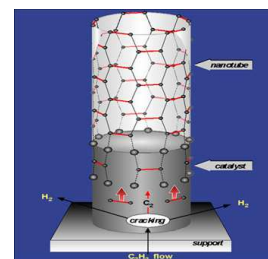




NANOFAC:



The Nanosciences at the University of Namur Belgium

Programme of the afternoon :

13h30: Welcome - Pr Robert Sporken, Dean of the Faculty of sciences

13h50: Pr Laurent Houssiau & Pr Jean-Jacques Pireaux, "*Nanosciences at LISE: new engineered materials and characterization techniques*", PMR/LISE

14h10: Dr Luc Henrard, "*Simulation of Spectroscopic Fingerprints at the Nanoscale*", PMR/LISE

14h30: Pr Carine Michiels, "*The Targan project: an example of the utilization of targeted radioactive nanoparticles in cancer*", URBC & LARN

14h50 - 15h10: Coffee break – poster session

15h10: Pr Zineb Mekhalif, "*Chemistry and Electrochemistry of Surfaces: from Nanofilms to Nanocomposites*", UCES

15h30: Dr Claire Bouvy, "*Optoelectronic materials: laser effect following a two-photon absorption process in disordered media*", UCNM

15h50: Pr Bernard Masereel, "*Evaluation of potential toxicity of nanomaterials. Nanotoxicology: from human blood biocompatibility to in vivo toxicity evaluation in rodent*"
Department of Pharmacy - Drug Design and Discovery Center

16h10: Pierre Fiasse, "*Presentation of open calls and future calls in the FP7 in nanotechnology*", NCP Wallonie

16h25: Conclusion

16h40: Closing drink and poster session

Laboratories working in the field :

Research center in Radiation interaction with Matter (PMR):

- Laboratory of electron spectroscopy LISE: J-J. Pireaux/L. Houssiau
- Solid state physics laboratory LPS: J-P. Vigneron/ L. Henrard
- Laboratory of analyses by nuclear reaction LARN: S. Lucas/G. Terwagne
- Laboratory of lasers and spectroscopies LLS: P. Thiry – M. Lepère
- Laboratory of Electronic Materials Physics : R. Sporken

Chemistry department:

- Research unit for surface (electro-)chemistry UCES: Z. Mekhalif/J. Delhalle
- Research unit for nanomaterials chemistry UCNM: B-L. Su
- Research unit of theoretical and structural physic-chemistry – lab of applied theoretical chemistry UCPTS-CTA : B. Champagne
- Research unit of organic chemistry – lab of organic and bio-organic supramolecular chemistry UCOBS-COMS: D. Bonifazi

Nanotoxico:

- Laboratory of analyses by nuclear reaction LARN : S. Lucas/G. Terwagne
- Research unit for surface (electro-)chemistry UCESA: Z. Mekhalif/J. Delhalle
- Department of Pharmacy- Drug Design and Discovery Center : B. Masereel
- Laboratory of cellular biochemistry and biology (URBC) : O. Toussaint
- Supported by “Atout Sciences”: M. Botman

Presentation 1:

Nanosciences at LISE: new engineered materials and characterization techniques

Laurent Houssiau and J.J. Pireaux

Research center in Radiation interaction with Matter (PMR): Laboratory of Electron Spectroscopy (LISE)

The nano era didn't take aback surface scientists at LISE. Their two long-developed objectives and expertises, (1) to engineer thin layers, with a control of **composition** and **structure** for specific applications; and (2) to improve and master **characterization techniques** capable to quantify such composition and structure... could easily be applied to **objects and ultra-thin films with nano-dimension(s)**. New materials are currently elaborated using physical deposition methods (evaporation, sublimation, plasma...), while X-ray, electron and ion based experiments are developed to study their properties at the nanoscale.

This progress will be illustrated with a few examples: the visual demonstration of the engineering of a sub-monolayer of organic molecules at a metal electrode to boost the efficiency of an organic light emitting diode; the tailoring of metal nano-clusters on carbon nanotubes with control of cluster size and size distribution thanks to plasma pre-treatment; the analysis of such nano hybrids by scanning transmission X-ray microscopy, revealing the surface chemistry and structure of a single (modified) carbon nanotube; the development of a new depth profiling technique in Time-of-Flight Secondary Ion Mass Spectroscopy to analyse thin organic layers, disclosing all elemental, chemical and molecular information through interfaces.

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Research activities

The laboratory activities focus mainly on:

- Fundamental research on solid materials, their surfaces and interfaces, on thin films, and on the radiation (UV excimer laser, RF plasma) interaction with matter.
- Study of the electronic and vibrational structure of fullerenes, ceramics, metal oxides, semiconductors, polymers, self-assembled monolayers and biomaterials.
- Analysis of surface properties of materials (X-rays, electrons, ions, UV laser, RF plasma) - determination of the electronic and vibrational structure of surfaces.

Projects in nanosciences

- [Interface design of metal nanocluster-carbon nanotube hybrids via control of structural and chemical defects in a plasma discharge \(NANO2HYBRIDS\)](#)
- [Interface-Control for Organic Devices \(ICONTROL\)](#)
- [Functional properties by mixed nanoorganic / metal oxide systems \(FOMOS\)](#)
- Combined SIMS-SFM Instrument for the 3-Dimensional Chemical Analysis of Nanostructures ([3D Nanochemiscope](#))
- [Physical chemistry of plasma-surface intercalations \(PA16/08\)](#)
- [Tailoring of active surface coatings for a better integration in the environment \(MIRAGE\)](#)
- [Elaboration and characterization of BCN thin films for micro- and nano-electronics future devices](#)
- NANOCOMPOSITE Platform (Nanocompo)

Equipments

- XPS Spectrometers (ESCA)
- TOF-SIMS IV secondary ion mass spectrometer
- HREELS high resolution electronic spectrometer

Posters presented by the lab:

1. Functionalising up to 5 g of carbon nanotube by plasma polymerization for new chemical and physical properties, p.22

Sami Abou Rich, Alexandre Felten, Jean-Jacques Pireaux

2. Surface characterization of silane nanofilms deposited by wet and plasma deposition methods on aluminium, p.23

A. Batan, F. Brusciotti, I. De Graeve, J. Vereecken, M. Wenkin, M. Piens, H. Terry, F. Reniers and J.J. Pireaux.

3. Deposition of nano-thin TiO_xC_y coating by low pressure plasma, p.24

M. Diallo, A. Batan, D. Mantovani, J.J. Pireaux

Presentation 2:

Simulation of Spectroscopic Fingerprints at the Nanoscale

Dr Luc Henrard

Research center in Radiation interaction with Matter (PMR): Solid state physics laboratory (LPS)

Numerical simulations are important tools for the understanding of physico-chemical science at the nanoscale. The properties of the matter indeed depend on the shape and size of the nanoparticles as well as on their composition. The diversity of the systems that can then be designed make prohibitive their precise experimental analysis. Moreover, most of the time, microscopic and spectroscopic analysis can hardly be interpreted without the support of simulations. In this presentation, I will focus on the role of simulation in the understanding of the spectroscopic fingerprints of two systems : optical properties of metal nanoparticles and structural analysis of the atomic structure of modified carbon nanotubes.

Optical properties of metal particles are due to the interaction of light with electronic excitation involving collectively the valence electrons of the particles (in opposition with the transitions between two electronic energy levels). These excitations are called plasmons and can be studied both by optical spectroscopy or electron energy loss spectroscopy (EELS). Only EELS can give information on the localization of the plasmon excitation and, consequently, link the particle shape and size with the optical properties. Let's mention that, even if it is not the main focus of this presentation, applications based on metallic nanoparticles surface plasmon excitations are numerous: biosensing, photothermal therapy, single molecule spectroscopy, plasmon induced transparency.

Carbon nanotubes main properties have not to be presented anymore (flexibility associated with high strength, very good electronic transport properties associated with possible dispersion in polymer matrix, ...). Their ability to be at the interface between the nanoworld and the macroscopic systems have boosted their study for both fundamental perspective and possible applications. We have developed an expertise in the analysis of their electronic and vibrational properties in the last 10 years. I will present the example of the study of the atomic structure of modified nanotubes by focusing on the boron and nitrogen doping. More particularly, we have studied the influence of the doping configuration on the electronic and transport properties and on the fingerprints by Scanning Tunneling Spectroscopy (STM).

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Research activities

The solid state physics laboratory deals theoretical physics of materials at the mesoscopic and nanoscopic scales. It works on two kinds of materials:

- Excited states of carbon nanostructures (fullerenes and carbon nanotubes)
- Photonic crystals as propagators of electro-magnetical waves to understand the colors produced by biological structures and to apply to new materials.

Projects in nanosciences

- Structural, electronic and optical properties [associated with chirality: from nanoscale to living species. Development of calculation device for theoretical physics and chemistry.](#) (FRFC-CHIRALITE)
- [Study of helical structures of carbon nanotubes](#)
- Novel, heteroatomic boron, nitrogen and carbon nanotubes (BNC)
- Study related to optical modelling [of amorphous silicon photovoltaic cells](#) (GVB)
- [Study of the influence of geometrical structuration of materials on the effectiveness of light emission and light absorption processes](#)
- Study of vibrational properties of carbon nanotubes
- Hygrochrom
- [Self-cleaning and anti-bacterial surfaces \(MIRAGE\)](#)
- NANOCOMPOSITE Platform (Nanocompo)

Equipments

- Scientific Interuniversity Computing Facility

Posters presented by the lab:

1. Growth and functionalisation of carbon nanotubes, p.25

Jean-François Colomer

2. Surface plasmon excitations of metallic nanoparticles investigated by EELS: a DDA study, p.26

N. Geuquet, J. Nelayah, M. Kociak, O. Stéphan, and L. Henrard

3. Control of the fluorescence dynamics of single emitters by coupled plasmonic modes, p.27

C. Vandenberg, D. Brayer, L. S. Froufe-Pérez and R. Carminati

4. STM simulations of Nitrogen and Boron doped single-wall nanotubes, p.28

B. Zheng, P. Hermet, L. Henrard

Presentation 3:

The Targan project: an example of the utilization of targeted radioactive nanoparticles in cancer

Dr Carine Michiels

Representing the Research center in Radiation interaction with Matter (PMR): Laboratory of analyses by nuclear reaction (LARN)

C. Michiels⁽¹⁾, B. Masereel⁽²⁾, O. Feron⁽³⁾, B. Gallez⁽⁴⁾, T. Vander Borgh⁽⁵⁾, S. Lucas⁽⁶⁾

(1) URBC, FUNDP – University of Namur, (2) Department of Pharmacy, FUNDP – University of Namur, (3) FATH, UCL, (4) CMFA, UCL, (5) IRME, UCL, (6) PMR-LARN, FUNDP – University of Namur

The Targan project aims to synthesize biocompatible radioactive nanoparticles that specifically target cancer vasculature to be used in radioimmunotherapy of lung cancer. This research is managed by a multidisciplinary team including physicists, biologists, pharmacists and physicians.

Small size carbon or gold nanoparticles that include several radioactive atoms are synthesized by a physical vacuum deposition. These nanoparticles are then amine-functionalized in situ, by a coating of PPAA (plasma-deposited polyallylamine). This coating allows the coupling of antibodies that specifically target tumor vasculature. We have demonstrated that CD105 (endoglin) is such a tumor endothelial cell specific antigen and that radioactive anti-endoglin antibodies specifically accumulate in tumor when injected in the tail vein of tumor bearing mice. The biodistribution of the nanocluster is currently under investigation. The next part of the project will be to study the effects of the radioactive nanoparticles coupled to the anti-endoglin antibody on tumor growth in mice. Finally, radioimmunotherapy with these antibody-coupled radioactive nanoparticles has been investigated from a dosimetric point of view: deposited doses, biological effective doses and tumor control probabilities have been determined by Monte Carlo dosimetric simulations. They showed that the efficacy with nanoparticles containing several radioactive atoms is much higher than with a single radionuclide coupled to each antibody. Hence, improvements in patient treatment is expected.

Acknowledgments: the Targan project is a Waleo 2 project from the Walloon Region

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Research activities

The laboratory deals with three domains:

- **Material sciences** : Synthesis of surface and interfacial materials with plasma and ion beams
- **Ion beam/radiation interaction with matter**: Fundamental study of Ion beam/radiation interaction with matter by means of a ion accelerator platform.
- **Life science**: experimental study of the cellular response to photon or particle radiations.

Projects in nanosciences

- [In vitro and in vivo toxicological study of three types of nanoparticles of economic interest in the wallon region \(NANOTOXICO\)](#)
- [Tumoral angiogenesis imaged and treated by radioactive nanoclusters \(TARGAN\)](#)
- Development of a measurement technique of nano-wears (nano-usures)
- [Metallic Nanoclusters deposited on planar substrates](#)
- [Ion luminescence of nanocrystal silicon synthesized by ion implantation for nanophotonic application \(SC-TEC-04\)](#)
- [Optimization of the luminescence of silicon nanocrystals for application in nanophotonic \(SC-TEC-2\)](#)
- [Self-cleaning and anti-bacterial surfaces \(MIRAGE\)](#)
- [Study of thick Li metallic coatings deposited by sputter evaporation.](#)
- [Optical and electronic properties of metallic oxynitride coatings produced by reactive magnetron sputtering](#)
- [Characterisation of layered structures by ion bombardment](#)
- [Development of radiation-responsive bioassays for biodosimetry applications.](#)
- NANOCOMPOSITE Platform (Nanocompo)

Equipments

- [Tandatron linear Accelerator \(ALTAÏS\)](#)
- Plasma pulverization chamber
- Variable energy Ion beam
- Ion implantation [150 kV](#)
- UHV beam line with low background detection system
- [Soft X-rays spectroscopy induced by electrons \(LEEIXS\)](#)

Posters presented by the lab:

1. TARGAN: tumoral angiogenesis detected and treated with labeled radioactive nanoparticles, p.29

N. Moreau, V. Bouchat, V. Valembois, O. Feron, B. Gallez, B. Masereel, C. Michiels, T. Vander Borght and S. Lucas

2. Synthesis of radioactive nanoparticles by magnetron sputtering, p.30

V. Bouchat, N. Moreau, V. Valembois, G. Genard, O. Feron, B. Gallez, B. Masereel, C. Michiels, T. Vander Borght and S. Lucas

Presentation 4:

Chemistry and Electrochemistry of Surfaces: from Nanofilms to Nanocomposites

Pr Zineb Mekhalif

Research unit for Surface (Electro-) Chemistry UCES

Two directions of the CES research dealing with the grafting of molecular connectors on surfaces will be presented. The first one focuses on the self-assembly of organic molecules on oxidisable metals while the second highlights the chemical functionalisation of carbon nanotubes (CNTs).

Although self-assemblies of organothiols on gold and copper have been extensively studied over the past years¹, less work has been reported on the more active metals such as nickel and zinc. In the first part, we will present our achievement in molecular functionalisation on copper, nickel and zinc by monolayer or multilayer assembly based on organothiol and organoselenol derivatives. Such systems are of particular interest since complicated structures can be designed and prepared with molecular precision and could provide new possibilities for technological applications using more common metals. We will particularly underline the critical effect of the surface chemical state and the way to control the interface favouring chemical and stable bonds.

The second part will be devoted to CNTs functionalisation by chemical grafting of organosilane molecules. The control of this step influences significantly the dispersion process in liquids, in polymers or metals and metal oxides matrices and furthermore the ultimate composite properties (electrical conductivity, mechanical properties, flame fire retardation...).

Financial Support: FUNDP, Région Wallonne, FNRS, Europe, Industries

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Research activities

GCES deals with design of surface and interface innovative materials and their synthesis by (electro-) chemistry and self assembling. Those surface materials correspond to organic and/or inorganic films assembly, thin or ultra thin, on both metallic, oxides or polymers substrates.

Researches followed at the GCES are clearly in the scope of the surface materials chemistry at micro or nanometric scales. Studies are aiming to maximize performance, chemical selectivity towards targets and structural control at a molecular level of (electro-) chemically synthesized compounds.

Projects in nanosciences

- Nanoscale Electrochemical and Bio-processes (Corrosion) at Solid-aqueous Interfaces of Industrial Materials (COST D33)
- NanoMembranes against Global Warming (NanoGLOWA)
- Composite materials Enforced non conventional matrices / Carbon nanotubes for spatial activities nanotubes (ESA-CNT)
- [In vitro and in vivo toxicological study of three types of nanoparticles of economic interest in the wallon region \(NANOTOXICO\)](#)
- Dispersion of carbon nanotubes : effects of solvent and functionalisation

Posters presented by the lab:

1. Fabrication of 2D ordered Ta₂O₅ films on a titanium substrate by electrodeposition of Ta from ionic liquid through a polystyrene template, p.31

Christelle Arnould, Joseph Delhalle and Zineb Mekhalif

2. Self-assembled Monolayers of Aliphatic Thiol, Dithiol and Dithiocarboxylic Acid on Electrochemically Reduced Polycrystalline Copper Substrates, p.32-33

Jessica Denayer, Joseph Delhalle and Zineb Mekhalif

3. Using of pyrene derivatives to characterize the carbon nanotubes surface, p.34

S. Detriche, S. Devillers, J.-F. Seffer, J. B.Nagy, Z. Mekhalif, J. Delhalle

4. Grafting PEG Fragments on Phynox[®] Substrates Modified with 11-Phosphoundecanoic Acid, p.35

Sébastien Devillers, Nathalie Cuvelier, Joseph Delhalle, Zineb Mekhalif

5. Electrochemical and Spectroscopic Study of C₁₂H₂₅X Molecules Adsorption on Copper Sheets, X (-SH,-S-S-, -SeH and -Se-Se-) , p.36

G. Fonder, C. Volcke, B. Csoka, J. Delhalle and Z. Mekhalif

6. Decoration of cuprous oxide nanoparticles on mutliwalled carbon nanotubes, p.37

Praveen Martis, Joseph Delhalle and Zineb Mekhalif

7. Characterization of MWCNT, SiC and TiC nanoparticles and the influence of the dispersion methods, p.38

Jorge Mejia, Stéphane Lucas, Zineb Mekhalif, Joseph Delhalle

8. Preparation of a PAN/MWNTs composite by surface-initiated ATRP on a stainless steel wire for solid-phase microextraction (SPME) of aromatic compounds, p.39-40

Isabelle Minet, Laszlo Hevesi, Manuel A. Azenha, Joseph Delhalle, Zineb Mekhalif

9. Effect of the counter-anion in the synthesis of SWNTs and DWNTs, p.41

J-F Seffer, S. Detriche, J. B.Nagy, Z. Mekhalif, J. Delhalle

Presentation 5:

Nanostructures and nanotechnologies

Dr Claire Bouvy

Research unit for nanomaterials chemistry UCNM

In recent years, new nanostructured materials organized on the nanometric scale contribute greatly to the improvement of our everyday-life. Thanks to their exceptional properties, they are considered as the most innovative and promising materials in many fields including optics, electronics, medicine, biology or even catalysis and are to be found in many applications such as light-emitting diodes, nanosensors, drug delivery systems, catalysts, etc. Nanostructured materials can be defined as integrated chemical systems, structurally ordered with nanometric dimensions. The design of such systems requires the organisation of the active components at the nanometric level and the control of their arrangement, their distribution and their properties inside a matrix. During this talk, an overview of the recent researches developed in our group will be given.

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Research activities

The laboratory deals with design, modelling, fundamentals and applications of nanomaterials and nanotechnology

Three axes have been defined in the laboratory:

- Conception and understanding at molecular and atomic level of hierarchically inorganic porous structures and nanostructures (nanotubes, nanowires, quantum dots, nanoplates,...) and application as catalysts, catalyst supports, adsorbents and drying agents in the petroleum processing, petrochemicals, chemicals, in hydrocarbons and gas separation processes and environmental protection.
- Synthesis, structure determination and theoretical simulation of new porous systems and molecular sieves.
- Theoretical and experimental study on Molecular recognition effect in porous systems and molecular sieves.

Projects in nanosciences

- Highly structured mesoporous thin films
- Development of porous inorganic matrixes suitable for the immobilization of cells for cell therapy
- New synthesis methods for photonic crystals: lesson from the living world and from the nature
- Conception of nanocomposites made of silica-based mesoporous thin films
- Development of porous matrices adapted to biological cells encapsulation for the cell therapy
- Silicon-based and carbon-based prepared from rice for the production of bio-fuel nanomaterials
- [Conception of inorganic materials by a new bottom-up approach: study of the synthesis processes \(INANOMAT\)](#)
- Conception of hybrid inorganic-biological nano-reactors for environmental goals : immobilization of cells and bacteria in silicon porous matrices
- Antimicrobial and self-cleaning surfaces (MIRAGE)
- Biomimeticism of the photosynthesis by immobilization of biosystems within a silica matrix: towards a new advance in the conception of "living materials"

Posters presented by the lab:

1. Design of highly sensitive and selective fluorescent nanosensors for the detection of mercuric ions, p.42-43

Jonathan Desmet and Bao-Lian Su

2. Synthesis hierarchical macro-mesoporous aluminosilicate with silicon to aluminium ratios close to one from a single precursor [(sBuO)₂-Al-O-Si-(OEt)₃], p.44

Arnaud Lemaire and Bao-Lian Su

3. Development of Porous Matrices Adapted to Biological Cells Encapsulation for the Cell Therapy, p.45

Grégory Leroux and Bao-Lian Su

Presentation 6:

Evaluation of potential toxicity of nanomaterials.

Nanotoxicology : From human blood biocompatibility to *in vivo* toxicity evaluation in rodent.

Pr Bernard Masereel

Department of Pharmacy – Drug Design & Discovery Center

The research fields of the Drug Design and Discovery Center (D3C) from the University of Namur focus on the design, the synthesis and the biological evaluation of original molecules endowed with therapeutical interest.

Since 2006 this laboratory, headed by Professor Bernard Masereel, is involved in the Nanotoxicology project. The aim of this research unit is to evaluate the potential toxicity of manufactured nanomaterials on human health. To reach this goal, relevant animal models were developed with a particular emphasis on the oral contamination and pulmonary inhalation. The effects of engineered nanomaterials were also studied on isolated human blood constituents.

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Research activities

The research fields are focused on the design, the chemical synthesis and the biological evaluation of original molecules endowed with therapeutically interest. We are also interested with the physicochemical properties of new compounds (pKa, Log P,...)

Projects in nanosciences

- Tumoral angiogenesis imaged and treated by radioactive nanoclusters (TARGAN)
- In vitro and in vivo toxicological study of three types of nanoparticles of economic interest in the wallon region (NANOTOXICO)

Posters presented by the lab:**1. Potential nanotoxicity in blood : Effects of engineered nanoparticles on human blood constituents, p.46**

Julie Laloy, Catherine Marbehant, Séverine Robert, François Mullier, Bernard Chatelain, Jean-Michel Dogné, Olivier Toussaint, Bernard Masereel, Stéphanie Rolin

Laboratory of cellular biochemistry and biology (URBC)

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Research activities

The URBC gathers several interdisciplinary research teams organized around different research topics. The URBC is presently composed of 46 researchers, amongst which 14 Ph.D. and 12 technicians. The URBC works in two domains: first in fundamental research aimed to understand cellular responses to stress in normal and pathological conditions and secondly in new molecular diagnostic technologies. The laboratory masters general techniques both in the domains of molecular biology, of biochemistry and cell biology, within leading edge facilities and thanks to performing technologies: FPLC, capillary electrophoresis, 2 mass spectrometers (MALDI and Q-TOF (MS-MS)), peptide synthesizer, confocal microscopy, differential display, 2 dimension gel electrophoresis and corresponding analysis system and lastly all the DNA array technology.

The laboratory is familiar with the manipulation of cells, proteins and genomes, such as cloning, sequences analyses, gene expression, and reporter genes.

Projects in nanosciences

- [In vitro and in vivo toxicological study of three types of nanoparticles of economic interest in the Walloon region \(NANOTOXICO\)](#)

The goal of the Nanotoxico project is to develop in vitro tests for nanoparticles toxicity assessment. This project involves several disciplines including [physics](#), [chemistry](#), [biology](#), [pharmacy](#) and [communication science](#). Each team will fulfil a specific mission in order to obtain an integrated view of nanomaterials physico-chemical properties and interaction with biological systems.

Equipments :

- TCS-SP Fluorescent confocal microscope
- Real time [PCR](#)
- DNA microarray technology
- MALDI-TOF Mass spectrometer
- Q-TOF2-LC MS-MS Mass [Spectrometer](#)

Posters presented by the lab:

1. TARGAN: Biocompatibility assessment of 3 types of gold nanoparticles on endothelial cells, p.47

M. Crespin, O. Feron, B. Gallez, B. Masereel, T. Vander Borgh, S. Lucas and C. Michiels

2. Relevance of Human Skin Equivalent (HSE) use for *in vitro* testing and ageing studies, p.48

J. Dedessus le Moutier, Thi Kim Duy Vo, N. Belot, H. Seltmann, M. Salmon C.C. Zouboulis, O. Toussaint

3. Effects of multi-wall carbon nanotubes on three cellular models of human skin, p.49

Vankoningsloo S, Piret JP, Saout C, Noël F, Mejia J, Delhalle J, Lucas S, Toussaint O

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Research activities

The laboratory for electronic materials studies the formation and properties of semiconductor heterostructures and/of metal/semiconductor contacts.

It works in close relationship with the Physics education group :

- 1) to develop and maintain physics experiments for laboratory and classroom use,
- 2) to supervise research projects for undergraduate physics students and,
- 3) to develop innovative tools for physics teaching at the high school level (multimedia, electronics in physics teaching).

Projects in nanosciences

- Study of epitaxial selective growth of II-VI semiconductors on silicon

Equipments :

- Scanning tunneling microscopy (STM)
- Photoelectron microscopy (PEEM)

Research center in Radiation interaction with Matter (PMR): Laboratory lasers and spectroscopies LLS

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Research activities

The laboratory deals with molecular spectroscopy and its applications: infrared spectroscopy for high resolution detection of traces of gas, characterization of surface-adsorbed or interface molecules with linear and non-linear optical (IR, Raman, SFG, DRSFG), electron spectroscopy (HREELS) and various microscopies (MEB, STM, AFM).

The laboratory develops firstly, theoretical models for vibrational and ro-vibrational analyses, and secondly high resolution spectrometers based on diodes and various lasers.

Projects in nanosciences

- [Development of new biological sensors and of adapted reading procedures](#)
- [Design and characterization by nonlinear optical spectroscopy and scanning probe microscopy of bioactive surfaces miming the cellular membranes](#)
- [Study of model biosensors and soft lithography techniques by nonlinear optical chemical imaging: towards the development of fast decoding and label-free high-density biosensors arrays](#)

Unit of theoretical and structural physico-chemistry - Applied Theoretical Chemistry Lab (UCPTS/CTA)

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Research activities

UCPTS brings together three laboratories : the Applied Theoretical Chemistry Lab (CTA), the structural biological chemistry lab (CBS) and the physico-chemistry informatics lab (PCI). UCPTS is developing research activities in molecular engineering and is aiming to characterize electronic and structural properties of macro-molecules. This group applies and develops a wide range of theoretical methods. In complement, the Unit develops an expertise in the domain macromolecular structures resolution through physicochemical experimental methods.

Quantum chemistry of polymer: Evaluation of structural and electronic properties of isolated stereoregular and modeling diagrams of polymer phases.

Non Linear optics: Research in non linear optics lends to emergence of a new discipline: photonic, source of development of modern ways of telecommunications and processing the information.

Projects in nanosciences

- Conception de nouveaux matériaux pour l'optique non-linéaire
- Conception d'interrupteurs moléculaires présentant d'importants contrastes optiques non-linéaires

Equipments

Development and applications of calculating methods of structural, electronic, optical properties – Interuniversity Scientific Computing Facilities (ISCF). Experimental determination of crystal structures – Single crystal X-Ray diffraction, In-plane X-ray powder diffraction.

Posters presented by the lab

1. Molecular Switches Presenting Second-Order NLO Responses : A joint Theoretical and Experimental Study, p.50

Aurélie PLAQUET

2. Theoretical modeling of the magnetic properties of boro-nitrogenous aromatic compounds and small supramolecular systems, p.51

Raphaël CARION

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Web page: www.fundp.ac.be/facultes/sciences/departements/chimie/recherche/groupe/qcobs/

Research activities

UCOBS brings together three laboratories : the synthesis organic chemistry laboratory (COS), the bio-organic chemistry laboratory (CBO) and the organic chemistry of supramolecular materials laboratory (COMS).

The COMS works in the organic chemistry of supramolecular materials, mainly on the synthesis and organization of molecules, at the molecular scale. The research topics are focused on weak interactions, organic nano-chemistry and innovative carbon-based materials. The interest is mainly on functionalization of the inner surfaces of carbon nanotubes with fluorescent molecules.

Projects in nanosciences

- Development of new organic materials for photovoltaic cells
- Supramolecular hierarchical self-assembly of organic molecules onto surfaces towards bottom-up nanodevices
- Cavity-confined Luminophores for advanced photonic materials

Posters presented by the lab

1. Surface-templated engineering of porphyrin-based supramolecules, p.52-53

Claudia Aurisicchio, Daniel Heim, Knud Seufert, Willi Auwärter, Johannes V. Barth and Davide Bonifazi

2. Organic functionalization of doubled-walled carbon nanotubes (DWCNTs) via lithiation-based reactions, p.54

Hassan Traboulsi and Davide Bonifazi

Functionalising up to 5 g of carbon nanotube by plasma polymerization for new chemical and physical properties

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The non-reactive nature of the carbon nanotube (CNT) surface appears as a constraint in several technological applications. The critical challenge is therefore to enhance dispersion and alignment of CNTs in the matrix of a composite. To overcome this problem, modification of the CNT surface by changing its chemical composition has proved to be efficient. To improve the processability, electrical, magnetic and optical properties of CNTs, some conjugated or conducting polymers are attached to their surfaces by plasma polymerization [1].

A low-temperature plasma process has been used for attaching specified molecular groups to carbon. This process does not involve the use of wet chemicals, does not involve exposure of the nanotubes to high temperatures, and generates very little chemical residue. In addition, this process can be carried out in a relatively simple apparatus and can readily be scaled up to mass production. We use Inductive RF plasma (13.56 MHz) to polymerize a monomer (Methyl MethAcrylate MMA, Styrene, AllylAmine AA, Phenyl Glucidyl Ether PGE) onto the CNTs surface.

In order to evaluate the chemical composition of the surface of the MWCNTs, XPS analyses were performed. The evolution of the polymer deposit by preliminary plasma onto the CNTs surface was studied by TEM. FTIR allows checking for the chemical structure of the deposited polymers.

In this work, we show that plasma fonctionnalization gives rise to C=O and C–O–C functional groups, C-F, and C-NH₂ at the MWCNT surface as a result of polymer deposited during the MMA, CF₄ and AA plasma treatments respectively. This process proves the efficiency and homogeneity of the grafted plasma polymers onto the 5 grams of CNTs.

This work is financially supported by the NanoCompo project (Région Wallonne)

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Surface characterization of silane nanofilms deposited by wet and plasma deposition methods on aluminium

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Silane nanofilms are applied to surfaces for various purposes, e.g., to form a protective layer against corrosion or to act as a primer layer for subsequent coating. Silane layers can be deposited by dry or wet processes, depending on the precursors and employed methods of application. In this work bis-1,2-(triethoxysilyl)ethane (BTSE) was used as a precursor to deposit silane films on Al 99.99% substrates with three different techniques: dipcoating (water based), vacuum plasma and atmospheric plasma. The aim of this investigation is to compare the surface and bulk characteristics of the differently prepared films, in order to get information on how the BTSE molecule is modified by the deposition technique. It should be emphasized that the literature did not report any previous deposition of plasma polymer BTSE films by vacuum and atmospheric plasma. Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy and FEG-SEM were used to characterize the structure, composition and surface morphology of the silane films.

BTSE films could be deposited by both vacuum and atmospheric plasma, besides the more traditional dipcoating technique. The layers deposited by vacuum plasma can be considered as “polymer-like films”, comparable in atomic and chemical compositions to the silane layers obtained by dipcoating. Atmospheric plasma treatment, however, leads to the formation of oxidized films richer in Si-O bonds; these films are more “inorganic”. XPS and FTIR measurements point out the presence of Si-O-Si bonds, while Si-O-Si, Si-O-C, Si-O and Si-CH₃ absorption bands are revealed by FTIR measurements.

A PAT (Pôle d'Attraction Technologique) project.

Deposition of nano-thin TiO_xC_y coating by low pressure plasma

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Under the theme of new materials, the treatment of atherosclerosis could benefit from the proactive development of modern nano-structured materials for the manufacture of new stents- Stents are medical devices placed inside partially blocked arteries to prevent the obstruction of blood flow and to act as internal scaffolding. This work involves the deposition by low pressure plasma of a TiO_xC_y -like multilayer on type 316L stainless steel, in order to achieve biocompatible coatings, having good mechanical properties, and preventing restenosis. Two configurations of TiO_xC_y multilayer were realized. The first one is composed of three layers with a gradient of carbon decreasing from the substrate, presenting at the surface a “mineral” layer; the second one also consists of a reversed order of layers, with a “polymer-like” surface layer. The plasma gas is a mixture of variable components (to get the gradient) of titanium isopropoxide vapour (TIP) and oxygen, with variable pressure and power in the discharge. Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Scanning Electronic Microscopy and Profilometry were used to characterize the structure, composition, surface morphology and thickness [20-100 nm] of the TiO_xC_y layers. The water contact angle measurement was also used to characterize the hydrophobicity of the surface. The XPS analysis shows the absence of metal from the substrate, and AFM maps show a few superficial cracks not reaching the interface (layer/substrate). The deposited layers adhere well to the substrate regardless of the configuration studied (no delamination); the first configuration is more oxidized than the second one. The first test of biocompatibility has shown that the surface layers are not toxic.

A WBI- Quebec bilateral research programme.

Growth and functionalisation of carbon nanotubes

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Carbon nanotubes (CNTs) are currently the focus of intense researches due to their unique properties and potential to impact broad areas of science and technology. However, the full potential of CNTs will not be realised until the growth of nanotubes can be further optimized and controlled. One way is the selective synthesis of vertically aligned carbon nanotubes on substrates. Indeed, the development of techniques to control and align CNTs on suitable substrates has received special attention for applications in the fields of displays, nanosensors, etc... Different methods have been successfully developed for the growth of aligned CNTs. Usually, through classical CDV, the CNTs are randomly oriented and the growth proceeds via a spaghetti-like distribution. Better alignment of the CNTs can be achieved through the deposition of a buffer layer on the substrate surface (e.g. Al_2O_3) aiming an optimal dispersion of the catalyst particles on the surfaces. In a first part, the synthesis of aligned multi-walled carbon nanotubes on substrates using or not a buffer layer, through classical chemical vapor deposition is reported.

Once the CNTs forests built, the nanotubes will be used as point of anchoring for all types of (organic, biological, etc...) molecules having quite specific properties in order to design new functional materials. So, the second part will concern the post growth modifications of the forest surfaces achieved using micro-wave plasma of O_2 and N_2 in order to introduce chemical functionalisation at the MWCNT tips.

Considering now the applications of the CNT powders (available commercially), a major challenge is to develop a range of reliable and effective functionalisation methodologies that allow the construction of CNTs-based materials keeping undamaged their electronic and optical properties. In this field, the synthesis and characterization of double-walled carbon nanotubes (DWCNTs) (Nanocyl[®]-2100) functionalized with Br_2 are reported (in the last part), first step to designing novel functionalized CNTs with specific properties, using metal catalyzed cross-coupling reactions.

Surface plasmon excitations of metallic nanoparticles investigated by EELS: a DDA study

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Metallic nanoparticles have unique optical properties related to the excitation by the electromagnetic waves of surface plasmon resonances (collective excitation of valence/conduction electrons). Beside the composition of the nanoparticles, surface plasmon excitation depends on the size, the shape of the particle and the dielectric environment. The more and more precise experimental growth control allows a tuning of the optical response properties of metallic nanoparticles and their use in several fields of nanotechnology, notably in bio-sensing and subwavelength colour imaging.

From the experimental point of view, besides optical measurements, the electromagnetic response of metallic nanoparticles can be investigated by Electron Energy Loss Spectroscopy using a Scanning Transmission Electron Microscope (STEM-EELS). In this poster, we will describe how the EELS response can be derived from a Discrete Dipole Approximation (DDA) model in which the nanoparticle is represented by a set of dipoles. For gold nanodecahedron, we will present comparison with recent experimental data. We will finally investigate the effects of coupling between the nanoparticle and the substrate surface, first, and between two interacting nanoparticles, secondly.

Control of the fluorescence dynamics of single emitters by coupled plasmonic modes

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It is well-known that the fluorescence lifetime of a dipole emitter (e.g. atom, molecule, and quantum dot) can be substantially modified close to a metal surface. Lifetime modifications are induced by changes in the local density of electromagnetic modes, and are quantitatively described by the classical electrodynamic response of the surface. The development of nearfield optics techniques has stimulated the use of metallic nanoantennas to modify the spontaneous emission features (fluorescence lifetime, fluorescence intensity, apparent quantum yield) of single emitters with nanometer-scale sensitivity. Efficient excitation and detection of the fluorescence of single molecules has been achieved through a plasmonic films, and the role of surface plasmons in the process has been analyzed [1,2]

In addition, control of plasmon-resonance frequencies can be achieved by playing with the shape of metallic structures. Another way of tailoring the resonance frequency is the coupling of plasmonic modes in nanostructures [3]. These hybrid plasmonic modes can lead to either radiative or non-radiative coupling depending on how strong they couple to free space. In this work, we study theoretically and numerically the possibility of controlling the fluorescence dynamics with systems involving coupled plasmon modes. We show three different cases: the dimers, the thin film and the sphere-film systems. Depending if the emitter is coupled to the radiative mode or the non-radiative mode, the apparent quantum yield and the fluorescence lifetime exhibit different behaviors.

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C. V. is a postdoctoral researcher of the FRS-FNRS and acknowledges a grant from the City of Paris that made possible a stay at ESPCI where part of this work was done. LS F.-P. is financially supported by the Juan de la Cierva program.

STM simulations of Nitrogen and Boron doped single-wall nanotubes

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The tuning of carbon nanotubes electronic properties are an important challenge for the design of nanoelectronic devices. The chemical doping is one of the possible methods to achieve such a controlled of electronic and optical properties. Beside the physical properties of modified carbon materials, the knowledge of the experimental fingerprints of doping configuration is crucial to analyzed the experimentally produced samples.

We have studied electronic properties and STM fingerprints of substitutional and pyridine-like doping by nitrogen and of substitutional doping by boron with different concentrations for metallic and semiconducting nanotubes in a Tersoff-Hamman formalism using density functional theory based calculations. These configurations are presently the most probable in doped carbon nanotubes. We will show the electronic structure modifications related with the n and p doping. For example, for metallic nanotubes, a shift of the Fermi level together with a localised donor (acceptor) states are observed for nitrogen (boron) substitution. Semiconducting tubes tend to become metallic under n and p substitutional doping. Finally, STM fingerprints of the localised states have been computed.

This work is supported by the BNC-TUBE STREP EU project (Project Number 033350).

TARGAN: tumoral angiogenesis detected and treated with labeled radioactive nanoparticles.

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In medicine, development of hybrid nanoparticles that can be targeted to vascular, extra-cellular or cell surface receptors is often considered as an attractive solution for cancer detection and treatment. The TARGAN project aims to synthesise biocompatible nanoparticles mixed with radioactive atoms that specifically target cancer vasculature. This research is managed by a multidisciplinary team including physicists, biologists, pharmacists and physicians.

The poster shows the physical part of this TARGAN project. Firstly, a new technique to synthesise inert and biocompatible nanoparticles such as carbon or gold nanoparticles is presented. This method is based on a physical vacuum deposition (PVD) process which combines DC magnetron sputtering and gas aggregation techniques in order to control their morphology, their size and their dispersion on any substrate. A second part of the poster deals with the amine-functionalisation of these nanoparticles. This functionalisation is very important for avoiding aggregation of these nanoparticles in a liquid environment and for making the bonds between the antibody and the nanoparticle. Finally, radioimmunotherapy with biological vectors labeled with radioactive nanoparticles has also been investigated from a dosimetric point of view. Deposited doses inside and around the tumor, biological effective doses and tumor control probabilities have been determined by simulations with the Monte Carlo code MCNPX. For these simulations, a new model of tumor has been developed in which the antibody distributions inside the tumor can be uniform, linear or exponential.

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Synthesis of radioactive nanoparticles by magnetron sputtering

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Due to their unique structural, chemical and physical properties, nanosized particles have shown promising interests in various fields such as electronics, optics and energy. More recently, nanoparticles have attracted considerable interest in medicine and biology. Quantum dots as fluorescent agents, gold nanoshells as cancer therapeutics, C₆₀ as drug delivery system and metallofullerenes as radiotracers are some examples of possible biomedical applications of nanomaterials. When combined with radioactive atoms, these nanomaterials are very promising for cancer detection and treatment.

The poster presents method to produce nanoparticles containing radioactive atoms by magnetron sputtering at high pressure. The idea is to put down the radioactive atoms on the cathode before pulverisation. The technique was tested for gold and carbon cathodes on which radioactive atoms, such as ^{99m}Tc or ⁵⁸Co, were deposited. Gold, as carbon, are well-know to be inert and biologically compatible. Mixed with radioactive atoms and linked to biological vector molecules, these nanoparticles could be used to enhance diagnostic sensitivity in medical imaging or to treat cancer.

Sizes and morphologies of these nanoparticles were analyzed by Transmission Electron Microscope (TEM) and CPS Disc Centrifuge. The sizes of the nanoparticles can vary between 2 and 15 nm. Activity was studied thanks to a CAPINTEC well counter or a HPGe detector. For analyzing the samples with very weak activities, a low background experimental setup for the HPGe was used. The Activity transfer, by sec and by cm², between the cathode and the samples of nanoparticles may vary between 5×10⁻⁸ and 10⁻⁷. At the present time, the best result obtained is 2 radioactive atoms for 1000 nanoparticles with a mean diameter of 2.6 nm but this result can be improved by increasing the initial activity of the cathode.

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Fabrication of 2D ordered Ta₂O₅ films on a titanium substrate by electrodeposition of Ta from ionic liquid through a polystyrene template

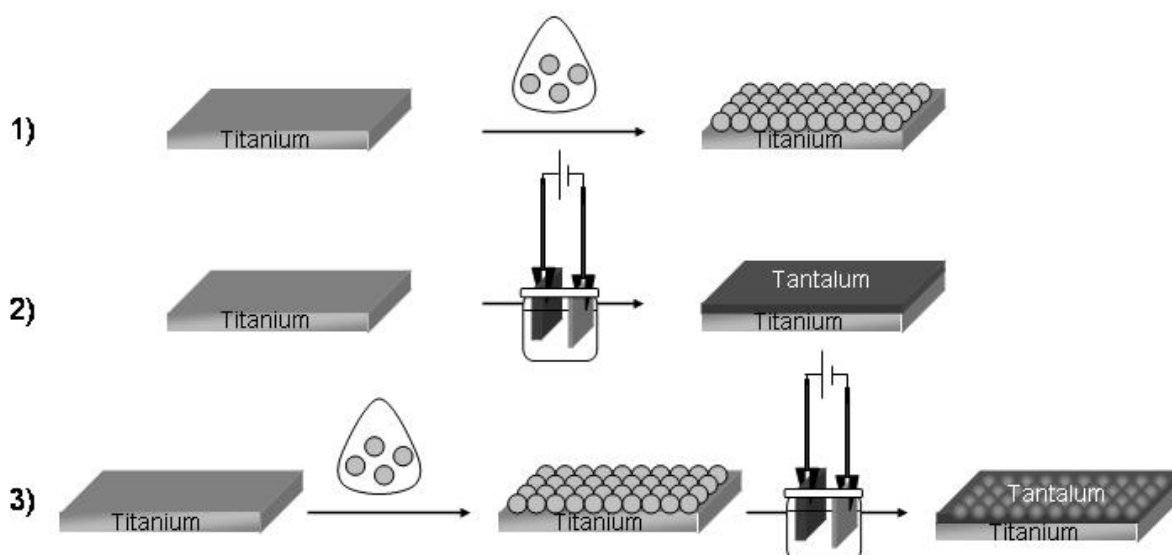
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The control of surface morphology is important to impart novel and interesting surface properties to materials in basic and applied sciences. The specific chemical and physical phenomena occurring inside spatially confined micrometer and sub-micrometer volumes are of particular interest. We focused on the study of titanium plate modifications for their use in biomaterials. Titanium and its alloys are widely used in orthopaedic domain but need some improvement. The deposition of a thin tantalum oxide layer could bring radiopacity, bioactivity and increasing corrosion resistance in body fluids. Among the numerous deposition methods developed in surface chemistry, our attention turned on the electrodeposition of the tantalum layer on this assembly, performed in an ionic liquid electrolyte in a glove box. The control of the surface morphology has been shown to influence the bacterial adherence to the implant. We report on the electrochemical deposition of 2D ordered tantalum oxide film through polystyrene (PS) templates formed on a titanium substrate. The different stages of the sample preparation are investigated by scanning electron microscopy (SEM) and compared to XPS data and electrochemical characterizations. The steps of the work are schematically depicted in graphical abstract.

Scheme of the three main steps followed in this paper



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Self-assembled Monolayers of Aliphatic Thiol, Dithiol and Dithiocarboxylic Acid on Electrochemically Reduced Polycrystalline Copper Substrates

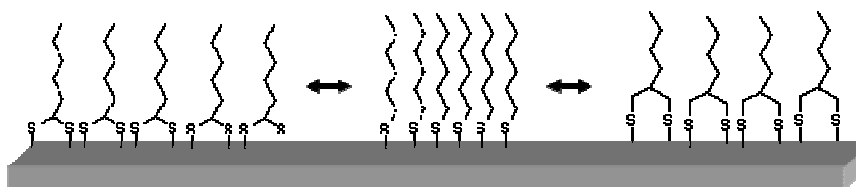
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Copper is an important metal in the chemical and microelectronics industries due largely to its high thermal and electric conductivities and low cost. There are two major disadvantages in the use of copper, the presence of copper oxide on his surface and the corrosion of this metal, especially in aqueous environments^[1].

Self-assembled monolayers on copper have been found to be promising inhibitor for copper corrosion. The presence of copper oxide layer on the top is problematic for the thiol adsorption. Chemical and/or electrochemical pretreatment are thus necessary^[2]. The alkanethiol monolayers have been show to form oriented densely packed films, which produce effective barriers to the penetration of corrosive chemicals to the substrate and to limit the oxidation of the metal^[3].

The present work affords a major progress in the field of SAMs derivated on alkanethiol on copper. The stability of the coating can be modified by the use of bipode molecule. The aliphatic dithiocarboxylic afford a coating less stable than normal alkanethiol^[4]. This kind of coating could be useful for temporary coating. The dithiol, for its part, afford a higher stability than alkanethiol, which is essential for further applications^[5].



Self-assembled monolayers of aliphatic dithiocarboxylic acid (a), thiol (b) and dithiol (c) on copper

Characterizations of the SAMs will be carried out using contact angles, XPS, PM-IRRAS and electrochemical studies (CV, LSV, SECM).

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Using of pyrene derivatives to characterize the carbon nanotubes surface.

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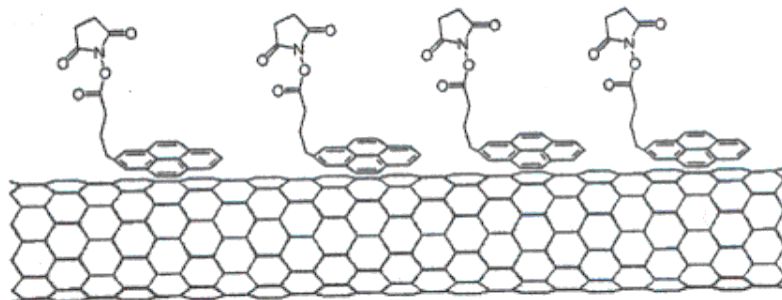
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Carbon Nanotubes (CNTs) are promising new materials identified in 1991 by S. Iijima¹. Their outstanding mechanical and electrical properties have kept the attention of researchers since their discovery. Among the several studies about CNTs; their interactions with pyrene derivatives have drawn the attention. Polyaromatics molecules are known to strongly interact with CNTs by physisorption on their surface. These compounds have been widely studied as interlinkers between CNTs and nanoparticules² or as surfactant for nanotubes solubilisation³.

This work presents two parts. The first one involves a systematic study of the interactions between six different types of CNTs and two pyrene derivatives. In this first part, we demonstrate a correlation between the CNTs surface state and the pyrene derivatives adsorption kinetics on this surface. In the second part, we can show that the utilization of pyrene derivatives allow us –by the use of various initial concentrations- to determine the available surface on the CNTs. This can be seen as a “chemical BET”, having an easier utilization compared with the “classic BET”. Surface determination by the use of pyrene derivatives also allows us to see the effect of several CNTs treatments on their surface quality and availability.

In conclusion, this work present pyrene derivatives not just as interlinker or surfactants but as “chemical probes” of the CNTs surface



Sample of pyrene derivative adsorption on carbon nanotube by π -stacking [4].

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Grafting PEG Fragments on Phynox[®] Substrates Modified with 11-Phosphoundecanoic Acid

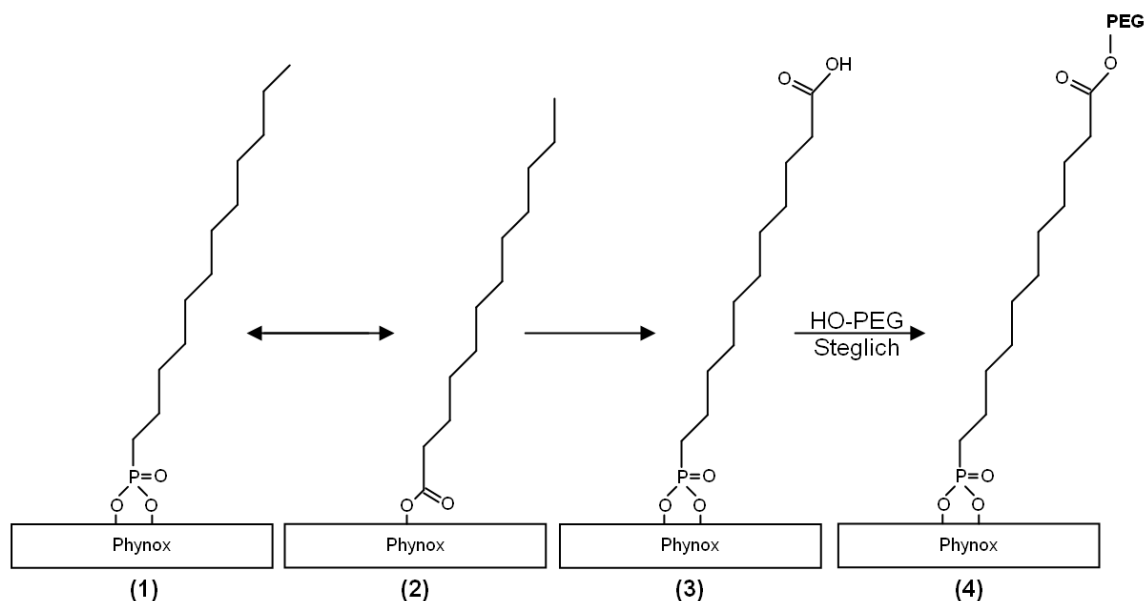
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Phynox[®], a cobalt-chromium alloy, exhibits interesting mechanical properties making it a valuable material for a number of applications. However, applications as biomaterial often require specific surface properties that can be imparted with suitable surface functionalizations. The aim of this work is to functionalize the Phynox[®] surfaces with 11-phosphoundecanoic acid monolayers, creating in this way a platform for a large variety of post-grafting chemical reactions, *e.g.* with alcohols and amines, to modify and control the surface properties. In a first part, we assess the interaction between the two terminal moieties of the 11-phosphoundecanoic acid and the Phynox[®] surface by studying the grafting of *n*-dodecylphosphonic acid and *n*-dodecanoic acid. To illustrate the potential of the 11-phosphoundecanoic acid monolayer, we report on our first attempts to post-graft small PEG fragments by the Steglich esterification reaction between the carboxylic end of the grafted 11-phosphoundecanoic acid molecules and the alcohol function of PEG fragments.



Schematic of the Phynox[®] surface modification methodology used in this work

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Electrochemical and Spectroscopic Study of C₁₂H₂₅X Molecules Adsorption on Copper Sheets, X (-SH, -S-S-, -SeH and -Se-Se-)

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This work has been a part in the scope of modifications of surfaces by the nowadays widely used organic molecular assemblies^{1,2}. In this work we will show on one hand that the chosen material to treat is an active metal, copper, and on the other hand that the nature of the anchoring groups on the surface are thiol and selenol. This purely fundamental study is motivated by the different perspectives of notably applications in microelectronics and connectors where copper is advantageous substitute of gold.

In opposition to gold that is an ideal substrate for adsorption of organothiols, using active metals substrates the presence of the superficial oxide layer appears to be an obstacle for the chemical adsorption of these molecules. Previous studies done in our laboratory³ resulted chemical and/or electrochemical pre-treatment methods to eliminate the oxide layer of metals (copper, nickel, zinc,...) and activate the surface where the thiol molecules are able to adsorb.

In this contribution, we explored the possibility of using selenol and selenide molecules to form self-assembled monolayers (SAMs) on copper, in order to check the influence of anchoring groups on SAMs quality and compared it to well-known thiolate assemblies (form with thiol and disulfide molecules). Precisely, monolayers of pure alkane chains have been self-assembled on electroreduced bulk copper. The different selected molecules present the following reactive anchoring groups: thiol (R-SH), disulfide (R-S-S-R), selenol (R-SeH) and diselenide (R-Se-Se-R), where R = C₁₂H₂₅-. Electrochemical (cyclic voltametry and scanning electrochemical microscopy) techniques and spectroscopic (X-ray photoelectron and polarization modulation infrared reflection absorption spectroscopy) have been used to characterise the surface composition and monolayer organisation. Atomic force microscopy (AFM) measurements complete this study.

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Decoration of cuprous oxide nanoparticles on multiwalled carbon nanotubes

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Carbon nanotubes (CNTs) have become one of the most important materials in the field of nanoscience and nanotechnology because of their exceptional properties that make them suitable for many potential applications as breakthrough materials for energy storage, electronics and catalysis. CNTs have been extensively used as supports for various nanoparticles such as TiO_2 , SiO_2 , Fe_3O_4 , CdS, Au, Pd, Pt, and Ag.

Among various metal oxide nanoparticles, increasing attention has been focused on copper and copper oxide nanoparticles due to their redox chemistry, extraordinary electrical, thermal, catalytic and sensing properties. Thus far, many attempts have been made to decorate copper and copper oxide nanoparticles on CNT's surface having the diameter ranging above 20nm.

In this study, we have reported homogeneous deposition of crystalline Cu_2O nano particles (8-80nm) on the surface of multiwalled carbon nanotubes (MWNTs) with an average diameter of 10nm, using copper (I) phenyl acetylide as the source of copper. MWNTs were oxygen-functionalized by treating them with a mixture of concentrated (H_2SO_4 : HNO_3) acids in 3:1 volume ratio before use. The samples were characterized by Transmission Electron Microscopy (TEM), X-ray Powder Diffraction (XRD), Field-Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray analysis (EDX) and X-ray Photoelectron Spectroscopy (XPS). Even though, the deposition of copper and copper oxide nanoparticles on CNTs in the literature is reported, they are either lengthy, tedious processes or in other cases surfactants and reducing agents have been used to control the size of the particles. Whereas, a facile and effective method of, uniform dispersion of nanoparticles without any usage of surfactants and reducing agents, is reported here. More importantly, the content of Cu_2O supported on MWNTs can be controlled by simply varying the relative ratio of Cu_2O to MWNTs.

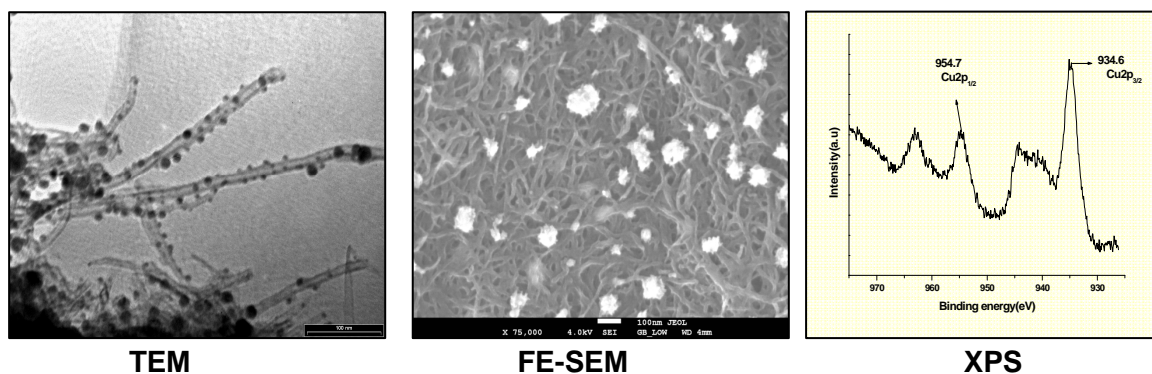


Figure 1: Analysis of cuprous oxide on carbon nanotubes

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Characterization of MWCNT, SiC and TiC nanoparticles and the influence of the dispersion methods

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The promising applications of multi-walled carbon nanotubes (MWCNT), Silicon Carbide (SiC) and Titanium Carbide (TiC) in medical and biomedical applications are huge and they continue to grow in number and variety. However, before such kind of nanomaterials can be incorporated into new devices, the toxicity and biocompatibility needs to be assessed thoroughly. In the case of an *in vitro* or *in vivo* toxicity assessment, biocompatible surfactants are typically used to enhance de-agglomeration and promote and individual nanomaterial – “object of study” contact (e.g. tissues, culture medium).

It is known that the unique nature of each type of nanomaterial expressed in their size, shape and surface characteristics plays an important role in their possible toxicological effects, so the type of surfactant and the dispersion method used (e.g. magnetic agitation, ultrasonication, centrifugation) will also affect the results of the tests being conducted. On the other hand, the use of surfactants contributes to modify the chemical composition and by consequence how they are integrated in any biological media, making it a better or worse dispersant agent in terms of biocompatibility.

Intrinsically, the dispersion process is related to another very important factor usually neglected: the surface chemical properties. Its proper knowledge is vital in biological interactions and whether they remain suspended as individuals or as agglomerates will depend upon it. Subsequently, a careful characterization of their properties before any test is necessary to control the possible degradation or modification of their raw properties. Moreover, nanomaterials can show defects, damages or changes in their extreme surface properties after ultrasonication cycles.

The effect of the Pluronic F108 solution (1%w/v) on the SiC, TiC nanoparticles and the MWCNT surface were studied before and after dispersion by XPS (extreme surface characterization), TEM (morphology), SEM (morphology), EDX (elemental composition) and Centrifugal sedimentation (size distribution) analyses. The results show modifications in the surface chemical composition, evidencing a partial wrapping by the Pluronic F108 that could modify their potential toxicity. Therefore, it is important not to disregard the effects of the dispersing methods on the nanoparticles when considering their potential toxicological effects.

This work is supported by the « Direction Générale des Technologies de la Recherche et de l’Energie » (DGTRE) of the Walloon Region of Belgium (Nanotoxico Project, RW/FUNDP Research convention N° 516252) and the University of Namur.

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Preparation of a PAN/MWNTs composite by surface-initiated ATRP on a stainless steel wire for solid-phase microextraction (SPME) of aromatic compounds

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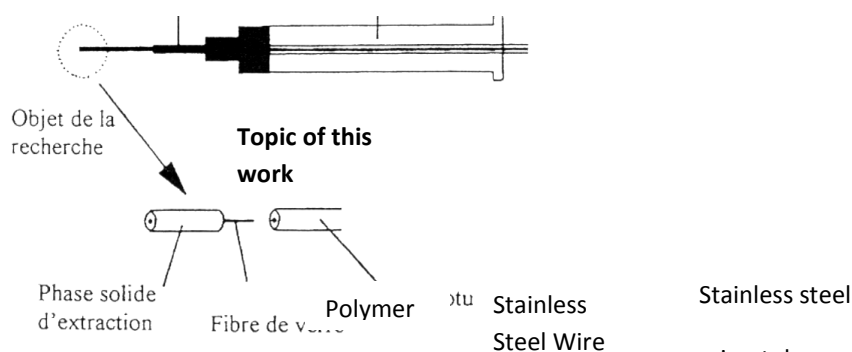
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Although the use of the initially designed SPME fibers (J. Pawliszyn, 1990) is increasingly gaining in popularity, they present some important drawbacks such as relatively low recommended operating temperature, their instability and swelling in organic solvents, the breakage of the fiber, the stripping of coatings and bending of the needle.

The goal of our project is to use stainless steel wires for SPME fibres. To reach this goal, we have worked out a "grafting from" method for the grafting of a layer of polymer, copolymer or composite materials onto the stainless steel surfaces. The first step is the grafting of a monolayer of ATRP (atom transfer radical polymerisation) initiators, 11-(2-bromo-2-methyl) propionyloxyundecylphosphonic acid, onto the stainless steel wires. Polymerisation from these surfaces is then performed under usual ATRP conditions.

The advantages of our method are twofold: the use of stainless steel as support ensures much greater mechanical robustness of the title objects and the onsite polymerisation technique allows for the synthesis of coating layers exhibiting a wide range of affinity towards the compounds to be extracted from various samples (SPME) and / or to be separated and identified (GC).



Indeed, these layers can consist of different homopolymers, statistical or block copolymers, as well as the same "doped" by unfunctionalised carbon nanotubes. Furthermore, since the coated layers are covalently bound to the stainless steel surfaces, good to excellent thermal stabilities are obtained as well as perfect resistance to solvents can be achieved.

The so prepared SPME fibers were evaluated for extraction of different classes of compounds (alcohols, BTEX...) from aqueous solutions. The optimization of the parameters affecting the extraction efficiency of the target compounds was studied (temperature and time of extraction).

The reproducibility of the coating procedure was evaluated resulting in a relative standard deviation lower than 10%. The repeatability for one fiber (n=10) was lower than 5%. The detection limits were lower than 2,5ng/L for BTEX. Taking into account the amount extracted per unit volume, the stainless steel fibers showed better extraction profiles in comparison with the commercial fibers (PDMS 7 μ m). The new SPME fibers have a lifetime of over hundred extractions. Thus, it is a promising alternative for low cost analysis, as the proposed fibers are robust and easily and inexpensively prepared.

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Effect of the counter-anion in the synthesis of SWNTs and DWNTs

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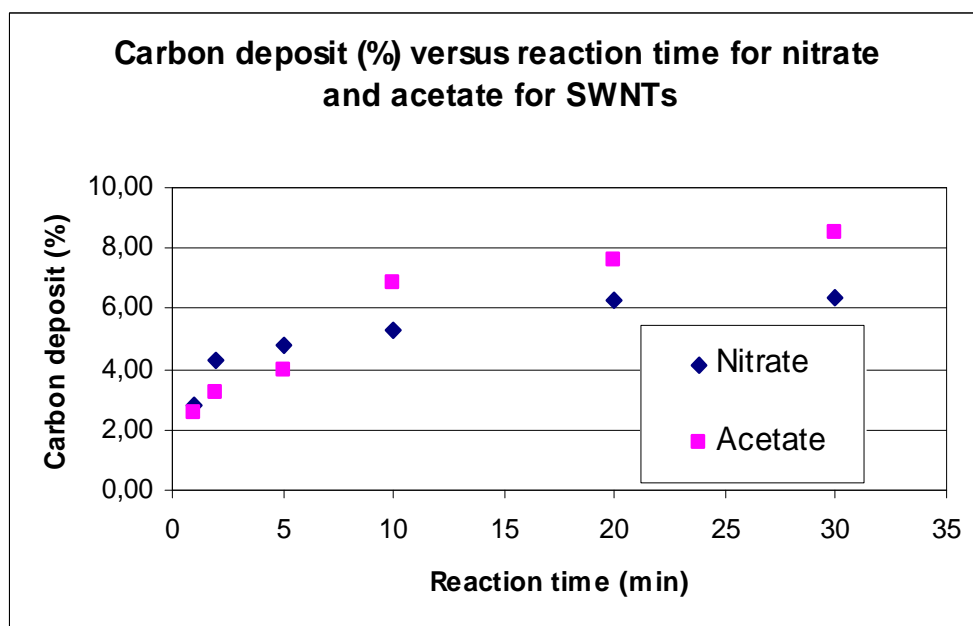
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In this study, we report a systematic screening of the role of the counter-anion in the synthesis of SWNTs and DWNTs. SWNTs and DWNTs are respectively synthesized on Co/MgO and Co-Mo/MgO catalysts. Four different cobalt salts were tested: acetate, nitrate, sulphate and chloride.

The best results are obtained for acetate and nitrate comparatively to sulphate and chloride which provide poor quality products. The poor results obtained with the sulphate catalyst are assumed to proceed from a "poisoning" of the catalyst by the sulphur.

This hypothesis has been confirmed by the increase of the quality of the products obtained on sulphate catalyst subjected to various pre-treatments before the synthesis.



Carbon deposit versus reaction time for nitrate and acetate for SWNTs

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Design of highly sensitive and selective fluorescent nanosensors for the detection of mercuric ions

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During the last decades, the interest of the scientists, including chemists as well as biologists, has been focused on the quantification within the environment and in waste industry of toxic heavy metals which cause serious damages on the human organism. Among them, mercury is considered as one of the most harmful due to its devastating effects on the environment and human health. In order to minimize the dramatic consequences of this highly toxic metal, it seems essential and urgent to design a new fluorescent detection method for the monitoring of mercuric ions based on the measurement of the photophysical changes of the fluoroionophore induced by these ions.

The present work aims at designing highly sensitive and selective fluorescent nanosensors for the detection of mercuric ions. To improve the efficiency of the device, we have planned to encapsulate the fluorescent sensor in a highly ordered mesoporous material in order to obtain a system more easy to handle, easily portable, able to perform field measurements and having the potentiality to be reuse due to the heterogeneity of the system. To achieve the aim of this project, different fluorescent probe molecules, responding all by a linear fluorescence enhancement proportional to the concentration of Hg^{2+} ions, have been synthesized and characterized successfully to be tested in their abilities, especially in terms of sensitivity and selectivity in the quantification of these metallic ions. In these syntheses, we have demonstrated the importance of considering both the fluorescent and chelating parts to envisage a sensitive and selective complexation of a specific ion. Indeed, we have considered respectively a substitution of sulfur atoms by selenium as chelating atoms to Hg^{2+} ions but also the grafting of an electron-withdrawing atom as bromine on anthracene,

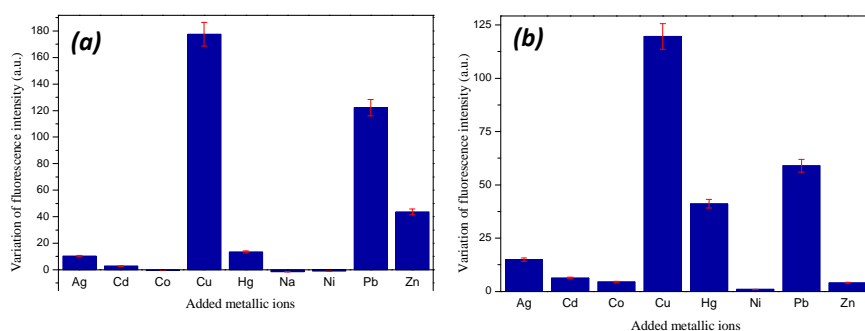


Figure 1 : Selectivity measurements (a) sulfur ionophore, (b) selenide ionophore

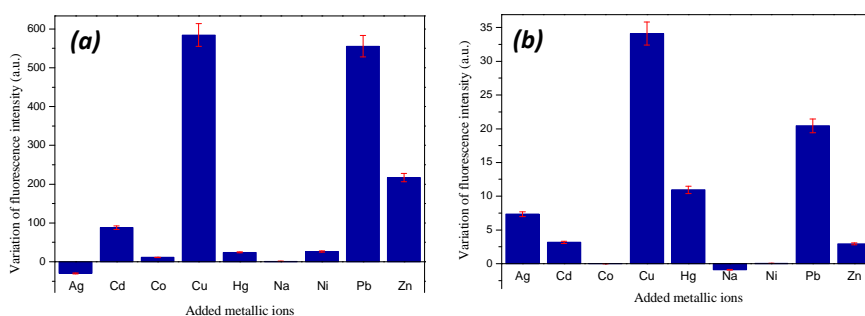


Figure 2 : Selectivity measurements (a) unmodified fluorescent moiety and (b) modified fluorescent moiety

the fluorescent moiety, to observe a potential increase of the sensitivity and selectivity of the fluorescent sensor towards Hg^{2+} ions. After these very promising tests, we have remarked generally that most of these molecules exhibited a significant

selectivity for Cu^{2+} and Pb^{2+} ions and less for Hg^{2+} ions. However, having considered a selenide ionophore instead of an ionophore based on sulfur atoms and the grafting of a

bromine atom on anthracene have been resulted in a strengthening of the selectivity of the probe towards Hg^{2+} ions (*Figure 1 and 2*). In view to encapsulate our future most efficient fluorescent probe in order to obtain our nanosensors adapted to the detection of Hg^{2+} ions, various highly structured mesoporous materials CMI-1 and SBA-15 were synthesized and characterized. Thanks to different characterization techniques, we could highlight the remarkable properties that possess these porous matrices for the designing of very efficient nanosensors.

Synthesis hierarchical macro-mesoporous aluminosilicate with silicon to aluminium ratios close to one from a single precursor [(sBuO)₂-Al-O-Si-(OEt)₃]

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With the decline in reserves of certain raw materials, coupled with the ever growing needs of the population, there is increased pressure on industries to devise novel synthetic processes. The Sol-gel process is one of the most promising technologies within inorganic chemistry. It permits the development of amazing materials featuring porous organisations at the nanometric scale and a controlled stoichiometry, such as aluminosilicate-based catalysts exhibiting hierarchical macro-meso porosity, as well as zirconosilicate mesostructured materials with very low Si/Metal ratios and an excellent homogeneity.

Recently, our laboratory has developed a new alkoxide-based synthesis pathway that targets materials with a hierarchical macro-mesoporosity without the need of any physical agent. This hierarchical porosity, auto-generated by the release of a porogen during fast reactions of hydrolysis and polycondensation, could lead to the synthesis of a single catalyst capable of undertaking a series of catalytic reactions with complete selectivity, with a performance rivalling a set of specific catalysts. This is the principle of a “one-pot reactor” and will allow us in the near future to save both time and money in terms of separation processes. Currently, our laboratory is able to synthesise macro-mesoporous aluminosilicates from a mixture of an aluminium alkoxide and an alkoxy silane. However, the aluminium precursor polymerises faster than the silica precursor and forms an undesirable binary oxide with poor selectivity. An elegant and original alternative, to the use of independent inorganic precursors, would be to exploit a single molecular source that possesses an intrinsic Si-O-Al link. This method has been realised by the use of di-sec-butoxyaluminumoxytriethoxysilane (sBuO)₂-Al-O-Si-(OEt)₃, an unique molecular precursor of aluminium and silica which features the Si-O-Al link. Fine tuning of the aluminium polymerisation of this single precursor is required to preserve the Al-O-Si linkages. This was achieved by the control of key parameters such as pH, use of chelating ligands and the addition of an inorganic co-precursor. These adapted conditions permit the design of macro-mesoporous aluminosilicates with a Si/Al ratio close to unity.

On the basis of this knowledge, other single precursors, containing Si-O-M linkages, have been used to create highly ordered mesoporous materials with a totally controlled stoichiometry. Indeed, the design of zirconosilicate mesostructured materials with interesting properties has been successfully achieved from a single precursor, avoiding an inhomogeneous repartition of zirconium atoms into the silica matrix due to the difference of polymerisation rates.

Development of Porous Matrices Adapted to Biological Cells Encapsulation for the Cell Therapy

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In recent years, the association of inanimate materials and living systems opens up great opportunities in the diagnosis and cure of major chronic diseases, like Type 1 diabetes. This disease is characterized by the attack of the insulin secreting beta cells by the body, which leads to their death. The treatments used at the moment improve the life's quality of patients but merely delay the complications of the disease. This pushes chemists and biologists to collaborate in the development of materials for encapsulation of beta cells to be transplanted in the body.

The principle consists in the immobilization of animal cells in porous matrices by sol-gel process, generating the matrix around the entity to encapsulate by using metal alkoxides undergoing hydrolysis reactions and condensation. This matrix has an obligation to be fully biocompatible; its nature should not interfere with the quality of the immobilized cells, while avoiding generating immune responses on the part of the host organism. It should also be stable over time and have a porosity adapted to the assimilation of nutrients and the removal of metabolites.

Titanium alkoxide would be suitable for immobilization of biological materials. Indeed titanium is one of the most biocompatible metals, with gold and platine. But if the silica way is widely used for biomolecules, enzymes, proteins and cells entrapment, the study on the titania as matrices for encapsulation of biomolecules is less spread. Indeed, as the titanium is a transition metal, the hydrolysis/condensation rate is very rapid and difficult to control compared to silica precursor.

We have prepared titania matrix using ethylene glycol as stabilizing agent. It is possible to obtain the latter without the employ of additional alcohol. We have used $\text{Ti}(\text{OiPr})_4$ and $\text{Ti}(\text{OBu})_4$ as precursors. The sol is obtained by mixing alkoxide precursor with ethylene glycol with ideal molar ratios of 1 : 14 ($\text{Ti}(\text{OiPr})_4$)

and 1 : 10 ($\text{Ti}(\text{OBu})_4$). The physiological pH is reached by the addition of NaOH. The addition of cells in suspension to these sols leads to the formation of gels entrapping the cells. The supercritical-dried aerogels present micropores and mesopores (*fig.1*).

The relative respiration of cells within the gels is shown by the *fig.2*. The problem of byproducts (alcohols released during the hydrolysis process) could be counter by the immobilization of alginate beads in the TiO_2 gels, the beads conferring a first protection to the cells.

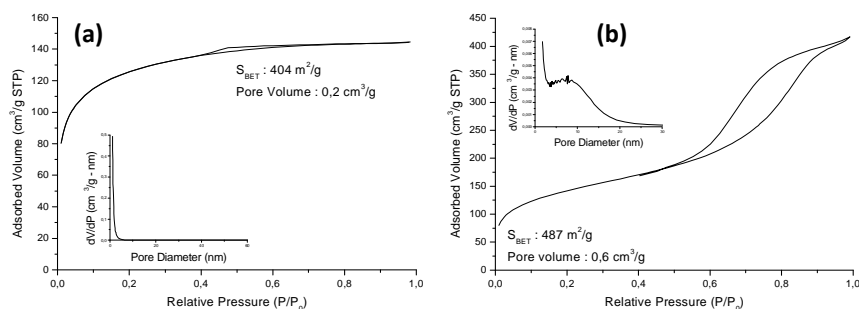


Fig.1: Isotherm and pore size distribution of a gel synthesized from (a) $\text{Ti}(\text{OBu})_4$ and (b) $\text{Ti}(\text{OiPr})_4$

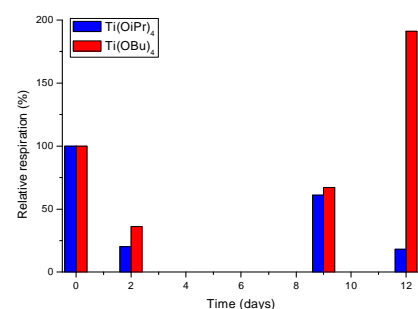


Fig.2: Relative respiration of cells immobilized in gels over time

Potential nanotoxicity in blood : Effects of engineered nanoparticles on human blood constituents

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Nanosciences and nanotechnologies are in constant evolution and development. Due to their remarkable mechanical, electrical, chemical, thermal, magnetic and biological properties, nanomaterials (<100 nm) are bearing of many hopes notably in chemistry, microelectronic and environmental domains. Nanomaterials also play a key role in nanomedicine with the development of drug delivery or drug detoxification nanosystems, imaging nanoprobe and diagnostic tools. These nanomaterials emerging as alternatives to conventional drugs must not only be designed as non toxic but also as biocompatible materials with blood and vasculature. Today, the effects of engineered nanomaterials on erythrocytes integrity (hemolysis) and on hemostasis (platelets aggregation and coagulation cascade) are not well known while it is a necessary part of preclinical development.

Here, we reported the potential toxicity of manufactured nanoparticles (MWCNT, SiC, TiC, SiO₂) in blood with a focus on potential impacts on human red blood cells, platelets and coagulation factors. Evaluation of haemolytic properties was performed using a spectrophotometric test for acute *in vitro* damage of red blood cells resulting with the release of haemoglobin. Platelet activation and aggregation properties were assayed using several state-of-the-art techniques such as impedance aggregometry, flow cytometry as well as transmission and scanning microscopy. Finally, the potential impact of manufactured nanomaterials on blood coagulation was investigated using the Calibrated Automated Thrombogram[®], a functional fluorimetric test for measuring blood hyper- and hypocoagulability.

TARGAN: Biocompatibility assessment of 3 types of gold nanoparticles on endothelial cells

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Radioimmunotherapy is an emerging therapeutic strategy to counter cancers but its efficiency could be improved at several levels: increasing the specificity of the antibody recognizing the tumorous antigen, increasing the number and the type of radioactive atoms per nanoparticle (NP) in order to kill more cancer cells, decreasing the size of the radioactive NP in order to facilitate its access inside the tumor, ...

In our lab, we have produced small diameter (4 to 6 nm) gold NPs coated or not with polyallylamine (PPAA). These NPs will then be coupled to a tumor endothelial cell specific antigen. The biocompatibility of these NPs has been assessed on EAhy926 endothelial cells and the results have been compared to the ones obtained with commercial gold NPs (10 nm and 20 nm diameter).

Unlike commercial gold NPs, after 24 hours incubation time, the gold NPs and the PPAA-coated gold NPs that we produced were toxic at a concentration of 1 and 0.5 ppm. After an incubation period of 72 hours, they inhibited cell proliferation in a concentration dependent way. When these NPs formed aggregates, no sign of toxicity was detected at the same concentrations. Moreover, we showed that cell death after an incubation period of 24 hours with gold NPs and PPAA-coated gold NPs was partly due to an activation of caspase 3 which leads to apoptosis. We also showed that, in the presence of gold NPs and commercial gold NPs, EAhy926 endothelial cells secreted interleukine-8. Finally, observations performed with a transmission electronic microscope showed that gold NP were internalized in intracellular vesicles.

These results indicate that gold NPs toxicity could be due to the size of the NPs, the small ones (4 to 6 nm diameter) could get into the cell, create an inflammatory context and induce apoptosis by activating caspase 3 while the larger ones were less toxic. We still have to investigate whether larger commercial gold NPs are internalized into the cell to the same extent than the smaller ones.

Acknowledgments: TARGAN is a waleo2 project from the walloon region.

Relevance of Human Skin Equivalent (HSE) use for *in vitro* testing and ageing studies

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Skin is our first natural protection against the environment. Huge interest exists in chemical and cosmetic compounds *in vitro* testing since European legislation imposes more safety and claims substantiation assessments in these fields. Various Human Skin Equivalent (HSE) models have been developed, which can comprise different cutaneous cell types in addition to keratinocytes and fibroblasts. These models are somewhat closer to the *in vivo* situation. However many *in vitro* studies are still conducted on monolayers of cells or less complex model like Dermal Equivalent (DE). In this study, we developed a new model of HSE which was characterized histologically. This model allowed to study the interactions between keratinocytes and fibroblasts at the gene expression level, using TaqMan low density RT-qPCR arrays. More characterization of these interactions was performed in a model of skin photo-ageing. A further step was to develop methodology allowing to study the effect of the age of the human donor of fibroblasts in this model of photo-ageing, on the gene expression of keratinocytes. This study on HSE demonstrates that keratinocytes and fibroblasts clearly interact, as shown from changes in gene expression patterns not observed in less complex models. Thus HSE should be considered as more representative models when studying skin-related issues involving at least fibroblasts or keratinocytes.

Acknowledgements : O. Toussaint is a Research Associate of the Belgian F.N.R.S and J. Dedessus le Moutier is Recipient of a FIRST-DEI fellowship, which is co-financed by the Walloon Region and StratiCELL SA

Effects of multi-wall carbon nanotubes on three cellular models of human skin

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The potential cytotoxicity of multi-wall carbon nanotubes (MWCNT) was investigated on three cellular models of human skin : a multi-layer *in vitro* reconstructed epidermis (RHE) including a corn layer, a keratinocyte cell line (IHK) and a sebocyte cell line (SZ95). The physico-chemical properties of MWCNT were characterized with various techniques (TEM, FEG-SEM, EDX, XRD, XPS, PIXE, BET). Then, MWCNT were dispersed into aqueous suspensions either by sonication, by coating with dispersive agents (hydroxypropylcellulose or Pluronic F108) or both. MWCNT were then diluted in culture medium to 100 µg/ml before cell incubation. Additionally, MWCNT dry powders were also applied on RHE. After 24h incubation, cell viability was determined by MTS conversion, LDH release and ³H-thymidine incorporation assays. These experiments were completed with morphological analyses by histology. Results show no significant harmful effects of MWCNT on RHE and SZ95. On the opposite, raw MWCNT induced slight toxicity in IHK cells (20% mortality) while sonicated MWCNT were much more harmful (70% mortality). However these effects were lost when MWCNT were sonicated in presence of dispersive agents.

Molecular Switches Presenting Second–Order NLO Responses: A joint Theroretical and Experimental Study

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Since a few years, optical chromophores are of particular interest in many different areas of the science and technology like new sensors, biosensors, data storage, optical communication or in new nanoscale electronic devices. This work deals with molecular switches possessing large contrasts in their second-order nonlinear optical (NLO) response called first hyperpolarizability, β ^[1].

The aim of this work is to optimize the contrast between the different commutable forms of different families of compounds: the spiropyran-merocyanin (Figure 1), the anils 4A and 4P (Figure 2), and the dihydroazulene (DHA) - vinylheptafulvene (VHF) (Figure 3) substituted with different donor and/or acceptor substituents^[2].

Calculations encompass geometry optimizations, analysis of the charge distribution, and evaluation of β by accounting for frequency dispersion, electron correlation, and solvent effects. The variations in β as a function of the substituent and the associated contrasts are explained in terms of donor-acceptor strengths and geometrical parameters. The NLO responses are theoretically investigated by using the hyper-Rayleigh scattering (HRS) technique.

Figure 1: Enol (E) and keto (K) tautomeric forms of anils derivatives.

ORXNCH3RRORXN+CH3RRRRRR-1231234455Spiropyran (S)Merocyanine (M)

Figure 2 : Labeling of the merocyanine-spiropyran systems and their substituents.

CNCNRRNCNRCNNCA Δ v Δ DHAVHF-cisVHF-trans

Figure 3 : Photo- and thermochromic equilibrium for the DHA-VHF system.

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THEORETICAL MODELING OF THE MAGNETIC PROPERTIES OF BORO-NITROGENOUS AROMATIC COMPOUNDS AND SMALL SUPRAMOLECULAR SYSTEMS

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Nowadays computational tools and quantum chemistry methods offer many efficient ways to address the structures and properties of complex systems. Our work consists in studying the characteristic magnetic responses of various kinds of chemical systems and their relationship to their aromatic nature. More precisely, we are interested in the rationalisation of the variation of the aromatic nature in a family of compounds, and thus on the variations of their magnetic properties.

One example of interest is the influence of the substitution of carbon-carbon pairs in aromatic hydrocarbons by “isoelectronic equivalents” such as the boron-nitrogen pair. In particular, the family of the boro-nitrogenous derivatives of the coronene molecule (which can be seen as a graphene fragment) displays significant variations of the magnetic properties and then large variations of their aromatic nature.

The second example deals with supramolecular systems. Indeed, the understanding of the Aromaticity concept is rather different when we consider a molecular or a supramolecular system: in the first case we restrict the analysis to the unique aromatic nature of the studied compound whereas in the second case we also consider the change in Aromaticity induced by the formation of the supramolecular entity.

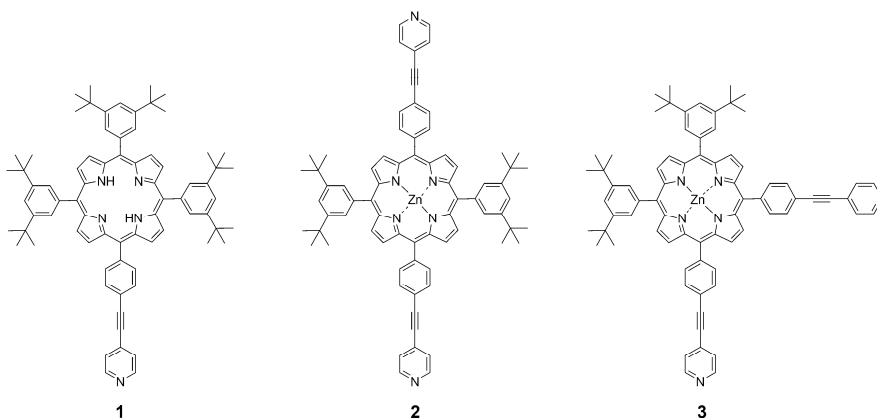
surface-TEMPLATED ENGINEERING OF porphyrin-BASED SUPRAMOLECULES

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Organic two dimensional (2D) networks featuring porous domains are of great interest since their cavities can be used as receptors for the confinement of functional molecules or nanoreactors for chemical transformations.^[1] Unfortunately, the investigation of these structures in solution presents several limitations due to the fact that the molecular components cannot be directly and individually addressed at the nanoscale level. In this respect, the deposition and the organization at interfaces is an obligatory passage towards the exploitation of these systems in real devices. Specifically, the engineering of such architectures on metal surfaces represents a promising first approach as the structure of the molecular-based assemblies can be studied by scanning probe microscopies, such as the Scanning Tunneling Microscope (STM) technique.^[2] One of the first example of self-assembled architectures featuring receiving pores at solid-liquid interfaces was reported by Drain and co-workers.^[3] Specifically, they have described the self-assembly of tetra-substituted pyridyl-porphyrin derivatives mediated by transition metals coordination interactions with Pd(II) and Pt(II) coordinating atoms. Following a similar approach, herein we report on self-organisation of bidimensional supramolecules obtained *via* self-assembly of pyridyl-derivatized porphyrins through transition-metal coordination on metallic surfaces under UHV conditions. In this respect, the synthesis of three different porphyrin molecular modules (see scheme) have been carried out (**1-3**). The synthetic strategy mainly involved the C(Sp²)-C(Sp) bond formation, achieved by exploiting cross-coupling-type Sonogashira reactions.^[4] The characterization of these arrays on surfaces has been accomplished by STM measurements.



Acknowledgements. We thank the SUNTUBE project from the “Région Wallonne”, the FNRS and the University of Namur for generous financial supports.

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Organic functionalization of doubled-walled carbon nanotubes (DWCNTs) *via* lithiation-based reactions

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Due to their low reactivity and poor solubility, Carbon Nanotubes (CNT) revealed to be very difficult to manipulate because of their aggregation.¹ For this reason, different types of organic and inorganic functionalization reactions have been performed to increase their processability,² as a large degree of functionalizations is usually needed in order to pave the road for CNT applications in functional materials and various molecular-based devices.³ Specifically, single-walled carbon nanotubes (SWCNTs) have been, by far, the most investigated carbon frameworks. Despite the large number of successful reports, one of the main drawbacks of the classical functionalizations techniques is that their electronic properties are profoundly affected as they usually introduce a large number of defects on the pi-conjugated wall breaking the extended conjugation.

In order to overcome this problem, in these studies we have focused our attention on double-walled carbon nanotubes (DWNTs), which can be regarded as SWNTs coated by an external carbon nanotube. In this work, we report on different covalent organic functionalizations of the external wall of the outer tube of DWNTs through reductive Birch reactions using different electrophilic groups bearing several functional groups, solubilizing alkyl chains and/or fluorescent appends. All functionalized materials have been greatly characterized via a large blend of spectroscopic and analytical techniques, such as microscopy (TEM, SEM and AFM), Raman spectroscopy, thermogravimetric analysis, X-Ray photoelectron spectroscopy (XPS), UV-Vis-NIR and IR spectroscopies. All together, the techniques allowed us to unambiguously proof the functionalization of DWNTs.

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