

Nano Singapore 2021 Virtual Conference

23 - 25 November, 2021

Book of Abstracts

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Nano Singapore 2021 Virtual Conference Program

23 - 25 November 2021 (GMT + 1 Time Zone)

November 23, 2021 Nano Singapore session I: Nanomaterials Fabrication / Synthesis / Characterisation		
Session's Chairs: Prof. Jacques Jupille, Institut des Nanosciences de Paris, France Prof. Fengzhou Fang, University College Dublin, Ireland		
09:00 - 09:30	Nano-structured composite materials for environmental benign antimicrobial technology Y. Zhang	Prof. Yugen Zhang , Institute of Bioengineering and Nanotechnology (IBN), A- Star, Singapore
09:30 - 10:00	Development of a next generation ion microscope aiming at single digit nanometer lithography, 3D imaging at the nanoscale and deterministic ion implantation J. Anton van Kan	Dr. Jeroen Anton van Kan , National University of Singapore, Singapore
10:00 - 10:30	Single-chain Knot/cyclized polymers from Controlled Multivinyl Monomer Polymerisation and Their Biomedical Applications W. Wang	Prof. Wenxin Wang, University College Dublin, Ireland
10:30 - 10:45	Nanosensor Detection of Synthetic Auxins in planta using Corona Phase Molecular Recognition M.C.Y. Ang , N. Dhar, D.T. Khong, T.T.S. Lew, M. Park, S. Sreelatha, J. Cui, A. Dehadrai, G.P. Singh, M.B. Chan-Park, S. Rajani and M.S. Strano	Dr. Mervin Chun-Yi Ang , Singapore-MIT Alliance for Research and Technology, Singapore
10:45 - 11:00	Understanding Active Site for Methanol Synthesis on CuZn and PdZn Nanoalloys U. Anjum and S.M Kozlov	Dr. Uzma Anjum , National University of Singapore, Singapore
11:00 - 11:30	Morning Break	
Session's Chairs: Prof. Jacques Jupille, Institut des Nanosciences de Paris, France Dr. Jeroen Anton van Kan, National University of Singapore, Singapore		
11:30 - 11:45	Crosslinked polypeptide films via RAFT mediated continuous as-sembly of polymers N.J. Chan , S. Lentz, P.A. Gurr, S. Tan, T. Scheibel and G. G. Qiao	Mr. Nicholas J. Chan, University of Melbourne, Australia
11:45 - 12:00	Field-induced nanoparticle-based diaphragms X. Tang and W. Wen	Ms. Xingwei Tang , Hong Kong University of Science & Technology, Hong Kong
12:00 - 12:15	Defect minimized hBN flake embedded Al2O3 thin film for flexible moisture barrier W. Jang , S. Han, T. Gu, H. Chae and D.Whang	Mr. Wonseok Jang, Sungkyunkwan University, Rep. of Korea
12:15 - 12:30	Impact of the Addition of Mixed Chlorinated Rubber, Graphene Oxide and Silicone Oil in Polyurethane as Anti- fouling Coatings O. F. Muslim , A. L. Juwono and Tulus	Dr. Opa Fajar Muslim , University of Indonesia, Indonesia
12:30 - 12:45	Growth of Patterned Vertically Aligned Carbon Nanotube Arrays With Marker Pen Stencilling L. Lum , Z. K. Ng, C. F. Siah, C. W. Tan, E. H.T. Teo and B. K. Tay	Mr. Lucas Lum, Nanyang Technological University, Singapore
12:45 - 13:30	Mid-Day Break	
Session's Chairs: Prof. Wenxin Wang, University College Dublin, Ireland Dr. Jean-Luc Bubendorff, University of Haute Alsace, France		
13:30 - 14:00	Plasmonics at the nanoscale J. Jupille	Prof. Jacques Jupille , Pierre et Marie Curie University CNRS Paris, France

14:00 - 14:30	Manufacturing III: Atomic and close-to-atomic scale manufacturing F. Fang	Prof. Fengzhou Fang, University College Dublin, Ireland
14:30 - 15:00	Graphene Oxide and Graphene-like Materials: Finding Their Place in the World of Commercial Carbon Materials E. Polyakova	Prof. Elena Polyakova , Graphene Laboratories Inc, NY, USA
15:00 - 15:15	A sustainable approach towards wood-based composites manufacturing by nanobiopolymer application P. Hochmańska-Kaniewska , D. Janiszewska and W. Bałęczny	Dr. Patrycja Hochmańska- Kaniewska, Łukasiewicz Research Network- Wood Technology Institute- Poznan, Poland
15:15 - 15:30	Application potential of multifunctional inorganic nanoparticles in textile and paper industries. M. Skwierczyńska , M. Runowski, A. Szczeszak, P. Kulpiński and S. Lis	Ms. Małgorzata Skwierczyńska, Adam Mickiewicz University- Poznan, Poland
15:30 - 15:45	2D Fluorographyne: Synthesis and Properties G. Abdi , A. Alizadeh, P. J. Leszczynski, Z. Mazej, W. Grochala and A. Szczurek	Dr. Gisya Abdi , University of Warsaw, Poland

Nano	November 24, 2021 Singapore session II.A: Nanoscale Electronics/Nano Electro	onics and Photonics
Dr. k	Session's Chairs: Cavitha Palaniappan, Newcastle Australia Institute of Higher Dr. Jean-Luc Bubendorff, University of Haute Alsac Prof. Renaud Bachelot, UTT Troyes, France	e, France
09:30 - 10:00	Road to Future Possibilities through Printed Electronics S. Agarwala	Prof. Shweta Agarwala , Aarhus University, Denmark
10:00 - 10:30	Plasmonic nanocavity for light manipulation and energy conversión L. Dangyuan	Dr. Lei Dangyuan, City University of Hong Kong, Hong Kong
10:30 - 11:00	Morning Break	
11:00 - 11:30	Enhanced Biodiesel Production through Nanocatalysts and Nano-material bound Microbial Enzymes K. Palaniappan	Dr. Kavitha Palaniappan, Newcastle Australia Institute of Higher Education, Singapore
11:30 - 11:45	Performance Improvement of Residue-free Graphene Field- Effect Transistor Using Au-assisted transfer Method Y.Jang , Y-M. Seo, H-S. Jang, K. Heo and D. Whang	Mr. Yamujin Jang, Sungkyunkwan University, Rep. of Korea
12:00 - 13:00	Mid-Day Break	
Nano Singapo	ore session II.B: Nanoscale Electronics/Nano Electronics and applications	d Photonics/ environmental
D	Session's Chairs: Prof. Jacques Jupille, Institut des Nanosciences de Pari r. Annarosa Gugliuzza, Institute on Membrane Technology (
13:00 - 13:30	Electrically switchable plasmonic nanoantennas H.W. Giessen	Prof. Harald W. Giessen , University of Stuttgart, Germany
13:30 - 14:00	Hybrid plasmonic nano-emitters: on the importance of controlling the spatial distribution of the active medium R. Bachelot	Prof. Renaud Bachelot , UTT Troyes, France
14:00 - 14:30	Graphene and bismuth telluride few layers entagled in nanostructured porous membranes for more sustainable water desalination A. Gugliuzza	Dr. Annarosa Gugliuzza, Institute on Membrane Technology (CNR-ITM), Italy
14:30 - 14:45	A new growth process for crystalline ultra-thin layers of conju- gated oligomers used in field-effect transistor applications J.L. Bubendorff , S. Renkert, S. Fall, T. Heiser, S. Motamen, L. Simon and G. Reiter	Dr. Jean-Luc Bubendorff, University of Haute Alsace, France
Nano S	ingapore 2021 - Session II.C: Nanomaterials for life science/	medical applications
	Session's Chairs:	
	Prof. Luigi Pasqua, University of Calabria, Italy Prof. Antonella Leggio, University of Calabria, Ita	
14:45 - 15:00	Engineered nanoparticles for targeted delivery of the anticancer drug Bortezomib A. Leggio , L. Pasqua and C. Morelli	Prof. Antonella Leggio , University of Calabria, Italy
15:00 - 15:15	Physical state of doxorubicin in Doxil® liposomal formulation: effect of temperature D.R. Perinelli , G. Bonacucina, M. Cespi and G.F. Palmieri	Dr. Diego Romano Perinelli, University of Camerino, Italy
15:15 - 15:30	Fundamental Chronobiological Changes and Charge Regulation Effects in Nanostructure of Bone Tissue A. A. Pavlychev , X.O. Brykalova and N.N. Kornillov	Prof. Andrey Pavlychev, Department of Physics, St.Petersburg State Univ., Russia
15:30 - 15:45	 Nanostructured Mesoporous Silica-Based Devices for Smart Chemotherapy L. Pasqua, C. Morelli and A. Leggio 	Prof. Luigi Pasqua , University of Calabria, Italy

15:45 - 16:00	Virus-based nanoparticles as multifunctionalized and targeted enzymatic nanoreactor for treatment of breast cancer	Duhalt , The National Autonomous University of
16:00 – 16:15	K. Chauhan and R. Vazquez-Duhalt A Qualitative Comparison between Two Different Microfluidic Devices with Roughened Surfaces Regarding Cavitation Inception M. Ghorbani	

November 25, 2021 Nano Singapore 2021 - Session III: Nanomaterials for life science/ medical applications		
Session's Chairs: Dr. Kavitha Palaniappan, Newcastle Australia Institute of Higher Education, Singapore Prof. Wenxin Wang, University College Dublin, Ireland		
09:00 - 09:30	Organic nanoparticles for sensing, imaging, and therapy B. Liu	Prof. Liu Bin , National University of Singapore, Singapore
09:30 - 10:00	Bioinspired Carbon Dots and Bio-templated Metal Nanoparticles for Sensing, Imaging and Nanomedicine Y. Nee Tan	Prof. Yen Nee Tan , Newcastle University, UK / NU International, Singapore
10:00 - 10:30	Genetic engineering of immune cells via nanoneedle array technology N.H. Voelcker	Prof.NicolasVoelcker,MonashUniversity,Australia
10:30 - 11:00	Morning Break	
11:00 - 11:30	Translational Nanomedicine: Crossing Borders in Drug Delivery M.G. Wacker	Prof. Matthias G. Wacker , National University of Singapore, Singapore
11:30 - 12:00	"Safe-by-Design" of Nanotechnology-Enabled Artificial Hip Joints For whole life use T. A. Wilkins , S. Lal, E.A. Caseley, R.M. Hall, J.L. Tipper	Prof. Terry Wilkins, University of Leeds, UK
12:00 - 12:15	Embedding of Antitumor Enzyme L-Lysine Alpha-Oxidase in the PolyGraphene and Using as Nanomatrixes for Cancer Prevention, Diagnosis and Treatment. A.S. Botin , A.Yu. Arinbasarova, A.G. Medentsev, T.S. Popova and D.V. Andreeva	Dr. Alexander Botin , Peoples' Friendship University of Russia, Moscow, Russia
12:15 - 12:30	Poly (photosensitizers) Nanoparticles for Enhanced in Vivo Pho-todynamic Therapy by Interrupting the π - π Stacking and Extend-ing Circulation Time N. Zheng	Dr. Nan Zheng , Dalian University of Technology, China
12:30 - 12:45	Design of RNA aptamer with highest affinityy to a specific long non-coding ribonucleic acid by the coarse-grained molecular mechanics S-P. Ju, H-W.Yang and T-F. Tseng	Mr. Tseng Ta Feng, National Sun Yat Sen University, Taiwan

Nano Singapore 2021 Posters Virtual Session

Posters are being displayed through the Virtual event solution. Discussions are to be done through the system chat features available to the attendees.

N.	Title	Author/Affiliation/Country
1.	Effect of Counter-ions on plasmonic response of citrate-stabilized gold nanoparticles K. Thammanatpong , S. Plengcharoensirichai and P. Swanglap	Mr. Kittimeth Thammanatpong, Silpakorn University, Thailand
2.	Utilizing of silver nanoparticle for Lead(II) ion detection S. Plengjaroensirichai , K. Thammanatpong and P. Swanglap	Mr. Sarawut Plengjaroensirichai , Silpakorn University, Thailand
3.	Green and eco-friendly synthesized gold nanoparticles with apple extracts for sensitive detection of Al3+ H. Park , W. Kim, M. Kim, J. Park, S. Jo, W. Kim, C. Kim, W. Lee and J. Park	Mr. Hyunjun Park, Korea University, Rep. of Korea
4.	The Formation of Covalently Bonded Aerogel Heterostructures Based on MXenes and Graphene Oxide M. Scheibe , C. Aparicio, K. Tadyszak, B. Peplinska, V. Ranc, M. Otyepka and B. Scheibe	Dr. Magdalena Scheibe , Palacky University Olomouc, Czech Republic
5.	Graphene-enhanced Raman spectroscopy for discrimination of amino acids Z. Chaloupková and V. Ranc	Dr. Zuzana Chaloupková , Palacky University Olomouc, Czech Republic
6.	Indoor-light harvesting of PVSK photovoltaics with double-sided irradiation to increase output power J-H. Lu , M-T. Cheng, T-H. Tsai, H-L. Hsu and C-P. Chen	Prof. Jong-Hong Lu , Ming Chi University of Technology, Taiwan
7.	The design and fabrication of nanoscale thermoelectric detector for near-field characterization of semiconductor lasers A. Piotrowska , A.Broda, A. Łaszcz, M. Zaborowski and D. Szmigiel	Dr. Anna Piotrowska , Institute of Microelectronics and Photonics-Warsaw, Poland
8.	High performance organic-inorganic hybrid encapsulant for smart windows M-J. Kang , D-J. Kang and H-G. Im	Mr. Min-Jung Kang , Korea Electrotechnology Research Institute (KERI), Rep of Korea
9.	Nano-Toxicant Method Using Artemia Franciscana and Multi-Object Tracking Algorithm M. Kim , J. Park, W. Kim, H. Park, S. Jo, W. Kim, C. Kim, W. Lee and J. Park	Mr. Minwoo Kim, Korea University, Rep. of Korea
10.	Zwitterionic Poly-photosensitizers as Carrier-free, Photosensitizer- Self-Delivery System for in Vivo Photodynamic Therapy N. Zheng and W. Song	Prof. Wangze Song , Dalian University of Technology, China

Nano Singapore session I: Nanomaterials Fabrication / Synthesis / Characterisation

Nano-structured composite materials for environmental benign antimicrobial technology

Yugen Zhang

Institute of Bioengineering and Bioimaging, 31 Biopolis Way, #07-01 The Nanos, Singapore 138669, Singapore

Abstract:

The worldwide spread of infectious diseases, exemplified by the current COVID-19 pandemic, and increasing instances of antimicrobial resistance, have raised the importance of disinfection and good hygiene. In addition, antimicrobial resistance (AMR) is also one of the most critical challenges in our modern society. The overuse of antibiotics. including non-therapeutic applications such agriculture as and environmental disinfection, represents one of the main causes for antimicrobial resistance. On the other hand, up to 80% of the germs are transmitted via surface contact. Therefore, killing bacteria/virus on the frequently touched surfaces is an effective way to avoid cross-infection. The common method to kill bacteria/virus on these surfaces relies on organic disinfectants (small molecules and polymers or organic coatings) which may lead to secondary contamination and drug resistance. Herein, we will introduce novel non-resistance, nano-structured antimicrobial technologies and green surface disinfection technology. Our disinfection surface technology coats various surfaces with nanopatterns or composites which kill adhered bacteria and fungi due to their physical structure through a rupturing mechanism or due to secondary ROS mecha-These disinfecting surface nism. and antimicrobial technologies are clean and safe, require no externally applied chemicals and can reduce healthcare-associated infections.

Keywords: Antimicrobial materials, surface disinfection, nanostructured surface, composite materials, antiviral.



Figure 1: Figure illustrating the bacteria killing mechanism of nano-structured surfaces.

Single-chain Knot/cyclized polymers from Controlled Multivinyl Monomer Polymerisation and Their Biomedical Applications

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Abstract:

Classical theory has long claimed that the polymerizations of multi-vinyl monomers (MVM) lead to insoluble cross-linked materials, as defined by P. Flory and W. Stockmayer 70 years ago (F-S theory)¹, and has since been numerously observed experimentally. Therefore, the (homo)polymerization of MVMs is still considered as a formidable task in chain growth polymerization. In recent decades, the introduction of controlled/living radical polymerizations (CRP) including atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) etc., has led to a significant advance in both synthetic polymer chemistry and physics. We first proposed a deactivation enhanced ATRP (DE-ATRP) method to homopolymerize MVMs². This approach has broken through two barriers for the polymerization of MVMs: uncontrollable homopolymerization and highly diluted reaction conditions, and successfully achieved the controlled homopolymerization of MVMs in concentrated conditions. Via this approach, a new class of single-chain knot/cyclized polymers can be formed due to the enhanced promotion of intramolecular cyclization and the suppression of intermolecular crosslinking^{3,4}.

Our breakthrough lies in the ability to alter the growth manner of polymerization by controlling the kinetic chain length together with manipulating chain growth conditions to achieve different polymer structures, which opened an efficient and practical road for the design and synthesis of knot/cyclized polymers from economical available monomers. The produced knot/cyclized polymeric materials significantly distinguish from crosslinked and hyperbranched polymers as they are no longer a combination of different polymer chains but indeed a self-knotted structure within a single chain, which have demonstrated the great potentials in biomedical applications^{5,6}.

Keywords: controlled/living radical polymerization, multi-vinyl monomers, single-chain knot/cyclized polymers, biomedical applications.



Figure 1: Controlled homopolymerization of MVM towards the formation of single-chain knot/cyclized architecture.

- 1. P. J. Flory, (1941) J. Am. Chem. Soc., 63, 3083-3090.
- W. Wang*, Y. Zheng, E. Roberts, C. J. Duxbury, L. Ding, D. J. Irvine, S. M. Howdle*, (2007) *Macromolecules*, 40, 7184-7194.
- Y. Zheng, H. Cao, B. Newland, Y. Dong, A. Pandit, W. Wang*, (2011) J. Am. Chem. Soc., 133, 13130-13137.
- Y. Gao, B. Newland, D. Zhou, K. Matyjaszewski, W. Wang*, (2017) *Angew. Chem.*, 56, 450-460.
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- Q. Xu, S. A, M. Venet, Y. Gao, D. Zhou*, W. Wang, M. Zeng, C. Rotella, X. Li, X. Wang, J. Lyu, B. J. Rodriguez, W. Wang*, (2019) *Angew. Chem.*, 131, 10726-10730.

Nanosensor Detection of Synthetic Auxins *in planta* using Corona Phase Molecular Recognition

M.C.Y. Ang¹, N. Dhar², D.T. Khong¹, T.T.S. Lew^{3,4}, M. Park³, S. Sreelatha², J. Cui³, A. Dehadrai³, G.P. Singh¹, M.B. Chan-Park^{1,5}, S. Rajani², M.S. Strano^{1,3}

¹Disruptive & Sustainable Technologies for Agricultural Precision IRG, Singapore-MIT Alliance for Research and Technology, Singapore

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³Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, USA

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⁵School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore

Abstract:

Synthetic auxins such as 1-naphthalene acetic acid (NAA) and 2,4-Dichlorophenoxyacetic acid (2,4-D) have been extensively used in plant tissue culture and as herbicides, since they are chemically more stable and potent than most endogenous auxins^{1,2}. A tool for rapid in planta detection of these compounds will enhance our knowledge about hormone distribution and signalling, and facilitate more efficient usage of synthetic auxins in agriculture. In this work, we show the development of real-time and non-destructive in planta NAA and 2,4-D nanosensors based on the concept of corona phase molecular recognition³ (CoPhMoRe), to replace current state-of-the-art sensing methods that are destructive and laborious. By designing a library of cationic polymers wrapped around single-walled carbon nanotubes (SWNTs) with general affinity for chemical moieties displayed on auxins and its derivatives, we developed selective sensors for these synthetic auxins, with particularly large quenching response to NAA (46%) and turn-on response to 2,4-D (51%). The NAA and 2,4-D nanosensors are demonstrated in planta across several plants species including spinach, Arabidopsis thaliana, Brassica rapa subsp. chinensis (Pak Choy) and Oryza sativa (Rice) grown in various mediums, including soil, hydroponics and plant tissue culture medium. After 5 h of 2,4-D supplementation to the hydroponics medium, 2,4-D is seen to accumulate in susceptible dicotyledon Pak Choy leaves while no uptake is observed in tolerant monocotyledon Rice leaves. As such, the 2,4-D nanosensor had demonstrated its capability for rapid testing of herbicide susceptibility and could help elucidate the mechanisms of 2,4-D transport and the basis for herbicide resistance in crops. The success of the CoPhMoRe technique for measuring these challenging plant hormones holds tremendous potential to advance plant biology study.

Keywords: plant nanobionics, nanosensors, carbon nanotubes, synthetic auxin, nanoparticles, herbicide, CoPhMoRe



Figure 1: Illustration of the concept of CoPh-MoRe which involves (1) design and synthesis of co-polymers for binding to SWNT; (2) discovery of unque corona phases selective for synthetic auxin analytes through library screening; (3) quantification and calibration of synthetic auxin binding via changes in SWNT emission spectra by monitoring the nIR fluorescence intensity changes or wavelength shifts.

- 1. Gianfagna, T. (1995) Natural and synthetic growth regulators and their use in horticultural and agronomic crops. *Plant hormones*, Springer 751-773.
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- Lew, T.T.S.; Sarojam, R.; Jang, I.-C.; Park, B.S.; Naqvi, N.I.; Wong, M.H.; Singh, G.P.; Ram, R.J.; Shoseyov, O.; Saito, K.; Chua, N.-H.; Strano, M.S. (2020) Speciesindependent analytical tools for nextgeneration agriculture. *Nat. Plants*, 6 (12), 1408-1417.

Understanding Active Site for Methanol Synthesis on CuZn and PdZn Nanoalloys

Uzma Anjum, Sergey M Kozlov,

Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

Abstract:

Methanol is used as an important precursor for the production of other industrially important chemicals such as formaldehyde and also regarded as potential environmentally friendly fuel. Cu and Pd based-ZnO catalysts are extensively used for the methanol synthesis because of their high catalytic activity and selectivity. Under reducing reaction conditions, Cu/ZnO and Pd/ZnO catalysts form the CuZn and PdZn surface alloys, respectively. In order to improve the production of methanol and developing efficient catalysts, the underline complex nature of the active sites in Cu/ZnO and Pd/ZnO catalysts needs attention. A detailed mechanistic study was conducted on CuZn and PdZn bimetallic nanoalloys to elucidate the complex nature of the catalytic active sites in nanoalloys that has not been completely understood because of the lack of experimental characterization with atomic resolution. Our sophisticated model and theoretical simulations provided a comprehensive understanding of the active sites in CuZn and PdZn nanoalloy catalysts for methanol synthesis. A stable CuZn (Figure1) and PdZn bimetallic chemical ordered nanoalloys were obtained from the density functional theory (DFT) calculations by fitting the topological based parameters [1],[2]. The most stable CuZn nanoalloy structure is shown in Figure1, in which most of the Zn atoms occupied the lower coordinated corner and edge sites. To uncover the effect of the position of Zn atoms on methanol synthesis in CuZn and PdZn nanoalloys, comprehensive structural dependent DFT calculations were performed. The adsorption energies of HCOO intermediate formed during the rate-determining step (CO₂(g) + H* \rightarrow HCOO*), were calculated on different coordinated sites of CuZn nanoalloy. For example, the binding energies of HCOO bidentate at the corner, edge, and terrace of Zn sites showed the following order $Zn_{corner}Cu_{corner} > \ Zn_{corner}Cu_{edge} > Zn_{corner}Cu_{terrace}$ depending on the coordination number. Hence, the Zn_{corner} and Cu_{corner} with the lowest coordination numbers was calculated to be the most favorable site (as shown in Figure 1) for HCOO binding. Similarly, The reaction energy for $CO_2(g)$ + $H^* \rightarrow HCOO^*$ elementary step was calculated to be highly exothermic at the same position (-1.21 eV).

Keywords: Density Functional Theory, Catalysts, Methanol synthesis, Nanoalloy.



Figure 1: Formate formation on the most favorable site of the most stable calculated CuZn nanoalloy structure. Zn and Cu atoms are represented in blue and beige colors, respectively.

- 1. Kozlov, Kovács, Ferrando, Neyman, How to determine accurate chemical ordering in several nanometer large bimetallic crystallites from electronic structure calculations, Chem. Sci. 2015, 6, 3868.
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Crosslinked polypeptide films *via* RAFT mediated continuous assembly of polymers

Nicholas J. Chan,^{1,2*} Sarah Lentz,^{1,2} Paul A. Gurr¹, Shereen Tan¹, Thomas Scheibel² and Greg G.

Qiao¹

¹ Department of Chemical Engineering, University of Melbourne, Melbourne, Australia ² Lehrstuhl Biomaterialien, Universität Bayreuth, Bayreuth, Germany

Abstract:

Polypeptide coatings are a cornerstone in the field of surface modification due to their widespread biological potential. As their properties are dictated by their structural features, subsequent control thereof using unique fabrication strategies is important. While deposition methods are a commonly known route, polymerization grafting methods offer an exciting strategy towards robust films. Our group has previously explored methods of yielding films with unique morphologies using various different polymerization techniques. Herein, we report a facile method of precisely fabricating densely crosslinked polypeptide films with unusually high random coil conformations and unique molecular through continuous assembly morphology polymerization via reversible addition-fragmentation chain transfer (CAP-RAFT). CAP-RAFT was fundamentally investigated using methacrylated poly-L-lysine (PLLMA) and methacrylated poly-L-glutamic acid (PLGMA) (Figure 1). Careful technique refinement resulted in films above 30 nm in thickness thick which could be increased above 90 nm upon multiple applications of this strategy. PLLMA and PLGMA films were found to have 30-50% random coil conformations despite the usual high α -helical propensity upon application of such polypeptides in other fim fabrication methodologies. Degradation by enzymes present in wound healing (Protease Type XIV) and the mammalian gut (α -chymotrypsin) was found, revealing positive potential for drug delivery, tissue engineering and other potential biological applications.

Keywords: CAP-RAFT, Polypeptide, NCA ROP, surface-initiated polymerization, crosslinked films, secondary structure, enzymatic degradation



Figure 1: Methodology for yielding crosslinked films *via* the continuous assembly of polymers with a polypeptide-based macrocrosslinker including a sample inset of the surface morphology as analysed by atomic force microscopy.

Field-induced nanoparticle-based diaphragms

Xingwei Tang, Weijia Wen

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Abstract:

The magnetic/electric field-induced vibration diaphragms are designed and fabricated by coating the magnetic/conductive nanoparticles on the polymer films¹. Such diaphragms (Figure 1) exhibit good vibration properties and frequency responses under the alternative magnetic/electric field². It is found that the frequency response of the diaphragms mainly depends on the rigidity of the film, nanoparticle size as well as coating thickness. In order to realize broadband response of the diaphragms to the audio frequency, different polymer films with various coating materials have been investigated from which the optimal parameters influencing the diaphragm's qualities are determined. The different patterns formed by the magnetic/conductive nanoparticles on the diaphragms are also studied and the results show that the local fields induced by magnetic/conductive patterns strongly dominate the vibration characters.

Keywords: magnetic/conductive films, magnetic/conductive nanoparticles, frequency responses



Figure 1: (A) is the magnetic/electric fieldinduced vibration diaphragm fabricated by coating the magnetic/conductive nanoparticles on the polymer films. (B) shows the vibration

character of a diaphragm induced by AC magnetic/electric field.

- Reznickova A, Orendac M, Kolska Z, et al. Copper nanoparticles functionalized PE: Preparation, characterization and magnetic properties[J]. Applied Surface Science, 2016, 390: 728-734.
- Reznickova A, Grulich L, Cizmar E, et al. Cu phthalocyanine, Cu and Fe@ Au nanoparticles grafted polyethylene: From structural to magnetic properties[J]. Materials Chemistry and Physics, 2020, 239: 1221

Defect minimized hBN flake embedded Al₂O₃ thin film for flexible moisture barrier

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Abstract:

Due to the vulnerability of organic optoelectronic devices to moisture and oxygen, thin-film moisture barriers have played a critical role in improving the lifetime of the devices. Here, we propose a hexagonal boron nitride (hBN) embedded Al₂O₃ thin film as a flexible moisture barri-er. After layer-by-layer deposition (LBL) of polymer and hBN flake composite layer as a template, Al₂O₃ was deposited by spatial plasma atomic layer deposition (PEALD). When Al₂O₃ was initially nucleated, Al-OH showed the defect act as path or channel of moisture and bind with hBN flake edge. The amine-functionalized hBN flakes suppress defect formation of Al₂O₃ thin film by forming aluminum oxynitride instead of Al-OH bonding. The hBN flake of Al₂O₃ thin film increase moisture diffusion path and inhibited crack propagation resulting in high mechanical flexibility. The flexible moisture barrier that has a value of 1.8×10^{-4} g/m² day WVTR and is stable in 3 mm bending radius fatigue tests is demonstrated by this synergistic effect.



Figure 1. Scheme of LBL templated process at (A) initial (B) mediate (C) saturation states (The figure below is a cross-section SEM image of each state. Scale bar is 100 nm)



Figure 2. (A) Al 2p (B) O 1s XPS spectra of LBL Al₂O₃ (C) relative content of atomic bonding in LBL and bare substrate Al_2O_3

Keywords: Hexagonal boron nitride, Exfoliation, Plasma enhanced atomic layer deposition, Point defect, Flexible moisture barrier

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Impact of the Addition of Mixed Chlorinated Rubber, Graphene Oxide and Silicone Oil in Polyurethane as Anti-fouling Coatings

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Abstract:

Many previous studies have reported that the polyurethane (PU) coatings exhibit excellent properties. Marine biofouling has made a serious problem on the marine devices and activities. Here, the use of anti-fouling additives based on mixed chlorinated rubber (CR), graphene oxide and silicone oil in the PU for marine coatings application was investigated. PU was prepared from polytetramethylene ether glycol (PTMEG) polyol then was called as part A, toluene diisocyanate (TDI) then was called as part B and thixotrope then was called as part C with the ratio of 100:60:1. In this study, the addition of a mixture of 1 phr of CR and 3 phr of 1 gram graphene oxide in 1000 ml of silicone oil were added in part A by mechanical stirring, subsequently part B and part C were added. The sample preparation was conducted under ambient condition. Initially, the samples were characterized for their mechanical properties and their chemical bonding using fourier transform infrared (FTIR) spectroscopy. The increasing of tensile strength of the samples were observed by the addition of the mixed CR, graphene oxide and silicone oil. The FTIR spectra showed the increasing of the intensity at the wavenumber of 1643 cm⁻¹ and 1269 cm⁻¹ which indicated a C=C strain group and Si bond of chemical compounds of PU, respectively. In order to investigate the role of the anti-fouling function, the samples were immersed in the sea for two months. Further the immersed samples in the sea were characterized using optical microscope and mechanical testing. The optical microscope observation on the samples with the addition of graphene oxide and silicone oil significantly decreased the growth of micro algae. Meanwhile, optical microscope observation showed that the samples with only CR addition significantly reduces the growth of micro barnacle. It was obtained that the addition of CR reduced the growing of micro barnacles until 35 %, while the addition of graphene oxide and silicone oil reduced the growing of micro algae until 48 % to the immersed sample for two months. To more elaboration, the electrochemical impedance spectroscopy (EIS) measurement was developed to investigate the impedance spectra on the samples of before and after immersed in the distilled water at temperature of 35°C for 120 hours. It showed that the total impedance increased at the immersed samples. Next, the equivalent circuit element from the impedance spectra was modelled to extract the series resistance, parallel resistance and capacitance. Interestingly, the series and parallel resistance increased and the capacitance decreased at the immersed samples which indicated anti-fouling element released during the immersion. Furthermore, the ageing test under ultraviolet (UV) light was performed for 500 hours to investigate the lifetime of the mechanical properties of the samples. It was observed that the UV light ageing initially increased tensile strength until 557 % at the duration below 80 hours exposure. In conclusions, it was obtained that the addition of mixed CR, graphene oxide and silicone oil improved not only the resistance to fouling but the mechanical property as well.

Keywords: polyurethane, coatings, chlorinated rubber, graphene oxide, silicone oil, mechanical properties, anti-fouling.



Figure 1: Optical microscope image shows the surface morphology of the PU coatings before and after immersion in the sea. It was obtained that the addition of mixed CR, graphene oxide and silicone oil improved the anti-fouling properties.

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Growth of Patterned Vertically Aligned Carbon Nanotube Arrays With Marker Pen Stencilling

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Abstract:

With the ongoing scientific interest in the properties and potential applications of carbon nanotubes (CNTs), the parameters and methods for the synthesis of CNTs have been well studied. One variety of CNTs with particular interest in the field of electronics packaging is the application of vertically align carbon nanotube (VACNT) arrays. The patterning of the VACNT arrays enables the fabrication of complex shapes and structures required in novel, CNT-based electronic device packaging. The default method for the fabrication of patterned VACNT arrays is by patterning substrates through photolithography before the deposition of the catalyst layer. However, as lithography is a chemical process that requires a clean room environment, room for an alternative patterning method can be seen especially in iterative environments experienced in the field of research and development. This paper reports a low cost, fast and simple technique of patterning substrates with marker pen stenciling. Permanent whiteboard marker ink is used as the sacrificial coating on substrates prior to the deposition of the catalyst layer for CNT growth. The marker pen ink then shows the ability to lift-off the catalyst layer in the defined regions, leaving defined catalyst patterns for the corresponsing growth of patterned VACNT arrays. This work will showcase the marker pen stenciling process as a cheaper, faster and more convenient alternative to conventional photolithography for millimetre-scale patterned VACNT applications.

Keywords: Vertically aligned carbon nanotubes, carbon nanotube synthesis, patterned catalyst deposition, electron beam deposition



Figure 1: (a) Optical image of a catalyst deposited SiO₂ wafer with stencilled marker pen ink; (b) Optical image of patterned VACNT growth from marker pen stencil.

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Plasmonics at the nanoscale

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Abstract:

Based on empirical knowledge dating back to Roman times, light scattering by nanoparticles was systematically used by medieval glass masters for the production of colored stained glass windows. The rationalization of the phenomenon in what is today called nanoplasmonics leads to innumerous applications in many fields [1]. After a brief introductory reminder, the talk develops three examples relating to the challenging topic of the supported metallic particles.

A focus is made on surface differential reflectivity spectroscopy (SDRS). This very sensitive and flexible method allows the analysis in situ and in real time of the growth of metal nanoparticles under conditions which fairly compare to X-ray scattering techniques practiced on synchrotrons, with the advantage of being operated in the laboratory [2]. SDRS emerges as a relevant tool for probing the size and the shape of particles with diameter in the 1-20 nm range. Firstly, applied to dielectrics-supported metal nanoparticles, the method reveals a never evidenced "universal" size-dependent behavior of the adhesion [3] which is shown to extend a Wulff-Kaishew description [4] of epitaxially strained particles. Then, SDRS allows scrutinizing the mechanism at work in buffer layers which promote the adhesion of noble metals on ceramics. In particular, it is demonstrated that seed layers in the sub-monolayer range can dramatically enhance the wetting of metals on substrates on which they otherwise do not even stick[5]. Such ability of small amounts of additives to promote film adhesion is of great practical interest. It shows the effectiveness of non-continuous and partially oxidized metal buffers which are close to realistic cases. Also, the anchoring of a film by discrete pre-deposited seed layers is more able to keep its functional properties intact.

In a third example, periodic arrays silver particles of a few hundred nanometers in size are obtained by solid-state dewetting of layers deposited on a substrate patterned by nanoimprint lithography. The self-organization of the nanoparticles is discussed in terms of thermodynamics and grain size. The key finding is that optical properties of the arrays are driven by not only the particle shape but also by the lattice period and the degree of order. A surface lattice resonance that disperses with the underlying period is evidenced experimentally and confirmed by optical simulations [6]. The opportunity to fabricate and tune such an assembly of plasmonic particles on transparent substrates opens prospects for both fundamental photonics and optical applications.

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Manufacturing III: Atomic and Close-to-atomic Scale Manufacturing

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Abstract:

This pleanary speech addresses the three paradigms of manufacturing advancement: Manufacturing I, craft-based manufacturing by hand, as in the Stone, Bronze and Iron Ages, in which manufacturing precision was at the millimeter or sub-millimeter scale; Manufacturing II, precision-controllable manufacturing using machinery whereby the scales of material removal, migration, and addition were reduced from millimeters to micrometers and even nanometers; and Manufacturing III, manufacturing objectives and processes are directly focused on atoms, spanning the macro- through the micro- to the nanoscale, whereby manufacturing is based on removal, migration, and addition at the atomic scale, namely, atomic and close-to-atomic scale manufacturing (ACSM). A typical characteristic of ACSM is that energy directly impacts the atom to be removed, migrated, and added. ACSM, as the next generation of manufacturing technology, will be employed to build atomicscale features for required functions and performance with the capacity of mass production. It will be the leading development trend in manufacturing technology and will play a significant role in the manufacturing of high-end components and future products.

Freeform optics find wide applications in various fields, such as virtual reality, augmented reality, high precision imaging and illumination systems. While it provides better optical performance, systems with freeform optics can be more compact in volume, lighter in weight, less in elements number and more in design freedom. This speech will further discuss about the manufacturing and measurement methods for complex shapes or structures. Typical applications developed in the presenter's laboratory together with industrial partners will be discussed. The research perspectives and the current application status of freeform optics will be outlined.

Keywords: Manufacturing III, Manufacturing paradigms, Manufacturing development, Atomic and close-to-atomic scale manufacturing, ACSM

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Graphene Oxide and Graphene-like Materials: Finding Their Place in the World of Commercial Carbon Materials

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Abstract:

Carbon atoms are the backbone of organic chemistry. A combination of these atoms can lead to the creation of an infinite variety of complex organic structures. For example, soot particles can form in nature and be synthesized in the lab quite easily, while each particle possesses a unique, complex geometric structure. Mankind produces a broad spectrum of carbon materials that are available in industrial qualities at reasonable prices including carbon fiber, carbon black, acetylene black, vapor-grown carbon fibers, micronized graphite, expanded graphite, spherical graphite, activated carbon, glassy carbon, synthetic graphite, fullerenes, and carbon nanotubes.

Over the last 15 years, a plethora of new materials marketed as "graphene" has emerged. It should be noted that graphene itself is an ideal rather than a real object, therefore it is more appropriate to label such materials as being 'graphene-like in nature. Graphene-like materials can be broadly classified as structures with a high aspect ratio and having a thickness of less than 10 nanometers. They are produced by various techniques that involve the exfoliation of graphite and synthesis using various forms of hydrocarbon sources. Unfortunately, graphene-like materials currently face fierce competition from commercially available carbon materials. For every new graphene-like material produced, there are several low-cost carbon alternatives that make it difficult to enter the commercial marketplace. We will provide a general overview of the similarities and differences between these materials as well as some suitable experimental techniques for their characterization.

More recently, Graphene Oxide is an emerging material that has been initially considered as a precursor for graphene production. Now, it is finding applications due to its unique chemical nature as well as its ability to be further chemically modified by a variety of chemical moieties. We will overview the revolutionary potential of this material as well as the challenges associated with its production and practical use

A sustainable approach towards wood-based composites manufacturing by nanobiopolymer application

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Abstract:

Recently, renewed interest in wood products for application in building and construction industry is resulted from the fact they are from renewable resources, have aesthetic values, great technological performance and much smaller carbon footprint than steel or concrete. However, there are still challanges addresed to obtain sustainable wood-based products reffering to the ecofriendly process of gluing and increasing durability of binder. The possibility to use bioadhesives in wood-based materials technology was developed within BioAdSIL project. An ecological alternative to currently used adhesive amino resins, which are a source of harmful formaldehyde emissions, has been obtained using nanocellulose modified with silanes. Nanocellulose can act as modifying and reinforcing agent of amine resins improving mechanical performance and reducing formaldehyde emission. However, hydrophilic nature of nanocellulose can limit its application in wood adhesives and lead to mechanical failure of wood-based panels. To obtain high-performance products, modification processes are required. Silane compounds, because of their chemical diversity and functionality, can be successfully used as cellulose fiber modifiers. Silane-modified nanocellulose has proven to be a promising nanobiopolymer in enchancing the adhesive and particleboard properties. The results showed that resins modified with nanocrystalline cellulose (CNC) kept their rheological behaviour and the proper viscosity after 4-week storage. Therefore, CNC can be used as a stabilizer extending the pot-life of resin. Particleboards prepared with resin containing CNC showed a reduction in formaldehyde and VOC emission as well as increase in bending strength and modulus of elasticity compared to the boards produced with commercial amine resins.

Keywords: nanocellulose, nanobiopolymer, bioadhesive, reinforcing agent, stabilizer, silane, sustainable wood-based products, formaldehyde emission, building and construction application



Figure 1: The BioAdSIL project approach to CNC application in wood-based composites manufacturing

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Application potential of multifunctional inorganic nanoparticles in textile and paper industries.

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Abstract:

Nanoparticles have gained considerable attention in past decades due to their unique properties (in comparison to their bulk counterpart) that enable their applications in various fields. Transition to the nanoscale allows employment of the particles for modification of materials in macro scale, for instance polymers, such as cellulose.

Here we report the wide range of inorganic nanoparticles (e.g. fluorides, phosphates, ferrites) that may be used for modification of cellulose fibers in order to give them additional properties, such as luminescence,¹ upconversion,² magnetism, or even a combination of these properties.^{3,4} By controlling the size and quantity of the introduced nanoparticles, the mechanical properties of cellulose fibers, important from the the processing point of view, can be mantained. These fibers can be processed into fabric or paper that can be used to produce the final products (e.g. documents, cloths and labels).

Thi work was supported by a grant no. POWR.03.02.00-00-I026/16 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education, the Polish National Science Centre (grant no. 2019/33/N/ST5/000325) and The National Centre for Research and Development (grant no. LIDER/39/0141/L-9/17/NCBR/2018).

Keywords: multifunctional nanoparticles, lanthanide(III) ions core/shell nanomaterials, documents and textiles protection, luminescence & magnetism



Figure 1: Photographs of luminescent-magnetic modifier colloid under UV-irradiation, before (left) and after (right) magnet capture

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2D Fluorographyne: Synthesis and Properties

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Abstract:

The graphyne structure is one of the new carbon allotropes composed of sp and sp²-hybridized carbon atoms, reported by Bughman et al. [1]. For instance, the γ -graphyne family is geometrically formed by linking acetylenic chains (– C=C–) between the adjacent benzene rings. Heteroatoms in carbon materials (e.g., N, F and P) result in enhancement of electrochemical activity by modifying the band gap and changing the surface characteristics.

In this research, two-dimentional graphyne-like structures with uniform pores and unique properties have been synthesised and characterized (Figure 1).



Figure 1: 2D graphyne-like structure with ordred triazine rings as heteroatom's sources.

Post modification was applied to introduce fluorine atoms by covalent functionalization. The colour of graphyne-like structure dispersed in water is brown while that of flourinated material is yellow. UV-Vis absorption shows the influence of heteroatoms on the band gaps (shifted from 0.4 to 2.3 eV after modification).

XPS characterization of resulting materials and the quantified atomic percentages of carbon, oxygen, nitrogen and fluorine are presented in Figure 2.

The resulting fluorinted materials showed photocatalytic activity in destroying organic polluttents like benzylalcoholes under solar simulated light.



Figure 2. XPS survey scan of modified graphyne like structures.

Ctotoxicity test was performed using the CellTiter Blue Reagent to investigate the effect of the flourinated substance on HEK cells. The results proved the cells retained the ability to reduce resazurin into resorufin (at concentration over $300 \mu g/ml$), which shows the metabolic capacity of cells after addition of flourinated materials.

Keywords: graphyne-like structures, Conjugated structure, covalent functionalization, two-dimentional graphyne-like structures, electronic properties.

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Nano Singapore session II.A: Nanoscale Electronics / Nano Electronics and Photonics

Road to Future Possibilties through Printed Electronics

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Abstract:

Although the electronics is now more efficient, faster and consumes low power, it still lacks in flexibility and conformality. The electronic components and devices are stiff and rigid. This has become a potential issue for new-generation wearable and smart textiles that need to provide comfort and have ergonomical structures. One challenge is that flexible and textile substrates are not compatible with conventional electronic fabrication. This has led the research community to look at alternate ways of fabricating electronics. Printed electronics is an umbrella of technologies that hold the promise to put electronis where ti is not envisioned before.

Contact printing has been well-researched and reported. However it tends to damage the substrate surfaces. Inkjet and Aerosol jet printing are noncontact modes and have shown great promise to fabricate flexible, stretchable and conformal electronics. My talk will focus on the processes and materials used for printing electronic components on flexible, stretchable and biocompatible substartes. I will discuss ink-substrate interactions happening at the interface to achieve homogeneous and coffee-ring effect free printing. Printing electronic inks on low-temperature substrates opens new challenges of sintering, as traditionally heat is used. Alternate post-processing methods will be detailed that may help sinter the printed tracks without damaging the low-temperature substrates. The talk will also report on various new application areas that are opening up due to laying electronics on unconventional surfaces.

Keywords: Printed electronics, 3D printing, inkjet printing, flexible electronics, wearable electronics, nano-inks.



Figure 1: Figure illustrating the landscape of my research in printed electronics, which spreads from synthesis of nano-inks, process technology, nano-devices to post-processing techniques.

Note: The submission is for a invited talk consideration.

Enhanced Biodiesel Production through Nanocatalysts and Nanomaterial bound Microbial Enzymes

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Abstract:

Transesterification of vegetable oils has been found to be one of the sustainable and renewable ways to meet the world's energy demand in the near future. This transesterification process yields biodiesel which can be used either directly or with some modifications in compression-ignition diesel engines. It is also known to produce less carbon monoxide, sulfur dioxide, oxides of nitrogen and unburned hydrocarbons compared to traditional petroleum-based fuel. The transesterification process is done by letting the vegetable oil to react with a primary alcohol in the presence of a suitable catalyst. A wide range of catalysts such as chemical catalyst, supercritical fluids, biocatalysts, etc. have been well explored in the literature. Recent studies have shown that nanocatalysts and nanomaterial bound microbial enzymes improve the efficiency of transesterification process by increasing the activity, selectivity and stability of the reactants involved in the process. The efficiency of various nanocatalysts such as nano-cerium oxide particles, nanocrystalline CaO, KF/CaO-Fe₃O₄ nanocatalyst, lithium impregnated calcium oxide solid nanocatalyst, lithium-doped CaO nanocatalyst, nanostructured mixed-metal oxides, cadmium oxide and tin oxide nanocatalysts supported by magnetic material, sulfated zirconia nanoparticle catalysts, carbon-based nanostructured catalysts and nanotube catalysts are reviewed and analysed in this study. Nanocrystalline CaO was found to provide 100% biodiesel efficiency, a rate that none of the other nanocatalysts could achieve¹. However nanocrystalline CaO lasted only for 3 cycles compared to KF/CaO nanocatalyst, which was able to serve for 16 cycles and yield an efficiency of 96%². As nanomaterials possess a large surface area to volume ratio, they also help in catalysis by being good enzyme immobilization supports. This study analyses the various types of enzyme immobilization techniques such as adsorption immobilization, covalent immobilization, entrapment immobilization and cross-linking immobilization techniques on nanoparticles, carbon nanotubes and nanofibers. 100% biodiesel conversion from waste cooking oil was observed using nano-immobilized lipase from a strain of *Candida antarctica* through the carrier epoxy- Fe_3O_4 -SiO₂³. However, this nanocarrier lasted only for 6 cycles compared to epoxy silica nanocarrier which was able to provide 99% biodiesel conversion efficiency from canola oil using *Thermomyces lanuginosa*'s lipase enzyme and can stand for 20 cycles⁴. As both nanocatalysts and nanomaterial bound microbial enzymes have found to increase biodiesel yield in a significant manner in laboratory studies, scale-up processes at industrial level need to be explored to see the cost-effectiveness of such catalysts for the transesterification process.

Keywords: transesterification, biodiesel, nanocatalysts, microbial enzymes, nanomaterial carriers, lipase enzyme.

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Performance Improvement of Residue-free Graphene Field-Effect Transistor Using Au-assisted transfer Method

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Abstract:

We report a novel graphene transfer technique for fabricating graphene field-effect transistors (FETs) that avoids detrimental organic contamination on a graphene surface. Instead of using an organic supporting film like poly(methyl methacrylate) (PMMA) for graphene transfer, Au film is directly deposited on the as-grown graphene substrate. We transferred graphene onto the target substrate via this method and then analyzed its surface using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). We confirmed the removal of organic residues by evaluating the electrical properties of a graphene fieldeffect transistor (GFET) fabricated using the proposed method. Graphene FETs fabricated using the established organic film transfer method are easily contaminated by organic residues, while Au film protects graphene channels from these contaminants. In addition, this method can also simplify the device fabrication process, as the Au film acts as an electrode. We successfully fabricated graphene FETs with a clean surface and improved electrical properties using this Au-assisted transfer method.

Keywords: Graphene; Field-effect transistor; Graphene transfer; Electrical property



Figure 1: The I(D)/I(G) Raman mapped image of (a) graphene transferred using PMMA and (b) graphene transferred using Au film. (c) The I(D)/I(G) ratio distribution graph. The 2D Raman mapped image of (d) graphene transferred using PMMA and (e) graphene transferred using Au. (f) The 2D position distribution graph. Scale bars, 5 µm.

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Nano Singapore session II.B: Nanoscale Electronics / Nano Electronics and Photonics / environmental applications

Electrically switchable plasmonic nanoantennas from metallic polymers: Active metasurfaces for beam steering

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Abstract: Metasurfaces based on plasmonic materials have revolutionized nanooptics [1]. The ability to shape beams with surfaces that are only a few hundred nanometers high has added tremendous design freedoms and functionalities to optics. In principle, plasmonic metasurfaces are the ultimate spatial light modulators that include amplitude and phase control on a deep subwavelength scale. The combination of propagation phase with geometrical phase allows for a full 2π phaseshift for each individual spatial element. The forefront of metasurface research is geared towards active metasurfaces. These devices allow for changing their functional properties. Examples include beam steering with varying angles, bifocal and zoom lensing, and, ultimately, switchable spatial light modulation.

Several approaches have been brought forward: Liquid crystals or polymers have been combined with plasmonic nanoantennas or high-index dielectric resonators, and an electric field can switch the refractive index next to the nanoantennas, hence shifting the resonance wavelength. Phasechange materials such as GST have been used in hybrid or high-index Mie resonator fashion to create metasurfaces in the infrared. Typically, materials of the GST family are switched by heat, as they can shift their refractive index drastically, depending on whether they are in the amorphous or crystalline state, which can be switched depending on heating and cooling parameters [2]. Another approach uses materials such as ITO which can shift its refractive index in the infrared depending on its charge carrier densitiy. In combination with a perfect absorber geometry, this results in electrical switchable functionalities such as beam steering for LIDAR applications. Other possibilities include metal-to-insulator transition materials such as Mg or VO2, which can be switched by proton incorporation or heating [3].

All of the previous approaches have their individual benefits and drawbacks. Hybrid approaches often suffer from the fact that the plasmonic resonances are shifted only spectrally, hence influencing other wavelengths. This holds true also for several of the GST approaches. Perfect absorber geometries that can in principle give the full 2π phaseshift and can be electrically switched commonly work in reflection geometries with very low reflectances, hence making applications such as LIDAR difficult. Nanoantennas that can switch plasmonic resonances on or off have switching speed issues, as incorporation of protons from the hydrogen gas phase often requires palladium as molecule splitting catalyst and hence results in switching times of seconds [4].

Here, we present a completely different and novel approach to the above problem: We present electrically switchable nanoantennas made from metallic polymers whose plasmon resonance can be switched on and off electrically and individually [5]. We demonstrate video-rate switching times, hence overcoming the previous speed issues. In order to validate our concept, we combine our electrically switchable plasmonic nanoantennas in functional metasurfaces. In one implementation, we demonstrate beam steering. In another example, we demonstrate a flat metalens whose focusing ability can be switched on and off electrically. Our system can be operated in transmission as well as in reflection geometry. Our approach represents the breakthrough that will ultimately enable spatial light modulators with densities higher than 1000 lp/mm. This is the crucial element to make possible high-angle variable beam steering, electrically adressable zoom metalenses, and, ultimately, wide-angle holographic videos. These devices are key to enable compact augmented and virtual reality devices.

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Graphene and bismuth telluride few layers entagled in nanostructured porous membranes for more sustainable water desalination

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Abstract:

Water supply is in high demand due to the scarcity of freshwater sources and hydrogeological instability of the areas in which degradation and adverse weather conditions occur. Membrane technologies provide new greener and ecosustainable solutions to the wastewater treatment and water desalination management. Seawater can be regarded as a rich source of freshwater and numerous commercial elements such as minerals. Membrane Distillation (MD) and membrane crystallization (MCr) are two attractive technologies, which can make saline water into freshwater and reusable minerals. The scale up of these two technologies is actually limited by the low productivity, high-energy consumption and recovery of polymorphic species in mixture. Herein, we demonstrate how new concept nanocomposite membranes boost the production of freshwater from synthetic seawater (NaCl 35 gL⁻¹), while in specific cases there is also contrasted conductive heat loss and salt rejection close to 100 %. Undesired fouling and thermal polarization events, which can compromise the performance of the separation, are prevented over longer operational time. The good chemical and mechanical stability of the engineered membranes is confirmed under different working conditions. The key issue for this kind of membranes is that few layers graphene and dichacolgenide compounds entagled in PVDF networks (Fig. 1) stimulate fast and reversible chemisorption mechanisms, which accelerate water transfer through the membrane for a double effect: a) amplified production of freshwater; b) controlled formation of crystals with much more regular shape and size. As a result, enhanced water desalination can be implemented when equipping MD/MCr devices with these edge membranes. This family of nanocomposite membranes is expected to facilitate the fabrication of new frontier multifunctional devices counting interplay of complementary cooperative functions on nanoscale.

Keywords: 2D materials, graphene, bismuth telluride, PVDF membrane, water desalination, membrane distillation and crystallization.



Figure 1: Figure illustrating the SEM image collected onto the surface of a PVDF membrane engineered with few layers bismuth telluride.

Acknowledgements

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A new growth process for crystalline ultra-thin layers of conjugated oligomers used in field-effect transistor applications

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Abstract:

Most organic semiconductor materials dewet on silicon wafers with thermal oxide layers. While Si-wafers represent convenient substrates for building a field effect transistor (FET), dewetting largely destroys the possibility for obtaining a compact and continuous crystalline thin organic semiconductor film and thus limits the mobility in these systems. Using oligothiophenes, we present an approach where the initial dewetting process can be turned into an advantage for generating very thin but large crystalline domains of a size up to the millimetres with all molecules sharing a single orientation[1]. Our approach can be easily extended to other molecules, which have strongly differing growth velocities in the various directions of the crystal, for example due to directional π -stacking interactions. FETs devices based on such large crystalline domains showed charge carrier mobility's that were two orders of magnitude higher compared to non-crystallized films(figure 1).

Keywords: Field Effect Transistor, thin organic semiconductor films, dewetting,molecular electronic, π - π stacking growth mechanism, spin coating, mobility, control of the molecule orientation.



Figure 1: From the 5TBT molecule(A) to the FET application(E) through the formation of a

well-crystallized ultra-thin organic layer characterized by light microscopy(D) and AFM(C), using a new growth mechanism(B)

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Nano Singapore 2021 Session II.C: Nanomaterials for life science / medical applications

Engineered nanoparticles for targeted delivery of the anticancer drug Bortezomib

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Abstract:

Conventional cancer therapies often present adverse side effects since they show poor selectivity for cancer cells.

An important challenge in cancer treatment is to identify a strategy that addresses these issues through the development of devices able to release the antineoplastic drug selectively in the target cells avoiding normal cells.

Targeting particular biomarkers overexpressed specifically on tumor cells enables the selective delivery of drugs to cancerous tissue minimizing toxic side effects and improving the drug therapeutic index.

In the last few years, the engineering of nano drug delivery systems (DDS) made of mesoporous silica nanoparticles¹ has allowed the development of biocompatible devices efficient as drug delivery carriers.

The peculiar properties of mesoporous silica nanoparticles (MSN) and the ability to modulate their structural properties and chemical functionalization make them ideal delivery platforms. In fact, they present a solid framework with as high surface area, tunable dimensions and easy surface modification that allow to design versatile nanosystems able to host various therapeutic agents and to bind molecular targets that interact selectively with specific membrane receptors overexpressed in cancer cells.²⁻⁴

A MSN-based device, FOL-MSN-BTZ, for pHsensitive release of the antineoplastic drug bortezomib in cancer cells over-expressing folate receptor (FR) has been developed. It consists of a nanometric honeycomb-like silica frame that presents folic acid (FOL) as targeting function (folate receptor specific ligand) on the external surface and the antineoplastic drug bortezomib (BTZ), a proteasome inhibitor highly active for the treatment of multiple myeloma (MM), linked within the pores by means of a pH-sensitive bond. Once the nanosystem FOL-MSN-BTZ enters the tumour cells, it releases the free drug in response to the slightly acidic tumor microenvironment.

FOL-MSN-BTZ prototype was tested on cancer cells overexpressing the folate receptor (FR+

cells) and on FR- normal cells. Our experiments showed that FOL-MSN-BTZ induces death in FR+ cancer cells but not in FR- normal cells while free BTZ resulted toxic for all cell lines tested, including FR- normal cells. *In vitro* results demonstrate that FOL-MSN uptake by FR expressing cells occurs through FR mediated endocytosis. Finally, we assessed the biocompatibility of FOL-MSN and FOL-MSN-BTZ at increasing concentrations and the antitumor activity of FOL-MSN-BTZ by evaluating the efficacy of the system in mouse xenograft models.

A more specific and selective MSN-based Bortezomib delivery system in which the targeting molecule FOL is replaced by a small peptide (CD38L) recognizing the CD38 receptor highly expressed on MM cells surface has also been designed and synthesized. CD38L-MSN-BTZ prototype gave very promising results *in vitro*.

Keywords: mesoporous silica nanoparticles, drug delivery systems, anticancer drugs, Bortezomib, targeting molecules, biomedical applications.

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Physical state of doxorubicin in Doxil[®] liposomal formulation: effect of temperature

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Abstract:

Liposomes are unilamellar nanovesicles made of phospholipids of great interest as drug delivery carriers, able to encapsulate both hydrophilic and lipophilic compounds. Some liposomal formulations have reached the market, including the doxorubicin loaded PEGylated liposomal dispersion named Doxil[®]. These liposomes, composed of phosphatidylcholine, cholesterol and soy PEGylated phosphoethanolamine (mPEG-DSPE), have an average size of 80 nm and a stable loading of doxorubicin sulphate (DOX). When loaded, DOX originates fibrillar supramolecular structures as evidenced by X-rays scattering techniques and electron microscopy. However, no molecular information are available on the structural changes of DOX nanocrystals in a confined environment over temperature. The aim of this work is to characterize the thermal behaviour of DOX nanocrystals in the confined environment of the PEGylated liposomes. Doxil® and unloaded liposomes as reference were analyzed by differential scanning calorimetry (mDSC), high-resolution ultrasonic spectroscopy (HR-US), scattering techniques as dynamic light scattering (DLS) [1], small angle x-rays scattering (SAXS) and small angle neutron scattering (SANS) and spectroscopic techniques (UV and raman spectroscopy). All techniques confirmed the crystalline state of DOX inside PEGylated liposomes. Particularly, mDSC and HR-US resulted to be very sensitive to highlight the changes in the phase transition behaviour of the nanocrystals when subjected to different heating programmes. DOX nanocrystals were found to be stable after heating up to 90°C, but an irreversible thermal behaviour was observed after a prolonged heating at elevated temperatures, accompanied by drug leakage from the liposomes [3]. Moreover, thermal properties were investigated after concentration of the liposomal dispersions (loaded and unloaded) using the ultrafiltration process under nitrogen pressure. The ultrafiltration process resulted to be effective in concentrating both loaded and unloaded liposomal dispersions, which showed a particle size and thermal properties comparable to those of the non-concentrated ones (marketed formulation). Moreover, all liposomal dispersions were stable at least for 8 weeks after concentration without appreciable morphological changes as assessed by cryo-TEM images [2].

In summary, a detailed characterization of the thermal behaviour of PEGylated liposomes loaded with doxorubicin (Doxil[®]) was performed by combining different techniques, which high-lighted a dependence of the reversibility of DOX phase transition upon the applied thermal conditions. Overall, this study provides new insights for the characterization of the physical state of drugs in confined environments.

Keywords: PEGylated liposomes, thermal analysis, doxorubicin, nanocrystals, confined environment.



Figure 1: Heat flow (mDSC) and attenuation (HR-US) variation over temperatures (A) and SANS scattering profile in H_2O and D_2O at 37 °C (B) for Doxil[®].

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Fundamental Chronobiological Changes and Charge Regulation Effects in Nanostructure of Bone Tissue

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Abstract:

Mechanisms resulting in age-related and pathology-induced changes in nanostructure and molecular dynamics in bone are investigated by combining X-ray diffraction, Raman scattering, IR and X-ray absorption spectroscopy and innershell photoemission. Cortical bone of newborn, adult and mature health rats is used as object to study general regularities of age-dependent phenomena. Medial and lateral condyles of the femur resected during total knee arthroplasty in patients with medial compartmental knee osteoarthritis (OA) are used as samples to understand pathology induced chronobiological (intact \rightarrow partially \rightarrow completely damaged cartillage) changes in local electronic and atomic structure of femoral bone [1]. Analyzing the experimental data and applying the 3DSL model [2] we (i) extract the age-and site-dependent deviations of the spectroscopic and structural characteristics of mineralized bone, (ii) examine relationships between nanostructure and hierarchical organization of the skeleton, (iii) reveal the chrobiological changes at the subcellular level. Figure 1 illustrates the chrobiological changes in the Ca and P 2p binding energies (solid lines), crystallinity (yellow diagram) and lattice constants a and c(dashed lines) of hydroxyapatite crystallographic cell. The chronobiology in OA-damaged areas is found closely related with forming non-apatite chemical bonds [1]. It is shown that dominant role of apatite Ca²⁺ states in bone is an indicator of its health [1]. The site-depent density of the apatite states in OA areas is exhibited with blue diagram in Figure 1. Inspecting the Ca²⁺ 2p photoemission spectra we approximate the Ca 2p BE as an exponential function of the ratio of age t to life expectancy $\langle T \rangle$. The substantial interference of the chronobiological and charge regulation effects in bone tissue is discussed.

The experiments were carried out with the support of the SPbU Resource Centers for (i) Physical Methods of Surface Investigation (ii) Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics and (iii) X-ray diffraction studies. This work is supported by RFBR grant 19-02-00891.

Keywords: bone tissue, hierarchcal matter, chronobiology, electronic and atomic structure, biomedical applications, age effects, osteoarthritis.



Figure 1. The fundamental chronobiological changes in nanostructure of cortex in young, adult and mature rats (upper) and femoral bone in OA knee compartment. The left and right scales correspond to the changes in electron BEs and lattice constants, respectively.

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Nanostructured Mesoporous Silica-Based Devices for Smart Chemotherapy

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Abstract:

Mesoporous silica with its regular nanostructure, good biocompatibility, large surface areas, large void volumes, high homogeneity in the pore diameter, represents an ideal nanoarchitecture to develop nanostructured devices able to interact with biological structures. We have developed (1) a class of hybrid bi/multi-functional Mesoporous Silica Nanoparticles (MSN) that allows the complete engineering of the release of a chemotherapeutic agent. The main limitations of current chemotherapies are poor selectivity for cancer cells and severe toxicity to normal cells that causes the dose responsive effect. Highly aggressive doses are thus necessary to eradicate tumours. Therefore, localized drug delivery would, ideally, improve the therapeutic efficacy, minimizing side effects.

In our approach mesoporous silica is functionalized on the external silica surface using a receptor specific ligand that is recognized by cancer cells receptors. An anticancer drug is grafted on the silica surface of the pore walls usually using a pH-sensitive bond. In this way our device is internalized by cancer cells through a receptorspecific mechanism and, in cancer cells organelles, the pH decrease induce the release of the drug.

Until now mainly folic acid has been used as receptor-specific ligand because its receptors are overexpressed by many kind of tuimor cells but other kind of molecules, such as peptides, can be employed. Encouraging results have been obtained *in vitro* because MSN are internalized in cancer cells but not in normal cells as represented in Scheme 1 (2) and *in vivo* where our smart chemotherapy has shown higher therapeutic efficacy if compared to free drug administration.



Scheme 1: MSNs structure and selective interaction with target cells.FOL- MSNs do not enter FR-negative cells and only induce growth arrest in FR-positive cell.

Keywords: Hybrid mesoporous silica, stimuliresponsive materials, multifunctional materials drug targeting, silica-based biomaterials, intracellular drug release, smart chemotherapy.

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Virus-based nanoparticles as multifunctionalized and targeted enzymatic nanoreactor for treatment of breast cancer

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Abstract:

Background: Tamoxifen is the standard endocrine therapy for breast cancers, which require metabolic activation by cytochrome P450 enzymes (CYP). However, the lower and variable concentrations of CYP activity at the tumor remain major bottlenecks for the efficient treatment, causing severe side-effects. Combination nanotherapy has gained much recent attention for cancer treatment as it reduces the drug-associated toxicity without affecting the therapeutic response.

Results: Here we show the modular design of P22 bacteriophage virus-like particles for nanoscale integration of virus-driven enzyme prodrug therapy and photodynamic therapy. These virus capsids carrying CYP activity at the core are decorated with photosensitizer and targeting moiety at the surface for effective combinatory treatment. The estradiol-functionalized nanoparticles are recognized and internalized into ER+ breast tumor cells increasing the intracellular CYP activity and showing the ability to produce reactive oxygen species (ROS) upon UV365nm irradiation. The generated ROS in synergy with enzymatic activity drastically enhanced the tamoxifen sensitivity in vitro, strongly inhibiting tumor cells.

Conclusions: This work clearly demonstrated that the targeted combinatory treatment using multifunctional biocatalytic P22 represents the effective nanotherapeutics for ER+ breast cancer.

Keywords: Cytochrome P450; Photodynamic therapy; Reactive oxygen species; Tamoxifen; Virus-like particle.

P22 virus nanoplatform for targeted synergic breast cancer therapy



Figure 1: Multifunctionalized biocatalytic P22 nanoreactor for combinatory treatment of ER+ breast cancer. The virus-like nanoparticles containing cytochrome P450 activity are functionalized with polyethylene glycol and a estradiol derivative for tumor targeting and with a photosensitizer for photodynamic therapy.

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A Qualitative Comparison between Two Different Microfluidic Devices with Roughened Surfaces Regarding Cavitation Inception

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Abstract:

Small bubbles generated via hydrodynamic cavitation as a result of the decrease in pressure within flow restrictive elements have wide applications. The recent studies have demonstrated their potentials in the biomedical applications, image processing and energy sectors. Therefore, the formation of the cavitation bubbles with the consideration of the surface topology has taken considerable attention particularly in the micro scale. In this study, two different microfluidic devices, which house significantly and slightly roughened microchannels, were fabricated to investigate the inception of the cavitation phenomenon. The roughness elements were created as nano grasses on the surface of the channels with the aid of the techniques adopted from semiconductor based microfabrication. Accordingly, the liquid flow was guided into the devices at different upstream pressures to record the inception of the cavitation and to investigate the size effect of the surface roughness.

Cavitating flows do not extend along the microchannel for the device with smaller roughness element (the peak-to-peak roughness is about 1 μ m) even at high upstream pressures. The concept of this study could be employed in the design of microfluidic devices, which could use to facilitate intense cavitating flows.

In this study, cavitation is qualitatively investigated inside the microfluidic devices with different roughened surfaces at various upstream pressures. The surfaces of the devices have peak to peak roughnesses of 1 and 2 µm, while the hydraulic diameter of the all devices is 75 µm. The results show that the surface roughness elements have substantial effects on the inception of the cavitation and development of the cavitating flow in micro scale. Recently, it was demonstrated that apart from the working fluid inside microfluidic devices, surface roughness elements have a significant effect on the generation of cavitation bubbles [1]. The experiments were performed at various upstream pressures from 2 to 4 MPa for the device with surface roughness elements (1 μm), however, in spite of the high upstream pressure, no cavitation inception was recorded for this device. The experiments were carried out for an identical microfluidic device with a surface roughness of 2 µm height to investigate the cavitation bubbles generation. The results of this device were presented in Figure 1, where the cavitation inception was observed at upstream pressure of 2 MPa. The cavitating flow does not develop along the microchannel, and the length of the twin cavities on the wall of the microchannel is almost constant from the inception condition to the high upstream pressure of 4 MPa. These results indicate that although the cavitation bubbles do not reach to the end of the channel and supercavitation flow regime does not form, this device with a 2 µm height roughness elements is capable of generation of cavitation bubbles.

Keywords: cavitation, microfluidic device, inception, pressure, roughness



Figure 1: Cavitating flow inside the microfluidic device with 2 μ m surface roughness at different upstream pressures

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Nano Singapore 2021 Session III: Nanomaterials for life science / medical applications

Organic nanoparticles for sensing, imaging, and therapy

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Abstract:

There is an increasing trend of using organic nanoparticles and especially light-harvesting conjugated polymer nanoparticles as active materials for sensing, imaging and therapy applications. The recent results show that conjugated polymer nanoparticles could be fabricated to have tunable sizes and emission, with over 10-fold brightness as compared to inorganic quantum dots with a similar dimension. In addition, their large absorption cross-sections have also enabled them to be used as photoacoustic contrast agents and for photothermal and photo dynamic therapy.

In this talk, I will discuss different strategies to form water-dispersible conjugated polymer nanoparticles and their applications as signal reporters or signal amplifiers for chemical and biological sensing/imaging and therapy. In addition, I will also briefly introduce our recent progress in organic nanoparticles with aggregation-induced emission features as replacement for quantum dots in various applications.

Keywords: Organic nanoparticle, photothermal therapy photoacoustic imaging, biomedical applications.

Bioinspired Carbon Dots and Bio-templated Metal Nanoparticles for Sensing, Imaging and Nanomedicine

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Abstract:

Inspired by Natural biomineralization processes, our research focuses on the rational design of peptide- and nucleic acid-based biomolecular templates for the synthesis of multifunctional carbon¹⁻⁵ and metallic nanomaterials⁶⁻¹¹ with tunable optical properties (i.e., plasmon absorption and light emission) and biofunctionalities for sensing, imaging, delivery and therapy. In particular, biofunctionalised metallic nanoparticles that exhibit a synergistic combination of biological and chemical properties resulting from the metal core and the biomolecular shell are well suited for biodetection.^{3, 6-15} By exploiting the colorimetric, fluorescence and light scattering properties of metal nanoparticles, we have developed a series of simple, fast and label-free nanobiosensors to detect bio-analytes ranging from small molecule drugs, protein biomarkers to cancer and bacteria cells. More recently, we have exploited the use of designer DNA and peptide templates to synthesize a palette of ultrasmall photoluminescent metal nanoclusters (NCs < 2nm in size) which could be used as multicolour probes for bioimaging, photodynamic therepy and multiplex sensing applications.^{7,8} We also took this biomimetic approach to 'turn' the native protein into bioactive fluorescent nanosensor for rapid drug screening without tedious genetic engineering.⁹ To enable greener synthesis with improve biocompatibility and functionalities, we employ the use of organic sources and biomass wastes in developing photoluminescent bioinspired carbon dots (biodots).¹ In these studies, we have uncovered the design principles of biodots derived from basic amino acids and DNA nucleobases with tailored-made structure-properties, which can be used to design multifunctional bioprobes for diagnostic and nanomedicine.²⁻⁵ For example, bioinspired antimicrobial biodots has been successfully developed for combating broad spectrum multi-drug resistant bacteria and used as ultrasensitive sensing probes for food pathogen detection (1 cfu/ml in < 0.5hr) in solution and. With further advances in bioinspired nanomaterials, we expect a far more extensive applications of these bio-smart nanomaterials for biological detection and therapy both in-vitro and in-vivo

towards early disease diagnostic, effective theranostic and personalized nanomedicine.^{7,16,17}

Keywords: carbon dots, metal nanoparticles, synthesis, functionalization, biomedical applications, biosensors, bioimaging, antibacteria, photosensitizer, photodynamic therapy, biomolecules, protein, DNA, peptides, fluorescent and plasmonic detection.

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Genetic engineering of immune cells via nanoneedle array technology

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Abstract:

Engineered cell–nanostructured interfaces driven by vertically aligned silicon nanoneedle arrays have become a promising platform for orchestrating key cell function, behaviour and cell fate conversion. The key advantage of ordered vertically aligned silicon nanoneedle arrays lies in their enhanced interaction at the interface between cells and nanoneedles due to their nanoscale dimension, enabling the bidirectional informational flow – biochemical/biophysical signals from or to the intracellular environment. The nanoneedle–cell interface open possibilities for implementing applications in biological applications such controlling cell behaviour or gene and protein delivery.

We have recently developed a suite of nanofabrication technologies combining colloidal or electron beam lithography techniques with wet or dry etching (wet: metal-assisted chemical etching; dry: deep reactive ion etching) to fabricate arrays of silicon-based nanoneedles with adaptable and programmable designs. And we have developed microscopy-based tools to study the effects of interfacing our nanoneedles with adherent and nonadherent cells. Our current research has the goal to establish nanoneedle-mediated gene delivery as a useful research tool and explore therapeutic approaches in cell therapy including in CAR-T therapy.

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Translational Nanomedicine: Crossing Borders in Drug Delivery

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Abstract:

For many years, nanocarrier delivery systems have been developed to deliver cancer therapeutics more efficiently to a specific site of action. With a rising number of drug products being approved, the quality and safety criteria are becoming a key concern of regulatory authorities globally [1].

Drug release testing is well accepted in early selection of formulation prototypes and during quality control. The assays detect even slight variations in the performance of the drug product. However, in the area of nanomedicines and when considering the limitations of existing clinical data, the correlation between the drug release rate and the *in vivo* response is difficult to establish.

In this ongoing investigation, the plasma concentration-time profiles of nanocarrier formulations were systematically analyzed and a physiologically-based pharmacokinetic model was created [2]. The *in silico* model comprises a compilation of the existing of human pharmacokinetic data to calculate the *in vivo* release rate of the nanocarrier. By establishing *in vitro-in vivo* correlations and applying this model to various nanomedicines including drug products such as Foscan®, Doxil®, and Myocet®, a comprehensive understanding of circulation and elimination of the carrier and the free drug was achieved.

For formulations of the photosensitizer temoporfin, Foslip[®] and Fospeg[®], an in vitro drug release assay was developed using the novel dispersion releaser (DR) technology. The release conditions were based on the expected physiological dissolution pressure and revealed a comparable release of the drug from pegylated and non-pegylated liposomes driven by the solubility of the drug. Additionally, the size and stability of the liposomes was monitored in presence of rat plasma. A vesicle size of 97 ± 3 nm for Foslip® and 97 \pm 1 nm for Fospeg® was observed. By using this sophisticated combination of *in vitro* and in silico methods, current efforts are focused on the evaluation of the formulation prototype NanoBB-1-Dox that has been recently evaluated in a phase I clinical trial [3]. The polymeric

nanoparticle formulation was developed to deliver the drug doxorubicin into the brain. To achieve this delivery, a receptor-mediated transport of the nanoparticles is addressed [4]. However, the rapid release of the drug from the carrier reduces the fraction of the drug available for this passage across the blood brain barrier and the *in silico* analysis revealed a race against time with regards to the drug release.

Keywords: doxorubicin, PLGA nanoparticles, *in vitro* release, pharmacokinetics.

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"Safe-by-Design" of Nanotechnology-Enabled Artificial Hip Joints For whole life use

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Abstract: A holistic approach to "Safe-by-Design" ¹ of nanoenabled replacement hip joints for arthroplasty is described (Figure 1). The design objective is for whole life in vivo achieved by coating of all joint components in nanostructured Si₃N₄ to substantially reduce friction, wear, stress induced nanoparticles, stress-induced metal ions and toxicity of all wear particles². All joint components were coated in silicon nitride by plasma enhanced chemical vapour deposition. Accelerated testing of whole joints under load was conducted usuing parallel series of robots with the joints encased in sealed flexible units containing bovine serum albumin and lubricin in isotonic phosphate buffered salin solution to simulate synovial fluid. Fluid samples containing wear debris were characterized by particle size, EDX and SEM, were incubated with human peripheral blood mononuclear cells (PBMNC) at 37°C/24 hrs 5% v/v CO2.. Cytokines released were subjected to assays for: a) oxidative stress; b) cytokine (TNF- α) release (ELISA); c) cytoxicity and d) DNA strandbreak (COMET). Irrespective of the phase structure, silicon nitride particles were non-cytotoxic and did not cause the release of TNF- α . Moreover, no significant production of reactive oxygen species was observed compared to the cells only negative control. Conversely, positive control cobalt chromium wear particles induced cytotoxicity and oxidative stress in the PBMNCs from at least one of the human donors after 24h. The results from this study indicate that silicon nitride has a low biological impact for the α , β and amorphous phases structures tested thus increasing current understandisng of this potential nanobiomaterial for healthcare applications. The design process and testing strategy has been incorporated into 2 new CEN Workshop Agreements CWA 17253-1 and CWA 17253-2. Together with the its patents and CEN standards, this technology provides Europe with a global competitive edge substantially reduces morbidity and mortality for patients by eliminating the need for orthopaedic surgical revisions.

Keywords: Safe-by-design, nanoenabled medical devices, hip hipjoints, ball & cup, toxicology, accelerated robotic testing, lifelong, in vivo, robotic wear testing, risk management framework, CEN Standards, morbidity & mortality reduction



Figure 1: The new design illustrated describes CoCrMo and TiALV joints in which the metal ball, socket and shaft are all coated in nanostructured Si_3N_4 by plasma vapouur deposition to substantially reduce joint friction, toxicity of wear nanoparticles and their toxicological.

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Embedding of Antitumor Enzyme L-Lysine Alpha-Oxidase in the PolyGraphene and Using as Nanomatrixes for Cancer Prevention, Diagnosis and Treatment.

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Abstract:

It is investigated that expanded graphite – Nanocomposite of PolyGraphene (PG) obtained after hydro-termic treatment of modified graphite became to be able to interact as sorbent PG with enzyme L-lysine alphaoxidase from Trichoderma cf. aureoviride Rifai.

It was studied the sorption properties of carbon material as an example of PolyGraphene (PG) concerning enzyme L-lysine alpha-oxidase from Trichoderma cf. aureoviride Rifai.

PG - version of ultrafine carbon sorbent, which was developed on the basis of the modified oxygen-containing expanded graphite (OCEG).

L-Lysine α -oxidase (LysOx) is one of the enzymes which are prospective in biotech-nology and medicine due to its antitumor and kinetic properties. An in vivo therapeutic effect was demonstrated on animals with tumor grafts: breast carcinoma SKBR3, Bro melanoma, intestinal cancer HCT116 and LS174T, ovary adenocarcinoma SCOV3, liver carcinoma.

This work aims to immobilize the extracellular L-lysine α -oxidase (LysOx) from Trichoderma cf. aureoviride Rifai VKM F-4268D on PolyGraphene and characterize some properties of adsorbed enzyme. Two types of PolyGraphene were used. Maximum adsorption equal to 5 or 11 µg protein/ mg of carrier was achieved, a high specific activity comparable to that of a free enzyme to take place.

LysOx adsorbed on PolyGraphene was shown to be a very stable system, namely high stability was revealed in the presence of chaotropic agent (urea) or proteolytic enzymes (pronase, chymotrypsin, trypsin).

Thus, the possibility of immobilization of LysOx on graphene with the full conservation of specific activity was shown.

In addition, LysOx is one of the enzymes that is promising in the enzyme therapy of tumors, based on the high sensitivity of tumor cells to the deficiency of growth factors, including amino acids.

Conclusions. Research work have the theoretical and practical importance, the received results and composit materials can be applied as matrix both in cancer screening, diagnosis, prevention and treatment and in using of other already known antitumor enzymes.

Keywords: L-lysine alpha-oxidase, immobilized enzyme, graphene, PolyGraphene, anticancer activity.

Poly (photosensitizers) Nanoparticles for Enhanced in Vivo Photodynamic Therapy by Interrupting the π - π Stacking and Extending Circulation Time

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Abstract:

The natural planar and rigid structures of most of the hydrophobic photosensitizers (PSs) (such as tetraphenyl porphyrin (TPP)) significantly reduce their loading efficiency in polymeric nanoparticles (NPs) due to the strong π - π interactions induced aggregation. The aggregation caused quenching (ACQ) will further reduce the quantum yield of singlet oxygen (102) generation and weaken the efficiency of photodynamic therapy (PDT). In addition, the small-molecular PSs exhibit short tumor retention time and tend to be easily cleared once released. Herein, poly (TPP) NPs, prepared by cross-linking of ROS degradable, thioketal linkers and TPP derivatives, followed by co-precipitation were firstly developed with quantitative loading efficiency (> 99%), uniform NP sizes (without aggregation), increased singlet oxygen quantum yield ($\Phi \Delta = 0.79$ in DMSO compared with 0.52 for original TPP), increased in vitro phototoxicity, extended tumor retention time, light-triggered on-demand release and enhanced in vivo antitumor efficacy, which comprehensively address the multiple issues for most of the PSs in PDT area.

Keywords: photodynamic therapy; π - π interactions; ROS degradable poly (TPP); quantitative TPP loading; improved singlet oxygen quantum yield



Figure 1: Figure illustrating the fundamental question that we are tempting to solve experimentally: what is the importance of silica surface modification nanoporous silica-based sol-gel glasses prepared from functionalized organosilane precursors on the parameters affecting the conformation, biological activity and functionality of encapsulated biomolecules.

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Design of RNA aptamer with highest affinity to a specific long noncoding Ribonucleic acid by the coarse-grained molecular mechanics

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Abstract:

A new prostate cancer marker:(Prostate cancer antigen 3(PCA3) long non-coding Ribonucleic acid(lncRNA) has been studied, and many studies have shown that PCA3 as a cancer marker has a higher accuracy than conventional prostate-specific antigen (PSA)[1].Therefore, a aptamer molecule that can quickly identify and target PCA3 molecules is designed by molecular recognition technology. For these reasons, the prevention and diagnosis of prostate cancer is of great importance and urgency.

The overall process begins with predicting the structure of lncRNA PCA3 through molecular dynamics, and then designing a suitable sequence to target PCA3. Simulation process with MARTINI Coarse-Grained(CG) model to increase simulation efficiency which is combined with Monte Carlo and simulated annealing (SA) methods and three global minimum search methods stochastic tunnelling(STUN), basin hopping(BH), and discrete molecular dvnamic(DMD), etc.Tens of thousands of structures are expected to be retrieved to predict the PCA3 global minimum structure, and then performing surface topology analysis of the tertiary structure of PCA3. The PCA3 lncRNA aptamer molecule was designed based on the complementary base pairing, and then analyzed for its adsorption energy, adsorption site, and structural stability to verify whether the designed sequences are identical to the two PCA3 RNA aptamer

ASO683: 5'- GCCATCAAGATTTTCTCGTC - 3' and

ASO735: 5'- GCTGCCTCATGTCATCACAG -3' sequences published by Dr. Sioss et al[2] to establish a standardized procedure for the search for fitness molecules.establish a standardized process for searching for the adaptor molecule.

Keywords: long non-coding Ribonucleic acid, lncRNA structure prediction, Prostate cancer antigen 3,molecule dynamic, molecule recognition, coarse grained model, prostate specific antigen.

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Posters Session

Effect of Counter-ions on plasmonic response of citrate-stabilized gold nanoparticles

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Abstract:

Gold nanoparticles are widely used as a sensor. However, spectroscopic behaviors of gold nanoparticles (AuNPs) change when disturbing by effect of anions. In this work, we study spectroscopic behaviors of AuNPs by adding mercury(II)perchlorate; $Hg(ClO_4)_2$ and mercury(II)chloride; HgCl₂ into AuNPs solution. Adding Hg(ClO₄)₂ led to precipitation of AuNPs but adding HgCl₂ led to color change of the AuNPs solution (Figure 1). UV-Visible spectroscopy was used to observe the wavelength shift of the AuNPs plasmon resonance. (Figure 2). These unique responses in the presence of different anions could be attributed to the different surface charge of AuNPs. Furthermore, addition of mercury salt led to drastically change of fluorescent emission. In fact, the emission spectra vanished after addition of 3.33 x 10⁻⁴ M HgCl₂. The evanescent of emission spectra show us the trait of fluorescent sensor. In the future, we will investigate this observation in details to develop AuNPs sensor without surface modification that easy to use and provide high sensitivity.

Keywords: Gold nanoparticles, UV-Visible spectroscopy, Fluorescence spectroscopy, Mercury, Fluorescent sensor, Counter-ion effect.



Figure 1: Citrate-stabilized gold nanoparticle without Hg, $Hg(ClO_4)_2$ and $HgCl_2$, respectively.



Figure 2: Absorbance spectra of AuNPs without Hg, with $Hg(ClO_4)_2$, and $HgCl_2$ that show wavelength shift .

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Utilizing of silver nanoparticle for Lead(II) ion detection

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Abstract:

The presence of Pb^{2+} in environment is an important problem due to its hazard towards living organisms. In this work, a novel naked eyes method for Pb²⁺ detection via yellow nanoparticles (Y-AgNPs) was successfully developed. To synthesize Y-AgNPs sensor and investigate selectivity of the sensor to Pb²⁺ for screening detection. The Y-AgNPs sensor was synthesized by a chemical reduction method with sodium borohydride as a reducer. Pb²⁺ selectivity of the sensor versus other metal ion were tested in solution and monitored by UV-Visible spectroscopy and naked eyes after 30 minutes of metal ion addition. The Y-AgNPs sensor provided high affinity toward Pb2+ with a distinguished precipitation, which was different compared to the presence of other metal ions (Figure 1). The high selectivity of the sensor could be attributed to the solubility product constant, and standard reduction potential of the Pb-salt and Pb2+, respectively. Moreover, we have demonstrated that the Y-AgNPs sensor could be used to detect Pb²⁺ in real sample and could be used as multisensor for Pb^{2+} , Hg^{2+} , Al^{3+} , Fe^{2+} (Figure 2). Therefore, the Y-AgNPs sensor is a candidate for Pb²⁺ screening due to its simplicity of preparation, and high selectivity.

Keywords: Y-AgNPs , Y-AgNPs sensor , $\rm Pb^{2+}$ screening detection, distinguished precipitation , multi-sensor .



Figure 1: Figure illustrating the YAgNPs sensor solution (left) and YAgNPs sensor solution after added Pb^{2+} Solution (left). The distinguished precipitations was observed.



Figure 2: Figure illustrating the YAgNPs sensor solution changes after added different cation. That showed YAgNPs sensor could be used as multi-sensor for Pb^{2+} , Hg^{2+} , Al^{3+} , Fe^{2+}

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Green and eco-friendly synthesized gold nanoparticles with apple extracts for sensitive detection of Al³⁺

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Abstract:

Aluminum has a high oxidizing property and it is easily ionized in water quality. Recently, there are reports that aluminum ions show a toxic effect. They can cause serious diseases associated with brain damage (Alzheimer, Parkinson's diseases, etc.). Therefore, the detection of Al³⁺ is very important. Recently, many studies detecting aluminum ions have been reported. These studies are including Atomic absorption spectroscopy(AAS), Inductive coupled plasma atomic emission spectroscopy (ICP-AES), Inductive coupled plasma mass spectroscopy(ICP-MS), Electrochemical method and Fluorescence analysis. However, the methods using such equipment have a limitation that the equipment is very large, expensive, and requires professional personnel. Here in we report a method to detect by colorimetric in which color changes when reacting with aluminum via gold nanoparticles synthesized using apple extracts (Ax-AuNPs). The aluminum ion solutions were added to the AuNP solutions with a 1:1 ratio. After 1 min, the color of the mixture solutions changed as confirmed by the naked eye. Especially, Ax-AuNPs are superior in reactivity with aluminum ions when compared with existing bare AuNPs, so it can be said that it is more sensitive (Figure 1). This is because the Ax-AuNPs are coated with pectin. Since pectin is a relatively large polymer structures compared to citrate which coated on bare gold nanoparticles, its reactivity with aluminum is greater than citrate. We developed an eco-friendly and enhanced colorimetric method for detection of aluminum ions in aqueous solution using pectin-rich AX-AuNPs synthesized from an apple extract solution. Also the sensitivity of the AX-AuNPs for the aluminum ions never decrease even in real sample experiments despite the presence of various interfering substances.

Keywords: Nanotoxicity, Gold nanoparticles, Green-synthesis, Eco-friendly, Colorimetry, Aluminum ions, Label-free, Real sample.



Figure 1: Cuvette images of AX-AuNPs (a) and conventional AuNPs (b) according to the reaction with different concentrations of aluminum ions in drinking water (0, 10, 12.5, 20, 25, 50, and 100 μ M). c,d) Absorbance ratio (A₆₁₀/A₅₃₀) results of AX-AuNP (c) and conventional AuNP solutions (d).

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The Formation of Covalently Bonded Aerogel Heterostructures Based on MXenes and Graphene Oxide

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Abstract:

Nowadays, the materials engineering field is dominated by trend of synthesis and application of two-dimensional (2D) nanomaterials, which are featured by remarkable properties and a wide spectrum of potential applications.¹ In the group of 2D nanomaterials among the others, the most investigated are graphene and its derivatives, transition metal dichalcogenides, hexagonal boron nitride, and the novel family of transition metal carbides and carbonitrides called MXenes.² This work presents the results of research on the formation of aerogel heterostructures based on Ti₃C₂T_x MXenes and graphene oxide (GO) monolayers. MXenes were prepared by etching of Al atoms from Ti₃AlC₂ MAX phase powder.³ The graphene oxide flakes were obtained using modified Hummers method.⁴ Prior to covalent bonding the MXene and GO flakes were characterized via scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray powder Diffraction (XRD), Raman and infrared (FT-IR) spectroscopies. For the aerogel hetero-structures formation two different approaches were investigated. In the first approach, the MXene and GO colloidal mixture was bonded by hydrothermal process with the addition of ethylenediamine (EDA). This resulted in formation of MXene-rGO hydrogel, which was liophilized. In the second approach, the MXenes and GO flakes reacted underwent reaction with 3-aminopropyltriethoxysilane (APTES). Flakes containing aminopropyl chains were crosslinked together by glutaraldehyde (GA). As-obtained colloidal solution was shock frozen using liquid nitrogen and liophilized. Prepared aerogels were characterized by XRD, SEM, Raman, FTIR techniques against their references, namely rGO, GO, and MXene aerogels formed in similar conditions.

Keywords: Ti₃C₂T_x, MXenes, Graphene Oxide, hydrogels, aerogels, structural characterization, *in vitro* culture cells scaffolds.



Figure 1: Figure presents AFM images of GO (A) and MXene (B) flakes, as well as SEM micrographs of rGO-MXene (C) and GO-MXene (D) aerogels crosslinked by EDA and APTES-GA, respectively.

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Graphene-enhanced Raman spectroscopy for discrimination of amino acids

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Abstract:

Amino acids are the basic "building blocks" that combine to form proteins. In every species, proteins are constructed from the same set of twenty amino acids. As well as forming proteins, enzymes and other body tissue they are also found throughout the body participating in a wide variety of chemical reactions, and are vital in basic energy production cycles, energy transfer and muscle activity. Raman spectroscopy has been demonstrated to be a valuable method for the study of biological molecules, in our case amino acids, with the availability of easily maintained and operated "benchtop" instruments. In most situations, a new characterization technique brings about a revolution in materials science, can upgrade the performance of new technologies. This synergistic action is also prominent in the research between graphene and SERS. Here we present a novel method for a determination of amino acids based on combination of graphene and Raman spectroscopy. Graphene and particularly graphene-enhanced Raman scattering (GERS) presents one of the most successful stories with many advanced applications because graphene, as 2D material, can increase the Raman signal due to its honeycomb lattice of sp²bonded carbon atoms due its amazing Raman scattering properties, which are related to its unique structure of electrons and phonons. Tryptophan, Phenylalanine, DOPA, Isoleucine, and Leucine were selected as model compounds for discrimination using GERS.

Keywords: amino acids, discrimination, graphene, Raman spectroscopy, GERS, Tryptophan, Phenylalanine, DOPA, Leucine, Isoleucine, biomedical applications.



Figure 1: Figure illustrating general scheme of the analyzed structure and analysis of amino acids.

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Indoor-light harvesting of PVSK photovoltaics with double-sided irradiation to increase output power

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Abstract:

With the rapid growth of Industry 4.0, Internet of Things (IoT), and Wireless Sensor Networks (WSN) applications, the demand for low-power wireless electronic devices in smart homes and wireless sensors has increased significantly. Electric power for low-consumption wireless electronic devices is usually provided by primary batteries. Based on environmental protection and maintenance convenience, it is hoped that indoor photovoltaics (IPV) can provide power for these low-consumption devices. IPV efficiency has intrinsic limitation, which had been discussed through theories.^(1,2) Because the light distribution of indoor illumination is different from a single solar source in outdoor, for the indoor light energy harvesting, the design of photovoltaics with double-sided transparent electrodes will possess higher output power than the conventional single-sided irradiation photovoltaics. The structure of the double-sided irradiation photovoltaics employed in this study is glass substrate\ ITO transparent electrode $NiO PVSK PC_{61}BM$ BCP\ Ag-ITO antireflection electrode. One end of the PVSK photovoltaics is an ITO transparent electrode and the other end is an Ag-ITO anti-reflection electrode. There are two different designs of Ag-ITO anti-reflection electrodes: (1) Ag 20 \sim 30 nm \ ITO 40 nm, and (2) Ag 0 \sim 2 nm \setminus ITO 40 nm \setminus Ag 8 nm \setminus ITO 40 nm. The experimental results show that the power conversion efficiency of single-sided irradiation PVSK photovoltaics is 20% to 28% under indoor light. The output power of PVSK photovoltaics with the same illuminance on both sides is increased by more than 50% compared to single-sided irradiation, the harvesting of indoor light energy greatly increasing. In this study, we also designed various optical filters to set up a white-light attenuation system, which can control white-light intensity and calibrate the relationship between LED irradiation power density and illuminance.

Keywords: Double-sided irradiation PVs, transparent electrodes, indoor light harvesting, anti-reflection, optical filters.



Figure 1: Double-sided irradiation PVSK photovoltaics samples, EQE measurement results on different sides, dashed lines (a), (b), (c), (d) are light incident from the ITO transparent electrode surface of the sample. The solid lines (a-1), (b-1), (c-1), and (d-1) are light incident from the surface of the Ag-ITO anti-reflection electrode; the Ag-ITO transparent electrode designs are respectively (a-1) Ag 20 nm \ITO 40 nm, (b-1) Ag 30 nm \ITO 40 nm, (c-1) ITO 40 nm \Ag 8 nm \ITO 40 nm, and (d-1) Ag 2 nm \ITO 40 nm \Ag 8 nm \ITO 40 nm. The curves (a) and (a-1), (b) and (b-1), (c) and (c-1), (d) and (d-1) represent the two sides of a sample, respectively.

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The design and fabrication of nanoscale thermoelectric detector for near-field characterization of semiconductor lasers

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Abstract:

The idea of this work is to develop a novel tool allowing for a fast, sensitive, and very precise analysis of the optical near-field and mode structure of semiconductor lasers within a wide spectrum of infrared wavelengths. The new approach is realized using a linear array of the multiprobe, nanoscale thermoelectric detectors, based on the Seebeck effect (voltage arises due to temperature difference between the measurement and reference points). Measurements of temperature distribution caused by beam interaction with the thermoelectric nanoscale detector are performed to reveal the radiation intensity spatial distribution in the laser near-field. The nanoscale thermoelectric detectors were made using a siliconcompatible MEMS process enhanced with the Focused Ion Beam (FIB) technique.

The paper describes the concept of the detector and outlines the development path from microscale down to nanoscale device (Fig. 1). A thermoelectric coefficient equal to 0.51 mV/K was found using a micro-thermocouple made in Pt/Ti/Si (p-type) process that was finally adapted for scaling down.

An important issue of the spatial measurement resolution is related to the outflow of heat i.e. the cross-talk between single thermoelements belonged to the multiprobe nanoscale detector.

As an infrared radiation source, a laser beam $(\lambda \approx 980 \text{ nm})$ with a Gaussian profile was used. The experimental setup also included: a CMOS camera, beamsplitters, a single mode fibre, a microscope objective, and single thermocouple detector. Furthermore, the thermocouple was connected to the universal thermocouple amplifier controlled by the LabView application. We used the CMOS camera to monitor the position of hot junctions with respect to the illuminating light beam, just to avoid heating-up the cold junction. Fig. 2 shows the measured beam intensity distribution expressed as voltage change as a function of thermocouple position in XY- plane. The optical power of the laser beam during the experiment was determined to 0.3 mW.

The obtained results indicate the application possibility of the fabricated multiprobe detector as a useful tool for laser beam characterization.



Figure 1: Thermoelectric structure in a 12-point configuration: (a) general view of the structure with cold and hot Seebeck junctions on the mono-Si substrate and (b) SEM image of parallel arrangement termocouples with 150 nm width of each thermocouples fabricated by FIB etching.



Figure 2: The normalized voltage values as a function of thermocouple position in XY-plane. The width of thermocouple used for the measurements was equal to 400 nm.

Keywords: nanothermocouple, FIB milling, micro- and nano-fabrication, Seebeck effect, laser beam characterisation

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High performance organic-inorganic hybrid encapsulant for smart windows

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Abstract:

Organic-inorganic hybrid materials fabricated by thermal polymerizations of various organic functional group have been studied in various application fields, as they have inherent advantages originating from their synergistically combined inorganic/organic networks. We designed and developed a high-performance organic/inorganic hybrid coating composed of surface-modified nanosilica (NS) as the nanofillers and a thermally curable epoxy polymer (EP) as the matrix. Colloidal NS was synthe-sized and surface-modified with glycidyl ligands by simple base-catalyzed sol-gel condensation reactions to endure homogeneous dispersion and cross-linking with EP. These results indicate that condensation reaction between surface silanol groups of the NS and glycidyl silanes successfully occurred via basecatalyzed sol-gel reaction, and the surface of the NS, as a result, was organically modified with glycidyl ligands.

We fabricated a nanosilica-incorporated hybrid coating as a high performance encapsulant. Synthesis was carried out using a simple and inexpensive sol gel process. We demonstrate the extended life of a smart window encapsulated with NS-EP resin under harsh condition. The NS-EP hybrids exhibited good coating quality, optical transparency over 90% in the visible range with strong adhesion, improved mechanical properties and improved moisture barrier performance. When the NS-EP coating was used as an encapsulation material, the Smart window lifetime was largely extended. We believe that this NS-EP hybrid can be used as a high-performance encapsulation material in various applications.

Keywords: Nanosilica, Silica nanoparticle, Surface modification, Organic-inorganic hybrid, Hybrid coating, Epoxy polymer, Smart window, Sol-gel reaction, Nanocomposite, Encapsulant, Hybrid material



Figure 1: Mocular structure of the NS-EP nanocomposite.

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Nano-Toxicant Method Using Artemia Franciscana and Multi-Object Tracking Algorithm

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Abstract:

Contamination of water with toxic materials such as mercury is a grave concern. Brine shrimp (Artemia franciscana) has widely been used as model organism in toxicity monitoring of water not only because it survives in high concentration of chloride, but also due to the high accessibility as a dry cyst, ease of culture, rapidity and low cost. Specifically, Faimali et al. investigated the feasibility of behavioral bioassay using larvae of Artemia, validating that an alteration of swimming speed is useful in evaluating water contamination. On the other hand, the behavior of Artemia is quantified through video analysis which became possible with the development of computation system and algorithm. In this research, we report a multi-tracking method to characterize the movements of Artemia franciscana exposed to a toxic substance (Hg(II)) for 1 h. For behavior analysis, we developed and verified fast and accurate automated tracking system, which can track multiple objects accurately and optimized considering unique backlash behavior of Artemia. We analyzed the changes in speed, trajectory and turning angle profiles due to different concentration of Hg(II). Interestingly, both stimulation and inhibition due to Hg(II) was observed which is called hormesis phenomenon. Using this manner, we were able to evaluate the toxicity of Hg(II) in real samples taken from the ocean. To test the toxicity with optimized automatic track-

ing system, we exposed Artemia to $Hg(\Pi)$. Among various toxicants, nano-size mercury material is one of the most dangerous material in ecosystem and to human because it easily dissolves in water to $Hg(\Pi)$. $Hg(\Pi)$ is widely distributed in ecosystem, and the toxicity to aquatic organism is well known. In spite of the severe toxicity of the Hg(Π), it is used extensively for numerous purposes, such as dental amalgam fillings, paint pads, and thermometers. Because of accumulation by food chain, ecosystem contaminated by mercury can be harmful to both human and aquatic organism, especially it can cause prenatal brain damage and movement disorder to human even at low concentration. Therefore, abundant studies about toxicity of $Hg(\Pi)$ has been conducted and can be used as representative toxic material. As a result of measuring the swimming sped using the optimized multi-object tracking system, as the concentration of mercury increases, the speed was slowed down. However, the directionality did not change In this study, acute toxicity assessment was performed using multi-object tracking of Artemia. It will be a useful tool in toxicity evaluation field by developing a system that has the advantage of providing fast and simple evaluation of toxicity.

Keywords: Nano-toxicity, brien shrimp, mercury ion, toxicological bioassay, trajectory analysis



Figure 1: Schematic of the toxicity test using multi-object tracking (MOT) system. (A) The 24 h old Artemia was exposed to Hg²⁺ solution for 1 h before the recording. Then the Artemia was transferred to behavior area on the recording stage for the recording. (B) Optical image of recording stage. The inset describes the center position (x,y) and heading direction (Φ) of Artemia. (C) The structure of the recording stage consists of a well plate lid, a mask, and cover glass. The depth of the behavior area is 700 µm, and the diameter is 12 mm. (D) The position coordinate and swimming direction of the Artemia was recorded using developed tracking algorithm for toxicity analysis. The processing speed of the tracking algorithm was accelerated using parallel computing. (E) By analyzing the behavior data from MOT system, the toxicity evaluation is achievable using various endpoints (i.e., trajectory, swimming speed, and turning angle).

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Zwitterionic Poly-photosensitizers as Carrier-free, Photosensitizer-Self-Delivery System for in Vivo Photodynamic Therapy

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Abstract:

Polymeric nanoparticles (NPs) have been widely established to deliver most of the hydrophobic chemo-drugs or photosensitizers (PSs) for cancer therapy. However, this strategy is usually hindered by the relatively low drug loading capacity and the undesired toxicity as well as the immunogenicity caused by the nontherapeutic, polymeric carriers. The carrier-free, drug selfdelivery systems, in which the chemo-drugs or their prodrugs themselves formed the NPs without the addition of nontherapeutic carriers, have been extensively developed to achieve a high drug loading capacity and low systemic toxicity. However, most of the driving forces to form the NPs were based on the strong hydrophobic interactions, which were the undesired forces for the porphyrin-based hydrophobic PSs due to the parasitic aggregation-caused quenching effect. Herein, the zwitterionic, watersoluble, and reactive oxygen species (ROS)-cleavable polyphotosensitizers (pPSs) were prepared by the polymerization method, which spontaneously introduced different charges associated with the "desired electrostatic effect" and reduced the "undesired aggregation" by separating the PS monomers using flexible and ROS cleavable linkers. The obtained pPS could be selfassembled into the nanocomplexes based on the electrostatic effect with a high PS loading capacity, improved singlet oxygen generation abilefficient ity, and phototoxicity. Upon poly(ethylene glycol) (PEG) or hyaluronic acid (HA) coating on the surface, both pPS/PEG and pPS/HA complexes exhibited enhanced stability under physiological environments and excellent in vivo antitumor efficacy. Moreover, HAcoated complexes also exhibited active tumor targeting. Such a polymerization strategy comprehensively addressed the parasitic issues for the hydrophobic PS selfdelivery system in the photodynamic therapy area.

Keywords: carrier-free, self-delivery, electrostatic effect, ACQ effect, PDT.



Figure 1: Formation of pPS Complexes Driven by the Electrostatic Effect as the Major Force and the Hydrophobic (π - π stacking) Interaction as the Minor Force.

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