluences Controlled Mechanical Properties, Cell Adhesion, and Antibacterial Property to TiN Coatings on Medical Titanium Alloy L. Li, M. L. Zhao, L. Dong and <b>D. J. Li</b>	<b>Prof. Dejun Li</b> , Tianjin Normal University, <b>China</b>
2.	Highly stable affibody-conjugated gold nanoparticles based en-hanced ELISA for dengue virus NS1 antigen <b>J. Bang</b> and S. Kim	Mr. Jinho Bang, Korea Institute of Ceramic Engineering and Technology, Rep. of Korea
3.	Fast and highly efficient antibody purification by the oriented immobilization of protein A on magnetic nanoparticles <b>S. Kim</b>	<b>Dr. Sunghyun Kim</b> , Korea Institute of Ceramic Engineering & Technology (KICET), <b>Rep. of Korea</b>
4.	A new approach for a physicochemical characterization of nano-particles in complex media: a pilot study. <b>T. Bastogne</b> , V. Jouan-Hureaux and M. Thomassin	<b>Prof. Thierry Bastogne</b> , Lorraine University, <b>France</b>
5.	Supramolecular Binding of Small Molecules on Self- Assembled Monolayer Protected Gold Nanoparticles <b>S. Boccardo</b> , D. Marson, Y. Yang, J. Trzcinski, S. Guldin and P. Posocco	<b>Mrs. Silvia Boccardo</b> , University of Trieste, <b>Italy</b>
6.	The functionalization of ZnO nanostructured coatings in metallic resorbable biomaterials towards personalized medicine <b>M.M. Alves</b> , S. Pinto, C. Santos and M.F. Montemor	Dr. Marta Alves, Lisbon University, Portugal
7.	A Silicon Nitride Nanopore Device on a Polymer Substrate with microsize pore W. Choi, C. Park, E. S. Jeon, K. Y. Chun, Y. R. Kim, K. B. Park, K. B. Kim, S. Na and <b>CS. Han</b>	<b>Prof. Chang-Soo Han</b> , Korea University- Seoul, <b>Rep. of Korea</b>
8.	Multimodal Targeted Nanoparticles for the Non-invasive Detection of Traumatic Brain Injury L.J. Cruz, M. Aswendt, M. Hoehn, E. Kaijzel, A. Chan and C. Löwik	<b>Dr. Luis Javier Cruz</b> , Leiden University Medical Center, <b>The</b> <b>Netherlands</b>
9.	Design, Obtention and Characterization of a Novel Bioactive Tri-layer Scaffold for Cartilage Tissue Engineering <b>Y. Campos</b> , G. Fuentes, A Almirall and Luis J. Cruz	<b>Ms. Yaima Campos</b> , Leiden University Medical Center, <b>The</b> <b>Netherlands</b>
10.	Thermosensitive hydrogel as controlled-release platform for in-traarticular delivery of etanercept <b>J.García</b> , G. Fuentes, A. Almirall and L. J. Cruz	<b>Ms. Jomarien García</b> , Leiden University Medical Center, The Netherlands
11.	Trends within Point-of-care Platform Development – The Grow-ing Influence of Nanomaterials <b>B. Regan</b> , R. O' Kennedy and D. Collins	<b>Mr. Brian Regan</b> , Dublin City University, <b>Ireland</b>
12.	Influence of synthesis parameters on the properties of the nanocomposite graphene / MFe2O4 (M=Ni, Co and Zn) Jedrzejewska, <b>D. Sibera</b> , R. Jedrzejewski, A. Bachmatiuk, R. Pełech and U. Narkiewicz	<b>Dr. Daniel Sibera</b> , West Pomeranian University of Technology, <b>Poland</b>
13.	Characterization of Nano-Graphenes and Graphene Nanoribbons by Atomic Force Microscopy with Atomic Precision D. Ebeling, Q. Zhong, L.F. Chi and <b>A. Schirmeisen</b>	<b>Prof. Andre Schirmeisen</b> , Justus- Liebig-University, <b>Germany</b>
14.	A Microawave Measurement Technique For 2D Material Characteriziation H. Krraoui, C. Tripon-Canseliet and I. Maksimovic	<b>Dr. Houssemeddine Krraoui</b> , UPMC University Paris 06, <b>France</b>
15.	Preparation of Highly Stable Black Phosphorus by Gold Decoration for High Performance Thermoelectric Generators <b>Y.H. Kang</b> , C.J. An, and S.Y. Cho	<b>Mr. Young Hun Kang</b> , Korea Research Institute of Chemical Technology, <b>Rep. of Korea</b>
16.	Modified consolidants of porous materials with enhanced per- formance <b>M. Remzová</b> . T.Brzicová and J. Rathouský	<b>Ms. Monika Remzová</b> , J. Heyrovsky Institute, <b>Czech</b> <b>Republic</b>

17.	Sol-gel synthesis of MeFe2O4 (Zn, Ni, Co, Cu and Mg) nanoparticles for water purification application G.Demeuova, A.Kurbanova, O.Mauit , M. Baisariyev, O. Ualibek, O. Toktarbaiuly and <b>G. Sugurbekova</b>	<b>Dr.Gulzat Demeuova</b> , Nazarbayev University, <b>Kazakhstan</b>
18.	Development of acoustic microscopy sensor with high resolution for characterization in thin films S. Lee, T. Park, D.Kwak and <b>I. Park</b>	<b>Prof. Ik Keun Park</b> , Seoul National University of Science and Technology, <b>Rep. of Korea</b>
19.	<ul> <li>AlGaN/GaN HEMT heterostructures for gas- and bio-chemical transducers</li> <li>B. Paszkiewic, B.K.Paszkiewicz, M. Wosko, K. Indykiewicz and <b>R. Paszkiewicz</b></li> </ul>	<b>Prof. Regina Paszkiewicz</b> , Wroclaw University of Science and Technology, <b>Poland</b>
20.	Engineering Self-protected MAPbBr3/Nitrogen-Doped Graphene Hybrids with High Stability for Photodetectors <b>M. Liang</b> , Y. Tang, C. Engelbrekt and Q. Chi	<b>Mr. Mingli Liang</b> , Technical University of Denmark, <b>Denmark</b> .
21.	Composition-Driven Magnetic and Structural Transformations in Doped Bismuth Ferrites <b>U. Khomchanka</b> and J. A. Paixão	<b>Dr. Uladzimir Khomchanka</b> , University of Coimbra, <b>Portugal</b>
22.	Electroluminescent Soft Elastomer Actuators with Adjustable Luminance <b>B.G. Ha</b> , J.Y. An, Y.R. Lee, and B.Y. Lee	<b>Mr. BeomGil Ha</b> , Korea University, Seoul, <b>Rep. of Korea</b>

October 24, 2018		
NanoMed 2018 / EGF 2018 / SMS 2018 – Joint Posters Session II Properties and applications		
	Posters Hall	
1.	Mesoporous Silica Nanoparticles for Targeted Delivery of Chemotherapeutic Drugs S. A. P. Pereira, A. Rahikkala, P. Figueiredo, M. L. C. Passos, H. A. Santos, M. L. M. F. S. Saraiva and <b>A. R. T. S. Araujo</b>	Dr. André R.T.S. Araujo, Polytechnic Institute of Guarda, Portugal
2.	The antifibrotic effect of Imatinib loaded CD44 targeted gold nanoparticles (Im-CD44-GNP) relies on alveolar macrophage regulation <b>V. Frangipane</b> , F. Meloni, M. Morosini, V. Codullo, S. Magni, H. Recalde, S. Inghilleri, L. Pandolfi, G. Comolli, E. Cova, C. Montecucco, M. Colombo and D. Prosperi	<b>Dr Vanessa Frangipane,</b> Foundation IRCCS Polyclinic San Matteo, <b>Italy</b>
3.	Therapeutic advantage of genetically engineered Salmonella typhimurium carrying small interfering RNA against inhibin alpha subunit in cancer treatment <b>W. Yoon</b> , Y. Yoo, Y. Seok Chae and S-H. Kee	<b>Prof. Wonsuck Yoon</b> , College of Medicine, Korea University, <b>Rep. of Korea</b>
4.	Incorporation of zinc phthalocyanine in biological nanovehicles for photodynamic cancer therapy <b>P. Lara</b> , R.V. Huis, S. Palma, M. Kogan and L.J.Cruz	<b>Mr. Pablo Lara</b> , Leiden University Medical Center, <b>Netherlands</b>
5.	Highly Efficient Protocol for Click Labeling of Biomolecules Using a Recyclable Cu2O nanowire-catalyst A.Makki, D. Sawant, K-W. Huang and J. Eppinger	<b>Dr. Arwa Makki</b> , King Abdullah University of Science and Technology- KAUST, <b>Saudi Arabia</b>
6.	A fast and straightforward procedure for vault nanoparticle purification and the characterization of its endocytic uptake <b>M. Pozzi</b> , E. Galbiati, M. Colombo, D. Prosperi and P. Tortora	<b>Ms. Maria Pozzi</b> , University of Milano-Bicocca, <b>Italy</b>
7.	SERS-Active Microgels contatining Highly Concentrated Gold Na- noparticles for Direct Analysis of Biological Fluids <b>Y.H. Kim</b> , S. Lee, D.J. Kim and S-H. Kim	Ms. Yeong Hwa Kim, KAIST- Daejeon, Rep. of Korea
8.	Possible effect of ionic fluid flow induced electric potential in a charged nano-channel on a diagnosis by POC S. Min and <b>J. Hong</b>	<b>Prof. Junghwa Hong</b> , Dept. Control & Instrument. Eng., Korea University, <b>Rep. of Korea</b>
9.	The toxicity effects of nano-particles on micro organism in bio-logical wastewater treatment process <b>S.J. Im</b> , S.H. Oh, S.H. Jeong and A.Jang	<b>Mr. Sung Ju Im</b> , Sungkyunkwan University, <b>Rep. of Korea</b>
10.	High intensity emitting Eu3+,Bi3+:LaF3 nanoparticles for luminescence bioimaging and X-ray computed tomography. <b>A.I. Becerro</b> , D. González Mancebo, A. Corral, M. Balzercyk and M. Ocaña	<b>Dr. Ana Isabel Becerro</b> , Materials Science Institute of Seville, <b>Spain</b>
11.	Blood circulation promotion by Integrated Functional Mineral Crystal (IFMC) <b>T. Hirata</b> , T. Fujimoto, T. Nomura and K. Hatakeyama	<b>Prof. Takamichi Hirata</b> , Tokyo City University, <b>Japan</b>
12.	Surface coating determines toxic potential of iron oxide nano- particles in renal cells M. Selc, N. Gregusova and <b>A. Babelova</b>	<b>Dr. Andrea Babelova</b> , Cancer Research Institute- BMC SAS, <b>Slovakia</b>
13.	A microfluidic model of the kidney – a platform for the determi-nation of nephrotoxicity <b>A. Gabelova</b> , K. Kozics, M. Sramkova, P. Pechacova, K. Kopecka, T. Knoll and Y. Kohl	<b>Dr. Alena Gabelova</b> , Cancer Research Institute- BMC SAS, <b>Slovakia</b>
14.	Graphene Nanocomposites Polymer based Films for Gas Sensing <b>M.Ehsani</b> , M.Prosheva, R.Fajgar, J.Blazevska, R. Tomovska and Y.Joseph	Ms.MaryamEhsani,BergakademieFreibergtechnicaluniversity,Germany
15.	Experimental investigation of the dynamic behaviour of Laminated Composite Reinforced with graphene using split Hopkinson pressure bars <b>M. Chihi</b> , M. Tarfaoui, K. Lafdi and C.Bouraoui	Dr. Manel Chihi, ENSTA Bretagne, France
16.	Thick Silica Foam Films with Aerogel-Like Thermal Conductivity and Bulk Density <b>T. Kangur</b> , M. Järvekülg and M. Timusk	<b>Dr Triin Kangur</b> , University of Tartu, <b>Estonia</b>

47	Hybrid multi-material microbraids for through-thickness	Ms. Caroline O'Keeffe, University of
17.	<b>C. O'Keeffe</b> , I. Partridge and G, Allegri	Bristol, United Kingdom
	Highly Integrated and Flexible Thermoelectric Module Fabricated by	Dr. Song Yun Cho, Korea Research
18.	Bruch-cast Doping of a Highly Aligned Carbon Nanotube Web	Institute of Chemical Technology,
	C.J. An, Y.H. Kang, and <b>S. Y. Cho</b>	Rep. of Korea
	Evaluation of Topography Effects of SThM Measurements on Thin	Prof. Guenther Benstetter,
19.	Thermoelectric Films	Deggendorf Institute of Technology,
	W. Lehermeier, C. Metzke, G. Benstetter, W. Frammelsberger	Germany
	Infectious risk after pose installation of prostheses and implants	Dr. Siham Azrou, University Saad
20.	osteoarticular implants	Dahlab-Blida 1, <b>Algeria</b>
	S. Azrou, M. Benamara, S. Berouaken ,R. Belouni, S. Abdi and M.	
	Hamidani	
	Photo-instability of ternary-Halide MAPb(Br1-x-ylxCly)3 Perovaksite	Prof. Young-Woo Heo, Kyungpook
21.	S-Y. Kim, H.J. Woo, H. Jo, S. Baek, J-H. Lee, J-J. Kim, S-W. Lee,	National University, Rep. of Korea.
	and <b>Y-W. Heo</b>	

NanoMed 2018 Plenary session I

## Tapered optical probes and optrodes for optogenetics and neurophotonics

M.De Vittorio,<sup>1,2,\*</sup> F.Pisanello,<sup>1</sup>

<sup>1</sup>Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia, Via Barsanti, Arnesano (LE), Italy

<sup>2</sup> Dip. Ingegneria dell'Innovazione, Università del Salento, Via Monteroni, 73100 Lecce (LE), Italy

## Abstract:

The combination of genetics, photonics, micromechanics electronics and is producing completely new technological approaches for physical and chemical sensors and actuators, which can be disposable, wearable or implantable in humans and animal models. These new approaches are opening the way to closed loop theranostics, i.e. device integrating capabilities and therapeutic diagnostic response.

For being able to monitor and control brain activity and disorders, low invasiveness probes need to be implanted and new effective methods are required, such as optogenetics. In optogenetics, opsins, which are light-sensitive proteins, are genetically targeted into specific neurons types in an animal model (typically a mouse), making possible the activation or inhibition of brain neurons by light. The development of new devices to optically interface with the mammalian brain in vivo has represented a revolution for experimental neuroscience, allowing to identify the role of specific population of neurons within specific neural circuits.

Recent advances on technologies for in-vivo optical stimulation and inhibition of neuronal activity in optogenetic experiments will be reported. It will be shown that modal manipulation in tapered optical fibers makes possible an effective and minimally invasive light delivery and recording in the mouse brain either for large brain volume or for selective stimulation/readout of multiple brain regions [1,2]. Nanomachining is also exploited for integrating arrays of microelectrodes and optical windows on tapered optrodes for combined extracellular

electrophysiology and optogenetic stimulation.

**Keywords**: optogenetics, brain technologies, optical fibers, electrophysiology.





**Figure 1**: a) Schematics of tapered fibers for broad emission, site selective illumination and optrodes; b) SEM image of a focus ion beam nanomachined tapered fiber (courtesy of OptogeniX srl, www.optogenix.com).

- F. Pisanello, L. Sileo, I. A. Oldenburg, M. Pisanello, L. Martiradonna, J. A. Assad, B. L. Sabatini, and M. De Vittorio, "Multipoint-Emitting Optical Fibers for Spatially Addressable In Vivo Optogenetics," Neuron, vol. 82, no. 6, pp. 1245–1254, May 2014.
- F. Pisanello, G. Mandelbaum, M. Pisanello, I. A. Oldenburg, L. Sileo, J. E. Markowitz, R. E. Peterson, A. Della Patria, T. M. Haynes, M. S. Emara, B. Spagnolo, S. R. Datta, M. De Vittorio, and B. L. Sabatini, "Dynamic illumination of spatially restricted or large brain volumes via a single tapered optical fiber," Nature Neurosci., vol. 20, no. 8, pp. 1180–1188, Jun. 2017.

## Nanomedical Implications for Parkinsons Disease: Silver Nanoparticles Inhibits Catechol O-methyltransferase

A. Usman<sup>1</sup>, K. Lobb<sup>2</sup>, BI Pletschke<sup>1</sup>, BS Wilhelmi<sup>1</sup>, CG Whiteley<sup>1\*</sup>

<sup>1</sup>Department of Biochemistry & Microbiology <sup>2</sup>Department of Chemistry Rhodes University; Grahamstown; South Africa

## Abstract:

Catechol O-methyltransferase (COMT) is a ubiquitous enzyme that catalyses the transfer of a methyl group from the cofactor, S-adenosyl-L-methionine (SAM) to a hydroxyl group of endogenous exogenous catecholand containing moieties. Control of the activity of this enzyme serves as an important drug target; its inhibitors are used as an adjunct to levodopa for the treatment of Parkinson's disease. Absorption, fluorescence and infrared spectroscopy as well as computational simulation studies show that silver nanoparticles inhibits human catechol Omethyltransferase. The nanoparticles form a corona with the enzyme and quenches the fluorescence of Trp143. This important amino acid keeps the planar catechol ring in its correct orientation during catalysis, by a static mechanism supported by a non-fluorescent fluorophore-nanoparticle complex. The enzyme has one binding site for AgNPs in a thermodynamically spontaneous binding and electrostatic interactions driven by confirmed by the negative  $\Delta G$  and  $\Delta H$  and positive  $\Delta S$ . Fourier transform infra-red spectroscopy within the amide I region of the enzyme indicates the interaction causes relaxation of its  $\beta$ -structures, while simulation studies indicate the involvement of six polar amino acids. The docking of silver nanoparticles with COMT was examined under a regime of molecular dynamics simulations. The simulation of the 'docking', first as a rigidbody complex, and eventually through flexiblefit analysis, creates 36 different complexes from four initial orientations of the nanoparticle strategically positioned around the surface of the enzyme. The structural deviations of the enzyme from the initial x-ray crystal structure during each docking simulation was assessed by comparative analysis of secondary structural elements, root mean square deviations (RMSD), B-factors, interactive bonding

energies, dihedral angles, radius of gyration  $(R_g)$ , circular dichroism (CD), volume occupied by  $C_{\alpha}$ , electrostatic potentials, solvation energies and hydrophobicities. Normalisation of the data narrows the selection to one 'final' structure.

**Keywords** Silver nanoparticles; Catechol Omethyltransferase; Parkinsons disease; Inhibition; Computer simulations





## References

1. Rutherford, K., Le Trong, I., Stenkamp,R.E., Parson, W.W., 2008. Crystal structures of human 108V and 108M catechol *O*-methyltransferase. J. Mol. Biol. 380, 120–130.

## NanoMed 2018 - Session I Bionanomaterials synthesis and characterization/ Nanomaterials for Medicine

# The vault complex: production and studies on its usage as nanovector

E. Galbiati,\* M. Pozzi, M. Colombo, D. Prosperi, P. Tortora

University of Milano-Bicocca, Department of Biotechnologies and Biosciences, Piazza della Scienza 2, 20126, Milan, Italy

### Abstract:

Vault is the largest eukaryotic ribonucleoprotein, yet its physiological role is so far unknow. This complex consists of 78-96 copies of the major vault protein (MVP, 97kDa), 8 copies of the poly-(ADP-ribose) polymerase (VPARP, 193 kDa), 2 copies of the telomerase-associated protein 1 (TEP1, 290 kDa) and several untranslated RNAs (vRNA). Despite its complex composition, the minimum vault structure can be produced by expressing MVP alone. The recombinant vault particle has properties suitable for a drug delivery system. Its overall dimensions are 41 x 41 x 72.5 nm and the large internal cavity makes it possible to encapsulate cytotoxic proteins, drugs and nucleic acids. Vault is also non-immunogenic and non-toxic, and can be easily modifed by biologically engineering either termini of MVP, or by chemically binding antibodies or small peptides. We produced the protein in insect cells and purified it by dialysis using a membrane with a molecular weight cutoff of 1 MDa and a subsequent size exclusion chromatography. The resulting complex displayed the expected chemical-physical properties, as shown by SDS-PAGE, western blot, TEM and Dynamic Light Scattering (DLS). We also studied vault's endocytic uptake by several cell lines using specific inhibitors for clathrin-mediated (chlorpromazine) and caveolae-dependent (genistein) endocytosis. The endocytosis was assessed by flow cytometry (FACS) and confocal microscopy analysis. We found that vault undergoes clathrin-mediated endocytic uptake in normal fibroblast and glioblastoma, but not in carcinoma cell lines. These results point to specific biological interactions between vault and surface receptors. To exploit vault as a vector in active targeting the protein chemically systems, was functionalized with trastuzumab (Tz), а monoclonal antibody recognizing the HER2 receptor, which is over-expressed in breast cancer. Vault-trastuzumab (vault-Tz) was proven to be effective in specific targeting and binding, and to be internalized in SKBR3 (HER2<sup>+</sup>) cells. These results show that vault is a promising

nanovector for drug delivery. The next steps include the encapsulation of pharmacologically active molecules or cytotoxic proteins and the evaluation of their activity *in vitro* and *in vivo*.

**Keywords**: major vault protein, baculovirus, endocytosis, targeting, breast cancer.



**Figure 1**. Outline of the newly developed purification procedure of the vault complex and its natural and engineered endocytic pathways.

- Stephen, A.G.; Raval-Fernandes, S.; Huynh, T.; Torres, M.; Kickhoefer, V.A.; Rome, L.H. Assembly of vault-like particles in insect cells expressing only the major vault protein. *J. Biol. Chem.* 2001, 276 (26), 23217-23220.
- Benner, N.L.; Zang, X.; Buehler, D.C.; Kickhoefer, V.A.; Rome, M.E.; Rome, L.H.; Wender, P.A Vault Nanoparticles: Chemical Modifications for Imaging and Enhanced Delivery. ACS Nano, 2017, 11 (1), 872-881.

## Titanium dioxide coating of porous silicon microparticles towards nanomedicine applications

E. Chistè,<sup>1\*</sup> M. Donini,<sup>2</sup> V. Cremers,<sup>3</sup> J. Dendooven,<sup>3</sup> C. Detavernier,<sup>3</sup> M. Scarpa,<sup>4</sup> S. Dusi,<sup>2</sup> and N. Daldosso.<sup>1</sup>

<sup>1</sup> University of Verona, Department of Computer Science, (Fluorescence Laboratory), Verona, Italy
 <sup>2</sup> University of Verona, Department of Medicine, (Division of General Pathology), Verona, Italy
 <sup>3</sup> Ghent University, Department of Solid State Sciences, (CoCooN Group), Gent, Belgium
 <sup>4</sup> University of Trento, Department of Physics, (Laboratory of Nanoscience), Trento, Italy

### Abstract:

Porous silicon (pSi) is a photoluminescent material with a sponge-like structure. The pSi light emitting microparticles are produced by anodization etching of crystalline Si wafer in HF solution and are stable for years in ethanol after a surface carboxyl-functionalization. They are biodegradable, biocompatible, inert and do not system. activate the immune response Furthermore, they have a porosity with large surface to volume ratio, thus being promising for targeting drug delivery and bioimaging. One of the main issues in the application of this material nanomedicine is its degradation to and photoluminescence (PL) fast quenching in environment. preserve aqueous То these properties, organic coatings are used (i.e. PEG, Chitosan). However, such thick coatings often limit the pore size volume and thus the loading capacity.

In this study, we deposited an inorganic (TiO<sub>2</sub>) thin layer on the pSi microparticles surface by ALD (Atomic Layer Deposition) in a rotary reactor, without modifying the structure, as it was confirmed by TEM images (Figure 1). We obtained PL stabilization for almost one year in aqueous media (i.e. PBS – phosphate buffered saline). To investigate the toxicity of pSi-TiO<sub>2</sub> microparticles, we performed in-vitro tests by incubating different amounts of microparticles in human DCs (dendritic cells). They were internalized without any toxic effect by the DCs and maintained the PL, as confirmed by two photon absorption experiment.

These promising results of optical stability and "compatibility" with human DCs open the way for future developments of inorganic coating of pSi microparticles to a complete platform for drug delivery achieve and bioimaging applications.

**Keywords**: Porous silicon, ALD, Photoluminescence, dendritic cells.



**Figure 1**: TEM images of representative pSi–TiO<sub>2</sub> microparticles.

- Ghafarinazari, A., Scarpa, M., Zoccatelli, G., Comes franchini, M., Locatelli, E., Daldosso, N. (2017) Hybrid luminescent porous silicon for efficient drug loading and release, *RSC Adv.*, 7(11), 6724-6734.
- 2. Longrie, D., Deduytsche, D., Haemers, J., Driesen, K., Detavernier, C. (2012), A rotary reactor for thermal and plasma-enhanced atomic layer deposition on powders and small objects, *Surf. Coat. Technol.*, 213, 183-191.
- Chistè, E., Ghafarinazari, A., Donini, M., Cremers, V., Dendooven, J., Detavernier, C., Benati, D., Scarpa, M., Dusi, S., Daldosso, N. (2018) TiO<sub>2</sub>-coated luminescent porous silicon micro-particles as a promising system for nanomedicine, *J. Mater. Chem. B*, 6, 1815-1824.

# Structure and properties of composite TiO<sub>2</sub>+TiN diffusive surface layers produced on NiTi shape memory alloys

J. Witkowska1\*, A. Sowińska2, E. Czarnowska2, T.Płociński1, T. Wierzchoń1

<sup>1</sup>Faculty of Materials Science and Engineering, Warsaw University of Technology, Poland <sup>2</sup> Pathology Department, Children's Memorial Health Institute, Warsaw, Poland \*justyna.aleksandra.witkowska@gmail.com

## Abstract:

The use of NiTi shape memory alloys in medicine for long-term implants requires enhancing its biocompatibility, mainly by increasing the corrosion resistance, reducing the amount of nickel ions released from the surface of the alloy into the biological environment and modeling biological response depending on the intended application [1]. Hence various surface engineering methods are used to improve the properties of the alloy, but not all of them allow to maintain the unique features, i.e. shape memory and superelasticity. Our previous work has shown that nitriding in a low-temperature plasma gives promising results in the context of the application of an alloy for bone implants [2]. In this study we present the results of plasma oxynitriding process conducted at the temperature of 300°C in two stages: nitriding and oxidizing. The inestigations of microstructure, surface topography, wettability and surface free energy, corrosion resistance, the amount of nickel iosn released from the surface, the biological response of osteoblasts, blood platelets and the adsorption of albumin were carried out to assess the properties of the NiTi alloy before and after the proposed surface treatment. The obtained results show greater surface roughness, less wettability, improved corrosion resistance, reduction of metallosis increased effect. osteoblast proliferation for NiTi alloy with a  $TiO_2 + TiN$ surface layer in comparison to the NiTi in initial state. Such results are promising in the context of medical applications as bone implants. The biological evaluation of the NiTi alloy with the oxynitrided layers indicate that the oxidation of the nitrided layer significantly changes the nature of the biological response of the cells in contact with the tested material.

**Keywords**: Nitinol, glow discharge oxynitriding, corrosion resistance, biocompatibility



**Figure 1**: AFM image of the surface of NiTi alloy before (a) and after (b) oxynitriding process; area  $1x1 \mu m$ .

- 1. Shabalovskaya S. (2002) Surface, corrosion and biocompatibility aspects of Nitinol as an implant material, *Bio. Med. Mater. Eng.* 12, 69–109
- Czarnowska E, Borowski T, Sowińska A et al. (2015). Structure and properties of nitrided surface layer produced on NiTi shape memory alloys by low temperature plasma nitriding, *Appl. Surf. Sci.* 334, 24-31

# Hybrid self-assembly of quantum dots and gold nanoparticles driven by protein pairing

Maxence Fernandez, <sup>1</sup> Laureen Moreaud, <sup>1,2</sup> Agnès Burel, <sup>1</sup> Agathe Urvoas, <sup>3</sup> Marie Valerio-Lepiniec, <sup>3</sup> Erik Dujardin, <sup>2</sup> Philippe Minard, <sup>3</sup> Pascale Even-Hernandez<sup>1</sup> and Valérie Marchi, <sup>1\*</sup>

<sup>1</sup> University Rennes 1, Institut of Chemical Sciences, UMR 6226 CNRS, Rennes, France
 <sup>2</sup> Groupe NanoSciences - CEMES-CNRS UPR 8011, Toulouse, France
 <sup>3</sup>I2BC, Univ Paris Sud, CNRS, CEA UMR 9198 - Bât. 430, F-91405 Orsay, France
 \*valerie.marchi@univ-rennes1.fr

### Abstract:

The broad field of nanotechnology has resulted in the design of hybrid nanomaterials featuring exclusive properties such as sensing, data or energy storage and biocide activity. Moleculedriven self-assembly of biomolecules led to the design of colloidal assemblies thanks to the direct recognition of specific molecular partners grafted onto nanoparticles. Direct coupling of nanoparticles has been achieved using DNA strands hybridization, peptide coupling or archetypal protein interactions. In this context, assemblies of gold nanoparticles were designed using artificial repeat  $\alpha$ Rep protein pairs of high affinity ( $K_D$  in the range of nM).<sup>1,2</sup> These promising proteins are able to self assembly complementary colloids in a controlled manner, by providing a control on the interparticle distance. Here we present the design of  $\alpha Rep$ proteins driven self-assemblies of semiconductor nanoparticles (Quantum dots, QDs) and gold nanoparticles (nPAu). First, to functionalize the QDs and the Au NP, the initial ligand polycystein peptidic derivatives at the surface of the NP are exchanged with the  $\alpha$ Rep proteins.<sup>3</sup> The efficiency of the protein grafting was demonstrated bv agarose gel electrophoresis. The molecular recognition the protein-functionalized properties of nanoparticles is evidenced by using Surface Plasmon Resonance technique. The selective formation of large colloidal assemblies of complementary nanoparticles are demonstrated by transmission electronic microscopy and finally characterized by fluorescence spectroscopy. These results open the route to the design of hybrid colloidal assemblies with original optical response.

**Keywords**: artificial proteins; gold nanoparticles; self-assembly; quantum dots.



Figure 1: a) Scheme of complementary nanoparticles grafted with  $\alpha$ Rep proteins.

- K. L. Gurunatha, A. C. Fournier, A. Urvoas, M. Valerio-Lepiniec, V. Marchi, P. Minard and E. Dujardin, ACS Nano, 2016, 10, 3176–3185.
- A. Guellouz, M. Valerio-Lepiniec, A. Urvoas, A. Chevrel, M. Graille, Z. Fourati-Kammoun, M. Desmadril, H. van Tilbeurgh and P. Minard, *PLoS ONE*, 2013, 8, 71512.
- T. Bizien, P. Even-Hernandez, M. Postic, E. Mazari, S. Chevance, A. Bondon, C. Hamon, D. Troadec, L. Largeau, C. Dupuis, C. Gosse, F.Artzner and V. Marchi, *Small*, 2014, 10, 3707–3716.

## Synthesis and characterization of SPIONs for smart theranostics

Matos J.C.\*<sup>1,2</sup>, Gonçalves M.C.<sup>1</sup>, Pereira L.C.J.<sup>2</sup>, Waerenborgh J.C.<sup>2</sup>

<sup>1</sup>CQE, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

<sup>2</sup> C<sup>2</sup>TN, Instituto Superior Técnico, Universidade de Lisboa, Bobadela, Portugal

### Abstract:

Superparamagnetic iron oxide nanoparticles (SPIONs), which are small particles of magnetite or maghemite, have shown great potential for biomedicine. SPIONs' coating is an important strategy to defeat their aggregation tendency, improving their dispersity and stability in liquid media, essential for biomedical applications.<sup>1</sup>

SPIONs were synthesized through an easy reduction-precipitation method run in air, based on Qu et al.<sup>2</sup>, and coated with four different polymers (PEG 1000/6000 and Dextran T10/T70).

All samples were structurally and magnetically characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Mössbauer spectroscopy and SQUID magnetometry. SPIONs with an average diameter of at least 7.5 nm showed the best magnetization results, with a saturation magnetization of  $\sim 64$ emu/g at 300 K, and a composition  $\leq 60\%$  of maghemite and  $\geq 40\%$  of magnetite. Concerning the SPIONs coatings, during their preparation procedure surfactants must be introduced after the SPIONs precipitation. Furthermore, it was observed that polymers with shorter chains do not affect the SPIONs magnetization performance, although longer chains polymers decrease the coated particle magnetization values, which is undesirable.

Future work will be directed towards magnetic performance of coated SPIONs.

**Keywords**: SPIONs, magnetite, maghemite, coating, PEG, dextran, magnetization.



**Figure 1**: (Left) Schematic of nanoparticles synthesis procedure. (Right) TEM and magnetization results for the coated SPIONs using four different polymers.

### **References:**

- Kandasamy, G., Maity, D. (2015) Recent advances in superparamagnetic iron oxide nanoparticles (SPIONs) for in vitro and in vivo cancer nanotheranostics, *Int. J. Pharm.*, 496, 191-218.
- Qu, S., Yang, H., Ren, D., Kan, S., Zou, G., Li D., Li M. (1999), Magnetite nanoparticles prepared by precipitation from partially reduced ferric chloride aqueous solutions, *J. Colloid Interface Sci.*, 215, 190-192.

## Acknowledgements:

Support for this work was provided by FCT through UID/Multi/04349/2013 and UID/QUI/00100/2013 projects.

Joana C. Matos acknowledges financial support from FCT, through ChemMat doctoral program (PD/BD/127914/2016).

## Microfluidic technologies for biomaterials nanofabrication for drug delivery applications

C.Palocci,1\* L..Chronopoulou,1A. Di Nitto1

<sup>1</sup>University of Rome "La Sapienza", Department of Chemistry, Rome, Italy

## Abstract:

Recently, the possibility to fabricate spatially well-defined, three dimensional (3D) nanostructures have attracted a lot of interest for the development of novel materials for biotechnological applications. To achieve this goal, three major aspects should be considered: (a) selection of biocompatible materials to construct 3D micro and nanostructures; (b) fabrication methods to control the size and uniform shape of the 3D microstructures; (c) the possibility to develop theoretical/numerical framing on the mechanism involved in controlling the nominal size and the size distribution of particles at nano/micro level. On this basis the emergence of microfluidic technologies provides a wide variety of novel strategies for synthesizing particles at the nanometer or micrometer length scale. Microfluidics can facilitate the manufacture materials with specially designed of structures and unique functions, such as core¿shell, Janus and hybrid capsule or microgel particles. The development of these micro- fluidic processes offers novel methods and knowledge for improving the of nanoparticles including properties particle size, size distribution, and physical, chemical or biological properties under a more mild and controllable environment. In the biomedical field, NPs find applications in drug delivery devices, targeted imaging, biomolecular sensing, and thin film coatings. NP size and polydispersity have a primary role in controlling their cellular interaction and biodistribution. Therefore, improving the control of NPs preparation is of critical importance for their successful clinical application. Our work is focused on the use of microfluidic devices to prepare biomaterials with proper size and morphology and also to establish modelling frameworks for interpreting experiments targeting the microfluidic-assisted nano and micro materials synthesis.



**Figure 1**: Figure illustrating the flow microfluidic reactor system used for the synthesis of PLGA NPs. The system consists of three inlets and one outlet (C) connected by a cross junction (d), creating a hydrodynamic flow-focusing with a central stream of dispersed phase (b) and two side streams of continuous phase (A and A').

- 1. Marco Bramosanti, Laura Chronopoulou, Fabiana Grillo, Alessio Valletta, Cleofe Palocci (2017) "Microfluidic-assisted nanoprecipitation of antiviral-loaded polymeric nanoparticles" *Colloids and Surfaces A*, 532, 369–376.
- Laura Chronopoulou, Carolina Sparago and Cleofe Palocci (2014) "A modular microfluidic platform for the synthesis of biopolymeric nanoparticles entrapping organic actives" J. Nanop. research, 16, 2703- 2709.

## NIR Photo-triggered hybrid copper sulphide nanoparticles functionalized with thermo-responsive polymers for on-demand drug delivery

Isabel Ortiz de Solorzano<sup>†‡§</sup>\*, Teresa Alejo<sup>†‡</sup>, Miriam Abad<sup>I</sup>, Carlos Bueno-Alejo<sup>†§</sup>, Gracia Mendoza<sup>†‡</sup>, Vanesa Andreu<sup>†‡</sup>, Silvia Irusta<sup>†‡§</sup>, Victor Sebastian<sup>†‡§</sup>, Manuel Arruebo<sup>†‡§</sup>

†Department of Chemical Engineering. Aragon Institute of Nanoscience (INA), University of Zaragoza, Spain
‡Aragon Health Research Institute (IIS Aragón), Zaragoza, Spain

§Networking Research Center on Bioengineering, Biomaterials and Nanomedicine, CIBER-BBN, Madrid, Spain lOrganic Chemistry Departament, Material Science Institute of Aragon (ICMA), Universidad de Zaragoza-CSIC,Spain

#### Abstract:

External stimuli activation of drug delivery vectors has become one of the main focus of attention in biomedical nanotechnological applications. Due to the possibility of being activated localy and after their administration in the body, these vectors allow the drug to be released directly in an specific target reducing side effects experimented with conventional drug administration routes. This activation is normally achieved by physical triggers such as magnetic fields, ultrasounds and near infrared (NIR) radiation<sup>1</sup>. Those vectors are composed of a material able to generate heat upon absorption of a specific electromagnetic radiation and another one that shows thermal responsiveness and hosts the transported drug. In this work we present a cleavable and thermo-sensitive drug delivery vector loaded with an anaesthetic drug potentially used for chronic pain treatment. By combining the photothermal ability of copper sulphide nanoparticles (NPs) upon excitation with Near Infrared (NIR) Light<sup>2</sup> and the thermo-responsive properties of the homemade oligo (ethylene glycol) methyl ether methacrylate copolymer we have obtained fragmentable nanocomposites able to release a carried drug on-demand after NIRlight triggering. (Figure 1) A complete physicochemical characterization of the resulting nanoparticles has been carried out and their degradation assessed at different temperatures. Herein, we have also evaluated the drug loading capacity of those nanoparticles and the temperature dependence in their drug release kinetics using bupivacaine hydrochloride as a model drug. Subcytotoxic doses on four different cell lines and their potential interference in cell metabolism, induction of apoptosis, and cell cycle have been evaluated.

**Keywords**: Thermosensitive polymer, cleavable nanoparticles, bupivacaine, drug delivery, photothermal; NIR.



**Figure 1**: Scheme of the nanoparticles and their biomedical applicatibility described in this work.

#### **References:**

- 1. T. Kawano, Y. Niidome, T. Mori, Y. Katayama, T. Niidome, PNIPAM gel-coated gold nanorods for targeted delivery responding to a near-infrared laser, *Bioconjug. Chem.* 20 (2009) 209–212.
- L. Guo, I. Panderi, D.D. Yan, K. Szulak, Y. Li, Y.T. Chen, H. Ma, D.B. Niesen, N. Seeram, A. Ahmed, B. Yan, D. Pantazatos, W. Lu, A comparative study of hollow copper sulfide nanoparticles and hollow gold nanospheres on degradability and toxicity, *ACS Nano*. 7 (2013) 8780–8793.

#### Acknowledgments:

The ERC Consolidator Grant program (ERC-2013-CoG-614715, NANOHEDONISM), is gratefully acknowledge.

# Study of neuronal guidance dynamics in neurodevelopmental disorders models by nano-engineered platforms

I. Tonazzini <sup>1,2</sup>\*, C. Masciullo<sup>2</sup>, G.M. Van Woerden<sup>1</sup>, M. Cecchini<sup>2</sup>, Y. Elgersma<sup>1</sup>

<sup>1</sup> Erasmus Medical Center, Dept. of Neuroscience, Rotterdam, the Netherlands <sup>2</sup> NEST, Istituto Nanoscienze – CNR, Pisa, Italy

## Abstract:

In the brain, cells are exposed to both physical and chemical extracellular stimuli determined by the micro/nano-environment within which they exist: these extracellular instructions orchestrate the wiring of the Although nervous system. central the dynamics of neuronal extracellular sensing is emerging as crucial for neuronal connectivity and functionality, little is known about these processes in pathological conditions (e.g. neurodevelopmental disorders). Nanoengineered substrates are emerging as tools for investigating and tailoring the processes that regulate neuronal extracellular sensing. Nano-structured substrates, for example nano-microgratings (GRs), are in fact able to induce specific topographical stimuli to neuronal cells, resembling in vitro several features of extracellular matrix (ECM) cues, and consequently to tune neuronal polarity and migration.

We here developed and demonstrated nanoengineered platforms to study neuronal sensing and migration processes in neurodevelopmental disorders. As pathological models, we focused on the unbalanced levels of ubiquitin ligase E3a (UBE3A), which leads to several neurodevelopmental such disorders, as Angelman Syndrome (AS) and 15duplication autisms (15dup). By exploiting electron beam, nanoimprint and/or replica molding, we engineered thermoplastic and elastomeric substrates patterned with GRs (i.e. alternating lines of ridges and grooves) having line-widths between 500 nm and 10 µm. We developed both physical and biochemical (i.e. ECM proteins) directional GRs patterns. Here we tested primary healthy-control, AS and 15dup neurons on nano-engineered chips by applying specific

biomimetic environmental physicobiochemical stimuli. We found guidance deficits in AS neurons, which correlate with defective focal adhesion pathway signaling. Our results were further confirmed in vivo, by in utero electroporation. We propose nano-engineered platforms as advanced devices for investigating neuronal guidance/migration dynamics in vitro, as in an enriched environment able to resemble closely the in vivo conditions. This work is supported by MSCA-IF-2017 grant Neuroguide (795948).

**Keywords**: nanostructured substrates; ubiquitin ligase E3a (UBE3A); contact guidance; Angelman Syndrome; autism; axonal guidance; cytoskeleton; micro-gratings; focal adhesions.



**Figure 1**: Confocal images of WT and AS hippocampal neurons cultured on GR (at Div4); inset= GR pattern.

## **References:**

1. Tonazzini, I., Meucci, S., Van Woerden, G.M., Elgersma, Y., Cecchini, M. (2016), Impaired neurite contact guidance in Ubiquitin ligase E3a (Ube3a)-deficient hippocampal neurons on nanostructured substrates, *Adv Healthcare Mat*, 5, 850-862.

## Biological characterization of osteoblast/osteoclast cell growth on polyamidoamine-coated bidimensional Buckypapers

A. Paolini<sup>1</sup>, G. Battafarano<sup>1</sup>, V. D'Oria<sup>1</sup>, F. Mura<sup>2</sup>, S. Sennato<sup>3</sup>, V. Mussi<sup>4</sup>, R. Risoluti<sup>5</sup>, S. Materazzi<sup>5</sup>, A. Del Fattore<sup>1</sup>, A. Masotti<sup>1</sup>

<sup>1</sup>Bambino Gesù Children's Hospital, IRCCS, Research Laboratories, Rome, Italy
 <sup>2</sup>Center for Nanotechnology for Engineering (CNIS), Sapienza University of Rome, Rome, Italy
 <sup>3</sup>Department of Physic and CNR-ISC UOS Roma, Rome, Italy
 <sup>4</sup>National Research Council, Institute for Complex Systems ISC-CNR, Rome, Italy
 <sup>5</sup>Department of Chemistry, Sapienza University of Rome, Rome, Italy

### Abstract:

Synthetic scaffolds based on carbon nanotubes (CNTs), generally referred as 'buckypapers', have been employed in bone, neural, muscle, and dental tissue engineering thanks to their properties at the nanoscale (i.e., high mechanical strength, electrical and/or thermal conductivity) [1,2,3]. To evaluate the adhesion and growth of bone cells on a novel hydrophilic polyamidoamine-coated bidimensional buckypaper, a 3D-printed device was fabricated to allow the growth of cells on these scaffolds.

Pristine BPs and polyamidoamine-coated BPs were enclosed in a home-made 3D-printed device and three different cell types (i.e., HEK-293T, osteoblast SAOS-2 and osteoclast) were seeded on them. The BPs surfaces were characterized by scanning electron microscopy, dispersive X-ray, energy atomic-force microscopy, thermogravimetric analysis and Raman microscopy techniques. BPs showed a network of CNTs with different length and a aspect. cross-linked The PAMAM functionalization is recognizable as a thin layer that covers the entire surface.

Pristine BPs after 1, 3 and 7 days from cell seeding showed a high toxicity compared to the PAMAM-coated BPs. The functionalization of BPs with PAMAM generated a suitable scaffold for cell growth as shown by cell clusters at different time points. PAMAM dendrimer was also able to increase the cell adhesion for the internalization of small oligonucleotides. Moreover, the presence of PAMAM on the BP surface allowed also to transfect the cells with a precursor miRNAs, showing great potential as a multifunctional material.

We highlighted the effective role of PAMAM in the coating of buckypaper scaffolds, that were able to generate suitable scaffolds for the growth of bone cells. **Keywords**: 3D Printing, PAMAM dendrimer, poly-lactic acid (PLA), scaffolds, microRNAs. Biomedicine



**Figure 1**: Schematic depiction of BPs enclosed within the 3D-printed device. The cells were seeded in the long wells designed on the upside face of the device. Confocal image of HEK-293T cells transfected with PAMAM-functionalized BP scaffold with FAM-labeled miRNA mimic (400X magnification). BCA protein assay of cells grown on BPs. (\*P<0.05 and \*\*P<0.01).



**Figure 2**: SEM images of human embryonic kidney HEK-293T cells, osteblasts (SAOS) and osteoclasts grown on pristine and PAMAM-functionalized buckypapers (scale bar  $10 \mu m$ ).

- 1. Price RL, Waid MC, Haberstroh KM, Webster TJ. 2003, Selective bone cell adhesion on formulations containing carbon nanofibers, Biomaterials, 24:1877-87
- 2. Hu L, Hecht DS, Grüner G. 2004, Percolation in transparent and conducting carbon nanotube networks, Nano Letters, 4:2513-2517
- 3. Correa-Duarte MA, Wagner N, Rojas-Chapana J, Morsczeck C, Thie M, Giersig M. 2004, Fabrication and biocompatibility of carbon nanotube-based 3D networks as scaffolds for cell seeding and growth, Nano Letters, 4:2233-2236

## Sorbtion and Desorbtion of Glycopeptide Antibiotics on the Surface of Nanocomposite PolyGraphene.

A.S. Botin,<sup>1,2,5,\*</sup> V.N. Buravtsev,<sup>5</sup> L.A. Baratova,<sup>3</sup> A.V. Timofeeva,<sup>3</sup> G.S. Katrukha,<sup>4</sup> I.I. Han,<sup>1</sup> T.S. Popova,<sup>2</sup>

<sup>1</sup> Institute of Biochemical Technology and Nanotechnology; Peoples' Friendship University of Russia, Moscow, Russia.

<sup>2</sup>N.V. Sklifosovsky Institute of Emergency Medicine, Moscow, Russia

<sup>3</sup> A.N. Belozersky Institute of Physico-Chemical Biology, Moscow State University, Moscow, Russia <sup>4</sup> G.F. Gause Research Institute of New Antibiotics, Russian Academy of Sciences, Moscow, Russia

<sup>5</sup> Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

#### Abstract:

It was discovered that expanded graphite -PolyGraphene (PG) obtained after hydrotermic treatment of modified graphite became to be able to interact as sorbent PG with glycopeptide antibiotics.

<u>Introduction.</u> In this work was studied the sorption properties of carbon material as an example of PolyGraphene (PG) concerning glycopeptide antibiotics clinically important groups, as well as study conditions desorption from PG of antibiotics of this group.

PG - version of ultrafine carbon sorbent, which was developed on the basis of the modified oxygen-containing expanded graphite (OCEG). PG is a potential sorbent for the separation of the antibiotic from the culture medium producing strain after the fermentation process. Originally studied sorption characteristics of PG with respect to antibiotics-standards as an example of clinically important glycopeptide (Vancomycin-Ristomycin) group to which are known antibiotics vancomycin, ristomycin, teicoplanin A2, ehremomitcin. The interest to antibiotics of this group is steadily increasing, it is associated with a sufficiently high their stability with respect to MDR Gram-positive microorganisms such as: Methicillin Resistant Staphylococus Aureus (MRSA), Methicillin Resistant Staphylococcus epidermidis (MRSE), Clostridium difficile, enterococcs, pneumococcs, and others, SO antibiotics -glikopeptids become indispensable in the treatment of infections caused by these microorganisms.

Sorption of antibiotics–glykopeptides on PG. Technological feature of PG as sorbent is need of filling of its openwork structure with solution in which tests were carried out it.

Follows from the obtained data that antibioticsglikopeptides possess ability to be occluded on PG in the chosen conditions. And the quantity of a sorbed antibiotic increases with increase in time of sorption.

For an eremomitsin, a vankomitsin and a teykoplanin the liquid phase of a sorbent served in all experiments as "transit area" - the antibiotic was immobilized on a carbon matrix and its share in a liquid phase of a sorbent didn't exceed 23% of all mass of the antibiotic accumulated on a sorbent. Thus, during the conducted research high sorption ability of a new sorbent of PG concerning a number of antibiotics-glikopeptides for the first time is established.

<u>Desorption of antibiotics from PG.</u> It is established that degree of a desorption of antibiotics from PG depends on properties of organic solvent and also on structure of the analyzed antibiotic. It is shown that antibiotics, stripped from PG, keep the physical and chemical properties and antibacterial activity. The obtained data by results of researches on sorption and a desorption allow to claim that PG can be used in practice of allocation of antibiotics – polypeptides from solutions.

<u>Conclusions.</u> Researches have the theoretical and practical importance, the received results can be applied both in screening new antibiotics, and at allocation and cleaning of already known antibiotics in production.

**Keywords**: PolyGraphene, sorption, desorption, glycopeptide antibiotics.

## Novel ultrashort self-assembling peptide bioinks for 3D culture of muscle myoblast cells

Wafaa Arab1, Sakandar Rauf1, Ohoud Al-Harbi2, Charlotte A. E. Hauser1\*

<sup>1</sup> Laboratory for Nanomedicine, Division of Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
<sup>2</sup> Electron Microsoften and Characterization Core Lab King Abdullah University of Science

<sup>2</sup> Electron Microscopy, Imaging and Characterization Core Lab, King Abdullah University of Science and Technology, Thuwal, KSA

## Abstract:

The ability of skeletal muscle to self-repair after a traumatic injury, tumor ablation, or muscular disease is slow and limited, and the capacity of skeletal muscle to self-regenerate declines with age. Tissue engineering of steeply functional skeletal muscle using 3D bioprinting technology is promising for creating tissue constructs that repair and promote regeneration of damaged tissue. Hydrogel scaffolds used as biomaterials for skeletal muscle tissue engineering can provide chemical, physical and mechanical cues to the cells in three dimensions thus promoting regeneration. Herein, we have developed two synthetically designed novel tetramer peptide biomaterials. These peptides are self-assembling into a nanofibrous 3D network, entrapping 99.9% water and the mimicking native collagen of an extracellular matrix. Different biocompatibility assays including MTT, 3D cell viability assay, cytotoxicity assay and live-dead assay confirm the biocompatibility of these peptide hydrogels mouse myoblast cells for (C2C12). Immunofluorescence analysis of cell-laden hydrogels revealed that the proliferation of C2C12 cells was well-aligned in the peptide hydrogels compared to the alginategelatin control. These results indicate that these peptide hydrogels are suitable for skeletal muscle tissue engineering. Finally, we tested the printability of the peptide bioinks using a commercially available 3D bioprinter. The ability to print these hydrogels will enable future development of 3D bioprinted scaffolds containing skeletal muscle myoblasts for tissue engineering applications.

**Keywords**: biomaterials; bioinks; 3D cell culture; 3D scaffold; tissue engineering; skeletal muscle cells.



**Figure 1**: Overlaid confocal fluorescence images of mouse myoblast cells encapsulated in peptide (4 mg/mL CH-01 and 3 mg/mL; CH02) and alginate-gelatin (1:1) hydrogels. The encapsulated cells were cultured for different days and finally analyzed using fluorescence confocal microscopy (Nucleus shown in blue, F-actin shown in red and vinculin in green). (A) Mouse myoblast cells cultured on tissue culture plate (TCP). Alginate-gelatin (B, C, D), CH-01 (E, F, G), and CH-02 (H, I, J) at day 2, 4, and 8, respectively. Scale bar is 20 µm.

## **References:**

 Hauser C A, Zhang, 2010, Designer selfassembling peptide nanofiber biological materials, 2010, Chem Soc Rev, 39(8): 2780–2790.

http://dx.doi.org/10.1039/B921448H.

 Sundaramurthi D, Rauf S, Hauser C A, 2016, 3D bioprinting technology for regenerative medicine applications. Int J Bioprint, 2(2): 117–135. http://dx.doi.org/10.18063/ IJB.2016.02.010.

## Incorporation of microgels in PLA monofilaments by wet spinning

Georg-Philipp Paar,<sup>1,2,\*</sup> Peter Reitzenstein<sup>1,2</sup>, Catalina Molano-López,<sup>3</sup> Andrij Pich,<sup>3</sup> Thomas Gries,<sup>2</sup> Stefan Jockenhoevel,<sup>2</sup> Andreas Blaeser<sup>1,2</sup>

<sup>1</sup> Dept. of Biohybrid & Medical Textile (BioTex), AME-Applied Biomedical Engineering, Helmholtz Institute Aachen, RWTH Aachen University, Aachen, Germany
<sup>2</sup> Institut für Textiltechnik of RWTH Aachen University, Aachen, Germany
<sup>3</sup> DWI-Leibniz Institute for interactive materials

### Abstract:

Biodegradable materials, such as polyglycolic acid (PGA) and polylactic acid (PLA), are used in medicine commercially for sutures. osteosynthesis systems and drug delivery systems. Furthermore filaments of the mentioned materials are commonly used for meshes and engineering tissue scaffolds. By using biodegradable materials for implants a second operation for implant removal and long-term foreign body reactions are prevented. In vivo degradation of PGA and PLA by hydrolysis results in release of degradation products, which can cause local acidosis and lead to dramatic clinical complications.

In the past, buffering of the pH drop by incorporation of various additives (e.g. caffeine, tricalcium phosphate, calcium hydroxide, calcium carbonate, magnesium hydroxide, magnesium oxide) into PGA filaments failed due to insufficient buffering capacity and instabilities in the spinning process [1]. However, amine based microgels were shown to be a successful buffering agent for acidic degradation products [2,3]. These pH-responsive colloidal polymer networks are heat sensitive and therefore have to be incorporated into filaments using solution spinning.

Dry spinning of PLA filaments with up to 10 wt.% of microgels was possible and buffering of the pH value successful. However dry spun PLA monofilaments are inferior because tensile strength is low and variation of tensile strength is high. This may result from kidney shaped cross section, which is characteristic for dry spun filaments.

Wet spinning showed to be a promising alternative solution spinning process, which allows production of PLA filaments with round cross section and increased tensile strength.

In wet spinning trials monofilaments were extruded from PLA/chloroform solution into

isopropanol. The influence of varied quantities of incorporated microgels on the mechanical characteristics of the filaments is evaluated by light microscopy and tensile testing.

**Keywords**: pH neutral degradation, polylactide, polyglycolide, microgels, wet spinning.

### **References:**

- 1. Schuster, P. (2014) Schmelzgesponnene Polyglykolid-Fasern mit pH-optimiertem Abbauverhalten, *Dissertation*, Shaker
- 2. Poggenburg, B., Fehér, K., Gries, T., Jockenhoevel, S. (2014) : Neutral abbaubare Polylactid-Fasern als Plattformtechnologie für innovative Medizinprodukte, *Kunststoffe in der Medizintechnik*, 139-152
- 3. Fehér, K., Romstadt, T., Böhm, C.A., Kolkenbrock, M., Blau, M.F., Molano-Lopez, С., Pich, A., Hannen, J., Bürgermeister, L., Schaaps, N., Vogt, F., Gries, T., Jockenhoevel, S. (2015) Microgelfunctionalised fibres with pH-optimised degradation behaviour – a promising approach medical for short-term applications, BioNanoMaterials, 16

## Acknowledgement

The Project "pHMed" is supported by the European Regional Development Fund North Rhine-Westphalia (EFRE.NRW).

## Bacterial Cellulose Membrane with Functional Properties

Andreia S. Monteiro<sup>1\*</sup>, Rafael R. Domeneguetti<sup>1</sup>, Michel Wong Chi Man<sup>2</sup>, Hernane S. Barud<sup>3</sup>, Carole Carcel<sup>2</sup> and Sidney J. L. Ribeiro<sup>1</sup>

<sup>1</sup> Institute of Chemistry- São Paulo State University – UNESP – Araraquara-SP, Brazil
<sup>2</sup> Institut Charles Gerhardt, Montpellier, UMR 5253 CNRS-ENSCM-UM, France
<sup>3</sup> University of Araraquara – Uniara – Araraquara –SP, Brazil

## Abstract:

Over the last decades, the design of high performance functional substrates with enhanced properties has been the subject of intense research, offering promising improvements in a plethora of scientific and technological areas.

Bacterial cellulose (BC) is secreted by a few strains of bacteria and consists of a cellulose nanofiber network with unique characteristics. Because of its excellent mechanical properties, outstanding biocompatibilities, and abilities to form porous structures, BC has been studied for a variety of applications in different fields, including the use as a biomaterial for scaffolds in tissue engineering. To extend its applications, BC is normally modified to enhance its properties [1,2].

This work reports the preparation of Bacterial Cellulose Membrane (BCM) with functional properties, namely cleaning properties (Easy-Cleaning and Self-cleaning properties). Initially, mesoporous silica nanoparticles functionalized with alkoxysilanes with easy-cleaning properties (SNs@F) and anatase SiO<sub>2</sub>@TiO<sub>2</sub> spherical nanocomposites with self-cleaning properties prepared. Subsequently, were these nanomaterials were incorporated into BCM, following two different methodologies: in situ and post-grafting. For in situ functionalization of BCM, the culture medium (CM) composition was charged with nanomaterials. In the case of postgrafting functionalization BCM was firstly prepared in culture and then modified (figure 1).

**Keywords**: Functional Bacterial Cellulose Membrane; Easy-Cleaning Properties; Self-Cleaning Properties; Anatase SiO<sub>2</sub>@TiO<sub>2</sub> nanocomposites; Photocatalytic Activity; Hybrid Mesoporous Silica Nanoparticles



**Figure 1:** Schematic representation of the preparation of bacterial cellulose membrane with easy-cleaning properties

- Pinto, E. R. D., Barud, H. S., Silva, R. R., Palmieri, M., Polito, M. L., Calil, V. L., Cremosa, M., Ribeiro, S. J. L., Messaddeq, Y., J. (2015), Transparent composites prepared from bacterial cellulose and castor oil based polyurethane as substrates for flexible OLEDs, *J. Mater. Chem. C*, 3, 11581-11588.
- Barud, H. S., Assunção, R. M. N., Martines, M. A. U., Dexpert-Ghys, J., Marques, R. F. C., Messaddeq, Y., Ribeiro, S. J. L. (2008), Bacterial cellulose-silica organic-inorganic hybrids, *J. Sol-Gel Sci. Technol.*, 46, 363-367

## EGF 2018 / SMS 2018 Plenary session I

## Towards future applications of graphene and other 2D materials - The Technology and Innovation Roadmap (TIR) of the Graphene Flagship

## T. Reiss<sup>1,</sup>

<sup>1</sup> Fraunhofer Institute for Systems and Innovation Research ISI, Karlsruhe, Germany

#### Abstract:

The Technology and Innovation Roadmap (TIR) within the Graphene Flagship aims to guide the community towards the development of products based on graphene and related 2D material (GRM). The TIR goal is to outline the principle rules to develop the GRM knowledge base, the means of production, and development of new devices, aiming at a final integration of GRM into systems. The contribution will illustrate the TIR approach and provide an overview of promising applications in key target markets: composites and coatings, electronics and photonics, biomedicals, and energy generation and storage. In addition, future value chains based on GRM for selected applications in energy storage - batteries and supercapacitors - will be discussed.

## Germanene: graphene's little sister

H.J.W. Zandvliet,1

<sup>1</sup> Physics of Interfaces and Nanomaterials and MESA<sup>+</sup> Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

### Abstract:

Germanene, the germanium analogue of graphene, is in many aspects very similar to graphene, but in contrast to the planar graphene lattice, the germanene honeycomb lattice is slightly buckled and composed of two vertically displaced sub-lattices [1]. Frist principles total energy calculations have revealed that freestanding germanene is a two-dimensional Dirac fermion system, i.e. the electrons behave as massless relativistic particles that are described by the Dirac equation, i.e. the relativistic variant of the Schrödinger equation.

Recently, it has been shown that germanene can be synthesized on various substrates, including  $MoS_2$  and  $Ge_2Pt$  [2-4]. As predicted germanene's honeycomb lattice is indeed buckled and the experimentally measured density of states exhibits a V-shape, which is one of the hallmarks of a two-dimensional Dirac system. Spatial maps of the Dirac point of germanene synthesized on  $MoS_2$  reveal the presence of charge puddles, which are induced by charged defects of the underlying substrate.

**Keywords**: germanene, scanning tunneling microscopy and spectroscopy, two-dimensional Dirac materials, charge puddles.



**Figure 1**: Scanning tunneling microscopy image (4.5 nm by 4.5 nm) of buckled honeycomb lattice of germanene. Sample bias -0.5 V, tunnel current 0.2 nA.

- 1. A. Acun et al. J. Phys. Cond. Mat. 27, 443002 (2015) and references therein.
- 2. P. Bampoulis et al. J. Phys. Cond. Mat., 26, 442001 (2014).
- 3. L. Zhang et al., *Appl. Phys. Lett.* **107**, 111605 (2015).
- 4. L. Zhang et al. *Phys. Rev. Lett.* **116**, 256804 (2016).
## Graphene Oxide Liquid Crystal and Relevant Functional Nanoscale Graphene Assembly

## Sang Ouk Kim\*

<sup>1</sup> National Creative Research Initiative Center for Multi-dimensional Directed Nanoscale Assembly, Department of Material Science & Engineering, KAIST, Daejeon 34141, Republic of Korea

## Abstract:

Graphene Oxide Liquid Crystal (GOLC) is a newly emerging graphene based material, which exhibits nematic type colloidal discotic liquid crystallinity with the orientational ordering of graphene oxide flakes in good solvents, including water. Since our first discovery of GOLC in aqueous dispersion <sup>[1]</sup>, this interesting mesophase has been utilized over world-wide for many different application fields, such as liquid crystalline graphene fiber spinning, highly ordered graphene membrane/film production, prototype liquid crystal display and so on <sup>[2-4]</sup>. Interestingly, GOLC also allow us a valuable opportunity for the highly ordered molecular scale assembly of functional nanoscale structures. This presentation will introduce our current status of GOLC research particularly focusing on the nanoscale assembly of functional nanostructures. Besides, relevant research works associated to the nanoscale assembly and chemical modification of various nanoscale graphene based materials will be presented <sup>[5,65]</sup>.

**Keywords**: graphene, liquid crystal, fiber, assembly, graphene oxide, membrane, film



**Figure 1**: GOLC in aqueous dispersion can be highly ordered into fiber structure by cost effective wet spinning. SEM cross-sectional image (left) and optical microscopy image of of highly aligned GOLC fiber between crossed polarizers (right).

## **References:**

 J. E. Kim, T.H. Han, S.H. Lee, J.Y. Kim, C.W. Ahn, J.M. Yun, S.O. Kim, *Angewandte Chemie International Edition* 50, 3043 (2011).

- R. Narayan, J.E. Kim, J.Y. Kim, K.E. Lee, S.O. Kim, *Advanced Materials* 28, 3045 (2016).
- 3. J.Y. Kim, S.O. Kim, *Nature Materials* **13**, 325 (2014).
- S. P. Sasikala, J. Lim, I. Kim, H. J. Jung, T. Y. Yun, T. H. Han, S. O. Kim, *Chemical Society Reviews* 47, 6013 (2018).
- U. N. Maiti, W. J. Lee, J. M. Lee, Y. T. Oh, J. Y. Kim, J. E. Kim, J. W. Shim, T. H. Han, S. O. Kim, *Advanced Materials* 26, 40 (2014).
- 6. S. H. Lee, D. H. Lee, W. J. Lee, S. O. Kim, *Advanced Functional Materials* **21**, 1338 (2011).

## Reversible generation of large retractive tensile forces in isometric chemo-mechanical actuators composed of nanocomposite hydrogels and aqueous NaCl solutions

K. Haraguchi,<sup>1\*</sup> Y. Kimura,<sup>1</sup> S. Shimizu<sup>1</sup>

<sup>1</sup>Nihon University, College of Industrial Technology, Department of Applied Molecular Chemistry, Narashino, Chiba, Japan

## Abstract:

Transparent Chemo-mechanical systems that transform chemical directly energy into mechanical energy have attracted significant attention due to their simple structures and mechanical-power-generating efficiencies. These systems are utilized in many fields such as artificial muscles, soft robots, smart valves, sensors, and drug-release technology. The most important factor in constructing an effective soft actuator is the generation of sufficiently large mechanical force and/or deformation to meet the needs of the application, preferably with excellent responsiveness, reversibility, and repeatability. However, it is difficult for polymer hydrogel actuators to satisfy each requirement.

Herein, we report a new nanocomposite hydrogel (NC gel)/stimulus system capable of generating high mechanical forces comparable to human muscle.<sup>1</sup> That is, the large mechanical forces were generated in muscle-like isometric actuator systems composed of stimuli-responsive NC gels and aqueous NaCl solutions. NC gels with poly(*N*-isopropylacrylamide)-clay (PNIPA-clay) network structures exhibit high mechanical toughnesses and reversible swelling/deswelling behavior in the absence/presence of NaCl. NC gels constrained to constant lengths in brine generate enhanced contractive forces due to the salt-induced coil-to-globule transitions that are more than ten times larger than those induced thermally.<sup>2</sup> A retractive tensile force (4 N/170 kPa), comparable to that of human muscle, was repeatedly generated at 20 °C using an appropriately composed NC gel, and by alternating the NaCl concentration between 0 and 5 M. This phenomenon is attributed to the combined effects of enhanced deswelling behavior resulting from the salt-induced coil-toglobule transition of PNIPA and the high stiffness of the deswollen gel due to the NaClstrengthened PNIPA-clay network.

**Keywords**: force generation, reversible process, nanocomposite hydrogel, muscle-like actuator, coil-to-globule transition, salt-induced transition,



**Figure 1**: Figure illustrating the large cyclic force profiles (red) for the NC2-m2 gel obtained by alternating  $C_{NaCl}$  in the surrounding aqueous solution between 5 M (40 min) and 0 M (20 min) at 20 °C, and the force profile (blue) for the NC2-m2 gel with alternating temperature (20–50 °C).

- Haraguchi, K., Kimura, Y., Shimizu, S. (2018) Reversible generation of large retractive tensile forces in isometric chemomechanical actuators composed of nanocomposite hydrogels and aqueous NaCl solutions, *Soft Matter*, 14, 927-933.
- Haraguchi, K., Taniguchi, S., Takehisa, T. (2005) Reversibel force gneraton in a temperature-responsive nanocomposite hydrogel consisting of poly(*N*-isopropyl acryl amide) and Clay, *Chem. Phys. Chem.*, 6, 238-241.

## Biomimetic approaches targeting dairy fouling mitigation of stainless steel

M. Jimenez<sup>1\*</sup>, S. Zouaghi<sup>1</sup>, M. Barry<sup>2</sup>, S. Bellayer<sup>1</sup>, S. Moradi<sup>3</sup>, S.G. Hatzikiriakos<sup>3</sup>, T. Dargent<sup>4</sup>, V. Thomy<sup>4</sup>, Y. Coffinier<sup>4</sup>, C. André<sup>1</sup>, M.A. Grunlan<sup>2</sup>, G. Delaplace<sup>1</sup>

<sup>1</sup> Université de Lille, Unité Matériaux et Transformations (UMET), UMR 8207, F-59000 Lille, France <sup>2</sup> Texas A&M University, Department of Biomedical Engineering, 5045 Emerging Technologies Building, 3120 TAMU, College Station, USA.

<sup>3</sup> The University of British Columbia, Chemical and Biological Engineering Department, V6T-1Z3Vancouver, BC, Canada

<sup>4</sup> Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), UMR 8520, F-59000 Lille, France

## Abstract:

Fouling is an ongoing issue in dairy industries, where thermal treatments are essential to ensure food safety and extend the products' shelf-life. The heat-induced accumulation of proteins and minerals on the equipment walls impairs the proper execution of thermal treatments. It also burdens the processes' cost and environmental impact through production loss and heavy water and chemical use (clean-in-place procedures). Fouling control would then allow to progress toward less expensive and more eco-responsible processes. Modification of the surface properties of stainless steel is one possible pathway toward fouling mitigation, as it would impact the interactions at the substrate/fluid interface. Previous research showed that, in isothermal conditions, control of protein adhesion on stainless steel was crucial to fouling limitation<sup>1</sup>.

This work presents the antifouling behaviour of several innovative and bioinspired surfaces targeting fouling reduction - namely atmospheric plasma-sprayed silane-based thin films<sup>2</sup>, femtosecond laser textured lubricated slippery surfaces<sup>3</sup> and amphiphilic coatings - designed through cutting-edge technologies. Fouling tests were conducted on a pilot scale pasteurization plant fed with a model whey protein and calcium solution. Tested samples were placed in isothermal holding-like conditions. Detailed characterizations of the substrates before and after fouling test allowed connecting their surface properties to their antifouling properties.

The antifouling performances of the engineered surfaces were all interesting, as, on the one hand both the slippery surfaces and the plasma coatings showed great fouling-release properties (-100% wt. and -90% wt. of fouling compared to stainless steel after a simple water rinse). On the other hand, the amphiphilic Si-PEO coatings exhibited outstanding antifouling properties and stayed perfectly clean for 5 consecutive 1.5 h pasteurization (Figure 1).

**Keywords**: dairy process, antifouling coatings, biomimetism, atmospheric plasma, liquid infused surfaces, stainless steel, amphiphilic, protein



**Figure 1**: Antifouling effect on heat exchanger plate covered with Si-PEO amphiphilic coating (n°8) compared to untreated plates

### **References:**

- 1. Zouaghi S. et al. (2018) , Influence of stainless steel surface properties on whey protein fouling under industrial processing conditions, *Journal of Food Engineering*, 228, 38-49.
- 2. Zouaghi S. et al. (2018) Atmospheric pressure plasma spraying of silane-based coatings targeting whey protein fouling and bacterial adhesion management, *Applied surface science*, 455, 392-402.
- 3. Zouaghi, S. et al. (2017) Antifouling Biomimetic Liquid-Infused Stainless Steel: Application to Dairy Industrial Processing, *ACS Appl. Mater. Interfaces*, 9, 26565-26573.

Acknowledgements: French national research agency (ANR-17-CE08-0032/ ECONOMICS)

## EGF 2018 - Session I Graphene Synthesis, Growth, Functionalization and Characterization

## Graphene vs. Heat Transfer: from thermally conductive nanomaterials to heat shealding under flame exposure

A. Fina, F. Carosio, G. Ferraro, M. Eleuteri, L. Maddalena, A. Di Pierro

Politecnico di Torino, DISAT department, Alessandria, Italy

## Abstract:

Graphene (single layer) is well known for its outstanding thermal conductivity. Despite the exploitation of graphene in bulk materials is still very much limited by its avaialbility, graphenerelated materials (GRM) such as multi-layer graphene and graphene nanoplatelets (GNP) are currently of high interest for the exploitation in thermally conductive materials. On the other hand, there is an increasing interest and need for thermally-conductive polymer-based materials, allowing the manufacturing of a range of heat exhangers, taking advantage of the corrosion resistance and ease of processing typical of polymers. While the combination of polymers and graphene-related materials into nanocomposites obvious, is quite the performances obtained are very variable and depend, among other paramenters, on nanoparticles size, defects, dispersion and processing. Furthermore, thermal conductivity in nanomaterials is strongly limited by the interfaces, each of those acting as a thermal resistance to the heat transfer. The first part of this talk will deal with recent research work in the preparation and properties of GRM polymer nanocomposites and nanopapers, as well as the functionalization of GNPs to produce molecular junctions acting as thermal bridges.

Surprisingly enough, GRM may also be used to deliver an heat shield in extreme conditions, for instance when a flame is applied onto the surface of a GRM-coated polymer foams. The second part of the talk will deal with recent results on the development of coating methods and the flame retardancy performance obtained with thin layers of graphene oxide or GNP onto soft polyrethane open foams, which may find applications in upholstered furniture, building insulation and transport.

**Keywords**: Graphene and related materials, thermal conductivity, nanocomposites, nanopapers, flame retardancy, flame resistance, heat shielding, polyurethane foams.

- Bernal M.M., Di Pierro A., Novara C., Giorgis F., Mortazavi B., Saracco G., Fina A. (2018). Edge-Grafted Molecular Junctions between Graphene Nanoplatelets: Applied Chemistry to Enhance Heat Transfer in Nanomaterials. ADVANCED FUNCTIONAL MATERIALS, 1706954.
- Di Pierro A., Saracco G., Fina A. (2018). Molecular junctions for thermal transport between graphene nanoribbons: Covalent bonding vs. interdigitated chains. COMPUTATIONAL MATERIALS SCIENCE vol. 142 p. 255–260
- Colonna S., Monticelli O., Gomez J., Novara C., Saracco G., Fina A. (2016). Effect of morphology and defectiveness of graphene-related materials on the electrical and thermal conductivity of their polymer nanocomposites. POLYMER, vol. 102, p. 292-300
- Tortello M., Colonna S., Bernal M.M., Gomez J., Pavese M., Novara C., Giorgis F., Maggio M., Guerra G., Saracco G., Gonnelli R., Fina A. (2016). Effect of thermal annealing on the heat transfer properties of reduced graphite oxide flakes: A nanoscale characterization via scanning thermal microscopy. CARBON, vol. 109, p. 390-401
- Carosio F., Maddalena L., Gomez J., Saracco G., Fina A. (2018) Graphene Oxide Exoskeleton to Produce Self-Extinguishing, Nonignitable, and Flame Resistant Flexible Foams: A Mechanically Tough Alternative to Inorganic Aerogels, ADV. MATER. INTERF. In press
- Fina A., Colonna S., Maddalena L., Tortello M., Monticelli O. (2018) A facile and low environmental impact approach to prepare thermally conductive nanocomposites based on polylactide and graphite nanoplatelets. ACS SUSTAINABLE CHEMISTRY AND ENGINEERING, in press

# Coordination chemistry of metal-containing molecules with graphene-based materials and their catalytic applications

## Sungjin Park<sup>1</sup>

<sup>1</sup> Department of Chemistry and Chemical Engineering, Inha University, Republic of Korea

## Abstract:

Chemical designing on nano-materials in molecular level would be a promising route to create new hybrid materials and to control various properties of nano- and molecular materials. Organometallic compounds have been a center of molecular catalysts with preeminent catalytic activity and selectivity in a wide range of chemical transformations. As carbon-based nanomaterials, such as graphene-based materials, carbon nanotubes, and carbon nitrides, are sterically bulky, and they exhibit a wide spectrum of electrical properties, they can dramatically tune the catalytic behavior of transition metalactive species. Hybridization based of organometallic complexes with graphene-based materials can give rise to enhance catalytic performances. In this presentation, I will discuss my recent research activities on the fundamental chemistry of carbon-based nano-materials as well as catalytic applications.

**Keywords**: Chemically modified graphenes, organometallic complexes, catalysts, heterogenous catalysts, coordination, surface



**Figure 1.** A scheme to reduce oxygen using Cobased molecular active species generated on the N-doped graphene-based materials

## **References:**

 Kim, S., Jang, D., Lim, J., Oh, J., Kim, S. O., Park, S. (2017) Co-based active species molecularly immobilized on carbon nanotubes for oxygen reduction reaction. *ChemSusChem* 10, 3473-3481.

 Han, J, Sa, Y. J., Shim, Y., Choi, M., Park, N., Joo, S. H., Park, S. (2015) Coordination chemistry of Co(acac)<sub>2</sub> with N-doped graphene: Implications for oxygen reduction reaction reactivity of organometallic Co-O<sub>4</sub>-N species. *Angew. Chem. Int. Ed.* 54, 12622-12626.

## Cristallization path of CVD graphene on Ge(001) substrate

L. Di Gaspare,<sup>1,</sup> L. Persichetti,<sup>1</sup> F. Fabbri,<sup>2</sup> A. Sgarlata,<sup>3</sup>,M. Fanfoni,<sup>3</sup> A. Notargiacomo,<sup>4</sup> A. M. Scaparro,<sup>1</sup> V. Miseikis,<sup>2</sup> C. Coletti,<sup>2</sup> and M. De Seta,<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze, Università Roma Tre, Viale G. Marconi, 446- 00146 Rome, Italy <sup>2</sup>Center for Nanotechnology Innovation @NEST, Italian Institute of Technology, Piazza San Silvestro 12, 56127 Pisa, Italy

<sup>3</sup>Dipartimento di Fisica, Università di Roma "Tor Vergata," Via della Ricerca Scientifica, 1-00133 Roma, Italy

<sup>4</sup>Institute for Photonics and Nanotechnology, CNR, Via Cineto Romano 42, 00156 Rome, Italy

### Abstract

"Real-world" technological applications of graphene opto-electronics with full in exploitation of its innovative properties still need a further improvements of graphene quality and the achievement of CMOS-compatible metal contamination-free graphene. To this end, CVD graphene grown directly on Ge substrates can represent a significant advancement toward the full compatibility with CMOS-technology. As for the graphene grade, in particular using Ge as substrate, the influence of the temperature and the early stage of nucleation should be further investigated to shed light on the main mechanism involved in the crystallization process and on their influence on the graphene properties and quality.

In this work we investigated the early stage of the CVD growth o graphene on Ge(001) by a combined use of m-Raman and x-rav photoelectron spectroscopies, and scanning tunnelling microscopy and spectroscopy. We identified, at the early stage of the growth, the carbon precursor phase to graphene nucleation made of C atoms and/or CH<sub>x</sub> aggregates. The C precursor phase evolves in graphene domains through a crystallization process that in turn results in the formation of a uniform single layer graphene (SLG). The nucleation of the small graphene domains is accomplished by the Ge surface "proto-faceting" that evolves in the characteristic Ge nano-faceting of SLG on Ge(001) with the exposure of the same  $\{107\}$ -{1010} facets at all the stage of the crystallization process. The influence of growth temperature on the crystallization process of graphene film is also investigated. We found that graphene quality depends dramatically on the temperature revealing a strong interplay among nanofaceting, temperature and healing of graphene defects.

**Keywords**: CVD, Graphene, Germanium, early stage of gowth.



**Figure 1**: Scheme of the cristallization process of graphene on Ge(001) substrate.

- 1. Lee, J. et al. (2014) Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium, *Science*, 344, 286–289
- 2. Wang, G.; et al. (2013) Direct Growth of Graphene Film on Germanium Substrate, *Sci. Rep.* 3, 2465.
- 3. A. M. Scaparro et al. (2016) Investigating the CVD Synthesis of Graphene on Ge(100): toward Layer-by-Layer Growth, ACS Applied Materials and Interfaces 8, 33083-33090.
- L. Di Gaspare et al. (2018) Early stage of CVD graphene synthesis on Ge(001) substrate, *Carbon* 134, 183-188.

## Spontaneous deformations of carbon nanotubes: twisting and shrinking

A. Pérez-Obiol,<sup>1\*</sup> V. Jakubský,<sup>2</sup>

<sup>1</sup>Kochi University of Technology, Laboratory of Physics, Kochi, Japan <sup>2</sup>Nuclear Physics Institute, Department of Theoretical Physics, Řež, Czech Republic

## Abstract:

Carbon nanotubes are one of the most promising materials for the future of electronic devices. Their electronic properties are intimately related to their shapes and mechanical deformations, allowing them to be either semiconductors or conductors. In particular, at low enough temperatures, spontaneous deformations might modify their electronic gap. This phenomenon, known as Peierls instability, has been studied for Kekulé deformations, showing that a gap opens for metallic nanotubes. We investigate the twisting and shrinking of single-wall carbon nanotubes at zero temperature. Using a tightbinding model with deformation-dependent hopping energies, we show that all nanotubes tend to shrink about 3%, while all but symmetric nanotubes twist a few radians every 10 micrometers. All carbon nanotubes of radiuses between half and one nanometer have been considered. Figure 1 illustrates the explicit values of the deformation parameters for each one of these carbon nanotubes, labeled according to their chirality (n, m). We have also studied how these spontaneous deformations affect the electronic properties of the nanotubes. In particular, the changes of the spectral gap associated with the twisting and shrinking are shown to depend on the chirality of the nanotubes.

**Keywords**: carbon nanotubes, spontaneous deformations, electronic properties, tight-binding model, chirality.

- Mintmire, J. W., Dunlap, B. I., White, C. T. (1992) Are fulleren tubules metallic?, *Phys. Rev. Lett* 68, 631.
- Jakubsky, V., Pérez-Obiol, A. (2017) Spontaneous twisting and shrinking of carbon nanotubes, *Phys. Rev. B95, 245431.*



**Figure 1**: Spontaneous twisting (top) and shrinking (bottom) of carbon nanotubes at zero temperature. All possible carbon nanotubes of radiuses between half and one nanometer are considered. Nanotubes with smaller radiuses and chiralities tend to twist more, and symmetric nanotubes stay non-twisted. The shrinking is about 3% in all nanotubes, varying very little with the chirality and the radius.

## TAO-DFT and Its Applications to Carbon Nanomaterials

## Jeng-Da Chai\*

Department of Physics, National Taiwan University, Taipei, Taiwan

## Abstract:

I will briefly describe thermally-assistedoccupation density functional theory (TAO-DFT) [1], the density functional approximations to TAO-DFT (TAO-DFAs) [2], the hybrid TAO-DFT schemes (i.e., the inclusion of exact exchange in TAO-DFT) [3], the self-consistent fictitious temperature scheme in TAO-DFT [4], and the applications of TAO-DFT to carbon nanomaterials (e.g., acenes, zigzag graphene nanoribbons, cyclacenes, PAHs, linear carbon chains, etc.) [5, 6, 7, 8, 9]. In contrast to Kohn-Sham density functional theory (KS-DFT), TAO-DFT is a density functional theory with fractional orbital occupations given by the Fermi-Dirac distribution (controlled bv а fictitious temperature), for the study of large electronic systems with strong static correlation effects. Due to its computational efficiency, TAO-DFT has been recently applied to the study of various carbon nanomaterials with strong static correlation effects (which are challenging systems for conventional electronic structure methods). Some interesting results will be presented.

**Keywords**: density functional theory, strong static correlation effects, carbon nanomaterials.

## **References:**

- 1. Chai, J.-D. (2012), Density functional theory with fractional orbital occupations, *J. Chem. Phys.*, 136, 154104.
- 2. Chai, J.-D. (2014), Thermally-assistedoccupation density functional theory with generalized-gradient approximations, *J. Chem. Phys.*, 140, 18A521.
- 3. Chai, J.-D. (2017), Role of exact exchange in thermally-assisted-occupation density functional theory: a proposal of new hybrid schemes, *J. Chem. Phys.*, 146, 044102.
- Lin, C.-Y., Hui, K., Chung, J.-H., Chai, J.-D. (2017), Self-consistent determination of the fictitious temperature in thermallyassisted-occupation density functional theory, *RSC Adv.*, 7, 50496-50507.
- 5. Wu, C.-S., Chai, J.-D. (2015), Electronic properties of zigzag graphene nanoribbons

studied by TAO-DFT, J. Chem. Theory Comput., 11, 2003-2011.

- 6. Yeh, C.-N., Chai, J.-D. (2016), Role of Kekulé and non-Kekulé structures in the radical character of alternant polycyclic aromatic hydrocarbons: a TAO-DFT study, *Sci. Rep.*, 6, 30562.
- Seenithurai, S., Chai, J.-D. (2016), Effect of Li adsorption on the electronic and hydrogen storage properties of acenes: a dispersioncorrected TAO-DFT study, *Sci. Rep.*, 6, 33081.
- 8. Wu, C.-S., Lee, P.-Y., Chai, J.-D. (2016), Electronic properties of cyclacenes from TAO-DFT, *Sci. Rep.*, 6, 37249.
- 9. Seenithurai, S., Chai, J.-D. (2017), Effect of Li termination on the electronic and hydrogen storage properties of linear carbon chains: a TAO-DFT study, *Sci. Rep.*, 7, 4966.

## Multilayered graphene grafted copper wires

Lee-Woon Jang<sup>1</sup>, Luman Zhang<sup>1</sup>, Mariela Menghini<sup>2</sup>, Hyunjin Cho<sup>3</sup>, Jun Yeon Hwang<sup>4</sup>, Dong Ick Son<sup>4</sup>, Jean-Pierre Locquet<sup>2</sup>, and JinWon Seo<sup>1\*</sup>

<sup>1</sup> KU Leuven, Department of Materials Engineering, Leuven, Belgium

<sup>2</sup> KU Leuven, Department of Physics and Astronomy, Leuven, Belgium

<sup>3</sup> Chonbuk National University, Department of Organic Materials and Fiber Engineering, Republic of Korea

<sup>4</sup> Korea Institute of Science and Technology, Institue of Advanced Composite Materials, Republic of Korea

### Abstract:

Graphene has various properties such as strong mechanical strength, high electrical conductivity, and chemical stability. It has been applied in the fields of energy, mechanics, and electronics. Recently, graphene grafted copper (Cu) wires have received great attention as an alternative functional structure that overcomes the limitation of Cu with low thermal and chemical resistance. High electrical and thermal conductivity of graphene has enabled thermally stable electronics and high-power devices [1]. Strong mechanical strength and chemical stability of graphene have facilitated the fabrication of mechanically reinforced composites and non-corrosive electrodes [2]. Potential applications of using graphene in ultra-fast electronics and lightweight conductors for aerospace have also been demonstrated [3]. However, despite application fields of graphene grafted Cu wires have markedly increased, detailed growth behavior of graphene on the wire structure has not been investigated extensively. Moreover, the influence of the graphene quality on the Cu wire performance and the degradation process of Cu during thermal and chemical treatments have not yet been reported in detail. In this study, we investigate the growth mechanism of graphene on Cu wires and their performance [4]. Sensitive growth parameters such as the reactor pressure and the surface morphology of Cu wires are controlled to obtain entirely covered graphene on Cu wires. The graphene growth is pursued by using acetylene and methane as carbon sources. The obtained graphene is analyzed and compared to identify the link to the chemical resistance, mechanical strength, thermal and electrical performances. Structural defects are identified as the main pathway of chemical etching and thermal oxidation, which strongly affect the performance of Cu wires. Our results demonstrate that the Cu wires with graphene grafting can overcome the initial limitation of oxidation and corrosion and can effectively

enhance mechanical, electrical as well as thermal properties and corrosion resistivity.

**Keywords**: multilayered graphene, graphene grafted copper wires, chemical vapor deposition, graphene quality, dynamic mechanical analysis, electrical property, thermal oxidation, chemical etching.



**Figure 1**: Schematic structure of the graphene grafted Cu wires and photographes illustrating the electrical, mechanical, and chemical analyses.

- 1. Mehta, R., Chugh, S., Chen, Z. (2015) Enhanced electrical and thermal conduction in grapheneencapsulated copper nanowires, *Nano Lett.*, 15, 2024-30.
- Kim, SJ., Shin, DH., Choi, YS., Rho, H., Park, M., Moon, BJ., Kim, YS., Lee, SK., Lee, DS., Kim, TW., Lee, SH., Kim, KS., Hong, BH., Bae, SK. (2018) Ultrastrong graphene-copper coreshell wires for high-performance electrical cables, *ACS Nano*, 12, 2803-2808.
- 3. Siochi, EJ. (2014) Graphene in the sky and beyond, *Nat Nanotechnol.*, 9, 745-7.
- Jang, LW., Zhang, L., Menghini, M., Cho, H., Hwang, JY., Son, DI., Locquet, JP., Seo, J. (2018) Multilayered graphene grafted copper wires, *Carbon*, in press, doi: 10.1016/j.carbon.2018.07.033.

## Grafting of polymer chains onto graphite oxide sheets : Towards the design of functional composites

Aline Guimont,<sup>1</sup> Abdelwaheb Dhahri,<sup>1,2</sup> Mohamed Hassen V Baouab,<sup>2</sup> Emmanuel Beyou<sup>1</sup>\*

<sup>1</sup>Ingénierie des Matériaux Polymères, CNRS UMR 5223, Université de Lyon, France, <sup>2</sup>Laboratoire de Microélectroniques et Instrumentations, Université de Monastir, Faculté des Sciences de Monastir, Monastir, Tunisia

## Abstract:

From an industrial application point of view, the most promising method for large scale production of graphene is based on the oxidation of graphite leading to graphite oxide (GO), which can subsequently be functionalized, followed by its reduction to restore electrical conductivity, if necessary. First the treatment of GO with polyethylene and chitosan (CS) through two main routes will be discussed as well as their characterization with the usual techniques (stability in solvent mixture (Figure 1), thermogravimetric analysis, etc...). Then, the polyethylene-grafted graphene oxide sheets were compounded at various contents in a polyethylene matrix and the corresponding composites were studied through electrical, rheological and electron microscopy measurements. In addition, the CS-grafted GO nanohybrid material was doped with gold nanoparticles and its catalytic activity was studied.

Rheological and electrical percolation thresholds were found between 10 and 15 wt% for polyethylene-functionalized graphene oxide composites while the graphite/PE composites at the same loading percentage did not reach any percolation threshold.

In addition, for Gold-based nanohybrids (Figure 2), it was found that this material exhibits a catalytic activity toward the reduction of nitrophenol to aminophenol.

The covalent functionalization of GO with polymer chains permits to ensure good dispersion of GO sheets in a polymer matrix ensuring improved electrical, mechanical and permeation properties of the corresponding composites.

**Keywords**: graphite oxide sheets, functionalization, polyethylene, chitosan, dispersion of fillers, electrical properties, catalytic activity.



**Figure 1**: Illustration of the effect of PE grafting onto the GO surface on the stability of dispersions in DMF/Heptane (50/50 v/v ;  $c = 0.36 \text{ mg.mL}^{-1}$ )



**Figure 2**: SEM images of gold nanoparticles adsorbed onto the surface of CS-grafted GO

- 1. Guimont A. Beyou E. Alcouffe P. (2013) Grafting of polyethylene onto graphite oxide sheets: a comparison of two routes *Polym*. *Chem.*,4, 2828-2835
- Dhahri A. Beyou E. Alcouffe P. Serghei A. Baouab M. (2016) Synthesis and characterization of Au-immobilized nanoparticles onto celluloseethylenediamine-grafted reduced graphite oxide, *Mat. Chem. Phys.*, 171, 303-311

## Towards Modified Graphene Oxide and Functional Derivatives for Industrial Applications

B. Gjoka,<sup>1\*</sup> R. Wendelbo,<sup>1</sup>

<sup>1</sup> Abalonyx As, Forskningsveien 1, 0373, Oslo, Norway

## Abstract:

Graphene and its functional derivatives (GO and rGO) have since their synthesis found a broad range of possible applications due to their remarkable chemical and physical properties.<sup>1</sup> graphene oxide, an oxidized Particularly, graphite sheet containing oxygen-type functionalities on the basal plane and on the edges, offers a unique opportunity to change the chemical and physical properties by modifying and engineering its surface.<sup>2,3</sup> Importantly, the excellent electrical and thermal conductivity of rGO has opened new possibilities in scientific fields such as electrochemistry, optics, capacitors and biological sensing. In this work graphene prepared was Hummer's oxide using methodology.<sup>4</sup> Subsequently, it was chemically modified using appropriate organic or inorganic molecules to further allow incorporation of the required material. This was done chemoselectively, in the presence of functional groups such as epoxy, hydroxyl on the surface and carbonyl and carboxylic groups on the edge. For example, GO is modified using an amino based polymer such as polyethyleneimine (PEI), covalently forming an amide with carboxylic acid groups on the edge of GO (Figure 1) leaving the other functional groups intact.<sup>5</sup> This route will provide efficiently; economically materials for carbon dioxide capture. Subsequent modification of rGO having different degree of oxygencontaining functionalities was also explored. This represents an excellent opportunity to fine tune the chemical and physical properties of the GO/rGO produced in order to confer to the subsequent material the desired properties e.g. thermal and electrical conductivity (rGO). Finally. we aim to combine different methodologies to characterize GO/rGO and their correspondent modified derivatives. In order to allow a systematic study of the morphological, structural and functionalization information of the GO and rGO materials, various techniques were employed such as FT-IR, SEM, XPS, XRD; NMR solid state, FT-Raman and TGA.

**Keywords**: Graphene oxide, reduced graphene oxide, functionalization, incorporation

organic/inorganic molecules, controlled oxygentype functionalities, characterization modified GO/rGO.



**Figure 1**: General scheme for GO functionalization with polyethyleneimine (PEI).

- 1. Chen, D., Feng, H., Li, J. (2012), Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications, *Chem. Review*, 112, 6027-6053.
- Loh, K.P., Bao, Q., Eda, G., Chhowalla M. (2012), Graphene oxide as a chemically tunable platform for optical applications, *Nat. Chem.*, 12, 1015-1024.
- Johnson, D.W., Dobson, B.P., Coleman. K. S. (2015), A manufacturing perspective on graphene dispersions, *Curr. Opin. Colloid Interface Sci.*, 367-382.
- 4. Hummers, W.S., Offeman, R.E. (1958) Preparation of Graphitic Oxide, *J. Am. Chem. Soc.*, 80, 1339.
- Chen, B., Liu, M., Zhang, L., Huang, J., Yao, J., Zhang. Z. (2011), Polyethylenimine-functionalized graphene oxide as an efficient gene delivery vector *J*. *Mater. Chem*, 21, 7736-7741.

## Synthesis of Multifunctional Graphene Based Nanocomposites for 3D Printing Applications

M. Soria Sánchez,<sup>1,\*</sup> G. Tobías Rossell,<sup>1</sup>

<sup>1</sup> Institute of Material Science of Barcelona, ICMAB (CSIC), Department of Solid State Chemistry, Bellaterra, Barcelona, Spain, <sup>\*</sup>msoria@icmab.es

#### Abstract

In recent years, several research groups and companies are working on finding new materials advanced properties with suitable for the development of 3D printed prototypes. Layered graphene is an emerging material for 3D printing<sup>1</sup> due to the combination of its impressive conductivity and the 3D nature of the printed structures, enabling the generation of high surface areas with good electrical properties and hierarchical pore structures. The main aim of this work is to study the impact of modified graphene nanoplatelets integrated in the structure of selected polymer matrix. The chemical modification of graphene is expected to improve its integration into commercially available polymers. An improved dispersion has a direct impact on the polymer/graphene interfacial interaction, which has shown to be a critical parameter for the stress transfer from the nanoparticles to the matrix.<sup>2,3</sup>

#### Experimental

Graphene nanocomposites have been synthesized through two different methods: 1. Direct intercalation of the previously reduced graphene oxide (rGO) into the polymer by exposing the filler to polymer molecules dissolved into appropriate solvents and, 2. Reduction "in situ" of the graphene oxide (GO) during the intercalation process. Hydrazine and ascorbic acid have been employed as reducing agents during these synthesis. Most common polymers like ABS, PLA and PCL has been used in this work. These graphene nanocomposites were prepared with a graphene loading of 3, 6, 9 and 12 wt%, in order to compare the mechanical and electrical properties before being used in 3D-printing. Extensive characterization of the synthesized materials has been carried out, including TGA, DSC, STEM, SEM, XPS or measurements of SAXS/WAXS with synchrotron radiation.

#### **Results and Discussion**

As can be seen in the Figure 1, the synthesis of graphene oxide (GO) and reduced graphene oxide (rGO) have been successfully carried out. Figure 2 shows raman spectra of ABS/RGO (3%) and PCL/RGO (3%) nanocomposites. As can be seen in these spectra, the integration of rGO into the polymer has been achieved, since the typical bands corresponding to the rGO as well as for the corresponding polymers can be observed in the graphs. Integration of the graphenic structures into

the rest of the polymers has been also achieved, which has also been evidenced by XPS spectra.



Figure 1: Raman spectra and TGA of the graphenic structures



Figure 2: a) Raman spectra of ABS and PCL nanocomposites

Thermal characterization of the composites show an increment in the decomposition temperature, which can be traduced like an increment in the thermal stability of the samples, attributed to the effect of the graphenic structures into the polymer which reinforces the polymeric structures due to the nucleation effect of the graphene in the composite. Complementary characterizaction of the samples has also established that nanocomposites with improved mechanical, thermal and electrical properties can be synthesized by adding graphene derivates into the polymer. So, it has been established that a well dispersed rGO renders not only improves properties in relation to strength and fracture toughness, but also conductivity of the composite, which it's not possible to get by adding GO. Future work will involve the extrusion of the nanocomposites filaments for being used in 3D printing.

#### **References:**

- 1. X. Wei1 et al., *Sci Rep.*, 5: 11181 (2015).
- 2. Tang, L.-C et al., Carbon, 60, 16-27 (2013).
- 3. Rafiee et al., ACS Nano, 3(12): 3884-3890 (2009).

#### Acknowledgments:

Authros would like to thank to the Marie Curie program –European Commission for the concession of the project 3D-Printgraph that has allowed the realization of this work.

# Controlled pore tuning on freestanding graphene using focused ion beam and electron beam induced platinum deposition

Timur Ashirov<sup>1</sup>, Doolos Aibek uulu<sup>2</sup>, Kemal Celebi<sup>3</sup>, Ali Coskun<sup>1</sup>

<sup>1</sup> University of Fribourg, Department of Chemistry, Fribourg, 1700, Switzerland
<sup>2</sup> Computer and Electrical Mathematical Science and Engineering, KAUST, Thuwal, 23955, KSA
<sup>3</sup> ETH Institute of Polymers, ETH Zurich, Zurich, 8093 Switzerland

## Abstract:

Since its discovery, graphene has been widely used in many potential applications. Being atomically thin, graphene has can be used for membranes with ballistic flow mechanics. FIB is a good tool for making uniform pores. However, for direct gas sieving or water desalination pores below 5 nm are required. Making such pores using FIB is challenging. For smaller pores fabrication TEM can be used, but it is limited to area and time consuming, which makes it not feasible for membrane applications. We have found an applicable way to tune pores below 5 nm using Pt electron beam induced deposition using FIB. Pt deposition reduces pore radius, controlling parameters will lead to pores below 5 nm.



Figure 1: (A) SEM image of transferred graphene sample onto SiNx frame, here 5x5 6 µm pores are fully covered with graphene without any tears. (B) Close look SEM image of one of the pores. (C) 52 ° tilted SEM image of single SiNx pore covered with graphene, tilted images provide better information about morphology of graphene. (D) SEM image of pore perforated graphene with FIB and Pt deposited at 0.40 nA using 1 µs dwell time and 100 passes to narrow down pores (Pt deposited site is indicated with Pt). (E-F) Close look SEM image of graphene pores perforated with FIB and tuned with Pt EBID. (G) High-angle annular dark-field scanning transmission electron microscope image (HAADF-STEM) of graphene pores opened with FIB and narrowed using Pt EBID. (H) HAADF-STEM image of single perforated graphene pore tuned with Pt deposition.

**Keywords**: graphene membranes, 2D materials, graphene transfer method, nanopores, controlled pore tuning, FIB, Pt electron beam induced deposition.

- K. S. Novoselov, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov. Electric Field Effect in Atomically Thin Carbon Films. Science 2004;306:666-669.
- K. Celebi, J. Buchheim, R.M. Wyss, A. Droudian, P. Gasser, I. Shorubalko, et al., Ultimate Permeation Across Atomically Thin Porous Graphene. Science. 2014;344:289–292.

## Carbon atomic structures promoting twisted growth of second Graphene layer at magic angles 21.78° and 27.8°.

G. Gawlik<sup>1\*</sup>, Z. Kozioł<sup>2</sup>, J. Jagielski<sup>1,2</sup>, P. Ciepielewski<sup>1</sup>.

<sup>1</sup> Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, POLAND,

<sup>2</sup> National Centre for Nuclear Research, A Soltana 7, 05-400 Otwock. POLAND.

\* Corresponding author: Email: grzegorz.gawlik@itme.edu.pl Tel.: +48 604618009; Fax: +48 (22) 864

54 96; Postal address: Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw,

Poland

### Abstract:

Graphene CVD growth on copper foil may leads to nucleation and growth of islands of second graphene layer or multiple graphene. There is frequently observed twisted orientation of the second and next layers of graphene regarding to the orientation of the graphene substrate layer at some fixed angles. Hexagonal shape of the graphene islands with very well defined straight allows observation edges and angles determination of such screwed multilayer structures by Scanning Electron Microscope (SEM) imaging. Two specific angles 21.780 and 27.80 of screwing of subsequently growing graphene layers were observed. Interaction between two atomic layers twisted at different angles were simulated on the basis of the Van der Waals force by summarizing attractive part of forces for each atom of the second layer. Two atomic configurations elementary were determined which revealed metastable positions twisted at exactly observed angles. Both structures are composed from one hexagon of carbon atoms with center located over carbon atom of the substrate layer and two carbon atoms attached to them in the form of diatomic chain in case of twisting at angle 21.780 or chain of three carbon atoms in case of twisting angle 27.80. Attaching of next two such chains of carbon atoms to the central hexagon stabilizes twisted position of such structure. However, subsequent attaching of next carbon atoms generally diminishes metastability the of twisted configuration. It should be pointed out that such elementary structures with metastable twisted position are periodically created during growth by attaching carbon atoms to the graphene edge because identical structures are arranged periodically over the entire surface of twisted graphene. Graphene layers of higher area consist of many elementary structures metastable at twisted position which may stabilize such twisted configuration. suggests It that twisted

configuration of second graphene layer is established after creation of some configuration of carbon atoms specific for each observed angle and then this angle is preserved during subsequent growth..

**Keywords**: graphene, multilayer, growth, twisted structure



**Fig.** Geometry of twisted graphene AB positioned carbon heksagon with attached carbon chains; a) twist angle  $27.8^{\circ}$  in case of three atoms chains, b) twist angle  $21.78^{\circ}$  caused by attached chains of two carbon atoms

## SMS 2018 - Session I Novel Materials, Micro/Nano Systems, Composite and Functional Materials

## Silicon-Carbon Films Synthesis by High-Frequency Deposition

Alexandr Temirov1,\*, Ilya Kubasov 1, Roman Zhukov1, Dmitry Kiselev, Mikhail Malinkovich1, Yurii Parkhomenko1

<sup>1</sup>National University of Science and Technology "MISiS", Moscow, Russia

## Abstract:

Silicon-carbon diamond-like thin films are a promising class of amorphous materials. Due to its unique physical properties – high hardness, low coefficient of friction, high chemical resistance and radiation resistance, they find an application in various fields of industry, mainly as protective coatings.

There are many methods of synthesis of diamondlike films. However, currently the development of new technologies is an important task.

This work presents a method of silicon-carbon films production by high-frequency deposition from the vapor mixture. This method is based on the diamond-like films synthesizing technology described by Parkhomenko et al.<sup>1</sup> Here we managed to resolve the main drawback of this technology - the uncontrollable amount of background impurities in the resulting films.

The specimens described in this work were investigated by atomic force microscopy and ESCA. The absence of background impurities in the samples, and the presence of the ratio of sp2 and sp3 links, typical for silicon-carbon films. The method of receiving allows creating doped silicon-carbon films with well-defined physical properties, primarily conductivity, eliminating the influence of background impurities.

The research was financially supported by the National University of Science and Technology "MISiS" (K2-009-2017).

**Keywords**: Silicon-carbon film, High Frequency Deposition, Protective coating, Diamond-like film.



Figure 1: Schematic view of an apparatus for growing doped silicon-carbon films

## **References:**

1. Yu. Parkhomenko, M. Malinkovich, E. Scryleva, M. Shupegin, (2005) Izvestia vuzov, 3, 12-16. (In Russian)

## Static Alignment of Polyvinylidene Fluoride nanofibers by electrospinning

M. Fawzy<sup>1,2</sup>, E. Elnabawy<sup>1</sup>, A. Hassanain1,3, N. Shehata,<sup>1,4,5,6 \*</sup>

<sup>1</sup>Center of Smart Nanotechnology and Photonics (CSNP), Alexandria University, Alexandria, Egypt <sup>2</sup>Department of Electrical Engineering, Faculty of Engineering, Alexandria University, Alexandria,

Egypt

<sup>3</sup>Department of Textile Engineering, Faculty of Engineering, Alexandria University, Alexandria, Egypt <sup>4</sup>Kuwait College of Science and Technology, Jahraa, Kuwait

<sup>5</sup>Faculty of Science, Utah State University, Logan, Utah, United States

<sup>6</sup>Department of Engineering Mathematics and Physics, Faculty of Engineering, Alexandria University, Alexandria, Egypt

## Abstract:

Piezoelectric polymer consider as highly flexible type of polymers which can be deformed by stretching, compression or bending resulting an orientation of net dipole moment of monomers into particular directions so that polling accurse. Polyvinylidene Fluoride (PVDF) and its copolymer have been intensively used for piezoelectric applications; with increasing relatively  $\beta$  phase content. Electrospinning is one of the most popular techniques for nanofiber (NF) fabrication [9-12], in which an increasing of  $\beta$  phase content can resulted through stretching of polymers at high electric filed that force the dipole moment to be aligned in specific direction so natural polling produced. Our work focuses on making a static alignment of the generated electrospun nanofibers based on 2 metallic bars of the collector side in design the electrospinning setup. A study of electrostatic field distribution, along with piezoelectric generated voltage has been analyzed under applied weights as mechanical stress with sensitivity up to 7.5 mV/g.

**Keywords**: piezoelectric, nanofibers, electrospinning, PVDF.



Figure 1: SEM image of aligned PVDF



Figure 2: Electric field distribution of 2-bars collector



**Figure 3**: Piezoelectric response of aligned PVDF nanofibers mat.

- 1. Baytekin, B., H.T. Baytekin, and B.A. Grzybowski, Retrieving and converting energy from polymers: deployable technologies and emerging concepts. Energy & Environmental Science, 2013. 6(12): p. 3467-3482.
- Karan, S.K., D. Mandal, and B.B. Khatua, Selfpowered flexible Fe-doped RGO/PVDF nanocomposite: an excellent material for a piezoelectric energy harvester. Nanoscale, 2015. 7(24): p. 10655-10666.

## Spinel MgFe<sub>2</sub>O<sub>4</sub> nanoparticles prepared by two way sol-gel method for photocatalytic application

A.Kurbanova, G.Demeuova, O.Mauit, M. Baisaryev, O.Ualibek, O.Toktarbaiuly, G.Sugurbekova

National Laboratory Astana, Nazarbayev University, Kabanbai batyr avenue 53, Astana, Kazakhstan

#### Abstract:

The following work is based on comparison of 2 sol gel methods for synthesis of spinel magnesium ferrite  $MgFe_2O_4$  nanoparticles, where target was to obtain nanoparticles with the maximum content of specified ferrites, uniform particles with high crystallinity for photodegradation application.

In the first method,  $MgFe_2O_4$  nanoparticles was synthesised by co-precipitation of magnesium and iron hydroxides by 2 steps: in the 1<sup>st</sup> step mixture of  $Mg(OH)_2$  and  $Fe(OH)_3$  with mole ratio 1:2 were co precipitated at pH 7 with ammonium carbonate; 2<sup>nd</sup> step based on drying at 80 °C followed by annealing at 600 °C. Isoelectric point (IEP) of this solution was achieved at pH 7.

The second sol-gel method is based on magnesium acetate and iron nitrate precursors. In this process, the sole evolves gradually towards the formation of a gel like network containing both a liquid phase and a solid phase. The experimental procedure of modified sol-gel method [1] consists of three stages: 1<sup>st</sup> stage is the preparatory stage, where chemicals are added and mixed together in the three neck round bottomed flask; 2<sup>nd</sup> stage is heating and stirring of the mixture for sol and gel formation using magnetic stirrer and hot plate; 3<sup>rd</sup> final stage is anneling at 400-600°C for growth of magnetic nanoparticles.

Structure and morphology of MgFe<sub>2</sub>O<sub>4</sub> nanoparticles were characterized by XRD and SEM. According to XRD pattern, 100% spinel ferrite with crystallinity of 77.6% has been achieved at pH=7.0, where zeta potential  $\xi$ =0.0002mV and annealing performed at 600°C. Also, SEM images showed the most uniform particle size distribution with crystallite size of 10-50 nm.Nanoparticles obtained using second method showed phase content of Fe<sub>2</sub>O<sub>3</sub> 23.8% and MgFe<sub>2</sub>O<sub>4</sub> 76.2% with crystallinity of 74.3%.

The photocatalytic activity of  $MgFe_2O_4$  was investigated by using photo-decomposition of methylene blue (MB) dye under solar light irradiation [2]. Total degradation of MB with  $MgFe_2O_4$  obtained from first method was achieved in 2 hours and 15 min at concentration 0.4 g/L of photocatalyst. It is one of the promising photocatalysts for waste water treatment.



**Figure 1**: Magnetic separation of MgFe<sub>2</sub>O<sub>4</sub> and photo degradation of MB with time.

This research was supported under the target program No 0115PK03029 "NU-Berkeley strategic initiative in warm-dense matter, advanced materials and energy sources for 2014-2018" from the Ministry of Education and Science of the Republic of Kazakhstan

**Keywords**: MgFe<sub>2</sub>O<sub>4</sub>, ferrite, sol-gel, isoelectric point, the points of of zero charge, pH, coagulation threshold, photodegradation, photocatalytic activity.

- 1. Lee Sanghoon. (2012) Ferrimagnetic MgFe<sub>2</sub>O<sub>4</sub> nanoparticles for intra-arterial hyperthermia agent applications, *PhD Thesis.*, National University of Singapore., 27-33.
- M. Shahid, L. Jingling, Z. Ali, Imran Shakir, M.F.Warsi, R. Parveen, M. Nadeem. Photocatalytic degradation of methylene blue on magnetically separable MgFe<sub>2</sub>O<sub>4</sub> under visible light irradiation, *Materials Chemistry and Physics* 139 (2013) 566-571

## Distributed control for a morphing wing with a macro fiber composite actuator

F. Svoboda,<sup>1</sup> M. Hromcik,<sup>1</sup>

<sup>1</sup> Czech Technical University in Prague, Department of Control Engineering, Prague, Czech Republic

## Abstract:

This work offers a new look at morphing wing control, where a dynamical model is represented as a set of agents and distributed control is used (Figure 1). The background theme of this work is the most important of all aeroelastic phenomena causing unstable self-excited vibrations of aeroelastic structures like a wing or aileron. This instability called flutter occurs above the critical (flutter) speed where at least one of the modes is no longer damped. Of course, aeroelasticity is relevant for the design of various structures including bridges, wind turbines, helicopter blades, etc. However, this work considers only flexible wing flutter. Flutter can take various forms involving different interacting modes and often leads to catastrophic structural failure. Reduction of structural weight to maximize efficiency and agility for modern aircraft also reduces stiffness and thereby increases the likelihood of flutter. A solution to this problem without structural modifications is active control. The general principle of active suppression approach is that available information is processed about unwanted movements of flexible parts which must be damped. Typically accelerations at a few points on a wing are measured, and control commands for dedicated aerodynamic surfaces are generated. Active flutter suppression systems become even more important with the new generation of light-weight materials and structures.

In the last 20 years, recent developments in SMART materials helped to examine a new concept of morphing wings. This new promising technology works with the idea of changing the enabling a mission-adaptive wing shape performance. Current conventional wings are usually designed for either a single cruise flight condition or by using a weighted combination of multiple flight conditions, and they are thus not optimal for a wide range of flight modes. wing geometry Continuous variable has significant efficiency, minimize drag, and it is silent compared to wings with conventional flaps with gaps producing a considerable noise source. Moreover, smart materials are removing energy conversions such as electrical to mechanical to hydraulic forces, reduces the number of individual parts and thus reduce the probability of failure.

Macro-Fiber Composite (MFC) has been used as an actuator for the morphing wing segment model presented in this work. These new aircraft actuation possibilities also motivate novel approaches to control design of active damping and flutter suppression systems, which we believe are thus far not commonly used in the field of aircraft control systems thus far. Especially interesting for this purpose are the distributed and cooperative control concepts dealing with a problem of controlling a multi-agent system, entities where multiple dynamic share information to accomplish a common goal.

**Keywords**: morphing wing, smart materials, macro fiber composite, aeroelasticity, flutter.



**Figure 1**: The dynamics of a morphing wing divided into several wing segments represented as a group of agents.



**Figure 2**: Figure illustrating the mechanical structure of the morphing wing segment.

## **References:**

- 1. T. A. Weisshaar, Morphing aircraft systems: Historical perspectives and future challenges. Journal of Aircraft, vol. 50, pp. 337-353, 2013.
- J. Hetrick, R. Osborn, S. Kota, P. Flick, and D. Paul, Flight testing of mission adaptive compliant wing, 48<sup>th</sup> AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 2007.
- F. Svoboda, M. Hromcik, and K. Hengster-Movric, Distributed State Feedback Control for Aeroelastic Morphing Wing Flutter Suppression, 26<sup>th</sup> Mediterranean Conference on Control and Automation (MED), June 2018.

### Acknowledgment:

This work was supported by the Czech Republic Grant Agency grant No. 16-21961S.

## Control of Vibration Suppression of Planar Structures Using Actuation by Clusters of Piezopatches

J. Volech<sup>1</sup>, Z. Šika<sup>1</sup>, F. Svoboda<sup>2</sup>, M. Hromčík<sup>2</sup>, J. Zavřel<sup>1</sup>, J. Karlíček<sup>1</sup>

<sup>1</sup>Czech Technical University in Prague, Department of Mechanics, Biomechanics and Mechatronics, Prague, Czech Republic

<sup>2</sup>Czech Technical University in Prague, Department of Control Engineering, Prague, Czech Republic

## Abstract:

"Intelligent materials" are nowadays the perspective subject of research. Thanks to development of piezo material price, the structure with many very cheap piezo elements will be reasonable in the near future. Such material can still have lightness, flexibility and approximately other aspects of the original material, but with the added energy these properties may be partially modified. The paper deals with optimization and control of vibration suppression of the planar flexible systems equipped by regular and dense matrix of multiple sensors and actuators. The control concept was firstly tested on the steel cantilever beam with three piezoelectric patches. FEM model of such concept was created to test its accuracy compared to reality. A detailed description of this problem could be seen in [1]. On this model, the H-infinity controller was designed and subsequently tested on the real experiment with promising results. Based on these results, the model was extended to a square plate with distributed piezo patches [2] in the 5x5 grid (Figure 1). The results of decentralized control law synthetized by the H-infinity control has been presented in [3]. The results are very promising, however, the ultimate goal of the research is to map the various variants of control of dense actuator networks, including the merger of actuators into groups with a common control signal from a single source. An important task is also to find the actuator and sensor architecture best suited to the ability to easily modify the basic found control for different shapes and boundary conditions of the damped planar structures. Within this paper the control is optimized and tested for several clusters of piezo patches which are powered with a single amplifier. The variants of these groups were found using optimization of controllability. The results show that the system can be controlled with minimum energy loss for each mode with reduced number of control inputs (amplifiers). The simulation as well as experimental results of this research are presented.

**Keywords:** distributed actuators; distributed sensors; distributed control; vibration suppression, piezo patches, clusters of actuators



**Figure 1:** The top view of an experimental demonstrator with a grid of 5x5 actuators and collocated sensors

#### **References:**

- Karlíček, J., Šika, Z., Volech, J., Svoboda, F. and Hromčík, M., "Vibration suppression of cantilever beam using collocated piezoelectric," Bulletin of Applied Mechanics, vol. 13, no. 42, pp. 1-6, 2017.
- Preumont, A., Mechatronics. Dynamics of Electromechanical and Piezoelectric Systems, Springer, 2006
- Šika, Z., Hromčík, M., Svoboda, F., Volech J., J., Zavřel J. Karlíček, Decentralized and distributed MIMO H-infinity robust control of vibration suppression of planar structures In: Proceedings of ISMA2018, (paper ID 588) Leuven: Katholieke Universiteit, 2018.

### Acknowledgements

The work has been supported by the Czech Science Foundation project Mechatronic structures with heavily distributed actuators and sensors, 16-21961S.

## Self-stratifying fire-retardant coatings

C. Lemesle<sup>1, 2</sup>, A. Beaugendre<sup>1</sup>, S. Bourbigot<sup>1</sup>, S. Duquesne<sup>1</sup>, A.S. Schuller<sup>2</sup>, M. Casetta<sup>1</sup>, M. Jimenez<sup>1</sup>

<sup>1</sup>Université de Lille, Unité Matériaux et Transformations (UMET), UMR 8207, F-59000 Lille, France <sup>2</sup>Mäder, 130 rue de la Mer Rouge, 68200 Mulhouse, France

## Abstract:

The design of innovative coatings with multifunctional properties is very challenging. Self-stratification can be an alternative as it is an eco-efficient process allowing the formation, in only one application, of a multi-layer film gathering the following properties: adhesion to a substrate, a functional property such as flame retardancy and weathering protective properties and potentially many others. This effective and economical concept thus allows reducing the number of steps to coat a substrate, while providing a coating with equivalent or better performances than a common three layers process (primer-functional coating-topcoat), also reducing the amount of energy used, the pollution and waste generation<sup>1</sup>.

For self-stratification to occur, liquid coatings must contain at least two partially incompatible thermosetting and thermoplastic polymers dissolved in a common solvent blend<sup>2</sup>. In this work, an innovative self-stratifying coating based on epoxy (DGEBA)/silicone blend has been and applied developed on polycarbonate substrate. Perfect self-stratification was evidenced by microscopic analysis coupled with X-ray mappings<sup>3</sup> (Figure 1). Flame retardant additives (2-10 wt.-%) were added to the formulation and the fire properties were evaluated via the determination of the Limiting Oxygen Index (LOI), UL94 and via Mass Loss Calorimetry (MLC). Some of the coatings allowed the formation of a protective barrier against fire and led to V0 rating at UL94 test and an increase of 28% to 35% in oxygen at LOI test. However, the increase in more stringent regulations on toxicological and environmental aspects now leads to the need of "green" flame retardant self-stratifying coatings. In this work, a "greener" self-stratifying coating with bio-based epoxy resin and specific solvent blend replacing xylene (Figure 2) will be presented and fully commented.

**Keywords:** Self-stratifying coating, fire retardant, epoxy/silicone blend, bio-based coating.



**Figure 1**: SEM micrograph of a cross section of a DGEBA/silicone based coating in butyl acetate : xylene (1:1); (a) self-stratified coating (b) EDS mapping of Silicon.



**Figure 2**: SEM micrograph of a cross section of a bio-based epoxy/silicone based coating; (a) self-stratified coating (b) EDS mapping of Silicon.

### **References**:

- 1. A. Beaugendre *et al.* (2017), "Selfstratifying coatings: a review," *Prog. Org. Coatings*, 110, pp. 210-241.
- A. Toussaint (1996), "Self-stratifying coatings for plastic substrates," *Prog. Org. Coatings*, 28, pp. 183–195.
- 3. A. Beaugendre *et al.* (2017), "Selfstratifying epoxy/silicone coatings," *Prog. Org. Coatings*, 103, pp. 101–110.

Acknowledgements: French National Research Agency (ANR-14-CE27-0010), Matikem competitiveness cluster and Mäder company.

## Water and Thermally-Induced Scratch Healing *Metallo*-Supramolecular Amphiphilic Polymer Conetworks

Clément Mugemana,<sup>1</sup> Patrick Grysan,<sup>1</sup> Reiner Dieden,<sup>1</sup> David Ruch,<sup>1</sup> Nico Bruns<sup>2</sup> and Philippe Dubois<sup>3</sup>

<sup>1</sup> Luxembourg Institute of Science and Technology, Materials Research and Technology (MRT), 5 Avenue des Hauts-Fourneaux, L-4362 Esch/Alzette, Luxembourg

<sup>2</sup> Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

<sup>3</sup>Center of Innovation and Research in Materials & Polymers - Laboratory of Polymeric and Composite Materials, Université de Mons, Place du Parc, 23B-7000 Mons, Belgium

#### Abstract:

One of the outstanding feature inspired from nature, is the ability of biological system to autonomously heal damages. In order to adapt the biological-inspired self-healing feature to manmade materials, the design of smart materials which can repair themselves in response to damage has exponentially increased over the last decade.<sup>1</sup>

The current challenge lies in the design of materials which combine the self-healing ability and robust mechanical properties.<sup>2</sup> One of the strategies which has been recently used to overcome this limitation, is based on the design of phase-separated nanostructured polymers.<sup>3</sup> While one phase provides good mechanical properties, the other one embedded with the supramolecular interactions endows the materials with self-healing behavior. Amphiphilic polymer conetworks (APCNs) represent ideal candidate as the covalently interconnected hydrophobic and hydrophilic polymer chains results in phaseseparated morphologies with excellent mechanical properties.<sup>4</sup>

Through this contribution, *metallo*supramolecular amphiphilic polymer conetwork based on poly(*N*- (pyridin-4-yl)acrylamide)*linked* by polydimethylsiloxane (PNP4A-*l*-PDMS) polymer conetworks are presenteted. Phase-separated morphologies embedded with reversible interactions of pyridine-Zn(II) complexed exhibit water and temperatureinduced self-healing behaviour.

**Keywords**: Amphiphilic polymer conetworks (APCNs), Self-Healing, *Metallo*-supramolecular interactions.



**Figure 1**: a) Amphiphilic polymer conetworks (PNP4A-*l*-PDMS) cross-linked by Zn(II) ions b) AFM phase mode image showing phaseseparated morphologies (scale bar: 100 nm) c) AFM height mode images showing the scratchhealing of the polymer conetworks.

#### **References:**

1. Hager, M. D.; Greil, P.; Leyens, C.; van der Zwaag, S.; Schubert, U. S., Self-Healing Materials. *Advanced Materials* **2010**, 22 (47), 5424-5430.

2. Richard, H., Hard Autonomous Self-Healing Supramolecular Materials—A Contradiction in Terms? *Angewandte Chemie International Edition* **2012**, 51 (48), 11942-11944.

3. Mozhdehi, D.; Ayala, S.; Cromwell, O. R.; Guan, Z., Self-Healing Multiphase Polymers via Dynamic Metal–Ligand Interactions. *Journal of the American Chemical Society* **2014**, 136 (46), 16128-16131.

4. Bruns, N.; Scherble, J.; Hartmann, L.; Thomann, R.; Iván, B.; Mülhaupt, R.; Tiller, J. C., Nanophase Separated Amphiphilic Conetwork Coatings and Membranes. *Macromolecules* **2005**, 38 (6), 2431-2438.

## Sensing fT magnetic fields by magnetoelectric metglas / bidomain y+140°-cut lithium niobate composite

<u>Andrei V. Turutin<sup>1,2</sup></u>, João V. Vidal<sup>3</sup>, Ilya V. Kubasov<sup>1</sup>, Alexander M. Kislyuk<sup>1</sup>, Mikhail D. Malinkovich<sup>1</sup>, Svetlana P. Kobeleva<sup>1</sup>, and Nikolai A. Sobolev<sup>1,2</sup>

<sup>1</sup>National University of Science and Technology MISiS, 119049 Moscow, Russia

<sup>2</sup> Department of Physics and I3N, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>3</sup>Department of Physics and CICECO - Aveiro Institute of Materials, University of Aveiro, 3810-193

Aveiro, Portugal

## Abstract:

Bidomain lithium niobate crystals are a promising material for precise actuators and magnetic sensors based on composite multiferroic structures [1–3]. Previously it was shown that a magnetoelectric (ME) coefficient of at least 578 V/(cm·Oe) can be obtained under resonance conditions in a laminate composite "bidomain crystal – metglas".

In this study we investigated ME properties of a composite based on  $Y+140^{\circ}$ -cut lithium niobate plates with an antiparallel polarized "head-to-head" domain structure; metglas was used as a magnetostrictive layer. Samples with a length of 20 mm and a width of 5 mm were studied. The thicknesses of the piezoelectric and magnetostrictive layers were 410  $\mu$ m and 29  $\mu$ m, respectively.

A series of bidomain samples was prepared by annealing upon out-diffusion of  $Li_2O$  from LiNbO<sub>3</sub> with a resultant growth of an inversion domain. The best sample for further studies was selected by testing the crystals as cantilevered piezoelectric actuators and measuring the deflection at the voltage of ±500 V. The movement amplitude of the free end of the chosen specimen was only 13% smaller than the theoretically predicted value for an ideal bimorph. This confirmed a high quality of the domain structure.

Measurements of the direct ME effect were carried out at room temperature and at a frequency of 110 Hz in the quasi-static regime with an applied modulation magnetic field  $\delta H = 0.1$  Oe. The maximum measured quasi-static ME coefficient was as large as  $|\alpha_{E31}| = 1.9$  V/(cm·Oe).

The dynamic ME coefficient was measured as a function of the modulation frequency with an applied optimum bias field of 5 Oe corresponding to the maximum ME effect as measured in the quasi-static regime. We found giant bending resonant ME coefficients of up to 1704  $V/(\text{cm} \cdot \text{Oe})$  at a resonance frequency of

6862 Hz. The ME composite exhibits a giant conversion value of 69.9 V/Oe, and in this case the measured magnetic noise density is only 92  $fT/Hz^{1/2}$ , which is quite respectable for this resonance frequency (Fig.1). We observed a good correspondence between the experimental results and the ones calculated in the framework of the unidimensional model.



**Fig.1** - Equivalent magnetic noise spectral density measured as a function of the frequency in the metglas / y+140°-cut LNC composite, as well as a calculated curve.

**Keywords**: Magnetic sensors, lithium niobate, bidomain crystals, magnetoelectric effect, cantilever, low frequency.

- 1. A. S. Bykov et al. Russ. Microelectron. 43 (8), 536 (2014).
- 2. I. V. Kubasov et al. Cryst. Reports 60 (5), 700 (2015).
- 3. J. V. Vidal et al. IEEE Trans. Ultrason. Ferroelect. Freq. Control 64 (7), 1102 (2017).

## High Temperature Sensor For Detecting Low Frequency Vibrations

I. V. Kubasov,<sup>1,\*</sup> A. M. Kislyuk<sup>1</sup>, A. V. Turutin<sup>1</sup>, A. A. Temirov<sup>1</sup>, R. N Zhukov<sup>1</sup>, A. S. Bykov<sup>1</sup>, M. D. Malinkovich<sup>1</sup>, Yu. N. Parkhomenko<sup>1</sup>

<sup>1</sup> National University of Science and Technology "MISiS", Moscow, Russia

## Abstract:

Crystalline ferroelectric bulk materials are widely used for producing of electromechanical systems, (e.g. vibration sensors and precision actuators) due to their outstanding piezoelectric properties. Commonly, such devices are made of PZT (PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>) because these materials possess very high piezoelectric coefficients, which can be varied in relatively wide range. On other PZT demonstrates the hand. hysteresis, electromechanical creep, strong temperature dependence of properties and contains lead, which is toxic and harmful for the environment.

In this study, we used a novel lead-free ferroelectric single crystalline material in order to create vibration sensor with high sensitivity and wide range of operating temperatures. Plates of single domain lithium niobate (LiNbO<sub>3</sub>) crystals were annealed in non-uniform thermal field near Curie point for formation of two oppositely polarized ferroelectric domains. Such bidomain structure is equivalent to traditional PZT bimorph, but in contrast to it based on the only one crystal and do not possess any glue layers. Cantilever-fastened bidomain crystal is able to produce voltage when bend due to direct piezoelectric effect. We discovered that the  $70 \times 5 \times 0.5$  mm<sup>3</sup> cantilevered bidomain crystal was able to produce 1  $\mu$ V/nm at low frequency vibrations (down to 10 Hz) and more than 25 mV/nm at the first resonance mode (100 Hz).

Our sensor prototype has piezoelectric element which demonstrates an ability to detect low frequency excitations with output coefficient up to 8.654 V/g (here g = 9.8 m/s2 is acceleration of gravity). Sensitivity at resonance is more than 100 V/g.

Due to high Curie point, weak temperature dependence of piezoelectric coefficients of lithium niobate and absence of glue layer in the construction, bidomain LiNbO3-based sensor is able to withstand more than 450 °C.

The study was supported by the Ministry of Education and Science of the Russian Federation (Federal Targeted Programme for Research and Development in Priority Areas of Development of the Russian Scientific and Technological Complex for 2014-2020) (Project ID RFMEFI57816X0187).

**Keywords**: lithium niobate, vibrational sensor, sensitivity, vibrations, ferroelectric, bidomain crystal.



**Figure 1**: Voltage, which was generated by  $70 \times 5 \times 0.5$  mm<sup>3</sup> cantilevered single crystalline bimorph at harmonic sine excitations with different frequencies

# Electrodepostion of biopolymer layers on fibrous matrices – preliminary results

E. Pabjanczyk-Wlazlo,<sup>1,\*</sup> G. Szparaga,<sup>1</sup> Z. Draczynski<sup>1</sup>

<sup>1</sup> Lodz University of Technology, Faculty of Material Technologies and Textile Design, Departement of Material and Commodity Science and Textile Metrology, Stefana Zeromskiego Str. 116, 90-924, Lodz, Poland, \* <u>ewelina.pabjanczyk-wlazlo@p.lodz.pl</u>

## Abstract:

The mechanism of electrophoretic deposition (EPD) comprises deposition of charged particles on the electrode under the influence of an applied electric field. Recently, there is a big increase in EPD especially in industrial applications due to its high versatility and low cost of equipment and maintenance [1]. Furthermore, despite the fact that the EPD is a wet process, it ensures control over the thickness and to some extent the morphology of the coating formed by adjusting the deposition time and the applied potential.

However, the electrodeposition of various types of coatings on metal substrates is relatively well established technique compared to the use EPD for surface modification of fibrous biomaterials. While the last one comprises a set of different characteristics, which are significantly different from metal substrates e.g. mechanical, thermal, electrical properties and etc. A major limitation in the case of fibrous materials is that most of them have poor conductivity, which often precludes the use of electrophoretic deposition. In contrast, a number of advantages of various types of fibrous structures (e.g. porous structure, flexibility, possibility for obtaining composite structures with the application for prospective bioactive materials for implantantion) caused a significant increase of interest in these carriers and methods of their potential modifications [2]. In this respect, the electrophoretic deposition of biopolymer layers on fibrous matrices brings interesting prospects for biomimetic and bioactive implantable materials.

**Keywords**: electrodeposition, fibrous structures, hyaluronic acid, alginate, surface modification

## Acknowledgments

The project "Electrodeposition of ultra-thin polymer layers as the novel method of modification of fibrous biomaterials" is financed by National Science Centre in Poland based on the decision number DEC-2015/19/N/ST8/02456.

- 1. Besra, L., Liu, M. (2007) A review on fundamentals and applications of electrophoretic deposition (EPD), *Prog. Mat. Sci.*, 52, 1–61
- 2. Corni, I., Ryan, M.P, Boccaccini, A.R. (2008), J. Eur. Ceram. Soc., 28, 1353–1367

## Anti-wetting Behavior of Mussel-inspired Materials Coated Antifouling Membrane

S.J. Choi,<sup>1</sup> S.S Kim<sup>2</sup>, D.S. Hwang<sup>2</sup>, A. Jang<sup>3</sup> and S. Kang<sup>1,\*</sup>

<sup>1</sup> Dept. of Civil & En.vironmental Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

<sup>2</sup> Division of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, Republic of Korea

<sup>3</sup> Department of Civil, Architectural and Environmental System Engineering, Sungkyunkwan University, Suwon, Republic of Korea

### Abstract:

Membrane distillation (MD) is a thermally driven process, where water molecules in hot feed vaporizes at the liquid/membrane interface and diffuses across a hydrophobic porous membrane. In MD process, membrane wetting, originated from membrane fouling, has been considered as a major problem. Recently, researches in marine biology have observed thin organic coating layer on mussels named periostracum and the main components of it, oleamide, was proven to have superior antifouling ability. In this study, to improve antiwetting properties, mussel-inspired oleamide was coated on the polypropylene membrane and membrane properties were evaluated. In the batch experiments using colloidal latex particles, the number of attached particles was decreased 61% in the 1 wt% oleamide coated membrane compared to virgin membrane. Moreover, contact angle of membrane was increased 5% in the presence of oleamide in comparison with the absence of it. Liquid entry pressure, typical parameter to indicates wettability of the membrane, was increased twice for the oleamide coated membrane compared to the virgin membrane. Furthermore, oleamide coated membrane showed stable MD performance against humic acid fouling without any wetting, while virgin membrane suffered severe wetting. From this study, the applicability of musselinspired materials as anti-wetting coating on membrane surface was successfully revealed.

**Keywords**: Mussel-inspired, oleamide, antifouling, membrane distillation, wetting



**Figure 1**: Number of attached colloidal latex particles on the virgin and oleamide (0.1 and 1 wt%) coated membrane

### **References:**

- Chen, Y., Tian, M., Li, X., Wang, Y., An, A. K., Fang, J., & He, T. (2017). Antiwetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact membrane distillation of emulsified wastewaters. *Journal of Membrane Science*, 535, 230-238.
- Kang, J.-Y., Bangoura, I., Cho, J.-Y., Joo, J., Choi, Y. S., Hwang, D. S., & Hong, Y.-K. (2016). Antifouling effects of the periostracum on algal spore settlement in the mussel Mytilus edulis. *Fisheries and Aquatic Sciences*, 19(1), 7.

### Acknowlwdgments:

This research was supported by the National Research Foundation of Korea Grant funded by the Ministry of Science, ICT and Future Planning (code 4.0016204.01)

## Synthesis of thermoelectric magnesium-silicide pastes for 3D printing and electrospinning

A. C. Marques1, Davide Miglietta2, A.C. Baptista1, G. Gaspar3, A. Gaspar, C. Bianqui1 R. C. da Silva5, A. Gonçalves6, F. Giorgis2, I. Ferreira1

<sup>1</sup>CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal

<sup>2</sup> Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

<sup>3</sup> Department of Physics & I3N, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>4</sup> CICECO, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>5</sup> IPFN-IST/UL, Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela, Portugal

<sup>6</sup> C2TN, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal

## Abstract:

The synthesis of eco-friendly Magnesiumsilicide semiconducting thermoelectric pastes (*n*-type) for building components to energy harvesting devices through 3D printing and electrospinning were developed and tested for the first time. The pastes synthesis consisted in ball milling Mg- and Si- powders and thermally annealing the resulting mixture under a particular atmosphere (*i.e.* vacuum, Ar or N<sub>2</sub>) for obtaining the Mg<sub>2</sub>Si phase, which was next blended with xylene solvent and Polysterene binder in 3 different mass to mass proportions. The best paste formulation for 3D printing and electrospinning was determined. The annealing steps required for eliminating the binder, and improving mechanical consolidation of the pieces and electro-spun fibres were determined. The materials produced in every single stage of the pastes synthesis were characterised by a variety of techniques that unequivocally proven the pastes' viability for producing thermoelectric parts and components. These can certainly trigger further research and development in green thermoelectric generators (TEGs) capable of adopting any form or shape with enhanced thermoelectric properties to compete with the common toxic materials such as Bi<sub>2</sub>Te<sub>3</sub>. Processes herein presented are cheap, efficient, easy and scalable.

**Keywords**: Mg<sub>2</sub>Si-based thermoelectric materials, mechanical alloying, 3D printing, electrospinning



Figure 1: Magnesium-silicide printed piece.

## NanoMed 2018 - Plenary session II: Nanotechnology in Therapy / Pharmaceutical Nanotechnology

## Local and targeted delivery of nanomedicines for the treatment of glioblastoma

V.Prreat,<sup>1,2,\*</sup> C.Bastiancich, P.Ganipineni, EL. Bozzato, M.Zhao, J.Bianco, F.Danhier

<sup>1</sup> University of Louvain, Louvain Drug Research Institute, Advanced drug delivery ad Biomaterials Brussels, Belgium

## Abstract

Glioblastoma (GBM) is one of the most aggressive and deadliest central nervous system tumors, and the current standard treatment is surgery followed by radiotherapy with concurrent chemotherapy. Nevertheless, the survival period is notably low mainly due to local recurrences. Although ample research has been performed to develop an effective therapeutic strategy for treating GBM, the success of extending patients' survival period and quality of life is limited. We hypothesized that the local delivery after surgical resection and targeted systemic delivery of anticancer drug-loaded nanomedicines would improve the treatment of GBM (1,2)

Targeted nanotheranostics are promising multifunctional system characterized by nanosize, possibility of surface functionalization, diagnostic and therapeutic capabilities. Due to the loss of BBB integrity in the GBM area, we showed that active targeting or magnetic targeting of SPIO/paclitaxel loaded nanoparticles enhanced the biodistribution of the nanoparticles in the brain and enhanced the survival time of GBM bearing mice after IV administration. (3)

Among the strategies that have been adopted to find new and efficacious therapies for the treatment of GBM, the local delivery of chemotherapeutic drugs in the tumor resection cavity emerged. We developed two formulations of anticancer nanomedicines that can be injected perisurgically in the resection cavity of orthotopic GBM. Both PEG-DMA photopolymerisable hydrogel containing paclitaxel-loaded PLGA nanoparticles and lauroyl-gemcitabine lipid nanocapsules that spontaneously form a gel significantly improved the survival of the GBMbearing mice. (4, 5).

Keywords: glioblastoma, nanomedicine, drug delivery

Nanomedicines for systemic and local GBM treatment



**Figure 1**: Figure illustrating the use of nanomedicne for the targeted and local treamtment of glioblastoma (1-5)

- 1. Ganipineni LP, Danhier F, Préat V. (2018) Drug delivery challenges and future of chemotherapeutic nanomedicine for glioblastoma treatment. *J Control Release*. 10, 281:42-57.
- Bastiancich C, Danhier P, Préat V, Danhier F. (2016) Anticancer drug-loaded hydrogels as drug delivery systems for the local treatment of glioblastoma. *J Control Release*. 10;243:29-42.
- Ganipineni LP, Ucakar B, Joudiou N, Bianco J, Danhier P, Zhao M, Bastiancich C, Gallez B, Danhier F, Préat V. (2018) Magnetic targeting of paclitaxel-loaded poly(lactic-co-glycolic acid)-based nanoparticles for the treatment of glioblastoma. *Int J Nanomedicine*. 13, 4509-4521.
- 4. Zhao M, Danhier F, Bastiancich C, Joudiou N, Ganipineni LP, Tsakiris N, Gallez B, Rieux AD, Jankovski A, Bianco J, Préat V. (2018) Post-resection treatment of glioblastoma with an injectable nanomedicine-loaded photopolymerizable hydrogel induces long-term survival. *Int J Pharm.* 548, 522-529.
- Bastiancich C, Bianco J, Vanvarenberg K, Ucakar B, Joudiou N, Gallez B, Bastiat G, Lagarce F, Préat V, Danhier F. (2017) Injectable nanomedicine hydrogel for local chemotherapy of glioblastoma after surgical resection. J Control Release. 264, 45-54.

## Long-term graft tolerance induction by NFATc pathway inhibition in innate immune cells

Gornati L., Cigni C., Mingozzi F., Marongiu L., Rotem R., Colombo M., Zanoni I., Prosperi D., Granucci F.<sup>1</sup>

Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126 Milano, Italy

## Abstract:

Transplantation is a viable therapeutic approach for failing organs and severe illnesses. The most feared complication of transplantation is rejection, the immune response of the recipient against mismatched donor antigens that may lead to graft loss. This pathological process is mediated by the instauration of alloreactive T cells that undergo clonal expansion supported by the activation of the Nuclear Factor of Activated T cells (NFAT). To avoid this issue, grafted patients undergo life-long administration of immunosuppressive drugs, which completely abrogate the immune response, against not only the graft but also potential pathogens or cancer cells. Here, we aim at evaluating NFAT as a potential specific therapeutic target to prevent rejection of mismatched grafts without causing immune paralysis. complete Bv using nanoparticles (NPs) delivering a specific NFAT inhibitor peptide and taking advantage of the natural ability of phagocytes to uptake NPs, we managed to abolish NFAT activation in these cells without affecting T cells. Remarkably, the administration of our NPs in a model of mismatched skin graft reduces allograft rejection. When transplanting NFATc2 KO skin, the rejection is delayed, corroborating the crucial role of NFAT in the process. Indeed, NFAT inhibition impairs absence or vessels permeability and thus migration of T cells from bloodstream to the graft as well as dendritic cells (DCs) migration to the draining lymph nodes, preventing activation of alloreactive T cells.

Furthermore, we noticed an increase in the CD4+ CD25+ Foxp3+ T cells compartment in spleen and draining lymph nodes in NPs treated recipients, suggesting regulatory T cells expansion and tolerance. We are currently investigating the role of a putative molecule probably responsible for tolerance induction that seems to be upregulated by DCs after NPs treatment.

## Smart Hybrid nanocrystals as Trojan horses for effective theranostic applications

Valentina Cauda,<sup>1,\*</sup> Bianca Dumontel,<sup>1</sup> Francesca Susa,<sup>1</sup> Marta Canta,<sup>1</sup> Luisa Racca,<sup>1</sup> Andrea Ancona,<sup>1</sup> Nadia Garino,<sup>1</sup> Tania Limongi,<sup>1</sup> Giancarlo Canavese,<sup>1</sup> Marco Laurenti,<sup>1</sup> <sup>1</sup> Politecnico di Torino, Department of Applied Sience and Technology, Turin, Italy

## Abstract:

Zinc oxide nanocrystals (ZnO NCs), thanks to their unique properties, are receiving much attention for their use in nanomedicine, in particular for therapy against cancer [1]. To be employed efficiently as diagnostic and therapeutic (yet theranostic) tools [2], highly dispersed, stable and non-toxic nanoparticles are required. In the case of ZnO NCs, there is still a lack of knowledge about cytotoxicity mechanisms and stability in the biological context, as well as immunological response and haemocompatible features. We thus propose a novel approach to render stable, immune and hemocompatible these ZnO NCs in various biological media using artificial and natural phospholipidic bilayers.

We synthesized amino-functionalized ZnO NCs, then shielded with phospholipid bilayers either from synthetic origin or natural biovesicles. We characterized their structural, morphological, physico-chemical properties, focusing on the coupling mechanism between ZnO NCs and the lipid vesicles. The stability behavior of different hybrid nanocrystals was evaluated, comparing biodegradation profiles their in different inorganic and biological media. The studies aim to investigate how the particle surface chemistry and charge could influence their aggregation/ degradation in the different media and interaction with cells. We actually proved their haemocompatibility in human plasma and their internalization into cancer cells and related cytotoxicity mechanisms. A stimuli responsive activation by UV-light was investigated for inducing high mortality of cancer cells based on the hybrid NCs. We demonstrated that pristine ZnO NCs strongly aggregate when suspended in both simulated and biological media, showing small dissolution into potentially cytotoxic Zncations, also slightly affecting their crystalline structure [3]. In contrast, high colloidal stability and integrity was retained for hybrid lipidshielded ZnO NCs in all media [3,4], accompanied by high biocompatibility, efficient cell internalization and effective killing ability only upon stimuli-activation. These features

render these hybrid ZnO NCs ideal "Trojan horses" for further theranostic applications.

**Keywords**: Zinc oxide nanocrystals, phospholipid bilayer, stimuli-responsive therapy, theranostics.



**Figure 1**: Scheme of the hybrid nanocrystal, as a Trojan horse showing higher bio and haemocompatibility, long-term stability in various biological and inorganic fluids, improved cell internalization with respect to pristine ZnO NCs. A stimuli responsive behavior, guided by UV-light, is also reported.

### **References:**

- Racca L, Canta M, Dumontel B, Ancona A, Limongi T, Garino N, Laurenti M, Canavese G, Cauda V (2018) "Zinc oxide nanostructures in biomedicine" in Ciofani G Ed. Smart Nanoparticles for Biomedicine, Elsevier Inc, 171-187.
- 2. Lim E, Kim T, Paik S, Haam S, Huh Y, Lee K (2015), Chem. Rev. 115:327–394.
- Dumontel B, Canta M, Engelke H, Chiodoni A, Racca L, Ancona A, Limongi T, Canavese G, Cauda V (2017) Enhanced Biostability and Cellular Uptake of Zinc Oxide Nanocrystals Shielded with Phospholipid Bilayer. J. Mater. Chem. B, 5,8799-8813.
- Ancona A, Dumontel B, Garino N, Demarco B, Chatzitheodoridou D, Fazzini W, Engelke H, Cauda V, (2018) Lipid-Coated Zinc Oxide Nanoparticles as Innovative ROS-Generators for Photodynamic Therapy in Cancer Cells. *Nanomaterials* 8, 1-15.

Acknowledgment to ERC Starting Grant (GA.678151) and Compagnia di Sanpaolo.

# Bio-engineered colloidal nanoparticles for therapeutic applications

## M. Colombo,<sup>1</sup>

<sup>1</sup> NanoBioLab, University of Milano-Bicocca, Department of Biotechnologies and Bioscience, Milano, Italy

## Abstract:

Multifunctional nanoparticles are promising bimodal tracers for noninvasive diagnosis and treatment of cancer and inflammatory dideases in vitro and in vivo. The design of bio-engineered colloidal nanoparticles needs careful optimization of size and shape, optical and magnetic properties, and efficient functionalization with ligands improve homing to the signal amplification and target selectivity toward malignant cells. One of the greatest challenges in designing nanoparticles functionalized with homing peptides and proteins to optimize molecular recognition resides in the possibility to finely control the ligand orientation on the nanoparticle surface.

To support the research in new drug delivery nanosystems, in the past few years new administration methods of nanoparticles rather than traditional intravenous ones have been explored. This is a highly innovative approach that is nearly unexplored at present. Because of parenteral administration drawbacks, alternative administration routes have been investigated. Among all, the oral and topical administration are the most interesting to obtain a local effect and gain a better patients compliance.

**Keywords**: colloidal nanoparticles, biofunctionalization, alternative administration methods, suicide gene therapy, cancer theranostic, acute and chronic disease treatment.



**Figure 1**: Magnetic nanoparticles functionalized with Trastuzumab or Ab fragments for targeting and treatment of breast cancer cells *in vitro* and *in vivo* 

- 1. L. Fiandra, et al. ACS Nano, 2013, 7, 6092
- 2. S. Mazzucchelli, M. Colombo, et al. *Angew. Chem., Int. Ed.* 2013, 52
- 3. M. Colombo et al. *Chem. Soc. Rev.*, 2012, 41, 4306
- 4. M. Colombo, et al. ACS Nano, 2010, 4, 5693.
- 5. F. Corsi, et al. ACS Nano, 2011, 8, 6383.
- 6. M. Colombo, et al. Angew. Chem. Int. Ed., 2012, 51, 496.
- 7. M. Colombo, et al. Small, 2012, 8, 1492.
- 8. M. Colombo, et al. Angew. Chem. Int. Ed., 2012, 37, 9272
- 9. M. Colombo, et al. *Nature Commun.* 2016, 7, 13818.
- 10. L. Salvioni, et al. *Pharmacol. Res.* 2016, 110, 122

## Bioelectronic Platform for Programmable Capture and Release of Circulating Tumor Cells

## Peilin Chen

Reseach Center for Applied Sciences, Academia Sinica, Tiapie, Taiwan

## Abstract:

In this study, we employed a novel onestep electrospinning process to fabricate poly(ethylene oxide) (PEO)/poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) core/shell nanofiber structures with improved water resistance and good electrochemical properties. We then integrated a biocompatible polymer coating with three-dimensional (3D) PEDOTbased nanofiber devices for dynamic control over capture/release performance of the rare circulating tumor cells (CTCs) (Figure 1), as well as the label-free detection by using organic electrochemical transistors (OECTs). The capture/release behavior the detailed of circulating tumor cells was studied using an organic bioelectronic platform comprising PEO/ PEDOT:PSS nanofiber mats with 3 wt % (3glycidyloxypropyl) trimethoxysilane as an additive. We have demonstrated that these nanofiber mats deposited on five-patterned indium tin oxide finger electrodes are excellent candidates for use as functional bioelectronic interfaces for the isolation, detection, sequential collection, and enrichment of rare CTCs through electrical activation of each single electrode. This combination behaved as an ideal model system displaying a high cell-capture yield for antibodypositive cells while resisting the adhesion of antibody-negative cells. Taking advantage of the electrochemical doping/dedoping characteristics of PEDOT:PSS materials, the captured rare cells could be electrically triggered release through the desorption phenomena of PLL-g-PEG-biotin on device surface. More than 90% of the targeted cancer cells were captured on the 3D PEDOTbased nanofiber microfluidic device; over 87% of captured cancer cells were subsequently released for collection; approximately 80% of spiked cancer cells could be collected in a 96-well plate. For the OECT design, it was demonstrated for CTC-capture monitoring performance and identifying cancer cell phenotypes. This 3D PEDOT-based bioelectronic device approach appears to be an economical route for the largescale preparation and detection of systems for

enhancing the downstream characterization of rare CTCs.

**Keywords**: circulating tumor cells, conducting polymer, organic electronics



**Figure 1**: Schematic illustration of PEDOT:PSS nanofiber mats as bioelectronic device platform for the enrichment of rare CTCs by five multiple/sequential rounds of ES.

- "Poly(3,4-ethylenedioxythiophene)-Based Nanofiber Mats as an Organic Bioelectronic Platform for Programming Multiple Capture/Release Cycles of Circulating Tumor Cells", C.-C. Yu, B.-C. Ho, R.-S. Juang, Y.-S. Hsiao\*, R V. R. Naidu, C. W. Kuo,Y.-W. You, J.-J. Shyue, J.-T. Fang\*, and P. Chen\*, ACS Appl. Mater. Interfaces 2017, 9, 30329-30342.
- Yu-Sheng Hsiao,\* Shyh-Chyang Luo, Shuang Hou, Bo Zhu, Jun Sekine, Chiung-Wen Kuo, Di-Yen Chueh, Hsiao-hua Yu,\* Hsian-Rong Tseng,\* and Peilin Chen\*,"3D Bioelectronic Interface: Capturing Circulating Tumor Cells onto Conducting Polymer-Based Micro/Nanorod Arrays with Chemical and Topographical Control" Small, 2014, **10**, 3012

## Targeted vaccine delivery using functionalized gold nanocages characterized in small intestine orgnoid system

C. Yu,<sup>1,2,\*</sup> T. Tong,<sup>1</sup> Q. Wang,<sup>3</sup> C. Miller<sup>4</sup>

<sup>1</sup> Iowa State University, Department of Agricultural and Biosystems Engineering, Ames, IA 50010, USA

<sup>2</sup> National Seafood Engineering Center, Dalian Polytechnic University, Dalian, China
<sup>3</sup> Iowa State University, Department of Chemical and Biological Engineering, Ames, USA
<sup>4</sup> Iowa State University, Department of Biomedical Sciences, Ames, USA

#### Abstract:

The intestinal epithelium forms an essential element of the mucosal barrier and plays a critical role in the pathophysiological response to different enteric disorders and diseases. It is also a barrier for oral vaccine delivery. Here, we demonstrated the feasibility of purposefully designing immunogen-carrying gold nanocages functionalized with  $\sigma$ -1 proteins from T1L reovirus to deliver immunogens across the mucosal barrier to enhance immunological responses. The immunogen delivery was characterized in small intestine orgnoid system. Primary isolated intestinal stem cells were used to create these orgnoids. M-cells, which are the targets for  $\sigma$ -1 functionalized nanocages, were induced in these orgnoids to allow easy pass of the nanovaccine complexes from inside-out through the lumen of the orgnoids. Both 3-D orgnoids and layered artificial lumen structures were utilized to investigate the effects of the  $\sigma$ -1 aided targeted delivery. Here, we demonstrated this proof-ofconcept targeted nanoviccine nano-vaccine system that will have a wide variety of applications in the development of oral vaccines for infectious diseases.

Keywords:  $\sigma$ -1 protein, gold nanocages, nanovaccines, intestinal stem cells.



**Figure 1**: Figure illustrating the mechanism of targeted vaccine delivery using gold nanocages functionalized by  $\sigma$ -1 proteins from reovirus to deliver immunogens through orgnoids made from small intestinal stem cell to facilitate vaccine delivery across mucosal barrier to stimulate strong immune-responses.

- 1. Chappell, J.D., A.E.Prota, T.S.Dermody, and T.Stehle. Crystal structure of reovirus attachment protein sigmal reveals evolutionary relationship to adenovirus fiber. The EMBO Journal Vol 21. Nos 1 & 2 pp, 1-11, 2002.
- Peng, H., C. Wang, X. Xu, C. Yu and Q. Wang, An Intestinal Trojan Horse for Gene Delivery. Nanoscale, DOI: 10.1039/C4NR06377E, published on line Jan 2015.
- Ikoba, U., H. Peng, H. Li, C. Miller, C. Yu, Q. Wang, Nanocarriers in Therapy of Infectious and Inflammatory Diseases. Nanoscale, DOI: 10.1039/C4NR07682F, published online Feb 2015
### NanoMed 2018 - Session II: Nanotechnology in Therapy / Pharmaceutical Nanotechnology

### Glycosaminoglycan-Coated Superparamagnetic Iron Oxide Nanoparticles for Theranostic Applications

C. Bongio<sup>1</sup>, M. Mauri<sup>2</sup>, G. Torri<sup>3</sup>, E. Vismara<sup>1</sup>

<sup>1</sup>Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano,

Milano, Italy;

<sup>2</sup> Department of Materials Science, University of Milan Bicocca, 20125 Milano, Italy; <sup>3</sup>Institute for Chemical and Biochemical Research "G. Ronzoni", 20133 Milano, Italy;

### Abstract:

The purpose of this work is to obtain a composite nanoscale biomaterial based on assembling iron nanoparticles with glycosaminoglycans, capable to combine therapeutic and diagnostic imaging aid functions. Super Paramagnetic Iron Oxide Nanoparticles (SPIONs) were selected due to their capability to act as MRI negative contrast agents. SPIONs were functionalized with Hyaluronic Acid (HA), a glycosaminoglycan (GAG) embodying a targeting moiety selectively directed to CD44 receptors of tumor cells<sup>[1]</sup>. On the other hand, SPIONs were derivatized with Low Molecular Weight Heparins (LMWHs), which target both heparanase<sup>[2]</sup> and selectins<sup>[3]</sup>, thus moderating tumor cell arrest, extravasation and metastasis.

An auxiliary decoration with Bovine Serum Albumine (BSA) was performed on both nanosystems, since BSA enhances their biocompatibility features and provides suitable depot sites for carrying hydrophobic drugs.

In details, SPIONs were grafted with both HA (5400 Da) and BSA, by means of a chemical conjugation with dopamine (DA)<sup>[4]</sup>. These Fe<sub>3</sub>O<sub>4</sub>·DA-BSA/DA-HA nanoparticles efficiently entrapped and released the hydrophobic anticancer drug Paclitaxel (PTX). Moreover, paramagnetic relaxation properties define our samples as excellent candidates as contrast agents. Biological evaluation MRI (cytotoxicity and in vivo experiments) are currently in progress. Given the chemical similarity between the considered GAGs, the attachment of LMWHs to SPIONs by means of a similar synthetic strategy that gave Fe<sub>3</sub>O<sub>4</sub>·DA-BSA/DA-HA was explored. A preliminary characterization of Fe<sub>3</sub>O<sub>4</sub>·DA-BSA/DA-LMWH nanosystems has been performed.

**Keywords**: superparamagnetism, iron oxide nanoparticles, glycosaminoglycans, hyaluronic acid, low molecular weight heparins, Paclitaxel, magnetic resonance imaging.



Figure 1: A schematic protocol of the envisioned  $Fe_3O_4$ ·DA-BSA/DA-HA nanoparticle

- Misra, S.; Heldin, P.; Hascall, V.C.; Karamanos, N.K.; Skandalis, S.S.; Markwald, R.R.; Ghatak, S. (2011), HA/CD44 interactions as potential targets for cancer therapy. *FEBS J*, 278, 1429–1443.
- Vlodavsky, I.; Singh, P.; Boyango, I.; Gutter-Kapon, L.; Elkin, M.; Sanderson, R.D.; Ilan, N. (2016) Heparanase: From Basic Research to Therapeutic Applications in Cancer and Inflammation. *Drug Resist Updat.*, 29:54-75.
- 3. Bendas, G.; Borsig, L. (**2012**) Cancer cell adhesion and metastasis: Selectins, integrins, and the inhibitory potential of heparins. *Int. J. Cell Biol.*, 676731.
- Vismara, E.; Bongio, C.; Coletti, A.; Edelman, R.; Serafini, A.; Mauri, M.; Simonutti, R.; Bertini, S.; Urso, E.; Assaraf, Y.G.; Livney, Y.D. (2017), Albumin and Hyaluronic Acid-Coated Superparamagnetic Iron Oxide Nanoparticles Loaded with Paclitaxel for Biomedical Applications, *Molecules*, 22(7):1030.

### Conjugation with anti-transferrin receptor antibody increases PLGA nanoparticles uptake in Glioblastoma cells

M. J. Ramalho<sup>1\*</sup>, J. Lima<sup>2,3,4</sup>, M. A. N. Coelho<sup>1</sup>, J. A. Loureiro<sup>1</sup>, M. C. Pereira<sup>1</sup>

<sup>1</sup>LEPABE - Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal

<sup>2</sup>Faculty of Medicine, University of Porto, Alameda Prof. Hernâni Monteiro, Porto, Portugal
 <sup>3</sup>Instituto de Investigação e Inovação em Saúde, University of Porto, R. Alfredo Allen, Porto, Portugal
 <sup>4</sup>Institute of Molecular Pathology and Immunology of the University of Porto, Porto, Portugal

#### \*mjramalho@fe.up.pt

#### Abstract:

Poly (d,l-lactic-co-glycolic acid) (PLGA) polymer have been widely studied as an efficient drug delivery system due to its well established clinical safety and its ability to enhance drug therapeutic benefits [1] In. this work, we propose PLGA nanoparticles (NPs) for the delivery of temozolomide (TMZ), an alkylating agent used for glioblastoma multiforme (GBM) treatment. The classical TMZ therapy is rarely curative, due to this type of tumor heterogeneity's, anatomic location and high proliferation rate [2]. As many other chemotherapeutic drugs, TMZ exhibits some limitations as high toxicity and low availability in the target tissues. To overcome these imitations, TMZ was encapsulated in PLGA NPs, and a targeting approach was envisaged using NPs modified with antitransferrin receptor (TfR) monoclonal antibody (mAb), since this receptor is overexpressed in GBM cells [3]. PLGA NPs were prepared using the single-emulsion evaporation method, and in vitro assays using two human GBM cell lines, U251 and U87, were conducted. The developed nanocarriers showed mean diameters of about 200 nm and encapsulation efficiency of 45%. The antiproliferative effect of TMZ entrapped in the PLGA NPs was evaluated on human GBM cell lines, demonstrating that the cytotoxicity effect of TMZ is enhanced by the nanoencapsulation comparatively with free TMZ. Fluorescence studies showed that modification of the PLGA NPs surface with mAb for TfR significantly increased the cellular internalization in the studied GBM cell lines, and confocal studies displaying NPs in late endosomes/lysosomes suggest that these NPs are selectively uptaken by TfR-mediated endocytosis. Future in vivo studies will allow evaluating the potential of the

developed nanocarriers for the treatment of GBM.

**Keywords**: glioblastoma multiforme, yemozolomide, poly(lactic-co-glycolic acid), nanoparticles, monoclonal antibody, transferrin receptor



Figure 1: Laser scanning confocal microscopy image of U87 cells treated with mAb- PLGA NPs for 72 h. The nuclei are marked in blue and the PLGA NPs in green using coumarin-6 dye. Scale bar:  $25 \mu m$ .

#### Acknowledgments

This work was the result of the project POCI-01-0145-FEDER-006939 (LEPABE – UID/EQU/00511/2013) funded by the European Regional Development Fund (ERDF), through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia; and NORTE-01-0145-FEDER-000005 – LEPABE- 2 ECO-INNOVATION, supported by North Portugal Regional Operational Program (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); and TRANSCAN/0001/2012, European project "NanoEFEct" financed by FCT and Portuguese Cancer League; and FCT doctoral grant (PD/BD/105984/2014).

- Ramalho, M.J., M.A.N. Coelho, and M.C. Pereira. (2018) Nanocarriers for the delivery of temozolomide in the treatment of glioblastoma: A review in *Design and Development of New Nanocarriers*, A.M. Grumezescu, Editor. William Andrew Publishing, Elsevier: Oxford, United Kingdom. p. 687-722.
- 2. Batash, R., et al. (2017) Glioblastoma Multiforme, Diagnosis and Treatment; Recent Literature Review, *Current Medicinal Chemistry*, 24, (27), 3002-3009.
- 3. Sun, T., et al. (2017) Targeting transferrin receptor delivery of temozolomide for a potential glioma stem cell-mediated therapy, *Oncotarget*, 8, (43), 74451-74465.

### Targeted Multifunctional Theranostic Nanoparticle for Efficient Tumor Imaging and Therapy

J. Lee<sup>1</sup>, W. I. Choi<sup>1,\*</sup>

<sup>1</sup> Center for Convergence Bioceramic Materials, Convergence R&D Division, Korea Institute of Ceramic Engineering and Technology (KICET), Republic of Korea

### Abstract:

Introduction of targeting ligands may lead to better pharmacokinetics, enhanced specificity, increased internalization and intracellular delivery of nano-systems, and more importantly, increased local concentration of drugs at the target site, reduced systemic toxicity, and target-to-background contrast improved in imaging.<sup>1</sup> Trastuzumab (Herceptin®) is a humanized monoclonal antibody for targeting the human epidermal growth factor 2 (HER2), which is overexpressed in ovarian, lung, gastric carcinomas, and especially human breast cancer  $(20 \sim 30\%$  incidence).<sup>2</sup> In this study, we prepared iron oxide nanoparticle and doxorubicin-loaded multifunctional nano-carrier (IONP/DOX-MFNC), capable of simultaneous cancer targeting via a herceptin monoclonal antibody, controlled anticancer drug delivery, as well as imaging modalities of magnetic resonance imaging and near-infrared fluorescence imaging (Figure 1). IONP and DOX were efficiently loaded into the nanocarrier, and a desirable pHresponsive release of DOX was achieved by MFNC. The nano-carrier showed much higher cellular uptake and stronger cytotoxicity to HER2 overexpressed SK-BR-3 (human breast cancer cells) than MCF-7, a negative control cell, suggesting specific cancer targeting via HER2 receptor. In an in vivo tumor xenograft model, IONP/DOX-MFNC showed higher tumor uptake and significantly enhanced tumor regression than the nano-carrier without the antibody. Thus, DOX-loaded, multi-functional nano-carrier with HER2 antibody was effective for both imaging and therapy, showing the potential for early stage cancer diagnosis and simultaneous therapy.

**Keywords**: NIR imaging, Herceptin, Active targeting, Doxorubicin, Pluronic.



**Figure 1**: *In vivo* NIR fluorescence image and MRI image of nude mice bearing SK-BR-3 tumors after intravenous injection of IONP/DOX-MFNC (with Herceptin).

- 1. Bae, Y. H. (2009) Drug targeting and tumor heterogeneity, *J. Control. Release*, 133, 2-3.
- Steinhauser I., Spänkuch B., Strebhardt K., Langer K. (2008) Trastuzumab modified nanoparticles: optimisation of preparation and uptake in cancer cells, *Biomaterials* 27, 4975-4983.

### New compounds for targeted photodynamic therapy of cancer

T. Michy<sup>2,3</sup>, C. Bernard<sup>2,3</sup>, X. Jiang<sup>1,2</sup>, JL. Coll<sup>1,2</sup>, I. Texier<sup>5</sup>, A. Hurbin<sup>1,2</sup>, G. Royal<sup>1,4</sup>, V. Josserand<sup>1,2</sup>

<sup>1</sup>INSERM U1209, Institute for Advanced Biosciences, F-38000, Grenoble, France
 <sup>2</sup>Univ. Grenoble Alpes, F-38000 Grenoble, France
 <sup>3</sup>CHU Hôpital, Nord CS 10217, 38000 Grenoble, France
 <sup>4</sup>UMR CNRS 5250, Département de Chimie Moléculaire, F-38000 Grenoble, France.
 <sup>5</sup>CEA-LETI MINATEC/DTBS, Grenoble, France.

#### Abstract:

For most solid tumors, surgery is the first therapeutic indication and the vital prognostic of patients is directly related to the completeness of tumor resection. Unfortunately, some tumor fragments resected due to the multifocal cannot be dissemination and/or their close contact with vital areas. It would therefore be extremely advantageous to potentiate the effectiveness of surgery by applying an intraoperative targeted chemotherapy at the end of surgery. PhotoDynamic Therapy (PDT) is a therapeutic approach that displays great potential for this application and is currently used in the clinic for the treatment of several cancers. However its specificity for tumor tissue is limited as well as its efficacy in deep tissues and hypoxic tumor areas that cause recurrence.

Our therapeutic strategy is based on the combination of lipid nanoparticles (lipdots®) as a tumor-targeting vector (1, 2) and an original photochromic derivative of the dihydropyren family (DHP) (3). DHP is capable of producing singlet oxygen when it is illuminated, but it can also store singlet oxygen and then gradually release it under the effect of temperature (37°C), regardless of the presence of oxygen, that is to say including in hypoxic tutmor regions.

The present work evaluated the biological behavior of DHP compounds compared to Verteporfin as a reference agent, first in vitro in cancer cell cultures and then in vivo in tumor bearing mice. Cytotoxicity under illumination was demonstrated in human ovarian cancer cells (SKOV3) as well as safety in the absence of illumination. Internalization and trafficking within the cells was assessed by confocal microscopy and flow cytometry and demonstrated a strong uptake and retention in tumor cells. The in vivo biodistribution and pharmacokinetics were evaluated by noninvasive fluorescence imaging in mice bearing either subcutaneous tumors or peritoneal carcinomatosis from ovarian cancer after intravenous injection of the photosensitizers in the lipidots®. encapsulated or not This demonstrated a high and long lasting tumor uptake of lipidots<sup>®</sup> (tumor signal was maximal from 5 to 48 hours post injection and tumor/healthy tissue = 4.8).

Finally, the safety and therapeutic efficacy were evaluated *in vivo* in mice with ovarian cancer (SKOV3). A single intravenous injection of the photosensitizers encapsulated or not in the lipidots<sup>®</sup> was followed by sequential illumination (5 min at 680 nm, 150 mW/cm<sup>2</sup>) after 15 minutes, 5, 24 and 48 hours. These therapeutic experiments are still in progress and results will be presented at the time of the congress.

**Keywords**: Cancer, Photodynamic therapy, photosensitizer, singlet oxygen, drug delivery.



**Figure 1**: Non-invasive Near Infra Red fluorescence imaging of tumor uptake of lipidots® 24 hours after intravenous injection in mice.

- 1. Hirsjarvi, S., Dufort, S., Bastiat, G., Saulnier, P., Passirani, C., Coll, J. L., and Benoit, J. P. Surface modification of lipid nanocapsules with polysaccharides: from physicochemical characteristics to in vivo aspects. *Acta biomaterialia.* **2013**; 9(5):6686-6693.
- Laine, A. L., Gravier, J., Henry, M., Sancey, L., Bejaud, J., Pancani, E., Wiber, M., Texier, I., Coll, J. L., Benoit, J. P., and Passirani, C. Conventional versus stealth lipid nanoparticles: formulation and in vivo fate prediction through FRET monitoring. *J Control Release*. 2014; 188:1-8.
- 3. Cobo, S., Lafolet, F., Saint-Aman, E., Philouze, C., Bucher, C., Silvi, S., Credi, A., and Royal, G. Reactivity of a pyridinium-substituted dimethyldihydropyrene switch under aerobic conditions: self-sensitized photo-oxygenation and thermal release of singlet oxygen. *Chemical communications*. **2015**; 51(73):13886-13889.

# Application of hydroxyapatite as an innovative carrier for bacteriophages

A. Fulgione<sup>1,\*</sup>, M. Iannaccone<sup>2</sup>, M. Papaianni<sup>2</sup>, F. Contaldi<sup>2</sup>, C. Colletti<sup>3</sup>, M. Lelli<sup>3</sup>, N. Roveri<sup>3</sup>, R. Capparelli<sup>2</sup>

<sup>1</sup> University of Sannio, Department of Science and Technology, Benevento, Italy <sup>2</sup> University of Naples, Department of Agriculture, Portici, Naples, Italy <sup>3</sup> Bioecoactive s.r.l., Granarolo dell'Emilia, Bologna, Italy

### Abstract:

"Bacteriophage therapy" represents a valid approach against the spread of antibiotic-resistant bacterial strainsbut - at the same time - displays some disadvantages (low stability, short half-life, no resistance to acid pH condition), which make difficult phage delivery to thespecific sites of infection suchas the gastrointestinal environment. Since many years, hydroxyapatite is being explored as vehicle for drug targeting, transfection, bone scaffolds and implant coating materials and, for these reasons we evaluated the effect of this mineral for the bacteriophage therapy. The results have highlighted that Salmonella Rissen bacteriophage displays antimicrobial activity against tenSalmonella speciesisolated from food.

Complexed with hydroxyapatite, the bacteriophages have shown an increased half-life and a resistance at acid pH conditions.

Experiments have demonstrated the ability of bacteriophages - carried by HA -to penetrate inside liver cancer cells (HepG2) more efficiently than phages alone and, so, killing intracellular bacteria.

Furthermore, the hydroxyapatite/bacteriophage complex was able to reduce the bacterial load of SalmonellaRissen in previously infected minced meat, respect to bacteriophage or hydroxyapatite alone (Figure 1).

Future research will be focused on the study of the effect of hydroxyapatite complexed with other bacteriophages.

**Keywords**: bacteriophages, hydroxyapatite, *Salmonella* Rissen, meat.



Figure 1: Bacterial reduction assay on minced meat. The samples of the meat were infected with S.Rissen (103 CFU/mL) and were treated with: hydroxyapatite (HA; 100 mg/mL) or bacteriophage  $(\phi 1; 10^8)$ PFU/mL) or bacteriophage-hydroxyapatite complex ( $\phi$ 1-HA; 10<sup>8</sup> PFU/mL and HA; 100 mg/mL). Positive control (Control) was represented by S. Rissen infected meat. \*\*\* p<0,001. Each value is the mean  $\pm$  DS of 3 independent experiments with 3 replicates each. Statistical analysis was performed with Student's t test.

- 1. Cisek, A.A., Dąbrowska, I., Gregorczyk, K.P., Wyżewski, Z. (2017), Phage Therapy in Bacterial Infections Treatment: One Hundred Years After the Discovery of Bacteriophages, *Curr. Microbiol.*, 74(2), 277-283.
- Uskoković, V., Uskoković, D.P. (2011), Nanosized hydroxyapatite and other calcium phosphates: chemistry of formation and application as drug and gene delivery agents, *J. Biomed. Mater. Res. B Appl.Biomater.*, 96(1),152-191.
- 3. Fox, K., Tran, P.A., Tran, N. (2012), Recent advances in research applications of nanophase hydroxyapatite, *Chemphyschem.*, 13(10), 2495-2506.

# Pemetrexed-loaded nanoparticles targeted to malignant pleural mesothelioma cells: an *in vitro* study

Laura Pandolfi<sup>1</sup>, Emanuela Cova<sup>1</sup>, Simona Inghilleri<sup>1</sup>, Monica Morosini<sup>1</sup>, Vanessa Frangipane<sup>1</sup>, Simona Mrakic-Sposta<sup>3</sup>, Miriam Colombo<sup>2</sup>, Patrizia Morbini<sup>4</sup>, Manuela Monti<sup>5</sup>, Giulia Stella<sup>1</sup>, Ymera Pignochino<sup>7</sup>, Silvia Benvenuti<sup>7</sup>, Davide Prosperi<sup>2</sup>, Federica Meloni<sup>6</sup>.

 <sup>1</sup> Clinic of respiratory apparatus diseases, IRCCS Fondazione Policlinico San Matteo, Pavia, Italy;
 <sup>2</sup>Department of di Biotecnology e Bioscience, Università di Milano-Bicocca, Milano, Italy;
 <sup>3</sup>Institute of bioimaging and molecular physiology, Consiglio Nazionale delle Ricerche (CNR), Segrate (Milano), Italy;

<sup>4</sup>Department of Molecular medicine, Unit of Anatomical pathology, Università di Pavia, Pavia, Italy;
 <sup>5</sup>Research center of rigenerative medicine, IRCCS Fondazione Policlinico San Matteo, Pavia, Italy;
 <sup>6</sup>Department od internal medicine, Unii of Pneumology, Università degli Studi di Pavia, Pavia, Italy
 <sup>7</sup>IRCCS Candiolo Cancer Institute, Candiolo, Torino, Italy

### Abstract:

Malignant Pleural Mesothelioma (MPM) is an aggressive tumor characterized by poor prognosis and increasing incidence due to widespread asbestos exposure. There is still no effective therapy for MPM<sup>1</sup>. Pemetrexed (Pe) is one of the few chemotherapeutic agents approved for advanced-stage disease, although the objective response to the drug is limited. The use of gold nanoparticles (GNPs) as drug delivery system represents a promising issue for diseases, such as MPM. GNPs specifically target malignant cells and they could: increase intracellular drug accumulation, avoid excessive systemic toxicity and administer the treatment directly into the pleural space<sup>2</sup>. This study aims to identify a new targeted therapy for MPM patients based on nano-delivery system.

Commercial MPM cell lines and primary cultures obtained by pleural effusions from MPM patients overexpressed CD146. In fact, GNPs decorated with a monoclonal anti-CD146 antibody (GNP-HC) were be internalized by MPM cell lines within 1 h. Treatment of Pe-loaded GNP-HC (GNP-HCPe) on MPM cell lines was very promising: both cell viability and motility of MPM cells were significantly affected by nanoparticles treatment compared to Pe and clonogenic capacity was completely inhibited following nanoparticles internalization. So, GNP-HCPe treatment displayed in vitro antineoplastic action and is more effective than Pe alone in inhibiting MPM cell line malignant phenotype. The novelty of this work is represented by the use of specifically decorated GNPs and opens the chance to avoid toxic effect on normal mesothelial cells in the perspective of a local intrapleural administration. This approach

is very promising since nowadays pharmacological systemic treatments for MPM are poorly effective.

**Keywords**: Gold nanoparticles, nano-drug delivery, mesothelioma, pemetrexed, intrapleural delivery.



**Figure 1**: GNP-HCPe fluorescent labeled (green) internalized by MPM cells.

- 1. Carbone, M. et al. (2002) The pathogenesis of mesothelioma, *Semin. oncol.*, 29: 2-17.
- 2. Cova et al. (2017) Bioengineered gold nanoparticles targeted to mesenchymal cells from patients with bronchiolitis obliterans syndrome does not rise the inflammatory response and can be safely inhaled by rodents, *Nanotoxicology*.

### Preparation and characterization of Pistacia Lentiscus var. Chia essential oil-loaded poly(lactic acid) nanoparticles as novel wound healing agent

I. Vrouvaki,<sup>1</sup> E. Koutra,<sup>2</sup> M. Kornaros,<sup>2</sup> K. Avgoustakis,<sup>1</sup> F. N. Lamari,<sup>1</sup> S. Hatziantoniou,<sup>1,\*</sup>

<sup>1</sup> Laboratory of Pharmaceutical Technology Dept of Pharmacy, School of Life Sciences, and <sup>2</sup> Department of Chemical Engineering, Patras, Greece

#### Abstract:

Dating back to the first century AD, ancient Greek physicians (Hippocrates, Dioscorides, Galenos) reported the therapeutic properties of Pistacia Lentiscus var. Chia (mastic tree of Chios). The plant derivatives are well known for treatment of stomach disorders, preservation of oral hygiene and wound healing action. Extended research suggests that the essential oil possess mainly antimicrobial and anti-inflammatory properties, thus attracting considerable interest as a potential wound healing agent. Issues like its poor water solubility and volatility, as well as its caustic nature when in large quantity, hinder the development of technological means for cutaneous administration. Further research has reported anticancer activity, raising significantly the demand of investigating possible means of administration. Encapsulating the essential oil in nanoparticles (NPS) provides a method of protection and controlled release for the oil constituents enclosed in the core of the nanoparticles. In this study, poly(lactic acid) (PLA) is chosen as the most appropriate shell biocompatibility, material due to its biodegradability hydrophobic nature. and allowing thus the incorporation of oily compounds. A comparative study has been carried out for the investigation of surfactant type on the produced nanoparticles, using poly(vinyl alcohol) and lecithin. Nanoparticles made by solvent evaporation method are evaluated according to mean size, shape, polydispersity Encapsulation index and zeta-potential. efficiency is determined utilizing GC-MS, technique of high accuracy and limited use in literature. Stability data and the in vitro release study indicated that polyvinyl alcohol-NPs remarkably firmer exhibit structure in comparison with lecithin-NPs. The results of this research demonstrate a potential for a novel sustained release system of a particular essential oil, maintaining though the possibility of expansion by two means; investigation of the

different biomedical applications and furthermore, encapsulation of a variety of essential oils.

**Keywords**: Pistacia Lentiscus var. Chia essential oil, encapsulation, nanoparticles, poly(lactic acid), nanotechnology, wound healing.



**Figure 1**: Utilizing scientific means in order to achieve application of the beneficial effects of the essential oil derived from Pistacia Lentiscus var. Chia. Figure illustrating the original plant and its resin (left part), stages of the experimental approach such as the stability diagram and part of the chromatogram of GC-MS (right part) and a SEM picture of the successfuly formulated nanoparticles.

- 1. Koutsoudaki, C., Krsek, M., Rodger, A. (2005), Chemical composition and antibacterial activity of the essential oil and the gum of Pistacia Lentiscus var. Chia, *J. Agric. Food Chem.*, 53, 7681-7685.
- Spyridopoulou, K., Tiptiri-Kourpeti, A., Lampri, E., Fitsiou, E., Vasileiadis, S., Vamvakias, M., Bardouki, H., Goussia, A., Malamou-Mitsi, V., Panayiotidis, M. I., Galanis, A., Pappa, A., Chlichlia, K. (2017), Dietary mastic oil extracted from Pistacia Lentiscus var. Chia suppresses tumor growth in experimental colon cancer models, *Sci. Rep.*, 7:3782, 1-14

### Graphene and the Brain: the Neurobiology of the Interaction between Graphene and Primary Neurons, Astrocytes and Microglia

F. Cesca,<sup>1,\*</sup> M. Bramini,<sup>1</sup> F. Benfenati<sup>1,2</sup>

<sup>1</sup> Istituto Italiano di Tecnologia, Center for Synaptic Neuroscience and Graphene Labs, Genova, Italy <sup>2</sup> University of Genova, Department of Experimental Medicine, Genova, Italy

### Abstract:

There is an increasing interest toward the use of graphene (G) and G-related materials (GRMs) for biomedical applications, especially for targeting the central nervous system. To fulfil this goal, it is mandatory to characterize the effects elicited by different types of G when in contact with the main neural cells populations, with the goal to evaluate G biocompatibility and accordingly any unwanted effects that G-based materials could potentially induce to living systems. We are conducting our research within the Graphene Flagship European project, focusing our attention on primary neurons [1], glial and microglia cells [2]. We are characterizing the molecular mechanisms of G flake internalization together with the possible inflammatory responses. Our results show that although exposure to G materials does not impact cell viability and network formation, it does nevertheless have important effects on neuronal and glial physiology. We demonstrated that G oxide (GO) flakes impact on several cellular synaptic processes including activity, intracellular Ca2+ dynamics and astrocyte glutamate uptake, thus on one side warranting caution when planning to employ this material for neurobiological applications, but on the other side suggesting GO materials could have protective effects in neuropathologies characterized by hyperexcitability. Moreover, we are exploring the possibility of using G-based supports as biocompatible scaffolds for biomedical applications, trying to exploit the conductive properties of this material to modulate and control the activity, differentiation and connectivity of neural networks grown in strict contact with such scaffolds. Finally, we are investigating the molecular and cellular mechanisms by which G and GRMs interact with the blood-brain barrier [3], to assess the possibility of using these materials for drug delivery applications targeted to the central nervous system.

**Keywords**: graphene and graphene oxide flakes, primary neurons and glia, blood-brain barrier, 2D/3D biocompatible scaffolds, biomedical applications.



**Figure 1**: Scanning electron microscopy (SEM) was used to study the interaction of flakes with neuronal cells. The image represents neurons that had been exposed to GO flakes for 96 h, fixed, and prepared for SEM analysis. A large number of flakes (white arrowheads) were found in contact with the cell membrane; however, cell morphology and network development were substantially unaffected [1].

- Bramini, M., Sacchetti, S., Armirotti, A., Rocchi, A., Vázquez, E., León Castellanos, V., Bandiera, T., Cesca, F., Benfenati, F. (2016) Graphene Oxide Nanosheets Disrupt Lipid Composition, Ca<sup>2+</sup> Homeostasis, and Synaptic Transmission in Primary Cortical Neurons. ACS Nano, 10(7):7154-71.
- Chiacchiaretta, M., Bramini, M., Rocchi, A., Armirotti, A., Giordano, E., Vázquez, E., Bandiera, T., Ferroni, S., Cesca, F., Benfenati, F. (2018) Graphene oxide upregulates the homeostatic functions of primary astrocytes and modulates astrocyteto-neuron communication, Under revision.
- Bramini, M., Ye, D., Hallerbach, A., Nic Raghnaill, M., Salvati, A., Aberg, C., Dawson, K.A. (2014) Imaging approach to mechanistic study of nanoparticle interactions with the blood-brain barrier. *ACS Nano*, 8(5):4304-12.

### A new lipopolyplex formulation with enhanced dendritic celltargeting ability for mRNA/adjuvant vaccine delivery

S. Persano,<sup>1,\*</sup> M.L. Guevara,<sup>1</sup>

<sup>1</sup> Children's Hospital of Eastern Ontario (CHEO) Research Institute; Department of Biochemestry, Microbiology and Immunology, University of Ottawa

### Abstract:

Messenger RNA (mRNA) is a novel and highly promising therapeutic agent for the treatment of different diseases, using strategies based on the induction of *de novo* synthesis of a specific and functional protein<sup>1</sup>. The use of mRNA is undergoing a growing interest particularly, for the development of infectious diseases and cancer vaccines<sup>2</sup>. However, so far, the implementation of mRNA for therapecutic applications has been limited due its extreme sensitivity to degradation by ribonucleases. Moreover, naked mRNA fails to target and transfect antigen-presenting cells (APCs) in vivo, limiting its efficacy as a vaccine<sup>1</sup>. For this reason, a delivery system with mRNA protective and APC-targeting properties is highly desirable.

In this framework, a new lipopolyplex vector, incorporating the immune adjuvant  $\alpha$ -galactosylceramide ( $\alpha$ -GalCer) and a multivalent cationic lipid, was proposed for *in vivo* delivery of mRNA into antigen presenting cells (APCs).

The transfection efficiency of the nanovector was analyzed using enhanced green fluorescence protein (eGFP) and luciferase mRNA. Furthermore, immunogenicity and therapeutic efficacy of the vaccine formulation were investigated. The results indicate that our lipopolyplexes possess a natural ability to target dendritic cells in vivo and to transfect them with high efficency. Moreover, we showed for the first time how mRNA-vaccine efficacy could be potentiated by codelivering mRNA, encoding for a tumor-associated antigen (TAA), with  $\alpha$ -GalCer adjuvant. Indeed, our vaccine formulation significantly enhanced the induction of antigenspecific CD8+ T-cells both systemically and intratumorally and increased tumor-infiltrating NK cells. All this correlated with a marked tumor growth retardation and increased survival of B16-F10 melanoma-bearing mice treated with α-GalCer/mRNA-loaded lipopolyplex the vaccine.

These data may have important implications in the design of novel formulations combining mRNA with lipidic adjuvants for the development of cancer vaccines with potentiated antitumor properties.

**Keywords**: Nanomedicine, Vaccines, mRNA, Cancer, Lipopolyplex, Non-viral vectors, adjuvants.



**Figure 1**: Figure illustrating the mechanism of action of the  $\alpha$ -GalCer/mRNA-loaded liopolyplex vaccine. After i.v. administration, antigen-mRNA and adjuvant are released simultaneously into dendritic cells which present the antigen, after processing, to the lymphocytes in order to promote an antitumor immune response.

- 1. Ugur Sahin, Katalin Karikó and Özlem Türeci. mRNA-based therapeitics— Developing a new class of drugs. Nat Rev Drug Discov. 13, pages 759–780 (2014).
- Norbert Pardi, Michael J. Hogan, Frederick W. Porter, and Drew Weissman. mRNA vaccines — a new era in vaccinology. Nat Rev Drug Discov. 2018 Apr;17(4):261-279.

### Biophysical and biological contributions of polyamine-coated carbon nanotubes and bidimensional buckypapers in the delivery of miRNAs to human cells

A. Celluzzi,<sup>1</sup> A. Paolini,<sup>1</sup> V. D'Oria,<sup>1</sup> R. Risoluti,<sup>2</sup> S. Materazzi,<sup>2</sup> M. Pezzullo,<sup>1</sup> S. Casciardi,<sup>3</sup> S. Sennato,<sup>4</sup> F. Bordi,<sup>4</sup> A. Masotti,<sup>1</sup>.

<sup>1</sup> Bambino Gesù Children's Hospital, IRCCS, Research Laboratories, Rome, ITALY. <sup>2</sup> Department of Chemistry, Sapienza University of Rome, Rome, ITALY.

<sup>3</sup> Department of Occupational and Environmental Medicine, Epidemiology and Hygiene, National Institution for Insurance Against Accidents at Work (INAIL Research), Monte Porzio Catone, ITALY. <sup>4</sup> CNR-ISC UOS Roma, Department of Physics, Sapienza University of Rome, Rome, ITALY.

#### Abstract:

Recent findings in nanomedicine have revealed that carbon nanotubes (CNTs) can be used as a potential novel gene delivery vector system. In our previous work, we functionalized CNTs polymers. with polyamine two polyethyleneimine (PEI) and polyamidoamine dendrimer (PAMAM). These compounds have low cytotoxicity, are able to conjugate microRNAs and transfect them efficiently to endothelial cells. The diameter and length of CNTs are important parameters to be taken into account when evaluating the effects on drug delivery efficiency. In order to investigate the biophysical and biological contributions of polymer-coated CNTs in delivery of miRNAs to human cells, we decided to investigate three different preparations, characterized by different dimensions and aspect ratios. Three different solutions of PEI- or PAMAM-coated CNTs were prepared. The amount of polymer bound to CNTs was assessed by thermogravimetric analysis (TGA), whereas the size by dynamic light scattering (DLS). Cytotoxicity of polymercoated CNTs was analyzed on HEK 293T cells using MTT assay, whereas the cellular uptake of miRNAs complexed to polyamine-coated CNTs was evaluated by confocal microscopy. A homemade support of buckypapers (BPs) was realized by filtering a suspension of PAM-CNTs and cell growth and transfection were examined by optical and confocal microscopy. We extensively characterized long and very short polymer-coated CNTs that resulted to have different properties. We found that longer CNTs may also transfect cells by "piercing" cells effectively, ultimately contributing to overall transfection. Interestingly, bidimensional sheets of CNTs (ie, BPs) are versatile supports for cell cultures, and when properly functionalized they have a reduced toxicity. The characterization of the biophysical and biological properties of polyamine-coated CNTs and bidimensional BPs allowed us to evaluate precisely their contributions in microRNA delivery to human cells.

#### Keywords:

carbon nanotubes, buckypapers, polyamines, cytotoxicity, cell transfection

### Polyamine-coated carboxylated carbon nanotubes (CNTs-COOH) and nanohorns (NHs-COOH) in the delivery of miRNAs to human cells

A. Celluzzi,<sup>1,\*</sup> A. Paolini,<sup>1</sup> L. Lo Tufo,<sup>1</sup> Z Abbaszadeh,<sup>1</sup> R. Risoluti,<sup>2</sup> S. Materazzi,<sup>2</sup> D. Pozzi,<sup>3</sup> G. Caracciolo,<sup>3</sup> A. Masotti,<sup>1</sup>.

<sup>1</sup> Bambino Gesù Children's Hospital, IRCCS, Research Laboratories, Rome, Italy
 <sup>2</sup> Department of Chemistry, Sapienza University of Rome, Rome, Italy
 <sup>3</sup> Department of Molecular Medicine, Sapienza University of Rome, Rome, Italy

#### Abstract:

Pristine and carboxylated carbon nanotubes (CNTs and CNTs-COOH) have received considerable interest as promising drug delivery systems. We previously reported a novel strategy to deliver miRNAs by polyamine (PEI and PAMAM) coated-CNTs. These polymers impart hydrophilicity to CNTs, which facilitates their suspension in aqueous solutions and generate a positively charged surface able to bind negatively charged nucleic acids. Here, we exploited the higher solubility of carboxylated CNTs compared to pristine ones and we compared the transfection efficiency of compounds having different lengths (CNTs and NHs).

The amount of polymer bound to CNTs was assessed by thermogravimetric analysis (TGA), whereas the size by dynamic light scattering (DLS). Cytotoxicity of polymer-coated CNTs was analyzed on HeLa cells using MTT assay, whereas the cellular uptake of miRNAs complexed to polyamine-coated CNTs was evaluated by confocal microscopy. Cellular internalization was evaluated also with cytofluorimetry by using different inhibitors of endocytic pathways.

All of the compounds are able to bind polymers independently by the size. These compounds are also quite stable for long time. The toxicity of PAM-CNTs-COOH and PAM-NHs-COOH resulted quite modest even at high doses. The transfection on HeLa cells by CNTs-COOH is good although the shorter NHs-COOH seem to have a better efficiency. PAM-CNTs-COOH were internalized with a caveolin-dependent endocytosis mechanism while for NH-CNTs-COOH the mechanism is more complex, maybe due to the size of these compounds.

We suggest that CNTs-COOH or NHs-COOH may be used as alternative drug delivery compounds for miRNA delivery into human cells.

**Keywords**: carboxylated carbon nanotubes, carbon nanohorns, polyamines, PEI, PAMAM, transfection, miRNAs, biomedical applications.

# The effect of surface functionalization and pH on protein-gold nanoparticle interactions

B. Meesaragandla,<sup>1,2,\*</sup> I. Garcia,<sup>3</sup> L.M. Liz-Marzán<sup>3,4</sup> and M. Delcea<sup>1,2</sup>

<sup>1</sup> Institute of Biochemistry, University of Greifswald
 <sup>2</sup> ZIK HIKE, University of Greifswald, Germany
 <sup>3</sup>CIC biomaGUNE and CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain
 <sup>4</sup>Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

### Abstract:

Nanoparticles (NPs) can stimulate and/or suppress the immune response when they interact with the proteins in the blood.<sup>1</sup> The conformational changes of proteins after conjugation with NPs are an important aspect for the immunogenicity. The compatibility of the NPs with the immune system is mainly determined by their surface chemistry.<sup>2</sup> In this work, we have studied the human serum albumin (HSA) protein-gold nanoparticle (AuNP) interactions focusing on the nature of AuNP surface and pH of the medium. HSA exhibit different isomeric forms and undergo conformational changes at different pH conditions (e.g. pH 3.8, 7.4, and 9.3).<sup>3</sup>

15 AuNPs with nm different surface functionalization (citrate, PEG-SH, PEG-COOH, PEG-NH<sub>2</sub>, and glycan) were chosen to understand the effect of surface functionalization on protein conformation. Both UV-Vis and dynamic light scattering (DLS) measurements have indicated the formation of protein corona. No significant change (or a slight red shift) is observed in the localized surface plasmon resonance (LSPR) position (at 523 nm), which may indicate the weak interaction between core AuNPs and HSA. In addition, increase in protein corona size is not due to the aggregation of the NPs. Circular dichroism (CD) spectroscopy studies suggested that HSA conjugated to AuNPs undergoes a change in the secondary structure (decrease in alpha-helix) at various pH for all functionalized AuNPs. This change in protein secondary structure might be due to the type of dominant interaction between NPs and HSA (i.e electrostatic, hydrogen bonding). Our results indicated that both surface charge and pH of the medium influences the changes in HSA structure.

**Keywords**: gold nanoparticles, human serum albumin, protein corona, circular dichroism spectroscopy, surface modification, pH, immunogenicity.



**Figure 1**: Schematic representation of the formation of AuNP-HSA corona at different pH conditions. The inset shows the variety of functional groups at the NPs surface to understand the nature of interaction between NPs and HSA.

- 1. Dobrovolskaia, M. A., McNeil, S. E. (2007), Immunological properties of engineered nanomaterials, *Nat. Nanotechnol.*, 2, 469-478.
- 2. McNeil, S. E. (2005), Nanotechnology for the biologist. J. Leukoc. Biol. 78, 585–594.
- Chatterjee, T., Pal. A., Dey. S., Chatterjee B. K., Chakrabarti. P. (2012) Interaction of virstatin with human serum albumin: spectroscopic analysis and molecular modeling. *PLOS One.*, 7, e37468. doi: 10.1371/journal.pone.0037468.

### EGF 2018 / SMS 2018 Joint Plenary Session

### Infrared and THz inter-subband optics of few-layer 2D materials

### Celal Yelgel

National Graphene Intitute, Univesity of Manchester, Booth St E, M13 9PL, Manchester, UK

### Abstract:

The science and applications of electronics and optoelectronics have been driven for decades by progress in the growth of semiconducting heterostructures. Many applications in the infrared and terahertz frequency range exploit transitions between quantized states in semiconductor quantum wells (intersubband transitions). However, current quantum well devices are limited in functionality and versatility by diffusive interfaces and the requirement of lattice-matched growth conditions. Here, we introduce the concept of intersubband transitions in van der Waals quantum wells, such as atomically thin films of MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub> and posttransition metal chalcogenides (PTMC), InSe and GaSe. These are materials where a strong covalent bonding of atoms inside individual layers coexists with a weak van der Waals coupling of the consecutive layer of the bulk crystal. Van der Waals quantum wells are naturally formed by two-dimensional materials and hold unexplored potential to overcome the aforementioned limitations — they form atomically sharp interfaces and can easily be combined into heterostructures, without latticematching restrictions.

At the same time, van der Waals nature of these crystals coexists with strong hybridizations of separately - conduction and valence band orbitals in the consecutive monolayers in the film, making the band structure of few-layer atomically thin TMDs and PTMCs sensitive to the number of layers in them [1,2]. In particular, few-layer films acquire multiple subbands in their electronic spectra, with a strong coupling of inter-subband transitions of carriers (electrons in n-doped and holes in p-doped materials) with out-of-plane polarised photons. Here, we show that, when n- or p-doped, few-layer films of TMDs and PTMCs become absorbers and emitters of infrared (IR) and THz light [1,2]. Our density functional theory modelling and a specially designed hybrid k·p theory for the monolayers of these materials, combined with the tight-binding model description of the interlayer hopping, predicts that optical activity of few-layer films of these two classes of compounds densely covers the range from IR (1.5 micron) for bilayer films to THz for the films with 3-10 layers.

The predicted spectral characteristics are confirmed [3] by SNOM studies of atomically thin films of WSe<sub>2</sub>. In a way, these thin films are analogous to quantum wells in conventional semiconductors, and, by choosing the number of layers, and/or n- or p-doping in one of TMD and PTMC compounds, one can tune such intersubband transition energy to the desirable application range, offering a new way how 2D materials can be harnessed for developing new technologies. This work enables the exploitation of intersubband transitions with unmatched design freedom and individual electronic and optical control suitable for photodetectors, lightemitting diodes and lasers.

- M. Danovich, D. Ruiz-Tijerina, C. Yelgel, V. Zólyomi, V. Fal'ko, Phys. Rev. B 98, 035411 (2018)
- S. Magorrian, V. Zólyomi, V. Fal'ko, Phys. Rev. B 97, 165304 (2018)
- P. Schmidt, F. Vialla, S. Latini, M. Massicotte, K.-J. Tielrooij, S. Mastel, G. Navickaite, M. Danovich, D. Ruiz-Tijerina, C. Yelgel, V. Fal'ko, K. Thygesen, R. Hillenbrand, F. Koppens, Nature Nanotechnology (2018)

### Electronic Properties of Graphene on Different Substrates: A Theoretical Perspective

### E. Voloshina

University of Shanghai, Deaprtment of Physics and ICQMS, Shanghai, P.R. China

### Abstract:

Epitaxial graphene on various substrates is an exciting field of materials chemistry and physics from different points of view. For example, technologically, the growth of graphene on metals is the main and the most perspective way for the large-scale preparation of high-quality graphene layers of different thicknesses with controllable properties. Furthermore, the obtained systems might be used for many applications, like spin filters, gas sensors, or in case of graphene/metal moiré structures as templates for the preparation exceptionally well-ordered nano-cluster of lattices. Along with the practical view on these experimental systems, and theoretical investigations of graphene/substrate interfaces gave rise variety of fundamental questions [1]. Two of them are: (i) nature of bonding between graphene and substrate and (ii) origin of modifications of the electronic structure of graphene in vicinity of the Fermi level. Aiming to shed more light on the problem of the interaction of graphene with the substrates and modification of its electronic structure, different examples of the graphene/metal interfaces have been considered. Based on the analysis of a large amount of experimentally and computationally obtained band structures, we proposed a universal model, which allows one to describe qualitatively any graphene/metal system [2]. All experimental observations can be understood in the framework of this approach. This work summarizes the long-term debates regarding connection of the bonding strength and the valence band modification in the graphene/metal systems and paves a way for the effective control of the electronic states of graphene in the vicinity of the Fermi level.

**Keywords**: graphene-metal systems, interface properties, DFT

### **References:**

1. Voloshina, E., Dedkov, Y. (2012), Graphene on metallic surfaces: problems and perspectives, *Phys. Chem. Chem. Phys.* 14, 13502. 2. Voloshina, E., Dedkov, Y. (2014), General approach to understanding the electronic structure of graphene on metals, *Mater. Res. Express* 1, 035603.

### Smart Inspection Tools for Zero Defect Manufacturing Strategy

### Cristina Cristalli

<sup>1</sup> Loccioni, Research for Innovation, Angeli di Rosora (AN), Italy

### Abstract:

In modern digital factories, performing in-line quality control on 100% of production is a key strategy to target a zero-defect production. This is particularly relevant in multistage production systems, since real-time and early identification of deviations and trends, performed at single stage level, allows to prevent the generation of defects and their propagation to downstream processes, enabling the entire manufacturing system to perform early detection of process deviations and self-adaptation to varying conditions. In such a context it becomes clear that requires а zero-defect strategy reliable information to support any decision. Reliable information requires measured data from the process and the product. Currently, sensors are designed just to capture the phenomenon to be observed and the associated acquisition board digitalizes the acquired signal, offering a limited level of processing. Classification of the acquired data aiming to take appropriate decision is realized using algorithms running on separate hardware. However, in a Zero-Defect-strategy context, measurement systems should be improved to be able to take decision and react to specific situations, like the human brain takes instantaneous decisions based on sensorial inputs. Indeed, this means empowering quality control systems with some intelligence that can be embedded with the sensor.

These concepts have been explored by recent EU-funded projects, among which the GO0D MAN [1] and the GRACE [2] projects are two examples worth mentioning. Indeed, both aim to integrate process and quality control in manufacturing system. In particular, the GOOD MAN project is implementing, in multi-stage manufacturing production lines, a distributed system architecture built on a joint use of agent based Cyber-Physical Systems (CPS) and smart in-line quality control systems. Born from the union of physical devices with network computing, CPSs can be considered essential for the future of industry in general, as they have been identified as core enabling and disruptive technology, with enormous social and economic importance. However, the pervasive and extensive use of CPSs in the industrial domain will be possible only if suitable connective architectures, cognitive structures and appropriate sensors able to provide reliable information are designed, developed and integrated.

**Keywords**: zero defect manufacturing, smart inspection system, multi-agent system, in-line quality control.

- 1. Web site of GO0DMAN Project: http://go0dman-project.eu/
- Web site of GRACE Project http://graceproject.org/

### Nanotechnology-based nanocoating and printed electronics in Smart Textiles

A. Braz Costa,<sup>1,2,\*</sup>

CeNTI – Centre of Nanotechnology and Smart Materials CITEVE – Technological Centre for Textile and Clothing Industries in Portugal

### Abstract:

Nanotechnology is considered a Key Enabling Technology (KET) in Horizon 2020, the European framework Program for Science and Technology, since it allows for cheaper productions, less energy, avoid resource intensive production processes and more effective products, through the exploitation of unique properties achieved at the nanoscale. In this sense, over the last years, CeNTI has been using Nanotechnologies to process materials at the nanoscale for a full range of applications.

Nanotechnologies and nano-enabled materials are being used at CeNTI as a KET for the development of innovative products and processes for several industrial applications. Several examples will be given to show the benefits of using Nanotechnologies to develop Functional and Smart Materials, focusing on the development of innovative textiles, in comparison with the use of conventional technologies. The increased comfort and hand-feel, increased durability and performance and the innovative applications for the textiles, are some of the benefits achieved when using nanotechnologies and nano-enabled materials in their development. Additionally, some examples will show how the use of nanotechnologies can provide new functionalities and intrinsic smartness of materials for smart applications, boosting the potential range of textile applications in everyday products and in cutting edge textile based technical applications.

**Keywords**: Advanced Textiles, Printed electronics, printed lightning, nanoparticules, nanocoating, smart textiles, fibre nanotecnologies

# Smart carbon based textile reinforcement for sensing infiltration of water in concrete structures

G. Dittel,<sup>1\*</sup> Y. Goldfeld,<sup>2</sup> G. Perry,<sup>2</sup> T. Quadflieg,<sup>1</sup> T. Gries<sup>1</sup>

<sup>1</sup> Institut fuer Textiltechnik of RWTH Aachen University, Aachen, Germany
<sup>2</sup> Technion - Israel Institute of Technology, Faculty of Civil and Environmental Engineering, Haifa, Israel

### Abstract:

In this study, we aim to examine the feasibility of textile reinforced concrete (TRC) smart structures with inherent sensing capabilities. The approach combines the advantages of thin walled glass fiber based TRC with the structuralelectrical properties of carbon rovings knitted in the textile grid. The paper aims to demonstrate that by means of simple electronic and structural manipulations, rovings made of carbon filaments can become an embedded sensory agent, which provides meaningful information regarding the functional and the structural health condition of the TRC load bearing element. In that sense, it aims to provide the structural system with the sensory features required for an intelligent system.

The study focuses on the ability of the rovings to sense infiltration of water through cracked zones along the structure. To examine this concept and its potential feasibility, a cracked TRC beam specimen with carbon sensory rovings knitted in a glass fiber fabric is tested and monitored under different environmental conditions. The study will look into the ability of the embedded carbon rovings to detect wetting through the comparison of various electrical schemes and sensing concepts. The results of the tests will demonstrate the features of each sensory scheme and reveal its potential use as a basis for functional monitoring in TRC structures. **Keywords**: textile reinforced concrete, sensory carbon rovings, smart textiles, sensing infiltration of water, intelligent concrete systems

### EGF 2018 / SMS 2018 - Joint Session II: Novel Materials / Graphene for Energy and Environment applications

### Advances in Nanoscale Electrical and Thermal Characterization of Surfaces and Thin Films

G. Benstetter,\* W. Lehermeier, C. Metzke

Deggendorf Institute of Technology, IQMA, Deggendorf, Germany

### Abstract:

Thin film devices and thermoelectric materials have gained a growing importance in sustainable energy harvesting because of their ability to convert energy directly. For higher efficiency, their thermal conductivity needs to be reduced while at the same time Seebeck coefficient and electrical conductivity should be increased or at least remain unchanged.

The presentation reviews advances in selected physical characterization methods to study structural, electrical and thermal properties of materials and thin films. Selected characterization methods are discussed such as scanning probe microscopy (SPM), electron microscopy-based techniques and the  $3\omega$  method to study the impact of material structure and film thickness on the transport properties. Case studies are presented for different thin film materials and systems ranging from sputter deposited semiconductors to laser-sintered nanoparticle thin film. The  $3\omega$  method is used to determine the thermal conductivity of thin films. Conductive atomic force microscopy (CAFM) is applied to analyze correlations between film morphology and 2D current distribution, supported by electron backscatter diffraction (EBSD) and scanning transmission electron microscopy (STEM). Local IV characteristics are obtained to reveal electrical conduction mechanisms with high spatial resolution. This work has been partially supported by the Bavarian State Ministry of the Environment and Consumer Protection via the project "UMWELTnanoTECH" and the Federal Ministry of Education and Research (BMBF), Germany.

Keywords: scanning probe microscopy, conductive atomic force microscopy, electron backscatter diffraction, thermoelectric materials,  $3\omega$  method.



**Figure 1**: Numerical analysis of the heat propagation into a thin film by using the  $3\omega$  method. Depending on the heater width relative to the film thickness either cross-plane or inplane thermal conductivity of thin films can be evaluated.

- B. Stoib, T. Langmann, N. Petermann, S. Matich, M. Sachsenhauser, H. Wiggers, M. Stutzmann, M.S. Brandt, Phys. Status Solidi A 210 (2013) 153–160
- D.G. Cahill, T.H. Allen, Appl. Phys. Lett. 65 (1994) 309.
- 3. D.G. Cahill, K. Goodson, A. Majumdar, J. Heat Transfer 124 (2002) 223.
- 4. G. Benstetter, A. Hofer, D. Liu, W. Frammelsberger, M. Lanza, "Conductive Atomic Force Microscopy. Applications in Nanomaterials", (2017), Wiley VCH
- 5. M. Bogner, A. Hofer, G. Benstetter, H. Gruber, R.Y. Fu, Thin Solid Films 591 (2015) 267–270.

### Molecular dynamics study of thermo-responsive oligomer endgrafted onto graphene oxide and quartz: the effect of the surface coverage

G. Forte,<sup>1\*</sup> G. Consiglio<sup>2</sup>

<sup>1</sup>University of Catania, Department of Scienze del Farmaco, Catania, Italy <sup>2</sup>University of Catania, Department of Scienze Chimiche, Catania, Italy

#### Abstract:

Both structural and dynamical properties of 40mer of thermos responsive polymer PNIPAM end-grafted to graphene oxide and silica were studied at various temperatures by using molecular dynamic simulations in explicit solvent. The radial distribution functions (RDF) together with evolution of the radius of gyration analysis (Rg) suggest how functional groups onto surfaces, e.g. -OH, affect the coil-to-globule transition of PNIPAM by means of electrostatic interactions, increasing the lower critical solution temperature of the free polymer which, experimentally, is found to be  $305 \text{ K}^1$ , Figure 1. These interactions are mainly represented by Hbond and hinder the transition to the globular form. Conversely hydrophobic groups located on the surface contribute to the globular collapse. A significant alteration in the arrangement of water molecules around the polymer is testified by the absence of the second peak, in the radial distribution functions, at the same temperatures radius gyration at which of decrease. Furthermore the H-bond correlation function indaicates that: i) hydrogen bond between boundtosurface PNIPAM acceptor groups (O=C<) and hydrogen atoms of water molecules are weaker than H-bond formed between free PNIPAM acceptor groups and water; ii) H-bond between PNIPAM acceptor groups and hydroxyl groups onto quartz surface are longer lived than those formed in the graphee oxide. We present a study which supplies a better insight to design nanoscale stimuli-responsive platforms wth potential applications in the drug-delivery, controlled release and surface modification.

**Keywords**: PNIPAM, stimuli-responsive platforms, silica surface, graphene oxide, polymer hydration, biomedical applications.



**Figure 1**: Figure illustrating the evolution of PNIPAM  $R_g$  at different temperatures: it decreases respectively at 310 K, when the polymer is end-grafted to graphene oxide (above), and at 315 K when end-grafted to quartz (below). Comparison show that higher degree of -OH surface coverage increase the LCST of the polymer up to 315 K.

#### **References:**

1. Wu, C., Wang, X. (1998) Globule-to-coil transition of a single homopolymer chain in solution, *Phys. Rev. Lett.*, 18, 4092-4094.

### Single Molecular Imaging of Fluorescent-Tagged Peptides Diffusing on a Surface of Boron Nitride

P. Li,<sup>1,\*</sup> T. Seki, <sup>1</sup> L. Sun, <sup>1</sup> Y. Hayamizu,<sup>1</sup>

<sup>1</sup>Tokyo Insitute of Technology, Schoole of Materials Science and Engineering, Tokyo, Japan

### Abstract:

Specific peptides can spontaneously organize on a solid surface. Functionalization of surfaces of inorganic materials with these peptides is essential for biological applications, such as biosensor, drag delivery. Recently, engineered peptides on two-dimensional materials have demonstrated a spontaneous organization into long-range ordered nanostructures with six-fold symmetry. During the process of selforganization, there are three steps: (1) binding, (2) diffusion, and (3) ordering.<sup>1</sup> It is important to investigate these processes individually for the control of the self-organization. While the ordering of peptides has been studied, the diffusion process is not fully understood, due to technical difficulties in the atomic force microscopy. In the kinetics of peptide selforganization, the diffusion process is needed to be studied more systematically.

In this work, we utilized a high-sensitive fluorescent microscopy with fluorescent tagged peptides for a single molecular imaging to quantitatively investigate the diffusion process. As the results of fluorescent microscope imaging, peptides at low concentration (~pM) diffuse on the BN surface with a random walk for a short time interval. The value of its diffusion coefficient is comparable with previously reported polymers solid on surfaces. Interestingly, in contrast, peptides at relatively high concentration (~nM) show an anisotropic diffusion in certain orientations via molecular recognition of surface. In the presentation, we will discuss quantitative physical parameters in the diffusion process.

**Keywords**: surface binding peptide, boron nitride, self-assembly, surface diffusion, single molecular imaging, single molecular tracking, anisotropic diffusion.



**Figure 1**: (a) Schematic of peptide self-assemble process on boron nitride surface: (i) binding, (ii) diffusion and (iii) ordering. (b) Fluorescent image of fluorescent-tagged peptide diffusing on BN suface at low concertation. (c) Fluorescent image of anisotropic diffusion at high concertation.

- So, C. Y., Hayamizu, Y., Yazici, H., Gresswell, C., Khatayevich, D., Tamerler, C., Sarikaya, M. (2012), Controlling selfassembly of engineered peptides on graphite by rational mutation, ACS NANO, 6(2), 1648-1656.
- Skaug, M. J., Mabry, J. N., Schwartz, D. K. (2014), Single-molecule tracking of polymer surface diffusion, *J. Am. Chem. Soc.*, 136, 1327-1332.

# Nanographene oxide as an efficient photocatalyst in the degrdation of Rhodamine 6 B dye and solvent free oxidation of benzyl alcohol

Daisy Theresa<sup>1</sup>, N Nagaraju<sup>1</sup>, H. Kathyayini<sup>2</sup>, Shanty Mathew<sup>1\*</sup>

<sup>1</sup> St. Joseph's College Research Center, Shanthinagar, Bengaluru, Karnataka, 560027, India.
<sup>2</sup> Centre for Incubation, Innovation Research and Consultancy (CIIRC), Jyothy Institute of Technology, Tataguni, Off Kanakapura Road, Bengaluru, 560082.

### Abstract:

The nano graphene oxide (NGO) was prepared from graphite by Modified Hummer's method. The prepared NGO was characterized by powder X-ray diffraction (PXRD), Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX). Conversion of graphite to NGO and particle size was confirmed by XRD. Presence of C-O and C=C bonds were analysed using FTIR. Exfoliation of graphite sheets is confirmed by SEM images. EDX confirmed the presence of carbon and oxygen. The photo catalytic activity of nano graphene oxide was assessed through the degradation of Rhodamine 6-B dye in an aqueous solution under solar radiation. 97% photo degradation of dye occurred in 4 hours. NGO was also used for the oxidation of benzyl alcohol to benzaldehyde under solvent free conditions. It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of the catalytic activity. It can be recovered by filtration, washed with water and subjected to other trials. The experimental results demonstrated that nano graphene oxide have promising applications in photo catalysis and in organic reactions.

**Keywords**: Nano graphene oxide, Rhodamine 6 B dye, photodegradation, oxidation of benzyl alcohol, solvent free.



Figure 1. SEM image of nanographene oxide

- Paulchamy B, Arthi G and Lignesh BD. A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial. Nanomedicine & Nanotechnology. (2015) 6:1
- Krishnamurthy, Karthikeyan & Mohan, Rajneesh & Kim, Sangjin. Graphene oxide as a photocatalytic material. Applied Physics Letters. 98 (2011)
- 3. R. Aarthi, K.C.Lalithambika, *Influence of chemical reactions over the formation of Graphene oxide nanoparticles*, RASAYAN J.Chem.vol.7.No.4.340-342.(2014).
- 4. Ali Gharib,Leila vojdani Fard ,Nader Noroozi Pesyan, Mina roshani. A new application of nano graphene oxide(NGO) as a heterogeneous catalyst in oxidation of Alcohols types.American institute of science.vol.1 no.5.151 -158. (2015)
- DanielR,Dreyer,SungjinPark,Christopher W.Bielawski and Rodney S.Ruoff. chemistry of grapheme oxide. chemical. society reviews (2009) 34

### Electrochemically Controlled Winding and Unwinding of HOPG Supported Carbon Nanoscroll

H. Tarábková,\* Z. Zelinger, P. Janda

J. Heyrovský Institute of Physical Chemistry ASCR, Prague, Czech Republic

### Abstract:

The carbon nanoscroll (CNS) represents carbon nanostructure similar to that of multi-walled carbon nanotube (CNT), but with a spiral-like rolled-up geometry and open edges at the ends. CNSs have properties as other graphitic system such as high mechanical strength, high electrical conductivity, nontoxicity. In contrast, the novel CNS topology exposes a number of unique properties. The CNS core size is more easily tunable, because to overcome van der Waals interlayer interactions in CNS structure requires less energy than the deformation of sp2 carbon bond in close tubular CNT structure. These properties lead to a number of proposed aplications[1] such as hydrogen storage, tunable nanochannel and nanoactuator.

CNSs were first reported as byproducts of arc discharge experiments using graphite electrode in 1960 [2] . Later, several different methods [1] producing CNSs at high yield and offering better control of final product were developed.

In our study[3], we have used CNSs spontaneously formed on freshly cleaved basal plane HOPG serving as a CNS support and working electrode at the same time. The CNS actuation was driven by applying potential (E) from 0 V to -0.9 V in an aqueous 0.1 M H2SO4 solution and monitored by in-situ AFM (Figure 1). Reversible changes of radial dimension exceeding 10 nm in axial and 50 nm in lateral direction were observed. Periodic dimensional changes take place selectively on scrolled nanostructures, while other parts of HOPG surface including planar areas, lifted and simple bended steps remain intact. The mechanism explaining observed phenomenon is discussed.

The work was supported by Czech Science Foundation project (No. 17-05167S) with potential optical applications.

**Keywords**: carbon nanoscroll, nanoactuator, electrochemically controlled scrolling, atomic force microscopy



**Figure 1**: Figure illustrating the electrochemically controlled winding and unwinding of CNS observed by in situ atomic force microscopy (AFM). *E* denotes applied potential.

- Perim, E., Machado, L. D., Galvao, D. S. (2014) A Brief Review on Syntheses, Structures, and Applications of Nanoscrolls, *Front. Mater.* 1, 1-7.
- 2. Bacon, R. (1960), Growth, Structure, and Properties of Graphite Whiskers, *J. Appl. Phys.*, 31, 283–290.
- Tarabkova, H., Zelinger, Z., Janda, P. (2018) Electrochemically controlled winding and unwinding of substrate-supported carbon nanoscrolls, *Phys. Chem. Chem. Phys.* 20, 5900-5908.

### Graphene devices for high frequency optoelectronic applications

P. Legagneux,<sup>1</sup> A. Montanaro,<sup>1</sup> O. Bezencenet,<sup>1</sup> B. Poupet,<sup>1</sup> J. Cholet,<sup>1</sup> M-B. Martin,<sup>1</sup> M. Rosticher,<sup>2</sup> B. Placais,<sup>2</sup>

<sup>1</sup>Thales R&T, Palaiseau, France

<sup>2</sup> Laboratoire Pierre Aigrain, ENS, Universities of PSL, Sorbonne, Paris Diderot, CNRS, Paris France.

#### Abstract:

Thanks to its broadband optical absorption, high carrier mobility and short photocarrier lifetime (< 1ps), graphene devices are particularly promising for broadband optoelectronic applications<sup>1</sup>. We report the mixing of high frequency (up to 67 GHz) electrical and optical signals within a graphene coplanar waveguide (CPW) fabricated on a thermally oxidized high resistivity silicon substrate (SiO<sub>2</sub>/Si-HR). Two different kinds of devices have been tested. The first one is based on a 2 inches CVD graphene film transferred on SiO<sub>2</sub>/Si-HR by Graphenea<sup>2</sup>. An optimized fabrication process<sup>3</sup> have been implemented to fabricate devices integrating low-doped CVD graphene and exhibiting a good carrier mobility. The second one is based on a h-BN/graphene/h-BN stack obtained by mechanical exfoliation. After device fabrication, both devices have been passivated with an Al<sub>2</sub>O<sub>3</sub> film obtained by atomic layer deposition. Using dedicated test devices we measured the room temperature field effect mobility. The mobility value is 3000  $cm^2/V.s$  for the Al<sub>2</sub>O<sub>3</sub>/G/SiO<sub>2</sub> structure and  $25.000 \text{ cm}^2/\text{V.s}$  for the h-BN/G/h-BN stack.

We also fabricated coplanar waveguides (CPWs) and perform high frequency optoelectronic mixing as shown on figure 1. An intensity-modulated laser at frequency fopt (67 GHz) illuminates the graphene channel and an electrical RF signal at frequency  $f_{\mbox{\scriptsize ele}}$  is injected in the CPW. This leads to the generation of two electrical signals at the CPW output, the first one at frequencies | fele - fopt | named intermediate frequency (IF) and the second one at  $(f_{ele} + f_{opt})$ . For the down-converted signal, we measured the conversion power efficiency, i.e. the output electrical power at IF divided by the input electrical power. For CPWs based on the h-BN/G/h-BN stack,  $P_{IF}/P_{RF}$  is between -44 and -54 dB for IF varying between 2 and 65 GHz. These results open interesting perspectives in graphene optoelectronic mixers for high speed communications.

**Keywords**: graphene, high frequency, optoelectronics, nanotechnology.



**Figure 1**: Optoelectronic mixing with a coplanar waveguide based on h-BN/graphene/h-BN stack. A 2-65 GHz electrical signal is mixed with a 67 GHz modulated optical signal leading to a 2-65 GHz downconverted signal. This figure plots the output power at intermediate frequency (IF) divided by the input power as a function of IF.

#### Acknowledgments

The research leading to these results have received partial funding from the European union Seventh Framework programme under grant N°696656 Graphene Flagship

- 1. A. Montanaro et al., "Thirty Gigahertz Optoelectronic Mixing in CVD Graphene, Nano Lett. 16, 2988 (2016).
- 2. Graphenea, https://www.graphenea.com/
- 3. S. Mzali et al., "Stabilizing a Graphene Platform toward Discrete Components", Appl. Phys. Lett. 109, 253110 (2016).

### Photodetector based on CVD grown 2D materials in a van der Waals heterostructure

B Sompalle<sup>1,2</sup>, CD Liao<sup>1</sup>, J Borme<sup>1</sup>, V Saxena<sup>1</sup>, F Cerqueira<sup>1,2</sup>, S Sadewasser<sup>1</sup>, P Alpuim<sup>1,2</sup>

<sup>1</sup>INL - International Iberian Nanotechnology Laboratory, Braga, Portugal <sup>2</sup>CFUM - Center of Physics, University of Minho, Braga, Portugal

### Abstract:

2D van der Waals heterostructures have great potential for optoelectronic applications [1][2]. High-quality two-dimensional atomic layers are essential for high performance optoelectronic applications because of their very high responsivity under illumination. The studies to date have been largely limited to stacked, exfoliated flakes, the controlled growth of such heterostructures remaining а significant challenge. Here we report the CVD growth of submillimeter sized single crystal graphene (as a conductor), hexagonal boron nitride (an insulator), MoSe<sub>2</sub> (the active semiconductor layer) and stacking of these layers as a photodetector with a planar structure, as shown in the figure. The (secondary) photocurrent is parallel to the substrate. This configuration is advantageous to couple the photodetector with light-emitting molecules (fluorophores) and devices, or to integrate with microfluidic devices, such as in biosensing applications. We also report a direct van der Waals growth of large-scale Graphene/hBN vertical bilayer. CVD grown MoSe<sub>2</sub> is stacked using all dry visco elastic stamping setup on to a graphene/hBN vertical bilayer. The direct growth of high-quality van der Waals junctions marks an important step toward high-performance integrated optoelectronic devices and systems. Direct growth avoids contamination between layers, defects due to transfer process and guarantees enhanced lightmatter interactions, leading to enhanced photon absorption and electron-hole collection in transparent graphene electrodes. This allows development of extremely efficient flexible optoelectronic devices for future electronics.

**Keywords**: Graphene, van der Waals heterostructure, photodetector, CVD



**Figure 1**: Figure shows the schematic of photodetector proposed by CVD grown 2D layers stacked in the form of vertical van der Waal heterostrcutre. **2**: Figure shows millimeter sized single crystal graphene used as electrodes for the device.

- L. Britnell, R. M. Ribeiro, A. Eckmann, R. Jalil, B. D. Belle, A. Mishchenko, Y. Kim, R. V Gorbachev, T. Georgiou, S. V Morozov, A. N. Grigorenko, A. K. Geim, C. Casiraghi, A. H. C. Neto, and K. S. Novoselov, "Strong Light-Matter Interactions Thin Films," vol. 340, no. June, 2013.
- J. Y. Lee, J.-H. Shin, G.-H. Lee, and C.-H. Lee, "Two-Dimensional Semiconductor Optoelectronics Based on van der Waals Heterostructures," *Nanomaterials*, vol. 6, no. 11, p. 193, Nov. 2016

## Electrochemical modulation of MoS<sub>2</sub> photoluminescence behavior in various electrolyte aqueous solutions for potential biological sensing

T. Seki,<sup>1</sup> K. Yatsu,<sup>1</sup> Y. Hayamizu<sup>1</sup>

<sup>1</sup> Tokyo Institute of Technology, Tokyo, Japan

### Abstract:

Functionalization of field effect transistors and optical sensors with biomaterials such as proteins and DNA has been widely employed to enable a specific selectivity and high sensitivity to target molecules. As for sensing materials, a group of transition metal dichalcogenides (TMDC), e.g., MoS<sub>2</sub> and WS<sub>2</sub>, has attracted much attention due to their superior optoelectronic properties as well as its atomically flat surface. Single layer (SL)-MoS<sub>2</sub> has shown photoluminescence (PL) and has been demonstrated that surrounding environments, such as molecular adsorption and solvent, largely affect its PL behavior [1,2]. Although it is not studied yet, SL-MoS<sub>2</sub> can be a candidate for an optical biosensor under physiological condition due to its high sensitivity to the environments. To this end, it is required to know how optical property of MoS<sub>2</sub> behaves under various aqueous conditions of pH and ions. However, despite of intensive studies on MoS<sub>2</sub> PL behavior under air or vacuum condition, the understanding of MoS2 PL behavior under aqueous solution of various ions species is still limited.

n this work, to address the problem, we have investigated ionic effects on PL of MoS2 in aqueous solutions and also investigated a correlation between electron density of MoS2 and its PL behavior by applying electrochemical bias in aqueous solutions. MoS<sub>2</sub> was synthesized by chemical vapor deposition on Si wafer. Then Au deposited electrode was on MoS<sub>2</sub> by photolithography. The MoS<sub>2</sub>/Au sample was transferred to a transparent glass substrate via a polymer thin film. Then various aqueous solutions were placed on the MoS<sub>2</sub>/Au sample, followed by insertion of a Pt electrode into the droplet. Immediately electrochemical bias was applied to the system. Finally, we measured MoS<sub>2</sub> PL images and spectra under modulated surface potential of MoS<sub>2</sub>. In this measurement, we utilized normal pulse voltammetry (NPV) to analyze time-dependent modulation of PL intensity against ion adsorption upon applying voltage. Compared to the case of unmodified  $MoS_2$ ,  $MoS_2$  modified with self-assembled peptides showed large time-dependency of PL modulation under various ionic aqueous solution, which may indicate strong interaction between ionic species and surface peptides layer with a monomolecular thickness on MoS2. In the presentation, we will discuss the effect of ionic species and type of peptides on PL timedependency upon NPV.

**Keywords**: transition metal dichalcogenide, MoS<sub>2</sub>, surface functionalization, peptide selfassembly, electrochemical photoluminescence measurement, bio-sensing.



**Figure 1**: (a) Schematic illustration of experimental setup. MoS2 substrate is conenected with a counter electrode via Au electrode. (b) PL image of MoS<sub>2</sub>/Au device sample.

- 1. Mouri, S.; Miyauchi, Y.; Matsuda, K. *Nano Lett.* **2013**, *13* (12), 5944–5948.
- Mao, N.; Chen, Y.; Liu, D.; Zang, J.; Xie, L. Small 2013, 9 (8), 1312–1315.

### A fully organic battery made of electrospun fibers

A.C. Baptista,<sup>1\*</sup> I. Ropio,<sup>1</sup> J.I. Martins,<sup>2,3</sup> J.P. Borges<sup>1</sup>, I. Ferreira<sup>1</sup>

 <sup>1</sup> CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
 <sup>2</sup> Universidade do Porto, Faculdade de Engenharia, Departamento de Engenharia Química, 4200-465 Porto, Portugal
 <sup>3</sup> Lab2PT, Instituto de Ciências Sociais, Universidade do Minho, 4710 - 057 Braga, Portugal

### Abstract:

Considering the growing need for power source miniaturization and the replacement, cost and risk inherent to conventional implantable medical devices, there is a need for the development of new electrical power source concepts.

A novel cellulose-based bio-battery made of electrospun fibers activated by biological fluids has been developed [1]. This work reports a new concept for a fully organic bio-battery that takes advantage of the high surface to volume ratio achieved by an electrospun matrix composed of sub-micrometric fibers that acts simultaneously as the separator and the support of the electrodes. This work presents the development of flexible, lightweight non-toxic and conductive cellulosebased electrospun fibers functionalized with Polypyrrole (PPy) and Polyaniline (PANI). Since cellulose is an environmentally friendly, cost effective and versatile material, a cellulosebased energy storage device will have significant advantages in comparison with many currently used batteries and supercapacitors.

In order to obtain highly conductive fibers, the *in situ* polymerization of pyrrole and aniline was carried out on the surface of cellulose acetate electrospun fibers (**Figure 1**). The polymerization conditions were extensively studied and lately the composite membranes were evaluated as electrodes for biobatteries.

A fully polymeric bio-battery was tested with physiological simulated solution as electrolyte, showing a maximum power density of 1.7 mW g<sup>-1</sup>, which is a promising power value considering the power requirements of common implantable medical devices.

Since harvesting energy directly from the environment is probably the most effective and promising approach for powering long-term biomedical devices, the bio-batteries can take advantage of the ionic content of the physiological fluids (such as blood or sweat) to generate electrical energy. When fully developed, they should be able to power a variety of ultralow-power consumption biomedical devices, such as pacemakers, artificial retinas, insulin pumps, cochlear implants and other future devices that will monitor bodily functions.



**Figure 1**: SEM image of cellulose acetate electrospun fibers functionalized with PPy.

### **References:**

1. AC. Baptista et al., Cellulose-based electrospun fibers functionalized with polypyrrole and polyaniline for fully organic batteries, J. Mater. Chem. A, 2018, 6, 256–265.

### Flexible Solid-State Supercapacitors Based on Tussock-Like Metal Oxide Nanowire Arrays

X. Cao, J. Ø. Duus and Q. Chi\*

### NanoChemistry Group, Department of Chemistry, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

### Abstract:

Flexible solid-state supercapacitors (FSSSCs) are of considerable interest as mobile power supply for future portable electronics [1,2]. Ternary transition metal oxides such as NiCo2O4 and MnCo<sub>2</sub>O<sub>4</sub> have received increasing attention as high-performance supercapacitor electrode materials due to their enhanced conductivity and electrochemical activity compared to binary transition metal oxides [3,4]. However, few attempts have been reported to date regarding the development of CuCo<sub>2</sub>O<sub>4</sub> based FSSSCs. In this study, a microwave assisted hydrothermal method combined with a simple thermal annealing process is employed to in-situ synthesize CuCo<sub>2</sub>O<sub>4</sub> nanowire arrays on commercial graphite papers. Phosphoric acid preactivation on graphite papers can effectively enrich their surface active sites for growth of CuCo<sub>2</sub>O<sub>4</sub> nanowires. Through the synergestic structureadjustment effects of polyvinyl pyrrolidone and Cu<sup>2+</sup>, a tussock-like highly-porous microstructure assembled from CuCo<sub>2</sub>O<sub>4</sub> nanowires is uniformly constructed onto the surface of graphite papers (Figure 1). The resulting electrode material was very conducive to realiazing multidimensional electron transport and rapid electrolyte ions diffusion. Thanks to these merits, the as-prepared flexible paper electrode can deliver a high specific capacitance of 1787 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in 1 M KOH in a two-electrode system, as well as superior cycling stability and good rate performace. An asymmetric supercapacitor composed of the as-prepared CuCo<sub>2</sub>O<sub>4</sub> based positive electrode, an activated carbon based negative electrode and a polyvinyl alcohol based gel electrolyte is being fabricated and tested. The initial results have laid a solid foundation for developing practical high-performance FSSSCs and further applying them for powering diverse portable electronics.

**Keywords**: flexible solid-state supercapacitors, portable electronics, transition metal oxides, nanowire arrays, graphite papers, paper electrodes, gel electrolyte.



**Figure 1**: (A) A scanning electron microscope image of tussock-like  $CuCo_2O_4$  nanowire arrays (top view); (B) a scanning electron microscope image of  $CuCo_2O_4$  nanowire arrays loaded on graphite papers (tilted side view) with C, Co, Cu and O mapping results; (C) a schematic of the proposed FSSSC.

- Dubal, D. P., Chodankar, N. R., Kim, D. -H., Gomez-Romere, P. (2018) Towards flexible solid-state supercapacitors for smart and wearable electronics, *Chem. Soc. Rev.*, 47, 2065-2129.
- Lu, X., Yu, M., Wang, G., Tong. Y., Li. Y. (2014) Flexible solid-state supercapacitors: design, fabrication and applications, *Energy Environ. Sci.*, 7, 2160-2181.
- Chen, D., Wang, Q., Wang, R., Shen, G. (2015) Ternary oxide nanostructured materials for supercapacitors: a review, J. Mater. Chem. A, 3, 10158-10173.
- Lu, Z., Wu, X., Jing, M., Wang, J., Liu, J., Lei, X., Sun, X. (2014) Transition metal oxides/hydroxides nanoarrays for aqueous electrochemical energy storage systems, *Sci. China Mater.*, 1, 59-69.

### Cul-based thin films for planer, highly flexible and transparent pn thermoelectric generators.

Bruno Miguel Morais Faustino<sup>\*1</sup>, Joao Coroa<sup>1</sup>, Jaime Faria<sup>1</sup>, Catarina Bianchi<sup>1</sup>, Ana Marques<sup>1</sup>, Isabel Ferreira<sup>1</sup>.

<sup>1</sup>CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, 2829-516, Portugal

### Abstract:

N-type transparent oxides with thermoelectric (TE) potential are vastly seen in today's technology. However, their p-type counterpart is often limited given the nature of the oxygen 2p orbitals and the delocalization of electrons at the top of the valence band. P-type transparent CuI thin films with thermoelectric properties have been produced by three different methods in order to maximise optical transparency (>70% in the visible range), electrical  $(\sigma = 1.1 \times 104 \text{ Sm}-1)$  and thermoelectric properties 1. The production and study of fully transparent CuI p-n modules into flexible Kapton CS substrates have resulted into the first planar, highly flexible and transparent p-n thermoelectric generators (TEG) using galliumdoped zinc oxide (GZO) as the n-type material.

**Keyword**s: thermoelectric, p-type, copper iodide, transparent, flexible

#### References

1. Morais Faustino, B. M. *et al.* CuI p-type thin films for highly transparent thermoelectric p-n modules. *Sci. Rep.* **8**, 6867 (2018).

# Supraparticles - complex particles as smart objects for interactive materials and processes

K. Mandel <sup>1,2</sup>

<sup>1</sup>Maximilians-University Würzburg, Germany <sup>2</sup>Fraunhofer Institute for Silicate Research ISC, Würzburg, Germany

karl-sebastian.mandel@isc.fraunhofer.de

### Abstract:

During the last decade nanoparticles have demonstrated great potential in making materials and processes more advanced for a variety of potential applications.

The next step further is to shift from dealing with individual nanoparticles to dealing with so-called supraparticles, *i.e.*, particles made from particles, the latter being nanoparticulate building-blocks.

Such multicomponent particle complexes and/or distinct nanostructured particle architectures bear great potential to yield unique functionalities (Fig. 1).

Novel processes are possible with such supraparticles. For instance merging magnetic and adsorber functionalities in one supraparticle system enables new approaches of water purification<sup>1-3</sup> and substance detection<sup>4-5</sup>.

Sophisticated architectures of nanoparticles forming supraparticles may furthermore change the properties of a material drastically – an example are super-lightweight magnetic microballoons<sup>6</sup>.

Moreover, with supraparticles, surfaces can be equipped with (inter)active properties.

Examples include coatings with refreshable, antibacterial functionality<sup>7</sup> or surfaces that may switch their visual (optical) properties upon magnetic<sup>8</sup> or gas triggering.

**Keywords**: smart materials; smart particles; supraparticles; switchable materials; multifunctional materials; novel nanostructures; complex particles



**Figure 1**: Supraparticles : Unique functionalities *via* multicomponent particle complexes and/or distinct nanostructured particle architectures.

- K. Mandel\*, A. Drenkova-Tuhtan, F. Hutter, C. Gellermann, H. Steinmetz, G. Sextl "Layered double hydroxide ion exchangers on superparamagnetic microparticles for recovery of phosphate from waste water" *Journal of Materials Chemistry A*, 1 (2013) 1840-1848.
- A. Drenkova-Tuhtan, M. Schneider, M. Franzreb, C. Meyer, C. Gellermann, G. Sextl, K. Mandel, H. Steinmetz,
   "Pilot-scale removal and recovery of dissolved phosphate from secondary wastewater effluents with reusable ZnFeZr adsorbent @ Fe3O4/SiO2 particles with magnetic harvesting" Water Research, 109 (2017) 77-87.
- M. Schneider, A. Drenkova-Tuhtan, W. Szczerba, C. Gellermann, C. Meyer, H. Steinmetz, K. Mandel\*, G. Sextl "Nanostructured ZnFeZr oxyhydroxide precipitate as efficient phosphate adsorber in waste water: understanding the role of different material-building-blocks" *RSC Environmental Science: Nano*, 4 (2017) 180 - 190.
- 4) T. Wehner, K. Mandel\*, M. Schneider, G. Sextl, K. Müller-Buschbaum\*
  "Superparamagnetic luminescent MOF@Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> composite particles for signal augmentation by magnetic harvesting as potential water detectors"
  ACS Applied Materials and Interfaces, 8 (2016) 5445-5452.
- T. Wehner, M. T. Seuffert, J. R. Sorg, M. Schneider, K. Mandel, G. Sextl, K. Müller-Buschbaum\*
   "Composite materials combining multiple luminescent MOFs and superparamagnetic microparticles for ratiometric water detection" *Journal of Materials Chemistry C*, 5 (2017) 10133-10142.
- T. Granath, A. Sanchez-Sanchez, A. Shemliov, V. Nicolosi, V. Fierro, A. Celzard, K. Mandel\* "Hollow Superparamagnetic Microballoons from Life-Like, Self-Directed Pickering Emulsions Based on Patchy Nanoparticles" ACS Nano, 10 (2016) 10347–10356.
- 7) T. Ballweg, C. Gellermann, K. Mandel\*"Coatings with a mole-hill structure of

nanoparticle raspberry-containers for surfaces with abrasion-refreshable reservoir functionality" *ACS Applied Materials and Interfaces*, 7 (2015) 24909–24914.

8) K. Mandel\*, T. Granath, T. Wehner, M. Rey, W. Stracke, N. Vogel, G. Sextl, K. Müller-Buschbaum\*
 "Smart Optical Composite Materials: Dispersions of Metal-Organic

Framework@Superparamagnetic Microrods for Switchable Isotropic-Anisotropic Optical Properties"

ACS Nano, 11 (2017) 779-787.

### Graphene -based hybrids for solar thermal evaporation of saline water

Nadhira Laidani<sup>1,\*</sup>, Francesca Marchetti<sup>1,2</sup>, Hafeez Ullah<sup>1,3</sup>, Gloria Gottardi<sup>1</sup>, Ruben Bartali<sup>1</sup>, Marina Scarpa<sup>2</sup>, E. Moser<sup>2</sup>, Said Makhlouf<sup>4</sup>, Ilyes Mitiche<sup>5</sup> and Omar Lamrous<sup>5</sup>

\* Corresponding author: Tel.: +39 0461 314 453; email: laidani@fbk.eu

<sup>1</sup> Fondazione Bruno Kessler, Materials & Systems Centre, Trento, Italy

<sup>2</sup> University of Trento, Department of Physics, Trento, Italy

<sup>3</sup> Department of Physics, Gomal University, Dera Ismail Khan 29220, KP, Pakistan

<sup>4</sup>University Mouloud Mammeri of Tizi-Ouzou, Mechanics, Structure and Energetics Lab, Tizi-Ouzou, Algeri

<sup>5</sup> University Mouloud Mammeri of Tizi-Ouzou, Quantum Chemistry and Physics Lab, Tizi-Ouzou, Algeria.

### Abstract:

Access to clean water, suitable for human consumption and domestic uses, is increasingly becoming the most important issue facing people around the world. For countries with plenty of solar light and scarce water, direct solar energy use for desalination is most appropriate for a large exploitation by non-industrial communities. Nanomaterials, graphene in particular, are increasingly gaining interest in this field, thanks to its peculiar electronic, thermal and optical properties. Among the recent advances purification for water by direct solar evaporation, the most promising mechanism by which nanomaterials can be active is based on a bio-inspired phenomenon which governs "transpiration" in plants which exploits a capillary-driven pumping. In this work, graphene and oxide/graphene hybrids suspensions in water and as hydrogels were tested for their ability to increase the light-toheat conversion and water evaporation efficiency. Hybrid powders were developed by means of radio-frequency sputtering of oxides (Nb2O5 and SiO2) onto graphene powder. Hydrogels of graphene were also produced by wet chemistry and tested for water evaporation enhancement under solar irradiation simulation.

A positive effect of graphene on saline water evaporation rate measured under a 1 sun-solar simulator was observed (Fig.1), whatever if in suspensions or as hydrogels, while the presence was found to improve the of the oxides graphene dispersion in water. The samples were characterized by means of X-ray photoelectron Raman spectroscopies. and UV-Vis spectrophotometry was employed to characterize the treated powder suspension stability in water.

**Keywords**: solar water evaporation; graphene; oxides; nanomaterials, hydrogels.



**Figure 1**: Figure illustrating the positive effect of graphene on the evaporation rate of water under solar simulator.

#### **References:**

- Y. Fu, T. Mei, G. Wang, A. Guo, G. Dai, S. Wang *et al.*, Appl. Therm. Eng. 114 (2017) 961
- 2. H. Liu, X. Zhang *et al.*, Nanoenergy 42 (2017) 115
- 3. Y. Li, T. Gao, Z. Yang *et al.*, Nanoenergy 41 (2017) 201

#### Acknowledgments:

The research leading to these results has received funding in Italy from "Ministero degli Affari Esteri e della Cooperazione Internazionale, Direzione Generale per la Promozione del Sistema Paese".

# Graphene oxide/TiO<sub>2</sub> heterojunction for efficient photocatalytic degradation of persistent aquatic pollutants

R. Zouzelka, <sup>1</sup> M. Remzova, <sup>1</sup> L. Brabec, <sup>1</sup> J. Rathousky<sup>1</sup>

<sup>1</sup> J. Heyrovsky Institute of Physical Chemistry of the CAS, v.i.i., Prague, Czech Republic

### Abstract:

Persistent aquatic pollutants represent a huge challenge to the environment. Among emerging pollutants in wastewaters, a special role is played by phenols, which are highly toxic to aquatic and human life, even at very low concentrations. By conventional methods, organic pollutants are often only pre-concentrated or transformed to other organic compounds, without achieving a complete mineralization.

Advanced oxidation processes (AOPs) are suitable alternatives to conventional approaches. One of the AOPs most suited to water treatment is heterogeneous photocatalysis using which the complete mineralization of organic compounds can be achieve.

In our research, we developed an optimized quantitative electrophoretic deposition (EPD) technique for the preparation of composite graphene oxide/titanium dioxide porous layers. They were deposited on rigid substrates (stainless steel, conductive glass and silicon wafer) without sintering and use of dispersive additives, which removes any potential contamination of the layers. The structure properties of the layers were determined using Raman and UV-Vis spectroscopies. Their morphology and texture properties were carried out by scanning electron microscopy and krypton adsorption experiments, respectively.

The layers showed very good mechanical photocatalytic enhanced stability and performance in the degradation of  $10^{-4}$  M aqueous solution of 4-chlorophenol. Compared to the pristine TiO<sub>2</sub>, the composite layers exhibited a three-fold increase of the first-order reaction rate constant with almost complete pollutant mineralization. The composite structure beneficially influenced the degradation of 4chlorophenol by increased formation of hydroxyl radicals, which was confirmed by time-resolve fluorescence measurements.

Owing to their excellent mechanical and photocataytic properties, these layers are suitable for a broad range of environmental applications. **Keywords**: aquatic pollutants, advanced oxidation process, heterogeneous photocatalysis, electrophoretic deposition, graphene oxide, TiO<sub>2</sub>, mineralization.



Figure 1: Photocatalytic degradation of 4chlorophenol on the composite graphene oxide /  $TiO_2$  layer.

#### **References:**

1. Zouzelka, R., Remzova, M., Brabec, L., Rathousky, J. (2018) Photocatalytic performance of porous TiO<sub>2</sub> layers prepared by quantitative electrophoretic deposition from organic solvents. *Applied Catalysis B: Environmental*, 227C, 70–78.
## NanoMed 2018 - Session III: Nanotechnology in Medical Diagnostics / Pharmaceutical Nanotechnology

## Developing laser-synthesized optically-tuned SERS sensors for drug detection

E. Fazio,<sup>1</sup> S. Trusso,<sup>2</sup> C. Zanchi,<sup>3</sup> A. Lucotti,<sup>3</sup> M. Santoro,<sup>1</sup> S. Spadaro,<sup>1</sup> F. Neri,<sup>1</sup> M. Casazza,<sup>4</sup> E. Ciusani,<sup>4</sup> U. de Grazia,<sup>4</sup> M. Tommasini,<sup>3\*</sup> P.M. Ossi,<sup>5</sup>

<sup>1</sup> Università di Messina, Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Messina, Italy

 $^{2}$  IPCF – CNR, Messina, Italy

<sup>3</sup> Politecnico di Milano, Dipartimento di Chimica, Materiali e Ing. Chimica "G. Natta", Milano, Italy

<sup>4</sup> Fondazione I.R.C.C.S. Istituto Neurologico Carlo Besta, Milano, Italy

<sup>5</sup> Politecnico di Milano, Dipartimento di Energia, Milano, Italy

(\*) Corresponding author: matteo.tommasini@polimi.it

## Abstract:

Therapeutic Drug Monitoring (TDM) is a clinical practice to determine the drug concentration in a biological fluid, usually blood plasma. TDM is critically important for Narrow Therapeutic Index (NTI) drugs, including Anti-Epileptic Drugs (AEDs), for which often small differences separate therapeutic and toxic doses. Blood concentration of AEDs is performed in the lab via immunoassay tests, or High- Performance Liquid Chromatography coupled to Mass Spectrometry (HPLC-MS). Both techniques are time consuming and costly. We discuss the use of light scattering with *ad hoc* engineered plasmonic and substrates as а fast comparatively inexpensive TDM approach for AEDs, complementary to the existing ones. Noble metal (Au) nanoparticles (NPs), grown by pulsed laser ablation of a high purity target are synthesized along two possible paths. If ablation is carried out in a transparent liquid a colloidal solution of Au NPs is obtained, if it is performed in a highdensity inert, massive gas (Ar) NPs form in the expanding plasma plume and are deposited on an inert support (100-Si). We illustrate the role of the few relevant process parameters on the size, size distribution, shape and optical properties of the NPs and of the NP arrays that self-assemble on the support. Such parameters are the ambient gas pressure and the laser pulse number for gasphase synthesis as well as the pulse duration and the laser energy density for liquid-phase ablation. In particular it is possible to adjust the wavelength of the Surface Plasmon Resonance (SPR) peak. This opens the way to Surface Enhanced Raman Scattering (SERS) measurements on samples of different origin with various AEDs at concentrations of clinical

interest [1;2]. We will present new results of our investigation on the SERS response of the newgeneration AED Perampanel (EISAI) of relevant clinical interest.

**Keywords**: Anti-Epileptic drugs, noble metal nanoparticle, gas-phase pulsed laser ablation, pulsed laser ablation in liquid, SERS, Perampanel

- Zanchi, C., Lucotti, A., Tommasini, M., Trusso, S., de Grazia, U., Ciusani, E., Ossi, P.M. (2017) Laser tailored nanoparticle arrays to detect molecules at dilute concentration, *Applied Surface Science* 396, 1866–1874.
- Santoro, M., Fazio, E., Trusso, S., Tommasini, M.m, Lucotti, A., Saija, R., Casazza, M., Neri, F., Ossi, P.M. (2018) SERS Sensing of Perampanel with Nanostructured Arrays of Gold Particles Produced by Pulsed Laser Ablation in Water, *Medical Devices and Sensors*, in the press.

## Plasmonic biosensors: a powerful tool in diagnostics

<u>A. Minopoli<sup>1,\*</sup></u>, B. Della Ventura<sup>1</sup>, C. Schiattarella<sup>1,2</sup>, R. Velotta<sup>1</sup>

<sup>1</sup>Department of Physics "E. Pancini" – Università di Napoli *Federico II* – Via Cintia, 26 Ed. 6 – 80126 Napoli (Italy)

<sup>2</sup>Institute for Microelectronics and Microsystems, National Research Council, Via P. Castellino 111, 80131 Napoli (Italy)

## Abstract:

Metallic surfaces can strongly confine electromagnetic field through its coupling to the surface plasmons. This interaction allows a large enhancement of the electromagnetic field intensity which provides an increase of excitation rate, a raise of quantum yield and an amplification of fluorescence signal by several orders of magnitude. The coupling of metallic nanostructures, like periodic array of nanostructured islands or nanoparticles, with specific bio-elements, as the antibodies, make them a powerful biosensors. In order to optimize the surface functionalization. we have employed the Photochemical Immobilization Technique (PIT), that is based on antibody activation by UV irradiation. The PIT ensures that the antibodies cover surface binding covalently and upright[1]. Figure 1 shows the detection scheme of functionalized gold nanoparticles (AuNPs). If the antigens are recognized by the antibodies, the AuNPs aggregate. The greater size of aggregates causes a change of color solution from red to violet visible by naked eye due to a red-shift of Localized Surface Plasmon Resonance (LSPR) frequency[2]. Figure 2 depicts the principle of Metal-Enhanced Fluorescence (MEF). The light emitted by fluorescent tags resonates with the electrical dipole of gold islands leading a fluorescent signal[3] rather than the fluorescence quenching expected in metals. Both proposed biosensors are suitable in protein detection. We are able to detect human IgG at a concentration level lower than 100 ng/mL[4]. We are testing the detection efficiency for small molecules like 17βestradiol.

**Keywords:** biosensors, AuNPs, colorimetric test, colloidal solution, functionalization, LSPR, MEF medical application.





Figure 1: Antigen detection by using functionalized AuNPs.

#### Figure 2: Sandwich scheme for MEF achievement.

- Della Ventura B, Schiavo L, Altucci C, Esposito R, Velotta R. 2011 Light assisted antibody immobilization for bio-sensing. *Biomed. Opt. Express* 2, 3223. (doi:10.1364/BOE.2.003223)
- Njoki PN, Lim I-IS, Mott D, Park H-Y, Khan B, Mishra S, Sujakumar R, Luo J, Zhong C-J. 2007 Size Correlation of Optical and Spectroscopic Properties for Gold Nanoparticles. J. Phys. Chem. C 111, 14664– 14669. (doi:10.1021/jp074902z)
- Aslan K, Gryczynski I, Malicka J, Matveeva E, Lakowicz JR, Geddes CD. 2005 Metalenhanced fluorescence: An emerging tool in biotechnology. *Curr. Opin. Biotechnol.* 16, 55–62. (doi:10.1016/j.copbio.2005.01.001)
- Iarossi M, Schiattarella C, Rea I, De Stefano L, Fittipaldi R, Vecchione A, Velotta R, Della Ventura B. 2018 Colorimetric Immunosensor by Aggregation of Photochemically Functionalized Gold Nanoparticles. ACS Omega 3, 3805–3812. (doi:10.1021/acsomega.8b00265)

## A novel optical biosensor for ochratoxin A based on aptamer-antibody sandwich assay and total internal reflection ellipsometry

A.G. Al-Rubaye <sup>a,†</sup>, A.Nabok <sup>a</sup>, T. Smith<sup>b</sup>, G. Catanante<sup>c</sup>, J-L. Marty<sup>c</sup>, E. Takacs<sup>d</sup>, A. Szekacs<sup>d</sup>

<sup>a</sup>Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, UK, S1 1WB

<sup>b</sup>Biomolecular Sciences Research Centre, Sheffield Hallam University, Sheffield, UK, S1 1WB

<sup>c</sup>University of Perpignan, Department of Biochemistry and Molecular Biology, France

<sup>d</sup> National Agricultural Research & Innovation Centre, Agro-Environmental Research Institute, Budapest, Hungary

## Abstract:

The main aim of this work is the development of novel optical sensing technologies for detection of mycotoxins. The method of total internal reflection ellipsometry (TIRE) developed in the last decade as a combination of spectroscopic ellisometry and SPR was proved to be a highly sensitive analytical tool in bio-sensing, particularly attractive for detection of low molecular weight analytes, such as mycotoxins [1]. The main advantage of the TIRE method, as compared to traditional SPR, is the recording of spectra of two ellipsometric parameters  $\Psi$  and  $\Delta$ , where  $\Psi$  and  $\Delta$  represent, respectively, the amplitude ratio and phase shift between p- and scomponents of polarized light.  $\Delta$ -spectra, which are typically recorded in TIRE, gave high sensitivity of detection. The detection of one of the mycotoxins, i.e. ochratoxin A (OTA) in aptamer assay using TIRE method was successfully attemted recently [2], howevere because of the small size of both the bio-receptor (aptamers) and target (mycotoxins) the spectral shift is quite small and difficult to detect. The use aptamer-antigen-antibody sandwich assay of [3] can amplify the TIRE sensor response because of a substantial spectral shift typically with large size molecules associated of In this work, we utilize antibodies. this advantageous aptamer-antibody sandwich assay in combination with highly sensitive tecthiques of TIRE to detect OTA. To the best of our knowledge, this is the first attemp of that type of sensor.

The anti-OTA aptamers (from Microsynth, Switzerland) were immobilized the surface on 25 nm thick gold films via thiol groups. A typical series of TIRE  $\Delta$ -spectra recorded after consequitive binding steps is shown in Figure 1. As one can see binding OTA of 0.1 ng-ml concentration to aptamers causes a small "blue" shift caused by aptamers wrapping around the target. The second part of assay, e.g. binding antibodied to OTA/aptamer complex, causes much larger "red" shift associated with the increase in the film thickness. Then antibodies were washed out using Twin20, and the assay was repeated for a larger concentrations of OTA resulting in a progressive "red" spectral shift in Fig. 1.

**Keywords:** Optical biosensor, TIRE, sandwich assay, aptamer, ochratoxin A, antibody.



**Figure 1.** TIRE spectra of detection of Ochratoxin A in the sandwich assay with aptamers-antibodies, Immobilisation aptamer on gold and sandwish aptamer - antibody is shown on inset.

## **References:**

- 1. Nabok, A., Tsargorodskaya, A. (2008), The method of total internal reflection ellipsometry for thin film characterisation and sensing, *Thin Solid Films*, 516 (24), 8993-9001
- Al Rubaye, A., Nabok, A., Catanante, G., Marty, J. L., Takacs, E., & Szekacs, A. (2018). Detection of ochratoxin A in aptamer assay using total internal reflection ellipsometry. *Sensors and Actuators B: Chemical*, 263, 248-251.
- 3. Guo, L., & Kim, D. H. (2012). LSPR biomolecular assay with high sensitivity induced by aptamer–antigen–antibody sandwich complex. *Biosensors and Bioelectronics*, *31*(1), 567-570.

## Acknowlegement:

This work was funded by NATO SPS program, project NUKR.SFPP 984637.

# Non-invasive monitoring of flap oxygenation using photoacoustic imaging

M. Aribert<sup>1,2,3</sup>, M. Henry<sup>1,2</sup>, JL. Coll<sup>1,2</sup>, G. Bettega<sup>1,2,3</sup>, V. Josserand<sup>1,2</sup>

<sup>1</sup> INSERM U1209, Institute for Advanced Biosciences, F-38000, Grenoble, France
 <sup>2</sup> Univ. Grenoble Alpes, F-38000 Grenoble, France
 <sup>3</sup> CHU Hôpital, Nord CS 10217, 38000 Grenoble, France

## Abstract:

**Purpose:** Reconstructive surgery aims to restore anatomical defects with autologous tissues called flaps and non-invasive assessment of flap viability remains an unmet clinical need. Indeed, vascular thrombosis may occur and lead to a partial or complete loss of the flap, with dramatic functional and esthetic consequences and increased morbidity if not rapidly treated (1).

Photoacoustic imaging (PAI) is a recent technology that can be used for the noninvasive evaluation of hemoglobin content (HbT) and tissue oxygen saturation (StO2) in preclinical models and in humans (2). In this study we assessed potential benefits from PAI for the continuous monitoring of flap oxygenation in a preclinical model.

**Methods:** 10 rats were operated by lifting an abdominal skin flap followed by arterial or venous occlusion of the flap pedicle, simulating extended thrombosis. PAI was performed using the vevoLAZR (LZ550 transducer) at 750 and 850 nm before surgery, after lifting the flap and after vascular occlusion.

**Results:** Venous and arterial thrombosis-induced flap color modifications (blue color or paleness) were visible about 2 hours after clamping, although this was not evident in all flaps. Following arterial clamping, HbT rapidly decreased and stabilized at 73±16% of initial values, whereas there was only a temporary and nonsignificant increase following venous clamping. In contrast, the StO2 values dropped very rapidly in 3-4 minutes from 63.3±9.6% down to 10.0±6.2% after an arterial occlusion, and down to 21.0±4.5% after a venous one. When compared to initial levels, the StO2 had decreased by 83±11% following an arterial occlusion and by 65±10% after a venous clamp.

**Conclusion:** PAI allows noninvasive and early detection of compromised flaps with clear distinctions between arterial and venous thrombosis.

**Keywords**: Reconstructive surgery, Flap monitoring, Photoacoustic imaging, Tissue oxygenation, biomedical applications, medical diagnosis.



**Figure 1**: Photoacoustic imaging derived StO2. Upper panel: before and after surgery. The black line represents the 10 mm<sup>2</sup> ROI that was used for quantitative analysis. Middle panel : 5 and 20 minutes after venous clamping. Lower panel: 5 and 20 minutes after arteria clamping.

- 1. Smit, J. M., Zeebregts, C. J., and Acosta, R. Timing of presentation of the first signs of vascular compromise dictates the salvage outcome of free flap transfers. *Plastic and reconstructive surgery*. **2008**; 122(3):991-992.
- Valluru, K. S., Wilson, K. E., and Willmann, J. K. Photoacoustic Imaging in Oncology: Translational Preclinical and Early Clinical Experience. *Radiology*. 2016; 280(2):332-349

## Creating a sandwich assay of magnetic and gold nanoparticles for tau-protein quantification using ID-SERS Making Alzheimer's disease diagnosis reliable

C Frank,<sup>1,\*</sup> V. Maurer,<sup>1,2</sup>, S. Wundrack<sup>1</sup>, S.Schmidt<sup>1</sup>, S. Zellmer<sup>2</sup>, G. Garnweitner<sup>2</sup>, R. Stosch<sup>1</sup>

<sup>1</sup> Physikalisch-Technische Bundesanstalt, Metrology in Chemistry, Braunschweig, Germany <sup>2</sup> TU Braunschweig, Institute for Particle Technology, Braunschweig, Germany

## Abstract:

Neurodegenerative diseases are amongst the major challenges for the healthcare systems in the aging societies of the Western World with currently over 44.4 million affected world-wide. This number will likely double in the next 20 years due to the aging population. The most common form of dementia is Alzheimer's disease with about 70 % of all cases. However, according to epidemiological data, only half of the patients suffering from Alzheimer's disease are currently identified, and, even if detected, then often only in advanced stages of the disease. Up to now, Alzheimer's disease is only reliable diagnosed post mortem.

One of the established biomarkers for Alzheimer's disease is the tau protein measured in cerebrospinal fluid (CSF). Due to the very low concentrations physiological and small collectable sample volumes the quantification is very challenging which becomes obvious in clinical ring trials. Reference methods ensuring traceability of the results to the SI are therefore urgently required. Those methods are currently being developed within the framework of the European Metrology Programme for Innovation and Research (EMPIR). Therefore, metallic and magnetic nanoparticles provide versatile sensing platforms for those biological and biomedical applications in human medicine. Here, a sandwich immuno-assay for surface-enhanced Raman scattering (SERS) based determination of tau protein will be established. The developed assay will be used to separate the target analyte from the matrix with the help of magnetic nanoparticles as well as for the quantification of the protein by utilisation of a sensitive SERS active marker coupled to gold nanoparticles. The linkage of both nanoparticles to the protein will be ensured by immunoreaction with specific antibodies (Figure 1). Especially the sensitivity of the SERS active marker makes this approach suitable for very low sample volumes and analyte concentrations typically found in CSF samples

while highest accuracy is achieved through the isotope dilution approach<sup>1</sup>.

Keywords: Alzheimer's disease, gold nanoparticles, magnetic nanoparticles, SI traceability, tau biomarker protein, quantification, isotope dilution surface enhanced Raman scattering (ID-SERS), biomedical applications.

**Figure 1**: Top: TEM Immage of the sandwich assay (The black spheres are the gold nanoparticles; Bottom: Schematic depiction of the sandwich assay in its natural composition

## **References:**

 Zakel, S., Wundrack, S., O'Connor, G., Güttler, B., Stosch, R. (2013) Validation of isotope dilution surface-enhanced Raman scattering (IDSERS) as a higher order reference method for clinical measurands employing international comparison schemes, J. Raman Spectrosc., 44(9) 1246-1252.

Acknowledgement: This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

# Functionalization of single-layer graphene transistors for immunoassays

P. D. Cabral<sup>1,2</sup>, E. Fernandes<sup>1</sup>, M. F. Cerqueira<sup>1,2</sup>, O. Bondarchuck<sup>1</sup>, D. Y. Petrovykh<sup>1</sup>, J. Borme<sup>1</sup>, P. Alpuim<sup>1,2</sup>

<sup>1</sup> International Iberian Nanotechnology Laboratory, 4715-330, Braga, Portugal <sup>2</sup> Center of Physics, University of Minho, 4710-057, Braga, Portugal

## Abstract:

The remarkable properties of graphene have generated a new trend in advanced materials for biomedical applications [1, 2]. The possibility of fast and sensitive electrical transduction makes it an ideal candidate for biosensing applications. However, graphene hydrophobicity is a challenge for biomolecules stability. To improve and understand the stability of the biomolecules on graphene, an exhaustive study of each step involved in graphene functionalization was done. Single layer graphene surfaces that mimic fieldeffect transistor channels are modified with a pyrene-derivative linker, followed by the immobilization of a monoclonal antibody specific to a stroke analyte (Matrix Metalloproteinase-9, MMP-9), and by passivation with a blocking agent to prevent non-specific binding. The functionalized graphene surface is characterized spectroscopy, contact by Raman angle measurements, x-ray photoelectron spectroscopy (XPS) and quartz crystal microbalance (QCM) measurements. The results show a stable graphene surface after modification with the heterobifunctional linker, and a high degree of completion of the linker-antibody and linkerblocking agent reactions. After validation, the strategy is used for the functionalization of the electrolyte-gated channel of field-effect transistors (EGFETs), where the graphene channel works as a transduction element through local gating by the charged analyte during the biorecognition event.

Detection of MMP9 in a range from 0.01 up to 10 ng/mL is achieved, with the signal increasing approximately linearly as a function of the model analyte concentration. This functionalization strategy is versatile and can be used in the graphene-based development of immunobiosensors where multiple immunoassays for the simultaneous detection of a panel of biomarkers is required. Chips containing 88 transistors, divided into 4 regions that can be differently functionalized for multiplex detection, were fabricated at the wafer scale. The chips are directly inserted into the connector of an integrated electronics board, which is connected to a PC via USB cable, for fast acquisition and processing of the signal.

**Keywords**: graphene; biofunctionalization; immunoassay; immuno-FET



**Figure 1**: Biofunctionalization and immunodetection strategy using a single-layer graphene EGFET. (A) Surface modification with the heterobifunctional linker, PBSE; (B) covalent immobilization of the antibody; (C) blocking with ethanolamine; (D) biorecognition of MMP-9 target.

- 1. Rodríguez, S.J., Makinistian, L., Albanesi, E.A. (2017) Graphene for amino acid biosensing: Theoretical study of the electronic transport, *Appl. Surf. Sci.* 419, 540–545.
- Novoselov, K.S., Fal'Ko, V.I., Colombo, L., Gellert, P.R., Schwab, M.G., Kim, K. (2012), A roadmap for graphene, *Nature* 490, 192–200.

## SI traceable quantification of hemoglobin using an ID-SERS active immunoassay

S. Schmidt\*, C. Frank, S. Wundrack, R. Stosch

Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany

#### Abstract:

The hemoglobin concentration in blood is the most often measured parameter in laboratory medicine. Being influenced by many diseases like erythrocytosis anemia. jaundice, or hemoglobinopathies, those measurements allow to obtain a first overview of patients' health status. Even though it is measured frequently in clinical laboratories, the only reference method approved by the World Health Organization spectrophotometric (WHO) is the cyanmethemoglobin method but this one is not traceable to the International System of Units (SI) which the WHO demands. Furthermore, the methods toxicity due to the use of potassium cyanide raises the need for non-toxic alternatives. Additionally, national medical associations define in their guidelines such as the one published by the German Medical Association for quality assurance in medical laboratories. guideline lists the most important This biomarkers and clinical laboratories must prove in stated intervals that they are able to measure them correctly within given limits of equivalence. To develop and establish a new potentially higher method order reference for hemoglobin quantification in blood, as a matter of course SI traceable and non-toxic. surface-enhanced Raman scattering (SERS) was combined with the isotope dilution (ID) approach to achieve highest accuracy and sensitivity. For this purpose, gold nanoparticles were coated with a Raman active marker being able to detect the protein of interest indirectly. Using the marker in its native and an isotopically labelled form results in a bond shift in the Raman spectra and the hemoglobin concentration in the sample can be derived from evaluating intensity ratios rather than absolute intensities. The hemoglobin was linked onto the AuNP surface via a specific monoclonal (mc) antibody. For purification a nitrocellulose membrane was chosen which was functionalized with a polyclonal (pc) antibody targeted against other binding sites than the first one to immobilize the captured hemoglobin. The method presented here (Figure 1) can be considered as a prove of principle for a universally applicable

procedure for quantifying a variety of protein biomarkers.

**Keywords**: biomarker, immunoassay, nanoparticles, isotope dilution, SI traceability, surface enhanced Raman scattering, metrology



**Figure 1**: Scheme of ID-SERS based immunoassay for quantitative detection of hemoglobin in blood.

We gratefully acknowledge the support of the Braunschweig International Graduate School of Metrology B-IGSM and the DFG Research Training Group GrK1952 "Metrology for Complex Nanosystems".

- Frank, C., Brauckmann, C., Palos, M., Arsene, C.G., Neukammer, J., del Castillo Busto M. E., Zakel, S., Swart, C., Güttler, B., Stosch, R. (2017) Comparison of potential higher order reference methods for total haemoglobin quantification – an interlabo- ratory study, *Anal. Bioanal. Chem.*, 39, 2341-2351.
- Hashemi, P., Luckau, L., Mischnick, P., Schmidt, S., Stosch, R., Wünsch, B. (2017) Biomacromolecules as tools and objects in nanometrology – current challenges and perspectives, *Anal. Bioanal. Chem.*, 409, 5901–5909.

## Graphene Oxide acts as an imitative of Progesterone on spermoviduct interactions and sperm physiology

M.Ramal-Sanchez,<sup>1,2,\*</sup>, G.Tsikis<sup>2</sup>, V. Labas<sup>3</sup>, X. Druart<sup>2</sup>, P. Mermillod<sup>2</sup>, M.Saint-Dizier<sup>2</sup> and N.Bernabò,<sup>1</sup>

<sup>1</sup> University of Teramo, Unit of Basic and Applied Biosciences, Teramo, Italy <sup>2</sup> INRA-Centre Val de Loire, PRC, Nouzilly, France <sup>3</sup>INRA, CIRE-PAIB, Nouzilly, France

#### Abstract:

Graphene Oxide (GO) has lately acquired a spotlight role in regenerative medicine and biotechnology thanks to its interesting properties. For that reason, our group has recently focused the attention in the modifications derived from the use in vitro of GO on swine spermatozoa, finding out not only that the lowest concentrations of GO (0.5 and 1  $\mu$ g/mL) did not cause toxicity but they also showed a positive effect in the fertilization outcome, probably due to an interaction with membrane cholesterol[1]. Afterwards and with the aim of studying the sperm-GO interactions in other mammalian species and in a more physiological condition, bovine sperm  $(4x10^{6}/mL)$ were co-incubated with bovine oviductal epithelial cells (BOEC) for 30 min. After collecting the unbound spermatozoa (UnS), GO (1µg/mL) and Progesterone (P4, previously studied by our group as an inductor of sperm release) (100 ng/mL) were added to the sperm-BOEC culture for 1h. Then, released spermatozoa (P4-ReS and GO-ReS) were collected. A group of spermatozoa was similarly manipulated without BOEC nor P4 or GO (CTRL) and other groups were treated with P4 or GO without BOEC (P4-CTRL and GO-CTRL). In this in vitro model, the attachment of sperm to BOEC simulate the "sperm reservoir" in the oviduct, where sperm storage, capacitation, fertilization and early embryo development take place [2]. Proteomic and lipidomic profilings were studied on Intact Cells by Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry (ICM-MS). The presence of Binder of Sperm Proteins (BSP)-1, -3 and -5, the most important seminal plasma proteins involved in sperm-BOEC binding, was studied by Western-Blotting. Fluorescence Recovery After Photobleaching (FRAP) analysis by confocal microscopy were performed to evaluate the changes in sperm membrane fluidity, an event directly related to capacitation. The most surprising aspect is that GO and P4 action seems to modify the sperm in the same way: binding to BOEC and then P4 or GO-induced release from BOEC triggers major changes in sperm proteins and lipids composition while P4 and GO by their selves have a moderate effect. A loss of BSPs at the sperm surface and an increase in sperm membrane fluidity were evidenced on P4 and GOreleased sperm from BOEC, suggesting a membrane destabilization probably responsible for the increase in the fertilizing competence of this In conclusion, the interesting population. similarity between P4 and GO treatment open the way for the study of these non-physiological graphene-related widespread materials as substitutes for the development of future bionsensors or nanodevices that could be applied in the reproductive field.

**Keywords**: sperm cells, graphene oxide, progesterone, BOEC.



**Figure 1**: Principal Component Analysis (PCA) of two random m/z (mass/charge) peaks from the proteomic profiling representing CTRL-spz (red), P4-ReS (green) and GO-ReS(blue), these last two with the same distribution profile.

#### References

- 1. Bernabò, N. et al (2018) Graphene oxide affects in vitro fertilization outcome by interacting with sperm membrane in an animal model, *Carbon* 129, 428-437.
- 2. Lamy, J. et al (2017), Steroid hormones regulate sperm-oviduct interactions in the bovine, *Reproduction*, 154, 497-508.

**Aknowledgements**: MRS research was supported by MarieSkłodowska-Curie ITN REP-BIOTECH 675526.

## Detection and Characterization of Different Neuronal and Glial Populations of Plasma Exosomes by Surface Plasmon Resonance imaging

S. Picciolini<sup>1,2\*,</sup> A. Gualerzi<sup>1</sup>, A. Sguassero<sup>1</sup>, F. Gramatica<sup>1</sup>, M. Masserini<sup>2</sup>, M. Bedoni<sup>1</sup>

<sup>1</sup> Laboratory of Nanomedicine and Clinical Biophotonics (LABION), IRCCS Fondazione Don Carlo Gnocchi ONLUS, Milan, Italy

<sup>2</sup> Nanomedicine Center NANOMIB, School of Medicine and Surgery, University of Milano-Bicocca, Monza, Italy

## Abstract:

The use of exosomes (EXOs) for diagnostic and disease monitoring purposes is becoming particularly appealing, considering that the pathological status greatly affects the EXOs content. Moreover, brain-derived EXOs present in blood plasma could be seen as a direct readout of the condition of the brain and can thus be studied as peripheral biomarkers of neurological disorders<sup>1</sup>. Inspired by remarkable development of plasmonic biosensors, we have designed an antibody array using Surface Plasmon Resonance imaging (SPRi) with the aims to detect CNSderived EXOs present in human plasma and to characterize them according to the presence and the relative amount of membrane molecules.

EXOs were isolated from plasma of healthy volunteers by size-exclusion chromatography and characterized by nanoparticles tracking analysis, transmission electron microscopy, western blot and a colorimetric test. The SPRi array was optimized for the detection of EXOs subpopulations, by using a suitable surface chemistry and specific antibodies for each class of vesicle to be detected.

With this strategy we demonstrated the possibility to simultaneously distinguish EXOs derived specifically from neurons, microglia, astrocytes and oligodendrocytes. Moreover, the presence and relative amount of another membrane constituent (GM1) were evaluated, showing a different composition of EXOs according to their cellular origin<sup>2</sup>.

In conclusion, SPRi can be used to discriminate different populations of circulating EXOs and to perform their concomitant characterization. The optimized SPRi biosensor represents a promising platform for the possible use of EXOs as clinical biomarkers of neurological diseases. **Keywords**: exosomes, Surface Plasmon Resonance imaging, biophotonics, neurological diseases, circulating biomarkers, biosensor.



**Figure 1**: we optimized a SPRi-based biosensor for the simultaneous detection and analysis of different neural subpopulations of human plasma EXOs, using an extremely limited amount of peripheral blood.

- Kanninen, K. M., Bister, N., Koistinaho, J., Malm, T. (2016), Exosomes as new diagnostic tools in CNS diseases. *Biochim Biophys Acta*, 1862 (3): 403-10
- Picciolini, S., Gualerzi, A., Vanna, R., Sguassero, A., Gramatica, F., Bedoni, M., Masserini, M., Morasso, C. (under revision), Detection and characterization of different brain-derived subpopulations of plasma exosomes by Surface Plasmon Resonance imaging., *Anal.Chem*

## EGF 2018 / SMS 2018 - Joint Session III.A: Energy applications

## An emerging material application in nanoelectronic devices and electrical performance

Hui-Lin Chang<sup>1, 2</sup>

<sup>1</sup> Material Science and Engineering Department, National Chiao Tung Unviersity, HsinChu, Taiwan <sup>2</sup> Device Department, Micron Technology at Manassas, VA, 20110

#### Abstract:

Sustaining Moore's law into the future requires continuous transistor scaling. Therefore, the adoption of emerging materials has become of great importance for the development of future nanoelectronics applications. Various emerging devices have been found to be promising candidates to extend Moore's law, such as Si nanowires, carbon nanotubes, and III-V compound field effect transistors (FETs). In this study, a systematic analysis and characterization of the structures and corresponding properties of the following emerging materials was conducted [Fig. 1]: random oriented SiCN tubes, nanowire / conical rods and 2D graphite/seaweed structures. This study addresses the growth mechanisms and electronic properties of the aforementioned nanostructured materials. The development of nanostructured materials is critical for enhancing emerging device applications. The integration of carbon nanotubes (CNTs) into Si-based metaloxide semiconductor field effect transistors (MOSFETs) or new nanoelectronics remains a challenge in the areas of transistors and interconnects. CNTs are recognized candidates for use in molecular electronics to overcome the physical limitations of currently used Si transistors and Cu interconnections [1-2]. Bundles of CNTs are naturally deposited in the vertical dimension, since they tend to adhere to each other vertically. The feasibility of realizing this vision depends on direct approaches to selective deposition in the trench or holes of Si wafers. Bundles of CNTs in the trenches and holes can provide sufficient current density in the form of channels and conductors, respectively. This paper systematically elucidates the synthesis of CNTs by microwave plasma CVD (MPCVD). In this study, Fe catalysts, CoSi2 films, and NiSi2 films employed frequently as gate electrodes and as a contact material in Si nanoelectronics are applied. The selective growth of CNTs in trench/hole/planar approaches is also investigated. Furthermore, the morphology and

nanostructures of CNTs are characterized. The field emission characteristics and ballistic conduction behaviors of CNTs deposited in the trenches and holes are addressed to determine electronic performance.

**Keywords**: nanoelectronic device, graphene, carbon nanotube, 2 dimension, 1 dimension, nano scale characterization.



**Figure 1**: The field emission J–E plots of the Si– C–N films for (a) Samples 1 and 2, (b) Samples 3 and 4, (c) Samples 5 and 6, (d) Samples 7 and 8.

- 1. S. K. Hwang, K. D. Lee and K. H. Lee: Jpn. Appl. Phys. Lett. 40 (2001) L580.
- Y. Avigal and R. Kalish: Appl. Phys. Lett. 78 (2001) 2291.

## NanoMed 2018 / EGF 2018 / SMS 2018 Joint Posters Session I Synthesis / Characterization / Properties

## Ag+Cu Ion Implantation Fluences Controlled Mechanical Properties, Cell Adhesion, and Antibacterial Property to TiN Coatings on Medical Titanium Alloy

L. Li<sup>1,2</sup>, M. L. Zhao<sup>1,2</sup>, L. Dong<sup>1,2</sup>, D. J. Li<sup>1,2,\*</sup>

<sup>1</sup> College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
<sup>2</sup> Tianjin International Joint Research Centre of Surface Technology for Energy Storage Matrials, Tianjin 300387, China

## Abstract:

Owing to medical titanium alloy (Ti-6Al-4V) has relatively poor hardness, corrosion resistance and antibacterial activity, it is essential to take some surface modification treatments on the medical titanium alloy. In consideration of the excellent mechanical, cell adhesion, and antibacterial properties of implant materials, titanium nitride coatings combined with Ag and Cu ion implantation become the preferred chioice for the surface modification of medical titanium alloy.

TiN coatings were synthesized by multi-arc ion plating system, with medical titanium alloy (Ti-6Al-4V) as substrates. To obtain good cell growth antibacterial property, Ag and Cu ions were implanted to the surface of TiN coatings at different fluences via ion implantation system. The structure was observed by TEM and SEM. The hardness and elastic modulus of TiN coatings before and after ion implantation were surveyed using a Nanoindenter XP system. Cytocompatibility and antibacterial property of TiN coatings at different Ag and Cu ion fluences was evaluated by osteoblast and Escherichia  $coli(E. coli, DH5\alpha)$  in vitro. The hardness and elastic modulus increase with the increasing Ag and Cu contents, and the maximum value achieves 35 GPa and 330 GPa when he Ag+Cu ion fluence reaches  $5 \times 10^{17}$  ions/cm<sup>2</sup>. In the cell proliferation

experiment, compared with the group without ion implantation, the number of living cells grown on the surface with Ag+Cu ion implantation was more and had no downward trend in seven days. The antibacterial property of TiN coatings at  $5 \times 10^{17}$  ions/cm<sup>2</sup> was extremely ideal and almost no E. coli growth.

**Keywords**: ion implantation; TiN coatings; multi-arc ion plating; antibacterial property; cytocompatibility.

- 1. C.M. Tîlmaciu, M. Mathieu, J.P. Lavigne, K. Toupet, G. Guerrero, A. Ponche, J. Amalric, D. Noël, P.H. Mutin, 2015, In vitro and in vivo characterization of antibacterial activity and biocompatibility: a study on silver-containing phosphonate monolayers on titanium, *Acta Biomater*. 15, 266-277.
- H. Cao, X. Liu, F. Meng, P.K. Chu, 2011, Biological actions of silver nanoparticles embedded in titanium controlled by microgalvanic effects, *Biomaterials*. 32, 693-705.

## Highly stable affibody-conjugated gold nanoparticles based enhanced ELISA for dengue virus NS1 antigen

Jinho Bang,<sup>1,2,\*</sup> Sunghyun Kim,<sup>1</sup>

<sup>1</sup> Korea Institute of Ceramic Engineering and Technology, Center for Convergence Bioceramic Materials, 202 Osongsaengmyeong 1-ro, Cheongjusi, Chungcheongbuk-do, South Korea <sup>2</sup> Department of Bioengineering, Hanyang University, Seoul, 133-791, South Korea

#### Abstract:

Infection with dengue virus (DENV) is a serious health issue that causes severe dengue fever and occasionally lethal complications, such as dengue hemorrhagic fever. Therefore, rapid and sensitive DENV detection is important to reduce morbidity and mortality. Here, we screened dengue NS1specific affibodies and developed highly stable anti-NS1 affibody-functionalized AuNPs to improve the detection sensitivity of NS1 antigen in ELISA. First, we screened NS1 antigenspecific affibody molecules (Z<sub>NS1</sub>12, Z<sub>NS1</sub>16, and Z<sub>NS1</sub>46) from the affibody phage library. The affibodies were then expressed and purified from Escherichia coli. Among them, the Z<sub>NS1</sub>12 affibody showed the highest equilibrium binding constant ( $K_d$ ) of 1  $\mu$ M and was sufficiently stable high temperatures. This affibody was at functionalized on AuNPs measuring 20 nm in diameter and were used as carriers to achieve amplification of the signal in ELISA. The developed anti-NS1 affibody-functionalized AuNPs  $((Z_{NS1}12)_2 - AuNP)$ showed good properties, such easy synthesis, high number of affibodies conjugation on AuNPs, and excellent stability under harsh conditions with high salt concentrations and temperature. In addition, this nanoparticle-based enhanced ELISA resulted in a 14.2-fold signal amplification performance for dengue NS1 detection in comparison with affibody-based ELISA. This novel and sensitive method using (Z<sub>NS1</sub>12)<sub>2</sub>-AuNP may have applications in the detection of DENV in infected patients at an early stage and for the detection of other pathogens in clinical diagnostics.

**Keywords**: Dengue virus, NS1 antigen, affibody, gold nanoparticles, highly stable, enhanced enzyme-linked immunosorbent assay.



Figure 1: The enhanced ELISA procedure for dengue NS1 detection using affibody-AuNPs conjugates compared with affibody-based ELISA.

#### **References:**

 J. Bang, H. Park, W. Choi, D. Sung, J.H. Lee, K.Y. Lee, S. Kim. (2018) Sensitive detection of dengue virus NS1 by highly stable affibody-functionalized gold nanoparticles, *New J. Chem.*, 42, 12607-12614.

# Fast and highly efficient antibody purification by the oriented immobilization of protein A on magnetic nanoparticles

Sunghyun Kim<sup>1</sup>

<sup>1</sup> Korea Institute of Ceramic Engineering & Technology (KICET), Center for convergence bioceramic materials, Cheongju-si, Republic of Korea

## Abstract:

In this study, we prepared the protein A grafted magnetic nanoparticles for industrial large-scale purification of antibodies with enhancement of binding capacity and immobilization by controlled orientation with chlorophenylsilane (CPTMS) on the surface. For site-specific immobilization of protein A, the genetically modified protein A with cysteine residue was expressed in E.coli and purified by affinity chromatography. To improve surface area to volume and increase immobilization amount of protein A, chlorophenylsilane functionalized magnetic nanoparticles (CPTMS@MNPs) were prepared smaller nanoparticles with average diameter of 20 nm than commercial magnetic microparticles (Dynalbeads) with average size of 2.8  $\mu$ m. The CPTMS@MNPs showed the enhancement of protein A immobilization and binding capacity to antibodies for 11.5-folds, and 7-folds higher than those of commercial Dynalbeads, respectively. In addition, the CPTMS@MNPs retained about 80% of the initial protein binding capacity until the third stage of recycling. Therefore, protein A grafted CPTMS@MNPs may be useful to industrial large-scale purification of antibodies.

**Keywords**: Chlorophenylsilane; Orientation; Immobilization; Magnetic nanoparticles; Antibody



**Figure 1**: Schematic description of protein A conjugated on magnetic nanoparticles by sitedirected orientation. (A) the unoriented immobilization of protein A on commercial magnetic microparticles (> 1  $\mu$ m) (B) the oriented immobilization of protein A on chlorosilane-functionalized magnetic nanoparticles (15 ~ 20 nm)

## **References:**

 Sunghyn Kim, Daekyung Sung, Jeong Ho Chang. (2018) Highly efficient antibody purification with controlled orientation of protein A on magnetic nanoparticles, MedChemComm, 9, 108-112

## A new approach for a physicochemical characterization of nanoparticles in complex media: a pilot study.

T. Bastogne<sup>1,2,3</sup>, V. Jouan-Hureaux<sup>1</sup>, M. Thomassin<sup>1</sup>

<sup>1</sup>UMR 7039 UL-CNRS, CRAN, Vandoeuvre-lès-Nancy, France
 <sup>2</sup>INRIA BIGS, Vandoeuvre-lès-Nancy Cedex, France,
 <sup>3</sup>Cybernano, Telecom Nancy, 54602 Villers-lès-Nancy, France

## Abstract:

Current techniques used to measure the physicochemical characteristics of nanoparticles in simple media are poorly predictive of their behavior observed during *in vivo* experiments<sup>1</sup>. As a consequence, some pharmacokinetic or toxicokinetic issues are detected too late. In this contribution, we are proposing an innovative approach to tackle this challenge<sup>2</sup>. The goal is to develop a generic characterization process that could be used in any laboratory with different categories of measurement technologies. The proposed solution is composed of three main steps:

- 1. Sample preparation;
- 2. Measurement phase;
- 3. Statistical analysis.

The sample preparation relies on a set of n serum-free media initially designed for cell culture but used herein to mimic heterogeneity of biological context. Each culture medium is composed of a large number (p), around a hundred, of biological compounds (proteins, vitamins, mineral salts, etc.), which may individually and synergistically interact with the nanoparticle surface. The nanoparticle to be characterized is added to each medium of the kit with the same concentration.

The resulting mixtures are then analyzed by an appropriate technology compatible with complex media to measure the size distribution of constitutive nano-objects.

In a third step, all the experimental data coming from the n series of measurement are used to solve a "large p small n" regression problem. This statistical analysis informs about the most likely medium compounds to affect the size distribution of nanoparticles compared to their initial dimensions. This communication presents the first results of a pilot study in which the proposed approach was tested on gold nanoparticles mixed in n=8 cell free culture media provided by Thermo Fisher Scientific. The nanoparticle size distributions were measured by a Dynamic light scattering system (Nanosight, Malvern). A partial least squares method was

used to solve the "large p small n" regression problem. Preliminary results confirms significant changes of the size distribution between the culture media and the feasibility of the statistical method to identify a set of medium compounds that may explain those variations.

**Keywords**: nanoparticle, physicochemical characterization, complex media, statistics.



**Figure 1**: Measured average size distributions of particles for nine samples in which the same concentration of gold nanoparticles are mixed in nine different serum free culture media. Those data are then used in a "large p small n" regression problem to identify biological compounds of the medium that modify the size distribution of the nanoparticle.

- C. Gollwitzer, et al., "A comparison of techniques for size measurement of nanoparticles in cell culture medium," Analytical Methods, vol. 8, no. 26, pp. 5272–5282, 2016.
- 2. T. Bastogne, "Improvement process of media cultures for the physico-chemical characterization of nano-materials in complex and serum free and controlled biological media." INPI Patent Deposit, No. 1661671, 2017.

## Supramolecular Binding of Small Molecules on Self-Assembled Monolayer Protected Gold Nanoparticles

S. Boccardo,<sup>1,2,\*</sup> D. Marson,<sup>1</sup> Y. Yang,<sup>2</sup> J. Trzcinski,<sup>2</sup> S. Guldin,<sup>2</sup> P. Posocco,<sup>1</sup>

<sup>1</sup> University of Trieste, Department of Engineering and Architecture, Trieste, Italy <sup>2</sup> University College London, Department of Chemical Engineering, London, United Kingdom

## Abstract:

Various strategies have been developed for construction of molecular aggregates with rationally designed properties, geometries, and dimensions that promise to provide solutions to both theoretical and practical problems in areas such as drug delivery, medical diagnostics, and biosensors, to name but a few. Several studies have reported an enhanced antimicrobial activity of the antiseptic photosensitizer crystal violet (CV) in the presence of gold nanoparticles covered with self-assembled monolayers. While the effectiveness of CV against gram-negative and gram-positive bacteria was demonstrated on multiple occasions, the detailed molecular mechanism of the synergistic interaction pathway between gold nanoparticles and CV remains poorly understood. We conducted a systematic investigation on the binding principles for CV attachment to the nanoparticle shell through a combined computational and experimental approach.

In particular, 2 nm gold core nanoparticles coated with undecanesulfonicacid (MUS)-containing ligands were considered.

The evidences obtained so far show a significant influence of the environmental conditions on CV interaction properties. Moreover, based on computational models resembling experimental conditions, the molecular binding principles were elucidated, showing a preferential binding mode of the CV to the monolayer.

**Keywords**: gold nanoparticles, self-assembled monolayer, molecular simulation, supramolecular binding, biomedical applications.



**Figure 1**: Molecular view of the interaction mode of CV and MUS-coated gold nanoparticle in solution.

## **References:**

Macdonald, T. J. et al. (2016) Thiol-Capped Gold Nanoparticles Swell-Encapsulated into Polyuretane as Powerful Antibacterial Surfaces Under Dark and Light Conditions, *Sci. Rep.* **6**, 39272

This work was supported by MIUR (grant RBSI14PBC6, SIR "FunctiOn at the Nanoparticle bioInterfAce").

## The functionalization of ZnO nanostructured coatings in metallic resorbable biomaterials towards personalized medicine

Marta M. Alves <sup>a</sup>, Sandra Pinto <sup>b</sup>, Catarina Santos <sup>a, c</sup>, Maria F. Montemor <sup>a</sup>

<sup>a</sup>CQE Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049-001, Lisboa, Portugal

<sup>b</sup>CQFM Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049-001, Lisboa, Portugal

<sup>c</sup>EST Setúbal, CDP2T, Instituto Politécnico de Setúbal, Campus IPS, 2914-508 Setúbal, Portugal

## Abstract:

The growing demand of materials that are able to respond to the increasing health challenges of a growing older population is now turning medical care into personalized medicine. With it, the development of materials fine-tuned to patients' needs are increasingly desirable. In the particular case of resorbable materials, the interaction with the host organism is crucial to modulate material's resorption. In this complex event, material's degradation will in turn modulate the healing process of host tissues. From the billions of substances that can be ascribed for their positive physiological role in bone healing, chemical elements as by far the simpler ones. From the reported resorbable materials, the metallic ones standout for bone healing due to their mechanical resistance. Within this class of materials, Zn has been increasing in attention. This is due to its degradation rate being compatible with that of bone healing and the resulting degradation products being innocuous for adjacent tissues. By functionalizing the surface of Zn with ZnO nanostructured coatings, an improved antimicrobial activity can be attained, which will contribute to preventing microbial adhesion to the surface of the material. On the top of this, an additional functionalization with Fe or Cu can be used to target specific health requirements: while Fe can bring an add-value in anaemia situations, Cu can aid in vascularization processes. Moreover, Cu as a physiological antagonist of Zn, can even prevent some local toxicity upon Zn dissolution. The physicochemical characterization of these functionalized ZnO nanostructured coatings revealed distinct distributions for Fe and Cu. The degradation rate of these materials, a property of extreme importance in bioresorbable materials, was physiological assessed under mimicked conditions and the resulting degradation

products carefully characterized. The presence of Fe or Cu had important effects in the corrosion rate of the material and consequently, in the degradation products formed. The physiological implication of Fe and Cu on these nanostructured coatings was further evaluated by hemocompatibility and vascularization testes. The possible repercussion of these elements in functionalized ZnO nanostructured coatings on Zn-based biomaterials for personalized medicine are discussed in detail.

# A Silicon Nitride Nanopore Device on a Polymer Substrate with microsize pore

W. Choi,<sup>1</sup> C. Park<sup>1</sup>, E. S. Jeon,<sup>1</sup> K. Y. Chun,<sup>1</sup> Y. R. Kim,<sup>2</sup> K. B. Park,<sup>3</sup> K. B. Kim,<sup>3</sup> S. Na<sup>1</sup>, C. -S. Han,<sup>1,\*</sup>

<sup>1</sup>Korea University, School of Mechanical Engineering, Seoul, S. Korea <sup>2</sup>Kyunghee University, Department of Food Science and Biotechnology, Yongin, S. Korea <sup>3</sup>Seoul National University, Department of Materials Science and Engineering, Seoul, S. Korea

## Abstract:

DNA translocation through nanopore device has been extensively investigated. Although solidstate nanopore device has advantages such as long-term stability and facile fabrication, there are sequencing resolution, insufficient frequency bandwidth of electronics, short-term use etc.

For the first time, we introduce the polymer substrate to support the nanopore membrane, made of silicone nitride. To place the nano mebrane, we fabricated the microsize pore on the polymer substrate. And the silicone nitride is transferred on top of polymer substrate. We replaced the Si/SiO2 with Polyimide substrate. For this we fabricated the microsize pore using nano laser ablation process.

Next, we measured the I-V characteristics for evaluate the nanopore size and ion transport. We found that the noise was greately reduced in a polymer substrate device. And DNA is successfully translocated by this nanopore device with high S/N ratio [1].

**Keywords**: nanopore device, DNA translocation, .polymer substrate, laser ablation, low noise

## **References:**

 Choi, W., Jeon, E.S., Chun, K.Y., Kim, Y.R., Park, K.B., Kim, K.B., Han, C.S. (2018) A Low-Noise Silicon Nitride Nanopore Device on a Polymer Substrate, *PloS One*, 2018, 13, e0200831.

## Multimodal Targeted Nanoparticles for the Non-invasive Detection of Traumatic Brain Injury

Luis Javier Cruz (Dept. of Radiology, Leiden University Medical Center (LUMC; The Netherlands)) Markus Aswendt, Mathias Hoehn (In-Vivo-NMR Laboratory, Max Planck Institute for Neurological Research in Cologne, Cologne, Germany), Eric Kaijzel, Alan Chan and Clemens Löwik (Dept. of Radiology, Leiden University Medical Center (LUMC; The Netherlands))

## Abstract

**Introduction:** Necrosis is a form of cell death that occurs only under pathological conditions such as ischemic diseases and traumatic brain injury (TBI). Non-invasive imaging of the affected tissue is a key component of novel therapeutic interventions and the measurement of treatment responses in patients. Here, we report a bimodal approach for the detection and monitoring of TBI.

PLGA Methods: NPs with entrapped perfluorcarbon and near-infrared fluorescently labelled was prepared using an o/w emulsion and solvent evaporation-extraction method (1). The PLGA NP surface was coated with a polyethylene glycol (PEG)-lipid layer and targeted delivery to necrotic cells was facilitated by coating the PLGA NP with IRdye-800CW. PLGA NPs were characterized by transmission electron microscopy (TEM), dynamic light scattering and Zeta potential (2). Brain cryo-lesion was induced in the front part of the parietal lobe for 60 seconds, followed by i.v. injection of targeted PLGA NP at different concentrations. The Pearl Impulse Small Animal Imaging System was used to image whole-body fluorescence signals at 3 h, 6 h, 24 h and 48 h post injection. MRI was carried out on a 11.7 T horizontal bore machine with a homebuilt transmit/receive single-loop surface coil. A <sup>19</sup>F image was acquired with matching geometry but lower resolution.

Results: Targeted PLGA NP had an average measured size of 200 nm in diameter and these PLGA NP harbored NIR and perfluorcarbon (PFC) in a single particle. Here, we show necrosisspecific in vivo detection by optical imaging and fluorine magnetic resonance imaging (<sup>19</sup>F MRI) using newly designed PLGA NP(NIR700 + PFC)-PEG-800CW. Quantitative ex vivo optical imaging and <sup>19</sup>F MRI of NIR-PFC content in injured brain regions and in major organs correlated well. Both modalities allowed the in vivo identification of necrotic brain lesions in a mouse model of TBI, with optical imaging being more sensitive than <sup>19</sup>F MRI. Our results confirm an increased blood pool residence time of PLGA NP coated with PEG layer and the successful targeting of TBI-damaged

tissue. A single PLGA NP containing NIR-PFC enables both rapid qualitative optical monitoring of the TBI state and quantitative 3D information from deeper tissues on the extent of the lesion by MRI. **Conclusion**: The results showed that necrosis targeted PLGA NPs reach the TBI and can potentially be used in the clinic for diagnosis of the brain injury and to deliver regenerating compounds for tissue repair.

## **References:**

- Srinivas M, Cruz LJ, Bonetto F, Heerschap A, Figdor CG, de Vries IJ. Biomaterials. 2010 Sep;31(27):7070-7.
- 2. Cruz LJ, Tacken PJ, Fokkink R, Figdor CG. Biomaterials. 2011 Oct;32(28):6791-803.

## Learning objectives

- Designing an effective nanoparticles for the non-invasive detection of traumatic brain injury
- Demonstrate the necrosis targeting capacity of the multimodal nanoparticles
- Assessing the visualization of traumatic brain injury in mouse model with optical imaging and <sup>19</sup>F MRI

## Acknowledgments

This work was supported by project grants from the EU Programme H2020-MSCA-2015-RISE (644373 – PRISAR) and MSCA-ITN-2015-ETN (675742 - ISPIC) and H2020-MSCA-2016-RISE (734684 - CHARMED)".

## Design, Obtention and Characterization of a Novel Bioactive Trilayer Scaffold for Cartilage Tissue Engineering

Y. Campos,<sup>1,2,\*</sup> G. Fuentes,<sup>1</sup> A Almirall1 Luis J. Cruz<sup>2</sup>

<sup>1</sup> Havana University, Biomaterials Centre, Metallic and Ceramic Materials Department, Havana, Cuba <sup>2</sup> Leiden University Medical Centre, Radiology Department, Leiden, The Netherlands

## Abstract:

biomaterials for cartilage Several tissue engineering has been widely used in recent years because techniques for treating cartilage affections, together with palliative treatments, have not been effective so far. For that reason, this research is aimed to design, obtain and characterize a new porous and bioactive trilayer scaffold based on natural polymers for their potential use in a possible cartilage regeneration and restoration. The surface morphology of the chitosan/collagen material (with hydroxyapatite incorporated in the calcified layer) was characterized by Scanning Electron Microscopy (SEM) showing an adequate porosity able to allow the nutrients exchange and cell movility through the matrix. In vitro studies of cell viability and proliferation were carried out with human C-28 chondrocyte cell line, by MTS and Live/Dead assays (Figure 1). The scaffold allowed cell viability and proliferation in a period of 14 days, showing that it was non cytotoxic. The bioactive behavior of the calcified layer was also evaluated by the immersion of the material in a Simulated Biological Fluid (SBF) solution for a period of 28 days. The specimen was analyzed by SEM at 3, 7, 14 and 28 days of immersion in solution. Some apatite nuclei were observed on the surface after 3 days, a higher population of nuclei at 14 days and an apatite layer covering almost the entire surface at 28 days. This fact guarantees the osseointegration of the scaffold with subchondral bone. The results obtained are encoring, proposing this novel porous trilayer scaffold as a promising candidate for cartilage tissue engineering.

**Keywords:** bioactive porous trilayer scaffold, collagen, chitosan, hydroxyapatite, cartilage tissue engineering



**Figure 1**: Cell viability assay results. Confocal micrographs from the LIVE/DEAD® assay at (A) 3 days, (B) 7 days, (C) 10 days and (D) 14 days of culture, revealing rapid growth and proliferation of chondrocytes. At 14 days, the wells and specimens were completely covered with living cells.

- 1. Kokubo, T, Takadama, H, (2006) How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials*, 27(15), 2907-2915.
- 2. Secretan, C., Bagnall, K, M, Jomha, N, M, (2010) Effects of introducing cultured human chondrocytes into a human articular cartilage explant model. *Cell and tissue research*, 339(2), 421-427.

## Thermosensitive hydrogel as controlled-release platform for intraarticular delivery of etanercept

J.García,<sup>1,2,\*</sup> G. Fuentes,<sup>1</sup> A. Almirall,<sup>1</sup> L. J. Cruz,<sup>2</sup>

<sup>1</sup> Havana University, Biomaterials Center, Department of Polymeric Biomaterials, Havana, Cuba <sup>2</sup> Leiden University Medical Center, LUMC, Department of Radiology, Leiden, The Netherlands

## Abstract:

Arthritis, including osteoarthritis (OA) and rheumatoid arthritis (RA), remains one of the major challenges in medical research and the clinic. These deseases are characterized mainly by cartilage degradation, which produce pain, stiffness, and loss of motion in the joint. Their management is directed towards pain relief achieved with different classes of drugs among which non-steroidal and steroidal antiinflammatory substances are the most frequently used agents. Nevertheless, the oral or systemic administration of such drugs is hindered by numerous side effects, which could be overcome by their intra-articular (IA) administration as dosage forms capable of gradually releasing the active substance. The aim of this work was to evaluate the behavior of Etanercept (ETA) release from thermosensitive hydrogels based on the physical mixing of Chitosan/Pluronic F127 (CS/PF) with and whithout tripolyphosphate (TPP, crosslinker agent) as IA drug delivery system. For the preparation of hydrogels, chitosan (1% w/v) and pluronic (25% w/v) were mixed. Scanning electron microscopy analysis showed that the crosslinked CS/PF-25 hydrogel with TPP has a different morphology respect to the uncrosslinked hydrogel. Infrared spectroscopy analysis indicated the main functional groups of each component of the hydrogel. The cytotoxicity and cell viability of the hydrogels were assessed by MTS and LIVE/DEAD® assays, where the results demonstrated non-cytotoxic effect of the crosslinked and uncrosslinked hydrogels on the human chondrocyte cell culture (C-28). ETA was with CS/PF-25 hydrogel mixed at the concentration of 0.05 µg/µL. In vitro release study showed that both samples released around 40% of drug in 24 hours and after that the crosslinked hydrogel had a lower release time respect to the uncrosslinked hydrogel during the 7 days studied. This study suggests the potential of CS/PF-25 hydrogel as an injectable carrier for future applications of delivering therapeutics.

**Keywords**: thermosensitive hydrogels, intraarticular administration, chitosan, pluronic, etanercept, biomedical applications.



**Figure 1**: Figure illustrating the percent cumulative in vitro drug release profile of Etanercept from crosslinked and uncrosslinked CS/PF-25 hydrogels in phosphate buffer solution

- 1. Yap, L.S., Yang, M.C. (2016) Evaluation of hydrogel composing of Pluronic F127 and carboxymethyl hexanoyl chitosan as injectable scaffold for tissue engineering applications, *Colloids and Surfaces B: Biointerfaces.*, 146, 204-211.
- 2. Aalbers, C., et al. (2015) Intra-articular etanercept treatment in inflammatory arthritis: A randomized double-blind placebo-controlled proof of mechanism clinical trial validating TNF as a potential therapeutic target for local treatment. *Joint Bone Spine.*, 82, 338-344.

## Trends within Point-of-care Platform Development – The Growing Influence of Nanomaterials

B. Regan,<sup>1</sup> R. O' Kennedy,<sup>2</sup> D. Collins,<sup>1</sup>

<sup>1</sup> Dublin City University, Department of Biotechnology, Dublin, Ireland <sup>2</sup>Hama Bin Khalifa University, Research Complex, P.O. Box 34110 Doha, Qatar

Correspondence: Brian Regan (brian.regan3@mail.dcu.ie)

## Abstract:

Point-of-care (POC) platforms are becoming widespread within increasingly healthcare diagnostics, aiding in the assessment of various types of diseases and illnesses. Most notably the management of patient health is heavily dependent upon the rapid and effective identification of an occurring health issue, an aspect which is highly beneficial to the treatment of cardiovascular disease (CVD). Critically, aiming to improve the sensitivities of these platforms and other assays in general is crucial to the early recognition of CVD. The area concerning biosensor development is continuously expanding and is a significant precursor to the fabrication of POC platforms. Many of these sensors are integrating the use of nanomaterials to attain sensor performances that exceed what has previously far been accomplished. Nanomaterials are utilized in many ways with a broad diversity of materials being employed, in addition to novel applications leading to the emergence of new detection techniques. This poster will present some of the most prominent uses of nanomaterials in biosensors aimed detecting at cardiac biomarkers, in addition to highlighting the subsequent impact on the biosensor fabrication. Furthermore, some of the most highly sensitive techniques targeting cardiac troponin I, a cardiac biomarker with high specificity, will be detailed in conjunction to outlining the potential for POC platform integration.

Keywords: point-of-care, biosensor, nanoparticles, upconverting nanoparticles, cardiac troponin I, metal organic framework



**Figure 1**: Illustration depicting various nanoparticles used in enhanced surface Raman spectroscopy. This technique was implemented in a lateral flow assay, an ideal format for point-of-care testing.

## **References:**

 T. Bai *et al.*, "Functionalized Au@Ag-Au nanoparticles as an optical and SERS dual probe for lateral flow sensing," *Anal. Bioanal. Chem.*, vol. 410, no. 9, pp. 2291–2303, Mar. 2018

# Influence of synthesis parameters on the properties of the nanocomposite graphene / MFe<sub>2</sub>O<sub>4</sub> (M=Ni, Co and Zn)

Jedrzejewska,<sup>1</sup> D. Sibera,<sup>1\*</sup> R. Jedrzejewski,<sup>2</sup> A. Bachmatiuk,<sup>3</sup> R. Pełech,<sup>4</sup> U. Narkiewicz<sup>1</sup>

 <sup>1</sup>Institute of Chemical and Environment Engineering, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Szczecin, Pułaskiego 10, Poland
 <sup>2</sup>Institute of Materials Science and Engineering, Faculty of Mechanical Engineering and Mechatronics, West Pomeranian University of Technology, al. Piastów 19, 70-310 Szczecin, Poland
 <sup>3</sup>Centre of Polymer and Carbon Materials- Polish Academy of Sciences, M. Curie-Sklodowskiej 34,

41-819 Zabrze, Poland

<sup>4</sup>Institute of Organic Chemical Technology, Faculty of Chemical Technology and Engineering, West Pomeranian University of Technology, Szczecin, Pułaskiego 10, Poland

## Abstract:

Due to its fascinating properties such as high surface area, very good electrical and thermal conductivity, excellent mechanical, optical and electrochemical properties, graphene may be the ideal material as a substrate of nanocomposites for applications in electronics. Layer of graphene can be used as a conductive matrix allowing good contact between the crystallites of nanomaterials. Graphene is an ideal material for electrochemistry because it exhibits improved features, such as very large 2-D electrical conductivity, very fast heterogeneous electron transfer, large surface area and low cost.

In this work, we are demonstrating the results of studies on the effects of synthesis parameters on the properties of graphene composites. Graphene/NiFe2O4, graphene / CoFe<sub>2</sub>O<sub>4</sub> and graphene/ZnFe<sub>2</sub>O<sub>4</sub> nano hybrid composites were prepared using а solvothermal strategy in microwave reactor and autoclave. Pressure treatment in the autoclave was performed for 12 to 24 h (with an increment of 4h) and temperature of 120°C, 160°C and 200°C. The pressure treatment in the microwave solvothermal reactor was much shorter, the solution was treated there for 15 to 45 min (change every 15 min), under a pressure of 40 to 50 atm (change every 5 atm). A series of experiments was conducted using a commercially available graphene (Graphene Nanopowder AO-3) or graphene obtained using the Hummers' method. The syntheses were carried out in a solution of ethanol.

We investigated the effect of synthesis parameters on the quality of the obtained nanocomposites. The morphology of the nanocomposites was investigated using transmission electron microscopy. Effect of synthesis parameters on phase composition of the obtained samples was investigated using Xray diffraction. The impact of dopant and the synthesis conditions on the surface area and electrical conductivity of the samples was also examined. Thermogravimetric studies were carried out on the selected materials.

#### Acknowledgement:

This work was supported by project: LIDER/496/L-6/14/NCBR/2015 financed by The National Centre for Research and Development.

## Characterization of Nano-Graphenes and Graphene Nanoribbons by Atomic Force Microscopy with Atomic Precision

D. Ebeling<sup>1</sup>, Q. Zhong<sup>2</sup>, L.F. Chi<sup>2</sup>, A. Schirmeisen,<sup>1,\*</sup>

<sup>1</sup> Justus-Liebig-University Giessen, Institute of Applied Physics, Giessen, Germany <sup>2</sup> Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, China

## Abstract:

Nano-graphenes and graphene nanoribbons (GNR) exhibit extraordinary electronic, chemical and mechanical properties that make them ideal candiates for widespread applications ranging from nanoscale electronic devices to drug delivery agents. For example their electrical properties can be tailored by the controlling the exact atomic structure of the graphenes. Although the two-dimensional parent material graphene semimetallic behaviour, exhibits quantum confinement and edge effects render all graphene nanoribbons with widths smaller than 10nm semiconducting. Nano-graphenes, as e.g. triangulene, are predicted to exhibit even magnetic properties at the zigzag edges that make them promising candidates for molecular spintronics. Essential for controlled nanographene engineering is reliable imaging of their precise atomic structure.

Here we present images of nano graphenes as well as graphene nano ribbons on gold surfaces using scanning probe microscopy techniques at liquid helium temperatures. With the scanning tunneling microscope we can determine the size and geometry of the on-surface synthesized graphene structures, but the exact atomic structure remains unresolved (Figure 1, top). Therefore we functionalize the SPM tip with a CO-molecule, and use the non-contact atomic force microscope, which allows imaging of the precise atomic structure of nanoscale graphene objects<sup>1</sup>. Due to the flexibility of the CO-tip distortions typically image lead to an overestimation of the bond lengths<sup>2</sup>. A direct comparison of the AFM scans with image contrast simulations allow a better match experimentally between measured and theoretically predicted structures (Figure 1. bottom). Further we shows tunneling spectroscopy images, which allow to characterize the internal electronic structure of the graphenes.

**Keywords**: Nano graphene, Graphene nano ribbons, atomic force microscopy, scanning tunneling microscopy.



**Figure 1**: Top: Imaging of the graphene nanoribbon with functional Cl side groups at 4 K by STM. Center: Imaging of the atomic structure of the GNR by non-contact AFM with CO-functionalized tip. allows structure idenfication at the chemical bond level. Bottom: Comparison of AFM scan with theoretical structure.

- Gross, L., Mohn, F., Moll, N., Liljeroth, P. & Meyer, G. (2009), The chemical structure of a molecule resolved by atomic force microscopy. *Science* 325, 1110–1114
- 2. Hapala, P. et al. (2014), The mechanism of high-resolution STM/AFM imaging with functionalized tips. *Phys. Rev. B* 90, 085421

## A Microawave Measurement Technique For 2D Material Characteriziation

H. Krraoui,<sup>1,\*</sup> C. Tripon-Canseliet,<sup>1</sup> I. Maksimovic<sup>1</sup>

<sup>1</sup> UPMC Université Paris 06, Laboratoire de Physique et Etude des Matèriaux, 75005 Paris, France

## Abstract:

Graphene is a 2D structure with  $sp^2$  chemical bounding of carbon atoms providing remarkable electronic and mechanical properties [1]. A number of different methods for preparing graphene thin films have appeared, and a wide range of experiments are being carried out on them [2].

There is a great deal of variability in the quality of films prepared, and even when identical methods are used, the film properties between successive batches may be quite different. The accepted method for characterising the electrical properties of graphene films is to measure the mobility. However, this generally requires patterning of the films and making electrical contact.

In this paper, we present a new method for conductivity and surface impedance measurements of monolayer graphene samples in broad frequency range. This parameters are extracted from the transmission between two antennas through a bistatic reflection method.

The schematic diagram of the free space bistatic measurement system is given in Fig.1. It consists of a pair of collinear horn antennas that operate as the feeds for the focusing lens.

Furthermore, positioners are used to control the position of the sample holder with a precision of  $10\mu m$  in the three directions of the Cartesian space.

The surface impedance of the global structure Zin is equal to the parallel connection between the surface impedance of the graphene sheet Zs and the surface impedance of the dielectric slab  $Z_0(z_0)$ .

Then, after some analytical manipulations, the real and the imaginary part of the surface impedance and the conductivity of the graphene can be measured in broad frequency range.

**Keywords**: free space, graphene, conductivity, surface impedance, radio frequency (RF).



**Figure 1**: Free space measurement of Graphene printed on a substrate dilectric.

- B. Kiraly, R. M. Jacobberger, A. J. Mannix, G. P. Campbell, M. J. Bedzyk, M. S. Arnold, M. C. Hersam, and N. P. Guisinger\* "Electronic and mechanical properties of Graphene-Germanium interfaces grown by Chemical Vapor Deposition," Nano Lett. vol. 15, pp 7414–7420, 2015.
- Z. Zhu, L. G.-Gancedo, A. J. Flewitt, H. Xie, F. Moussy and W. I. Milne, "A Critical Review of Glucose Biosensors Based on Carbon Nanomaterials: Carbon Nanotubes and Graphene," Sensors, vol. 12, pp. 5996-6022, 2012.

## Preparation of Highly Stable Black Phosphorus by Gold Decoration for High Performance Thermoelectric Generators

Young Hun Kang, Cheng Jin An, and Song Yun Cho\*

Division of Advanced Materials, Korea Research Institute of Chemical Technology, 141 Gajeong- ro, Yuseong-gu, Daejeon 34114, Republic of Korea

## Abstract:

Atomically thin black phosphorus (BP) as a new member of two-dimensional (2D) material, has attained considerable interest due to its unique electronic and optical properties. The fascinating properties suggest that BP is not only promising materials for application for nanoscale optoelectronic device but also for intrinsically efficient thermoelectric (TE) device. Its great potential as a high performance TE material has been demonstrated with ultrahigh Seebeck coefficient in the order of approximately 10 mV K<sup>-1</sup>. However, the excellent TE properties was realized by applying large external voltage on dielectric gate for Fermi-level tuning of 2D BP to increase the carrier concentration.

In this work, the surface transfer method was utilized to manipulate the electronic properties of BP to provide a stronger nonvolatile doping capability, as compared with the electrostatic modulation via an external electrical field. Surface transfer doping relies on the interfacial charge transfer without introducing significant defects into the lattice structure of the as-doped materials, thereby nearly maintaining their fundamental transport properties. The electronic property of exfoliated BP was delicately tuned by decoration of Au nanoparticle (NP) through simple and facile solution process. Consequently, the electrical conductivity of the Au-decorated BP was significantly improved from 0.001 to  $63.3 \text{ S cm}^{-1}$ , at the same time, the reduction in Seebeck coefficient of BP, which is dependent on the carrier concentration, was efficiently suppressed by the formation of energy barrier at the interface of Au-BP heterostructure. This considerable enhancement of the electrical conductivity by Au NP incorporation outweigh the moderate reduction of the Seebeck coefficient, contributing to a high power factor of 68.5 from  $0.025 \ \mu\text{W} \text{ m}^{-1} \text{ K}^{-2}$ . Moreover, the instability of BP in air, which tremendously bothers the practical uses of BP for TE generator, was dramatically improved by occupying the energetic defects or edge sites with novel metal

elements, showing no significant change in internal resistance for one week without any encapsulation. Finally, the vertical TE generator composed of Au-decorated BP as a p-type source was stably fabricated, showing much higher power output than pristine BP. This cost-effective and versatile approach for highly stable BP material with unique electrical and thermoelectric properties will open the door for new TE materials with wide-ranging applications.

**Keywords**: black phosphorus; gold nanoparticle; decoration; air stability; thermoelectric generator.



**Figure 1**: (a) Schematic illustration of the preparation of the Au-decorated BP sheet and (b) Fabrication and power generation of the vertical TE generator.

- 1. Churchill, H. O.; Jarillo-Herrero, P. (2014) Two-dimensional Crystal: Phosphorus Joins the Family. *Nat. Nanotechnol.*, *9*, 330-331.
- Saito, Y.; Iizuka, T.; Koretsune, T.; Arita, R.; Shimizu, S.; Iwasa, Y. (2016) Gate-tuned Thermoelectric Power in Black Phosphorus. *Nano Lett.*, 16, 4819–4824.

# Modified consolidants of porous materials with enhanced performance

M. Remzová,<sup>1,2,\*</sup> T.Brzicová,<sup>3</sup> J. Rathouský<sup>1,2</sup>

<sup>1</sup> J. Heyrovsky Institute of Physical Chemistry of the CAS, v.i.i., Prague, Czech Republic
 <sup>2</sup> Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Rep.
 <sup>3</sup> Institute of Experimental Medicine of the CAS, v.i.i., Prague, Czech Republic

## Abstract:

Silicon alkoxides have long been used as consolidants of weathered stone monuments. However, their physical properties are not ideal, for example, their microporosity leads to cracking of formed gels. To enhance their properties, we prepared and characterized modified ethylsilicates, and tested their effectiveness as potential consolidants (Figure 1). The ethlysilicate consolidants were modified by a combination of two ways: by selection of catalyst (either organometallic compounds or amines<sup>1</sup>) and nanoparticle type (SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO). FTIR spectroscopy was used to follow the sol-gel process to determine irs rate. The porosity of the solidified material was determined using sorption experiments. To test the performance of developed modiefied consolidants they were applied to different types of sedimentary rocks. During the process of maturation, the stone's surface properties and microstructure, such as wettability, capillarity and water transport, were analyzed using various techniques. Elastic modulus and hardness of the specimen were obtained from load-displacement measurements in nanoindentation tests<sup>2</sup>. To evaluate the effectiveness of each consolidant, the drilling resistance measuring system (DRMS) was used to determine the drilling resistance force and penetration depth. Ethylsilicate gels modified by octylamine and nanoparticles did not crack, penetrated deeper into the pore structure of the stone and increased the hardness of the treated material. Finally, only nanoparticles with a minimal adverse effect on both the health and the environment were used. The cytotoxicity tests in human lung A549 cells showed that while no cytotoxicity was observed for TiO2 and octylated SiO<sub>2</sub> nanoparticles, unmodified SiO<sub>2</sub> and ZnO nanoparticles decreased cell viability in both WST-1 and LDH assays. Importantly, these materials did not significantly alter the natural characteristics of the stone. Thus, our work ethylsilicates suggests that modified by

octylamine and nanoparticles are highly promising consolidants.

**Keywords**: stone consolidation, ethysilicates, nanoparticles, nanoindentation, drilling resistance measurement system, cytotoxicity test.



**Figure 1**: A scheme summarizing all the steps in the development of modified ethylsilicate consolidants with improved performance.

- Mosquera M.J., De Los Santos D.M., Valdez-Castro L., Esquivias L. (2008) New route for producing crack-free xerogels: Obtaining uniform pore size. J. Non. Cryst. Solids., 354, 645–50.
- Remzova, M., Sasek, P., Frankeova, D., Slizkova, Z., Rathousky, J. (2016) Effect of modified ethylsilicate consolidants on the mechanical properties of sandstone. *Constr. Build. Mater.*, 112, 674–681.

## Sol-gel synthesis of MeFe<sub>2</sub>O<sub>4</sub> (Zn, Ni, Co, Cu and Mg) nanoparticles for water purification application

G.Demeuova, A.Kurbanova, O.Mauit , M. Baisariyev, O. Ualibek, O. Toktarbaiuly, G. Sugurbekova National Laboratory Astana, Nazarbayev University, Astana, Kazakhstan

#### Abstract:

Water purification and environmental remediation has been one of critical issues arising with increasing demand for portable water. Industrial effluents, primarily synthetic colourings from textile dyes such as methylene blue contribute predominantly to water pollution [1]. Therefore, the aim of this study was to investigate efficient degradation of MB employing metal ferrite (Zn, Ni, Co, Cu and Mg) photocatalysts under solar light irradiation.

The experimental procedure is based on modified sol gel technique [2], where  $Fe(NO_3)_2 \times 9H_2O$  was used as metal precursor, providing  $Fe^{3+}$  ions, which is highly soluble in organic solvents. Magnesium (II), cobalt (II), nickel (II), zinc (II) and cupper (II) acetates, in the form of powder, contributed to the required  $Mg^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Co^{2+}$  ions for metal ferrite formation. Iron nitrate and metal acetate were weigthed in required stoichiometric ratio and dissolved in ethanol, followed by addition of acetic acid to enhance hydrolysis. Solution was continuously stirred while 2-MOE was poured as a solvent coupled with ethylene glycol that served as a precursor to polymers. The obtained solution was dried overnight and further calcined at 600 °C for 8 hrs.

Phase composition, crystallinity, structure and surface morphology were studied by XRD and SEM. According to X-ray diffraction pattern (Fig 1), samples are polycrystalline nanoscale structures, as evidenced by the broadening and low intensity of the diffraction peaks. Phase analysis based on those diffractograms showed 100% spinel cubic MgFe<sub>2</sub>O<sub>4</sub> and tetragonal CuFe2O4 have been achieved with crystallinity of 75.6% and 77% respectively, whereas the rest are iron-containing oxides of cubic structure. As for FeCoO and FeZnO samples, formation of a structure characteristic of hematite Fe<sub>2</sub>O<sub>3</sub> is observed. The formation of the hematite phase in the structure can be caused by thermal annealing at a temperature of 600 ° C, which is characteristic for the phase transformation of iron oxide into hematite. SEM analysis in Figure 2 represent uniform particle size distribution with particle size varying from 10-60 nm. Photocatalytic property of obtained samples was investigated by photodegradation of methylene blue (MB) under solar light irradiation. The photocatalytic activity of MgFe<sub>2</sub>O<sub>4</sub> was investigated by using photodecomposition of methylene blue (MB) dye under solar light irradiation [1].



Figure 1: X-ray Diffraction patterns of metal ferrites



Figure 2: SEM analysis of obtained samples

Total degradation of MB with  $MgFe_2O_4$  was achieved in 2 hours and 45 min at concentration 0.4 g/L of photocatalyst.

**Keywords**: water treatment, photocatalyst, ferrites, sol-gel, photocatalytic activity.

- 1. 1. Z.Y.Kong et al. (2014). The application of magnesium ferrite photocatalyst for photo treatment of methylene blue. *Journal of Engineering Science and Technology. Special issue on SOMCHE & RSCE 2014 Conference.* pp 1-10.
- Lee Sanghoon. (2012) Ferrimagnetic MgFe<sub>2</sub>O<sub>4</sub> nanoparticles for intra-arterial hyperthermia agent applications, *PhD Thesis.*, National University of Singapore., 27-33.

## Development of acoustic microscopy sensor with high resolution for characterization in thin films

S. Lee<sup>1</sup>, T. Park<sup>1</sup>, D.Kwak<sup>1</sup>, I. Park<sup>1\*</sup>

<sup>1</sup> Seoul National University of Science and Technology, Department of Mechanical & Automotive Engineering, 232 Gongneung-ro, Nowon-gu, Seoul 01811, Korea

## Abstract

The acoustic microscopy system (AMS) is a non-destructive method for the evaluation of he micro/nano structures of materials using ultrasonic waves. Recently, the development of a high-frequency acoustic microscopy sensor has been required, as the thickness of thin films has decreased. In this study, we developed a high-resolution AMS sensor to evaluate the microstructure of thin films. For the fabrication of a piezoelectric transducer, various thicknesses of ZnO thin films were deposited on a sapphire lens using RF magnetron reactive sputtering. Using the fabricated sensor, the velocity of the leaky surface acoustic wave and acoustic image of the thin film were analyzed. Based on the results, the developed high-resolution AMS sensor will be used for the diagnosis/inspection of micro/nano structural damages in thin films.

**Keywords**: Acoustic microscopy system (AMS), High-resolution sensor, RF-magnetron sputter, Thin films, Piezoelectric transducer

## AlGaN/GaN HEMT heterostructures for gas- and bio-chemical transducers

B. Paszkiewicz, B.K.Paszkiewicz, M. Wosko, K. Indykiewicz, R. Paszkiewicz

Faculty of Microsystem Electronics and Photonics, Wroclaw University of Science and Technology, Z. Janiszewskiego 11/17, 50-372 Wroclaw, Poland

## Abstract:

In recent years an increase is observed in application of nitrides materials for gas- and biochemical sensors. In this sensor two essential elements could be distinguished: transducer part and receptor part. In a result of interaction of analyte with receptor part specific physicchemical reactions occur in it that cause changes in the properties of the transducer part. Depending on the type of applied transducer the chemical information is changed on other type of energy in form of electrical, optical or acoustic signal. Typically the semiconductor transducers utilize the field effect. The operation of MISFET (MOSFET), MESFET and HEMT transistors are based on this effect. In the general case, the transistors could be used as a transducer in which the metallic gate was replaced by receptor part. From many years the silicon ISFET transistors were used as a transducer. In recent years, because of higher electrons mobility, the ISFET transistors are replaced by HEMT transistors. Two dimensional gas electrons in the channel of HEMT transistors, fabricated in classical AIIIBV semiconductors, have very high mobility but in this case the semiconductor surfaces are chemically and electrically unstable and could be biologically incompatible (or even toxic for cells cultures). Because of it the AlGaN/GaN heterostructure with different cap layers (AlGaN, AlN, GaN, SiN) were proposed for HEMT transistors fabrication process. The operation of AlGaN/GaN HEMT transistors is based on the modulation of the sheet carrier concentration of 2DEG, in triangular potential well, that is formed in the GaN layer near the AlGaN/GaN interface. The electrical response of AlGaN/GaN HEMTtype transducer could be the change of the channel resistance, alteration of the drain saturation current or the change of pinch-off voltage of the channel. Depending on the type of applied receptor layer the open-gated HEMT type AlGaN/GaN transducers could be used for sensing of various types of biological and chemical substances [1] (Figure 1).



**Figure 1:** Matrix of 5 AlGaN/GaN HEMT type transistors with open gates of various lengths.

There was also found that exposed surface of transducers reacts on changes of electrolyte pH that should enable elaboration of semiconductor pH sensor and [2, 3]. However, in hydrogen sensor as a receptor part the thin metal layer of palladium or platinum are applied that catalyse the dissociation of gas molecules.

The result of the research, performed at WUST, on the design, fabrication and measurement of AlGaN/GaN HEMT transducers for biochemical sensor application will presented and discussed (Figure 2 and Figure 3).

**Keywords**: AlGaN/GaN heterostructures, HEMT-type transducers, open-gated transistors, gas sensors, and bio-chemical sensors, 2DEG



**Figure 2**: Part of transducer chip designed and fabricated in WUST: A-transistor with metallic gate, B-transistor with electrolytic gate, C-counter electrode.



**Figure 3:** Transient characteristics of AlGaN/GaN HEMT transistors with electrolytic gates and a metal gate transistor (Urs = Ugs) for various pH of electrolite.

#### Acknowledgement:

This work was co-financed by the National Centre for Development Research grants and TECHMATSTRATEG No. 1/346922/4/NCBR/2017, the National Science Centre grant No. DEC-2015/19/B/ST7/02494, Wroclaw University of Science and Technology statutory grants and by the Slovak-Polish International Cooperation Program. This work was accomplished thanks to the product indicators and result indicators achieved within the projects co-financed by the European Union within Regional the framework of the European Development Fund, through a grant from the Innovative Economy (POIG.01.01.02-00-008/08-05) and by the National Centre for Research and Development through the Applied Research Program Grant No. 178782 and LIDER No. 027/533/L-5/13/NCBR/2014,

## **References:**

- Liu, H.Y.; Hsu, W.C.; Chen, W.F.; Lin, C.W.; Li, Y.Y.; Lee, C.S.; Sun, W.C.; Wei, S.Y.; Yu, S.M., (2016), Investigation of AlGaN/GaN ion-sensitive heterostructure field-effect transistors based pH sensors with Al2O3 surface passivation and sensing membrane, *IEEE Sens. J. 16, 3514–3522*.
- Sansalvador, I.; Fay, C.D.; Cleary, J.; Nightingale, A.M.; Mowlem, M.C. Diamond, D., (2016), Autonomous reagent-based

microfluidic PH sensor platform. Sens. Actuator B-Chem., 225, 369–376.

3. M. Hojko, D. Paszku, B. Paszkiewicz, (2013), Measurements of AlGaN/GaN heterostructures for sensor applications, *Optica Applicata, XLIII, 1, 35-38.* 

## Engineering Self-protected MAPbBr<sub>3</sub>/Nitrogen-Doped Graphene Hybrids with High Stability for Photodetectors

M. Liang,<sup>1</sup> Y. Tang,<sup>1</sup> C. Engelbrekt,<sup>1</sup> Q. Chi,<sup>1,\*</sup>

<sup>1</sup>Technical University of Denmark, Department of Chemistry, Kongens Lyngby, Denmark.

## Abstract:

Metal-halide perovskites (MHPs) have emerged at the forefront of light absorber materials due to their unique physicochemical properties such as large light absorption coefficients, a broad absorption range, high carrier mobility, customizable optical properties and superior solution processability. These materials show great potential in design and fabrication of new generation optoelectronic devices. However, poor stability could be a fatal barrier for application of halide perovskites. To overcome this issue, materials such as Al<sub>2</sub>O<sub>3</sub>, ZnO<sub>2</sub>, polymer and organic ligands have been used as protective layers on the perovskite materials. However, this has caused poor conductivity and mismatch between materials. Herein, we report a simple and versatile solution method towards chemical decoration of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> (MAPbBr<sub>3</sub>) perovskites to obtain perovskitebased molecular hybrids. Nitrogen-doped graphene (N-rGO) was chosen due to its large specific surface area, excellent stability and high charge mobility. Further, N-rGO has rich chemically active sites, e.g., N atoms and residue oxygen-containing groups. These functional groups hold advantages for chemical linking through hydrogen bonding between N-rGO and MAPbBr<sub>3</sub> perovskites. The hybrid MAPbBr<sub>3</sub>/NrGO materials were prepared in-situ by a facile method. Photodetector devices were fabricated with the hybrid materials to investigate their optoelectronic properties. The photodetectors displayed high stability against moisture and impressively, light. More the hybrid optoelectronic devices show 120-fold enhanced photoresponsivity compared to these devices based on pure perovskites. The as-designed hybrid is thus a promising candidate for photodetection applications.

**Keywords**: metal-halide perovskites, nitrogendoped graphene, optoelectronic properties, optoelectronic devices, high stability, photodetector.



**Figure 1**: Hybrid MAPbBr<sub>3</sub>/N-rGO materials showing high stability against moisture and light under ambient conditions. The material is in-situ synthesized via hydrogen bonding and displays excellent optoelectronic performance.

- 1. Pan, R., Li, H., Wang, J., Jin, X., et al. (2018) High-responsivity photodetectors based on formamidinium lead halide perovskite quantum dot–graphene hybrid, *Part. Part. Syst. Charact.*, 35, 1700304.
- 2. Lee, Y., Kwon, J., Hwang, E., et al. (2015), High-performance perovskite–graphene hybrid photodetector, *Adv. Mater.*, 27, 41– 46.
- Luo, Q., Zhang, Y., Liu, C., Li, J., et al. (2015), Iodide-reduced graphene oxide with dopant-free spiro-OMeTAD for ambient stable and high-efficiency perovskite solar cells, *J. Mater. Chem. A.*, 3, 15996–16004.

## Composition-Driven Magnetic and Structural Transformations in Doped Bismuth Ferrites

U. Khomchanka,<sup>1,\*</sup> J. A. Paixão<sup>1</sup>

<sup>1</sup> University of Coimbra, CFisUC/Department of Physics, Coimbra, Portugal

## Abstract:

Magnetoelectric multiferroics exhibit the simultaneous existence of spin and electric dipole ordering, making them promising for future technological applications [1, 2]. While BiFeO<sub>3</sub> is the most thoroughly studied magnetic ferroelectric compound, the properties of its solid solutions remain a matter of intensive debate. In this paper we show how variation in the chemical composition of Bi1- $_{x}Ae_{x}Fe_{1-x}Ti_{x}O_{3}$  (Ae=Ca, Sr, Ba) perovskites affects their crystal structure and magnetic behavior. In particular, our research demonstrates that Ca/Ti and Sr/Ti cycloidal substitutions suppress the antiferromagnetic structure specific to the parent compound, thus stabilizing a weak ferromagnetic ferroelectric state. The Ba/Tidoped solid solutions retain the magnetic behavior characteristic of the pure BiFeO<sub>3</sub>. The composition-driven changes in the magnetic properties of the  $Bi_{1-x}Ae_xFe_{1-x}Ti_xO_3$ compounds correlate with the evolution of lattice parameters, thus confirming the existence of a tight coupling between the magnetic and structural/electric dipole order in these materials.

**Keywords**: BiFeO<sub>3</sub>, crystal structure, magnetic properties, multiferroics, spin-cycloid instability.

- 1. Dong, S., Liu, J.-M., Cheong, S.-W., Ren, Z. (2015), ultiferroic materials and magnetoelectric physics: symmetry, entanglement, excitation, and topology, *Adv. Phys.*, 64, 519-626.
- Fiebig, M., Lottermoser, T., Meier, D., Trassin, M. (2016), The evolution of multiferroics, *Nat. Rev. Mater.*, 1, 16046.

## Electroluminescent soft elastomer actuators with adjustable luminance

Beom Gil Ha, Jong Yeop An, Ye Rim Lee, and Byung Yang Lee

Department of Mechanical Engineering, Korea University, Seoul 02841, Korea

## Abstract:

Multifunctional soft-material-based light-emitting actuators that can actively deform and emit light are essential factors for future lighting and display Therefore, flexible and applications. soft electroluminescent (EL) devices that can accommodate large mechanical strains such as bending, twisting, stretching and folding have been studied extensively. In this study, we demonstrate a soft actuator that can control the strain and luminance individually by using electrical stimulation. By inserting an EL layer between dielectric elastomer films, we could fabricate a soft actuator with controllable strain and electroluminance while applying a combination of AC and DC signals. The AC signal component mainly controlled the luminance of the device, while the DC signal controlled the strain of the device. The electrode of the device is composed of hybrid structure of nanowires and carbon nanotubes. The fabricated EL actuator exhibits a maximum strain of 85% and a maximum luminance of  $300 \text{ cd/m}^2$ . We also attempted to use liquid metal to improve the performance. When the liquid metal was not mixed with the electrode, the luminance characteristic was lowered at a voltage value higher than a certain level. However, when the liquid metal was mixed with the electrode, the luminance characteristic was increased more than the conventional value. That is, with the use of liquid metal electrodes, the actuator performance can be improved, and a reduction in power consumption can be expected. We believed that this work will contribute to the new development of soft skin or muscle.

**Keywords:** electroluminescent soft actuators, multifunctional soft devices, strain, luminance



**Figure1**: Schematic of fabrication process of the Electroluminescent Dielectric Elastomer Actuator (ELDEA).

#### **References:**

Ye Rim Lee, Hyung Ho kwon, Do Hoon Lee and Byung Yang Lee (2017) Highly flexible and transparent dielectric elastomer actuators using silver nanowire and carbon nanotube hybrid electrodes, *Soft Matter*, 13, 6390-6395
## NanoMed 2018 / EGF 2018 / SMS 2018 Joint Posters Session II Properties and applications

## Mesoporous Silica Nanoparticles for Targeted Delivery of Chemotherapeutic Drugs

S. A. P. Pereira,<sup>1</sup> A. Rahikkala,<sup>2</sup> P. Figueiredo,<sup>2</sup> M. L. C. Passos,<sup>1</sup> H. A. Santos,<sup>2,3</sup> M. L. M. F. S. Saraiva,<sup>1</sup> <u>A. R. T. S. Araujo<sup>1,4</sup></u>

<sup>1</sup> LAQV, REQUIMTE, University of Porto, Department of Chemical Sciences, Faculty of Pharmacy, Porto, Portugal

<sup>2</sup> University of Helsinki, Drug Research Program, Division of Pharmaceutical Chemistry and Technology, Faculty of Pharmacy, Helsinki, Finland

<sup>3</sup> University of Helsinki, Helsinki Institute of Life Science (HiLIFE), Helsinki, Finland <sup>4</sup> Research Unit for Inland Development (UDI), Polytechnic Institute of Guarda, Guarda, Portugal

#### Abstract:

Mesoporous silica nanoparticles (MSNs) (Figure 1) present unique features that make them a promising drug delivery carrier for cancer therapy, such as: high drug loading efficiency, high degree of tunability regarding size, controlling drug release, high biocompatibility, biodegradability and chemical flexibility. Their structural properties allow the targeted delivery of chemotherapeutic drugs to enhance drug efficacy and reduce adverse effects. The functionalization of MSNs with targeting ligands to a specific tissue/cell and stimuli-responsive capping materials to seal drugs inside the MSNs pores have been widely studied for biomedical and pharmaceutical applications. Furthermore, multiple stimuli-responsive MSN-based drug delivery systems have been developed to enhance the delivery of chemotherapeutic drugs to their specific target and thereby improve the release of the drugs at the intended site [1,2]. In addition, several toxicity studies have been conducted to evaluate the biosafety and biocompatibility of MSNs. Although MSNs can induce cytotoxicity associated with oxidative stress, different modifications to control morphology and surface composition can be performed to overcome the biocompatibility concerns [3].

On the other hand, the number of reports where nanoparticles have been used coupled to a flowbased strategy or as a part of a microfluidic device has been increasing, aimed for their characterization, synthesis and toxicity evaluation, and also for analytical determinations and nanomedicine. The prospect of associating the MSNs with flow-based analytical methods is envisioned as it would permit confined, costeffective and reliable analysis, guaranteeing precise and reproducible control of the reaction conditions, within a shorter timeframe, while exploiting the features of the MSNs.

**Keywords**: mesoporous silica nanoparticles (MSNs), chemotherapeutic drugs,



functionalization, targeting, toxicity, flow analysis systems.

**Figure 1**: Surface functionalization of some types of MSNs.

- 1. Alvarez-Berríos, M.P, Sosa-Cintron, N., Rodriguez-Lugo, M., Juneja, R, Vivero-Escoto, J.L. (2016), Hybrid nanomaterials based on iron oxide nanoparticles and mesoporous silica nanoparticles: overcoming challenges in current cancer treatments, *J Chem*, 2016, 1-15.
- Martínez-Carmona, M., Colilla, M., Vallet-Regí, M. (2015), Smart mesoporous nanomaterials for antitumor therapy, *Nanomaterials-Basel*, 5, 1906-1937.
- Lee, S., Yun, H.S., Kim, S.H. (2011), The comparative effects of mesoporous silica nanoparticles and colloidal silica on inflammation and apoptosis, *Biomaterials*, 32, 9434-9443.

## The antifibrotic effect of Imatinib loaded CD44 targeted gold nanoparticles (Im-CD44-GNP) relies on alveolar macrophage regulation

V. Frangipane,<sup>1</sup> F. Meloni,<sup>1,2</sup> M. Morosini,<sup>1</sup> V. Codullo,<sup>3</sup> S. Magni,<sup>1</sup> H. Recalde,<sup>4</sup> S. Inghilleri,<sup>1</sup> L. Pandolfi,<sup>1</sup> G. Comolli,<sup>5</sup> E. Cova,<sup>1</sup> C. Montecucco,<sup>3</sup> M. Colombo,<sup>6</sup> D. Prosperi<sup>6</sup>

<sup>1</sup> Respiratory Deseases, IRCCS San Matteo Foundation, Pavia, Italy
<sup>2</sup>University of Pavia, Department of Internal Medicine, Pavia, Italy
<sup>3</sup>Rheumatology, IRCCS San Matteo Foundation, Pavia, Italy
<sup>4</sup>University of Pavia, Pavia, Italy
<sup>5</sup> Diagnostic Medicine, IRCCS San Matteo Foundation, Pavia, Italy
<sup>6</sup>University of Milan Bicocca, Department of Biotechnology and Biomedicine, Milan, Italy

#### Abstract:

We have previously demonstrated in vitro and in vivo the efficacy of the delivery of Im-CD44-GNP. TEM analysis of the treated lungs (by intratracheal delivery of Im-CD44-GNP to bleomycin-induced lung fibrosis) showed that Im-CD44-GNP were predominantly located into alveolar macrophages (AM), thus suggesting that they could be a therapeutic target. Aim of the present study was to assess the in vitro effect of Im-CD44-GNP on activation, viability, pro-fibrotic polarization and activity of monocyte-derived macrophages (MDM). MDM were obtained from normal donor buffy coats by density gradient and differentiated by LPS or platelet lysate for 2-6 days, treated with a 2 hrshot of Im-CD44-GNP, CD44-GNP or Imatinib alone (Im), and evaluated after 24 hrs for: CD14, CD206 expression, viability, IL8 and TGFb release. Results MDM viability was significantly reduced by Im-CD44-GNP with respect to controls and Im alone (<0.01 for both comparison), IL8 release was also significantly lower in Im-treated cells, either delivered by CD44-GNP or alone (both p s <0.001). Im-CD44-GNP decreased % of CD14+CD206+ cells with respect to controls (13.3 vs 35.6, p=0.06). This effect was more pronounced than with Im alone (29.5%). CD206 MFI was also significantly reduced. TGF-beta release was not significantly affected by GNP. Interestingly a lower but significant biologic effect was also present with CD44 coated drug-UN-loaded GNPs. Our results indicate that MDM polarization, activation and viability are impaired by Im-CD44-GNP, thus MDM represent a possible target of this local therapeutic strategy.

**Keywords**: Gold nanoparticles, nano-drug delivery, monocyte-derived macrophages.



**Figure 1**: Figure illustrating the experimental plan of our work.

- 1. Cova, E., Inghilleri, S., Pandolfi, L., et al. (2017) Bioengineered gold nanoparticles targeted to mesenchymal cells from patients with bronchiolitis obliterans syndrome does not rise the inflammatory response and can be safely inhaled by rodents., *Nanotoxicology.*, 11(4):534-545.
- Karta, M.R., Gavala, M.L., Curran, C.S., et al. (2014) LPS modulates rhinovirus-induced chemokine secretion in monocytes and macrophages., *Am J Respir Cell Mol Biol.*, 51(1):125-34.

### Therapeutic advantage of genetically engineered *Salmonella typhimurium* carrying small interfering RNA against inhibin alpha subunit in cancer treatment

Wonsuck Yoon<sup>1</sup>, Young Yoo<sup>2</sup>, Yang Seok Chae<sup>3</sup>, Sun-Ho Kee<sup>4</sup>

<sup>1</sup>Allergy Immunology Center, College of Medicine, Korea University, Republic of Korea, <sup>2</sup>bepartment of Pediatrics, College of Medicine, Korea University, Republic of Korea, <sup>3</sup>cepartment of Pathology, College of Medicine, Korea University, Republic of Korea, <sup>4</sup>Department of Microbiology, College of Medicine, Korea University, Republic of Korea

#### Abstract:

Inhibin, a dimer composed of alpha and beta subunits, suppresses the synthesis and secretion follicle-stimulating hormone (FSH). of In contrast to its well-known endocrine function, the role of inhibin in cancer development and therapeutic response is unclear. We found that the alpha subunit of inhibin (INHA) was more highly expressed in human colon cancer and melanoma cell lines and tissues compared to their normal counterparts. We also found that RNA interference (RNAi)-mediated knockdown of INHA exerted a moderate cytotoxic and apoptotic effect against colon cancer and melanoma cells. Salmonella, particularly less toxic attenuated Salmonella strains, are used to treat cancer in two ways. First, Salmonella accumulate around tumors, penetrate the cell barrier, and replicate inside the tumors. Second, Salmonella can act as a vehicle for delivering anti-cancer agents or pro-apoptotic genes to attack tumors. In this study, we aimed to develop a suitable cancer therapeutic strategy by genetically modifying attenuated Salmonella typhimurium to harbor small interfering RNA (siRNA) expression plasmids targeting INHA (si-INHA). Attenuated S. typhimurium bearing si-INHA (S. typhimurium/si-INHA) invaded cancer cells, inducing cytotoxicity. Cancer cells infected with S. typhimurium/si-INHA underwent both apoptosis and necrosis. Subcutaneous administration of S. typhimurium/si-INHA efficiently inhibited tumor growth and prolonged the survival of immunocompetent BALB/c mice bearing CT26 colon carcinoma or B16F10 melanoma, compared with administration of PBS, unmodified S. typhimurium, or S. typhimurium bearing a control scrambled siRNA (S. typhimurium/si-Cont). Collectively, our results suggest that tumor-targeted therapy using S. typhimurium/si-INHA may provide a novel cancer treatment option.

Keywords: Inhibin alpha subunit (INHA); Genetically modified attenuated Salmonella typhimurium; **RNA** interference (RNAi): Syngeneic mouse models utilizing immunocompetent mice bearing tumors; Treatment option for cancer therapy

#### siRNA therapy using Salmonella typhimurium



INHA siRNA induced therapeutic effects against cancer

Figure 1: siRNA Cancer therapy using Salmonella. Recombinant S. typhimurium expressing inhibin alpha siRNA were constructed by pcDNATM6.2-GW/EmGFP-miR expression using electrophoration. vector administration Subcutaneous of S. typhimurium/si-INHA efficiently inhibited tumor growth and prolonged the survival of in mouse cancer model.

- 1. Lee CH. (2016) Employment of Salmonella in Cancer Gene Therapy, *Methods Mol Biol.*, 1409:79-83.
- 2. Yoon W, Park YC, Kim J, Chae YS, Byeon JH, Min SH, Park S, Yoo Y, Park YK and Kim BM. (2017) Application of genetically engineered Salmonella typhimurium for interferon-gamma-induced therapy against melanoma, *European journal of cancer.*, 70:48-61.

## Incorporation of zinc phthalocyanine in biological nanovehicles for photodynamic cancer therapy

P. Lara,<sup>1,2,\*</sup> R.V. Huis,<sup>1</sup> S. Palma<sup>2</sup>, M. Kogan<sup>2</sup>, L.J.Cruz<sup>1</sup>

<sup>1</sup> Leiden University Medical Center, Department of Radiology, Leiden, Neatherlands <sup>2</sup> University of Chile, Advanced Center for Chronic Diseases, Santiago, Chile

#### Abstract:

Zinc phthalocyanine (ZnPc) is a promising photosensitizer for cancer therapy because of his optimal tissue penetration, excelent photodynamic action and absortion between the therapeutic window zone. Unfortunayly this compound proprieties are limited for his low solubiliy and poor selectivity [1].

On the other hand, exosomes are endogenous nanosized extracellular vesicles with a great potential for drug delivery as they are able to transport cargos to specific cells, protecting its contents from degradation processes. Furthermore, they are beneficied from the enhanced permeability and retention effect which allows them a passive targeting in tumor tissue [2].

In this work, we incorporate ZnPc in exosomes (Zn-Exo) and evaluate its potential in photodynamic therapy against cancer cells.

Zn-Exo were effectively incorporated in B16F10 exosomes after direct incubation and purification through size exclusion columns. We did not observed changes in size distribution, polydispersity, surface charge, protein markers in relation with control exosomes. Moreover, Zn-Exo were able to efficiently incorporate in tumor MC38 cells in a time dependent maner and resulted to be non toxic without light exposure. Interestingly, after photodynamic exposure at the sames concentrations, Zn-Exo produced total cell dead while ZnPc dissolved in DMSO only produced around 30%

Overall the incubation method was an effective way to incorporate ZnPc in exosomes and increase his therapeutic potential in cancer therapy

**Keywords**: exosomes, photodynamic therapy, Zinc phthalocyanine, targeted therapy, theranostics



**Figure 1**: Incorporation of ZnPc in exosomes isolated from B16F10 cells. Exosomes are extracellular vesicles originated from the endocitic pathway. After isolation, these vesicles are incubated with ZnPc by direct incubation and passed through a size exclusion column for purification

- 1. Oliveira, D.M., et al., Zinc phthalocyanine/magnetic fluid complex: a promising dual nanostructured system for cancer treatment. J Nanosci Nanotechnol, 2006. **6**(8): p. 2432-7.
- Batrakova, E.V. and M.S. Kim, Using exosomes, naturally-equipped nanocarriers, for drug delivery. J Control Release, 2015. 219: p. 396-405.

## Highly Efficient Protocol for Click Labeling of Biomolecules Using a Recyclable Cu2O nanowire-catalyst

Arwa Makki<sup>1,2</sup>, Dinesh Sawant<sup>1</sup>, Kuo-Wei Huang<sup>1</sup>, Jörg Eppinger<sup>1\*</sup>

 <sup>1</sup> King Abdullah University of Science and Technology KAUST, Biological & Organometallic Catalysis Laboratories, Biochemistry Department BOC; KAUST Catalysis Center, KCC Thuwal 23955-690, Kingdom of Saudi Arabia
<sup>2</sup> Department of Biochemistry, Faculty of Science, Center for Science and Medical Research, University of Jeddah, Jeddah 80203, Saudi Arabia

#### Abstract:

Copper catalysed azide-alkyne cyclo-addition (CuAAC) reactions have found widespread application in chemistry and life science for the modification of ligands, polymers, supramolecular compound of challenging architecture, peptides, proteins or DNA. In vivo and in vitro modifications of biological molecules are a particularly active field for the development of the bio-orthogonal AAC reaction. Recently, several metal-free click reactions were developed, since the toxicity of the required copper concentrations prevents its use in combination with living cells. [1]. Here we present the use of ultra-thin Cu<sub>2</sub>O layers on Cu nanowires as AAC catalysts, which are active at ppm concentrations of Cu<sup>+</sup> in water at room temperature. Based on this observation we developed a new heterogeneous CuAAC protocol for the bio-conjugation of biomolecules in vitro and in vivo. Combination with the incorporation of unnatural amino acid into proteins such as p-Azido- or p-Ethynylphenylalanine (pAzF, pEynF) this protocol allows the efficient site-selective modification of proteins on living cells.

**Keywords**: Copper catalysed azide–alkyne cyclo-addition (CuAAC), bio-orthogonal AAC reaction, bio-orthogonal AAC reaction, bio-conjugation, Cu nanowire, proteins, living cells.

#### **References:**

1. Liu, C. C. & Schultz, P. G. Adding New Chemistries to the Genetic Code. Annu. Rev. Biochem. 79, 413–444 (2010).



**Figure 1:** Cu-catalyzed click reaction for sitespecific bio-conjugation by using recyclable catalyst

### A fast and straightforward procedure for vault nanoparticle purification and the characterization of its endocytic uptake

M. Pozzi<sup>1</sup>, E. Galbiati<sup>1</sup>, M. Colombo<sup>1</sup>, D. Prosperi<sup>1</sup>, P. Tortora<sup>1</sup>

<sup>1</sup>Department of Biotechnologies and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, I-20126, Milano, Italy

#### Abstract:

Vaults are eukaryotic ribonucleoproteins composed of up to 78 copies of the 97 kDa major vault protein (MVP) that assembles into a barrellike, "nanocapsule" enclosing poly(ADPribose) polymerase (VPARP, 193 kDa), telomeraseassociated protein-1 (TEP-1, 290 kDa) and small untranslated RNAs (vRNA). Overall, the molecular mass of vault particles amounts to about 13 MDa. Although it has been implicated in several cellular functions (such as transport processes, drug uptake and modulation of signal transduction), its physiological roles remain poorly understood. Thanks to its huge size (41x41x72.5 nm) and the presence of a large internal cavity, plenty of investigations are being carried on to exploit it as a nanovector for drug delivery. Here, we report a purification protocol, which is simpler and faster than those currently available. Using the baculovirus expression system, vault was expressed in Sf21 cell lines. Starting from crude extracts, the procedure only consisted of a dialysis step with a 1 MDa molecular weight cutoff membrane, and a subsequent size exclusion chromatography. As supported by transmission electron microscopy and dynamic light scattering, authentic vault was obtained. We then assessed vault's endocytic uptake by a normal fibroblast and several cancer cell lines using specific inhibitors of either clathrin-mediated (chlorpromazine) or caveolae-dependent (genistein) endocytosis. By flow cytometry and confocal microscopy (Figure 1), we found that all of them internalized vault via clathrin-mediated endocytosis, as shown by the inhibitory effect of chlorpromazine. In contrast, no significant caveolin-mediated endocytosis was detected, as supported by the ineffectiveness of genistein. Noteworthy, endocytosis was considerably slower in some cancer cell lines assayed compared with the fibroblasts. These results provide the first evidence for an intrinsic propensity of the vault complex to undergo endocytic uptake in cultures of eukaryotic cells and point to specific biological interaction between vault and surface receptors.

**Keywords:** major vault protein, baculovirus, endocytosis, protein nanoparticles, SEC purification.



**Figure 1:** Vault endocytic uptake, as detected by confocal microscopy. The images show the merged signals of vault (green), cell membranes stained with Alexa fluor-555-conjugated wheat germ agglutinin (red) and DAPI (blue). The cell lines under investigation were preincubated with either chlorpromazine or genistein, or in the absence of any effector, then incubated at 37°C for the indicated times.

- 1. Kedersha, N. L.; Rome, L. H. Isolation and characterization of a novel ribonucleoprotein particle: large structures contain a single species of small RNA. *J. Cell. Biol.* **1986**, *103* (3), 699-709.
- 2. Stephen, A.G.; Raval-Fernandes, S.; Huynh, T.; Torres, M.; Kickhoefer, V.A.; Rome, L.H. Assembly of vault-like particles in insect cells expressing only the major vault protein. *J. Biol. Chem.* **2001**, *276* (26), 23217-23220.

## SERS-Active Microgels contatining Highly Concentrated Gold Nanoparticles for Direct Analysis of Biological Fluids

Yeong Hwa Kim<sup>1</sup>, Sangmin Lee<sup>1</sup>, Dong Jae Kim<sup>1</sup>, and Shin-Hyun Kim<sup>1\*</sup>

<sup>1</sup> Department of Chemical and Biomolecular Engineering, KAIST, Daejeon 34141, South Korea

#### Abstract:

Surface-enhanced Raman scattering (SERS) is promising for molecular detection as it provides dramatically-intensified Raman signals of molecules near metal nanostructures. For example, it is possible to detect rhodamine B at ultralow concentration of 10<sup>-20</sup> M using a metal sandwich-like composed nanostructure of Au@Al<sub>2</sub>O<sub>3</sub>@Au arrays.<sup>1</sup> However, metal nanostructures are prone to con-tamination caused by irreversible adsorption of proteins in most biological fluids, which interrupts the Raman analysis of small target molecules. To overcome the problem, metal nanoparticlesloaded microgels have been designed.<sup>2</sup> The hydrogel matrix with con-sistent mesh size provides molecular size-selective permeability and a cut-off threshold of permeation, enabling in-situ separation of small target molecules. However, it is still challenging to make highly SERS-active metal nanostructures within the while maintaining microgel, high signal reproducibility. In this work, we design the microgels containing highly concentrated gold nanoparticles as a SERS-active substrate using a microfluidic technology. With a capillary microfluidic device. water-in-oil-in-water double-emulsion drops are prepared, of which water phase contains innermost gold nanoparticels and hydrogel precursors. By imposing positive osmotic pressure on the droplets, water in the core is selectively pumped out through oil shell for 3 days, concentrating gold nanoparticles; the concentration factor is controlled in the range of 10-50 depending on the osmotic pressure. The hydrogel precursor is crosslinked by irradiating ultraviolet, which results in the formation of microgels containing the concentrated gold nanoparticles. Finally, oil shell is ruptured to obtain the microgels suspended in water. As the mesh size of the microgels is controlled to exclude large protein while allowing small molecules, the microgels enable the direct detection of small molecules without interruption of protein. In addition, the gold nanoparticles even dispersed within the the

microgel provides high Raman signal reproducibility. The gold nanoparticles form nanogaps as highly concentrated, which serve as hot spots for significant enhancement of Raman signal through SERS. We believe that our microgel SERS platform is useful for point-ofcare analysis in the field of drug detection and medical diagnostics.

**Keywords**: Raman, SERS, microgels, microfluidics, permeation, sensors



**Figure 1**: Schematic for fabrication procedure of a microgel containing highly concentrated gold nanoparticles.

- Yang, C.; Chen, Y.; Liu, D.; Chen, C.; Wang, J.; Fan, Y.; Huang, S.; Lei, W. Nanocavity-in-Multiple Nanogap Plasmonic Coupling Effects from Vertically Sandwich-like Au@ Al2O3@ Au Arrays for Surface–Enhanced Raman Scattering. ACS appl. Mater. Interfaces, 2018, 10, 8317-8323.
- Kim, D. J.; Jeon, T. Y.; Park, S. G.; Han, H. J.; Im, S. H.; Kim, D. H.; Kim, S. H. Uniform Microgels Containing Agglomerates of Silver Nanocubes for Molecular Size-Selectivity and High SERS Activity. Small, 2017, 13, 1604048.

## Possible effect of ionic fluid flow induced electric potential in a charged nano-channel on a diagnosis by POC

Sungki Min,<sup>1</sup> Junghwa Hong,<sup>2</sup>

#### <sup>1</sup>Research & Development Center, BNR, Seoul, South Korea <sup>2</sup>Dept. Control & Instrument. Eng., Korea University, Sejong, South Korea

Recently, Kelvin probe Abstract: force microscopy [1] have been used for the detection of toxic metal ions in a label-free manner. This method can improve the sensitivity to the pM level. However, those has suffered from background noises, because the ion-mediated ligand-receptor interactions were measured. Particularly, theses charged particles are are floating in a liquid when the electric potential is measured. Since ionic fluid flow generates a significant electrical potential, it could be a error source during the potential measurement. Furthermore, if a subtrate has a charge the flow induced potential could be augmented. In this study, a ionic fluid flow induced electric potential in a electrically charged nano-channel was theoretically analyzed to understand a caused possible measurement error. This result could be used for the error corrections when a subtle electric potential is measured for the point of care applications. The ionic fluid (physiological saline) in a nano-channel having the circular corss section is surrounded by a pre-charged subtrate, which forms the boundary condition (the external potential) and affects the charge density of the nano-channel. To include the external potential effects, a modified transient charge density equation\* is used. In addition, the Navier–Stokes equation\*\*, considering the effects of the total potential on the nano-channel flow, is applied. For the analysis, a commercial finite element (ABAQUS) was utilized with a FORTRAN user subroutine that was developed for this study. To obtain variations in the electrical potential, the subtrate and nano-channel modeled were using the axisymmetric piezoelectric element (FAX4) and fluid link element (FLINK), respectively. The annular fluid space in the nano-channel was 100 nm. A step pressure differnece of 100 kPa (physiologically possible maximum pressure gradient) was applied to the nano-channel for 0.5 s using the AMPLITUDE option, and then removed. A constant potential of -10 mV, which is approximately equal to the averaged value of the

variations of the charge of the general living cell, was considered in this study. A significant generation in the ionic fluid flow induced electric potential was predicted in this study. The generated peak electrical potential values under the step pressure application were +1.6 mV and -1.3 mV during the loading and unloading, respectively. In the previous study, Kelvin probe force microscopy [30] can detect the subtile electric potential up to 1 pM of aluminum ion in the tab water. The reported resolution of the detction sensitivity by the study was 1 pM when the measurand was the surface electric potential. The resolution is very dependent on the stanard deviation error since the measurement results were discerned by the statistical difference. Including the ionic fluild flow analysis to the measurement using the electrochemical or direct detection of electric potential, therefore, the resolution of sensitivity could be significanltly improved.

\*  $\frac{1}{D}\frac{\partial \rho_f}{\partial t} = \nabla^2 \rho_f - \kappa^2 \rho_f + \kappa^2 \epsilon_f \nabla^2 \phi$  where D is the diffusion coefficient,  $\rho_f$  is the charge density,  $\nabla$  is the del operator,  $\kappa$  is the inverse Debye length,  $\epsilon_f$  is the dielectric permittivity of fluid, and  $\phi$  is the external potential.

\*\*  $\mu \nabla^2 \mathbf{u} - \rho \frac{\partial \mathbf{u}}{\partial t} = \nabla \mathbf{p} + \rho_f \nabla \Phi$  where  $\rho$ ,  $\mu$ ,  $\rho_f$ , p, u, and  $\Phi$  are the fluid density, viscosity of fluid, charge density, pressure, fluid velocity, and total electric potential ( $\Phi = \psi + \phi$ ) which is the sum of the internal and external potentials, respectively.

**Keywords**: electrically pre-charged substrate, ionic fluid flow, flow induced electric potential, nano-channnel, modified transient charge density equation, modified Navier–Stokes equation

#### **References:**

1. Kim, W. et al. (2018), Sensors and *Actuators B*, 255, 2179–2186.

## The toxicity effects of nano-particles on micro organism in biological wastewater treatment process

Sung Ju IM, Sang Hun OH and, Sang hyun JEONG and Am JANG $^*$ 

Graduate School of Water Resources, Sungkyunkwan University (SKKU), 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do 16419, Rep. of Korea

\* Corresponding author: Tel.: +82-31-290-7526, Fax: +82-31-290-7549, E-mail: amjang@skku.edu (Am Jang)

#### Abstract:

Cosmetics, pharmaseuticals, and skin care products are major examples of nano-particles containing products. As the application of nanomaterials increases in many industry areas, the exposure possiblity of nanomaterials to ecosystems is increasing. natural When nanoparticles were discharged into the water, it is aggregated to grow into secondary particles of micron level. In addition, aggregates are precipitated and remained for a long time in water ecosystem. As the results, micro level containing the nano-particles bound with an organic substances reduced or inhibited to microorganism growth rate due to tocixity of nano-particles. Therefore this study evaluated the growth rate of microorganisms in the wastewater with various concentrations and type of nanoparticles.

The growth inhibition rate of Pseudomonas by ZnO was 2.75% and the growth inhibition rate by TiO<sub>2</sub> was 6.68%. Compared to Bacillus, it has been found to be relatively less affected by nanomaterials. Also, ZnO showed the highest growth inhibition rate at 75 ppm concentration. However, in the case of TiO2, nano-particles were less affected since growth tendency is observed to be similar with control under various concentration conditions. On the other hand, Bacillus showed that the growth inhibition rate of ZnO was significant, comparing to control (93%). However, in the case of Pseudomonas, growth inhibition rate by ZnO and TiO<sub>2</sub> was less than 10%, which is different tendency with Bacillus. Therefore, it is necessary to check whether it influences microbial growth by increasing the concentration of nano-particles.

Keywords: Nano-particle, toxicity, microorganism growth, biological wastewater treatment

(a) *Bacillus* 



**Figure 1**: Growth inhibitation rate at various concentration of nano-particles a) *Bacillus* b) *Pseudomonas*.

#### **References:**

- 1. Okkyoung Choi, Kathy Kanjun Deng, Nam Jung Kim, Louis Ross Jr, Rao Surampalli, Zhiqiang Hu, (2008), The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth, Water research, 42, 3066-3074.
- Makarand A. Patil, Parimal A. Parikh, (2014), Investigation on likely effects of Ag, TiO2, and ZnO nanoparticles on sewage treatment, Bull envionmetal contam toxicol, 92, 109-114.

#### Acknowledgement

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT, & Future Planning (2017R1A2B3009675).

# High intensity emitting Eu<sup>3+</sup>,Bi<sup>3+</sup>:LaF<sub>3</sub> nanoparticles for luminescence bioimaging and X-ray computed tomography

A.I. Becerro,1\* D. González Mancebo,1 A. Corral,2 M. Balzercyk,2 M. Ocaña1

<sup>1</sup> Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Seville, Spain. \*anieto@icmse.csic.es <sup>2</sup> Centro Nacional de Aceleradores (US, JA, CSIC), Seville, Spain

#### Abstract:

Rare earth (RE)-based inorganic nanoparticles doped with active lanthanide ions (Ln:NPs) are an excellent choice for potential use as phosphors in luminescent bioimaging and as contrast agents in X-rays computed tomography. Among the different RE salts, RE fluorides are preferred as phosphors matrices because of their low toxicity and low phonon energy of the fluoride lattice, which provides improved quantum efficiency to the phosphor.<sup>1,2</sup> Ln:NPs suffer, however, from an important drawback due to the low emission intensity of lanthanide ions. Different strategies been developed to have overcome this inconvenient including energy transfer from the NP matrix to the doping lanthanide ion in singly doped NPs or among co-doping ions in codoped NPs. Herein, we have used the latter to obtain a nanoparticulated, high emission intensity red phosphor based on the energy transfer from Bi<sup>3+</sup> to Eu<sup>3+</sup> in Eu<sup>3+</sup>,Bi<sup>3+</sup> codoped LaF<sub>3</sub>. Lanthanum has been chosen as the matrix cation due to the identical ionic radii of La3+ and Bi3+, which facilitates the co-doping process. We have used an interesting synthesis approach, based on the use of polyols, that renders hydrophilic and uniform NPs at room temperature without using additives (Fig. 1a). The NPs obtained produce an intense red emission after excitation with UV light thanks to the efficient energy transfer from  $Bi^{3+}$  to  $Eu^{3+}$  (Fig. 1b). Finally, thanks to the high atomic number of Bi, La and Eu, the NPs present an excellent X-ray attenuation efficacy, which is higher than that of Iohexol, a clinically approved X-ray computed tomography contrast agent (Fig. 1c). In summary, Eu<sup>3+</sup>,Bi<sup>3+</sup>:LaF<sub>3</sub> NPs, synthesed in polyol medim, are promising candidates as dual bioprobes for both luminescence imaging and X-rays computed tomography.



**Figure 1**: a) TEM micrograph of Eu<sup>3+</sup>,Bi<sup>3+</sup>:LaF<sub>3</sub> NPs synthesized at room temperature. b) Emission spectra of Eu<sup>3+</sup>,Bi<sup>3+</sup>:LaF<sub>3</sub> NPs showing the much higher emission intensity when excited through Bi<sup>3+</sup> (250 nm) than through Eu<sup>3+</sup> (393 nm). c) X-ray attenuation of Eu<sup>3+</sup>,Bi<sup>3+</sup>:LaF<sub>3</sub> NPs compared with that of a clinically used contrast agent for X-ray computed tomography.

- A.I. Becerro et al (2016) Ligand-Free Synthesis of Tunable Size Ln:BaGdF5 (Ln = Eu3+ and Nd3+) Nanoparticles: Luminescence, Magnetic Properties, and Biocompatibility, *Langmuir*, 32, 411.
- D. Gonzláez-Mancebo et al. (2017) Crystal structure, NIR luminescence and X-ray computed tomography of Nd<sup>3+</sup>:Ba<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>2.7</sub> nanospheres, *Dalton Trans.*, 46, 6580.

## Blood circulation promotion by Integrated Functional Mineral Crystal (IFMC)

T. Hirata,<sup>1,2,\*</sup> T. Fujimoto,<sup>3,1,2</sup> T. Nomura,<sup>4</sup> K. Hatakeyama<sup>5</sup>

<sup>1</sup> Mineral Crystal Research Center, Advanced Research Laboratories, Tokyo City University, Tokyo, Japan <sup>2</sup> Department of Medical Engineering, Tokyo City University, Tokyo, Japan <sup>3</sup> Clinic F, Tokyo, Japan <sup>4</sup> Professor Emeritus, Osaka City University, Osaka, Japan

<sup>5</sup> TEIKOKU Pharmaceutical Company, Osaka, Japan

#### Abstract:

Hot springs are more than valuable "hot tub" for relaxation and health. Hot springs, spa and spa therapy have a rich history and are valued in many parts of the world. Many hot springs have thermal effects, hydraulic effects, buoyancy effects. As an example of this, Ghoneum and Ogura investigated the immunomodulatory activity on human natural killer (NK) cells of Marina Crystal Minerals (MCM), a crystallized mixture of minerals and trace elements from sea water [1].

From the above-mentioned background, the mechanism by which Integrated Functional Mineral Crystal (IFMC), is a mixture in a specific ratio of mineral components extracted from natural minerals, promotes blood circulation was investigated. In particular, detailed assessment of vasorelaxation factors was performed.

SEM images of IFMC are shown in Figure 1. Crystals of different sizes may be observed. In addition, according to the element mapping images, the distribution of sulfur (S), manganese (Mn), iron (Fe), zinc (Zn), and neodymium (Nd) originating in mineral components extracted from natural minerals was confirmed.

Changes in the temperature of the back of the hand when sprayed with IFMC were measured using a thermograph. The subject was a 22-yearold woman who habitually felt cold in her hands and feet. The back of her hand was sprayed directly with IFMC solution, and the surface temperature was measured at intervals of 1 min during a total measurement period of 10 min.

Thermo-images of body surface temperature are shown in Figure. 2. Before spraying, the temperature of the back of the hand was 30–32°C, and that of the finger area was lower at 28–30°C, indicating that the peripheral circulation was poor. At 1 min after direct spraying with IFMC solution, a temporary drop in surface temperature due to the heat of evaporation of the liquid was measured. However, at 3 min after spraying, thick blood vessels stood out across practically the whole of the back of the hand, and, at the same time, there was an increase in the temperature of the peripheral blood vessels in the fingers. The surface temperature, which had been around 30°C, rose to 32°C or higher in the vicinity of the blood vessels. After 5 min, the temperature of the whole hand had risen, and this increase in temperature was caused by improved blood flow due to a clear vasodilatory effect.

From the above results, a trend was found for vasodilation to shift incrementally from thick blood vessels to fine blood vessels. Therefore, the results showed that the endothelium-derived relaxing factor (EDRF) in the blood vessel increased after IFMC.<sup>TM</sup> application.

**Keywords**: integrated functional mineral crystal, blood circulation promotion.



**Figure 1**: Scanning electron microscopy (SEM) image of IFMC. x1000 and x5000



Figure 2: Thermograph images of hand surface temperature.

#### **References:**

1. M. Ghoneum and T. Ogura, Nutrition Research, 19 (1999), pp.1287-1298.

## Surface coating determines toxic potential of iron oxide nanoparticles in renal cells

M. Selc,<sup>1</sup>, N. Gregusova,<sup>1</sup>, A. Babelova,<sup>1,\*</sup>

<sup>1</sup>Cancer Research Institute BMC SAS, Department of Nanobiology, Bratislava, Slovakia

#### Abstract:

Iron oxide nanoparticles (IONs; magnetite) are verv promising candidates for combating unspecificity and unwanted side effects of the traditional therapy. Their real potential in medical applications, however, strongly depends on their physico-chemical properties, especially coating. The surface of metal-core nanoparticles is usually coated with inert polymers shielding them from reticuloendothelial system. In biological systems, this coating interacts with serum proteins forming so called protein corona. Consequent interactions between cells and nanoparticles can also lead to disturbance of cell well-being, reactive oxygen species production<sup>1</sup>, genotoxicity<sup>2</sup>, as well as release of inflammatory cytokines<sup>3</sup>. Here, we report the influence of polyethylene glycol (PEG) and bovine serum albumin (BSA) coatings of IONs on the renal toxicity in vitro in one of the most important cell types involved in kidney blood filtration - renal podocytes. We isolated primary mouse podocytes, because they represent the best model for in vitro studying of podocyte responses towards different stimuli. The type of IONs coating turned to be determinative in inducing toxic response in podocytes. Moreover, IONs differing in solely outer coating induce very different inflammatory response in these cells, which was manifestied by diverse induction of inflammatory cytokine TNFa (Figure 1) as well as other inflammatory factors. This study contributes to the enlightment of nano:bio interactions that are crutial for developing a biocompatible nanotherapeutics. As only biocompatible nanomaterial biotoxicity would not overrun the therapeutic gain.

**Keywords**: IONs, toxic response, podocytes, kidney, inflammatory response, biocompatible nanomaterial.



**Figure 1**: Figure illustrating different inflammatory respons of primary mouse podocytes to IONs nanoparticles coated with BSA or PEG after a short- (5h) and long- (24h) term incubation.

Acknowledgement: This work was supported by the following grants: SASPRO Programme 0084/01/02, VEGA 2/0113/15, and APVV 16/0579.

- 1. Celardo, I., Pedersen, J.Z., Traversa, E. ., Ghibelli, L. (2011), Pharmacological potential of cerium oxide nanopartices, *Nanoscale.*, 3, 1411-1420.
- Buliakova, B., Mesarosova, M., Babelova, A., Selc, M., Nemethova, V., Sebova, L., Razga, F., Ursinyova, M., Chalupa, I., Gabelova, A., (2017), Surface-modified magnetite nanoparticles act as aneugen-like spindle poison, *Nanomedicine: Nanotechnology, Biology, and Medicine.*, 13 (1), 69-82.
- 3. Deng, Z.J., Liang, M., Monteiro, M., Toth, I., (2011), Nanoparticle-induced unfolding of fibrinogen promotes Mac-1 receptor activation and *inflammation*, *Nat. Nanotechnol.*, 6, 39-44.

## A microfluidic model of the kidney – a platform for the determination of nephrotoxicity

A. Gabelova<sup>1</sup>, K. Kozics<sup>1</sup>, M. Sramkova<sup>1</sup>, P. Pechacova<sup>1</sup>, K. Kopecka<sup>1</sup>, T. Knoll<sup>2</sup> and Y. Kohl<sup>2</sup>

<sup>1</sup> Cancer Research Institute, BMC SAS, Dept. of Nanobiology, Bratislava, Slovakia <sup>2</sup> Fraunhofer Institute for Biomedical Engineering IBMT, Sulzbach, Germany

#### Abstract:

The renal proximal tubule is a primary site of nephrotoxicity and resulting drug attrition during pre-clinical stages of pharmaceutical development. The unpredicted emergence of kidney failure underlines the limitations of current in vitro and in vivo models, which fail to predict adverse drug effects on the kidney. The development of a reliable predictive models in the early stage during new drug discovery and development is therefore an urgent need. Microfluidic technology offers an alternative platform for toxicity screening. Microfluidic organ-on-a-chips provide a controllable culture microenvironment for living cells in micrometersized chambers that imitated the construction of minimal functional units and kept partial function of organs or tissues in vivo. Microfluidic devices could reduce the need for animal testing and become a great platform to replace the conventional screening techniques.

The chip-based microfluidic kidney module has the size of a microscopic slide and was established as device for (nano)toxicity screening (Figure 1). The human renal proximal tubule epithelial TH1 cells are cultured on a silicon nitride membrane in a microchip, integrated in the microfluidic module which is incorporated into a miniaturized incubator microscope enabling the optical analysis. Integrated electrodes guarantee impedance measurements of the tissue. This microfluidic system mimics the *in vivo* microenvironment including exposure to fluid shear stress.

**Keywords**: human renal proximal tubule cells, microfluidic kidney module, kidney-on-a-chip, nephrotoxicity, nanosafety testing, biomedical applications.



**Figure 1**: Schematic illustration of cell cultivation on the microchip. (A) Cross-section sketch of the open chip with electrodes, (B) the image of TH1 cells growing on the membrane

#### Acknowledgement:

The authors would like to acknowledge funding from H2020/2014-2020 under grant agreement no. 685817 – HISENTS

- 1. Kyung-Jin, J., Mehr, A.P., Hamilton, G.A., McPartlin, L.A., Chung, S., Suh, K.Y., Ingber, D.E. (2013), Human kidney tutbuleon-a-chip for drug transport and nephrotoxicity assessment, *Integr. Biol.*, 5, 1119-1129.
- Du, G., Fang, Q., den Toonder, J.M.J. (2016), Microfluidics for cell-based high throughput screening platforms – A review, *Anal. Chim. Acta*, 903, 36-50.

### Graphene Nanocomposites Polymer based Films for Gas Sensing

M.Ehsani,<sup>1\*</sup> M.Prosheva<sup>2</sup>, R.Fajgar<sup>3</sup>, J.Blazevska<sup>2</sup>, <sup>1</sup>R. Tomovska<sup>4</sup>, Y.Joseph<sup>1</sup>

<sup>1</sup> Technische Universität Bergakademie Freiberg, Institute of Electronic and Sensor Materials, Freiberg, Germany

<sup>2</sup> University St.Cyril and Methodius, Faculty of Technology and Metallurgy, Skopje, Macedonia

<sup>3</sup> Czech Academy of Sciences, Institute of Chemical Process Fundamentals, Czech Republic

 $^{\rm 4}$  University of the Basque Country, Institute for Polymer Materials, , San Sebastian, Spain

#### Abstract:

With the high carrier mobility, large specific surface areas, and controlled modification possibilities graphene nano-composites films based on polymer matrix, offer efficient sensing materials for highly sensitive and cost effective sensors <sup>[1]</sup>. Introducing of mixture of conductive nanofillers like graphene and multi-wall carbon nanotubes (CNTs) up to 1wt% as a functional nanomaterials into the polymer matrix enable conductivity of composite film, very good electronic properties and facilitate charge transfering. This has initiated interests in the development of highly sensitive and selective gas sensors based on polymer-based nanocomposite materials and their carbon group reinforcement <sup>[2]</sup>. In this paper, different synthesizing methods like blending and in-situ polymerization of nanocomposites films based on poly (methyl methacrylate-buthyl acrylateglycidyl methacrylate) (P(MMA-co-BA-co-GMA)) polymer matrix are presented. The polymer matrix were reinforced with graphene and carbon nanotubes in different ratio and the final films were characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). At the end, the nano-composite films were fabricated by using a spin coating method on a sensitive quartz crystal microbalance (QCM), as it is depicted in Figure.1. The sensing behavior of the sensors toward different kind of gas molecules was investigated by using home made high vacuum sensing measurement device. This paper focuses on the influence that the conductive nanofillers have on the change of the sensing behavior of the polymer-based nanocomposite films toward different kind of gas molecules.

**Keywords**: Graphene, Carbon nanotubes, Polymers, Gas, Sensing applications, Hybrid composites, Polymerization, Blending, nanocomposites film, X-ray photoelectron spectroscopy (XPS), Atomic force microscopy (AFM), Quarz crystal microbalance (QCM).



**Figure 1**: Schematic representation of nanocomposite films coated on QCM and sensing mechanism of the QCM gas sensor toward gas molecules.

- 1. Paszkiewicz, S., et al. "New functional nanocomposites based on poly (trimethylene 2, 5-furanoate) and few layer graphene prepared by in situ polymerization." Express Polymer Letters12.6 (2018).
- Das, Rashmita, A. J. Pattanayak, and Sarat K. Swain. "Polymer nanocomposites for sensor devices." Polymer-based Nanocomposites for Energy and Environmental Applications. 2018. 205-218.

## Experimental investigation of the dynamic behaviour of Laminated Composite Reinforced with graphen using split Hopkinson pressure bars

M. Chihi,<sup>1,2,\*</sup> M. Tarfaoui,<sup>1,3</sup> K. Lafdi,<sup>3</sup> C.Bouraoui,<sup>1,2</sup>

<sup>1</sup> ENSTA Bretagne, FRE CNRS 3744, IRDL, F-29200 Brest, France <sup>2</sup> ENISO, Université de Sousse, BP 264, Cité Erriadh, 4023 Sousse, Tunisia <sup>3</sup> University of Dayton, 300 College Park, Dayton, OH 45469-0256, USA

#### Abstract:

Mother of all the graphitic material, graphene is structurally characterized as a two-dimensional layer of bonded carbon. Since its advent in 2004 [1], graphene has been one of the most promising materials in nano-technology. This central role mainly stems from a combination of unique mechanical [2], electrical [3] and thermal [4] properties.

As a novel two-dimensional material, graphene can generate a huge enhancement at properties at very low filler contents. Despite the potential applications of composites reinforced with graphene to dynamic extremes, high strain-rate loading experimental techniques on such materials are essentially absent.

This work examines and assesses the out-ofplane dynamic behavior of polymer laminated composites based on Epoxy resin, carbon fibers fabric and graphene. Specimens with two mass fractions (0% as reference and 2%) of graphene have been tested. Dynamic compression tests were conducted using the Split Hopkinson Pressure Bars (SHPB) technique, Figure 1. Deformation histories and damage scenarios of specimens were recorded during impact by resorting to a high-speed camera. Experimental investigations have shown that the increase in the strain rate has a dramatic effect on the mechanical behavior and the damage scenarios of the material. The effect of mass fraction of graphene on the dynamic properties and damage kinetics was discussed, Figure 2.

**Keywords**: graphene , SHBP ,dynamic behavior, damage kinetics.



Figure 1: Split Hopkinson Pressure bar appartus.



**Figure 2:** Stress–strain curve for different mass fractions of graphene, P = 2 bars.

- 1. Novoselov, K. S. et al. Electric Field Effect in Atomically Thin Carbon Films. *Science* 306, 666–669 (2004).
- Go'mez-Navarro C, Burghard M, Kern K. Elastic properties of chemically derived single graphene sheets. *Nano Lett* 2008; 8:2045–9.
- 3. Novoselov KS, Morozov SV, Mohinddin TMG, Ponomarenko LA, Elias DC, Yang R, et al. Electronic properties of graphene. *Phys Status Solidi B* 2007; 244:4106–11.
- 4. Yu A, Ramesh P, Itkis M E, Bekyarova E, Haddon R C. Graphite nanoplatelet-epoxy composites thermal interface materials. *J Phys Chem C* 2007; 111:7565–9.

## Thick Silica Foam Films with Aerogel-Like Thermal Conductivity and Bulk Density

T. Kangur<sup>1</sup>, M. Järvekülg<sup>1</sup>, M. Timusk<sup>1</sup>

<sup>1</sup> University of Tartu, Institute of Physics, Tartu, Estonia

#### Abstract:

Over the last few decades new ingenious methods have been developed in the sol-gel processing of materials, combining knowledge and material processing methods from different fields of pushing the boundaries research and of xerogel/oxide conventional or aerogel preparation from a wet gel in a typical film, fiber or bulk material form. Notable examples of the reinvention of the sol-gel technique include the synthesis of oxide foams, which form an important class of materials due to their wide applicability for catalysis, electrochromic devices and high performance thermal insulation.

This work reports a novel method for the preparation of thick silica foam films that combines an alkoxide-based hydrolytic sol-gel process and in situ catalytic decomposition of hydrogen peroxide on a catalyst-coated support. A hydrogen peroxide/nitric acid aqueous solution was used to carry out acid-catalysed hydrolysis of tetramethoxysilane. The H2O2-loaded sols were sprayed on MnO<sub>2</sub>-coated substrates, heterogeneous resulting in catalytic decomposition of H<sub>2</sub>O<sub>2</sub> and effective foaming and simultaneous gel formation due to oxygen gas and water formation. Silica foam films with a well-defined closed-cell porosity were annealed at 600°C without any damage to the closed-cell porous film morphology. Up to 530 µm thick films were prepared with macropore sizes in the range of 29-47 µm, exceptionally thin macropore wall thicknesses of 16-50 nm and a bulk density as low as 64 kg/m<sup>3</sup>, comparable to that of the aerogels. The lowest measured thermal conductivity of the prepared foams was 0.018±0.001 W/(m\*K), which is also similar to silica aerogels, enabling the prepared foams to be used as efficient thermal insulation materials [1].

**Keywords**: silica foam, low-density material, closed-cell porosity, sol-gel, hydrogen peroxide, manganese dioxide.



**Figure 1**: SEM image of cross-section of silica foam film.

#### **Reference:**

 Timusk, M., Kuus, A., Utt, K., Kangur, T., Šutka, A., Järvekülg, M., Knite, M. (2016), Thick silica foam films through combined catalytic decomposition of H<sub>2</sub>O<sub>2</sub> and sol-gel processes, *Materials and Design*, 111, 80-87.

## Hybrid multi-material microbraids for through-thickness multifunctionality

C. O'Keeffe<sup>1</sup>, I. Partridge<sup>1</sup>, G, Allegri<sup>1</sup>

<sup>1</sup> University of Bristol, Department of Aerospace Engineering, Bristol, UK

#### Abstract:

Composites are made up of a combination of materials where each component provides a unique property to the final product [1]. Rapid advancements have been made in both material and structural designs, predominantly motivated by potential aerospace and medical industry applications. Material research and development is focused on the desire for mass and volume optimal performance reduction. and the subsequent cost savings. Traditional methods for design address load carrying and other functional requirements separately resulting in a loadbearing structure with parasitic-like functions True multifunctionality combines [2]. the capabilities of one or more subsystems with that of the load bearing structure, hence reducing the mass and volume of the total system [3]. This work describes the effects of tufted metallic carbon hybrid braided yarns in composite laminates. The effectiveness of the braids for through-thickness-resinforment (TTR) in addition to their self-sensing capability will be assessed according to ASTM D5528.

By tufting these hybrid yarns into preforms it will enable through-thickness multifunctionality within the composite material and extend its functionality beyond purely structural strength. Future work will address potential application potential applications for use in crack propagation and fault detection in automotive and aerospace industries.

**Keywords**: Multifunctionality, hybrid microbraids, tufting, fault and crack propagation detection



Figure 1: Titanium/ carbon fibre braids.

- K. Salonitis, J. Pandremenos, J. Paralikas, and G. Chryssolouris, "Multifunctional materials: Engineering applications and processing challenges," *Int. J. Adv. Manuf. Technol.*, vol. 49, no. 5–8, pp. 803–826, 2010.
- R. F. Gibson, "A review of recent research on mechanics of multifunctional composite materials and structures," *Compos. Struct.*, vol. 92, no. 12, pp. 2793–2810, 2010.
- K. K. Sairajan, G. S. Aglietti, and K. M. Mani, "A review of multifunctional structure technology for aerospace applications," *Acta Astronaut.*, vol. 120, pp. 30–42, 2016.

## Highly Integrated and Flexible Thermoelectric Module Fabricated by Bruch-cast Doping of a Highly Aligned Carbon Nanotube Web

Cheng Jin An, Young Hun Kang, and Song Yun  $\mathrm{Cho}^*$ 

Korea Research Institute of Chemical Technology, Division of Advanced Materials, Daejeon, Korea

#### Abstract:

With increasing attention on flexible or wearable power-conversion devices, intensive research efforts have been devoted to flexible organic thermoelectric (TE) modules to replace the brittle inorganic ones. In this study, a highly integrated and flexible TE module with a novel device architecture based on a carbon nanotube (CNT) web is proposed. The pristine CNT web shows superior electrical conductivity of 998.3 S cm<sup>-1</sup>, owing to the increased longitudinal carrier mobility derived from the highly aligned structure. To realize optimal TE property, the pristine CNT web is alternately doped with p- and n-type carriers using FeCl<sub>3</sub> and benzyl viologen, respectively, via a brush-casting method (Figure 1). Brush-casting is the simple doping process enables large-scale and continuous that fabrication of flexible TE modules by allowing precise doping of the localized area without a shadow mask. Flexible TE modules were then fabricated by repeated brushing and folding of the CNT webs. Owing to the synergic effect of the highly integrated high-performance TE material (highly aligned CNT web) and the facile doping process (brush-casting), flexible TE modules consisting of 120 p-n couples over an area of 8 cm<sup>2</sup> show a maximum power output of 17.41  $\mu$ W for a temperature difference of 3.3 K.

**Keywords**: directly spun carbon nanotube web, doping process, brush-casting, flexible thermoelectric module, thermal sensor.



**Figure 1**: Fabrication of the highly integrated and flexible TE module using a highly aligned CNT web by the brush-casting and folding method. (a) Doping of the CNT web with corresponding dopants by the brush-casting method and mechanical folding of the alternately doped CNT web. (b) Cutting the large barshaped TE module into several TE cells. (c) Embedding 6 TE cells into a silicon pad and electrically connecting them in series.

- An, C. J., Kang, Y. H., Lee, A. –Y., Jang, K. –S., Jeong, Y., Cho, S. Y. (2016) Foldable Thermoelectric Materials: Improvement of the Thermoelectric Performance of Directly Spun CNT Webs by Individual Control of Electrical and Thermal Conductivity, ACS Appl. Mater. Interfaces, 8, 22142-22150.
- An, C. J., Kang, Y. H., Song, H., Jeong, Y., Cho, S. Y. (2017), High-Performance Flexible Thermoelectric Generator by Control of Electronic Structure of Directly Spun Carbon Nanotube Webs with Various Molecular Dopants, *J. Mater. Chem. A*, 5, 15631-15639.

## Evaluation of Topography Effects of SThM Measurements on Thin Thermoelectric Films

W. Lehermeier, C. Metzke, G. Benstetter, W. Frammelsberger

Deggendorf Institute of Technology, IQMA, Deggendorf, Germany

#### Abstract:

Sustainabel energy generation is an important topic with respect to global warming. Therefore, advanced materials for energy storage and energy harvesting applications are needed. Of particular relevance are thin film materials with a high figure of merit [1], which is a result of high electrical conductivity and low thermal conductivity. Thermal characterization with the  $3\omega$  method provides an average value for crossplane and in-plane thermal conductivities. However, studies show [2] that, for example AlN thin films and CuI thin films, show grain structures with different thermal conductivity values for grains and grain boundaries. Therefore, high resultion measurements are needed for research and development to examine this observation in more detail.

Scanning thermal microscopy (SThM) is a technique, which maps qualitatively the local thermal surface conductivity of thin films. Therefore, SThM is a suitable method to investigate differences on local thermal conductivities of thermoelectric thin films. Our SThM experiments on a test sample (silcon with native oxide on top) show (Fig. 1) that, the topography is able to influence the thermal measurement results. Fig. 1a) shows the topography of the test sample, where a onedimensional array of rectangular steps is present. The thermal image of the test sample, Fig. 1b), do not show a thermal contrast for upper and lower planes but solely at the edges indicated by the bright lines. The reason for this observation is that, the amount of heat, which is locally exchanged between tip and sample, depends on the contact area of the interface of tip and sample. At the edges the contact area is much smaller than at the planes and thus the thermal exchange is reduced which leads to a larger SThM signal (Fig. 1d).

Therefore, it may not be excluded that the relative thermal conductivity measured by SThM is influenced by topographic features. Probe tip and surface do not only convolute in the topography image but also in the thermal image. The relevance of this influence strongly depends on the geometry of topographical features and the geometry of the probe tip and is currently widely unknown. Further research is necessary to analyse this effect in detail. One option could be to use different probe tips and different thin film materials and to correlate the images achieved. The relation of topography, tip geometry and thermal image may allow to deduce the severity of the mutual interference. Another option could be to artificially produce flat sample surfaces by, for example polishing or/and ion milling, and to evaluate the SThM measurement results. By this means, the thermal signal is widely decoubled from topographical features. Hence, grain bounderies and grains may still be discriminable by their thermal conductivity while the influence of the topography is minimized.

In future works we will follow both options. The poster explains the measurement setup and presents SThM images of thin films. The impact of the topography on the thermal image is demonstrated.

**Keywords:** thermoelectric thin films, scanning thermal microscopy, grain structure, topographic effects



**Figure 1**: Scanning probe measurements of a silicon test sample. The topography image (a) illustrates the one-dimensional array of rectangular steps. The thermal image (b) do not show a different thermal contrast for the upper and lower topographical planes. However, the transition from a high topographic region to a low topographic region is clearly observable in the thermal image due to the bright lines. A detailed graph for one line scan (corresponding to the blue lines in Figure a and b) is given for both, the topography measurement (c) and the SThM measurement (d)

- C. Yang, D. Souchay, M. Kneiß, M. Bogner, H. M. Wei, M. Lorenz, O. Oeckler, G. Benstetter, Y. Q. Fu, M. Grundmann. Transparent flexible thermoelectric material based on non-toxic earthabundant p-type copper iodide thin film. Nature communications, 8:16076, 2017.
- 2. W. Lehermeier. Thermal Characterization of Thin Film Materials. Master Thesis, Deggendorf Institute of Technology, Deggendorf, 2018.

### Infectious risk after pose installation of\_prostheses and implants osteoarticulaires

AZROU Siham \*, <sup>1, 2</sup>, Benamara Mounia<sup>1, 2</sup>, Samia Berouaken<sup>1,2</sup>, Benamara mounia<sup>2</sup>, Belouni Rachid<sup>1,2</sup>, Abdi Samia <sup>1,2</sup>, Mourad Hamidani <sup>1,3</sup>

#### <sup>1</sup>Faculty of Medicine, University Saad Dahlab-Blida 1

<sup>2</sup>Central laboratory of biology, University hospital centre Frantz Fanon, Blida

<sup>3</sup>the trauma and orthopaedic surgery unit, University hospital centre Frantz Fanon, Blida

#### Abstract:

The implantation of orthopaedic equipment (prosthesis, implants, osteosynthesis material) is currently an indispensable factor in the management of degenerative arthropathies and in the treatment of fractures [1]. On the other hand, it can lead to several complications, the most serious of which is osteo-articular infections (IOA) on material [2]. The objectives of our work are: estimate the prevalence of IOA on orthopaedic equipment, Assess the infectious risk after the installation of the equipment in orthopaedic surgery and determine the main aetiologies responsible for IOA on hardware. Our study is triennial and is intended to be retrospective over the period from 01 January 2015 to 31 December 2017. All patients who had undergone material placement and had their medical follow-up in the trauma and orthopaedic surgery unit of Blida University Hospital Center were included. Patients who were initially operated in other unit and patients who did not have a complete record, or who did not have a balance sheet, were excluded from the study. A standardized operating record for collecting clinical information on the patients and a bacteriological results record was documented for each patient included in the study. All of our data has been entered, uniformized and subsequently exploited on Excel.76% (3037/3856) of patients admitted to the orthopaedic and traumatological surgery department of the BLIDA CHU for a surgical procedure benefited from a placement of material: 2760 of osteosynthesis equipment, 164 total hip prosthesis (THA) ), 75 total knee arthroplasty (TKA), 50 intermediate

prostheses 38 Prosthesis and cervicocephalique (PCC).For 3037 equipment poses, there were 137 cases of infection with a prevalence rate of 0045 (4.51%). The infection occurs mainly on TKA 10.66% (8/75) followed by PCC 10.52%(4/38) and THA 6.09 (10/164), and finally intermediate prostheses 10% (5/50). The risk of infection on osteosynthesis material occupies the last round with a percentage of 4.05 (110/2760), although it is the most settled material)The Screw plate and external fixatives are the most infected osteosynthesis material with respective rates of 41.81 % (46/110) and 10% (11/110). The most frequently isolated organisms, regardless of the type of staphylococci: 31, 72% material, are (59/186)of Staphylococcus aureus (59/186) and 13, 44 %( 25/186) of Staphylococcus coagulase negative. In our series of 137 cases 110 patients have evolved well under antibiotic therapy, while 17 patients have relapsed and have been surgically resumed. The use of orthopaedic material implies a real infectious risk. The development of new safer orthopaedic implants is necessary.

**Keywords:** infection, osteoarticular, prosthesis, osteosynthesis, staphylococci

- 1. Zimmerli W, Trampuz A and Ochsner PE. Prosthetic-joint infections. N Engl J Med, 2004; 351: 1645-1654.
- Osmon DR, Berbari EF, Berendt AR, et al. Diagnosis and management of prosthetic joint infection: clinical practice guidelines by the Infectious Diseases Society of America. Clin Infect Dis, 2013; 56: e1e25.

### Photo-instability of ternary-Halide MAPb(Br<sub>1-x-y</sub>l<sub>x</sub>Cl<sub>y</sub>)<sub>3</sub> Perovaksite

Se-Yun Kim<sup>1</sup>, Han Jeong Woo<sup>2</sup>, Hyunil Jo<sup>2</sup>, Seoungtae Baek<sup>2</sup>, Joon-Hyung Lee<sup>2</sup>, Jeong-Joo Kim<sup>2</sup>, Sang-Wook Lee, and Young-Woo Heo<sup>2,\*</sup>

<sup>1</sup>Convergence Research Center for Solar Energy, Daegu Gyeongbuk Institute of Science & Technology (DGIST), Daegu 42988, Korea.

<sup>2</sup>School of Materials Science and Engineering, Kyungpook National University, Daegu, 41566, Korea.

#### Abstract:

Halide perovskite which has been reported 22.1% of power conversion efficiency in solar cell, have been actively investigated to apply optoelectronic devices, various such as photovoltaic, light emitting diode and photodetector, due to the high light absorption coefficient, excellent charge carrier mobility, facile solution processability and ease of band tuning characteristics. However, photo-induced instability in binary halide mixed perovskite, such as in CH<sub>3</sub>NH<sub>3</sub>Pb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, was commonly observed under the photo-irradiation.<sup>1-4</sup> Since the phase separation into I- and Br-rich phases under the photo-irradiation lead to significant drop in photocurrent, this photo-induced instability has become the critical problem of long term stability.<sup>5</sup> Various attempts have been made to improve the photo stability through A-cation and B-cation mixing in ABX<sub>3</sub> formula, however, it has never been attempted to improve the photostability through the additional composition engineering at X site, such as  $MAPb(Br_{1-x-y}Cl_xI_y)$ which may cause the entropic gain and lattice contraction effect. In this presentation, we investigated photo-instability of various compositions single phase perovskite, such as CH<sub>3</sub>NH<sub>3</sub>Pb(Br<sub>1-x-y</sub>Cl<sub>x</sub>I<sub>y</sub>)<sub>3</sub> ( $0 \le x \le 1$  and  $0 \le y \le 1$ ), using soft PL laser source (SPL) and hard PL laser source (HPL)(Figure 1). Based on the spinodal decomposition model, the PL spectral changes according to photo-irradiation time and power of PL source were interpreted, and it could be expected that the photo-stability improvement due to entropic gain and lattice contraction by ternary halide mixed perovskite would not occur.

**Keywords**: Halide perovskies, Photo-stability, Solar cell, Photoluminescence,



**Figure 1**: PL spectrum of a MAPb(Br1-xyI<sub>x</sub>Cl<sub>y</sub>)<sub>3</sub> film by various irradiation time by HPL

- Thermal Decomposition J. Am. Chem. Soc, 2014, 136, 12241-12244, DOI: 10.1021/ja5071398
- Bi, C.; Yuan, Y.; Fang, Y.; Huang, J. Low-Temperature Fabrication of Efficient Wide-Bandgap Organolead Trihalide Perovskite Solar Cells Adv. Energy Mater. 2015, 5, 1401616, DOI: 10.1002/aenm.201401616
- Yang, Z.; Cheh, c.-c.; Liang, P.-W.; Crump, M.I Lin, F.; Zhu, Z.; Jen, A. K.-Y. Effects of formamidinium and bromide ion substitution in methylammonium lead triiodide toward high-performance perovskite solar cells, Nano Energy 2016, 22, 328-337, DOI: 10.1016/j.nanoen.2016.02.033
- 4. Eric T. Hoke, Daniel J. Slotcavage, Emma R. Dohner, Andrea R. Bowring, Hemamala I. Karunadasa and Michael D. McGehee. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics, Chem. Sci. 2015, 6, 613-617, DOI: 10.1039/C4SC03141E
- Ian L. Braly, Hugh W. Hillhouse, Optoelectronic Quality and Stability of Hybrid Perovskites from MAPbI3 to MAPbI2Br Using Composition Spread Libraries, J. Phys. Chem. C, 2016, 120, 893–902, DOI: 10.1021/acs.jpcc.5b10728