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Abstracts

Sorted by chronological order of NISM meeting

Surface modified Ga-silicates catalysts prepared via the aerosol process

Loraine SOUMOY¹, Alvis Vivian¹, Luca FUSARO¹, Damien P. DEBECKER², Carmela APRILE^{1*}

¹CNANO, Department of Chemistry, University of Namur, 5000 Namur, Belgium

²IMCN, UCLouvain, 1348 Louvain-la-Neuve, Belgium

*E-mail: carmela.aprile@unamur.be

During the last decade, the decrease of fossil resources combined with increasing concerns about environmental pollution has led to changes in energy strategies. In this context, considerable attention has been devoted to the development of biofuels, above all biodiesel, as a promising alternative to fossil fuels. Nevertheless, the production of biodiesel yields approximately 10wt% of glycerol as by-product. Because of the increasing production of biodiesel, glycerol is now considered as a waste. A promising route to its sustainable valorization is represented by the condensation of glycerol with acetone into solketal thanks to heterogeneous catalysts displaying both Brønsted and Lewis acid sites. Indeed, it is already reported that porous silicates presenting a metal inserted as single site in the framework can be active and selective catalysts for this reaction.^{1,2}

In this work, the aerosol-assisted sol-gel process was used as a powerful tool to synthesize silica-based solids with gallium inserted as single-site in the structure.³ To investigate the role played by the hydrophobic/hydrophilic balance of the catalyst surface, a series of Ga-silicates displaying different degrees of methyl functionalization (5, 10 and 15 mol%) were synthesized. The solids were fully characterized by N₂ physisorption, XRD, TEM (figure 1a) and ICP-OES spectroscopy. The successful incorporation of gallium as single site within the silica framework was assessed via ⁷¹Ga Solid State NMR (figure 1b). The mesoporous Ga-silicates were tested in the acetalization of glycerol with acetone to produce solketal under solventless conditions, showing excellent catalytic performances. Our best catalyst outcompetes other solids reported in literature. Furthermore, it was reused in multiple cycles thus providing the stability of the material under selected reaction conditions. A positive influence of the functionalization on the performances of the catalysts was observed, especially when catalysts display a very low degree of functionalization.

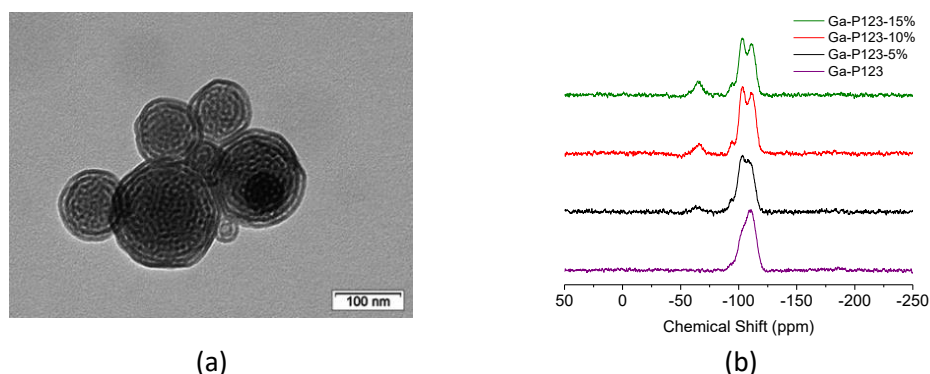


Figure 1 - (a) TEM micrograph of 5% methylated Ga-silicate and (b) Solid State Magic Angle Spinning ²⁹Si NMR spectra of synthesized materials.

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Polarized 2-D hierarchical B doped g-C₃N₄ nanoplates architectures for highly enhanced visible light photocatalytic activity

Yang Ding, Lina Huang, Tarek Barakat, Bao-lian Su*

Laboratory of Inorganic Materials Chemistry, University of Namur, 61 rue de Bruxelles, B5000, Namur, Belgium (Email: bao-lian.su@unamur.be)

A new type of boron-doped graphitic carbon nitride (B-g-C₃N₄/Pt) nanoplates was prepared by a benign one-pot thermal polycondensation process. Systematic studies revealed that a 4%B-C₃N₄/4%Pt (1at% B-g-C₃N₄) showed the best photocatalytic Rhodamine(RhB) degradation activity under visible light irradiation (>400 nm), which is more than 10 times that of the pristine g-C₃N₄ bulk. Detailed characterizations revealed that the high photocatalytic performance could be attributed to the combination of band structure engineering and morphological control^[1,2]. The novel g-C₃N₄/Pt nanoplates not only reduces the band gap to absorb more visible light but also exhibits a higher surface area of 4%B-C₃N₄/4%Pt (49.47 m²·g⁻¹) as compared to that of g-C₃N₄ bulk (8.24 m²·g⁻¹). In addition, the conductive Pt species promote the photo-induced carriers separation, which subsequently improve the photocatalytic performance drastically. This work demonstrates a synergistic strategy to prepare efficient B-g-C₃N₄/Pt nanoplates as a promising photocatalyst for RhB degradation under visible light with good stability.

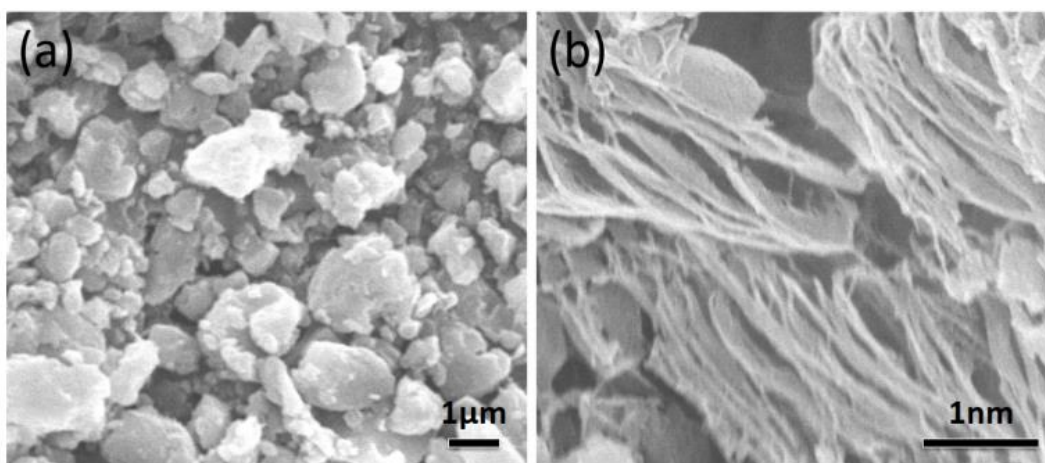


Figure. 1 SEM images of the as-synthesized g-C₃N₄ bulk(a) and B-g-C₃N₄/Pt nanoplates

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A tailored plasma process for tailored nanoparticles

Emile HAYE¹, Yan BUSBY¹, Mathieu DA SILVA PIRES¹, Florian BOCHESE¹ Thomas HAUET², Crosby SOON CHANG², Gabriela DUDEK³, Nathalie JOB⁴, Jaafar GHANBAJA², Laurent HOUSSIAU¹, Jean-Jacques PIREAUX¹

¹ *Laboratoire Interdisciplinaire de Spectroscopie Electronique (LISE), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium*

² *Institut Jean Lamour, UMR 7189, Université de Lorraine, 2 Allée André Guinier, 54011 Nancy, France.*

³ *Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland.*

⁴ *Department of Chemical Engineering – Nanomaterials, Catalysis, Electrochemistry, University of Liège, Building B6a, 4000 Liège, Belgium.*

emile.haye@unamur.be

An innovative plasma-based process has been developed for the synthesis of ~~new~~ metal-based nanoparticles. The process consists in the degradation of a solid organometallic (metal acetylacetonate) precursor in a radio frequency inductively coupled (ICP-RF) plasma, using an inert (Ar) or a reactive (N₂, O₂, NH₃) atmosphere.

This process offers a high flexibility in terms of fine control of the nanoparticles morphology and their chemical state, and avoids the extensive use of solvents. Moreover, the degradation of the organometallic and the subsequent nanoparticles generation can be monitored *in situ* by optical emission spectroscopy. Analytical *ex situ* characterizations (XRD, TEM-EDS, XPS) show that a wide variety of nanoparticles structures (amorphous, crystallized, core-shell), sizes, morphologies and chemical compositions (metallic, oxides, nitrides) can be obtained by varying the treatment conditions, and can be adapted for a specified application.

We will illustrate several different cases, namely the synthesis of photocatalytic ZnO nanoparticles, of Fe₃N nanoparticles with tuneable magnetic properties for pervaporation membranes, and of bimetallic nanoparticles for catalysis.

Keywords: nanoparticles, ICR-RF plasma, OES

Preparation of high crystalline quality, large area films of MoTe₂ by molecular beam epitaxy

Roshan Castelino, **Trung T. Pham**,* Alex Felten, and Robert Sporken
Namur Institute of Structural Matter (NISM), Department of Physics, University of Namur,
61 Rue de Bruxelles, B-5000 Namur, Belgium

*Presenter: Trung T. Pham; E-mail: trung.phamthanh@unamur.be

Thin two dimensional layered structures of transition metal dichalcogenides (TMDs) have attracted tremendous interest in scientific and technological communities due to their excellent physical and chemical properties compared to bulk form [1-3]. TMDs known by the form of MX₂ (M = Mo or W, X = S, Se, or Te) exist in several structural polytypes such as hexagonal (2H), octahedral (1T), monoclinic (1T') and orthorhombic (1T_d) [4] in which the semiconducting 2H phase is thermodynamically stable while the metallic 1T phase, under ambient conditions spontaneously relaxes into semi-metallic 1T' or T_d phase [5, 6]. According to the literature, monolayer semiconducting TMDs show sizable direct band gap [7], quantum confinement effects [8], large exciton binding energies [9] and large valley polarizations [10] and so on, which are very promising for high performance of electronics and optoelectronics.

Compared with MoS₂ and MoSe₂, monolayer 2H-MoTe₂ films have the smallest direct band gap which is similar to that of Si, making it an excellent candidate for applications in novel near infrared photonics and optoelectronics [11, 12]. Therefore, the controllable synthesis of large-area lateral growth of uniform mono- and double-layer 2H-MoTe₂ is highly desirable for device fabrication. Up to now, unfortunately it still maintains challenging although there have recently been several attempts to grow and transfer MoTe₂ on various substrates using different methods.

In this talk, we present here results which demonstrate the direct growth of large area and high crystalline 2H-MoTe₂ films on graphene terminated 6H-SiC(0001) substrates by using molecular beam epitaxy with appropriate conditions. We present furthermore scanning tunneling microscopy (STM) images together with diffraction patterns and X-ray photoemission spectroscopy/scanning tunneling spectroscopy (XPS/STS) spectra which establish unambiguously the 2H-MoTe₂ nature of the films. Our study indicates that control of MBE conditions can be used to synthesize stoichiometric, high crystalline, and phase stabilized 2H-MoTe₂ films.

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Influence of Al-doped Zn target phase composition on sputtering characteristic in PVD

Florian BOCCHESI¹, Aurélien BESNARD², Stéphane LUCAS¹

¹ *Laboratoire d'analyse par réactions nucléaires (LARN), Namur Institute of Structured Matter (NISM), University of Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium*

² *Arts et Metiers Paris Tech - LaBoMaP, 71250 Cluny, France*

E-mail: Florian.Bocchese@unamur.be

New technologies developed nowadays require new materials with particular properties. Thereby, a lot of researches are focused on the development of new materials and the influence of their composition on optoelectronic properties, durability properties or structural properties. However, final material also depends of the experimental technique of deposition. Among them, magnetron sputtering is very popular because it is scalable for industry and ecological. Nevertheless, using simulation to improve the prediction ability allows working more efficiently and consequently to significant material, energy and costing savings.

It is well known that the use of target containing at least two elements is a dynamic process due to preferential sputtering and local composition variation. As the sputtering yield, as well as energy and angular distributions of the sputtered atoms, is often used as input parameter for the process simulation chain, the initial simulation with SRIM has to be relevant and precise. Therefore, in the case of a composed target with several elements, the metallurgical state has to be studied: number, composition and fraction of the phases in presence.

In this study, we use a target with a nominal composition of 95 at.% of Zn and 5 at.% of Al. SRIM simulations were performed for different compositions from pure Zn to pure Al, as if the substrate was a single solid solution. The case where the target is a binary mixture of two phases is then considered, with the help of the phase diagram and experimental analyses of the target (XRD, SEM-EDX). Numerical results show that the description of the target microstructure has an effect on the sputter yield and on the angular distributions.

Phase controlled synthesis of MoTe₂ on graphene/SiC(0001) by MBE

Roshan CASTELINO, Trung T. PHAM, Robert SPORKEN

Namur Institute of Structured Matter,

Department of Physics, University of Namur, Rue de Bruxelles, Belgium

E-mail: roshan.castelino@unamur.be

Ever since its discovery, graphene has been researched for its fascinating properties. However, the lack of bandgap in graphene has motivated a search for similar intrinsically semiconducting two dimensional materials. Transition metal dichalcogenides (TMDs) have been considered as an alternative owing to their unique electrical and optical properties. Bulk TMDs exhibit a wide variety of polymorphs, the important ones being *2H* and *1T'*. The *2H* phase is semiconducting while the *1T'* phase is metallic and the controlled transition from one phase to other has been investigated and the stabilization of one phase over the other is highly desirable. Among all the TMD tellurides, molybdenum telluride (MoTe₂) exhibits co-existence of both *2H* and *1T'* phases at room temperature due to the small energy difference between them [1]. While this co-existence is very promising for a large number of applications, it is also a challenge for the phase-specific synthesis of large area, highly crystalline films. Although there have been several studies on the Molecular Beam Epitaxy (MBE) synthesis of MoTe₂ on various substrates [2-4], growth mechanism, the influence of substrate temperatures on the structure and crystalline quality, the transition between the phases as well as the stabilization of one phase over another are not fully reported yet.

In this study, we present a systematic study of the growth of MoTe₂ on graphene/SiC(0001) by MBE at various substrate temperatures. The synthesized films were characterized by Reflection High Energy Electron Diffraction (RHEED), Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), X-ray Photoelectron spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). For a given Te:Mo flux ratio, the crystalline quality of the films depends strongly on substrate temperature. At substrate temperatures between 150°C and 250°C, films containing co-existing phases are obtained. The *2H* phase can be stabilized by annealing the films with and without Te flux. Annealing without Te flux produces *2H* phase with higher number of defects and the domain edges are terminated by nanowires of Mo₆Te₆. Annealing with Te flux improves the crystalline quality with uniform domains with smooth edges. STM analysis of the domains shows a network of inversion domain boundaries. Moiré patterns confirm the rotational alignment and symmetry seen in LEED.

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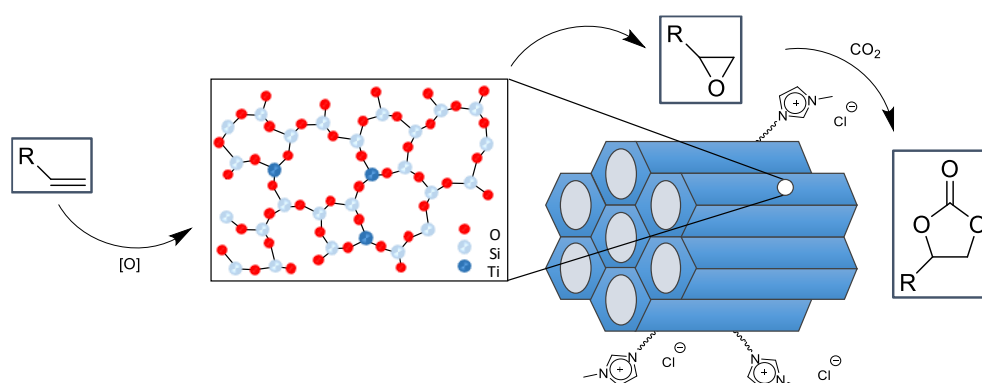
Synthesis of Ti-SiO₂ based catalysts for cascade reactions

Adrien COMES, Rémy PONCELET, Carmela APRILE

Group of Applied Materials Chemistry (CMA), Unit of Nanomaterials Chemistry (CNANO),
Department of Chemistry, University of Namur – Rue de Bruxelles, 61, 5000 Namur, Belgium

E-mail: adrien.comes@unamur.be

During the past years, there was a rising interest of the scientific community towards the conversion of carbon dioxide into valuable compounds. The reaction between CO₂ and epoxides lead to the synthesis of highly demanded chemicals: the cyclic carbonates. Various homogeneous or heterogeneous catalysts were already developed for this reaction. Among those, imidazolium salts display excellent catalytic activity.^[1, 2] However high temperature are usually required. An efficient way to decrease the reaction temperature while preserving good CO₂ conversions is the use of co-catalysts (usually Lewis acid centres). Recently, we proved that the insertion of Zn and Sn as single site within the silica framework followed by the post-functionalization with imidazolium salts allow obtaining a bi-functional catalyst with improved performances.^[3] Here, we explored the insertion of titanium in the silica architecture as Lewis acid centre to favour the ring opening of the epoxides. Moreover, it is known that the Ti-SiO₂ catalysts (e.g. Ti-MCM-41)^[4] display high catalytic activity for the epoxidation of alkene. Therefore, it should be possible to form the cyclic carbonates directly from their corresponding alkene ^[5] in a cascade reaction using a titanium-based catalyst functionalized with imidazolium salts as depicted on Scheme 1. All the materials were fully characterised in terms of textural, structural and catalytic properties. The solids were used in a cascade reaction: the oxidation of an alkene into epoxide and the conversion of this epoxide into the corresponding cyclic carbonate with excellent results. The stability of the best solid was proved in multiple catalytic cycles.



Scheme 1: Cascade reaction using a Ti-SiO₂ based catalyst functionalized with imidazolium salts.

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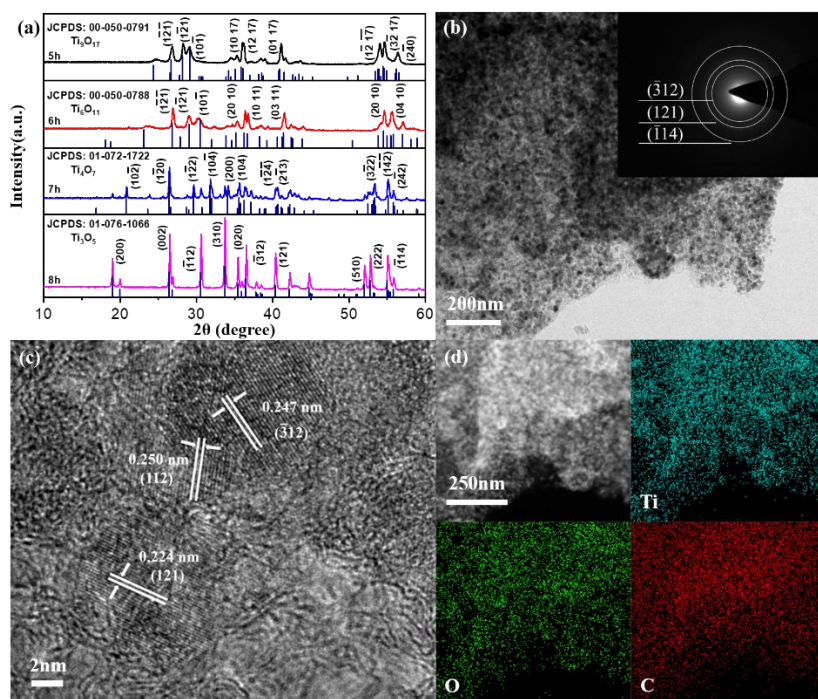
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Synthesis of magnéli Ti_nO_{2n-1} for PEC water splitting

Yingying Wang, Yan-xin Chen, Tarek Barakat, Bao-lian Su

Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium. Email: yingying.wang@unamur.be;

Abstract: The titanium suboxides with a generic formula Ti_nO_{2n-1} ($3 \leq n \leq 10$) are called Magnéli materials (in honor of Arne Magnéli, who was the first to study these compounds). The Magnéli phases have unique crystal structures derived from TiO_2 , which are made up of two dimensional chains of TiO_6 but with an oxygen deficiency in every n titanium octahedral sites. This kind of semiconductor-metal phase transition is antihunt without any further calcination and along with substantial adjustment in optical, electrical and magnetic properties. Until now, the Magnéli phases have been well characterised and already applied in many areas, such as batteries, fuel cells, electrocatalysis and energy conversion. Various magnéli Ti_nO_{2n-1} were synthesized by reductive hydrochar derived from glucose. The crystallization process and the phase of the as-prepared Ti_nO_{2n-1} have been studied systematically. The photoelectrochemical performances of as-prepared samples under solar light illumination are also investigated. We think that this result can serve important contribution to researchers in the fields of Photocatalytic / Photoelectrochemical and energy-related sciences.



Fluorescent silica nanoparticles for photocatalytic application

Yeromina Alexandra ^{1,2}, Davide Bonifazi ^{1,2}, Carmela Aprile ¹

1) Group of Applied Materials Chemistry (CMA), Unit of Nanomaterials Chemistry (CNANO), Department of Chemistry, University of Namur – Rue de Bruxelles, 61, 5000 Namur, Belgium

2) Bonifazi Research group, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

E-mail: oleksandra.yeromina@unamur.be

Photocatalytic transformations and in particular those driven by the solar-light have recently emerged as a relevant and sustainable class of reactions. To achieve these transformations, in classical photocatalysis a light-harvesting photosensitizer (mainly, Ru(II)- or Ir(III)-based complexes) and a semiconducting photocatalyst (ZnO, TiO₂, e.g.) are needed. [1] Due to metal depletion, a modern society is seeking for metal-free alternatives and as such, organic chromophores (OCs) are getting huge attention nowadays. [2] The OCs can be used to trigger the photocatalytic transformations under visible light, acting both as photocatalyst and photosensitizer. [3] In addition, their optical properties can be easily tuned via rational molecular design. [4] Recently, different heteroatom-doped polycyclic aromatic hydrocarbons of perylene and *peri*-xanthenoxanthene types chromophores were synthesized and proved to be efficient in the photoredox dehalogenation of different aromatic bromo derivatives under homogeneous conditions. [5]

To improve the stability and recyclability of the photocatalysts, the chosen fluorophores were synthesized and covalently anchored on mesoporous silica nanoparticles (Figure 1). The new and easy methodology was developed in this work. The obtained fluorescent materials were characterized by solid-state ¹³C and ²⁹Si NMR, UV/Vis and IR spectroscopy, their morphology was studied via TEM and the porosity was analyzed by N₂ physisorption experiments. Preliminary photocatalytic tests of 4-bromacetophenone debromination reaction using XS-PDI solid indicate its photocatalytic activity, although further optimization is needed.

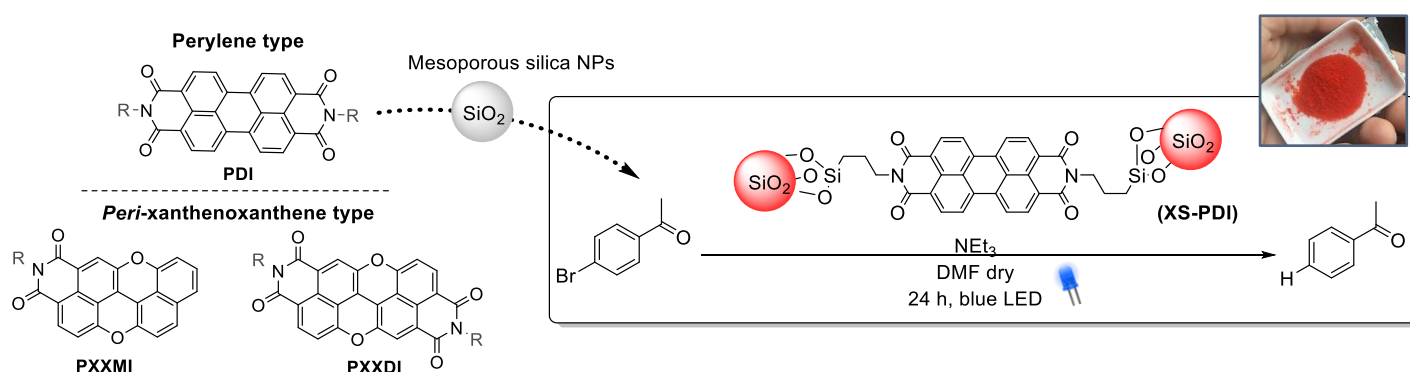


Figure 1. The OCs synthesized (on the left) and the photocatalytic test performed (on the right).

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Evaluating the electronic and vibrational contributions to second and third harmonic scattering responses

Pierre BEAUJEAN and Benoît CHAMPAGNE

*Laboratory of Theoretical Chemistry, Namur Institute of Structured Matter,
University of Namur - 61, Rue de Bruxelles, B-5000 Namur, Belgium,
E-mail: pierre.beaujean@unamur.be*

The second harmonic (β_{SHS}) and third harmonic (γ_{THS}) scattering hyperpolarizabilities and depolarization ratios of small molecules (water, carbon tetrachloride, chloroform, dichloromethane, chloromethane, and acetonitrile) have been evaluated at the coupled cluster response theory level of approximation^[1,2] and compared to experimental data. Besides the static and dynamic β_{SHS} and γ_{THS} responses, the depolarization ratios, which reveal the nature of the responses, are calculated. For γ_{THS} these constitute the first quantum chemical investigations^[3,4], following two recent publications on their measurements^[5,6].

This contribution will address i) the choice of a suitable atomic basis set, ii) the importance of electron correlation contribution as a function of the chemical composition, iii) the frequency dispersion of the responses, iv) the amplitude of the vibrational contributions (pure vibrational and zero-point vibrational average^[7]) in comparison to their electronic counterpart, and v) the relationships between the hyperpolarizabilities/depolarization ratios and the chemical composition.

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Scattering of ultraviolet light by avian eggshells

M. Ladouce¹, T. Barakat², B.-L. Su^{2,3,4}, O. Deparis¹ and S. R. Mouchet^{1,5}

¹*Department of Physics and Namur Institute of Structured Matter (NISM), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*

²*Laboratory of Inorganic Materials Chemistry (CMI) and Namur Institute of Structured Matter (NISM), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*

³*State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, Wuhan, Hubei 430070, China*

⁴*Department of Chemistry and Clare Hall College, University of Cambridge, Herschel Road, Cambridge CB3 9AL, United Kingdom*

⁵*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK*

E-mail: mathieu.ladouce@student.unamur.be & sebastien.mouchet@unamur.be

Eggshell is essential for the reproduction of birds. The optical properties of their shells may have an impact on biological functions such as heat and UV protection, recognition by the parents or camouflage. While ultraviolet reflection by bird eggshells has been superficially described in the scientific literature, the physical origin of this phenomenon remains poorly understood. In this contribution, reflectance peaks in the near UV range were observed by spectrophotometric measurements of different varieties of hen, duck and quail eggshells. This optical response was discussed in terms of the visual sensations of hens and human beings. In addition, electron microscopy imaging (Figure 1) revealed the presence of pores within the so-called “calcified shell” part (i.e., between ca. 20 μm and ca. 240 μm deep from the outer surface). The average radii of these pores range from 120 to 160 nm, depending on the egg varieties. Mercury intrusion porosimetry allowed to highlight a distribution of pores’ radii around 175 nm. Spectral measurements of excitation and emission by fluorescence revealed the presence of fluorophores embedded in the shells. In addition, preliminary analytical and numerical predictions using the Mie diffusion theory and the rigorous coupled-wave analysis suggest that these pores are responsible for the optical response observed in the UV.

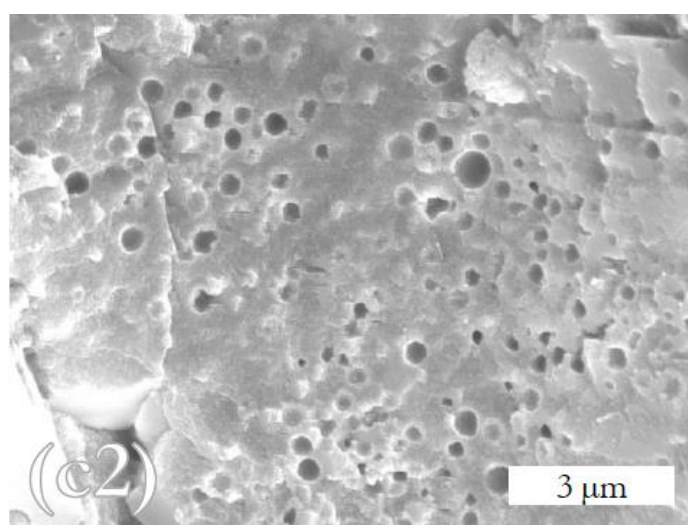


Figure 1 – Cross-section of the hen white eggshell displaying pores with an average radius equal to 121 nm in the so-called “calcified shell” part of the shell.

Control of fluorescence emission in a beetle's 3D photonic structures

M. M. Lobet¹, A. M. Kaczmarek², D. Mara², R. Van Deun², O. Deparis¹ and S. R. Mouchet^{1,3}

¹*Department of Physics and Namur Institute of Structured Matter (NISM), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*

²*L³ – Luminescent Lanthanide Lab, Department Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium*

³*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK*

E-mail: marie.lobet@student.unamur.be & sebastien.mouchet@unamur.be

The optical structures found in some beetles' scales are generally associated with photonic crystals [1-4]. These structures are periodic along one, two or three dimensions. Such periodicities affect the propagation of electromagnetic waves inside the structured material through light interference. In addition to this optical effect, fluorescence emission can also occur in beetles' scales due to the presence of fluorophores which are naturally embedded within the structures' materials [3]. This phenomenon is however underinvestigated. In this study, we analysed the fluorescence emission controlled within *Eupholus linnei* beetle's 3D photonic structures. This beetle is characterised by turquoise-striped black elytra. The turquoise colour of these stripes is due to scales exhibiting various photonic domains ranging from orange to blue under incident white light. Under ultraviolet light, the turquoise stripes emit light in the visible spectrum. Using electron microscopy, 3D photonic structures were found in the beetle's scales. In addition to measurements of the scales' reflectance and the analysis of these scales' colours in terms of chromaticity, the optical response of the observed nanostructures was predicted using the dominant reflected wavelength formula as well as optical simulation methods such as the Rigorous Coupled-Wave Analysis (RCWA) [4]. Furthermore, the fluorescence properties of the scales were measured by spectrofluorimetry. The related decay time was evaluated to be longer at a wavelength within the photonic bandgap of the structures than outside this photonic bandgap. The quantum yield of the fluorescent scales was estimated to be rather low (about 21%), suggesting that fluorescence emission does not play a role in the visual appearance of the investigated weevil.

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Coherent and Incoherent response in Second Harmonic Generation: Seeing at the Nanoscale

Pierre-François BREVET

Institut Lumière Matière, UMR CNRS 5306 Université Claude Bernard Lyon 1, France

E-mail: pfbrevet@univ-lyon1.fr

Second Harmonic Generation (SHG) is the process whereby two photons at a fundamental frequency are converted into a single photon at the harmonic frequency. In non centrosymmetric media, it is an efficient coherent process when the matching of the two waves is achieved, a condition defined as the phase matching condition.

Besides coherent SHG, incoherent Second Harmonic Scattering (SHS) takes place in centrosymmetric media like liquids. SHS has been extensively used to determine the first hyperpolarizability of organic molecular compounds, with great success. Furthermore, a polarization analysis of the SHS light reveals the symmetry properties of the compounds and has helped tremendously to develop the design of highly efficient nonlinear optical molecular probes for quadratic susceptibility processes. More recently, SHS has also been used to investigate nanoparticles, and metallic nanoparticles in particular, and unravel the competition between size and shape, yielding a morphological view of the nanoparticles.

In liquids however, one key fundamental feature is the absence of orientational correlations between molecules since the concentrations used are low. Distances between molecules or particles preclude any interactions. Hence, random orientation of the molecules is ensured and indeed experimentally observed.

In neat liquids however, when one repeats the measurements to investigate the solvent molecules themselves, this condition breaks down as the intermolecular distances are very short. Not only short but also long range correlations are then exhibited and can be revealed by specific experimental polarization configurations with SHS. These correlations have been recently observed for neat and salty water [1].

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Adapted polarizing microscopy technique for the determination of birefringence patterns in parchments

Julie BOUHY

Department of physics, NISM member, University of Namur

E-mail: julie.bouhy@unamur.be

Conventional as well as nonlinear (SHG or TPEF) optical microscopies are used to investigate the physical properties of various tissues in which collagen plays structural and mechanical functions [1]. Specific collagen fibre assemblies dictate the tissue's properties [2][3]. Collagen-based tissues are optically anisotropic and exhibit both intrinsic and form birefringences. Intrinsic birefringence arises from the tropo-collagen molecules whereas form birefringence originates from their hierarchical organization at the macromolecular level (fibrils and fibres). Therefore, birefringence can be used as a tissue's structural indicator.

Parchment originates from the dermis of animal skin, treated to obtain a strong, durable writing support [4]. Its strength results from the organization of a complex network of parallel collagen fibers. Various factors, as mechanical stresses from different origins or ambient conditions, modify this structure, hence, the parchment's optical properties. The study of the resulting birefringence patterns is interesting for conservators and curators since it can help them determining the state of parchment's degradation, and understanding the impact of repairing techniques.

The aim of the present study is to measure the spatial distribution of birefringence (retardance and slow axis orientation) in parchments. For this purpose, we adapted a technique originally developed by Shribak and Oldenbourg [5], which involves single-wavelength measurements of two-dimensional birefringence distribution and image processing algorithms. The method, which relies on the use of five polarization settings and image processing, allows extraction of both retardance and slow axis orientation in each pixel. The non-invasive and contactless features of this technique are advantageous in the context of parchment studies.

The experimental set-up is built around a polarizing optical microscope (BX53-P, Olympus) with polarizing condenser removed, mirror added in order to redirect the laser beam toward the sample, and a polarization-grade plane achromat objective (Fig.1) [6]. The birefringence measurement requires a stable, bright and monochromatic light source, here a 633-nm HeNe laser (HNLS008R-EC, Thorlabs).

Parchments conserved at the Moretus Plantin university library (Namur, Belgium) were made available for the study. Among them, an English deed (1682) was examined (Fig. 1). Preliminary observations of damages (Fig. 1a,b) and bends (Fig. 1c,d) were made using the unmodified microscope in transmission mode and crossed-polarizers configuration. In the damages zone, strong changes of birefringence patterns were observed as the sample stage was rotated (Fig. 1a,b) whereas, in the bend zones, no such patterns were observed (Fig. 1c,d). A bend (e.g. the lowest horizontal bend, thick arrow) was identified as a stripe on the image by focusing alternately inside and outside the bend. Outside this stripe, on both sides of it, brighter and colorful birefringence patterns were observed and changed upon rotation. The absence of such patterns in the bend could be due to damages of the parchment's fibrous structure upon folding, which would result in a loss of anisotropy, hence birefringence. Interestingly, a reduced contrast between inside and outside of the bend stripe was noticed in less severe bends. This trend still needs to be confirmed quantitatively by performing spatially resolved birefringence

measurements. The related experiments are in progress and results will be presented at the meeting.

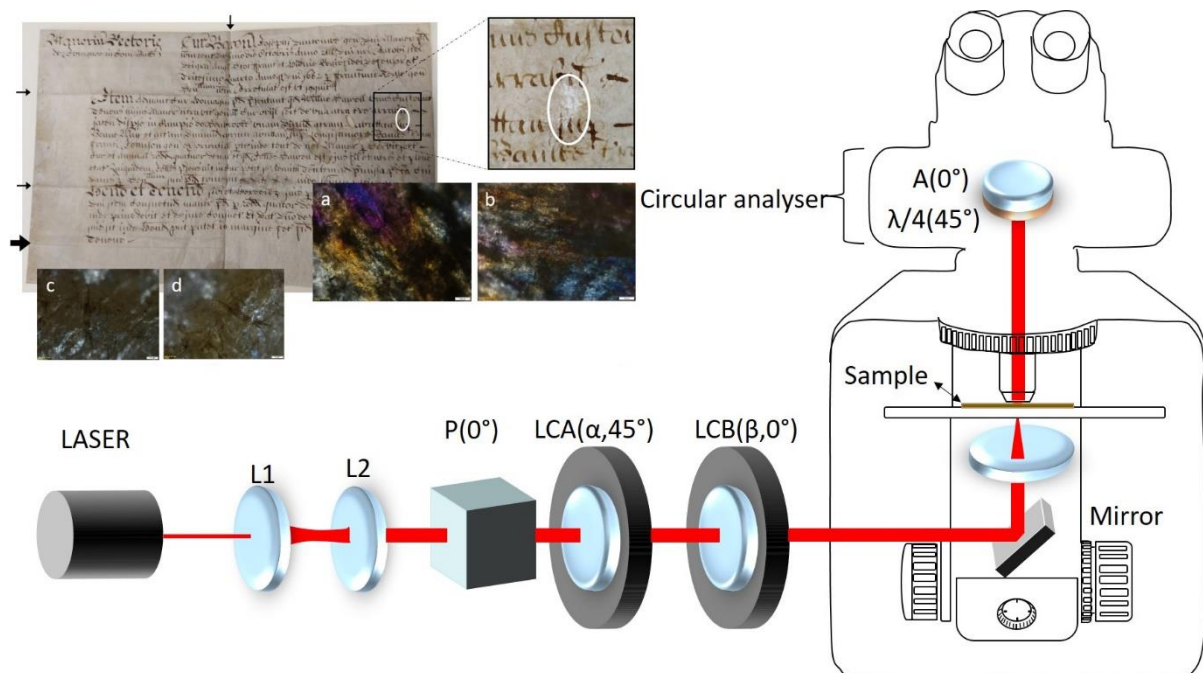


Fig. 1. A 633-nm He-Ne laser light beam is collimated by two lenses L1 and L2, and elliptically polarized by a linear polarizer (P) and two voltage-controlled liquid crystal compensators LCA and LCB, with slow axes at 45° to each other. Five elliptical polarizations are set by tuning liquid crystals retardation values. The beam is focused by a lens (L3) on the sample (S) and redirected by a mirror (M) towards the circular analyzer, made of a quarter wave-plate ($\lambda/4$) and a linear analyzer (A). The five microscope images obtained are processed in order to extract sample's birefringence pattern. The photograph of the historical parchment under test shows bends (indicated by arrows) and damages (circle). Inset: polarized light microscopy images of damage (a,b) and lowest horizontal bend (c,d).

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Interaction of photon pairs in a maximally entangled polarisation state with thin metallic films

M. Remy¹, B. Bokic², M. Cormann¹, W. Kubo³, Y. Caudano¹, and B. Kolaric^{2,4}

¹ Department of Physics, University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium
NISM and naXys Institutes

² Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

³ Department of Electrical and Electronic Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan

⁴ Micro- and Nanophotonic Materials Group, University of Mons, Place du Parc 20, 7000 Mons, Belgium

We investigate the interaction between a system in a maximally entangled Bell state $|\phi_+\rangle$ with continuous or nanostructured, thin, metallic films at normal incidence by quantum tomography [1]. This state is produced by the help of two BBO of type one in an orthogonal configuration. The photon pairs of identical frequency are spontaneously emitted along two superimposed emission cones. They are entangled in polarisation and spatially. The tomography is realised on the polarization state of the photon pairs to obtain the density matrix associated to the most likely quantum state that produced the polarization correlations measured by photon coincidence counting. We compare the quantum features of the incident and transmitted states (fidelity between the states before and after the film and entanglement of formation of the state). To do that we use the code developed by Paul Kwiat's quantum information group [2]. We compare the results obtained with and without nanostructures.

In the case of the continuous film, we also realise a complete tomography in function of the angle of incidence. We study the evolution of the transmitted density matrix (after interaction with the metallic film) from the tomography results. The entanglement and the similarity between the initial and final states decrease slowly. In fact, with the theoretical transmission coefficient obtained with the transfer matrix method, we propose a simple explanation of the phenomenon. It is due to the asymmetry between the transmission coefficients for polarisation s and p in function of the incident angle.

We observe and conclude that, at normal incidence, we do not need nanostructures to preserve quantum entanglement in transmission through metallic films. Indeed, standard isotropic material conserve of the biphoton polarization state in transmission at normal incidence because the complex transmission coefficient is the same for all polarisations. When the angle of incidence increases, the diverge between the s and p transmission coefficients predict really well the asymmetry observed in the density matrix components.

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Understanding the magnetron PECVD of DLC films in an acetylene admixture with a hybrid PICMC/DSMC model

Antoine FAUROUX¹, Andreas PFLUG², Stéphane LUCAS¹

1) *Namur Institute of Structured Matter (NISM) - LARN,
University of Namur – Rue de Bruxelles 61 - 5000 Namur, Belgium*

2) *Fraunhofer Institute for Surface Engineering and Thin Films,
Braunschweig, Germany*

E-mail: antoine.fauroux@unamur.be

Diamond-like carbon (DLC) coatings are well known for their exceptional properties, but complex substrate geometries and variable arrangements like those occurring in everyday DLC coating business are challenging in terms reproducibility, scalability or film homogeneity. The aim of this study is to improve our understanding of magnetron PECVD (Plasma Enhanced Chemical Vapor Deposition) of DLC with acetylene as precursor [1] through simulations and experiments.

The complex chemistry of hydrocarbon plasma usually favor fluid models but their validity is limited for low-pressure and nonequilibrium processes like magnetron PECVD, and although PICMC models are a great tool for investigating low-temperature plasmas, they are limited to small volumes, simple chemistries and short simulation times due to their high computational cost. This is why we present a PICMC (Particle-in-Cell Monte-Carlo) model made with a validated highly parallelized software [2], with a carefully chosen set of chemical reactions and surface interactions [3], coupled with a DSMC model for the transport of radicals and ions in an accurate 3D meshed model of our experimental reactor. The PICMC model takes account of the competing target sputtering and pollution mechanisms and its effect on the plasma. The transport of particles is done in a DSMC model with variable-soft-sphere collisions taking account of the gas recycling.

This study aimed at predicting the dependence in power and acetylene flux of the hysteresis point between the carbon-free and the fully polluted mode, which is of crucial importance for film deposition. Only low power are attainable with PICMC simulations due to computational limits, but we show that our results could be extrapolated to higher powers. Together with this theoretical study, spectroscopic measurements and sample characterization are conducted in order to validate our predictions on the plasma chemistry, on the discharge behavior and on the deposition.

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Study of the effect of cocrystallization on a N-salicylideneaniline switch using a combination of periodic and embedded quantum theory methods.

Jean QUERTINMONT & Benoît CHAMPAGNE

*Unité de Chimie Physique Théorique et Structurale, Namur Institute of Structured Matter,
University of Namur, 61 Rue de Bruxelles 5000 Namur, Belgium*

E-mail: jean.quertinmont@unamur.be

Cocrystallization is being developed as a strategy to tune the thermochromic and photochromic properties of molecular switches. As this grows into a powerful tool, quantum chemistry methods can provide insights on the effects of cocrystallization on the switching process as well as on the accompanying changes of properties. In this presentation, we focus on a single N-salicylideneaniline derivative, which tautomerizes between an enol and a keto form, and on its cocrystals where it forms intermolecular hydrogen bonds or halogen bonds with a variety of cofomers. First, using periodic boundary conditions density functional theory, the enol and keto forms are characterized (their relative energies, bond lengths, and electronic distributions) and are discussed at the light of the interactions between the N-salicylideneaniline switch and the conformer. In particular, we discuss the impact of co-crystallization on the keto/enol equilibrium and its relationship with the modifications of thermochromism observed experimentally. Then, using embedding methods combined with the second-order approximate coupled cluster singles and doubles model, CC2, the optical properties (UV/vis absorption spectra) are simulated and analyzed, highlighting the effect of the geometry and of the environment of the switch.

Bifunctional Lewis acid base catalysts derived from triptycene

Ali Ben Saïda, Guillaume Berionni*,

University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium

E-mail: guillaume.berionni@unamur.be

Although 9-phospha- and 9-sila-triptycenes are widely used as ligands and catalysts [1], bifunctional boron/phosphorus functionalized triptycenes have not been synthesized so far [2,3]. Recent theoretical investigations highlighted that such highly pyramidalized boron Lewis acid may give access to unique Lewis acidic properties [4].

The goal of our research was to synthesize this cage-shaped Lewis acid-base bora-phosphatriptycene, which we found to be one of the strongest Lewis acids known up to date (stronger than $B(C_6F_5)_3$) and which showed promising reactivities [5].

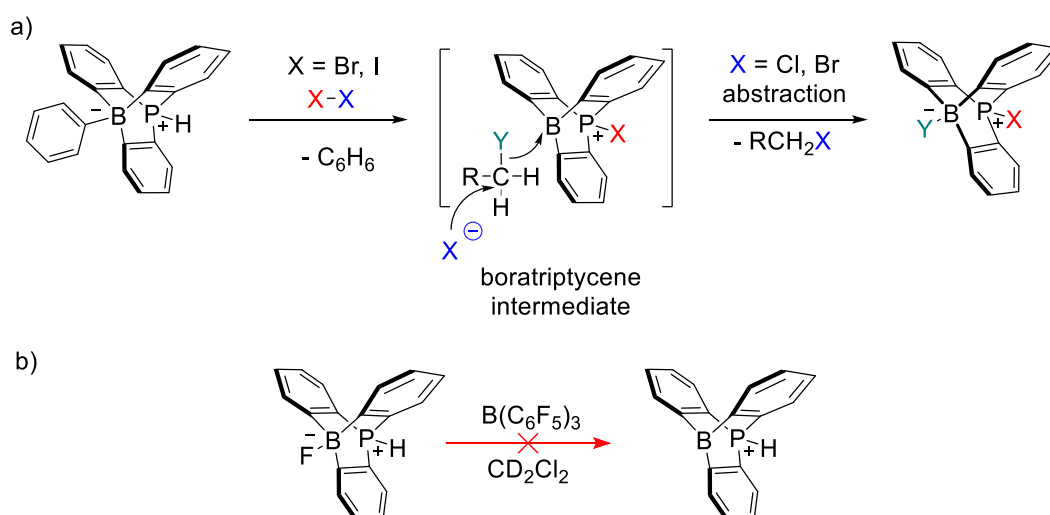


Fig. 1 – a) Mechanism of the generation of the boratriptycene-10-phosponium intermediate, of reaction of the fluoroborate triptycene with $B(C_6F_5)_3$

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Gold nanoparticles as radiosensitizers in proton therapy in 4T1 tumour in BALB/c model

Ewa Biela, Sébastien Penninckx, Félicien Hespeels, Stéphane Lucas, Anne-Catherine Heuskin

Department of Physics – LARN, Université de Namur, Rue de Bruxelles 61 - 5000 Namur
Belgique

e-mail: ewa.biela@unamur.be

Radiotherapy is a form of a local tumour treatment. It allows to deliver lethal dose of radiation to the tumour without affecting distant organs and tissues. Unfortunately, tissues surrounding the tumour (especially these on the path of the beam) are also affected by radiation. Using a specific radiosensitizer, harmless to cells in normal condition but increasing effect of radiation in its localisation could significantly improve effect of treatment and reduce damage to healthy tissues.

In simulations using of high Z nanoparticles increases the number of reactive oxygen species (ROS), which are able to cause DNA damage in cells and lead its death. Gold nanoparticles (GNP) were already tested as a radiosensitizer in radio- and protontherapy in several cancer cell lines in vitro and they indeed increased the death ratio (1). Additionally the second mechanism of radiosensitisation was described (2): after entrance to the cell GNP inhibit thioredoxin reductase (TRX). This enzyme neutralises free radicals and this way counteracts the damage caused by ROS. When TRX is inhibited cells lose its defence against radiation.

Until now only in vitro data of using of nanoparticles in radio- and protontherapy were provided (3–5). In our research we investigate potential benefits of using of GNP in 4T1 tumour in BALB/c mice. We tested thioredoxin reductase activity and nanoparticles intake by 4T1 cells, and TRX inhibition caused by nanoparticles. In clonogenic assay we investigate the influence of presence of nanoparticles during cells irradiation. Finally, we inoculated 4T1 tumour into the mammary fatpad of the mice to determine the growth ratio of the tumour and we tested TRX activity in the tumour model. In the next step we will investigate if using of nanoparticles can be beneficial for cancer radiotherapy in a living organism.

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Thermally Activated Delayed Fluorescence – Rational design using a joined synthetic and computational effort

Tom CARDEYNAELS

Tom CARDEYNAELS^{1,2}, Prof. Dr. Wouter MAES¹, Prof. Dr. Benoît Champagne²

¹*Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan – Building D, 3590 Diepenbeek, Belgium* – ²*Namur Institute of Structured Matter, University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*

E-mail: tom.cardeynaels@unamur.be

Thermally activated delayed fluorescence (TADF) relies on the reverse intersystem crossing (RISC) of triplet excitons formed under electrical excitation in organic light-emitting diodes (OLEDs).^[1] In order for this process to occur, the first excited singlet and triplet states need to be close to each other. Because there is no heavy atom present in these molecules, spin-orbit coupling (SOC) values are small and a second triplet state is needed in order for vibrational coupling (VC) to enhance the RISC.^[2] These conditions can be difficult to satisfy without knowledge of the energy levels and this, in turn, is difficult to measure experimentally. TADF molecule design is therefore often performed in conjunction with density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. Using these quantum chemical methods, the three-dimensional geometry can be optimized and properties such as the singlet and triplet energy levels can be obtained.

In this work, a novel compound is designed based on the known molecule DCyB-4Cbz, consisting of 9H-carbazole (Cbz) as the donor unit and 1,4-dicyanobenzene (DCyB) as the acceptor unit.^[3] In our design, the 9H-carbazole is replaced by 4H-dithieno[3,2-b:2',3'-d]pyrrole (DTP), which is a planar and highly electron rich donor material.

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Magnetically-induced current densities in helicenes

Emna Cherni,^{a,b,c} Benoît Champagne,^c Sameh Ayadi,^b and Vincent Liégeois^c

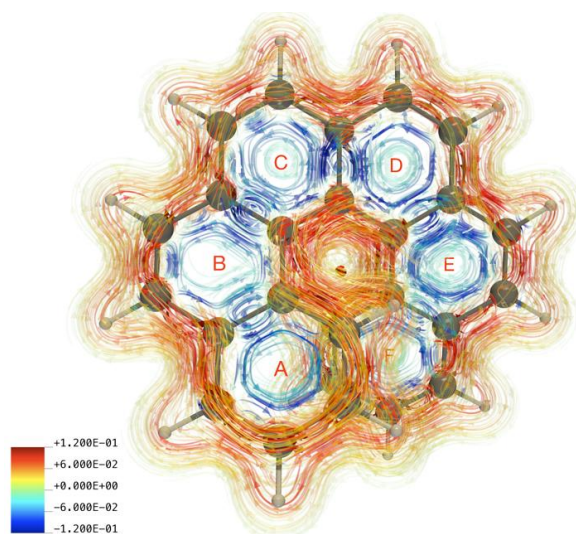
(a) Department of Chemistry, Faculty of sciences of Tunis, University of Tunis EL Manar

(b) Laboratory of materials molecules and applications, Preparatory Institute for scientific and technical studies, Carthage University

(c) Laboratory of Theoretical Chemistry, Unit of Theoretical and Structural Physical Chemistry Namur Institute of Structured Matter, University of Namur

E-mail: emna.cherni@fst.utm.tn

Magnetically-induced current densities as well as other aromaticity criteria such as NICS and bond length alternation (BLA)^[1] have been calculated and analyzed at the density functional theory level for a variety of ortho-fused polycyclic aromatic molecules by using the gauge including magnetically-induced current (GIMIC) method.^[2] All calculations were performed using the GAUSSIAN 16 program while the data analysis was carried out using DrawMol. Thereby, we investigated the aromatic character in the homologous series of carbohelicenes by increasing the number of fused benzene rings from six to twenty. To a great extent, all criteria clearly indicate that the two outer rings are the most aromatic ones since they exhibit the largest induced current, the most negative NICS(0) and NICS_{zz}(0), and BLA values close to zero. Then, in aza-helicenes, the induced currents are always smaller in the pyrrole rings than in the benzene ones.^[3]



3D Streamline plot of the current density for [6]-helicene. The magnetic field vector is represented in red and is oriented toward the reader so that clockwise (anti-clockwise) flows indicate diatropic (paratropic) current densities. They are drawn in reddish (bluish) color and are positive (negative).

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Thickness uniformity optimization of films deposited by PVD on complex substrates in motion.

Martin Evrard¹, Stéphane Lucas¹

¹University of Namur - NISM, Namur, Belgium

E-mail: martin.evrard@unamur.be

Plasma thin film ($\leq 10 \mu\text{m}$) deposition nowadays state-of-the-art technology is used to provide added value to 2D and 3D complex substrates. Nevertheless, films deposition with uniform thickness on 3D complex shapes is still a challenge for various deposition systems. In the case of magnetron sputtering, concavities and different substrate orientations lead to macroscopic shadowing and affect the thickness uniformity and films morphology. Also, thickness uniformity for each part may be strongly affected by the load ratio of the chamber. The aim of this work is to present the current state of the implementation of multiple algorithms to tackle the challenges: Firstly, the optimization of films thickness deposited by PVD on complex shapes in rotation. Secondly, investigate the influence of rotation types (simple or multiple) and shadowing uniformity.

First, we use oriented meshed objects to describe the complex shape of the substrate. Secondly, we compute the start positions, directions and energies of the particles. Thirdly, these are transported through the gas phase by a combination of a 3D Monte-Carlo simulation describing the transport and a "Verlet-linked-cells-list" algorithm to speed-up the simulation. For the detection of the atoms on the meshes, we use techniques of back-faces culling which take automatically into account the shadowing from the substrate itself or from other substrates in the chamber. This algorithms combination allows us to predict the films thickness on a high amount of substrates in motion in a chamber whatever the cathode shape, position and metal sputtered. A genetic algorithm combined to the transport code allows us to obtain the best experimental parameters leading to the maximum of uniformity for different level of shadowing. Experimental chrome deposition with a DC system on high shadowed substrates installed on planetary rotation axis has been performed to validate the code and confirm the optimal parameters of uniformity.

Characterization of gold films and gold nanoparticles synthesized by physical and chemical way

Ornella Fichera, Sébastien Penninckx, Anne-Catherine Heuskin and Stéphane Lucas

*Research center for the Physics of Matter and Radiation (LARN), Department of Physics,
University of Namur (UNamur), B-5000 Namur, Belgium*

E-mail: ornella.fichera@unamur.be

Due to technological advances, gold has become very popular in a variety of applications as in electronics, computer science and biomedical fields thanks to its better electrical conductivity, inertness and biocompatibility compared to others metallic elements^[1]. In the nanometer scale, novel specific properties emerge, including greater chemical reactivity and particular catalytic and optical properties that make gold a sought-after candidate in therapeutic and diagnostic applications^[2,3,4].

The research center for the Physics of Matter and Radiation (LARN) has some expertise in gold based materials. Gold films can be produced with variable thickness from 1 to 10 μm on different kind of substrates by physical vapor deposition (PVD) technique^[5]. LARN acquired also more knowledge in producing gold nanoparticles (AuNPs) by both physical (PVD) and chemical way (based on Turkevich method)^[6] with a particle size respectively from 1 to 10 nm and from 1 to 100 nm. Surface modification of gold with amine groups is performed to enhance dispersion in aqueous solutions and/or to target specific molecules for biological applications. Gold based materials are mainly applied in radiotherapy as radiosensitizing agent for the cancer treatment^[7] and are being studied for their application in a new topic related to the design of biosensors by using the surface plasmon resonance (SPR) phenomenon. Properties as size distribution, morphology, crystalline structure and surface chemistry of gold based materials are known to affect biological response^[8]. In order to understand their behavior in biological systems and to use them in the suitable application, their physicochemical characteristics are required. In this way, our work consists on their characterization by using numerous analytical techniques as X-ray photoelectron spectroscopy (XPS), Transmission Electron Microscopy (TEM), Atomic Force microscopy (AFM), Ultraviolet–visible spectroscopy (Uv-vis), X-ray Diffraction (XRD) and Centrifugal Liquid Sedimentation (CLS).

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Physicochemical characterizations and toxicity assessments of spray coating containing manufactured nanomaterials, generated by atomization

Ornella Fichera¹, Lütfiye Alpan², Anne-sophie Delvigne², Julie Laloy², Tijani Tabarrant¹, Julien Colaux¹, Jorge Mejia¹, Jean-Michel Dogné² and Stéphane Lucas¹

¹Research center for the Physics of Matter and Radiation (LARN), Department of Physics, University of Namur (UNamur), B-5000 Namur, Belgium

²Department of Pharmacy, Namur Nanosafety Centre (NNC), Namur Research Institute for Life Sciences (NARILIS), University of Namur (UNamur), B-5000 Namur, Belgium

E-mail: ornella.fichera@unamur.be

Manufactured nanomaterials (MNMs) are nowadays incorporated into many common products as cosmetics, foods, consumer electronics and textiles^[1,2]. Their increasing use in industrial applications induces many issues about environmental and human safety (EHS). Especially in the field of paints and coatings in which they represent a significant economic interest^[3,4] because they improve mechanical, physicochemical and antimicrobial properties^[5]. Spray painting is the predominant application in finishing industries^[6]. Therefore, workers are exposed to a high percentage of paint overspray^[7]. Inhalation is the major route of exposure to airborne nanoparticles (NPs) and their potential effects on the human health remains unclear^[8].

Our work aims to bring more knowledge about risk assessments of paint aerosol exposure containing MNMs to the human body. Titanium dioxide (TiO₂) or carbon black (CB) MNMs were added into water-based paints formulations and the physicochemical properties (particles size distribution, morphology and surface chemistry) at each characterization stage of paint materials (raw MNMs, suspensions of MNMs, paint containing them and paint aerosol produced) were evaluated to understand later the biological response. Several techniques such as X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Centrifugal Liquid Sedimentation (CLS) and Electrical Low Impactor (ELPI) were used to this objective. Acute and subacute experiments were performed in a whole-body (mice) exposure model to provide information (histopathological examinations) on the potential toxicity of paint aerosol. Moreover, quantification of MNMs on mice's lungs was achieved by using Particles Induced X-ray Emission (PIXE).

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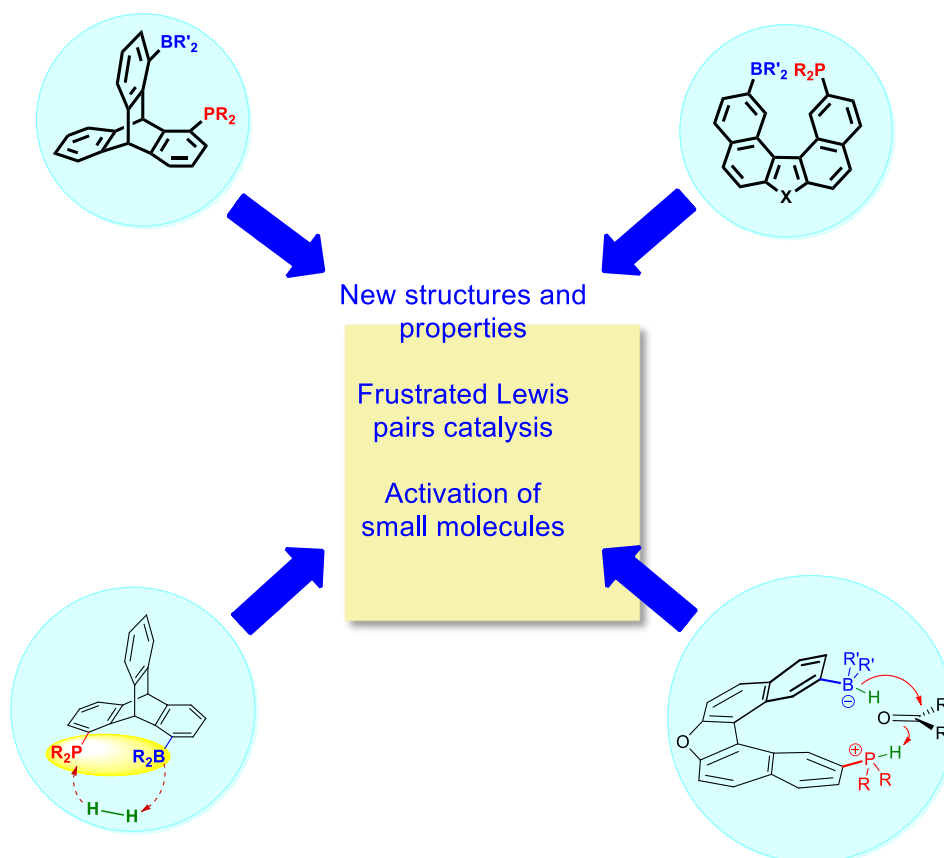
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Synthesis, structure and reactivity of frustrated Lewis pairs based on triptycene and [5]-helicene scaffolds

Mathieu Gama, Julien Janssens, Guillaume Berionni

Because of their unique chemical, physical and photophysical properties, boron and phosphorus compounds are playing an important role in materials science and organic chemistry^[1]. Due to the increasing importance of sterically hindered boron Lewis acid and phosphorus Lewis bases in catalysis, in particular in the field of frustrated Lewis pairs (FLPs) catalysis,^[2] we are interested in finding new molecular architectures to connect these reactive chemical functionalities.

The triptycene is a propeller shaped molecule with unique geometry for designing new types of ligands and catalysts. Triptycene based phosphines and boranes have been used as ligands for transition metals^[3] and as receptors for anions^[4] but have not yet been used as bulky phosphine in the field of frustrated Lewis pair. We are currently investigating the synthesis and properties of triptycene with a phosphine and a boron substituent located at different position on this tridimensional scaffold. Another tridimensional scaffold under investigation is the [5]-helicene. Helicenes are chiral and can be used in the field of asymmetric catalysis. Our future goal is to study the stereoelectronic properties of these new types of ambiphilic molecules for potential applications in FLPs catalysis.



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New bora-anthracenes as Lewis acids and anion sensors

Department of Chemistry, Namur Institute of Structured Matter
University of Namur, 5000 Namur, Belgium

Dr. Thu-Hong DOAN, email: thu-hong.doan@unamur.be;
Dr. Aurélien CHARDON, email: aurelien.chardon@unamur.be;
Prof. Guillaume BERIONNI, email: guillaume.berionni@unamur.be.

Trivalent boron compounds are widely used Lewis acids in academia and industry, and are playing an important role in chemistry and materials sciences.¹

With the purpose of developing a new class of boron Lewis acid, we aim at synthesizing and studying the Lewis acidity of bora-anthracene derivatives (Figure 1, top). Recently, our group has developed a straightforward methodology for introducing a variety of aryl groups attached to boron atom.

In this poster, we will describe the synthesis of new substituted bora-anthracene derivatives and their structural characterization in solution and in the solid-state. Beside Lewis acid properties, photophysical behavior of the system as well as influence of different aryl groups on changes of photophysical properties will be considered. Based on these characteristics, the bora-anthracene derivatives might be used as constituent of molecular receptors for toxic anions such as fluorides F^- and cyanides CN^- (Figure 1, bottom) and can find other applications in organic catalysis.

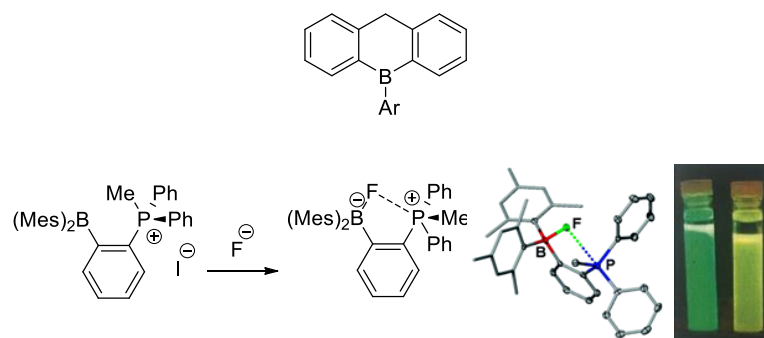


Figure 1. Target bora-anthracene compound (top) and example of a fluoride anion detector (bottom).²

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Ordered hierarchical porous carbon materials synthesized by dual-template method for advanced Li-Se battery

Hongyan Li¹, and Bao-Lian Su¹

hongyan.li@unamur.be

Laboratory of Inorganic Materials Chemistry, University of Namur, 61 rue de Bruxelles, B5000, Namur, Belgium

Lithium-selenium (Li-Se) battery as an alternative to its sulfur counterpart has some noticeable advantages such as extremely higher electrical conductivity of Se and better electrochemical performance [1-3]. In our work, a kind of three-dimensional microporous enough ordered hierarchical porous carbon material (MOHPC) with a wide range of porous sizes was synthesized with the help of templates and KOH activation, accompanying with Se worked as the cathode in Li-Se battery. The OHPC material showed a high specific surface area of 1265 m² g⁻¹. The unique structure delivered many advantages, for the microporous hosts as microcontainers for elemental Se could significantly absorb the polyselenides and minimize the shuttling effect, and the three-dimensional orderly connected channel structure constituted with meso- and macropore could let electrolyte come through the cathode much easier. Therefore, hierarchical porous carbon materials with various size of porous, could take advantages of different pore structures, no hesitate to be promising Se hosts for Li-Se battery.

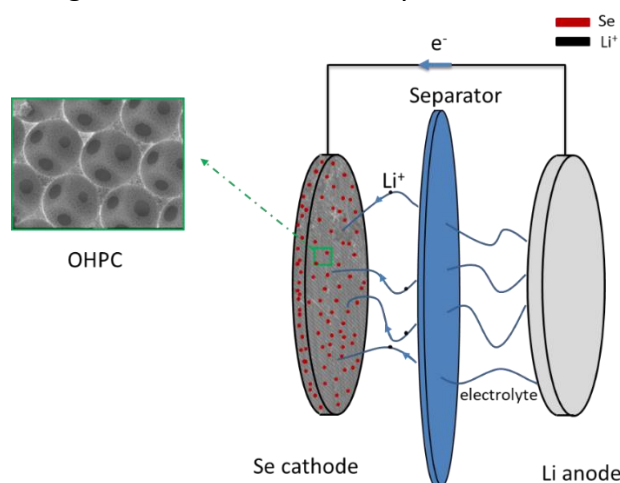


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Optimization of catalysts features and reaction conditions for the conversion of raw glycerol

Amélie Maertens, Alvise Vivian, Carmela Aprile*

Unit of Nanomaterials Chemistry (CNANO), Department of Chemistry, University of Namur, 5000 Namur, Belgium

* carmela.aprile@unamur.be

With the shortcoming of non-renewable energy sources and in particular fossil fuels, scientists focused their attention on the development of sustainable alternatives among which biomass conversion. An example is represented by the production of biodiesel. In this process, glycerol comes as a byproduct at an approximate proportion of 10 wt%^[1] and the constant increase in biodiesel production led to an excess of glycerol on the market. Glycerol coming from biomass conversion contains many impurities and its use requires a costly refining process. For this reason, the development of novel processes for a direct and efficient valorization of crude glycerol is an attractive perspective^[2]. Among the possible routes, one worthwhile to consider is the use of glycerol as platform for the synthesis of valuable chemicals. As an example, the ketalization reaction of glycerol with acetone leads to 2,2-dimethyl-1,3-dioxolane-4-methanol, shortly named “solketal” (Figure 1). Solketal can be used as a flavoring agent, plasticizer or fuel additive to reduce particles emission^[3].

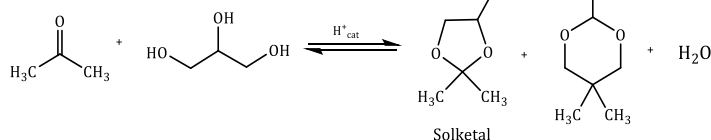


Figure 2. Ketalization reaction of glycerol with acetone under acidic catalysis

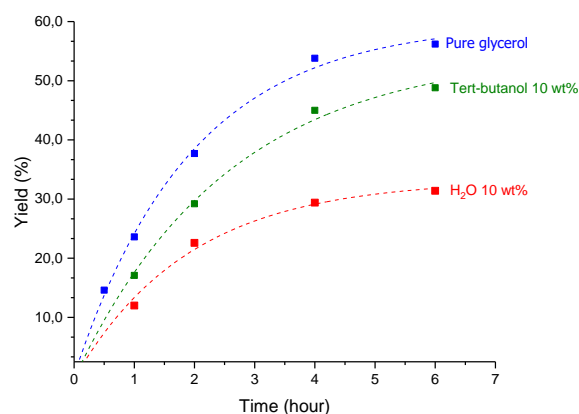


Figure 3. Kinetic study of the conversion of glycerol to solketal using pure glycerol, glycerol/*t*-but. mixture and glycerol/water mixture., Glycerol:Acetone 1:4, 10mg of cat., 80°C 800rpm

To perform this reaction, an acid catalyst is required and in the optic of green chemistry, the use of heterogeneous catalysts displaying both Brønsted and Lewis acidity is a sustainable option. Among the large range of materials exploited in the field of heterogeneous catalysis, MCM-41-base solid is one of the most known due to its bidimensional hexagonal phase, highly ordered mesoporous structure, narrow pore size distribution and high surface area^[4]. To take advantage of those properties and expand the range of possible applications, several options have been investigated among which the isomorphous substitution of a Si atom of the structure by a metal one (e.g. Al, Ti, Ga) to enhance its surface acidity.

Here the optimization of the synthesis of extra small size (diameter below 100 nm) MCM-41 particles with Ga inserted in the structure is presented. The influence of various parameter such as the particle size, the order of addition of Si and Ga precursors and different Ga loading were studied. All the materials were extensively characterized via N₂ physisorption, XRD, TEM, ICP-OES spectroscopy and ²⁹Si solid state magic angle spinning NMR and their catalytic performances were evaluated in the conversion of glycerol into solketal. The material displaying the best activity was used in further tests with glycerol/water mixture (Figure 3) with the aim of simulating the composition of raw glycerol and evaluated the influence of water on the catalytic activity.

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Optimization by a genetic algorithm of pyramidal structures made of one, two or three stacks of metal/dielectric layers for a quasi-perfect broadband absorption of UV to near-infrared radiations

Alexandre MAYER¹ and Michaël LOBET²

¹*Department of Physics, University of Namur, Namur, Belgium*

E-mail: alexandre.mayer@unamur.be

²*Centre Spatial de Liège, Angleur, Belgium*

E-mail: mlobet@seas.harvard.edu

We use a genetic algorithm to optimize 2-D periodic arrays of truncated square-based pyramids made of only one, two or three stacks of metal/dielectric layers. The objective is to achieve a quasi-perfect broadband absorption of normally incident radiations with wavelengths comprised between 420 and 1600 nm. Previous work by Lobet et al. has shown that ultra-broadband absorption can be achieved with periodic arrays of truncated square-based pyramids made of alternating metal/dielectric layers. By using 20 stacks of Au/Ge layers, they could indeed absorb 98% of incident radiations with wavelengths between 0.2 and 5.8 microns. This ultra-broadband absorption is essentially due to (i) an efficient anti-reflection property of these pyramidal structures and (ii) a well-designed coupling between the localized surface plasmons found at the metal/dielectric interfaces of each stack. Since the fabrication of structures made of 20 stacks of metal/dielectric layers is not practical, we use a genetic algorithm to establish simplified structures that consist of only 1, 2 or 3 stacks of metal/dielectric layers. We consider in particular the results one can obtain by considering (i) Ni, Ti, Al or Cr for the metal, and (ii) poly(methyl methacrylate) (PMMA) or TiO₂ for the dielectric. The parameters to determine for each metal/dielectric combination are (i) the period of the system, (ii) the lateral dimensions of each stack of metal/dielectric layers and (iii) the width of each dielectric. These parameters are subject to the constraint that the final structure must form a realistic pyramidal structure. The increased number of degrees of freedom in the structures considered is expected to compensate the reduced number of metal/dielectric layers. We use a Rigorous Coupled Waves Analysis (RCWA) method to compute the absorption spectrum of the structures considered. A parallel version of the genetic algorithm is then used to solve the optimization problem and establish optimal high-quality solutions. Our study shows that Ni/PMMA represents the best metal/dielectric combination. With an optimized structure made of only three stacks of Ni/PMMA, it is possible indeed to absorb 99.8% of the considered incident radiations. An integrated absorptance of 99.4% is achieved with three stacks of Ti/PMMA or Cr/PMMA layers.

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Synthesis of Novel Bifunctional Boron/Nitrogen Frustrated Lewis Pairs

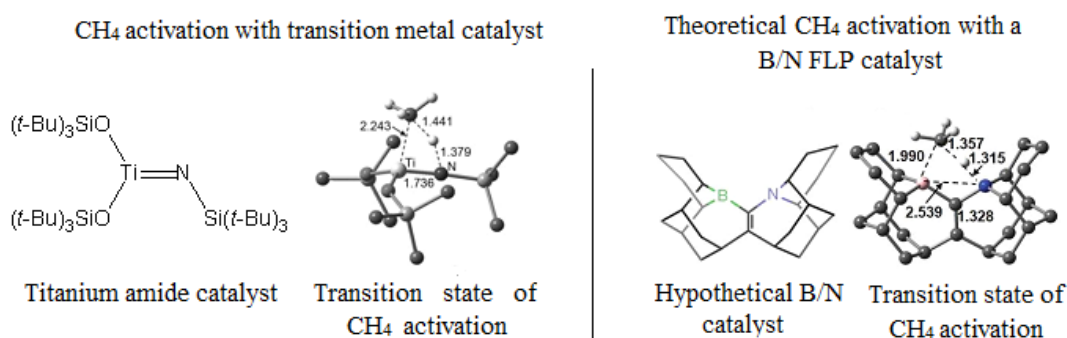
Loïc Mineur, Aurélien Chardon, Nikolay Tumanov, Guillaume Berionni*

University of Namur, Institute of Structured Matter – 61, rue de Bruxelles, Namur, Belgium

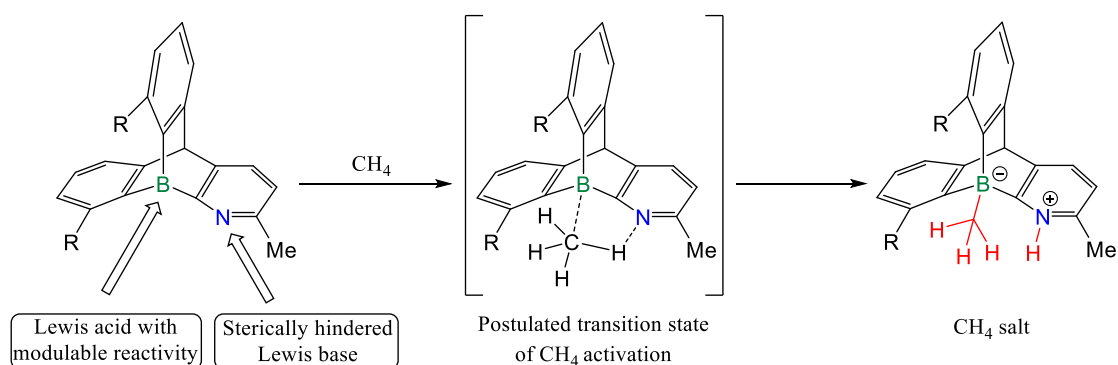
* guillaume.berionni@unamur.be (www.unamur.be/en/sci/chemistry/rco)

Methane is the second most potent anthropogenic greenhouse gas in our atmosphere.^[1] The activation of the CH bond of methane requires the use of transition metals,^[2] which are often rare, expensive and toxic. During this Master thesis, we aim to develop a metal-free catalyst for methane activation using abundant, light and inexpensive main-group elements. This catalyst contains a Lewis base and a Lewis acid connected with precise distances and orientation in order to mimic the properties of a titanium catalyst capable of activating methane (scheme 1a). Based on computational investigations^[3] (scheme 1a) we started to design a bifunctional Lewis acid/base metallomimetic catalyst^[4] based on a bora-triptycene scaffold (scheme 1b), which possess a highly reactive bridgehead pyramidal trivalent boron, a rigid structure, and good thermal stability.

a)



b)



Scheme 1: a) Transition metal catalyst (left) and hypothetical system capable of activating methane (right),

b) 9-Bora-azatriptycene synthesised during this work

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Multi-scale modelling of TCO coating deposited by reactive magnetron sputtering:

application to structured c-Si thin film solar cells

J. Müller⁽¹⁾, P. Moskovkin⁽¹⁾, A. Mayer⁽²⁾, O. Deparis⁽²⁾ and S. Lucas⁽¹⁾

(1) University of Namur (PMR-LARN-NISM), rue de Bruxelles 61, B-5000 Namur, Belgium

(2) University of Namur (PMR -NISM), rue de Bruxelles 61, B-5000 Namur, Belgium

Transparent conductive oxides (TCO) present a large range of applications such as optoelectronic devices, especially transparent front-side contact for solar cells. In this last case, aluminium doped zinc oxide (ZnO:Al or AZO) can be a good alternative to indium doped tin oxide (ITO). However, the electrical and optical properties of such coatings highly depend on the structuration of the substrate. The present study focuses on nano-scale characterizations of AZO thin film deposited on micro-scale patterns.

The first step consists of nano-scale modelling of AZO deposition by reactive magnetron sputtering [1] on mono-crystalline silicone substrates thanks to a kinetic Monte Carlo model [2]. For these simulations, metallic (Zn, Al), reactive (O) and neutral (Ar) fluxes can be defined individually, with their own angular and energy distributions. Moreover, in order to mimic large samples, the periodic-supercell method is used. Then, electrical and optical characterizations of the coating can be performed. Electrical properties

(effective electrical conductivity) are computed by the mean of a finite-element code solving the Maxwell-Faraday equation (hypothesis: near absence of varying magnetic field). Optical properties (effective optical index) are evaluated by using effective medium models (Maxwell-Garnett and/or Bruggeman). During all the process, a special attention is given to the substrate shape.

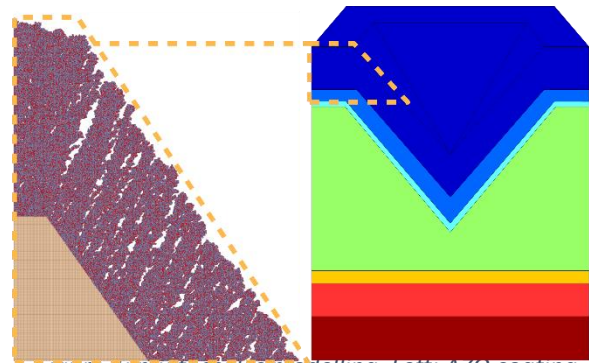


Figure 4: multi-scales modelling. Left: AZO coating on structured c-Si. Right: modelled solar cell.

The second step is based on a micro-scale modelling of a full multi-layered structured c-Si thin film solar cell. The optical characterization (optical efficiency, short circuit current density) is done by RCWA [3] allowing to predict complex optical phenomena like scattering or light trapping. The major novelty of such study is the introduction in the RCWA simulation of the effective refractive indices of AZO depending on the position on the substrate (flat or tilted section of the pattern).

Finally, a full optimization by genetic algorithm [4] is performed in order to find the layer thicknesses and the pattern size parameters providing the best short circuit current density.

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$^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ isotopic tracing of germanium diffusion

A. Nélis⁽¹⁾, I. Vickridge⁽²⁾, J.J. Ganem⁽²⁾ and G. Terwagne⁽¹⁾

(1) Université de Namur, LARN, département de physique, Namur, Belgique

(2) Université Pierre et Marie Curie, INSP, Paris, France

E-mail: adrien.nelis@unamur.be

Integration of semiconductor nanocrystals (Ge and/or Si) into optoelectronic devices has been in the center of many studies over last years, thanks to properties like quantum confinement or multiple exciton generation (MEG).

Germanium nanocrystals (Ge-nc) are formed by ion implantation into a dielectric layer (SiO_2/Si). Ge-nc formation requires a high temperature thermal treatment under controlled atmosphere (1100 °C during 1h under N_2), during which germanium diffuses towards the sample's surface and towards the interface. [1]

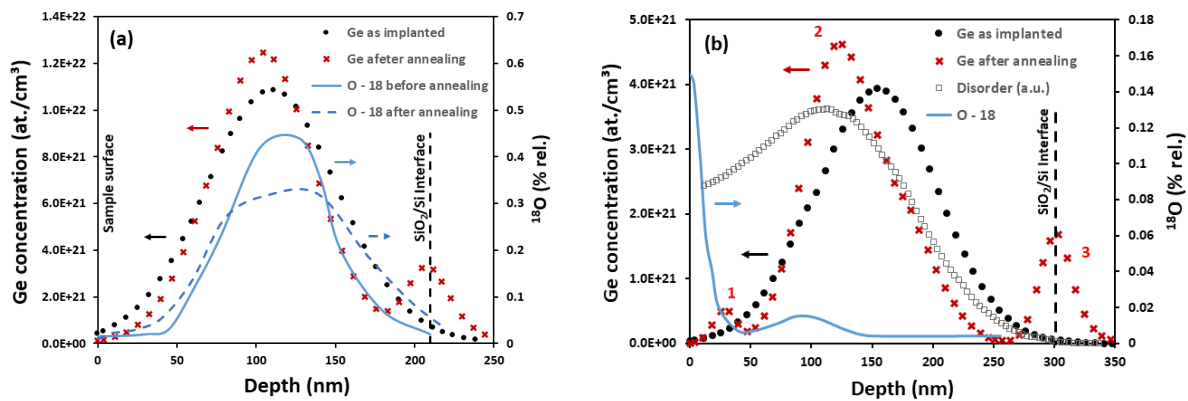


Figure 1 : RBS and NRP profiles before and after 1h annealing under (a) 100 % N_2 for ^{18}O -enriched oxide, (b) 99 % N_2 + 1 % $^{18}\text{O}_2$.

This diffusion is generally associated in literature to the presence of oxygen. [2] Germanium atoms are supposed to be linked to oxygen atoms to diffuse in the form of highly volatile GeO compounds during thermal treatments. Although oxygen contribution is widely accepted, the origin of this oxygen is still subject to debate.

This study proposes to highlight the origin of oxygen atoms involved in germanium diffusion by isotopic tracing, using $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ nuclear reaction at 151 keV.

Two different configurations have been tested : 1) annealings under contaminated atmosphere (99% N_2 + 1% $^{18}\text{O}_2$), and 2) ^{18}O -enriched oxides annealed under pure nitrogen atmosphere.

Combination of Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA) and Narrow Resonant Profiling (NRP) measurements allows us to evidence ^{74}Ge and ^{18}O depth-profiles.

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On the nature of the singlet and triplet excitations mediating thermally activated delayed fluorescence.

Y. Olivier¹, L. Muccioli², J.-C. Sancho-Garcia³, B. Yurash⁴, D. Hall⁵, A. Pershin⁶, V. Lemaury⁷, C. Adachi⁸, T.-Q. Nguyen⁹, E. Zysman-Colman¹⁰, D. Beljonne¹¹

^{1, 5, 6, 7, 11} Laboratory for Chemistry of Novel Materials, University of Mons, Mons, BELGIUM
yoann.olivier@umons.ac.be, dh82@st-andrews.ac.uk, Anton.PERSHIN@umons.ac.be,
Vincent.LEMAUR@umons.ac.be, David.BELJONNE@umons.ac.be

² Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, ITALY
luca.muccioli@unibo.it

³ Departamento de Química Física, University of Alicante, Alicante (Spain)
jc.sancho@ua.es

^{4, 9} Department of Chemistry and Biochemistry, Center for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, (United States of America)
byurash@ucsb.edu, guyen@chem.ucsb.edu

^{5, 10} University of St Andrews, St Andrews (United Kingdom)

dh82@st-andrews.ac.uk, eli.zysman-colman@st-andrews.ac.uk

⁸ Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka (Japan)
adachi@cstf.kyushu-u.ac.jp

Thermally Activated Delayed Fluorescence (TADF) process is the new paradigm for Organic Light-Emitting Diodes (OLEDs). Despite all the efforts, a complete mechanistic understanding of TADF materials has not been fully uncovered yet. Part of the complexity arises from the apparent dichotomy between the need for small energy difference between the lowest singlet and triplet excited states (ΔE_{ST}) which has to carry a significant charge transfer (CT) character; and for a significant spin-orbit coupling which according to El-Sayed rules requires the involved singlet and triplet excited states to have very different natures [1]. In this contribution, we will show:

(i) How this dichotomy can be resolved once accounting in a fully atomistic model of reference carbazole derivatives for thermal fluctuations of the molecular conformations and discrete electronic polarization effects in amorphous films [2]. Using both computational and experimental techniques [3], we demonstrate that, electronic excitations involved in the TADF process have a mixed CT-locally excited character being dynamically tuned by torsional vibrational modes. Hence, we will demonstrate that the conversion of triplet-to-singlet and light emission in TADF materials are both electronic processes that are vibrationally-assisted.

(ii) Unlike conventional TADF chromophores, how color purity is achieved together with small ΔE_{ST} and high photoluminescence quantum yield in boron-centered azatriangulene-like molecules [4]. Here, using highly correlated quantum-chemical calculations, we report this is driven by short-range reorganization of the electron density taking place upon electronic excitation of these multi-resonant structures. Based on this finding, we design a series of π -extended boron- and nitrogen-doped nanographenes as promising candidates for efficient TADF emitters with concomitantly decreased ΔE_{ST} , improved oscillator strength and core rigidity compared to previously reported structures, permitting both emission color purity and tunability across the visible spectrum.

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The high activity of aerosol-made Ga-silicate catalysts for solketal synthesis explained by a deep structural investigation

Alvise Vivian,¹ Loraine Soumoy,¹ Luca Fusaro,¹ Damien P. Debecker² and Carmela Aprile^{1,*}

¹ Unit of Nanomaterials Chemistry (CNANO), Department of Chemistry, University of Namur, 5000 Namur, Belgium, ² Institute of Condensed Matter and Nanosciences - UCLouvain., 1348 Louvain-la-Neuve, Belgium

E-mail: alvise.vivian@unamur.be

During the last decade, considerable attention has been devoted to the development of biofuels, above all biodiesel. The transesterification reaction to produce biodiesel yields as by-product an amount of glycerol around 10 wt % of the total biodiesel manufacture.^[1] A promising route to valorize glycerol is represented by its condensation with acetone to produce solketal, an added-value product with several applications.^[2] A sustainable way to perform this reaction envisages the use of heterogeneous catalysts displaying Brønsted and Lewis acidities. In particular, it has been already reported that Ga-MCM-41 nanoparticles are one of the most efficient catalysts in the conversion of glycerol into solketal.^[3] Here, the aerosol assisted sol-gel process^[4] was used to synthesize silica-based solids with Ga inserted as single-site in the structure. Three different materials bearing a Si/Ga ratio of 34, 74 and 148 were synthesized and extensively characterized via N₂ physisorption, XRD, TEM and ICP-OES.

To investigate the coordination number/geometry of the metal center inserted as single site within the silica matrix, a deep structural investigation of the materials was performed via solid state NMR of ⁷¹Ga under magic angle spinning (MAS). The challenging study of quadrupolar ⁷¹Ga allowed to observe a signal with a maximum at around 140 ppm that can be assigned to a predominant contribution of tetrahedral gallium present as single site in the silica framework (Figure 1, right).^[5] These aerosol-made mesoporous Ga-silicates showed excellent catalytic performance in the conversion of glycerol into solketal and the best catalyst displayed high turnover number and high selectivity. In order to further prove the stability of the solid under the selected reaction conditions, hot filtration tests were performed, demonstrating the absence of leaching of active sites.

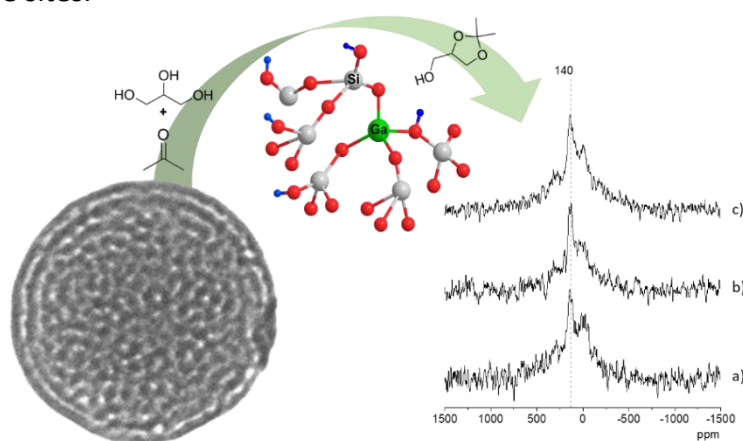


Figure 5 TEM micrograph of a Ga-silicate nanoparticle (left) and ⁷¹Ga MAS solid state NMR spectra of the three synthesized solids: Si/Ga=148(a), 74(b) and 37(c) (right)

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