



iPlasmaNano-VIII - 8th International Conference on Plasma Nanoscience

**Sunday 2 July – Thursday 6 July 2017
University of Antwerp, Belgium**

Programme

Book of Abstracts

Welcome

On behalf of the International Executive Committee and the Organising Committee, it is my pleasure to welcome you to the 8th edition in the iPlasmaNano conference series, iPlasmaNano-VIII. After the first 7 editions, held in Slovenia, Australia, Singapore, California, Spain, China and Greece, this year's edition is held in the beautiful city of Antwerp, Belgium, co-organised by UAntwerpen, UGent and IMEC.

The main theme of the iPlasmaNano conference deals with the fundamental science and applications of low-temperature plasmas, ion beams, lasers, and related approaches and its relation to the fabrication, synthesis, modification, and integration of nanoscale materials, structures and functional devices.

This year's edition has sessions dedicated to modelling and simulation, plasma catalysis, plasma medicine, nanomaterials, and plasmas for micro-electronics.

Additionally, for the first time, the conference now also introduces two dedicated poster sessions, intended in particular for students and people new to the field. We hope this will allow young people to interact with the experts in the field.

Furthermore, two separate sessions are dedicated to “beyond academics”: industrial applications, future prospects and perspectives, presented by recognized experts in the field.

We hope you will enjoy the science, the conference, the city, the food, and everything else. Welcome to Antwerp, welcome to iPlasmaNano-VIII!

Erik C. Neyts
Chair iPlasmaNano-VIII

iPlasmaNano International Executive Committee

Kostya (Ken) Ostrikov - Convenor of iPlasmaNano Series, Queensland University of Technology and CSIRO

Shuyan Xu, Nanyang Technological University, Singapore

Mohan Sankaran, Case Western Reserve University, U.S.A.

Angel Barranco, CSIC - Spanish National Research Council, Spain

Michael Keidar, George Washington University, U.S.A.

Uroš Cvelbar, Jožef Stefan Institute, Slovenia

Davide Mariotti, University of Ulster, UK

Erik C. Neyts, University of Antwerp, Belgium

Xingguo Li, Beijing University, P. R. China

Masaru Hori, Nagoya University, Japan

Xiaoxia Zhong, Shanghai Jiaotong University, P.R. China

Evangelos Gogolides, NCSR Demokritos, Greece

Organising Committee

Erik C. Neyts - conference chair, University of Antwerp

Stefan De Gendt, KU Leuven

Nathalie De Geyter, UGent

Annemie Bogaerts, University of Antwerp

Luc Van't dack, University of Antwerp

Scope

The scope of the iPlasmaNano conferences is plasma nanoscience/nanotechnology and its applications. Topics covered include:

- Fabrication of inorganic nanomaterials and nanostructures using vacuum or atmospheric plasmas or ion beams and control of their functionality and surface properties;
- Fabrication of organic nanomaterials and nanostructures and control of their functionality (materials include (but are not limited to): graphene, carbon, polymers, or other organic materials, biomaterials);
- New plasma processes in vacuum or atmospheric pressure for nanoscale fabrication, green nanofabrication, improvement of industrial processes, sustainable lifecycles of natural resources;
- Applications of plasma nanotechnology in life sciences and chemistry: diagnostics / monitoring (integration in sensors, biosensors, labs on chip, MEMS);
- Plasma nanocatalysis;
- Applications of plasma nanotechnology in photonics and plasmonics;
- Applications of plasma nanotechnology in energy and energy harvesting devices;
- Plasmas at new spatiotemporal scales: micro and nanoplasmas, nanosecond pulsing, nanoplasmas generated by ultrafast intense radiation;
- Modelling and diagnostics of plasmas during nanomaterial growth or etching;
- Plasmas formed at the surface or inside liquids;
- Entrepreneurial efforts in plasma nanotechnology (e.g., new spin-off companies and products);
- New vacuum or atmospheric plasma sources for plasma nanotechnology.

Background

The 8th International Conference on Plasma Nanoscience will continue the main theme of the conference series, in particular the fundamental science and applications of low-temperature plasmas, ion beams, lasers, and related approaches and its relation to the fabrication, synthesis, modification, and integration of nanoscale materials, structures and functional devices.

For the scope, aims, basic approaches, and recent advances in the field of plasma nanoscience, we refer to the following special issues, reviews and books:

- Special issue on: Plasma synthesis of nanoparticles. 2015 *J. Phys. D Appl. Phys.* **48**(31). iopscience.iop.org/0022-3727/48/31 (Sankaran R M and Kortshagen U; Eds.)
- Special issue on: Fundamentals of plasma–surface interactions. 2014 *J. Phys. D: Appl. Phys.* **47**(22). iopscience.iop.org/0022-3727/47/22 (Bogaerts A, Neyts E C and Rousseau A; Eds.)
- Special issue on: Plasmas for enhanced catalytic processes. 2015 *Catalysis Today* **256**, Part 1. www.sciencedirect.com/science/journal/09205861/256/part/P1 (Nozaki T, Neyts E C, Sankaran M, Ostrikov K and Liu C-j; Eds.)
- Review article on: Plasma nanoscience: from nano-solids in plasmas to nano-plasmas in solids. 2013 *Adv. Phys.* **62** 113-224. (Ostrikov K, Neyts E C and Meyyappan M) www.tandfonline.com/toc/tadp20/62/2 or arxiv.org/abs/1306.6711.
- Additional details about the conference topics can be found in our previous publication: Perspectives in plasma nanoscience. 2011 *J. Phys. D: Appl. Phys.* **44**. iopscience.iop.org/journal/0022-3727/page/Perspectives%20in%20plasma%20nanoscience (Ostrikov K, Cvelbar U and Murphy A B; Eds.)

Previous conferences and archive

- [iPlasmaNano-VII 2016](http://www.athens2016.iplasmanano.org/), Greece - www.athens2016.iplasmanano.org/
- [iPlasmaNano-VI 2015](http://www.huodongjia.com/event-3820443.html), China - www.huodongjia.com/event-3820443.html
- [iPlasmaNano-V 2014](http://www.barcelocongresos.com.es/iplasmanano-v/), Spain - www.barcelocongresos.com.es/iplasmanano-v/
- iPlasmaNano-IV 2013 California, U.S.A.
- [iPlasmaNano-III 2012](http://www.ntu.edu.sg/ias/upcomingevents/plasmanano12/Pages/default.aspx), Singapore - www.ntu.edu.sg/ias/upcomingevents/plasmanano12/Pages/default.aspx
- [iPlasmaNano-II 2010](http://www.acpo.csiro.au/iPlasmaNano/), Australia - www.acpo.csiro.au/iPlasmaNano/
- iPlasmaNano-I 2009, Piran, Slovenia

Conference programme

Monday, 3 July 2017

08:00 – 08:30	Registration
08:30 – 09:00	Opening
Session 1	Modelling and simulation
09:00 – 09:35	Keynote 1 – Michael Bonitz Towards a self-consistent theoretical description of the plasma Interface
09:35 – 10:00	Invited 1 – Pascal Brault Molecular Dynamics approach to plasma-surface and plasma-reactivity processes
10:00 – 10:25	Invited 2 – Daniil Marinov Kinetic Monte Carlo modelling of surface processes in reactive plasmas
10:30 – 11:00	Refreshment break
Session 2	Plasma catalysis I
11:00 – 11:35	Keynote 2 – J. Christopher Whitehead Plasma catalysis –is it just a question of scale?
11:35 – 12:00	Invited 3 – Volker Hessel Engineered nanomaterials by environmentally friendly atmospheric pressure microplasma process
12:00 – 12:25	Invited 4 – Leon Lefferts Plasma catalysis, walking up the thermodynamic hill?
12:30 – 13:30	Lunch
Session 3	Nanomaterials I
13:30 – 14:05	Keynote 3 – Toshiaki Kato Nanoscale plasma processing for atomic engineering of nano carbon materials
14:05 – 14:30	Invited 5 – Jinghua Fang Plasma enabled fabrication and applications of nanometamaterials using porous alumina
14:30 – 14:45	Contributed 1 – Pandiyarasan Veluswamy Selective patterned growth of ZnO nanorods/nanosheets on carbon fabric and their wearable properties
Poster session I 15:00 – 16:00	Plasma catalysis and nanomaterials
Session 4	Modelling, plasma catalysis and nanomaterials
16:00 – 16:25	Invited 6 – Sanjay Mathur Plasma CVD grown semiconductor metal oxide thin films and hetero-interfaces for solar hydrogen technologies
16:30 – 16:45	Contributed 2 – Athanasios Smyrnakis Plasma nanoassembly and plasma nanotexturing of polymers: controlling the transition from order to randomness towards versatile applications
16:45 – 17:00	Contributed 3 – Peter J. Bruggeman Silver nanoparticle synthesis at the plasma-liquid interface: mechanistic insights through modelling the plasma-liquid interface
17:00 – 17:15	Contributed 4 – Zahra Marvi Multiscale modelling of plasma-deposited hydrogenated amorphous silicon films
17:15 – 17:30	Contributed 5 – Igor Levchenko Nanostructures, metamaterials and nano-engineered surfaces in plasma thrusters: review and perspectives
17:30 – 17:45	Contributed 6 – Zhenhua Li Performance of Co/CNTs by hydrogen dielectric-barrier discharge plasma for Fischer-Tropsch synthesis
19:15	Dinner

Tuesday, 4 July 2017

Session 5	Plasma catalysis II
09:00 – 09:35	Keynote 4 – Hyun-Ha Kim Surface streamers and plasma catalysis
09:35 – 10:00	Invited 7 – Emiel J.M. Hensen Temperature-programmed plasma surface reaction
10:00 – 10:25	Invited 8 – Olivier Guaitella Seeking mechanisms of plasma/catalyst interaction with surface in situ diagnostics
10:30 – 11:00	Refreshment break
Session 6	Nanomaterials II
11:00 – 11:35	Keynote 5 – Chang-jun Liu Recent progresses in the applications of cold plasmas for CO ₂ conversion
11:35 – 12:10	Keynote 6 – Thierry Belmonte Nano-objects synthesized from Cu ₂₈ Ag ₇₂ electrodes by nanosecond-pulsed discharges in liquid nitrogen
12:10 – 12:35	Invited 9 – Wei-Hung Chiang Nanostructure engineering using atmospheric-pressure microplasmas: synthesis and applications
12:35 – 14:00	Lunch
14:00 – 18:00	Mid-session excursion: guided city walk
19:15	Dinner

Conference programme

Wednesday, 5 July 2017

Session 7	Plasma medicine I
09:00 – 09:35	Keynote 7 – Jean-Michel Pouvesle Biomedical applications of cold atmospheric pressure plasmas with a special focus on cancer treatment
09:35 – 10:00	Invited 10 – Annemie Bogaerts Plasma for cancer treatment: how can RONS penetrate through the cell membrane?
10:00 – 10:25	Invited 11 – Michael Keidar Plasma and nanoparticle applications in cancer therapy
10:30 – 11:00	Refreshment break
Session 8	Plasma medicine II
11:00 – 11:25	Invited 12 – Cristina Canal Liquid-mediated effects of cold plasma on bone cancer
11:25 – 11:50	Invited 13 – Sander Bekeschus Plasma, cancer, immunity - roads and challenges
11:50 – 12:15	Invited 14 – Jan-Wilm Lackmann Thiol chemistry as a molecular tool in plasma medicine
12:15 – 12:30	Contributed 7 – Sirui Li Plasma-liquid assisted synthesis of silver and rare earth nanoparticles for biomedical applications
12:30 – 13:30	Lunch
Session 9	Microelectronics I
13:30 – 13:55	Invited 15 – Jean-Francois de Marneffe Patterning challenges for ultimate CMOS and beyond CMOS nano-fabrication
13:55 – 14:20	Invited 16 – Fred Roozeboom InZnO grown by atmospheric plasma-enhanced spatial atomic layer deposition for application in high-mobility TFT circuits
14:20 – 14:45	Invited 17 – Huiying Yang Plasma enhanced performance in 3D printed flexible lithium ion batteries
14:45 – 15:10	Invited 18 – Angel Barranco Plasma-assisted oblique angle deposition of in-plane anisotropic ITO thin films
Poster session II 15:15 – 16:15	Micro-electronics and plasma medicine
Session 10	Micro-electronics II
16:15 – 16:40	Invited 19 – Romain Chanson Cryo-etching for integration in micro-electronic: silicon deep etch for contact etching and low-k integration in back end of line (BEOL)
16:40 – 17:05	Invited 20 – Athanasios Smyrnakis Plasma etched silicon nanowires with enhanced light trapping properties for axial or radial photovoltaic nanodevices
17:05 – 17:20	Contributed 8 – Quan-Zhi Zhang Protection mechanism for porous low-k materials during cryogenic etching
19:15	Conference dinner

Thursday, 6 July 2017

Session 11	Perspectives, industry and commercialisation I
09:00 – 09:20	Invited 21 – Ken Ostrikov Plasma-nano-synergies: catalysing cross-disciplinary collaborations
09:20 – 09:40	Invited 22 – Alquin Stevens Recent developments in digital μ PlasmaPrint surface engineering. From low volume science to high volume industrial applications
09:40 – 10:00	Invited 23 – Peter J. Bruggeman Challenges in controlling plasma processes in the plasma/nano-field: a personal perspective
10:00 – 10:20	Invited 24 – Gill Scheltjens Enabling functional thin films by soft atmospheric plasma polymerisation
10:20 – 11:00	Refreshment break
Session 12	Perspectives, industry and commercialisation II
11:00 – 11:25	Invited 25 – David Go The plasma-catalyst interaction: exploring synergistic effects at high temperature
11:25 – 11:50	Invited 26 – Mahendra Sunkara Nanowire as a model system for designing catalysts?
11:50 – 12:05	Invited 27 – Uroš Cvelbar Plasma and edge nanoelectronics
12:05 – 12:30	Conference closing and presentation iPlasmaNano-IX

Conference programme

Monday July 3rd, 2017

Poster session I: Plasma catalysis and nanomaterials

1. Damien U.B. Aussems: Atomistic simulations of graphite etching at realistic time-scales
2. Kristof M. Bal: Effect of plasma surface charging on the catalytic decomposition of carbon dioxide
3. Sotheara Chuon: Contribution to the CFD simulation of a magnetron discharge
4. Nathalie De Geyter: Study on plasma-induced modifications on pre-electrospinning polymer solutions and resultant nanofibres
5. Neda HafezKhiabani: Plasma-based conversion of CO₂ in a packed dielectric barrier discharge using coated silica spheres
6. Stijn Huygh: Insight in the surface reactions of the plasma catalytic dry reforming of methane on anatase (001)
7. Kenji Ishikawa: Programmed process for synthesis of calcium oxalate crystals in a buffered glucose solution by irradiation with non-equilibrium atmospheric-pressure plasma
8. Umedjon Khalilov: The role of hydrogen in the plasma modification of nanostructures
9. Igor Levchenko: Nanostructures, metamaterials and nano-engineered surfaces in plasma thrusters: review and perspectives
10. Alexander Parastayev: UV-Vis spectroscopy as a tool for in situ monitoring of catalyst temperature in a dielectric barrier discharge reactor
11. Harinarayan Puliyalil: Plasma catalysis for the efficient conversion of methane into valuable chemicals
12. Marleen Ramakers: Using a gliding arc plasmatron for CO₂ conversion
13. Jiann Shieh: Using plasma activation and platinum catalyst to grow carbon nanotubes at low temperature
14. Hiroo Suzuki: Wafer-scale integration of suspended graphene nanoribbon and its non-volatile optical memory operation
15. Charlotte Vets: Thermodynamic screening of bimetallic nanoparticles for chirality-selective carbon nanotube growth
16. Shengping Wang: Enhancement of CO₂ methanation performance on Ni/Al₂O₃ catalyst by plasma treatment
17. Bin Xu: Catalyst surface state control towards chirality controlled synthesis of single-walled carbon nanotube with plasma CVD
28. Athanasios Smyrnakis: Towards superhydrophobic polymers via atmospheric pressure plasma etching

Wednesday July 5th, 2017

Poster session II: Micro-electronics and plasma medicine

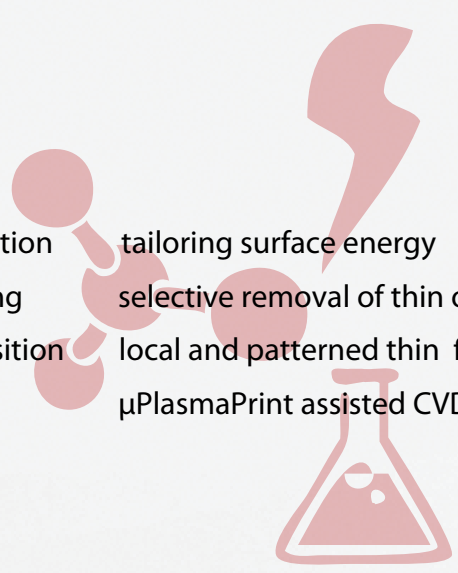
18. Rino Morent: Plasma treatment of polyactive nano-fibre conduits
19. Yuri Gorbanev: COST RF plasma jet: understanding the standard
20. Yuri Gorbanev: Plasma initiates radical reactions
21. Irina Grubova: Ab initio study of structural and electronic properties of the hydroxyapatite (001) / rutile (110) interface
22. Markus Heyne: Atomic layer etching of amorphous Si on MoS₂ for selectively patterned MX₂ heterostructures
23. Naresh Kumar: The stimulation of L6 skeletal muscle cell differentiation by non-thermal plasma modified electrically conductive fibres
24. Angela Privat Maldonado: Three-dimensional spheroid models to investigate the effect of low-temperature plasma treatments on metastatic processes of solid tumours
25. Jamoliddin I. Razzokov: Effect of plasma oxidation on the properties of globular proteins: an atomic scale study
26. Stefan Tinck: Cryogenic etching of porous SiO₂ with SF₆/O₂ plasmas
27. Maksudbek Yusupov: Understanding the role of aquaporins in the selective anti-cancer capacity of cold atmospheric plasmas



μ PlasmaPrint

InnoPhysics

printing nano surface modification with plasma activated molecules

- 
- activation tailoring surface energy
 - etching selective removal of thin organic films
 - deposition local and patterned thin film deposition
- μ PlasmaPrint assisted CVD & ALD

- low temperature ■
- non contact ■
- selective ■
- maskless ■
- digital, patterned, local ■

www.innophysics.nl



info@innophysics.nl



+31 40 2484774



Fransebaan 592a
Eindhoven NL



InnoPhysics

printing nano surface modification with plasma activated molecules

Key features

- 24 electrode digital micro-plasma generator
- 150 μm - 1 mm feature size typically
- smallest feature size commercially available

Application areas

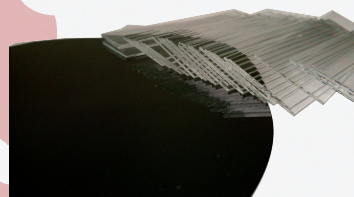
- bio-medical sensors, microfluidics, tissue scaffolds
- printed electronics
- Semicon, PCB, MEMS

μ PlasmaPrint R&D product solutions

μ PlasmaPrint toolkit



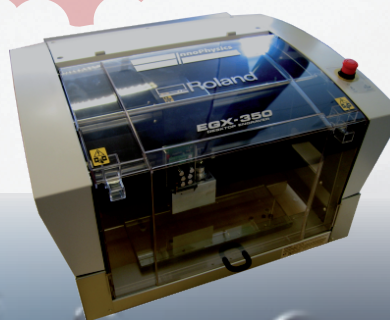
Sampling service



μ PlasmaPrint LP50 integration



μ PlasmaPrint Station



www.innophysics.nl



info@innophysics.nl



+31 40 2484774



Fransebaan 592a
Eindhoven NL



Monday July 3rd, 2017

08:00 – 08:30	Registration
08:30 – 09:00	Opening
Session 1	Modelling and simulation
09:00 – 09:35	Keynote 1 – Michael Bonitz Towards a self-consistent theoretical description of the plasma Interface
09:35 – 10:00	Invited 1 – Pascal Brault Molecular Dynamics approach to plasma-surface and plasma-reactivity processes
10:00 – 10:25	Invited 2 – Danil Marinov Kinetic Monte Carlo modelling of surface processes in reactive plasmas
10:30 – 11:00	Refreshment break
Session 2	Plasma catalysis I
11:00 – 11:35	Keynote 2 – J. Christopher Whitehead Plasma catalysis –is it just a question of scale?
11:35 – 12:00	Invited 3 – Volker Hessel Engineered nanomaterials by environmentally friendly atmospheric pressure microplasma process
12:00 – 12:25	Invited 4 – Leon Lefferts Plasma catalysis, walking up the thermodynamic hill?
12:30 – 13:30	Lunch
Session 3	Nanomaterials I
13:30 – 14:05	Keynote 3 – Toshiaki Kato Nanoscale plasma processing for atomic engineering of nano carbon materials
14:05 – 14:30	Invited 5 – Jinghua Fang Plasma enabled fabrication and applications of nanometamaterials using porous alumina
14:30 – 14:45	Contributed 1 – Pandiyarasan Veluswamy Selective patterned growth of ZnO nanorods/nanosheets on carbon fabric and their wearable properties
Poster session I 15:00 – 16:00	Plasma catalysis and nanomaterials
Session 4	Modelling, plasma catalysis and nanomaterials
16:00 – 16:25	Invited 6 – Sanjay Mathur Plasma CVD grown semiconductor metal oxide thin films and hetero-interfaces for solar hydrogen technologies
16:30 – 16:45	Contributed 2 – Athanasios Smyrnakis Plasma nanoassembly and plasma nanotexturing of polymers: controlling the transition from order to randomness towards versatile applications
16:45 – 17:00	Contributed 3 – Peter J. Bruggeman Silver nanoparticle synthesis at the plasma-liquid interface: mechanistic insights through modelling the plasma-liquid interface
17:00 – 17:15	Contributed 4 – Zahra Marvi Multiscale modelling of plasma-deposited hydrogenated amorphous silicon films
17:15 – 17:30	Contributed 5 – Igor Levchenko Nanostructures, metamaterials and nano-engineered surfaces in plasma thrusters: review and perspectives
17:30 – 17:45	Contributed 6 – Zhenhua Li Performance of Co/CNTs by hydrogen dielectric-barrier discharge plasma for Fischer-Tropsch synthesis
19:15	Dinner

TOWARDS A SELF-CONSISTENT THEORETICAL DESCRIPTION OF THE PLASMA INTERFACE

M. Bonitz*

Kiel University, Institut für Theoretische Physik und Astrophysik

Leibnizstrasse 15, 24098 Kiel, Germany

* e-mail: bonitz@theo-physik.uni-kiel.de

The interaction of low-temperature plasmas with a solid surface is highly complex due to the radically different electron densities, lengths and time scales. Additional difficulties arise from the non-equilibrium and non-isothermal character of the plasma. While the plasma kinetics are well accessible via PIC-MCC simulations, the inclusion of surface effects is typically done phenomenologically. On the other hand, the response of the solid to the plasma is usually done in linear response, assuming a weak and adiabatic answer.

This picture becomes highly questionable if the dimensions of the solid are reduced to the nanoscale or/and the plasma pressure increases. I will present the idea of an integrated approach to the plasma-solid system that we are presently developing in Kiel. It couples plasma simulations, state of the art solid simulations based on quantum kinetic equations [1], mesoscopic molecular dynamics and kinetic Monte Carlo simulations [2], and also takes into account non-adiabatic processes and electronic correlations in the solid [3].

- [1] Bonitz M 2016 *Quantum kinetic theory, 2nd edition*. (Berlin: Springer Verlag)
- [2] Abraham J W, Strunskus Th, Faupel F and Bonitz M 2016 *J. Appl. Phys.* **119** 185301
- [3] Balzer K, Schlünzen N and Bonitz M 2016 *Phys. Rev. B* **94** 245118

MOLECULAR DYNAMICS APPROACH TO PLASMA-SURFACE AND PLASMA-REACTIVITY PROCESSES

P. Brault*

CNRS / Université d'Orléans, GREMI UMR7344

14 rue d'Issoudun, P.O. Box 6744, 45067 Orléans Cedex 2, France

* e-mail: pascal.brault@univ-orleans.fr

Due to the atomic/molecular nature of the plasma surface interactions and the reactivity of the plasma core, molecular dynamics simulations are suitable for understanding the associated basic mechanisms. This is mainly due to availability of interaction potentials of high quality, especially many body and /or reactive potentials [1-3].

A great variety of processes can be thus rigorously investigated:

- atomic and molecular collisions in the gas phase;
- nanocluster/soot growth in the gas phase;
- plasma wall interactions and surface and sub-surface (nano-)structurisation;
- plasma (nano-)cluster and thin-film growth on materials;
- direct treatment of materials surface: nitridation, carbidisation, oxidation, ...;
- plasma grafting, functionalisation, ...;
- plasma reactivity on surfaces (including supported nanocatalysts, ...);
-

Beside the availability of the interaction potentials, careful modelling of the initial conditions for simulations, hopefully closed to experiments, is required [4]. Moreover there now exist strategies for including process long time dynamics in molecular dynamics simulations [5].

Due to the high fluxes encountered in molecular dynamics simulations, caution should be paid to the treatment of energy release during bond formation, unphysical collisions, heating, ...

The present lecture will illustrate the different methodological approaches in considering various contexts, in line with experiments, as:

- plasma (reactive) sputtering and deposition;
- plasma – catalysis;
- plasma chemistry, including involving biological media and radicals;
- plasma irradiation of materials.

[1] Graves D and Brault P 2009 *J. Phys D: Appl. Phys.* **42** 194011

[2] Special issue on “Three decades of many-body potentials in materials research”, 2012 *MRS Bull.* **37** 469-521

[3] Neyts E C and Brault P 2017 *Plasma Process. Polym.* **14** 1600145

[4] Brault P and Neyts E C 2015 *Catalysis Today* **256** 3-12

[5] Bal K M and Neyts E C 2015 *J. Chem. Theory Comput.* **11** 4545-4554

KINETIC MONTE CARLO MODELLING OF SURFACE PROCESSES IN REACTIVE PLASMAS

D. Marinov^{1,*} and V. Guerra²

¹ IMEC vzw

Kapeldreef 75, 3001 Leuven-Heverlee, Belgium

² Universidade de Lisboa, Instituto Superior Técnico, Instituto de Plasmas e Fusão Nuclear

Lisbon, Portugal

* e-mail: daniil.marinov@imec.be

Despite the remarkable progress in *ab-initio* modelling of plasma-surface interactions, atomistic simulations on the time and length scales that are relevant to real systems remain challenging. Therefore, coarse-grained deterministic models are often used in practice. In deterministic description, surface kinetics is formulated in terms of fractional coverages of different types of active sites and simulated by a system of differential equations. Such mesoscopic approach is simple and computationally efficient but it is inherently approximate because it does not account for the complex microscopic details of the underlying processes. In this contribution, Kinetic Monte Carlo (KMC) modelling of surface kinetics in plasmas is discussed. We demonstrate that KMC is particularly well suited to bridge the gap between the complexity of atomistic simulations and the effectiveness of deterministic models.

In KMC approach, the master equation for a given system is not explicitly solved, but instead the underlying Markov process is simulated numerically. KMC algorithms are exact, they can handle reaction probabilities that depend on the local configuration of the system and they are well suited to model heterogeneous surfaces that exhibit distributions of adsorption energy and reactivity [1, 2]. In this report, KMC modelling of atomic recombination and molecular formation on surfaces in contact with reactive plasmas is discussed. Simulations are benchmarked against the available experimental data. In particular, surface processes in systems with a distribution of active sites [3, 4] is analysed in detail.

- [1] Guerra V and Marinov D 2016 *Plasma Sources Sci. Technol.* **25** 045001
- [2] Marinov D, Teixeira C and Guerra V 2017 *Plasma Process. Polym.* **14** 1600175
- [3] Donnelly V M, Guha J and Stafford L 2011 *J. Vac. Sci. Technol. A: Vacuum, Surfaces, Film* **29** 10801
- [4] Guerra V, Marinov D, Guaitella O and Rousseau A 2014 *J. Phys. D: Appl. Phys.* **47** 224012

Acknowledgments. VG was partially supported by FCT, Projects UID/FIS/50010/2013 and PTDC/FIS-PLA/1420/2014 (PREMiERE).

PLASMA CATALYSIS – IS IT JUST A QUESTION OF SCALE?J.C. Whitehead*The University of Manchester, School of Chemistry
Oxford Road, Manchester M13 9PL, Great Britain

* e-mail: j.c.whitehead@manchester.ac.uk

The interaction of plasma with a catalytic material is a complex one about which we have only a little understanding [1]. In plasma-catalyst systems, a gas-phase process occurs more readily and with improved selectivity with an appropriate catalyst. The enhancement in performance that comes from this interaction arises from a range of parameters that when varied affect the physical, electrical and chemical performance of the discharge and may also modify the material properties of the catalyst. These modifications may be transient or longer term. The mechanical construction of the discharge and the way in which the catalyst is introduced to the plasma are of prime importance and their optimisation can be a very significant consideration in the performance of the hybrid plasma-catalyst system. The majority of our knowledge to date comes from experiments in which averaged properties such as product concentrations are measured usually downstream of the process and long-term changes to the catalyst are determined usually post processing. However, we are now able to make real-time, in situ measurements of the electrical properties of the discharge, the identity and behaviour of the chemical species created in the discharge and examine not just the bulk properties of the catalyst but its properties on a meso, nano, even molecular scale and how this affects the plasma-catalyst interactions. We can now describe the interaction of plasma and catalyst as a function of time and distance over a wide measurement scale and move from a description of the steady-state kinetics to the homogeneous and heterogeneous dynamics at molecular level.

[1] Whitehead J C 2016 *J. Physics D: Appl. Phys.* **49** 43001

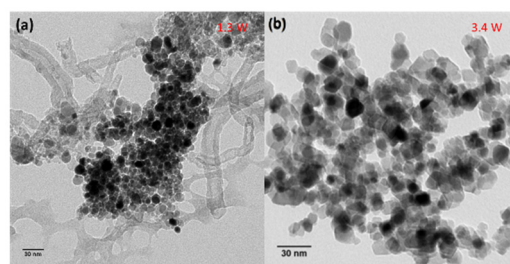
V. Hessel^{1,*}, L. Lin¹, W. Zhang^{1,2}, S.A. Starostine³ and S. Li¹

3 FUJIFILM Manufacturing Europe BV
P.O. Box 90156, Tilburg, The Netherlands

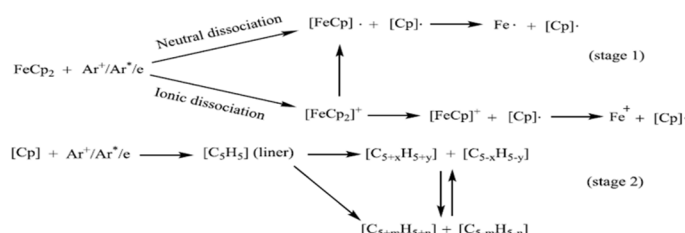
Introduction

Our background is plasma-chemical processing as a holistic process intensification tool and we have investigated the nitrogen fixation and CO₂ conversion. Recently, we developed a multifunctional microplasma system which allows flexible process control, easy assembly and direct product collection for nanomaterials synthesis. Based on this setup, titanium nitride (TiN) [1], iron oxides (Fe₂O₃ and Fe₃O₄) [2], nickel (Ni) and silver (Ag) nanoparticles (NPs) were prepared at very low plasma power consumption. A process-parameter based optimisation, mechanism analysis and the selected applications were investigated.

- The admixture of H_2 in the microplasma system can reduce the TiO_2 content during the TiN NPs synthesis by using $TiCl_4$ as precursor.
- The increase of reaction temperature and power help to enhance the ferrocene dissociation degree, while also lead to larger size particles of the iron oxides NPs.
- Carbon contaminations are suppressed and FCC-Ni NPs are preferentially formed at high plasma power (upper Fig. a and b).
- Using a silver ammonia complex as the precursor for the Ag NPs provides higher reaction efficiency than using silver nitrate.



- TiCl_4 and N_2 are dissociated by electrons and highly reactive species. Atomic Ti or ionised Ti moieties and atomic N radicals are formed in the plasma volume. Recombination reactions between Ti moieties and N radicals lead to the formation of TiN nanoparticles.
- The ferrocene dissociation process includes two stages (lower Fig.): the metal-cyclopentadienyl dissociation stage (stage 1) and the cyclopentadienyl ring dissociation stage (stage 2).

$$\begin{array}{lcl}
 \text{FeCp}_2 + \text{Ar}^+/\text{Ar}^*/\text{e} & \begin{array}{l} \nearrow \text{Neutral dissociation} \\ \searrow \text{Ionic dissociation} \end{array} & \begin{array}{l} [\text{FeCp}] \cdot + [\text{Cp}] \cdot \longrightarrow \text{Fe} \cdot + [\text{Cp}] \cdot \\ [\text{FeCp}_2]^+ \longrightarrow [\text{FeCp}]^+ + [\text{Cp}] \cdot \longrightarrow \text{Fe}^+ + [\text{Cp}] \cdot \end{array} \quad (\text{stage 1}) \\
 \\
 [\text{Cp}] + \text{Ar}^+/\text{Ar}^*/\text{e} & \longrightarrow & [\text{C}_5\text{H}_5] \text{ (liner)} \longrightarrow [\text{C}_{5-x}\text{H}_{5-y}] + [\text{C}_{5-x}\text{H}_{5-y}] \cdot \quad (\text{stage 2})
 \end{array}$$


- Magnetic properties of FCC-Ni NPs are much better than that of HCP-Ni NPs. The prepared magnetic nanomaterials will be used in the magnetic hyperthermia process to kill cancer cells. Other future bionano and marker applications will be presented as well.

Outlook

The process is environmentally friendly, as hardly any additional materials are needed than the reactants. It is chemically flexible as we can conduct both syntheses with gas only and gas-liquid biphasic system. Thus, it offers a wide range of applications for the synthesis and modification of nanostructures with different properties and chemical compositions, i.e., engineered nanomaterials.

- [1] Lin L, Starostin S, Wang Q and Hessel V 2017 *Chem. Engng. J.* **321** 447-457
- [2] Lin L, Starostin S, Hessel V and Wang Q 2017 *Chem .Engng. Sci.* submitted

Acknowledgements. The authors acknowledge the support from Chinese Scholarship Council (CSC) and European LIFE12 ENV_NL_000718 “Green plasma process technology for manufacturing of flexible electronics” project.

PLASMA CATALYSIS, WALKING UP THE THERMODYNAMIC HILL?L. Lefferts*

University of Twente, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, Catalytic Processes and Materials

Drienerlolaan 5, 7522 NB Enschede, The Netherlands

* e-mail: l.lefferts@utwente.nl

This lecture will present recent results on the effect of the placement of a catalyst inside or downstream of a DBD plasma for two hill-up reaction, i.e., non-oxidative coupling of methane and decomposition of CaCO_3 . It will be shown that the catalyst influences the product distribution by interaction with activated species during methane coupling, even when the catalyst is positioned outside the plasma. The energy efficiency of both reactions will be discussed. Furthermore, I am hoping to answer the question whether CaCO_3 decomposition in a DBD plasma is just a thermal effect or not.

NANOSCALE PLASMA PROCESSING FOR ATOMIC ENGINEERING OF NANO CARBON MATERIALS

T. Kato* and T. Kaneko

Tohoku University, Department of Electronic Engineering
Aoba 6-6-05, Aramaki, Aoba-Ku, 980-8579 Sendai, Japan

* e-mail: kato12@ecei.tohoku.ac.jp

Layered-semiconductor materials with atomic thickness attract intense attention due to its outstanding electrical and optical features. Single-walled carbon nanotubes (SWNTs), graphene nanoribbons (GNRs), and transition metal dichalcogenides (TMDs) are known as such atomic-scale and layered-semiconductor materials. Since the electrical and optical features of those materials are sensitive to their atomic structures, structural-controlled synthesis and functionalisation of the layered-semiconductor materials with atomic resolution are crucial issues for the practical use of those novel nanomaterials. We have applied nanoscale plasma processing to solve these problems and realised several innovative syntheses and functionalisation for those nanomaterials. (i) The preferential growth of specific chirality SWNTs has been realised with diffusion plasma CVD. (ii) The integrated synthesis of single crystal and monolayer TMD has also been demonstrated. (iii) A novel method for the integrated synthesis of suspended GNRs is established with rapid heating plasma CVD using Ni nanobar as a catalyst. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The precise tuning of growth conditions is carried out, resulting in the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98 %) (Fig. 1). We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the opto-electrical applications in industrial scale.

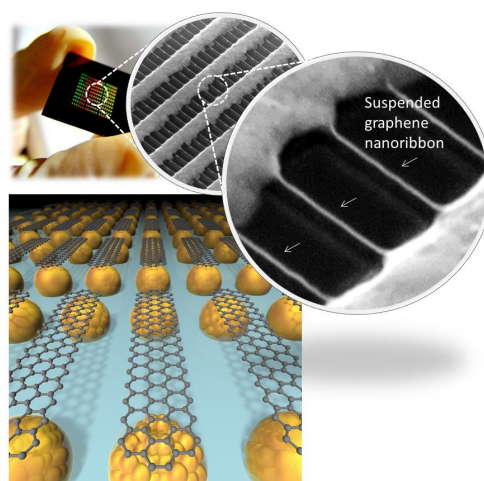


Figure 1. Large scale synthesis of suspended GNR array.

- [1] Kato T and Hatakeyama R 2008 *J. Am. Chem. Soc.* **130** 8101-8107
- [2] Kato T and Hatakeyama R 2010 *ACS Nano* **4** 7395-7400
- [3] Ghorannevis Z, Kato T, Kaneko T and Hatakeyama R 2010 *J. Am. Chem. Soc.* **132** 9570-9572
- [4] Kato T and Hatakeyama R 2012 *Nature Nanotechnol.* **7** 651-656
- [5] Kato T and Hatakeyama R 2012 *ACS Nano* **6** 8508-8515
- [6] Kato T and Kaneko T 2014 *ACS Nano* **8** 12777-12785
- [7] Suzuki H, Kaneko T, Shibuta Y, Ohno M, Maekawa Y and Kato T 2016 *Nature Comm.* **7** 11797-1-10
- [8] Kato T and Kaneko T 2016 *ACS Nano* **10** 9687-9694

PLASMA ENABLED FABRICATION AND APPLICATIONS OF NANOMETAMATERIALS USING POROUS ALUMINA

J. Fang^{1,*}, I. Levchenko², K. Ostrikov³ and D. Jin¹

¹ University of Technology Sydney, Faculty of Science, Institute for Biomedical Materials and Devices
2007 Ultimo, New South Wales, Australia

² NIE, Nanyang Technological University, Plasma Sources and Applications Center
637616 Singapore, Singapore

³ Queensland University of Technology, School of Chemistry, Physics, and Mechanical Engineering
4000 Brisbane, Queensland, Australia

* e-mail: jinghua.fang@uts.edu.au

Engineering a new class of hybrid materials that can enable ultra-sensitive sensors for bio-imaging, gas detection, air and food contamination control is critical to meet the global challenges of environment conservation and efficient use of energy and mineral resources, especially for point-of-use applications. Template-assisted synthesis is an elegant approach for achieving highly-controllable growth of arrays of various nanometamaterials. Anodic aluminium oxide (AAO) membranes are one of best template candidates to fabricate these promising materials such as arrays of carbon related or other noble metal nanotubes [1, 2] and nanowires [3, 4].

In this work, we report on several examples for the growth and functionalisation of nanometamaterials by exposing highly-periodic (hexagonally-symmetrical), porous anodic aluminium oxide templates to a low-temperature plasma. Characterisation using TEM, SEM, and EDS techniques have shown different nanostructures have been fabricated successfully and novel applications such as in gas sensing [5] and plasmonic effects [6] have been demonstrated. With plasma, our environmentally-friendly process is simple, fast and does not involve any pre-treatment for the samples. This novel fabrication and functionalisation technique constitutes another interesting application of alumina templates to different nanometalmaterials growth.

- [1] Gao H, Mu C, Wang F, Xu D, Wu K, Xie Y, Liu S, Wang E, Xu J, Yu D J 2003 *Appl. Phys.* **93** 5602-605
- [2] Sui Y C, Acosta D R, Gonzalez-Leon J A, Bermudez A, Feuchtwanger J, Cui B Z, Flores J O and Saniger J M 2001 *J. Phys. Chem. B* **105** 1523-1527
- [3] Zong R L, Zhou J, Li B, Fu M, Shi S K and Li L T 2005 *J. Chem. Phys.* **123** 094710
- [4] Liu C H, Yiu W C, Au F C K, Ding J X, Lee C S and Lee S T 2009 *Appl. Phys. Lett.* **83** 3168-3170
- [5] Fang J, Levchenko I, Yan W, Aharonovich I, Aramesh M, Prawer S and Ostrikov K 2015 *Adv. Optical Mater.* **3** 750-755
- [6] Fang J, Levchenko I and Ostrikov K 2015 *J. Hydr. Stor.* **40** 6165-6172

SELECTIVE PATTERNED GROWTH OF ZnO NANORODS/NANOSHEETS ON CARBON FABRIC AND THEIR WEARABLE PROPERTIES

P. Veluswamy*, F. Khan, S. Sakamoto, Y Hayakawa and H Ikeda

Shizuoka University, Graduate School of Science and Technology, Research Institute of Electronics

Johoku 3-5-1, Naka-ku, JP-432-8011 Hamamatsu, Shizuoka, Japan

* e-mail: pandiyarasan@yahoo.co.in

The central idea of this paper is to innovate a new approach for the development of wearable device materials through the selective patterned growth coating with ZnO nanostructures. The study was designed in order to have a clear understanding of the role of ZnO nanostructure as well as the modified carbon fabric thereof under investigation. Plasma pre-treated carbon fabric results revealed the uniform ZnO layers on the surface was successfully synthesised via a simple solvothermal method. The growth behaviours were investigated from morphology, structural, chemical composition, optical, electrical and thermos-power properties. It was found that the volume of the zinc nitrate, hexamine and reaction time played important roles for the formation of uniform ZnO coatings on carbon fabric. The ultraviolet ray protection factor (UPF) of the fibre coated with ZnO could reach up to 201.7 but bare carbon fibre will be 28.62, meaning that high concentration hexamine could dramatically enhance the UV-shielding property. Furthermore, the ZnO coated carbon fabric also reported excellent electrical conductivity. The thermos-power value of the ZnO coated carbon fabric could reach $-0.054 \mu\text{VK}^{-1}$. It was expected that such conductive fabric has extensive application in wearable thermoelectric devices.

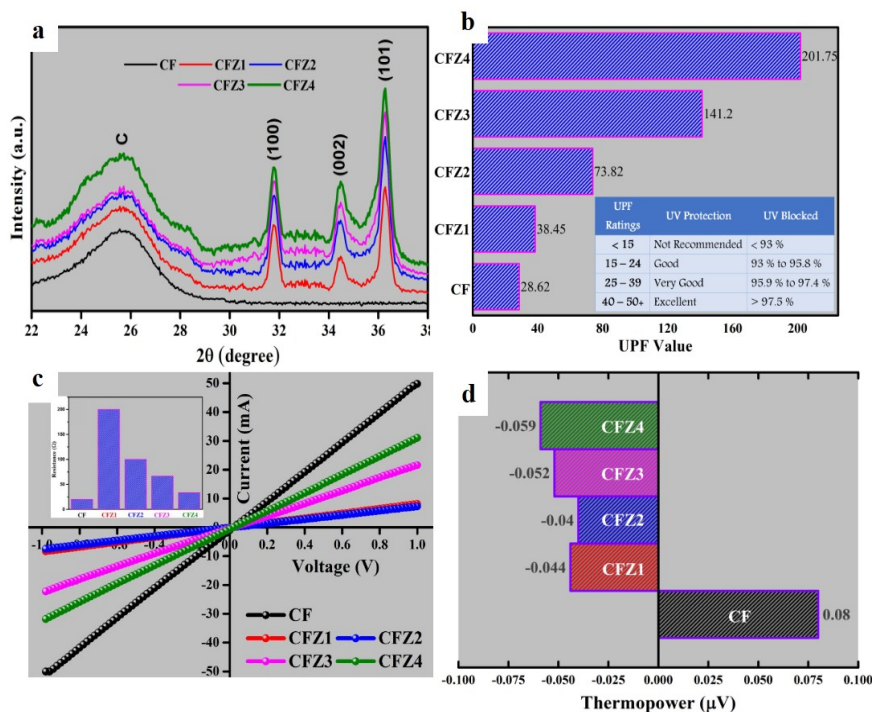


Figure 1. Plasma pre-treated carbon fabric with/without (a) XRD pattern, (b) UV shielding properties, (c) I-V curve (inset: resistance of the prepared samples), and (d) thermoelectromotive force.

- [1] Sun D, *et al.* 2006 *J. Mater. Process Tech.* **173** 172-177
- [2] Ling W, *et al.* 2013 *J. Clean. Prod.* **54** 323-331
- [3] Pandiyarasan V, *et al.* 2017 *Carbohydr. Polym.* **157** 1801-1808

PLASMA CVD GROWN SEMICONDUCTOR METAL OXIDE THIN FILMS AND HETERO-INTERFACES FOR SOLAR HYDROGEN TECHNOLOGIES

S. Mathur*

University of Cologne, Inorganic and Materials Chemistry
Greinstrasse 6, 50939 Cologne, Germany

* e-mail: sanjay.mathur@uni-koeln.de

Metal oxide nanostructures with hetero-contacts and phase boundaries offer unique platform for designing materials architectures for energy harvesting applications. As viable alternative to water electrolysis, photo-electrochemical (PEC) water splitting has emerged as a competitive technology being capable of converting solar energy directly into chemical energy using stable and efficient photo-catalysts for solar hydrogen production. Nanostructured metal oxides and composite materials are promising candidates for effective photo-anodes, which are fabricated using CVD, PE-CVD and ALD techniques for producing multilayered electrodes as oxygen evolution reaction catalysts.

Besides the size and surface effects, the modulation of electronic behaviour due to junction properties leads to modified surface states that promote selective decomposition of analytes and adsorbates. The growing possibilities of engineering nanostructures in various compositions (pure, doped, composites, heterostructures) and forms has intensified the research on the integration of different functional material units in a single architecture to obtain new photo-catalytic materials. In addition, new concepts of enhancing charge transduction by surface functionalisation are promising strategies to promote specific chemical interactions, however the challenge related to reproducible synthesis and device integration of nanomaterials persist. Chemical nanotechnologies have played, in the past few decades a major role in the convergence of life, physical and engineering sciences leading not only to simple collaboration among the disciplines but to a paradigm shift based on true disciplinary integration. This talk will present how chemically grown and designed thin films and bilayers of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies.

PLASMA NANOASSEMBLY AND PLASMA NANOTEXTURING OF POLYMERS: CONTROLLING THE TRANSITION FROM ORDER TO RANDOMNESS TOWARDS VERSATILE APPLICATIONS

A. Smyrnakis, A. Zeniou and E. Gogolides*

NCSR “Demokritos”, Institute of Nanoscience and Nanotechnology

15310 Aghia Paraskevi, Greece

* e-mail: e.gogolides@inn.demokritos.gr

Etching roughness is usually considered as an unwanted issue in plasma processing. However, there are cases, where plasma induced roughness is beneficial and may result in new functional materials with controlled properties [1]. Recently, we demonstrated plasma etching as a tool for surface nanotexturing of organic materials [2], and also as a simple, non-lithographic and low-cost process, to direct the assembly of sub-50 nm periodic dots on any polymeric surface, such as PMMA [3]. In all cases, roughness formation is a result of a combined fast etching of polymer and co-sputtered deposition of material from the reactor walls. In this work, we extend our study on plasma nanoroughening and present the ability to control roughness at will, and in addition to control, the transition from quasi-ordered nanoassembly to random nanotexturing. We propose the use of a new variable electrostatic shield [4], appropriate for both RIE and ICP systems, which allows full control of the flux of co-sputtered atoms from the substrate holder, the clamping ring, the electrode or their combination, ranging from complete elimination of co-sputtering to maximum possible co-sputtering, and, therefore, allows full control of roughness formation during plasma etching. The result is the formation of different surface morphologies ranging from random roughness to ordered polymeric nanodots. Moreover, by varying plasma parameters such as the bias power, etching time and temperature we achieve control over the size of the nanodots. We also examine the use of the fabricated nanodots as an etching mask to transfer the pattern to silicon substrates for the fabrication of Si nanopillars, nanowires or nanotips. These can be used as antireflective surfaces or as moulds for stamping polymeric materials. In addition, applications of the nanotexture in other fields, such as antiwetting, antifouling and antibacterial surfaces will be demonstrated.

- [1] Gogolides E, *et al.* 2011 *J. Phys. D: Appl. Phys.* **44** 174021
- [2] Tsougeni K, *et al.* 2009 *Langmuir* **25** 11748-11759
- [3] Vourdas N, *et al.* 2010 *Nanotechnology* **21** 85302
- [4] Greek Patent application no. 2106503181

SILVER NANOPARTICLE SYNTHESIS AT THE PLASMA-LIQUID INTERFACE: MECHANISTIC INSIGHTS THROUGH MODELLING THE PLASMA-LIQUID INTERFACE

V.S.S.K. Kondeti, U. Gangal and P.J. Bruggeman*

University of Minnesota, Department of Mechanical Engineering

111, Church Street SE, 55414 Minneapolis, MN, U.S.A.

* e-mail: pbruggem@umn.edu

Metal nanoparticles can be generated by the interaction of plasmas with liquids [1]. Plasmas enable the reduction of metal ions and the formed neutral metal atoms subsequently coagulate to form nanoparticles. In this contribution, we report on the synthesis of silver nanoparticles in solutions of AgNO_3 by a pulsed DC driven atmospheric pressure plasma jet operating in helium in contact with the solution.

The plasma generates many reactive species, such as e^- , H, OH, V(UV) photons and others, which could play a role or lead to competing reactions with reducing species that can influence the reduction of the metal ions. The reduction of Ag^+ has often been suggested to be due to plasma produced solvated electrons [2]. However due to the high reactivity of solvated electrons they can react with many other plasma produced species and competing radical-radical reactions at the plasma-liquid interface can strongly impact the reduction process.

In this contribution we investigate the impact of several plasma produced species on the reduction of Ag^+ , the initial step in the formation of the Ag-nanoparticle, through detailed chemical kinetic models of the liquid phase chemistry at the near plasma-liquid interface. The models are also complemented by experimental data on the nanoparticle formation. The study includes a comparison of conditions for which the solution is anode and cathode to assess the influence of electron injection into the liquid. Both transmission electron microscopy and absorption spectroscopy were used to detect the production of the nanoparticles.

The combination of model and experiment shows the importance of H-radicals in the reduction of Ag^+ . The importance of H over solvated electrons for the investigated conditions is due to the large species fluxes of the plasma to the liquid. The large fluxes lead to exceptionally large radical densities at the plasma-liquid interface, conditions for which radical-radical reactions strongly impact the species concentrations. These large radical densities also cause exceptionally large gradients in Ag, Ag^+ and pH near the plasma-liquid interface which has a profound impact on the reduction process. Such gradients have recently been reported even in the case when only electron injection is considered [3].

- [1] Chen Q, Li J and Li Y 2015 *J. Phys. D: Appl. Phys.* **48** 424005
- [2] Richmonds C and Sankaran R M 2008 *Appl. Phys. Lett.* **93** 131501
- [3] Gopalakrishnan R, Kawamura E, Lichtenberg A J, Lieberman M A and Graves D B 2016 *J. Phys. D: Appl. Phys.* **49** 295205

MULTISCALE MODELLING OF PLASMA-DEPOSITED HYDROGENATED AMORPHOUS SILICON FILMS

Z. Marvi^{1,2,*}, S. Xu,² G. Foroutan,³ K. Ostrikov⁴, I. Levchenko^{2,4} and H. Kersten¹

¹ Christian-Albrechts-Universität, IEAP
24098 Kiel, Germany

² Nanyang Technological University, National Institute of Education, Plasma Sources and Applications Centre
1 Nanyang Walk, 637616, Singapore, Singapore

³ Sahand University of Technology, Physics Department
51335-1996 Tabriz, Iran

⁴ Queensland University of Technology, School of Chemistry
4000 Brisbane, QLD, Australia

* e-mail: marvi@physik.uni-kiel.de

A sophisticated multiscale model developed on the basis of self-consistent surface and plasma-kinetics sub-models, including one-dimensional plasma sheath formalisation [1], was used to study the growth of amorphous hydrogenated silicon films in a low-temperature plasma. The model considers a whole range of key processes, the effect of surface temperature, ion flux, energy and other plasma-sheath parameters.

It was found that at $T_s \leq 400$ K and within the reasonable range of ion flux, the surface is primarily covered by SiH_3 radicals. At higher T_s , hydrogen abstraction proceeds via hydrogen attachment to SiH_3 radicals, resulting in fewer higher hydrides on the surface and higher rate of dangling bond (DB) production and film growth (Fig. 1). The hydrogen content in the film decreases with increasing of T_s due to enhancement of thermal H abstraction. This is quite compatible with experimental findings [2].

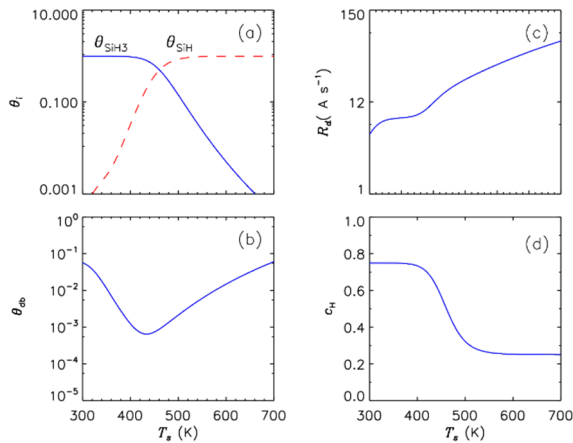


Figure 1. Surface coverage of SiH and SiH_3 (a), DBs (b), growth rate (c), and H content (d), as a function of T_s .

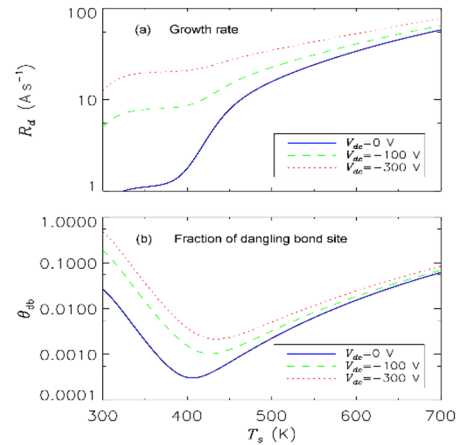


Figure 2. Dependence of (a) growth rate and (b) DBs site on T_s for different V_{dc} .

It was also found that θ_{db} exhibits non-monotonous behaviour with increasing surface temperature, which was explained in terms of combination of H with SiH_3 diffusing on surface, and domination of direct chemisorption over chemisorption of the physisorbed radicals at lower T_s . Such a

non-monotonous dependency is well known for the plasma-surface interaction by adsorption-desorption equilibrium and different reaction channels [3].

Increasing of substrate bias and consequently the ion energy and flux result in the increase of θ_{ab} and R_{d} (Fig.2). The effect of V_{dc} is more pronounced at lower T_{s} which is in good agreement with the relevant experimental results [4].

- [1] Marvi Z, Xu S, Foroutan G and Ostrikov K 2015 *Phys. Plasmas* **22** 13504
- [2] Askari S, Levchenko I, Ostrikov K, Maguire P and Mariotti D 2014 *Appl. Phys. Lett.* **104** 163103
- [3] Deutsch H, Kersten H and Rutscher A 1989 *Contrib. Plasma Phys.* **29** 263-284
- [4] Hishida M, Sekimoto T, Matsumoto M and Terakawa A 2016 *Energies* **9** 42

NANOSTRUCTURES, METAMATERIALS AND NANO-ENGINEERED SURFACES IN PLASMA THRUSTERS: REVIEW AND PERSPECTIVES

I. Levchenko^{1,2,*}, M. Lim¹ and S. Xu¹

¹ Nanyang Technological University, National Institute of Education, Plasma Sources and Applications Centre

1 Nanyang Walk, 637616, Singapore, Singapore

² Queensland University of Technology, School of Chemistry

4000 Brisbane QLD, Australia

* e-mail: levchenko.igor@nie.edu.sg

Efficient and reliable control systems are among the primary prerequisites for the successful cost-effective space exploration. Communication satellites, manned and cargo spacecraft, small satellites for space remote sensing, scientific instrument for the adjacent and deep space exploration – all of them require precise speed and orientation controls capable of long (several years), robust, and highly efficient operation in the adverse open-space conditions. The criterion of the control system efficiency in the terms of lowest required fuel and mass carrier flow rate, along with the energy efficiency, are the main parameters that directly influence the performance of the whole spacecraft. The electric propulsion-based control systems demonstrate superior characteristics, as compared with the compressed gas, liquid propellant and solid-fuelled thrusters. Without any physical limitations to the exhaust gas velocity (whereas any thermal engines are limited to $6,000 \text{ m}\times\text{s}^{-1}$), the electric propulsion systems and thrusters could ensure very mass-efficient operation. Nevertheless, these systems still require significant advance in the energy efficiency, reliability, service life and controllability. New materials, including the nanostructure-based structures and metamaterials, are among the most promising approaches that can help to solve these challenges. In this work we briefly review the unique features of the nanostructure-based materials in the contexts of their application in the electric propulsion systems and thrusters, with a strong focus to the Hall-effect thrusters which are regarded as the most promising candidates for the long-living space systems, spacecraft and satellites. In particular, the application of vertically-aligned nanotube patterns, nanotube- and graphene-based nanomaterials, as well as complex metamaterials involving nanoscaled structures and related physical effects is discussed. Advantages and disadvantages of these systems are considered. Moreover, a concept of the adaptive thruster is proposed capable of self-adjusting the operation mode by synthesising nanomaterials in the discharge, and depositing them to the proper areas of the acceleration channel, thus actively changing the channel wall conductivity and other characteristics influencing the discharge and thruster operation regime.

PERFORMANCE OF Co/CNTs BY HYDROGEN DIELECTRIC-BARRIER DISCHARGE PLASMA FOR FISCHER-TROPSCH SYNTHESIS

Z. Li*, S. Wang, M. Si and J. Lv

Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Chemical Engineering and Technology, Key Laboratory for Green Chemical Technology of Ministry of Education 300072 Tianjin, P.R. China

* e-mail: zhenhua@tju.edu.cn

Fischer–Tropsch (FT) synthesis is an important reaction that can produce hydrocarbons from syngas (CO and H₂) obtained from reforming of natural gas and gasification of coal, heavy oil or biomass. In recent years, increasing demand and fluctuating prices of energy, coupled with unstable fuel supplies and energy security concerns in many countries, have led to increasing interest in FT synthesis. Among the reported catalysts, cobalt catalysts are preferred due to their high productivities, high chain growth probability, high stability, low activity for the water gas shift reaction and lower price compared to noble metals.

In this report, carbon nanotubes (CNTs) supported cobalt catalyst was prepared by hydrogen dielectric-barrier discharge (H₂-DBD) plasma. Compared to the conventional hydrogen reduction method, H₂-DBD plasma treatment can not only decompose the cobalt precursor completely but also reduce the cobalt precursor efficiently at lower temperature with less time. The plasma prepared catalyst shows a similar catalytic performance for Fischer–Tropsch (FT) synthesis with the catalyst treated by conventional hydrogen reduction. This proves that the H₂-DBD plasma is an efficient alternative way to prepare the Co/CNTs catalyst for FT synthesis.

Monday July 3rd, 2017**Poster session I: Plasma catalysis and nanomaterials**

1. Damien U.B. Aussems: Atomistic simulations of graphite etching at realistic time-scales
2. Kristof M. Bal: Effect of plasma surface charging on the catalytic decomposition of carbon dioxide
3. Sotheara Chuon: Contribution to the CFD simulation of a magnetron discharge
4. Nathalie De Geyter: Study on plasma-induced modifications on pre-electrospinning polymer solutions and resultant nanofibres
5. Neda HafezKhiabani: Plasma-based conversion of CO₂ in a packed dielectric barrier discharge using coated silica spheres
6. Stijn Huygh: Insight in the surface reactions of the plasma catalytic dry reforming of methane on anatase (001)
7. Kenji Ishikawa: Programmed process for synthesis of calcium oxalate crystals in a buffered glucose solution by irradiation with non-equilibrium atmospheric-pressure plasma
8. Umedjon Khalilov: The role of hydrogen in the plasma modification of nanostructures
9. Igor Levchenko: Nanostructures, metamaterials and nano-engineered surfaces in plasma thrusters: review and perspectives
10. Alexander Parastaev: UV-Vis spectroscopy as a tool for in situ monitoring of catalyst temperature in a dielectric barrier discharge reactor
11. Harinarayan Puliylalil: Plasma catalysis for the efficient conversion of methane into valuable chemicals
12. Marleen Ramakers: Using a gliding arc plasmatron for CO₂ conversion
13. Jiann Shieh: Using plasma activation and platinum catalyst to grow carbon nanotubes at low temperature
14. Hiroo Suzuki: Wafer-scale integration of suspended graphene nanoribbon and its non-volatile optical memory operation
15. Charlotte Vets: Thermodynamic screening of bimetallic nanoparticles for chirality-selective carbon nanotube growth
16. Shengping Wang: Enhancement of CO₂ methanation performance on Ni/Al₂O₃ catalyst by plasma treatment
17. Bin Xu: Catalyst surface state control towards chirality controlled synthesis of single-walled carbon nanotube with plasma CVD
28. Anathasios Smyrnakis: Towards superhydrophobic polymers via atmospheric pressure plasma etching

ATOMISTIC SIMULATIONS OF GRAPHITE ETCHING AT REALISTIC TIME-SCALES

D.U.B. Aussems^{1,*}, K.M. Bal², T.W. Morgan¹, M.C.M. van de Sanden^{1,3} and E.C. Neyts²

¹ Dutch Institute for Fundamental Energy Research (DIFFER), Association EURATOM-FOM, Trilateral Euregio Cluster

De Zaale 20, 5612 AJ Eindhoven, The Netherlands

² University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

³ Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

* e-mail: d.aussems@diffier.nl

Hydrogen-graphite interactions are relevant to a wide variety of applications, ranging from astrophysics to fusion devices and nanoelectronics. To understand these interactions, atomistic simulation by Molecular Dynamics (MD) has shown to be an invaluable tool. MD, however, suffers from severe time-scale limitations. In this work we employ a novel method, collective variable-driven hyperdynamics (CVHD) [1] to extend the time-scale between impacts to a realistic value of 1 ms (flux of $10^{20} \text{ m}^{-2}\text{s}^{-1}$). The results show that the erosion yield, hydrogen surface coverage and species distribution are significantly affected by the time between impacts. This can be explained by the higher probability for C-C bond breaking due to the prolonged exposure to thermal stress, and the subsequent transition from ion- to thermal-induced etching. Remarkably, this latter regime of thermal-induced etching – chemical erosion – was accessed for the first time using atomistic simulations. In conclusion, this study demonstrates that accounting for long time-scales significantly affects ion bombardment simulations and may not be neglected in a wide range of conditions, in contrast to what is typically assumed.

[1] Bal K M and Neyts E C 2015 *J. Chem. Theory Comput.* **11** 4545

EFFECT OF PLASMA SURFACE CHARGING ON THE CATALYTIC DECOMPOSITION OF CARBON DIOXIDE

K.M. Bal*, S. Huygh and E.C. Neyts

University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: kristof.bal@uantwerpen.be

The microscopic mechanisms of the plasma-catalyst interactions in plasma-assisted catalysis remain largely unknown [1]. Compared to traditional thermal catalysis, any surface in contact with a plasma carries a sizable negative surface charge [2, 3]. These excess electrons modify the electronic structure of the exposed catalyst, which can be expected to have an impact on its chemical properties, but the precise effect of this phenomenon on the catalytic process has not yet been investigated [4]. In this contribution, we report on density functional calculations investigating the effect of a negative catalyst surface charge on the stability and activity of nanostructured single-atom transition metal catalysts ($M = \text{Ti, Ni, Cu}$) supported on Al_2O_3 , focussing on the energetics of CO_2 decomposition. The presence of a negative surface charge is found to increase the reductive power of the catalyst, therefore promoting the splitting of CO_2 to CO and oxygen. The relative activity of the investigated transition metals is also changed upon charging, suggesting controlled plasma-induced surface charging as a powerful additional parameter to tune catalyst activity and selectivity.

- [1] Neyts E C, Ostrikov K, Sunkara M K and Bogaerts A 2015 *Chem. Rev.* **115** 13408
- [2] Heinisch R L, Bronold F X and Fehske H 2012 *Phys. Rev. B* **85** 075323
- [3] Peeters F J J, Rumphorst R F and van de Sanden M C M 2016 *Plasma Sources Sci. Technol.* **25** 03LT03
- [4] Neyts E C 2016 *Plasma Chem. Plasma Process.* **36** 185

Acknowledgements. K.M.B. is funded as PhD fellow (aspirant) of the FWO-Flanders (Fund for Scientific Research-Flanders), Grant 11V8915N. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation - Flanders (FWO) and the Flemish Government – department EWI.

CONTRIBUTION TO THE CFD SIMULATION OF A MAGNETRON DISCHARGE

S. Chuon^{1,*}, J.-M. Bauchire¹, P. Brault¹ and E.C. Neyts²

¹ CNRS / Université d'Orléans, GREMI, UMR 7344

14 rue d'Issoudun, P.O. Box 6744, 45067 Orléans Cedex 2, France

² University of Antwerp, Department of Chemistry, Research Group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: sotheara.chuon@univ-orleans.fr

Sputtering deposition is used nowadays for coating synthesis in several domains (i.e., mechanic, optic, electronic...). Magnetron sputtering process allows the synthesis of dense coating and an increase of deposition rate thanks to higher electron collision frequency due to the magnetic field [1]. To better understand discharge phenomena, numerical simulations associated with experimental results appear as a reliable tool. Moreover, numerical simulations allow system behaviour prediction and thus to find optimal operating conditions for experimentations. Different models with analytic, continuum or fluid, particle and hybrid approach can be used [2, 3]. Among those, Particle-In-Cell/Monte Carlo Collision (PIC-MCC) is the most common despite the computing time drawbacks.

In this work, a DC magnetron discharge is simulated in a region close to the cylindrical symmetric target (size of the two-dimensional limited region perpendicular to the target 26.95×26.95 mm). The numerical simulation is performed using COMSOL Multiphysics[®] software and based on the theoretical model from Costin *et al.* [4]. This model allows the description of the evolution of the magnetron discharge parameters as the magnetic field, the electric potential, the electrons and ions densities and the mean energy.

The transport of the electrons and the positive ions is described by the first three moments of the Boltzmann equation: continuity, momentum transfer and mean energy transfer (only for electrons), coupled with the Poisson equation. The coupling with the magnetic field requires some assumptions: classical drift-diffusion expressions are used for fluxes in transport equations. In this case, the influence of the magnetic field is introduced in the electron flux and an effective electric field is considered for ions.

The results obtained will then be coupled, in further work, with Molecular Dynamic (MD) simulations applied to the target and the deposition process in order to build a multi-scale approach of the magnetron sputtering process.

[1] Swan S 1988 *Phys. Technol.* **19** 67-75

[2] Kondo S and Nanbu K 1999 *J. Phys. Appl. Phys.* **32** 1142-1152

[3] Kadlec S 2007 *Surf. Coat. Technol.* **202** 895-903

[4] Costin C, Marques L, Popa G and Gousset G 2005 *Plasma Sources Sci. Technol.* **14** 168-176

STUDY ON PLASMA-INDUCED MODIFICATIONS ON PRE-ELECTROSPINNING POLYMER SOLUTIONS AND RESULTANT NANOFIBRES

F. Rezaei, R. Morent and N. De Geyter*

Ghent University, Faculty of Engineering and Architecture, Department of Applied Physics, Research Unit Plasma Technology (RUPT)

St. Pietersnieuwstraat 41 B4, 9000 Ghent, Belgium

* e-mail: nathalie.degeyter@ugent.be

Electrospinning makes use of electrostatic forces to create a thin jet of a polymer solution. When the electric field overcomes the surface tension of the droplets of the polymer solution, a charged jet forms and nanofibres will collect on a collecting plate due to solvent evaporation [1]. Research on nanofibres has been strongly increasing due to the fact that they can be used in several applications, ranging from textile to biomedical applications. Smooth, continuous and “bead-free” nanofibres are desirable for the most effective use of nanofibrous mats. Formation of such fibres depends on many factors including “fixed parameters” such as molecular weight of the polymer and polymer solution properties (like viscosity, concentration of the solution, electrical conductivity, surface tension), and also “variable parameters” such as the applied electric potential, flow rate of the polymer solution, distance between the needle and the collecting plate, the motion of the collecting plate, and environmental conditions. Poly lactic acid (PLA) is a semi-crystalline polymer, which is broadly used in various biomedical applications and clinical uses due to its biodegradability, biocompatibility, and good mechanical properties [2]. In this study, an atmospheric-pressure argon plasma jet is used for the modification of PLA dissolved in a chloroform/dimethylformamide mixture with 6 % w/v concentration to enhance the electro-spinnability of the polymer solution. Plasma treatments are carried out with various exposure times and the viscosity, surface tension, and conductivity of the solutions is measured before and after plasma treatment. Optical emission spectroscopy (OES) is also performed during plasma treatment to investigate the characteristics of the atmospheric plasma jet generated in the solution. The plasma-modified and the untreated solutions are then used to produce nanofibres making use of electrospinning. The morphology and chemical structure of produced nanofibrous mats are examined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively.

[1] Chronakis I 2005 *J. Mater. Process. Technol.* **167** 283-293

[2] Cui W, Li X, Zhu X, Yu G, Zhou S and Weng J 2006 *J. Biomacromolecules* **7** 1623-1629

Acknowledgements. This research was supported by a research grant (G.0379.15N) from the Research Foundation Flanders (FWO) and has also received funding from the European Research Council (ERC) under the European Union’s Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement no. 279022 (PLASMAPOR) and ERC Grant Agreement no. 335929 (PLASMATS).

PLASMA-BASED CONVERSION OF CO₂ IN A PACKED DIELECTRIC BARRIER DISCHARGE USING COATED SILICA SPHERES

N. HafezKhiabani^{1,*}, V. Meynen² and A. Bogaerts¹

¹ University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

² University of Antwerp, Department of Chemistry, Laboratory of Adsorption and Catalysis
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: neda.hafezkhiani@uantwerpen.be

The effect of different titania, Ti-zeolites and alumina coated silica spheres has been studied in CO₂ conversion in a cylindrical dielectric barrier discharge. Spray coating of different powder suspensions on silica spheres was used to make core shell spheres by means of a pan coater (Fig. 1a).

To investigate the porosity and apparent surface area effect, nitrogen and argon volumetric sorption was carried out. SEM was also used to determine the pore size of the macroporous shells. UV-Vis diffuse reflectance measurements were applied to determine the photon induced electronic transitions of the materials. In order to access the structure and crystallinity of the core-shells, Raman spectroscopy and X-ray diffraction were applied.

The core-shell materials were tested in the DBD (Fig. 1b) to assess the impact of the shell material and shell thickness on the CO₂ conversion to CO and oxygen and its energy efficiency. Different coated spheres yielded different CO₂ conversion and energy efficiency in the plasma. This research is of interest for gaining more insight in the underlying physical and chemical effects of plasma catalysis.

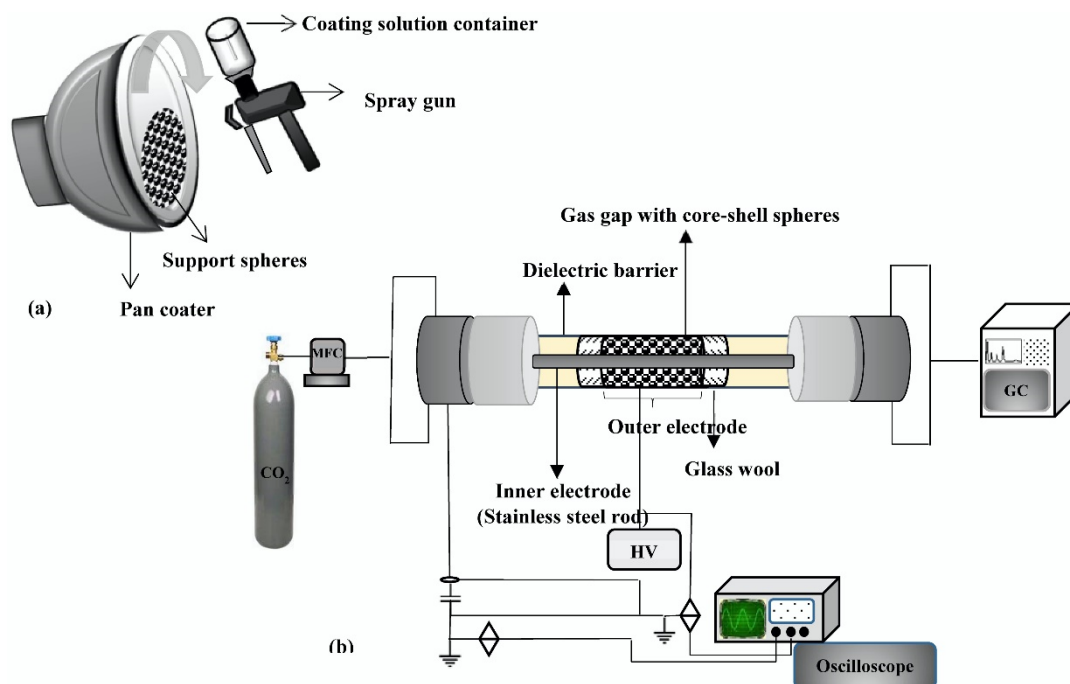


Figure 1. Schematic set up: (a) spray coating, (b) packed DBD plasma reactor.

Acknowledgements. This research was supported by the IOF-SBO "SynCO₂Chem" and the FWO "G.0254.14N" projects.

INSIGHT IN THE SURFACE REACTIONS OF THE PLASMA CATALYTIC DRY REFORMING OF METHANE ON ANATASE (001)

S. Huygh*, A. Bogaerts and E.C. Neyts

University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: stijn.huygh@uantwerpen.be

The conversion of greenhouse gases is a possible mitigation strategy for global climate changes. Conventional conversion methods of greenhouse gases have their disadvantages, such as a high energy requirement, sintering, and coke formation of the employed catalysts. It has been suggested that plasma-catalysis (PC) is a promising alternative to conventional reforming. The plasma will activate the feed gas by electron impact reactions, while the catalyst will lower the energy barrier for surface reactions. The hybridisation of a plasma with a catalyst can possibly result in synergistic effects due to the interactions of the plasma with the catalyst and vice versa. Due to the high complexity of the PC-system, there is still a lack of fundamental knowledge on the plasma-surface interactions. We studied the adsorption, desorption and surface reactions for the plasma catalytic DRM on TiO₂ anatase (001) surface using Density Functional Theory calculations. The results of this study show a significant decrease in the temperature threshold of the overall reaction, as the rate limiting dissociative adsorption of CH₄ in thermal reforming can be circumvented. This results from the availability of plasma generated methane derived radicals, which exhibit a higher adsorption rate than methane. Furthermore, coke formation, a typical problem in thermal DRM on nickel, will not be present on the TiO₂ surface. Within the PC-DRM methane derived radicals will form oxygenated products, which generate oxygen vacancies required for the reduction of CO₂. Based on the studied reaction mechanisms for the PC-DRM, we found that, in theory, it is possible to control and steer the reforming towards a desired composition of output gas by adjusting the temperature and plasma properties. Within the PC reforming the range in which the temperature can be adjusted is increased compared to thermal reforming, as the rate limiting adsorption of methane and coke formation are removed.

PROGRAMMED PROCESS FOR SYNTHESIS OF CALCIUM OXALATE CRYSTALS IN A BUFFERED GLUCOSE SOLUTION BY IRRADIATION WITH NON-EQUILIBRIUM ATMOSPHERIC-PRESSURE PLASMA

K. Ishikawa^{1,*}, N. Kurake¹, H. Tanaka¹, K. Nakamura², H. Kajiyama², F. Kikkawa², M. Mizuno², Y. Yamanishi³, Y. Ikehara⁴ and M. Hori¹

¹ Nagoya University, Graduate School of Engineering
Furo-cho, Chikusa, 484-8603 Nagoya Aichi, Japan

² Nagoya University, Graduate School of Medicine
65 Tsurumai, Showa, 466-8560 Nagoya Aichi, Japan

³ Kyushu University, Graduate School of Engineering
819-0395 Fukuoka, Japan

⁴ National Institute of Advanced Industrial Science and Technology
1-1-1 Higashi, 305-8561 Tsukuba, Ibaraki, Japan

* e-mail: ishikawa.kenji@nagoya-u.jp

Octahedral particulates several tens of microns in size were synthesized in a culture medium irradiated through contact with a plume of non-equilibrium atmospheric-pressure plasma (NEAPP). The particulates were identified in the crystalline phase as calcium oxalate dihydrate (COD) but thermodynamically stable calcium oxalate monohydrate (COM). The original medium contained constituents such as NaCl, D-glucose, CaCl₂, and NaHCO₃ but not oxalate or oxalic acid. The oxalate was clearly synthesized and crystallised in the medium as thermodynamically unstable COD crystals after the NEAPP irradiation.[1]

Plasma irradiation has also been shown to induce the crystallisation of proteins. For example, the crystallisation of a lysozyme in solution following plasma irradiation was reported [2]. We have recently reported the crystallisation of urinary stone-forming salts in plasma-irradiated solutions. Urinary stone-forming salts can be maintained in solution to the point of supersaturation; the precipitation of these salts is due to the failure of colloids to hold them in solution. Urinary stones are composed of ~80 % crystals of calcium salts (e.g., calcium oxalate or calcium phosphate). In general, it is not possible to synthesize artificial urine by mixing urinary crystalloids in the proportions in which they are normally found. The supersaturation of urine can be possible to control under a programmed process for stone formation in the plasma irradiated solution.

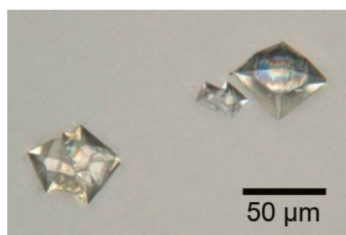


Figure 1. Morphology of the particulates synthesized during 24 h incubation [1].

[1] Kurake N, *et al.* 2016 *Appl. Phys. Express* **9** 096201

[2] Ito T, *et al.* 2011 *Appl. Phys. Express* **4** 026201

Acknowledgements. The authors would like to thank Profs H. Hashizume, K. Takeda, T. Tsutsumi, H. Kondo, and M. Sekine. This study was supported in part by MEXT KAKENHI Grant-in-Aid for Scientific Research on Innovative Areas (No. 24108002).

THE ROLE OF HYDROGEN IN THE PLASMA MODIFICATION OF NANOSTRUCTURES

U. Khalilov*, A. Bogaerts and E.C. Neyts

University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: umedjon.khalilov@uantwerpen.be

Precise control over the nucleation/growth of carbon nanotubes (CNTs) or the oxidation of Si nanowires (SiNWs) would enable their wide-scale use in a variety of electronic applications [1, 2]. While the plasma modification is a promising technique to obtain such nanostructures, the partial role of plasma species and thus the underline mechanisms are not properly understood.

Therefore, we study the role of H-radical as a plasma species using hybrid MD/MC simulation technique with experimental supports. In particular, we found that the H-effects such as dehydrogenation, rehydrogenation, and H etching can clarify a number of experimental observations on the CNT nucleation from hydrocarbon (C_xH_y) feedstocks: (1) the appearance of unstable carbon protrusions in *in-situ* TEM-observations; (2) the onset of MWNT nucleation in the case of low temperature and high H flux; and (3) the lower growth rate [1]. Also, the etching process of a carbon cap in a H_2 -plasma is similar to (the opposite of) the cap formation process in C_xH_y -based SWNT nucleation [3]. However, the etching onset of CNT is not similar to the etching character of a carbon cap. During the adsorption of H atoms and their coalescence, adsorbed ortho hydrogen pairs on CNTs induce higher shear stresses than axial stresses, leading to the elongation of HC-CH bonds. Indeed, the ortho H pairs more perpendicular to the tube axis ($\gamma \rightarrow 0^\circ$) are responsible for C-C bond breaking in CNTs. Consequently, this phenomenon leads to understand the onset of the selective etching of CNT using H_2 -plasma [4].

In the restructuring of the deposited Ni thin film, while the number of larger clusters subsequently increases and small clusters simultaneously disappear due to Ostwald ripening, the small nanoclusters remain in the case of H_2 plasma. It can be explained that the Ostwald ripening discontinues or is at least slowed down due to the H-termination of nanoclusters in the plasma regime [5].

We also studied the nanoscale mechanisms for room temperature SiNW oxidation by selected H-based plasma species. The hydroxylation processes were studied by monitoring the silanol (SiOH) and siloxane (SiOSi) groups in the SiNWs as well as the formed water (H_2O) molecules desorbing from the nanowire. The results demonstrate how the self-limiting oxidation behaviour depends on the oxidising plasma species [1].

In general, the obtained results strongly indicate that the precise control of H-concentration leads to control over the plasma modification of nanostructures.

- [1] Khalilov U, Bogaerts A and Neyts E C 2015 *Nat. Commun.* **6** 10306
- [2] Khalilov U, Bogaerts A and Neyts E C 2017 *Acc. Chem. Res.* **50** 796-804
- [3] Khalilov U, Bogaerts A and Neyts E C 2017 *Carbon* **118** 452-457
- [4] Khalilov U, Bogaerts A, Xu B, Kato T, Kaneko T and Neyts E C 2017 *Nanoscale* **9** 1653
- [5] Khalilov U, Bogaerts A, Hussain S, Kovacevic E, Brault P, Boulmer-Leborgne C and Neyts E C 2017 *J. Phys. D: Appl. Phys* **50** 184001

NANOSTRUCTURES, METAMATERIALS AND NANO-ENGINEERED SURFACES IN PLASMA THRUSTERS: REVIEW AND PERSPECTIVES

I. Levchenko^{1,2,*}, M. Lim¹ and S. Xu¹

¹ Nanyang Technological University, National Institute of Education, Plasma Sources and Applications Centre
1 Nanyang Walk, 637616, Singapore, Singapore

² Queensland University of Technology, School of Chemistry
4000 Brisbane QLD, Australia

* e-mail: levchenko.igor@nie.edu.sg

Efficient and reliable control systems are among the primary prerequisites for the successful cost-effective space exploration. Communication satellites, manned and cargo spacecraft, small satellites for space remote sensing, scientific instrument for the adjacent and deep space exploration – all of them require precise speed and orientation controls capable of long (several years), robust, and highly efficient operation in the adverse open-space conditions. The criterion of the control system efficiency in the terms of lowest required fuel and mass carrier flow rate, along with the energy efficiency, are the main parameters that directly influence the performance of the whole spacecraft. The electric propulsion-based control systems demonstrate superior characteristics, as compared with the compressed gas, liquid propellant and solid-fuelled thrusters. Without any physical limitations to the exhaust gas velocity (whereas any thermal engines are limited to $6,000 \text{ m}\times\text{s}^{-1}$), the electric propulsion systems and thrusters could ensure very mass-efficient operation. Nevertheless, these systems still require significant advance in the energy efficiency, reliability, service life and controllability. New materials, including the nanostructure-based structures and metamaterials, are among the most promising approaches that can help to solve these challenges. In this work we briefly review the unique features of the nanostructure-based materials in the contexts of their application in the electric propulsion systems and thrusters, with a strong focus to the Hall-effect thrusters which are regarded as the most promising candidates for the long-living space systems, spacecraft and satellites. In particular, the application of vertically-aligned nanotube patterns, nanotube- and graphene-based nanomaterials, as well as complex metamaterials involving nanoscaled structures and related physical effects is discussed. Advantages and disadvantages of these systems are considered. Moreover, a concept of the adaptive thruster is proposed capable of self-adjusting the operation mode by synthesising nanomaterials in the discharge, and depositing them to the proper areas of the acceleration channel, thus actively changing the channel wall conductivity and other characteristics influencing the discharge and thruster operation regime.

UV-VIS SPECTROSCOPY AS A TOOL FOR IN SITU MONITORING OF CATALYST TEMPERATURE IN A DIELECTRIC BARRIER DISCHARGE REACTOR

A. Parastaev*, A. Litke and E.J.M. Hensen

Eindhoven University of Technology, Inorganic Materials Chemistry group

5600 MB Eindhoven, The Netherlands

* e-mail: a.parastaev@tue.nl

Carrying out heterogeneous reactions in a plasma offers an alternative to thermal catalysis. Synergy between the plasma and the solid catalyst results in novel process windows allowing increased performance and energy efficiency. It is also argued to provide a way of converting surplus electricity in chemical energy. Until now, there is only limited mechanistic insight into the synergy between heterogeneous catalysts and plasma. Accurate comparison between plasma-catalytic and thermocatalytic reactions is often hampered because of the intricate complex nature of the plasma-catalyst system. The properties of the plasma depend on the filling material, usually comprising also the catalyst (e.g., increasing the dielectric constant enhances the electric field) [1], while on the other hand the permittivity and polarisation of the catalyst depend on the plasma parameters. A more solid understanding of the interplay between plasma and catalytic solids would be enabling towards further development of efficient plasma-catalytic processes.

A well-known complication in plasma-catalysis involves catalyst overheating, an effect which is relevant in the evaluation of plasma-catalytic performance. Measuring the temperature with a thermocouple in a high voltage environment cannot be done during the plasma-catalytic reaction and is therefore usually done after the plasma has been switched off. We recorded overheating profiles of various filling materials in the reactor upon exposure to CO₂ plasma with a conventional thermocouple and UV-Vis spectroscopy (Fig. 1). We use TiO₂ and SrTiO₃, not only because of their useful dielectric properties ($\epsilon(\text{TiO}_2) = 86$ and 170 , $\epsilon(\text{SrTiO}_3) = 310$) in the plasma context but also because of their optical properties. TiO₂ and SrTiO₃ exhibit a temperature dependent refractive index [2], which can be exploited to determine catalyst temperature *in situ*, without inserting a sensor inside the discharge zone. We used these solids to study plasma-catalytic CO₂ dissociation and hydrogenation.

Here we have presented a new method to estimate the overheating contribution of different catalytic supports for plasma-assisted reactions. The effects of overheating during plasma-catalysis have to be taken into account when comparing plasma-catalysts. Using this novel approach in combination with spectroscopy, it is possible to compare the activity and selectivity of catalysts in plasma-catalytic processes, and to evaluate the impact of plasma properties on these processes.

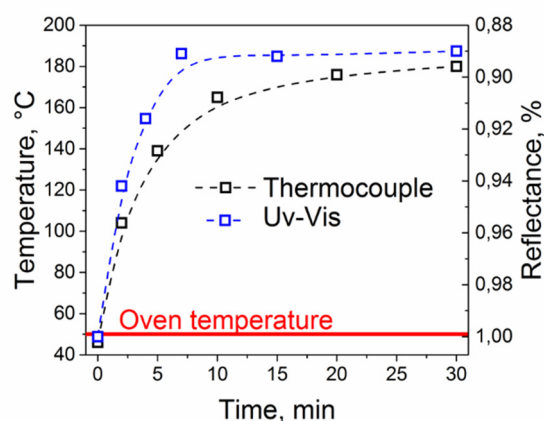


Figure 1. Temperature profile of r-TiO₂ at 50 °C of the oven at 1 kHz and 20 kV.

- [1] Van Laer K and Bogaerts A 2017 *Plasma Process. Polym.* **14** 1600129
- [2] Toyoda T and Yabe M 1983 *J. Phys. D: Appl. Phys.* **16** 251-255

PLASMA CATALYSIS FOR THE EFFICIENT CONVERSION OF METHANE INTO VALUABLE CHEMICALS

H. Puliyalil*, D.L. Jurković, A. Pohar and B. Likozar

National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering
Hajdrihova 19, 1000 Ljubljana, Slovenia

* e-mail: hari.puliyalil@ki.si

Motivated by the advantages of vast availability and lower emission of toxic gases compared to other fossil fuels, natural gas consumption has increased remarkably. Most of the natural gas deposits are in remote areas that demands long distance transportation to make it available in the market. However, due to high flammability and volatile nature, oxidative upgrading of methane into liquid chemicals has achieved significant attention. Conventionally used catalytic conversion has the disadvantages of carbon deposition and associated catalyst deactivation, high temperature operation and slow switch on and off time. These disadvantages could be overcome by using the methodology of low temperature plasma oxidation of methane with an active catalyst in the discharge zone [1].

Primarily, CO₂ reforming of CH₄ to syngas was carried out in a spark discharge in the presence and absence of an active Ni catalyst. The effects of plasma-catalyst synergy on the feeding gas conversion rate and syngas selectivity were studied. However, single step conversion of CH₄ to liquid chemicals is of greater interest compared to the syngas route. For this, controlled oxidation of CH₄ with O₂ was achieved inside an atmospheric pressure dielectric barrier discharge incorporated with various substrates including glass beads, zeolites, alumina and various active metals on these substrates. By combining the synergy between the plasma and the embedded material, a mixture of value added chemicals including methanol, formaldehyde and carboxylic acids were yielded. The liquid products obtained were then analysed and quantified by using standardized HPLC, whereas conversion rate and the yield of gaseous products were monitored with the help of micro GC gas analyser. Both the processes were optimized for various parameters such as gas flow rate, feeding gas ratio and plasma discharge power.

[1] De Bie C, van Dijk J and Bogaerts A 2015 *J. Phys. Chem. C* **119** 22331-22350

Acknowledgements. The authors gratefully acknowledge the European Commission, as the work was partially established within the ADREM project. This project has received funding through a Sustainable Process Industry through Resources an Energy Efficiency (SPIRE) call under the European Union's Horizon 2020 research and innovation programme (grant agreement no 680777).

USING A GLIDING ARC PLASMATRON FOR CO₂ CONVERSION

M. Ramakers*, G. Trenchev and A. Bogaerts

University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: marleen.ramakers@uantwerpen.be

There has been increased interest in the conversion of CO₂ by plasma to produce value-added chemicals and store renewable energy in chemicals [1]. Several types of plasmas have been applied for CO₂ conversion, but most research is carried out with one of the following types of plasmas: dielectric barrier discharges (DBDs) [2], microwave plasmas [3], and gliding arc discharges [4]. The latter are very promising in terms of energy efficiency.

In this work a gliding arc plasmatron is used to study CO₂ conversion. This is a three-dimensional gliding arc reactor in which the gas enters through a tangential inlet so that a vortex flow is obtained. A diagram of the experimental system is shown in Fig. 1. A mass flow controller is used to insert CO₂ into the gliding arc plasmatron. The reactor is powered by a DC current source type power supply. The plasma voltage and current are measured by a high voltage probe (Tek P6015A) and a current sense resistor of 10 Ω , respectively. With these values the plasma power can be calculated. In the reactor tube, which is placed after the gliding arc plasmatron, a thermocouple is inserted to measure the temperature of the out coming gas. The output gas composition is analysed online by gas chromatography.

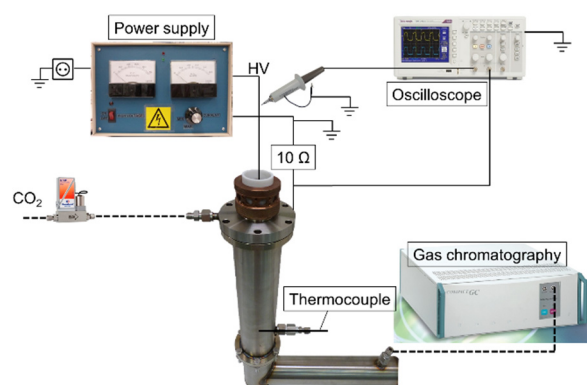


Figure 1. Schematics of the experimental system.

The main goal of this research is to obtain a better understanding of CO₂ conversion in this type of plasma reactor and how this process can operate in an energy-efficient way for industrial implementation of this technique. More particularly, the effect of the applied power and flow rate on CO₂ conversion and energy efficiency are studied. Furthermore, the influence of the electrode geometry is investigated in order to determine the effect of the vortex flow on CO₂ splitting.

- [1] Fridman A 2008 *Plasma chemistry*. (Cambridge: Cambridge University Press)
- [2] Wang S, Zhang Y, Liu X and Wang X 2012 *Plasma Chem. Plasma Process.* **32** 979
- [3] Spencer L F and Gallimore A D 2013 *Plasma Sources Sci. Technol.* **22** 015019
- [4] Nunnally T, Gutsol K, Rabinovich A, Fridman A, Gutsol A and Kemoun A J 2011 *J. Phys. D: Appl. Phys.* **44** 274009

USING PLASMA ACTIVATION AND PLATINUM CATALYST TO GROW CARBON NANOTUBES AT LOW TEMPERATURE

H.-Y. Lee, Y.-C. Huang and J. Shieh*

National United University, Department of Materials Science and Engineering,
2 Lienda, 36063 Miaoli, Taiwan

* e-mail: jshieh@nuu.edu.tw

Due to their excellent properties, carbon nanotubes (CNTs) have been widely studied for many years. To apply carbon nanotubes to electronic devices, however, low-temperature growth [1] without magnetic catalyst [2] remains a challenge. In this paper, we tried to fabricate CNTs with Pt catalyst at temperature as low as possible by plasma CVD. The key process is to transfer platinum film into nanoparticle morphology by plasma activation. The results show that without plasma treatment, carbon nanostructures sprouted but further growth was limited. As a low-temperature H_2/Ar plasma was applied to treat the catalyst for 10 min in advance, CNTs can be synthesized at 280 °C between silicon nanopillars (Fig. 1). Moreover, the density of CNTs increased with the duration of plasma treatment. Figure 2 shows that abundant CNTs were successfully synthesized by Pt catalyst at 250 °C as the pretreatment was extended to 30 min. These results suggest that it is possible to grow CNTs at low temperature through the assistance of plasma pretreatment and platinum nanoparticles, which is helpful in the developing of CNT-based nanodevices such as CNT/Si heterojunction solar cells [3].

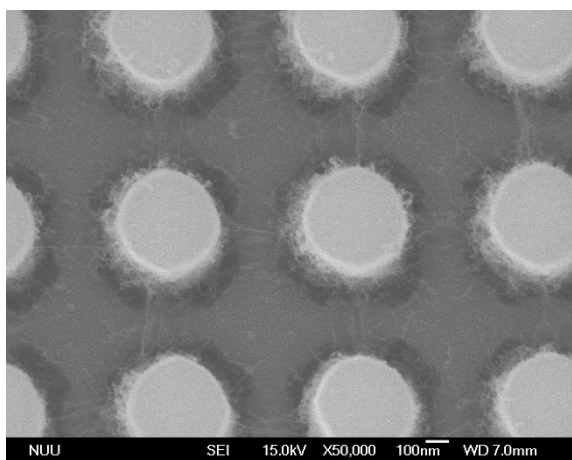


Figure 1. Carbon nanotubes grown at 280 °C between Si nanopillars.

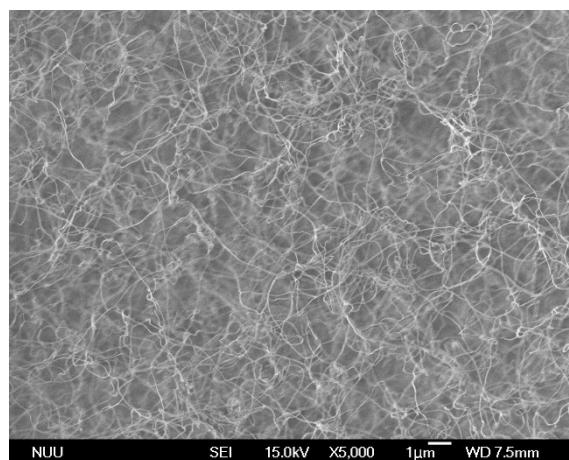


Figure 2. Abundant carbon nanotubes grown at lower temperature by longer plasma pretreatment.

- [1] Meyyappan M 2009 *J. Phys. D: Appl. Phys.* **42** 213001
- [2] Takagi D, Homma Y, Hibino H, Suzuki S and Kobayashi Y 2006 *Nano Lett.* **6** 2642
- [3] Shi E, Zhang L, Li Z, Li P, Shang Y, Jia Y, Wei J, Wang K, Zhu H, Wu D, Zhang S and Cao A 2012 *Sci. Rep.* **2** 884

Acknowledgements. We thank the Ministry of Science and Technology of Taiwan for financial support (grant no. MOST 104-2628-E-239-001-MY3).

WAFER-SCALE INTEGRATION OF SUSPENDED GRAPHENE NANORIBBON AND ITS NON-VOLATILE OPTICAL MEMORY OPERATION

H. Suzuki*, T. Kaneko, and T. Kato

Tohoku University, Department of Electronic Engineering
Aoba 6-6-05, Aramaki, Aoba-Ku, 980-8579 Sendai, Japan

* e-mail: suzuki12@ecei.tohoku.ac.jp

Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Up to now, we developed a novel method based on the advanced plasma CVD method with nanoscale Ni catalyst (Ni nanobar) for directly fabricating suspended GNRs devices [1]. However, the growth yield of suspended GNRs is low and understanding the growth mechanism is required to solve this problem. Based on this background, we attempted to elucidate the growth dynamics of GNRs in our method by the comparison of molecular dynamics simulation and phase diagram calculation with the systematically obtained experimental results. By following this growth model, the yield of suspended GNR growth can be drastically improved ($\sim 98\%$) and wafer-scale synthesis of 1,000,000 suspended GNRs has been realised (Fig. 1a-c) [2].

Furthermore, we measured photo-response of current in GNRs array under the field effect transistor (FET) configurations (Fig. 1d). It is found the current of GNR can be drastically changed by photo irradiation and the current change can be maintained for a long time even after stopping the photo irradiation, which is known as a persistent photoconductivity (PPC) (Fig. 1e). This phenomenon can be understood due to hot carrier trapping in some trapping sites, which is same as a kind of operation principal of non-volatile optical memory, indicating the wafer-scale GNR array grown by our method can be useful as a novel optical-memory device.

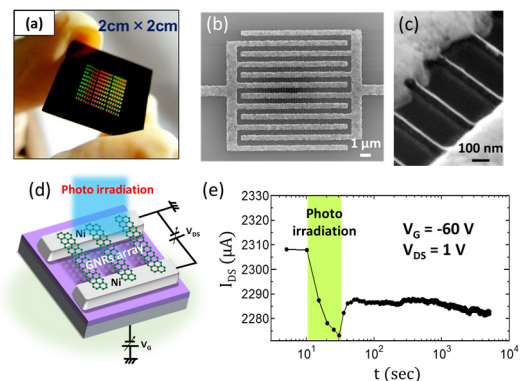


Figure 1. (a) Picture of wafer-scale integrated GNRs array. (b, c) Scanning electron microscope image of suspended GNRs array. (d) Schematic image of GNR array-FET under photo irradiation. (e) PPC of GNRs array.

[1] Kato T and Hatakeyama R 2012 *Nat. Nanotech.* **7** 651-656

[2] Suzuki H, Kaneko T, Shibuta Y, Ohno M, Maekawa Y and Kato T 2016 *Nat. Commun.* **7** 11797-11806

THERMODYNAMIC SCREENING OF BIMETALLIC NANOPARTICLES FOR CHIRALITY-SELECTIVE CARBON NANOTUBE GROWTH

C. Vets* and E.C. Neyts

University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: charlotte.vets@uantwerpen.be

Carbon nanotubes (CNTs) find many applications in diverse areas, such as fibers in composite materials, as sensors, actuators, transistor components, etc. The opto-electronic properties of CNTs, however, depend strongly on the CNT chirality, i.e., on the direction in which its hexagonal carbon network is rolled up, as shown in Fig. 1. Since this chirality is determined during CNT growth, it is of major importance to be able to control this catalytic process [2]. It has been demonstrated both experimentally and theoretically that bimetallic catalysts provide a possible means to achieve better chirality control [3, 4]. In this work, we perform a thermodynamic screening on NiFe, NiGa and FeGa nanocatalysts. We determine their most stable compositions and elemental distributions to gain insight in their structure, which is an important factor for chirality-selective CNT growth. We use density functional theory (DFT) calculations in order to first investigate the stability of nanocatalysts with various compositions and elemental distributions. We also include interstitial carbons to mimic the dissolution of carbon in the system during a typical growth process, i.e., catalytic chemical vapour deposition (CCVD) [5]. Since DFT calculations are conducted at 0 K, we subsequently employ Born-Oppenheimer molecular dynamics (BOMD) simulations to study a selection of stable nanocatalysts at 700 K, a typical temperature for CCVD [6].

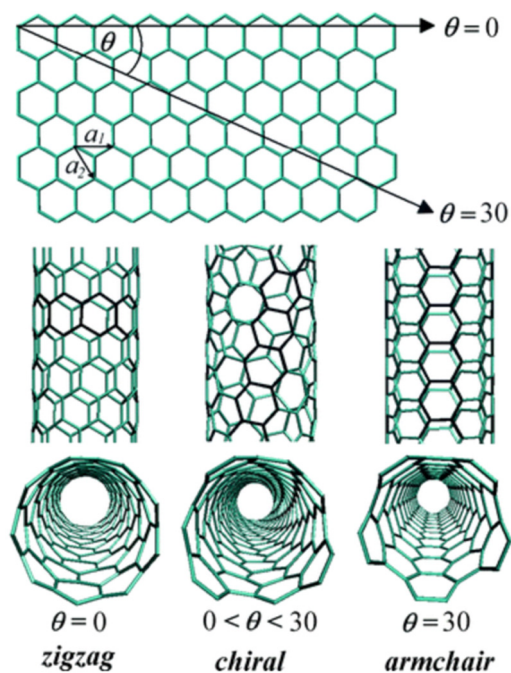


Figure 1. Definition of different CNT chiralities [1].

- [1] Galano A 2010 *Nanoscale* **2** 373-380
- [2] Neyts E C, *et al.* 2011 *J. Am. Chem. Soc.* **133** 17225-17231
- [3] Chiang W-H, *et al.* 2009 *ACS Nano* **3** 4023-4032
- [4] Silvearv F, *et al.* 2015 *J. Mater. Chem. C* **3** 3422-3427
- [5] Magnin Y, *et al.* 2015 *Phys. Rev. Lett.* **115** 205502
- [6] Elliot J A, *et al.* 2013 *Nanoscale* **5** 6662-6676

ENHANCEMENT OF CO₂ METHANATION PERFORMANCE ON Ni/Al₂O₃ CATALYST BY PLASMA TREATMENT

S. Wang*, L. Zhang and Z. Li

Tianjin University, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Chemical Engineering and Technology, Key Laboratory for Green Chemical Technology of Ministry of Education Tianjin 300072, China

* e-mail: spwang@tju.edu.cn

The 15 % Ni/Al₂O₃ catalysts were prepared via impregnation, co-precipitation and impregnation-precipitation method respectively. The catalytic performances of these catalysts for CO₂ methanation were investigated under atmospheric pressure. It was found that the catalyst prepared via impregnation-precipitation method has higher activity and better stability for CO₂ methanation than the other methods. DBD plasma treatment and CeO₂ additive further improved CO₂ methanation activity. The catalysts were characterised by BET, X-ray diffraction (XRD), temperature programmed reduction (H₂-TPR), temperature programmed desorption (CO₂-TPD), X-ray photoelectron spectroscopy (XPS), and TEM techniques. By comparing conventional thermal calcination method with dielectric barrier discharge (DBD) plasma, we found that either of CO₂ conversion or CH₄ selectivity was greatly enhanced on the catalyst prepared by DBD plasma. Furthermore, the additive CeO₂ improved the methanation performance with DBD plasma assistance.

CATALYST SURFACE STATE CONTROL TOWARDS CHIRALITY CONTROLLED SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBE WITH PLASMA CVD

B. Xu*, T. Kaneko and T. Kato

Tohoku University, Department of Electronic Engineering
Aoba 6-6-05, Aramaki, Aoba-ku, 80-579 Sendai, Japan

* e-mail: xu12@ecei.tohoku.ac.jp

Single-walled carbon nanotubes (SWNTs) are potential materials for future opto-electrical device applications due to their excellent optical and electrical properties. Since the opto-electrical characteristics of SWNTs strongly depend on their chirality, chirality-controlled synthesis of SWNTs still remain as a major issue in nanotube science and application community. In order to obtain SWNTs with specific chirality, our group focused on the catalyst, which plays a very important role in controlling SWNTs chirality. We make a systematic investigation to elucidate the correlation between catalyst state and the chirality species grown by plasma CVD. Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) are used to analyse the structures and surface states of the catalyst. It is found that the surface state of the catalyst can be controlled by a catalyst-pretreatment method, which is originally developed in this study. Furthermore, since SWNTs synthesis is carried out under very low temperature by the usage of plasma CVD, the catalyst surface state becomes very sensitive to the growth of a specific type of chiralities within similar diameter range. The dominant chirality species can be tuned from (6,5) to (6,4) SWNTs by controlling the catalyst surface state (Figs. 1a and 1b). This finding is very important for the synthesis of SWNTs with desired chirality species.

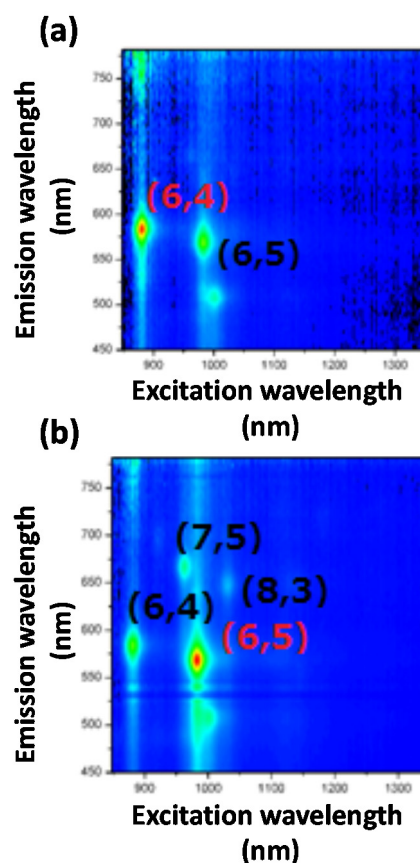


Figure 1. Photoluminescence-excitation mapping of (a) (6,4) dominant and (b) (6,5) dominant SWNTs grown by plasma CVD.

- [1] Ghorannevis Z, Kato T, Kaneko T and Hatakeyama R 2010 *J. Am. Chem. Soc.* **132** 9570-9572
- [2] Kato T and Hatakeyama R 2010 *ACS Nano* **4** 7395-7400
- [3] Xu B, Kato T, Murakoshi K and Kaneko T 2014 *J. Plasma Fusion Res.* **9** 1206075

TOWARDS SUPERHYDROPHOBIC POLYMERS VIA ATMOSPHERIC PRESSURE PLASMA ETCHING

P. Dimitrakellis, A. Smyrnakis and E. Gogolides*

NCSR “Demokritos”, Institute of Nanoscience and Nanotechnology

15310 Aghia Paraskevi, Greece

* e-mail: e.gogolides@inn.demokritos.gr

Superhydrophobic surfaces exhibiting high water contact angle ($> 150^\circ$) and low hysteresis ($< 10^\circ$) values are of great interest due to the numerous potential applications such as self-cleaning, anti-fogging, anti-icing, antifouling and drag reduction. Most studies so far have focussed on controlling the micro- and nanoscale surface topography in order to mimic the lotus leaf hierarchical structure. Plasma processing is one of the most promising techniques for the preparation of superhydrophobic surfaces as it is environmentally friendlier compared to the wet chemical methods. For polymeric materials, low pressure (reactive ion enhanced) plasma etching is typically applied using oxygen-rich plasma chemistry and proper micro-masking in order to create high aspect ratio structures. However, low pressure plasmas require expensive vacuum equipment, thus there is an increasing interest in atmospheric pressure plasmas as a low-cost alternative which also offer the possibility for in-line industrial processing. Yet, it is not clear how to induce simultaneous topography generation and chemical functionality with atmospheric plasmas. Here, we present one such approach, where a topography is introduced before plasma processing.

In this work we propose atmospheric pressure plasma etching combined with colloidal lithography in order to create hierarchical structures on flat polymeric substrates and induce superhydrophobic properties after coating with a low surface energy material. We have coated flat polymethylmethacrylate plates with polystyrene particles using spin-coating method and we have created an initial micro-scale topography. Next we applied helium-oxygen plasma using a novel dielectric barrier discharge source able for large-area and rapid etching of polymeric surfaces [1, 2]. The oxygen-rich plasma chemistry led to the rapid shrinking of polystyrene particles with the simultaneous creation of nanoscale roughness as indicated using SEM images. The optimisation of plasma etching process duration along with the deposition of a thin fluorocarbon film using led to the successful preparation of roll-off superhydrophobic surfaces presenting very high water contact angle values ($\sim 155^\circ$) and low hysteresis ($\sim 9^\circ$).

- [1] Dimitrakellis P, Zeniou A, Stratakos Y and Gogolides E 2016 *Plasma Sources Sci. Technol.* **25** 025015
- [2] Zeniou A, Puač N, Selaković N, Škoro N, Dimitrakellis P, Gogolides E and Petrović Z 2017 *J. Phys. D: Appl. Phys.* **50** 135204

Tuesday July 4th, 2017

Session 5	Plasma catalysis II
09:00 – 09:35	Keynote 4 – Hyun-Ha Kim Surface streamers and plasma catalysis
09:35 – 10:00	Invited 7 – Emiel J.M. Hensen Temperature-programmed plasma surface reaction
10:00 – 10:25	Invited 8 – Olivier Guaitella Seeking mechanisms of plasma/catalyst interaction with surface in situ diagnostics
10:30 – 11:00	Refreshment break
Session 6	Nanomaterials II
11:00 – 11:35	Keynote 5 – Chang-jun Liu Recent progresses in the applications of cold plasmas for CO ₂ conversion
11:35 – 12:10	Keynote 6 – Thierry Belmonte Nano-objects synthesized from Cu ₂₈ Ag ₇₂ electrodes by nanosecond-pulsed discharges in liquid nitrogen
12:10 – 12:35	Invited 9 – Wei-Hung Chiang Nanostructure engineering using atmospheric-pressure microplasmas: synthesis and applications
12:35 – 14:00	Lunch
14:00 – 18:00	Mid-session excursion: guided city walk
19:15	Dinner

SURFACE STREAMERS AND PLASMA CATALYSIS

H.-H. Kim*, Y. Teramoto and A. Ogata

National Institute of Advanced Industrial Science and Technology (AIST), Environmental Management Research Institute

305-8569 Tsukuba, Japan

* e-mail: hyun-ha.kim@aist.go.jp

Plasma chemistry is attracting considerable attentions due to the intrinsic characteristics brought by highly non-equilibrium state. These characteristic properties include ultra-fast reaction time ($\sim 10^{-4}$ s), mild reaction condition (ambient pressure and temperature), rapid start-up and shutoff. Plasma-catalysis, which combines non-thermal plasma with various catalysts, is based on the bilateral interaction. The potential applications of plasma-catalysis include hazardous VOCs removal, NO_x removal, ammonia synthesis, CO₂ conversion, and fuel reforming. Many of synergistic effects have been reported by many researcher groups in the past 10 years. However, the degree of enhancements seems to be dependent on the type of combinations (i.e., reactor configuration, power supply, type of catalysts, and operating conditions). In this regards, fundamental studies are necessary to accelerate the broad use of plasma-catalysis in many industrial fields.

This presentation will cover from the current understanding the interaction of plasma and catalyst to the possible applications in various chemical reactions.

- [1] Kim H-H, Teramoto Y, Nanba T, Takagi H and Ogata A 2016 *Plasma Chem. Plasma Processing* **36** 45-72
- [2] Kim H-H, Teramoto Y, Negishi N and Ogata A 2015 *Catalysis Today* **256** 13-22
- [3] Kim H-H, Teramoto Y, Nanba T, Takagi H and Ogata A 2017 *Plasma Process. Polym.* **14** 1600157

Acknowledgements. The authors would like to acknowledge financial support from the JSPS KAKENHI Grant Number JP26400539.

TEMPERATURE-PROGRAMMED PLASMA SURFACE REACTION

A. Parastayev¹, W.F.L.M. Hoebein², E.J.M. van Heesch², N. Kosinov¹ and E.J.M. Hensen^{1,*}

¹ Eindhoven University of Technology, Inorganic Materials Chemistry group
5600 MB Eindhoven, The Netherlands

² Eindhoven University of Technology, Electrical Energy Systems group
600 MB Eindhoven, The Netherlands

* e-mail: e.j.m.hensen@tue.nl

Plasma-enhanced heterogeneous catalysis offers opportunities with respect to thermal catalysis in view of synergies between the plasma and the solid catalyst. However, there is only limited mechanistic insight into the interaction of energetic electrons and excited molecules with heterogeneous catalysts. Accurate comparison of performance in a plasma-catalytic setting is complicated because of the intricate nature of the plasma-catalyst system: simultaneous reactions occurring in the gas-phase and at the catalytic surface and the dependence of the discharge on dielectric properties of the packed catalyst bed [1] and of the permittivity and polarisation of the catalyst on plasma parameters [2]. Thorough understanding of plasma-catalyst interactions would enable further development of efficient plasma-catalytic processes.

Here, we present a method of temperature-programmed plasma reaction (TPPR) that allows decoupling gas-phase processes from the surface plasma-induced reactions. Our approach comprises: (i) adsorption of the reactant on the catalyst surface at ambient temperature; (ii) flushing to remove gas-phase reactant molecules; (iii) exposure of the catalyst to a plasma at ambient temperature to remove weakly adsorbed species; and (iv) heating of the catalyst in plasma to drive catalytic reactions. We apply this to the plasma-assisted Sabatier reaction ($\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$) and show that a Co/CeZrO₄ is a promising catalyst for this purpose. The CeZrO₄ matrix provides CO₂ adsorption sites. Adsorbed CO₂ is plasma-activated at the metal-support surface and hydrogenated to CH₄ at milder conditions than possible in thermal catalysis.

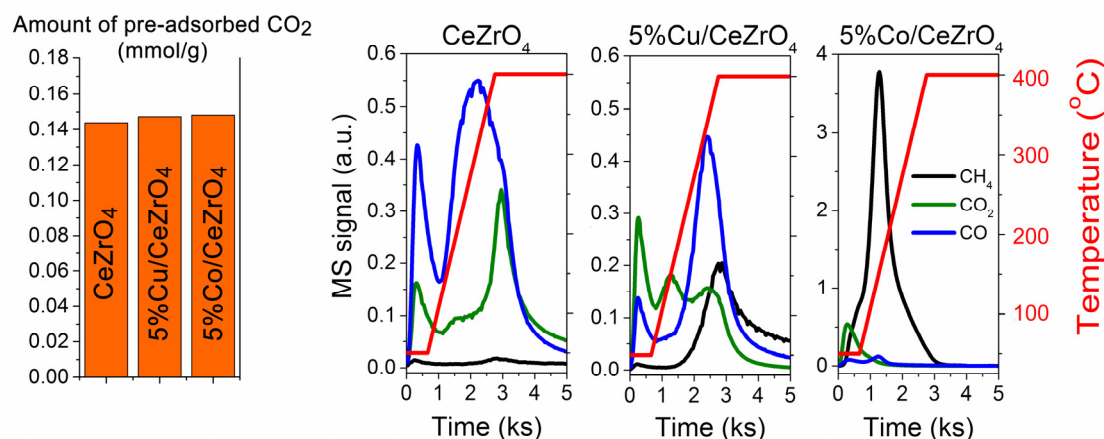


Figure 1. (left) Breakthrough adsorption of CO₂ on CeZrO₄ at 50 °C; (right); TPPR screening of CeZrO₄ catalysts in CO₂ hydrogenation (pulse duration 90 μs, frequency 1 kHz, ramp 10 °C/min).

A new method to compare the performance of different catalysts for plasma-driven catalytic reactions is presented. Using this novel approach in combination with spectroscopy, it is possible

to compare the activity and selectivity of catalysts in plasma-enhanced catalytic processes, and to evaluate the impact of electron-induced surface reactions on these processes.

- [1] Van Laer K and Bogaerts A 2017 *Plasma Process. Polym.* **14** 1600129
- [2] Heine C, Girgsdies F, Trunschke A, Schlögl R and Eichelbaum M 2013 *Appl. Phys. A* **112** 289–296

SEEKING MECHANISMS OF PLASMA/CATALYST INTERACTION WITH SURFACE IN SITU DIAGNOSTICS

O. Guaitella^{1,*}, A.S. Morillo-Candas¹, D. Yap¹, E. Slikboer^{1,2,3}, A. Sobota² and E. Garcia-Caurel³

1 CNRS / Ecole Polytechnique / UPMC / Université Paris-Saclay, LPP
91128 Palaiseau, France

2 Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

3 CNRS / Ecole Polytechnique / Université Paris-Saclay, LPICM
91128 Palaiseau, France

* e-mail: olivier.guaitella@lpp.polytechnique.fr

The interaction of plasma with surfaces is always a very challenging topic because of the multiplicity of phenomena modifying the surface but also because of the reverse influence of the substrate on the plasma properties. Therefore, most of the studies dedicated to plasma surface interactions are performed with very low pressure plasmas and ideal model surfaces. The situation is even more complex for plasma/catalyst interaction that usually involves transient filamentary discharges in contact with highly porous, reactive materials at elevated pressure. In order to get insight into the role of catalytic surfaces under plasma exposure, we are following two complementary approaches: (i) a pulsed low pressure (1 - 10 mbar) glow discharge is used to obtain condition in which the gas phase kinetic is controlled as much as possible and surface reactions are monitored with transmission infrared absorption through catalyst pellets exposed to this plasma; (ii) dielectric barrier discharges and plasma jets are used to compare the surface reactivity at elevated pressure (100 - 1000 mbar) and also to develop surface electric field diagnostics to get insight into the role of electric field in the modification of catalytic properties.

The *in situ* time resolved infrared absorption technique, similar to the one described in [1], has been used first in CO₂/CH₄ mixtures for gas reforming purposes. No proper conclusion on surface mechanisms can be drawn without an accurate description of the plasma to which the surface is exposed. In the case of the glow discharge, many diagnostics have been used such as step scan FTIR, high resolution TALIF and Raman scattering in order to obtain dissociation rate, vibrational excitation as well as gas temperature in the plasma. The measurements have been done with original catalysts based on metal oxides deposited on alginates structures.

The surface electric field measurements based on the technique described in [2], have been first performed with atmospheric pressure plasma jet because of their highly reproducible behaviour. An innovative polarimeter has been developed to obtain time resolved the charge deposited and the three components of the electric field induced by ionization waves on dielectric surfaces. The nature of the species responsible for charge deposition will be investigated. The technique is also being adapted to apply it with the same catalyst as the one studied with infrared absorption.

The combination of well controlled plasma conditions with *in situ* surface diagnostic techniques are a unique way to tackle the multiplicity of the mechanisms involved in plasma/catalyst interaction. The measurements currently done in CO₂ containing plasmas will illustrate the interest of this approach that could be used in many other field of applications, air treatment or biomedical application for instance.

- [1] Barakat C, Gravejat P, Guaitella O, Thevenet F and Rousseau A 2014 *Appl. Catalysis B: Environmental* **147** 302-313
- [2] Slikboer E, Guaitella O and Sobota A 2016 *Plasma Sources Sci. Technol.* **25** 03LT04

RECENT PROGRESSES IN THE APPLICATIONS OF COLD PLASMAS FOR CO₂ CONVERSION

C.-j. Liu*

Tianjin University, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering
300072 Tianjin, P.R. China

* e-mail: ughg_cjl@yahoo.com; coronacj@tju.edu.cn

CO₂ conversion and utilisation find applications not only in the emission control but also in spacecraft, submarine, fine chemical production, specific steel fabrication and indoor air treatment [1]. Cold plasmas have been extensively investigated for CO₂ conversion. There are two ways in general for cold plasma CO₂ conversion: one is the direct CO₂ conversion using cold plasmas [2-5] and the other is the catalyst preparation using cold plasmas for the next catalytic CO₂ conversion [6-8]. A high CO₂ conversion can be easily achieved with the use of cold plasmas [3-5]. The theoretical studies have confirmed that, if CO₂ molecule is electrically charges, the charged CO₂ conversion will be too easy with high selectivity [9]. The challenge is how to find a facile way to get the charged CO₂. The present plasma generation methodologies normally dissociate the CO₂ molecule into complex species, inducing complex reactions with poor selectivity of the objective products. The innovation in the plasma generation technologies is needed. On the other hand, cold plasmas can decompose the catalyst precursors under very different conditions from the conventional thermal treatment [6, 10]. This will result in unique catalyst with highly catalyst dispersion and desired structure for CO₂ reforming and CO₂ methanation. The cold plasma treatment of the catalyst precursor can also get specific hydrate, with which the high dispersion and desired structure can be also achieved after the thermal treatment. This also leads to an improved activity for CO₂ reforming.

- [1] Liu C 2017 Greenhouse Gases: Sci. Technol. (accepted)
- [2] Liu C, Xu G and Wang T 1999 *Fuel Process. Technol.* **58** 119-134
- [3] Snoeckx R, Heijkens S, Van Wesenbeeck K, Lenaerts S and Bogaerts A 2016 *Energy Environ. Sci.* **9** 999-1011
- [4] Eliasson B, Liu C and Kogelschatz U 2000 *Ind. Eng. Chem. Res.* **39** 1221-1227
- [5] Wang Q, Cheng Y and Jin Y 2009 *Catalysis Today* **148** 275-282
- [6] Liu C, Ye J, Jiang J and Pan Y 2011 *ChemCatChem* **3** 529-541
- [7] Zhu X, Huo P, Zhang Y, Cheng D and Liu C 2008 *Appl. Catal. B: Environmen.* **81** 132-140
- [8] Guo F, Xu J and Chu W 2015 *Catalysis Today* **256** 124-129
- [9] Wang J, Liu C, Zhang Y and Eliasson B 2003 *Chem. Phys. Lett.* **368** 313-318
- [10] Wang W, Anderson C, Wang Z, Wu W, Cui H and Liu C 2017 *Chem. Sci.* **8** 3310-3324

NANO-OBJECTS SYNTHESIZED FROM $\text{Cu}_{28}\text{Ag}_{72}$ ELECTRODES BY NANOSECOND-PULSED DISCHARGES IN LIQUID NITROGEN

H. Kabbara¹, J. Ghanbaja¹, C. Noël^{1,2} and T. Belmonte^{1,2,*}

1 Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198
54042 Nancy, France

2 CNRS, Institut Jean Lamour, UMR CNRS 7198
54042 Nancy, France

* e-mail: thierry.belmonte@univ-lorraine.fr

Benefiting from the properties of silver without supporting the cost of this element is an issue that can be solved by replacing silver atoms that are not solicited by atoms of another cheaper element. Copper (Cu) is about 100 times cheaper than Ag while possessing comparable bulk properties – its electrical conductivity is only 6 % less than that of Ag. Then, Cu-particles have been considered as an ideal substitute for Ag particles.

We present results about the synthesis of nanoobjects formed by erosion of $\text{Cu}_{28}\text{Ag}_{72}$ electrodes with spark discharges in liquid nitrogen. The $\text{Cu}_{28}\text{Ag}_{72}$ (composition expressed in at%) is a two-phase mixture made up of $\text{Ag}_{96.4}\text{Cu}_{3.6}$ and $\text{Cu}_{99.4}\text{Ag}_{0.6}$ phases. We observe the synthesis of 2D sheets composed of two allotropes (hexagonal and cubic) of the $\text{Ag}_{0.985}\text{Cu}_{0.015}$ phase. On the other hand, two distributions of nanoparticles are found: one around 5 ± 3 nm and one around 20 ± 10 nm. Electron Energy Loss Spectra indicate that nanoparticles are made of metallic copper and silver. EDS measurements show that these particles contain only a few percent of silver. Since they are not oxidised, we infer that silver in the as-formed CuAg alloy prevent air oxidation of the nanoparticles, pure copper nanoparticles produced in similar conditions being systematically oxidised in air to form CuO.

The erosion process leading to the formation of the observed nanoobjects is specific to each phase contained in the $\text{Cu}_{28}\text{Ag}_{72}$ electrodes and resembles those observed for pure metals, i.e., silver and copper. Such a behaviour has never been described till now. Furthermore, the possibility to grow 2D-objects as well as metallic copper nanoparticles doped by a small amount of silver opens up new perspectives in applications where Ag and Cu are needed.

NANOSTRUCTURE ENGINEERING USING ATMOSPHERIC-PRESSURE MICROPLASMAS: SYNTHESIS AND APPLICATIONS

W.-H. Chiang*

National Taiwan University of Science and Technology, Department of Chemical Engineering
No. 43, Sec. 4, Keelung Rd., Da'an District, 10617 Taipei, Taiwan

* e-mail: whchiang@mail.ntust.edu.tw

Microplasmas are a special class of electrical discharges formed in geometries where at least one dimension is less than 1 mm. As a result of their unique scaling, microplasmas operate stably at atmospheric pressure and contain large concentrations of energetic electrons (1 - 10 eV). These properties are attractive for a range of nanomaterials synthesis and nanostructure engineering such as metal nanostructures and carbon-based materials.

In this presentation, I will discuss these topics in detail, highlighting the advantages of microplasma-based systems for the synthesis of well-defined nanomaterials. These experiments will aid in the rational design and fabrication of nanomaterials and may also have significant impact in emerging applications. Recently, we found that the energetic species including radicals, ions and electrons generated in the microplasmas were capable of initiating electrochemical-assisted reactions for the nucleation and growth of graphene quantum dots. Moreover, we develop a simple synthesis of metal nanoparticles/graphene composites using a unique atmospheric-pressure microplasma-assisted electrochemical method. Systematic μ -Raman study indicates that the as-produced AgNP/graphene composites show exceptional SERS performance.

Wednesday July 5th, 2017

Session 7	Plasma medicine I
09:00 – 09:35	Keynote 7 – Jean-Michel Pouvesle Biomedical applications of cold atmospheric pressure plasmas with a special focus on cancer treatment
09:35 – 10:00	Invited 10 – Annemie Bogaerts Plasma for cancer treatment: how can RONS penetrate through the cell membrane?
10:00 – 10:25	Invited 11 – Michael Keidar Plasma and nanoparticle applications in cancer therapy
10:30 – 11:00	Refreshment break
Session 8	Plasma medicine II
11:00 – 11:25	Invited 12 – Cristina Canal Liquid-mediated effects of cold plasma on bone cancer
11:25 – 11:50	Invited 13 – Sander Bekeschus Plasma, cancer, immunity – roads and challenges
11:50 – 12:15	Invited 14 – Jan-Wilm Lackmann Thiol chemistry as a molecular tool in plasma medicine
12:15 – 12:30	Contributed 7 – Sirui Li Plasma-liquid assisted synthesis of silver and rare earth nanoparticles for biomedical applications
12:30 – 13:30	Lunch
Session 9	Microelectronics I
13:30 – 13:55	Invited 15 – Jean-François de Marneffe Patterning challenges for ultimate CMOS and beyond CMOS nano-fabrication
13:55 – 14:20	Invited 16 – Fred Roozeboom InZnO grown by atmospheric plasma-enhanced spatial atomic layer deposition for application in high-mobility TFT circuits
14:20 – 14:45	Invited 17 – Huiying Yang Plasma enhanced performance in 3D printed flexible lithium ion batteries
14:45 – 15:10	Invited 18 – Angel Barranco Plasma-assisted oblique angle deposition of in-plane anisotropic ITO thin films
Poster session II 15:15 – 16:15	Micro-electronics and plasma medicine
Session 10	Micro-electronics II
16:15 – 16:40	Invited 19 – Romain Chanson Cryo-etching for integration in micro-electronic: silicon deep etch for contact etching and low-k integration in back end of line (BEOL)
16:40 – 17:05	Invited 20 – Athanasios Smyrnakis Plasma etched silicon nanowires with enhanced light trapping properties for axial or radial photovoltaic nanodevices
17:05 – 17:20	Contributed 8 – Quan-Zhi Zhang Protection mechanism for porous low-k materials during cryogenic etching
19:15	Conference dinner

BIOMEDICAL APPLICATIONS OF COLD ATMOSPHERIC PRESSURE PLASMAS WITH A SPECIAL FOCUS ON CANCER TREATMENT

J.-M. Pouvesle* and É. Robert

CNRS / Université d'Orléans, GREMI, UMR 7344

14 rue d'Issoudun, P.O. Box 6744, 45067 Orléans Cedex 2, France

* e-mail: jean-michel.pouvesle@univ-orleans.fr

The last decade has seen an impressive increase of the research dedicated to the biomedical applications of low temperature plasmas, especially with plasma sources working at atmospheric pressure. In this new trend, beside decontamination/sterilisation and surface treatment, which have already a quite long story through low pressure plasma research and developments, medical applications are tacking an increasing place underlined by the actual numerous clinical trials. Medical applications of low temperature plasmas now concern a very wide range of domains, including primary hemostasis and blood coagulation, dental care, skin decontamination and hygiene, wound and ulcer treatment, dermatology, cancer treatment. Biological applications are also now extended to agriculture and, more recently, to cosmetic. Despite the huge number of *in vitro* and *in vivo* experiments there are still a large number of remaining questions concerning the processes leading to the observed results, but also the specific role of the different plasma components that are directly linked both to the plasma production devices and the presence of the living target (biological tissues and materials, organs and their direct environment). Taking the example of cancer treatment, beside the radical production, we will emphasize on the potential role of the strong electric field generated around the plasma plume of atmospheric plasma jet systems, and discuss possible changes induced in microenvironment of tissues or tumours. We will also emphasize on the fact that plasma diagnostics must be performed in real treatment conditions. In this talk, after a presentation of the context, the plasma devices, and the main applications, considering the specific case of cancer treatment, we will go through what have been already demonstrated concerning *in vitro* and *in vivo* experiments, what problems are directly linked with discharges including recent results on electric field measurements in plasma biological application conditions, what are the challenges in front us, and finishing trying to draw what are the main perspectives in the domain.

Acknowledgments: X. Damany, T. Darny, C. Douat, S. Dozias from GREMI, G. Busco, V. Vijayarangan from GREMI and CBM, A. Delalande, C. Grillon, C. Pichon, F. Fasani, S. Morrisset-Lopez, D. Gosset from CBM (Orléans), and A.L. Bulteau, M. Dezet from IPREM (Pau) have participated to part of the presented work.

This work is founded by APR PLASMEDNORM, ANR PAMPA, ARD 2020 Cosmetoscience PLASMACOSM project and by the Région Centre-Val de Loire.

PLASMA FOR CANCER TREATMENT: HOW CAN RONS PENETRATE THROUGH THE CELL MEMBRANE?

A. Bogaerts*, M. Yusupov and J. Van der Paal

University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: annemie.bogaerts@uantwerpen.be

In recent years, there is a lot of interest in cold atmospheric plasma (CAP) for cancer treatment [1]. However, the underlying mechanisms are still not fully understood. It is generally believed that reactive oxygen and nitrogen species (RONS) generated by CAPs play an important role in killing the cancer cells [2, 3]. A noticeable rise of intracellular ROS in cancer cells compared to normal cells has been reported, which might subsequently lead to oxidative damage of biomolecules inside the cells. The plasma species, however, first interact with the cell membrane, chemically modifying or oxidising its lipids. It is therefore important to study the behaviour of the oxidised cell membrane and its effect on the penetration of the reactive plasma species (i.e., various RONS) through the oxidised lipid bilayer.

This talk will give an overview of our recent simulation results on the permeation of RONS across oxidised and non-oxidised cell membranes. Specifically, I will show the effect of the presence of cholesterol, which is present in higher concentrations in the cell membrane of normal cells than cancer cells, and we found that it causes a drop in the probability of pore formation in the cell membrane and in the RONS penetration ability. This might be one of the explanations for the selectivity of plasma therapy towards cancer cells versus normal cells [4, 5]. Moreover, I will discuss the synergistic effect of the electric field together with lipid oxidation on the permeability of cell membranes [6].

In general, the computational results show that oxidation of the cell membrane leads to an increased permeability of RONS, thereby increasing the probability of RONS penetration to the cell interior. However, the energy barriers for RONS translocation across the membrane still remain relatively high, which indicates the need for specific protein channels (e.g., aquaporin) or pores created by an electric field to allow RONS penetration into the cytoplasm, eventually to cause oxidative damage.

- [1] Keidar M, Walk R, Shashurin A, Srinivasan P, Sandler A, Dasgupta S, Ravi R, Guerrero-Preston R and Trink B 2011 *Br. J. Cancer* **105** 1295-1301
- [2] Graves D B 2014 *Plasma Process. Polym.* **11** 1120-1127
- [3] Lu X, Naidis G V, Laroussi M, Reuter S, Graves D B and Ostrikov K 2016 *Phys. Rep.* **630** 1-84
- [4] Van der Paal J, Neyts E C, Verlack C C W and Bogaerts A 2016 *Chem. Sci.* **7** 489-498
- [5] Van der Paal J, Verheyen C, Neyts E C and Bogaerts A 2017 *Sci. Reports* **7** 39526
- [6] Yusupov M, Van der Paal J, Neyts E C and Bogaerts A 2017 *Biochim. Biophys. Acta – General* **1861** 839-847

PLASMA AND NANOPARTICLE APPLICATIONS IN CANCER THERAPYM. Keidar*The George Washington University
21209 Washington DC, U.S.A.

* e-mail: keidar@gwu.edu

Plasma medicine is a relatively new field that outgrew from research in application of low-temperature (or cold) atmospheric plasmas in bioengineering. One of the most promising applications of cold atmospheric plasma (CAP) is the cancer therapy. Convincing evidence of CAP selectivity towards the cancer cells has been accumulated. This talk will summarize the state of the art of this emerging field presenting various aspects of CAP application in cancer such as role of reactive species (reactive oxygen and nitrogen), cell cycle modification, *in vivo* application, CAP interaction with cancer cells in conjunction with nanoparticles, computational oncology applied to CAP. The efficacy of cold plasma in a pre-clinical model of various cancer types such as lung, bladder, breast, head, neck, brain and skin has been demonstrated. Both *in-vitro* and *in-vivo* studies revealed that cold plasmas selectively kill cancer cells. It was shown that: (a) cold plasma application selectively eradicates cancer cells *in vitro* without damaging normal cells. (b) Significantly reduced tumour size *in vivo*. The two best known cold plasma effects, plasma-induced apoptosis and the decrease of cell migration velocity can have important implications in cancer treatment by localizing the affected area of the tissue and by decreasing metastatic development. Recently mechanism of plasma selectivity based on aquaporin hypothesis has been proposed. Aquaporins (AQPs) are the confirmed membrane channels of H_2O_2 and other large molecules. We have demonstrated that the anti-glioblastoma capacity of plasma could be inhibited by silencing the expression of AQP in glioblastoma cells (U87MG) or using the aquaporins-blocker silver atoms. In general, expression of AQPs varies significantly among different cancer cell lines. Thus this study may facilitate the understanding on the diverse responses of cancer cells to plasma treatment.

LIQUID-MEDIATED EFFECTS OF COLD PLASMA ON BONE CANCER

C. Canal^{1,2,*}, I. Hamouda^{1,2}, J. Guillem-Martí^{1,2} and M.P. Ginebra^{1,2,3}

1 Technical University of Catalonia (UPC), Escola d'Enginyeria Barcelona Est (EEBE), Dept. Materials Science and Metallurgy, University Biomaterials, Biomechanics and Tissue Engineering Group
c/ Eduard Maristany 10-14, 08019 Barcelona, Spain

2 Technical University of Catalonia (UPC), Barcelona Research Center in Multiscale Science and Engineering
Barcelona, Spain

3 Institute of Bioengineering of Catalonia (IBEC)
c/ Baldori i Reixach 10-12, 08028 Barcelona, Spain

* e-mail: cristina.canal@upc.edu

Primary bone cancers (arising directly in bone) are usually treated by a combination of therapies, including surgery, chemo and radiotherapy but patients often relapse. Secondary or metastatic bone cancers found most often in patients suffering from breast or prostate cancer have no therapeutic treatment and associate many drawbacks for the patients. Atmospheric pressure plasmas have already demonstrated selective anti-tumour action in a number of carcinomas and in more relatively rare brain tumours [1], and could represent an alternative and/or complementary therapy for bone cancers.

Our preliminary data have shown proof of concept of the lethal efficacy of treating cell culture medium with an atmospheric pressure plasma jet (APPJ) generated with helium on one kind of bone osteosarcoma cells [2].

Herein, we are interested in expanding those studies and investigating the potential selectivity of plasma-activated liquids towards three different osteosarcoma cell lines (SaOS-2, MG63 and MC3T3) versus different healthy cells involved in the bone regenerative process (pluripotent or from either bone or connective tissue). In general, plasma-treated medium showed cytotoxic effects on bone cancer cells and certain treatment conditions lead to progressive bone cancer cell death through apoptosis, with alterations in the cell morphology, while bone healthy cells remained viable and essentially unaffected by the treatment.

Given the mediation of liquid media on the biological effects of plasmas, we discuss the relationship between these effects and the Reactive Oxygen and Nitrogen species (RONS) generated in liquid medium (cell culture medium) at different treatment times, and the effects of different parameters such as volume of liquid treated in the generation of these species. The results obtained provide a promising novel approach for improved bone cancer therapies.

[1] Graves D B 2014 *Plasma Process Polym.* **11** 1120

[2] Canal C, Fontelo R, Guillem-Martí J, Cvelbar U and Ginebra M P 2017 *Free Radic Biol Med.* (accepted, under revisions)

Acknowledgements. Authors acknowledge the financial support of MAT2015-65601-R project (MINECO/FEDER, EU) and from the ERC under the EU's Horizon 2020 research and innovation programme (grant agreement no. 714793).

PLASMA, CANCER, IMMUNITY – ROADS AND CHALLENGES

S. Bekeschus^{1,*}, V. Miller², A. Fridman² and K.-D. Weltmann¹

1 Leibniz-Institute for Plasma Science and Technology, ZIK plasmatis
Felix-Hausdorff Strasse 2, 17489 Greifswald, Germany

2 Drexel University, Nyheim Plasma Institute
200 Federal Street, 08103 Camden, NJ, U.S.A.

* e-mail: sander.bekeschus@inp-greifswald.de

Plasma oncology has rapidly developed to become a major topic in plasma medicine. Plasma killing activity has been shown numerous times in cancer cell cultures and subcutaneous tumour animal models. Yet, one of the major challenges in oncology are not primary or bulk tumours, which can be surgically excised. Rather, 90 % of cancer patients die of hard-to-reach or widespread metastasis and subsequent organ failure. In many instances, plasma application may be impractical to directly debulk metastatic sites throughout the human body. Much has been learned in oncology in the past decades with regard to antitumour immune responses. It is widely recognised today that tumours vividly interact with their stromal and immune microenvironment, which strongly contributes to either cancer growth or suppression. Especially evident is the frequent finding that patient prognosis is elevated the more tumour reactive immune cells are present, and vice versa for immunity-suppressive cells. Moreover, increasing the immunogenicity by immunogenic cell death (ICD) of tumours correlates with patient benefit. This effect is only seen with certain therapies, and many of them are of physical nature. Next to some specific chemotherapeutics, ionising radiation is well established and an ICD inducer. Additional physical approaches such as photodynamic therapy, electro chemotherapy, and high hydrostatic pressure have shown encouraging results in pre-clinical models. Firmly attached to this concept, cold physical plasmas may be the next promising approach in oncology. Although only applied locally, plasma therapy could exhibit systemic antitumour immune responses in the host, possibly aiding in eradicating distant metastasis through immunity that are key in patient survival. A main route of plasma effects are reactive species but with some sources, also electrical fields, UV radiation, and electrons and ions come into play. This oral contribution attempts to summarise key results from the community and the authors in plasma oncology research, and addresses important challenges that will need attention in the future.

THIOL CHEMISTRY AS A MOLECULAR TOOL IN PLASMA MEDICINE

J.-W. Lackmann^{1,2,*}, K. Wende³, B. Offerhaus¹, C.C.W. Verlackt⁴, C. Klinkhammer⁵, F. Kogelheide², D. Hüther¹, K. Sgonina¹, M. Havenith⁵, A. Bogaerts⁴, P. Awakowicz¹ and K. Stapelmann²

1 Ruhr University Bochum, Institute for Electrical Engineering and Plasma Technology
Universitätsstrasse 150, 44780 Bochum, Germany

2 Ruhr University Bochum, Biomedical Applications of Plasma Technology
Universitätsstrasse 150, 44780 Bochum, Germany

3 INP Greifswald, Plasma-Liquid Effects
Felix-Hausdorff-Strasse 2, 17489 Greifswald, Germany

4 University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

5 Ruhr University Bochum, Physical Chemistry II
Universitätsstrasse 150, 44780 Bochum, Germany

* e-mail: lackmann@aept.ruhr-uni-bochum.de

Cold technical plasmas (CAPs) are currently under investigation in various fields of industry and medicine. Clinical trials using CAPs for wound healing are in progress and the preliminary results are promising. Other fields, such as cancer treatment, offer promising findings as well. However, the chemical interactions between CAPs and their biological targets are only partly understood. The complex chemical cocktails generated by CAPs can impact various biological structures [1]. A better understanding of these reactions would allow to tune and adapt plasmas for specific tasks. One prevalent impact of plasma on biological targets is the chemical modification of thiol groups, which carry out various important tasks in the human body, such as cell signalling and protein structure formation. As thiols are involved in many regulatory and functional processes in tissues, an in-depth understanding of the impact of plasma treatment on thiols is highly relevant for a safe application of plasmas in medicine.

To shed light onto these interactions, various thiol-containing model substrates, such as the amino acid cysteine and larger target substrates, were investigated with different plasma sources [2, 3]. Using a normalised target substrate, the impact of the different plasma sources can be compared not by means of a physical characterisation but by their chemical impact. Stepwise increase of sample complexity allows monitoring how thiols are affected by plasma treatment in an ever more complex environment. The combination of experimental evidence and MD simulations permit a comprehensive overview of chemical processes induced by plasma treatment. This combined approach allows for a more throughout investigation of modifications on a molecular level and helps to understand fundamental plasma chemistry processes. Furthermore, knowledge about the substrate chemistry enables the use of test substrates as bio-probes for the investigation of plasma chemistry in other industrial fields [4].

[1] Lackmann J-W and Bandow J E 2014 *Appl. Microbiol. Biotechnol.* **98** 6205-6213

[2] Kogelheide F, *et al.* 2016 *J. Phys. D: Appl. Phys.* **49** 084004

[3] Lackmann J-W, *et al.* 2015 *J. Phys. D: Appl. Phys.* **48** 494003

[4] Offerhaus B, *et al.* 2017 *Plasma Process Polym.* (accepted)

PLASMA-LIQUID ASSISTED SYNTHESIS OF SILVER AND RARE EARTH NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

S. Li^{1,*}, W. Zhang^{1,2}, L. Lin¹, S. Starostin³ and V. Hessel¹

¹ Eindhoven University of Technology, Chemical Engineering and Chemistry Department
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

² Hebei University of Technology, School of Marine Science and Engineering,
Tianjin, P.R. China

³ FUJIFILM Manufacturing Europe, Tilburg Research Labs.
Tilburg, The Netherlands

* e-mail: s.li1@tue.nl

Owing to its excellent anti-bacteria properties, silver nanoparticles (NPs) have attracted great attention in the field of bio-decontamination. Rare earth nanoparticles with good optical properties show promising potential in fluorescence bioimaging. Our research on these two types of nanoparticles is presented including the synthesis methodology, particle characteristics and properties also related bio-applications.

Plasma-liquid interaction (PLI) is a simple, efficient and environment-friendly method for nanoparticle synthesis. Since toxic chemicals are not involved during the synthesis process, PLI is considered very suitable to fabricate nanomaterials for bio-application [1]. A multi-functional reactor system with modular design and exchangeable subunits was used for PLI reactions, through which silver and rare earth series nanoparticles of controllable size were prepared by controlling processing parameters [2]. In the case of silver nanoparticles, silver nitrate and silver ammonia complex were used as the precursor with sucrose as the dispersant. A variation of the sucrose/silver source molar ratio led clear changes in the SPR peak position and intensity of the UV-vis absorbance spectra (Fig. 1), indicating the amount of dispersant has an important impact on the size and yield of Ag NPs. Results also showed that the silver ammonia complex as the precursor to prepare Ag NPs has a higher reaction efficiency than using silver nitrate. When varying the plasma reaction time from 1 min to 20 min, a strong variation of the average nanoparticle size is visible (from about 10 - 36 nm) for silver nitrate precursor, while this effect is much less pronounced for the silver ammonia complexed as the precursor (from about 11 to 17 nm). The silver ammonia complexed system has a faster reaction rate, it can achieve the maximum conversion of the silver precursor to Ag NPs in a shorter reaction time. About 37 % of silver nitrate is converted to Ag NPs while about 75 % of silver ammonia is converted to Ag NPs in 5 minutes. In the case of rare earth nanoparticles, PLI with the rare-earth nitrates (yttrium nitrate) solution was used to form rare earth hydroxides, then followed by heat-treatment of the hydroxides at various temperatures, high purity crystalline rare earth nanoparticles (yttrium oxides) with adjustable sizes can be fabricated. Furthermore, the synthesised yttrium

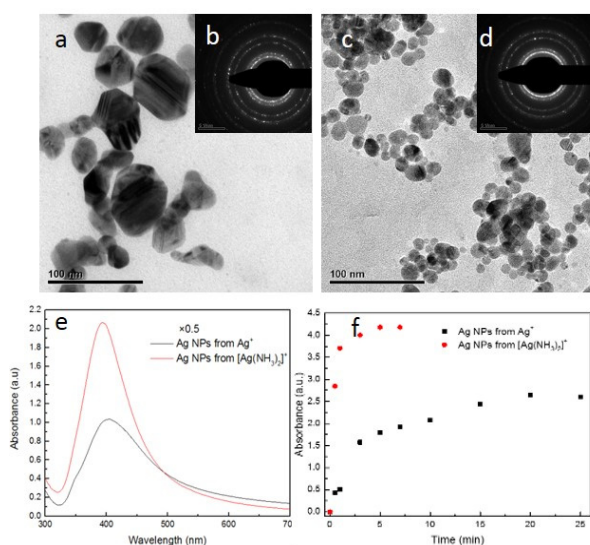


Fig. 1 TEM (a and c), SAED (b and d), UV-Vis absorbance spectroscopy (e) and time-dependent absorbance intensity (f) of the Ag NPs obtained from silver nitrate and silver ammonia.

Further, the synthesised yttrium

oxides will be used as the host materials for Eu doping. The $\text{Y}_2\text{O}_3/\text{Eu}$ composite showed a clear fluorescent signal emitted, indicating its great potential in a bio-imaging related application. On the other hand, decontamination of *E. coli* and *S. aureus* by using silver nanoparticles will also be tested.

- [1] Mariotti D and Sankaran R M 2010 *J. Phys. D: Appl. Phys.* **43** 323001
- [2] Lin L and Wang Q 2015 *Plasma Chem. Plasma Process.* **35** 925-962

PATTERNING CHALLENGES FOR ULTIMATE CMOS AND BEYOND CMOS NANO-FABRICATION

J.-F. de Marneffe*, F. Lazzarino, E. Altamirano-Sanchez and D. Piumi

IMEC vzw

Kapeldreef 75, 3001 Leuven-Heverlee, Belgium

* e-mail: marneffe@imec.be

Pattern transfer is the ability to move a shaped sacrificial material into a permanent substrate. Besides the usual requirement of pattern fidelity, aspects related to anisotropy, selectivity, amplification and low damage are of key importance for technological applications. Since thirty years, plasma etching became the workhorse of pattern transfer for nano-manufacturing, due to its superior capabilities with respect to the above requirements, and high throughput/low cost. By entering sub-10 nm scales, plasma etching enters the era of atomic resolution, where a single layer of atoms can have a tremendous importance for the good or bad behaviour of a nanodevice.

In this talk, we will present some patterning challenges driven by most advanced nanofabrication techniques. Traditional optical lithography methods, massively used in VLSI thanks to their high throughput, do not offer high enough resolution for sub-10nm dimensions, even by the use of extreme-UV (13.6 nm). They therefore require the assistance of specific deposition/etch steps for duplicating or quadruplicating the printed features, combined with multiple masks. Scaling boosters are also considered for enhancing device density, by use of self-aligned approaches.

Alternative lithography by scanning probe lithography methods (SPL), low-cost, mask-less, single-pass and high-resolution, typically requires tailored resist materials, showing specific physical and chemical characteristics, having considerable effect on their plasma performance. The need for high resolution requires also resist thickness of the order of 5 - 10 nm, as a consequence post-lithography resist hardening strategies need to be explored.

Finally, during the etch process, material damage should be kept within a single nanometre, which preclude the use of high energetic bombardment in ion-assisted mode, but favour the use of cyclic processes where chemical adsorption and physical/thermal activation are clearly separated, i.e., so-called atomic-layer etching approaches. Some examples will be given.

Acknowledgements. Part of the research leading to these results has received funding from the European Union's Seventh Framework Programme FP7/2007-2013 under grant agreement no. 318804 ("Single Nanometer Manufacturing for beyond CMOS devices" – acronym SNM).

InZnO GROWN BY ATMOSPHERIC PLASMA-ENHANCED SPATIAL ATOMIC LAYER DEPOSITION FOR APPLICATION IN HIGH-MOBILITY TFT CIRCUITS

A. Illiberi^{1,3}, I. Katsouras¹, S. Gazibegovic¹, B. Cobb¹, E. Nekovic¹, W. van Boekel¹, C. Frijters¹, J. Maas¹, F. Roozeboom^{1,2,*}, Y. Creighton¹, P. Poodt¹ and G. Gelinck^{1,2}

¹ Holst Centre / TNO

High Tech Campus 31, 5600 AE Eindhoven, The Netherlands

² Eindhoven University of Technology, Department of Applied Physics,
5600 MB Eindhoven, The Netherlands

³ Present address: ASM International, Leuven, Belgium

* e-mail: fred.roozeboom@tno.nl

Recently, In(Ga)ZnO was reported as a novel Amorphous Oxide Semiconductor (AOS) channel material replacing conventional amorphous silicon (a-Si:H) for application in thin-film transistor (TFT) circuits in display back panels.

In this presentation we will describe the growth of InZnO at atmospheric pressure and high deposition rates ($\sim$ nm/sec) using the technique of spatial atomic layer deposition (s-ALD) [2, 3]. We will start with a short explanation of the basics and the advantages of this novel deposition technique including the use of a special microplasma source design of the so-called Dielectric Barrier Discharge type [4]. Next, we will show that by varying the ratio of the trimethyl indium and diethyl zinc chemical precursor vapours, the In/(In+Zn) ratio of the film can be accurately tuned in the entire composition range from zinc oxide to indium oxide. TFT test structures with an [In/Zn] ratio of 2:1 show very high field-effect mobility (exceeding 30 cm²/V.s), and excellent stability. We demonstrate large-scale integration in the form of 19-stage ring oscillators operating at 200 kHz which outperform the state of the art.

This superior electrical performance, in combination with the intrinsic advantages of spatial atomic layer deposition conducted at atmospheric pressure, demonstrate the great potential of s-ALD as commercial manufacturing technique for low-cost and large-area electronics based on amorphous oxide semiconductors.

- [1] Kamiya T, Nomura K and Hosono H *J. Disp. Technol.* **5** 273-288
- [2] Poodt P, Lankhorst A, Roozeboom F, Spee C, Maas D and Vermeer A 2010 *Adv. Mater.* **22** 3564-3567
- [3] Illiberi A, Scherpenborg R, Roozeboom F and Poodt P 2014 *ECS J. Solid State Sci. Technol.* **3** 111-114
- [4] Creighton Y, Illiberi A, Mione M, van Boekel W, Debernardi N, Seitz M, van den Bruele F, Poodt P and Roozeboom F 2016 in: *Proc. Int. Conf. on Coatings on Glass and Plastics (ICCG 2016)*. (Braunschweig, Germany; June 12-16) 93-97

PLASMA ENHANCED PERFORMANCE IN 3D PRINTED FLEXIBLE LITHIUM ION BATTERIES

H. Yang*

Singapore University of Technology and Design

8 Somapah Road, 487372 Singapore, Singapore

* e-mail: yanghuiyang@sutd.edu.sg

In the next generation electronics devices, wearable electronics (such as google glasses, apple watch etc.) will dominate the market and emerge as the mainstream devices of future life-style [1]. Among various flexible electronics components, flexible lithium-ion batteries (LIBs) are one of the most potential candidates to address the energy storage issue because of their high energy density and output voltage, long life, and eco-friendly operation [2, 3]. In our research lab, we are working on meeting the flexible and thin requirements of devices, various novel materials, especially carbon materials such as activated carbons, carbon nanotubes, carbon fibres, graphene, and their composites, have been being explored as flexible electrodes. We have developed a breakthrough technology to achieve high electrochemical performance smart battery with shut down function and outstanding charge/discharge rates through digital manufacturing methods. The incorporation of temperature sensitive polymer into the printable ink imparts self-protection ability to the printed conducting trace, with rapid recovery of repeated large damages at the same or different locations without any user intervention or external trigger with 90 seconds. The printed system can be used to realize rapid prototyping of an object and patterning at low cost and has been tried in energy devices. The real-life applicability of the new self-healing concept can be demonstrated for different electrochemical sensors, and wearable textile-based electrical circuits, with considerable promise for widespread practical applications and long-lasting printed electronic devices.

- [1] Pan Z, Ren J, Guan G, Fang X, Wang B, Doo S G, Son I, Huang X and Peng H 2016 *Adv. Energy Mater.* **6** 1600271
- [2] Zhou G M, Li F and Cheng H M 2014 *Energy Environ. Sci.* **7** 1307-1338
- [3] Wang J G, Jin D D, Zhou R, Li X, Liu X R, Shen C, Xie K Y, Li B H, Kang F Y and Wei B Q 2016 *ACS Nano* **10** 6227-6234

PLASMA ASSISTED OBLIQUE ANGLE DEPOSITION OF IN-PLANE ANISOTROPIC ITO THIN FILMS

J. Parra-Barranco¹, J.R. Sanchez-Valencia¹, F.J. Aparicio¹, F. Garcia-Garcia¹, V. Rico¹, C. Lopez-Santos¹, A. Borrás¹, F.J. Ferrer², A.R. Gonzalez-Elipse¹ and A. Barranco^{1,*}

¹ Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla)
C/ Américo Vespucio 49, 41092 Sevilla, Spain

² Centro Nacional de Aceleradores (CSIC-Universidad de Sevilla)
Avda Thomas A. Edison 7, 41092 Sevilla, Spain

* e-mail: angel.barranco@csic.es

Oblique angle deposited (OAD) oxide thin films are quite interesting materials due to the wide variety of nanostructures that can be obtained with this method. Most important properties of the oxide OAD thin films rely in the possibility to tailor their nanostructure in the form of tilted columns and other more complex forms. This nanostructure is caused by geometrical shadowing effects during the thin film growth. Porous OAD films have been used as hosts or templates to fabricate new nanocomposite materials and other complex optical nanostructures like photonic crystals, dye sensitized solar cells, optical sensors and microfluidic devices [1-3]. In this work we study the fabrication of transparent and conducting indium tin oxide films (ITO) by a novel synthetic approach consisting in OAD deposition assisted by electron cyclotron resonance (ECR) microwave remote plasma. The ECR microwave discharges are fully compatible with the range of pressures required for the electron evaporation process utilised for the deposition of the ITO thin films. The objective of the plasma is to modify the growth mechanism of the OAD process in order to control the columnar microstructure, porosity and the properties of the films [4]. As it will be shown, the OAD ITO deposition assisted by the plasma discharge is a very effective process to develop in-plane anisotropy in the ITO films what determines the films optical and electrical properties.

- [1] Brett M J, *et al.* 2008 *Science* **319** 1192
- [2] Barranco A, *et al.* 2016 *Progress Mater. Sci.* **76** 59-153
- [3] González-García L, *et al.* 2012 *Nanotechnology* **23** 205701
- [4] Gonzalez-García L, *et al.* 2011 *Energy. Environ. Sci.* **4** 3426
- [5] Parra-Barranco J, *et al.* 2015 *ACS Appl. Mater. Interf.* **7** 10993

Acknowledgements. We thank the EU (FEDER) and MINECO-AEI for financial support (Projects MAT2016-79866-R, MAT2013-40852-R, MAT2013-42900-P, MINECO-CSIC 201560E055, IJCI-2014-21226, RECUPERA2020 and Marie Skłodowska-Curie Actions H2020-MSCA-IF-2014 PlasmaPerovSol grant Ref. ID 661480).

CRYO-ETCHING FOR INTEGRATION IN MICRO-ELECTRONIC: SILICON DEEP ETCH FOR CONTACT ETCHING AND LOW-K INTEGRATION IN BACK END OF LINE (BEOL)

R. Chanson^{1,*}, P. Lefauchaux², R. Dussart², P. Shen³, K. Urabe³, C. Dussarat³, K. Maekawa⁴, K. Yatsuda⁵, S. Tahara⁶ and J.-F. de Marneffe¹

1 IMEC vzw

Kapeldreef 75, 3001 Leuven-Heverlee, Belgium

2 CNRS / Université d'Orléans, GREMI, UMR 7344

14 rue d'Issoudun, P.O. Box 6744, 45067 Orléans Cedex 2, France

3 Air Liquide Laboratories

Tsukuba, Japan

4 TEL Technology Center, America, LLC

Albany, NY, U.S.A.

5 Tokyo Electron Ltd.

Tokyo, Japan

6 Tokyo Electron Miyagi Ltd.

Miyagi, Japan

* e-mail: romain.chanson@imec.be

Cryogenic etching is proposed as an alternative to the bosh process for silicon deep etching. The bosh process is known for its advantages as able to work at room temperature; this process is also robust and reproducible. Drawbacks are also known as the scalloping, the time waste during the passivation steps and process drifts due to passivation layer deposition on the reactor wall. The cryo-alternative avoids all these drawbacks; moreover, by-products of passivation are removed during the wafer warm up to room temperature (RT). The only one drawback is the need of a low process temperature.

More recently, cryogenic etching was proposed for low-k integration in the back end of line (BEOL). The aim is to use the micro-capillary condensation phenomenon in order to fill the low-k during plasma etching. The advantage is, in the one hand, to protect the organo-silicate methyl termination from chemical reaction. In the other hand, contrarily to pore stuffing protection by polymer, the condensate is desorbing when the wafer is warm up to RT. First proof of concept was shown with C₄F₈ recently, showing that low-k film could be etched without huge damages. However, this gas condense around -120 °C; such temperature is not compatible with industrial tools, which could only cool down around -60 °C. To work at higher temperature, Air Liquide provide new molecules allowing condensation at higher temperature. Moreover, these gases show very stable condensate. Damages involved by vacuum ultra violet (VUV) are evidenced but remain low after processing. Pattern transfer in 45 nm half pitch performed by TEL will be presented to highlight the interest for this cryo-etching process and its capability to reduce plasma induce damage (PID).

Acknowledgments. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 708106.

PLASMA ETCHED SILICON NANOWIRES WITH ENHANCED LIGHT TRAPPING PROPERTIES FOR AXIAL OR RADIAL PHOTOVOLTAIC NANODEVICES

A. Smyrnakis, P. Dimitrakis and E. Gogolides*

NCSR “Demokritos”, Institute of Nanoscience and Nanotechnology

15310 Aghia Paraskevi, Greece

* e-mail: e.gogolides@inn.demokritos.gr

Silicon nanowires (SiNWs) show unique structural, electrical and optical properties, that makes them a great candidate for high performance nanodevices such as energy conversion devices, photodiodes, sensors, and field effect transistors. In particular, SiNWs can offer several advantages for photovoltaic applications. Here, we report a top-down approach for the fabrication of highly ordered and perpendicular to the substrate, high aspect ratio (up to 40:1) silicon nanowires and nanopillar [1, 2]. Instead of conventional lithography, we use the cost effective process of colloidal particle self-assembly followed by cryogenic Si plasma etching, that offers smooth controllable sidewall profile and fast etch rate.

The optical properties of SiNWs are evaluated by reflectance measurements where extremely low total reflectance below 2 % is recognised. We experimentally demonstrate improved light absorption when moving from a perfectly ordered (after e-beam lithography) to a defective and quasi-ordered (after colloidal self-assembly) SiNW array [2]. We prove that even a small dimensional variability leads to dramatic reduction of the reflectance and increased light trapping inside the SiNW justifying their possible application in photovoltaic devices.

Plasma etched SiNW based photovoltaic devices are demonstrated [3]. We examine two different geometries and device configurations: (a) the axial type, in which the p-n junction is formed along the length of the wire; and (b) the radial type, where the p-n junction is formed from the outer to the centre of each wire. For the axial device, typical ion implantation is used for doping, while for the radial nanowires we use Spin-On-Dopant solutions for boron implantation and ultra-shallow p-n junction fabrication. Issues about the device configuration and electrical passivation by both methyl termination and hydrogen termination by plasma treatment are examined. Electrical characterization of the NWs was performed where promising results were obtained in terms of short circuit current (I_{sc}) increase and fill factor (FF) under illumination.

[1] Ellinas K, *et al.* 2011 *Microelectronic Engng.* **88** 2547-2551

[2] Smyrnakis A, *et al.* 2015 *Nanotechnology* **26** 085301

[3] Smyrnakis A, *et al.* 2017 *Microelectronic Engng.* **174** 74-79

PROTECTION MECHANISM FOR POROUS LOW-K MATERIALS DURING CRYOGENIC ETCHING

Q.-Z. Zhang*, S. Tinck and A. Bogaerts

University of Antwerp, Department of Chemistry, Research Group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerpen-Wilrijk, Belgium

* e-mail: quan-zhi.zhang@uantwerpen.be

A hybrid Monte Carlo - fluid model is employed to investigate cryogenic C_4F_8 plasma etching of porous organo-silicate materials. It is shown that the plasma induced damage gradually decreases with lowering the substrate temperature, which allows that C_4F_8 condenses inside the pores. Negligible plasma induced damage can be achieved around $-110\text{ }^{\circ}\text{C}$. However, the etching rate is reduced due to the pore filling with C_4F_8 . The simulation results of both etching rate and plasma induced damage as a function of temperature are validated by experimental results, performed at IMEC [1].

Furthermore, as shown in Fig. 1, the etching profile simulation also visually captures the permeation behaviour of the plasma species and their interactions with the pores in non-completely filled porous materials, which reveals the fundamental physics and chemistry mechanisms in cryogenic etching. Thus, these simulations provide a deeper understanding, which will help industry to improve the etching processing at cryogenic temperature.

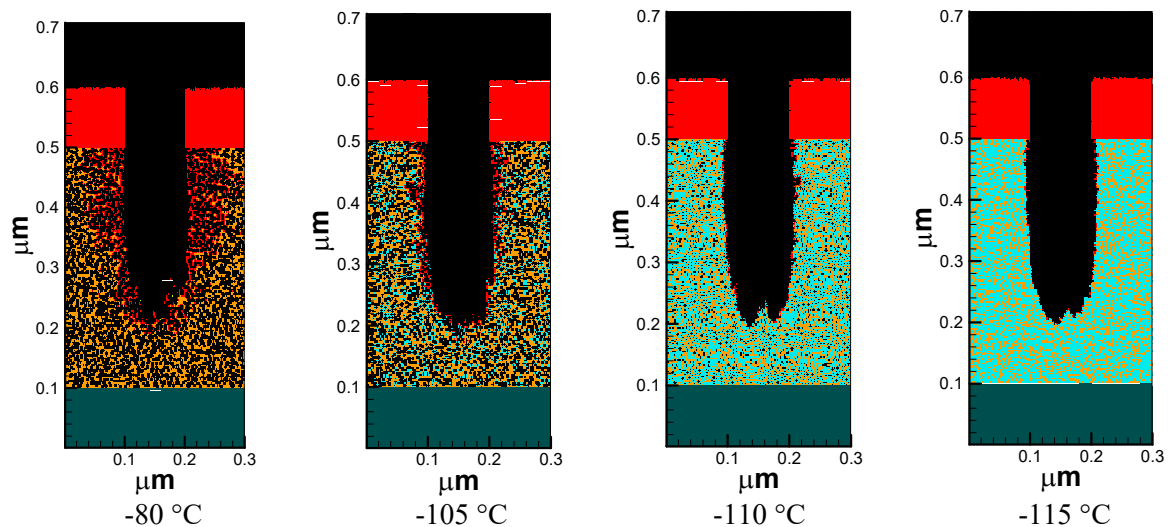


Figure 1. Etching profiles (for same depth) as a function of substrate temperature. The red lines indicate the permeation of plasma species, and their reactions with pores; the cyan colour indicates the filling of condensed C_4F_8 , and the filling percent for each temperature is 0 % ($-80\text{ }^{\circ}\text{C}$), 25 % ($-105\text{ }^{\circ}\text{C}$), 70 % ($-110\text{ }^{\circ}\text{C}$) and 100 % ($-115\text{ }^{\circ}\text{C}$).

[1] Zhang L P, Marneffe J F, *et al.* 2016 *J. Phys. D: Appl. Phys.* **49** 175203

Acknowledgements. We acknowledge the support from Marie Skłodowska-Curie actions (Grant Agreement no. 702604).

Wednesday July 5th, 2017**Poster session II: Micro-electronics and plasma medicine**

18. Rino Morent: Plasma treatment of polyactive nano-fibre conduits
19. Yuri Gorbanev: COST RF plasma jet: understanding the standard
20. Yuri Gorbanev: Plasma initiates radical reactions
21. Irina Grubova: Ab initio study of structural and electronic properties of the hydroxyapatite (001) / rutile (110) interface
22. Markus Heyne: Atomic layer etching of amorphous Si on MoS₂ for selectively patterned MX₂ heterostructures
23. Naresh Kumar: The stimulation of L6 skeletal muscle cell differentiation by non-thermal plasma modified electrically conductive fibres
24. Angela Privat Maldonado: Three-dimensional spheroid models to investigate the effect of low-temperature plasma treatments on metastatic processes of solid tumours
25. Jamoliddin I. Razzokov: Effect of plasma oxidation on the properties of globular proteins: an atomic scale study
26. Stefan Tinck: Cryogenic etching of porous SiO₂ with SF₆/O₂ plasmas
27. Maksudbek Yusupov: Understanding the role of aquaporins in the selective anti-cancer capacity of cold atmospheric plasmas

PLASMA TREATMENT OF POLYACTIVE NANO-FIBRE CONDUITS

R. Ghobeira¹, P. Wieringa², L. Moroni² and R. Morent^{1,*}

1 Ghent University, Department of Applied Physics, Research Unit Plasma Technology (RUPT)
Sint-Pietersnieuwstraat 41 B4, 9000 Ghent, Belgium

2 MERLN institute, Department of Complex Tissue Regeneration
P.O. Box 616, 6200 MD Maastricht, The Netherlands

* e-mail: rino.morent@ugent.be

Artificial guidance conduits are nowadays developed to repair peripheral nerve injuries while obviating the drawbacks of autografts. Enhancement of nerve regeneration via these conduits is strongly governed by mechanical, topographical and chemical properties of the surface. In this work, the copolymer poly(ethylene oxide terephthalate)/poly(butylene terephthalate) 300 55/45, commercially known as Polyactive (PA) is used due to its appropriate elasticity and strength, as well as its safe use in humans. The conduits are fabricated by an electrospinning process resulting in fibre meshes mimicking the neural extracellular matrix. The conduits comprised of PA nano-fibres have an average diameter of 1.3 μm and an average pore diameter of 2.5 μm . However, it remains a challenging task to bio-activate such a porous structure with narrow dimensions. Plasma treatment has the potential to modify the complex surface and should reach the central part of the porous conduits. A sub-atmospheric plasma treatment using an air or argon dielectric barrier discharge was used to treat the conduits. Chemical and physical surface changes are studied by XPS and SEM. Results indicate that air and argon plasmas increase the oxygen content with 7 % on the inner and outer conduit surface. This clearly shows the ability of the plasma to penetrate and modify the entire wall thickness of 140 μm . A small difference in the incorporated functional groups is observed between both treatments. A higher incorporation of C-O and O-C=O is found in the case of air plasma compared to argon plasma treatment. In the latter, also a small amount of C=O is incorporated. Different types of neural cells might sense these small differences thus generating detectable variances in their behaviour.

COST RF PLASMA JET: UNDERSTANDING THE STANDARD

Y. Gorbanev^{1,2,*}, P. Cos² and A. Bogaerts¹

1 University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

2 University of Antwerp, Department of Pharmaceutical Sciences
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: yury.gorbanev@uantwerpen.be

In recent years, gas discharges, known as non-thermal plasmas operating at atmospheric pressure have gained increased attention in biomedical applications [1]. However, the chemical and physical processes in plasma-exposed aqueous media still lack detailed understanding. For example, it was shown recently that in the case of a parallel-field kHz-frequency plasma jet all reactive species detected in the liquid sample exposed to plasma were generated in the gas phase plasma and subsequently delivered to the liquid sample [2]. However, both gas and liquid phase chemistry of the plasma jet depend on the specific type of plasma operation. A large number of research groups manufacture and study a particular jet, which adds to the complexity of the plasma research.

To address this, the COST RF plasma jet was introduced to set a comparison standard between the research of different research groups around the world [3]. The gas phase chemistry of the jet can be monitored via various spectroscopic techniques or predicted using available models [4]. At the same time, the liquid phase chemistry (most important for the biological applications, where water is an essential part of the milieu [5]) is scarcely studied.

In this investigation, we evaluate the phase in which the reactive species detected in the liquid are created. The use of isotopically labelled water introduced into different compartments of the jet combined with EPR analysis of the formed radicals and ¹H-NMR analysis of the isotope content of the aqueous solution allows distinction between the species that diffuse into the liquids from the gas phase and those formed from the liquid phase molecules.

The study provides insights into the mechanisms behind the action of the COST RF jet in biomedical applications.

- [1] Lu X, Naidis G V, Laroussi M, Reuter S, Graves D B and Ostrikov K 2016 *Phys. Rep.* **630** 1-84
- [2] Gorbanev Y, O'Connell D and Chechik V 2016 *Chem. Eur. J.* **22** 3496-3505
- [3] Golda J, Held B, Redeker M, Konkowski M, Beijer P, Sobota A, Kroesen G, Braithwaite N St J, Reuter S, Turner M M, Gans T, O'Connell D and Schulz-von der Gathen V 2016 *J. Phys. D: Appl. Phys.* **49** 084003
- [4] Murakami T, Niemi K, Gans T, O'Connell D and Graham W G 2014 *Plasma Sources Sci. Technol.* **23** 025005
- [5] Vermeylen S, De Waele J, Vanuytsel S, De Backer J, Van der Paal J, Ramakers M, Leyssens K, Marcq E, Van Audenaerde J, Smits E L J, Dewilde S and Bogaerts A 2016 *Plasma Proc. Polym.* **13** 1195-1205

Acknowledgements. This research was supported by the European Marie Skłodowska-Curie Individual Fellowship "LTPAM" within Horizon2020 (Grant no. 657304).

PLASMA INITIATES RADICAL REACTIONS

Y. Gorbanev^{1,2,4,*}, D. Leifert³, A. Studer³, D. O'Connell⁴ and V. Chechik²

1 University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

2 University of York, Department of Chemistry
University Road, Heslington, York YO10 5DD, Great Britain

3 University of Münster, Organic Chemistry Institute
Corrensstrasse 40, 48149, Münster, Germany

4 University of York, Department of Physics, York Plasma Institute
University Road, Heslington, York YO10 5DD, Great Britain

* e-mail: yury.gorbanev@uantwerpen.be

The recent development of non-thermal plasmas, which operate at atmospheric pressure and near room temperature, allows these plasmas to be used as sources of reactive species generated under mild conditions [1]. In general, the concentrations of the produced species are low [2], and the plasmas cannot be practically used in stoichiometric chemical reactions. The situation is different for the initiation of radical chain reactions, where only a small amount of an initiator is required to overcome chain termination processes.

In this work, we investigated the applicability of non-thermal plasma to be used as an initiator in radical reactions (Fig. 1). Three case studies were performed: 1) dehalogenation of the iodo-substituted arenes; 2) dehalogenation followed by 5-*exo*-trig cyclisation; and 3) trifluoromethylation with Togni-II reagent. These reactions were chosen to cover a range of solvents and reaction conditions, different types of chain transfer agents, intra- and intermolecular pathways, and different types of atmospheric pressure plasma reactors (jets).

Under optimised conditions, excellent yields were recorded for all three reactions, demonstrating that non-thermal plasmas can be efficiently used in the absence of any other added initiators. The short reaction times, mild conditions (e.g., absence of toxic or hazardous initiators, low level of UV, moderate temperatures, solvent-free reactions) make plasma an appealing alternative to conventional radical initiators [3].

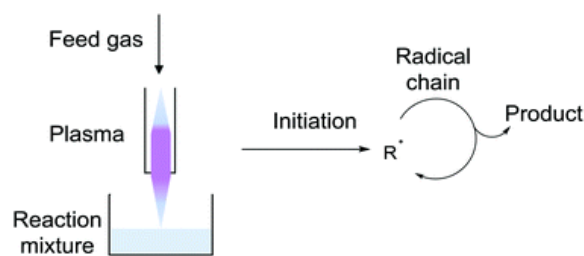


Figure 2. Non-thermal plasmas act as initiators in radical chain reactions.

- [1] Lu X, Naidis G V, Laroussi M, Reuter S, Graves D B and Ostrikov K 2016 *Phys. Rep.* **630** 1-84
- [2] Hefny M M, Pattyn C, Lukes P and Benedikt J 2016 *J. Phys. D: Appl. Phys.* **49** 404002
- [3] Gorbanev Y, Leifert D, Studer A, O'Connell D and Chechik V 2017 *Chem. Commun.* **53** 3685-3688

Acknowledgements. This work was supported by the Leverhulme Trust (grant RPG-2013-079) and EPSRC (EP/K018388/1 and EP/H003797/2).

AB INITIO STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF THE HYDROXYAPATITE (001) / RUTILE (110) INTERFACE

I. Grubova^{1,2,*}, M. Surmeneva¹, S. Huygh², R. Surmenev¹ and E.C. Neyts¹

¹ National Research Tomsk Polytechnic University, Department of Experimental Physics
Lenin Avenue 30, 634050 Tomsk, Russia

² University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: rodeo_88@mail.ru

The work of adhesion, interfacial energy, atomic and electronic structure of the amorphous hydroxyapatite (aHA) / rutile (110) interfaces were studied using ab initio calculations based on the density functional theory (DFT). Three kinds of rutile (Ru) slab with four atomic layers were adopted for interfacial model geometries, the stoichiometric (denoted as cRu), non-stoichiometric (denoted as Ru(Vo1) and Ru(Vo3)) and amorphous surfaces (denoted as aRu). The calculations concern three models of aHa/Ru interfaces each with 3 or 4 stacking configurations. Formation energies of bridging and sub-bridging oxygen vacancies considered in Ru (110) surface were evaluated and obtain results confirm that oxygen vacancies are more likely to form at the Ru surface than at subsurface [1]. The interfacial interaction at the interfaces was evaluated through the work of adhesion. For the aHA / Ru(110) interfaces, the work of adhesion is found to depend strongly on the chemical environment of the Ru surface. Electronic analysis indicates that the charge transfer is very small in the case of interface formation between aHA and crystalline Ru (110). In contrast, significant charge transfer occurs between aHA and aRu slabs during the formation of the interface. Charge density difference (CDD) analysis indicates that the dominant interactions in the interface have significant ionic character, and in particular the Ti-O bonds. Thus, the obtained results reveal that the aHA / aRu interface shows a more preferable interaction and is thermodynamically more stable than other interfaces. These results are particularly important for improving the long-term stability of HA-based implants.

[1] Cheng H and Selloni A 2009 *Phys. Rev. B* **79** 092101

Acknowledgements. This work was financially supported by the “PhD P.L.U.S.” scholarship funded by National Research Tomsk Polytechnic University, BOF Fellowships for International Joint PhD students funded by University of Antwerp (project number 32545), S.H. is funded as PhD fellow (aspirant) of the FWO-Flanders (Fund for Scientific ResearchFlanders), Grant number 11C0115N. Federal Target Program #14.587.21.0013 (application 2015-14-588-0002-5599), President's fellowships MK-7907.2016.8, MK-6459.2016.8, and 11.1233.2017/PCH.

ATOMIC LAYER ETCHING OF AMORPHOUS Si ON MoS₂ FOR SELECTIVELY PATTERNED MX₂ HETEROSTRUCTURES

M. Heyne^{1,2,3,*}, A. Goodyear⁴, J.-F. de Marneffe³, M. Cooke⁴, E.C. Neyts², I. Radu³ and S. De Gendt^{1,3}

¹ KU Leuven

Celestijnenlaan 200F, 3001 Leuven-Heverlee, Belgium

² University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

³ IMEC vzw

Kapeldreef 75, 3001 Leuven-Heverlee, Belgium

⁴ Oxford Instruments Plasma Technology

North End, Bristol BS49 4AP, Great Britain

* e-mail: markus.heyne@kuleuven.be

Few-atom thick nanosheet materials, such as MoS₂ and WS₂, are considered as building blocks for future nanoelectronics due to outstanding properties of their heterostructures [1]. To date there is no technique available to fabricate heterostructure devices with high density on small footprint and contact the two different nanosheets separately. Two fundamental issues occur during the patterning and integration steps: wet etching often causes failure due to poor substrate adhesion of the van-der-Waals layered films. Besides this, conventional plasma-based processes, used for opening contact areas, damage the sensitive films already with moderate ion energies. In addition, etch selectivity between different transition-metal dichalcogenides (TMD) is anticipated to be challenging due to similar chemical properties of the films.

We established a scalable method to grow arbitrarily patterned WS₂ on top of MoS₂. To this end, a thin amorphous Si layer (aSi) was deposited on MoS₂ obtained by MoO₃ sulphurisation and a PECVD SiO₂ hardmask was applied [2]. The remaining thin amorphous silicon layer was then etched by Cl-based atomic layer etching in an Oxford Instruments PlasmaPro 100 chamber equipped with an ALE kit [3]. The atomic layer etching process consists of the following consecutive steps: a chlorination pulse with a fast-switching valve, purging, and activation with a low table bias power. This soft process enables etch rates of 0.6 nm/cycle and allows the patterning the aSi layer on MoS₂ without damaging the TMD.

The hardmask and native oxide of the patterned aSi film were removed and passivated in a subsequent wet etch step in 0.5 % HF-solution and converted into WS₂ by high-temperature WF₆ and H₂S cyclic treatment [4]. As a result, individually patterned WS₂ on MoS₂ can be obtained.

- [1] Huo N, Kang J, Wei Z, Li S-S, Li J and Wei S-H 2014 *Adv. Funct. Mater.* **24** 7025-7031
- [2] Heyne M H, Chiappe D, Meersschaut J, Nuytten T, Conard T, Bender H, Huyghebaert C, Radu I P, Caymax M, de Marneffe J-F, Neyts E C and De Gendt S 2016 *J. Mater. Chem. C* **4** 1295-1304
- [3] Goodyear A and Cooke M 2017 *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film* **35** 01A105
- [4] Heyne M H, de Marneffe J-F, Delabie A, Caymax M, Neyts E C, Radu I, Huyghebaert C and De Gendt S 2017 *Nanotechnology* **28** 04LT01

Acknowledgements. M.H. acknowledges the agency Flanders Innovation & Entrepreneurship (VLAIO) for the support of this work.

THE STIMULATION OF L6 SKELETAL MUSCLE CELL DIFFERENTIATION BY NON THERMAL PLASMA MODIFIED ELECTRICALLY CONDUCTIVE FIBRES

N. Kumar^{1,*}, P. Shaw², E.H. Choi², P. Attri² and A. Bogaerts¹

¹ University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

² Kwangwoon University, Department of Electrical and Biological Physics, Plasma Bioscience Research Center
20 Kwangwon-Ro, Nowon-Gu, 139-701 Seoul, South Korea

Myoblasts are myogenic precursors that proliferate, activate, and differentiate on muscle injury to sustain the regenerative capacity of skeletal muscles. Therefore, myotube formation plays an important role in restoring muscular functions, and substrates to promote the differentiation of myoblasts to myotubes need to be developed for muscle tissue engineering. In this study, we developed a non-thermal plasma modified electrically conductive polyaniline polymer and fabricated it into nano-fibre substrates that were further used to investigate muscle L6 cell proliferation and differentiation. However, the expression and subcellular localisation of non-thermal plasma modified nano-fibres (plasma-modified polymers; PMP) in muscle development and myoblast differentiation are largely unknown. The PMP nano-fibres were cytocompatible and show higher proliferation and total protein content upon 8 days of muscle cell culture, whereas non-plasma modified polyaniline polymer nano-fibres (NMP) do not show significant effects on proliferation. Furthermore, the level of myogenin gene expression detected on day 8 of culture PMP nano-fibres was approximately 1 and 2 fold greater than the NMP nano-fibres. Similar results were observed for the expression of other genes including troponin (1.5-fold greater) and the myosin heavy chain gene (3-fold greater). These results indicate that PMP nano-fibre substrates can modulate the induction of myoblasts into myotube formation without additional electrical stimulation, suggesting that these nano-fibre substrates may have potential as a temporary substrate for skeletal tissue engineering.

THREE-DIMENSIONAL SPHEROID MODELS TO INVESTIGATE THE EFFECT OF LOW-TEMPERATURE PLASMA TREATMENTS ON METASTATIC PROCESSES OF SOLID TUMOURS

A. Privat-Maldonado^{1,2,*}, E. Smits² and A. Bogaerts¹

1 University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

2 University of Antwerp, Center for Cell Therapy and Regenerative Medicine, Solid Tumor Immunology Group,
Center for Oncology Research

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: angela.privatmaldonado@uantwerpen.be

Cancer is the second leading cause of death worldwide [1]. However, current treatments to control the spread of solid tumours are still highly toxic. Thus, new cancer treatments that are effective and have low impact on healthy cells are needed. In this context, low-temperature plasmas (LTPs) arise as an attractive anticancer therapy. The biological response of LTPs is mainly mediated by the reactive nitrogen and oxygen species generated in the plasma [2]. LTPs can induce DNA damage [3] and cell death in homogenous monolayers of cancer cells *in vitro* [4]. However, a model that better reflects the *in vivo* behaviour of cells in tumour tissues to evaluate the efficacy of LTP cancer treatments is required. We propose the use of a versatile 3-dimensional multicellular spheroid model that mimics the pathophysiological condition in tumours such as oxygen, nutrients, metabolites and proliferation gradients and complex architecture [5] to assess the effect of LTP treatment in metastatic processes of solid tumours. For this study, spheroids are generated using U87, LN229 and U251 glioblastoma cell lines and exposed directly or indirectly (plasma-treated PBS) to plasma (KinPen). We use live cell imaging tools to assess cell viability, spheroid morphology and extracellular matrix (ECM) integrity that inform about the ability of tumour cells to migrate, survive or proliferate in response to direct and indirect LTP treatment. This study provides insight in the effect of LTP treatment on solid tumours.

[1] Fitzmaurice C, *et al.* 2015 *Jama Oncology* **1** 505-527

[2] Graves D B 2012 *J. Phys. D: Appl. Phys.* **45** 263001

[3] Hirst A M, Simms M S, Mann V M, Maitland N J, O'Connell D and Frame F M 2015 *Br. J. Cancer* **112** 1536-1545

[4] Vermeylen S, *et al.* 2016 *Plasma Process. Polym.* **13** 1195-1205

[5] Vinci M, *et al.* 2012 *BMC Biol.* DOI: 10.1186/1741-7007-10-29

EFFECT OF PLASMA OXIDATION ON THE PROPERTIES OF GLOBULAR PROTEINS: AN ATOMIC SCALE STUDY

J.I. Razzokov and A. Bogaerts

University of Antwerp, Department of Chemistry, Research group PLASMANT

Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

* e-mail: jamoliddin.razzokov@uantwerpen.be

We perform molecular dynamics (MD) simulations in order to study the interaction of plasma species with proteins, more specifically with tubuline, which is a major component of the eukaryotic cytoskeleton. Recent experiments [1] showed the shrinkage of cancer cells after treating with CAP. Therefore, it is important to investigate the structural flexibility of tubuline in native as well as oxidised form, in various levels of oxidation, to elucidate how oxidation induced by plasma influences the protein configuration and stability. For this purpose, we performed MD simulations using the modified (or oxidised) amino acid residues with three oxidation levels of tubulin, i.e., 10, 20 and 30 % [2, 3]. The force field for the post-translational modifications of the amino acids is based on literature [4].

The results on the time evolution of the root mean square deviation (RMSD) of the native and oxidized tubuline show that the stability of the protein decreases upon increasing the oxidation degree; see Fig. 1.

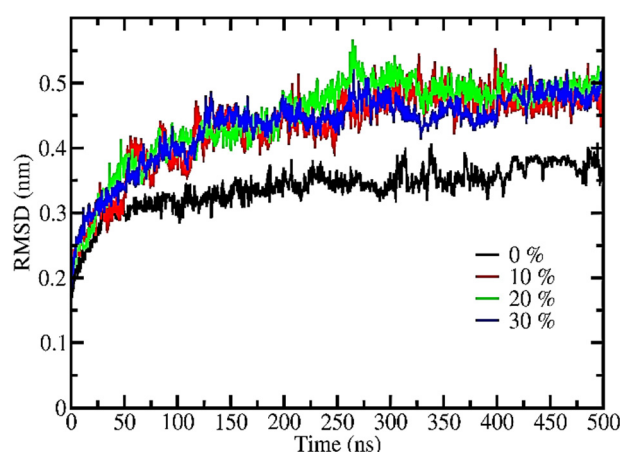


Figure 1. RMSD of native (0 %) as well as oxidized tubuline with 10, 20 and 30 % oxidatively modified solvent accessible residues.

This indicates that even a small fraction of oxidation (10 %) greatly affects the stability of tubuline by increasing its flexibility. These investigations are highly important for gaining fundamental insight into the plasma interaction with tubuline, and to better understand how plasma induces the shrinkage of cancer cells.

- [1] Kumar N, *et al.* 2017 *Sci. Rep.* (to be submitted)
- [2] Takai E, *et al.* 2014. *J Phys D: Appl Phys.* **47** 28
- [3] Stadtman E R 2006 *Free Radic Res.* **40** 1250-1258
- [4] Petrov D, *et al.* 2013 *PLoS Comput Biol.* **9**(7) e1003154

CRYOGENIC ETCHING OF POROUS SiO_2 WITH SF_6/O_2 PLASMAS

S. Tinck^{1,*}, T. Tillocher², R. Dussart², E.C. Neyts¹ and A. Bogaerts¹

¹ University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

² CNRS / Université d'Orléans, GREMI, UMR 7344
14 rue d'Issoudun, P.O. Box 6744, 45067 Orléans Cedex 2, France

* e-mail: stefan.tinck@uantwerpen.be

Porous low- k materials, like $\text{SiO}_2:\text{CH}_3$, have gained increasing interest in the microelectronics industry during the past decade due to their promising properties for advanced interconnect technologies in microchip manufacturing [1]. The main problem with etching these porous materials is plasma induced damage (PID). During etching with PID, the material is significantly damaged by ion bombardment, and especially by diffusion of reactive species (e.g., F atoms) into the material underneath the protective mask, effectively increasing its k -value and thus degrading the quality of the isolating porous material.

PID can be limited by cooling the wafer to about -100°C and etching it with SF_6/O_2 so that an oxifluoride passivation layer is formed on the surface of the pores that also reduces diffusion through the material. During SF_6/O_2 cryo-etching, first proposed in 1988 by Tachi *et al.* [3] a SiF_xO_y passivation layer is formed, which desorbs naturally when the wafer is brought back to room temperature, leaving a clean trench with no scalloping [4].

The underlying mechanisms of how the SiF_xO_y passivation layer is formed and automatically desorbs afterwards are not fully understood [5]. The aim of this work is to obtain a better understanding of this mechanism and to further improve the cryo-etching process by limiting PID. Both experimental and numerical investigations (including Monte Carlo - fluid plasma simulations and Molecular Dynamics) are carried out to obtain more insight in these processes.

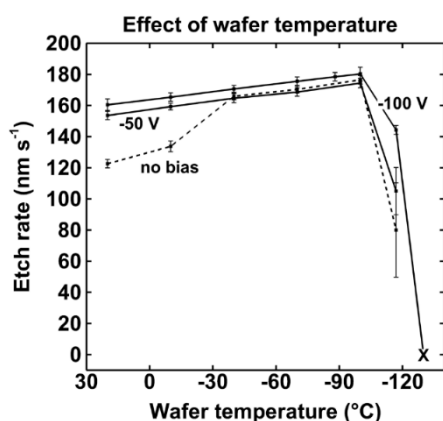


Figure 1. Measured etch rates a.f.o. temperature.

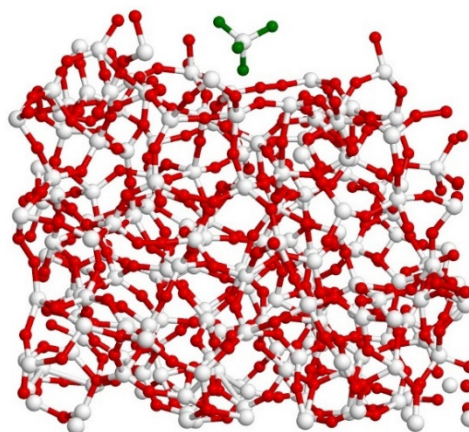


Figure 2. Molecular Dynamics of SiF_4 on SiO_2 .

- [1] McCoy M 2000 *Chem. Engng. News* **78** 17
- [2] Zhang L, *et al.* 2016 *J. Phys. D: Appl. Phys.* **49** 175203
- [3] Tachi S, *et al.* 1988 *Appl. Phys. Lett.* **52** 616
- [4] Dussart R, *et al.* 2004 *J. Micromech. Microengng.* **14** 190
- [5] Dussart R, *et al.* 2014 *J. Phys. D: Appl. Phys.* **47** 123001

UNDERSTANDING THE ROLE OF AQUAPORINS IN THE SELECTIVE ANTI-CANCER CAPACITY OF COLD ATMOSPHERIC PLASMAS

M. Yusupov^{1,*}, D. Yan², M. Keidar² and A. Bogaerts¹

¹ University of Antwerp, Department of Chemistry, Research group PLASMANT
Campus Drie Eiken, Universiteitsplein 1, 2610 Antwerpen-Wilrijk, Belgium

² The George Washington University, Department of Mechanical and Aerospace Engineering
Science & Engineering Hall, 800 22nd Street, NW, Room 3550, 20052 Washington DC, U.S.A.

* e-mail: maksudbek.yusupov@uantwerpen.be

Recently, cold atmospheric plasmas (CAPs) have shown their promising applications in cancer therapy [1]. The underlying mechanisms, however, still remain obscure. There are several studies in literature which proposed mechanisms to understand the selective effect of CAP in cancer treatment [2-4], and all of them are based on the noticeable rise of intracellular reactive oxygen species (ROS) occurring in cancer cells compared to normal cells [5-8]. One of the recently suggested mechanisms is based on aquaporins (AQPs), i.e., the only verified H₂O₂ channels on cells [2]. It was found that after CAP treatment, the CAP-generated H₂O₂ penetrate into cancer cells significantly faster than in homologous normal cells, which may contribute to the higher rise of ROS in cancer cells compared to normal cells [2].

In this study, we perform molecular dynamics (MD) simulations to determine the precise role of AQPs in the selective anti-cancer capacity of CAP. Specifically, we investigate the permeation (or diffusion) processes of H₂O₂ through the AQP1. The calculated free energy and diffusion rate profiles of H₂O₂ across AQP1 allow us to determine the permeability coefficient of H₂O₂ through AQP1, which might explain the faster H₂O₂ consumption speed of cancer cells. The calculated free energy profile of H₂O₂ across the AQP1 shows a lower energy barrier for penetration into the cytoplasm compared to that for the phospholipid membrane. This, in turn, can explain the need for protein channels or so-called electropores (see [9]) for delivery of ROS into cells. In addition, we measure the H₂O₂ consumption of several cancer cell lines. So far, we have found that the consumption speed of PA-TU-8988T cells, A549 cells, and MCF-7 cells in the first hour after culturing in H₂O₂-containing medium is 2.35, 2.69, and 2.69 pM/cell/second, respectively. The measured H₂O₂ consumption speed of cells will be correlated with the calculated permeability coefficient of AQP1. This study will give better insight into the role of AQPs in the selectivity of plasma for treating cancer cells.

- [1] Keidar M 2015 *Plasma Sources Sci. Technol.* **24** 033001
- [2] Yan D, *et al.* 2015 *Biointerphases* **10** 040801
- [3] Szili E J, Hong S-H and Short R D 2015 *Biointerphases* **10** 029511
- [4] Van der Paal J, Neyts E C, Verlaet C C and Bogaerts A 2016 *Chem. Sci.* **7** 489
- [5] Ishaq M, Evans M D and Ostrikov K 2014 *BBA-Mol. Cell Res.* **1843** 2827
- [6] Ishaq M, *et al.* 2014 *Mol. Biol. Cell* **25** 1523
- [7] Kaushik N K, Kaushik N, Park D and Choi E H 2014 *PLoS One* **9** e103349
- [8] Kim S J and Chung T 2016 *Sci. Rep.* **6** 20332
- [9] Yusupov M, Van der Paal J, Neyts E C and Bogaerts A 2017 *BBA-Gen. Subjects* **1861** 839

Thursday July 6th, 2017

Session 11	Perspectives, industry and commercialisation I
09:00 – 09:20	Invited 21 – Ken Ostrikov Plasma-nano-synergies: catalysing cross-disciplinary collaborations
09:20 – 09:40	Invited 22 – Alquin Stevens Recent developments in digital μ PlasmaPrint surface engineering - from low volume science to high volume industrial applications
09:40 – 10:00	Invited 23 – Peter J. Bruggeman Challenges in controlling plasma processes in the plasma/nano-field: a personal perspective
10:00 – 10:20	Invited 24 – Gill Scheltjens Enabling functional thin films by soft atmospheric plasma polymerisation
10:20 – 11:00	Refreshment break
Session 12	Perspectives, industry and commercialisation II
11:00 – 11:25	Invited 25 – David Go The plasma-catalyst interaction: exploring synergistic effects at high temperature
11:25 – 11:50	Invited 26 – Mahendra Sunkara Nanowire as a model system for designing catalysts?
11:50 – 12:05	Invited 27 – Uroš Cvelbar Plasma and edge nanoelectronics
12:05 – 12:30	Conference closing and presentation iPlasmaNano-IX

PLASMA-NANO-SYNERGIES: CATALYSING CROSS-DISCIPLINARY COLLABORATIONS

K. Ostrikov*

¹ Queensland University of Technology (QUT), School of Chemistry, Physics and Mechanical Engineering,
Science and Engineering Faculty
4000 Brisbane, QLD, Australia

² Queensland University of Technology (QUT), Institute for Future Environments
4000 Brisbane, QLD, Australia

* e-mail: kostya.ostrikov@qut.edu.au

With plasma nanoscience reaching a dozen years milestone, it is worth examining how research in this field catalyses cross-disciplinary collaborations. The focus of this presentation will be on the key features of nanoscale interactions of low-temperature plasmas with matter which make such plasmas a versatile tool in materials science and engineering and other areas such as chemical engineering and health sciences. Particular attention will be paid on synergistic effects of plasmas with common materials and processing methods and what difference it makes in diverse applications, with particular focus where nanoscale and atomic-scale features of materials play a role.

These localised interactions have opened opportunities for fundamental research and applications in the plasma nanoscience field. The focussed “what can plasma do for you” examples will be used to stimulate collaborative efforts even between researchers working in both academia and industry and normally in very diverse fields.

RECENT DEVELOPMENTS IN DIGITAL μ PLASMAPRINT SURFACE ENGINEERING - FROM LOW VOLUME SCIENCE TO HIGH VOLUME INDUSTRIAL APPLICATIONS

A. Stevens^{1,*}, J. Verheijen¹, J. Schep¹, T. Huiskamp^{1,2}, N. Van Hijningen¹ and H. De Haan¹

1 Innophysics BV

Franssebaan 592a, 5627 JM Eindhoven, The Netherlands

2 Eindhoven University of Technology

Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

* e-mail: alquin.stevens@innophysics.nl

Area-selective surface modifications by atmospheric pressure micro-plasmas allow cost-effective surface modifications and chemical functionalisation. Plasma patterning technologies are utilised for example in optical components production, semicon back-end, flexible electronics manufacturing, in combination with inkjet printing or fluid dispensing, and may also be implemented in biosensor and tissue engineering applications. InnoPhysics has developed and commercialises the μ PlasmaPrint technology, which enables area-selective functionalisation by means of a dot-wise patterning of the plasma treatment/deposition with resolutions from millimetres down to 150 μm . μ PlasmaPrint utilises a multi pin-to-plate dielectric barrier micro-discharge at atmospheric pressure which can be independently activated according to a digitally programmed pattern. In order to improve the μ PlasmaPrint resolution and to improve the processing and substrates flexibility, InnoPhysics has developed new hardware and process options. Recent developments will be shown related to process feedback through surface wettability mapping, in-situ monitoring of the plasma energy for improved process feedback and the development of a stand-alone μ PlasmaPrint head with integrated electrode to enable the application of μ PlasmaPrint not only on 2D, flat substrates, but also more complex, 3D workpieces. On the process side, developments will be presented to enable non-fouling hydrophilic coatings in plastic biomedical devices by combining μ PlasmaPrint with liquid coating dispensing. Furthermore recent developments which enable selective chemistry to obtain patterns of chemically functionalised substrates as an alternative to direct μ PlasmaPrint deposition will be shown. Examples will involve a plasma ALD-like approach to obtain TiO_2 for photocatalytic and electron transport layer applications, and the formation of selectively grown diamond patterns on Si wafer. These process options broaden the scope of potential applications of digital μ PlasmaPrint surface modifications at present for low volume science applications and for future high volume industrial applications.

ENABLING FUNCTIONAL THIN FILMS BY SOFT ATMOSPHERIC PLASMA POLYMERISATION

G. Scheltjens*

APEMCO

Z. 1 Researchpark 330, 1731 Zellik, Belgium

* e-mail: gill.scheltjens@apemco.eu

Plasma polymer thin films are of great interest in surface engineering in a wide range of applications. However, atmospheric plasma polymerisation usually highlights complex structures with a high degree of cross-linking due to a high fragmentation of chemical precursors and their random recombination, related to the excess of energy involved during the polymerisation process. Herein, by using soft atmospheric plasma deposition conditions, developed by FUNCOATS, and by adapting these conditions to the used perfluorodecyl acrylate (PFDA) and dodecyl acrylate (DOCA) precursors [1], it appears possible not only to get a high retention of monomer functionalities but a polymerisation close to conventional methods. Molecular investigation revealed the presence of polymeric moieties and the mechanism of plasma polymerisation of acrylates and/or methacrylates moieties has been mainly based on a selective activation of specific chemical groups and more precisely by activation of the ethylenic groups. The characterisation of such coatings, achieved in soft plasma conditions, by using a multi-techniques approach (FTIR, MALDI-TOF/MS and solid state NMR, XRD and DSC) highlighted a high control in the plasma polymerisation process by ensuring the preservation of the integrity of the monomers and limiting their dissociation[2, 3].

- [1] Petersen J, Becker C, Fouquet T, Addiego F, Toniazzo V, Dinia A and Ruch D 2013 RSC Advances **3** 4416-4424
- [2] Fouquet T, Mertz G, Delmee M, Becker C, Bardon J and Sato H 2016 *Plasma Process. Polym.* **13** 862-868
- [3] Fouquet T, Mertz G, Becker C, Fetzer L, Ziarelli F and Ruch D 2014 *Plasma Process. Polym.* **11** 931-942

THE PLASMA-CATALYST INTERACTION: EXPLORING SYNERGISTIC EFFECTS AT HIGH TEMPERATURE

D.B. Go^{1,2,*}, J. Kim² and J. C. Hicks²

1 University of Notre Dame, Department of Aerospace and Mechanical Engineering
46556 Notre Dame, IN, U.S.A.

2 University of Notre Dame, Department of Chemical and Biomolecular Engineering
46556 Notre Dame, IN, U.S.A.

* e-mail: dgo@nd.edu

Plasma-enhanced catalysis has shown significant promise for effective chemical processing ranging from chemical synthesis (e.g., gas reforming) to chemical elimination (e.g., VOC destruction). However, the precise physical and chemical mechanisms of the enhancement remain elusive as the both the plasma and the catalytic processes are independently complex, and when coupled, exceedingly so. In this work, we use dry reforming of methane with carbon dioxide to probe the impact of a dielectric barrier discharge (DBD) on thermal catalysis. At low temperatures, not surprisingly, thermal catalysis using nickel (Ni) is essentially inactive but the DBD alone (no Ni) can convert methane. At high temperatures, the opposite is true as thermal catalysis (with Ni) is active but the DBD alone (no Ni) shows no conversion. Interestingly, when at high temperatures with both the presence of a Ni catalyst and a DBD, there is enhancement above that seen from thermal catalysis alone. This suggests that the various active species produced by the DBD at higher temperatures interact in unique ways with the catalysts, even though they themselves are insufficient to convert methane. This work will overview our efforts to understand these interactions at high temperatures under both equilibrium and kinetically-limited conditions [1, 2]. Our results show that the plasma effectively reduces the activation barrier at higher temperatures, leading to enhanced catalytic activity.

[1] Kim J, Abbott M S, Go D B and Hicks J C 2016 *ACS Energy Lett.* **1** 94-99

[2] Kim J, Go D B and Hicks J C 2017 *Phys Chem Chem Phys* (in press)

NANOWIRE AS A MODEL SYSTEM FOR DESIGNING CATALYSTS?

M. Sunkara^{1,2,*}, P. Ajayi¹, A. Nambo^{1,2}, V. Atla¹, V. Kumar², J. He², T. Nguyen² and S. Vasireddi²

1 University of Louisville, Conn Center for Renewable Energy Research and Chemical Engineering
40292 Louisville, KY, U.S.A.

2 Advanced Energy Materials, LLC
311 E. Lee Street, 40208 Louisville, KY, U.S.A.

* e-mail: mahendra@louisville.edu

Nanowires are one-dimensional materials whose surfaces depend upon the growth direction. The resulting surfaces can be modified and used to define uniform surface sites for designing high performance catalysts and adsorbents. In this presentation, a perspective will be provided on the use of nanowire based materials and their performance with several chemical and plasma catalysis applications.

As a first example, we will consider the use of metal oxide nanowires for designing high performance catalytic adsorbents. Specifically, catalysts and their performance with ultra-deep desulphurisation using hydrogen and low amounts of hydrogen will be discussed for removing sulphur from diesels and other fuels from hundreds of ppm to 1 ppm [1]. In addition, the nature of active sites and how they can be manipulated for tuning the activity of both desulphurisation and aromatics hydrogenation will be discussed.

In the second example, how molybdenum oxide nanowires can be used to obtain sulphide surface sites necessary for high performance hydrogen evolution electro-catalysts [2]. The final example will deal with nanowire based materials for designing high performance adsorbents for carbon dioxide capture and electrochemical reduction of carbon dioxide [3].

- [1] Gupta M, He J, Nguyen T, Petzold F, Fonseca D, Jasinski J and Sunkara M K 2016 *Appl. Catalysis B: Environmen.* **180** 246-254
- [2] Chen Z, Cummins D, Clark E L, Reinecke B, Sunkara M K and Jaramillo T F 2011 *Nano Lett.* **11** 4168-4175
- [3] Kumar B, Atla V, Brian J P, Nguyen T, Kumari S, Sunkara M and Spurgeon J M 2017 *Angewandte Chemie* **56** 3645-3649

Acknowledgements. Advanced Energy Materials, LLC acknowledges support from National Science Foundation and Kentucky Science and Technology Corp. Conn Center acknowledges support from DOE-EPSCoR, NSF-EPSCoR and NSF-SOLAR grants.

PLASMA AND EDGE NANO ELECTRONICSU. Cvelbar*

Jožef Stefan Institute

Jamova cesta 39, 1000 Ljubljana, Slovenia

* e-mail: uros.cvelbar@ijs.si

The new development of electronic devices drives the technology into use of smaller and more precise systems like utilisation of 2D nanostructure edges, which recently showed great potential in applications of electronics. The electronic properties and edge properties of nanomaterials can be significantly influenced through functionalisation, which changes also the material band gap. There are more and more theoretical studies which unravel the edge effects and quantum confinement on the electronic properties of 2D nanomaterials like nanoribbons. The different edge functionalisation groups, such as H, F, Cl, OH, O and S, led either to semiconductor or metallic behaviour in systems like phosphorene nanoribbons in dependence to their edge chemical groups. However, very little experiments and measurements have been performed to prove the theoretical results. This is opening a number of opportunities for plasma nanoscience to actively participate in the ongoing research. The presented talk will outline the ongoing research and future opportunities as well as challenges for plasma nanoscience dealing with edge nanoelectronics.