



Wednesday, November 24th

Session Nanomaterials for Energy

10:50 – 11:20 Keynote

David MUNOZ-ROJAS, CNRS – LMGP, France

Abstracts

Keynote Speakers



David MUÑOZ-ROJAS

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Biography

David Muñoz-Rojas received his degree in Organic Chemistry at the Instituto Químico de Sarrià (IQS, 1999) and his PhD in Materials Science (2004) at the Instituto de Ciencia de Materiales de Barcelona. Thereafter, he worked as a postdoc at the Laboratoire de Réactivité et Chimie des Solides in Amiens, the Research Centre for Nanoscience and Nanotechnology in Barcelona and at the University of Cambridge. He is currently a CNRS researcher at Laboratoire des Matériaux et du Génie Physique in Grenoble. His research focuses on using and developing cheap and scalable chemical approaches for the fabrication of novel functional materials for electronic and optoelectronic applications. In particular, he has pioneered the development of the novel SALD technique for the deposition of active components for optoelectronic devices. He is currently developing SALD further to extend the possibilities and fields of application of this exciting technique through several ANRs (one as coordinator), regional and local projects, and a FET Open project that he coordinates. He (co)authored 78 publications, 6 book chapters, coedited a book and is (co)inventor of 6 patents.

SPATIAL ATOMIC LAYER DEPOSITION: A HIGH-THROUGHPUT, OPEN-AIR TECHNIQUE ALLOWING THE DEPOSITION OF PATTERNED FUNCTIONAL MATERIALS

Within the materials deposition techniques, Spatial Atomic Layer Deposition (SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. SALD relies on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[1] Thus, fluid dynamics play a role in SALD since precursor intermixing must be avoided in order to have surface-limited reactions leading to ALD growth, as opposed to CVD growth. Fluid dynamics in SALD mainly depend on the geometry of the reactor and its components.

While care is normally taken to prevent precursor crosstalk when using SALD, we have shown that the spatial separation principle can also be applied to perform CVD reactions (SCVD), i.e. growth not limited to the surface, yielding yet faster deposition rates while maintain the film quality and conformality typical of ALD and SALD. [2,3] We have also shown that selective deposition can be achieved by working in SCVD mode. In this new approach to area-selective deposition (ASD), the depositions are performed in static mode (i.e. no relative movement between the reactor and the substrate), and Computational Fluid Dynamics (CFD) simulations are used to control the effect of the different deposition parameters on the SCVD mode. [4]

In this presentation we will show how close-proximity SALD based on a manifold injection head working in the open air can be tuned to deposit custom patterns without the need of pre-patterning steps. This is achieved by using the system in static SCVD mode and by a proper design of the injection head using 3D printing. We will also show other new approaches to ASD developed with our SALD system and how it can be tuned to perform 3D printing of functional materials

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Keywords: thin films ; transparent conductive materials; energy materials; spatial atomic layer deposition; 3D printing; functional materials.

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Thematic Session: Nanomaterials for Energy

Keywords: Polyol Synthesis, Transition metal oxides, Electrochromism, Device

Nanopowders Based Transition Metal Oxides for Enhanced Electrochromic Properties

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Transition metal oxides such as tungsten, niobium, cerium and vanadium oxides and their derivatives are key players in the field of electrochromic materials. Electrochromism is the ability of materials and devices to change their optical properties when a voltage is applied [1, 2]. The applications of electrochromic devices, ECDs, are multifold from smart windows in cars, rear-view mirrors and protective eyewear as transmittive or reflective properties and visible or infrared domain are concerned [3]. As electrochromic applications enter a new phase of commercial exploitation, the requirement of robust electrochromic materials with high durability, different color transitions and fast-switching times becomes even more important.

Until now, various methods for the synthesis of nanostructured based transition metal oxides with various morphologies have been reported such as hydrothermal process, polyol treatment, pulsed laser irradiation, electro-deposition, and sol-gel method. Among these, the polyol process offers several advantages as compared to other chemical methods. Indeed, the polyol process is commonly considered as an energy efficient and environmentally benign process, also allowing the preparation of large quantity of ultra-fine powders.

In this study, various oxides powders were synthesized by the polyol process [4, 5]. The adjustment of the deposition technique for the preparation of films from the nanopowders using dip coating for thinner/transparent films and doctor blading for thick/opaque films, allows us to correlate the electrochromic behavior to several criteria including the film crystallinity and morphology. Unexpected electrochromic behavior will be in particular discussed for vanadium oxides in respect of the V/O stoichiometry.

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Thematic Session: Nanomaterials for Energy

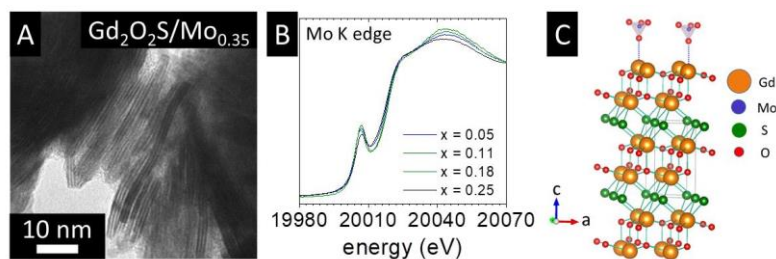
Keywords: Nanoplates, Molybdenum, Oxysulfides, XANES-EXAFS, Electrocatalysis

Molybdenum-Containing Oxysulfide Nanoplates: Characterization of their Structure and Active Sites for Electrocatalysis

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Molybdenum is found in compounds such as MoS₂ and MoO₃, studied for their electronic properties, but also as battery electrodes or as electrocatalysts.^{1,2} As mixed anion compounds, molybdenum oxysulfides of generic formula Mo_xO_yS_z are raising a recent interest due to their singular electronic properties. They are produced as thin films and amorphous powders and used in catalysis for instance.³ However, they are still scarcely described as nanomaterials, by lack of a suitable colloidal synthesis route.



Here, we designed a new synthetic route, using 2-nm thick nanoplates of gadolinium oxysulfide^{4,5} to support molybdenum active sites and produce a new family of compounds (fig. A). These were characterized in depth by X-ray absorption spectroscopy at Mo K-edge (fig. B),

Mo L-edges and S K-edge, X-ray diffraction on powder, X-ray photoelectron spectroscopy, pair-distribution function analysis and transmission electron microscopy. Based on this combination of characterizations, we propose a structural model (fig. C) with molybdate sites that are accessible to external stimuli and account for the observed catalytic activity in oxygen reduction reaction.

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Thematic Session: *Nanomaterials for Energy*

Keywords: Transparent conductive oxide recyclable organic photovoltaic (check)

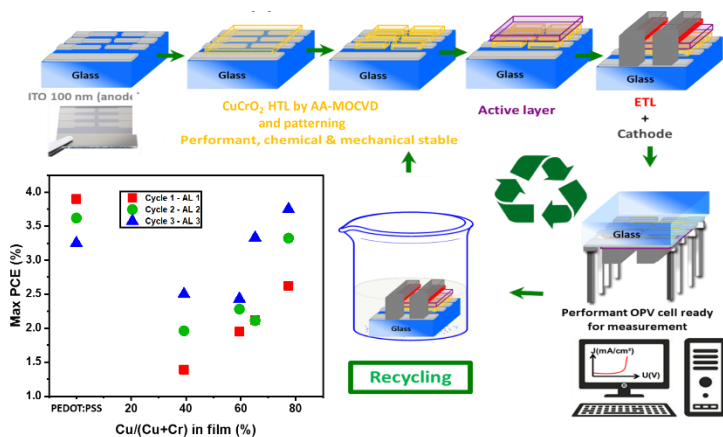
Optimized stoichiometry for CuCrO_2 thin films as Sustainable and semi-transparent Hole Transparent Layer in performant and recyclable organic solar cells

Lorenzo Bottiglieri (1), Ali Nouridine (2), Joao Resende (1,3), Carmen Jiménez (1), Jean-Luc Deschanvres (1)

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Abstract:

A promising approach to improve the performances and stability of Organic Solar Cells (OSC), is the replacement of chemical unstable and hygroscopic PEDOT:PSS¹ used as Hole Transport Layer (HTL) by p-type Transparent Conductive Oxides^{2,3}. Here, CuCrO_2 thin films with various cationic ratio, synthesized by Aerosol Assisted Chemical Vapour Deposition, were optimized to find a good compromise between transparency, conductivity and band alignment to improve the OSC performances. The resistivity,



transparency and bandgap are reduced for greater $\text{Cu}/(\text{Cu}+\text{Cr})$ in the films, with an optimal composition around 65%. The composition of the HTL was correlated to the performances of the solar cells. The strong chemical and mechanical stability of CuCrO_2 films allowed the reuse of the glass/ITO/ CuCrO_2 structure, permitting the optimization of the Active Layer (AL). The greatest Power Conversion Efficiency (PCE) was achieved for $\text{Cu}/(\text{Cu}+\text{Cr})=77\%$, as best

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trade-off between HTL's resistivity, energy gap, and morphology, resulting in a PCE of 3.75% after AL optimization. These results showed an improve in PCE of 15%, compared to the PEDOT:PSS based device. As highlighted result, the partial recyclability of the solar cell could open many promising routes in prototyping, reducing the manufacturing costs and time, enabling the development of new performant and sustainable semi-transparent organic photovoltaic devices.

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Acknowledgment:

This work was supported by the Ministère de l'Enseignement supérieur, de la Recherche et de l'Innovation, MESRI. The authors further acknowledge the Grenoble-INP, which is supported by the Centre of Excellence of Multifunctional Materials, CEMAM (n°ANR-10-LABX-44-01)

Experimental Evidence of the Role of Structural Short-Range Order on the Electrochemical Activity of Iridium Oxide

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Thematic Session: Nanomaterials for energy.

Keywords : Nanoparticles, macroporous, dihydrogen, aerosol.

We have recently developed a new type of architecture for noble metal and noble metal oxides-based catalysts.^{1,2} In these hierarchical porous structures, nanoparticles are assembled into macroporous microspheres (fig.1). These materials are made using aerosol, an easy and scalable synthesis technique.

In the case of pure iridium oxide, the state of the art catalyst for the oxygen evolution reaction (OER), we have shown that the surface state, the crystallization, crystallite size and therefore the electrochemical properties can easily be tuned by changing the post-synthesis thermal treatment.² In order to decrease the price for hydrogen production, we are aiming at developing catalysts with lower iridium content. In this work, we are taking the advantage of the versatility of this green synthesis technique to prepare a large panel of iridium-non-noble metal mixed oxides. In the case of IrMo mixed oxides, by introducing molybdenum along with iridium into the structure, we are able to delay the crystallization of the materials while the chemical transformation occurs in the same temperature range as for pure iridium. This uniqueness allows us to decouple the influence of the oxidation state from the structure of the material structure on the electrochemical activity. Using HRTEM, XRD, XPS, XAS characterizations, we rule out the influence of the oxidation state and provide an unambiguous proof of the impact of the structural ordering onto the electrochemical activity of iridium based materials towards the OER.

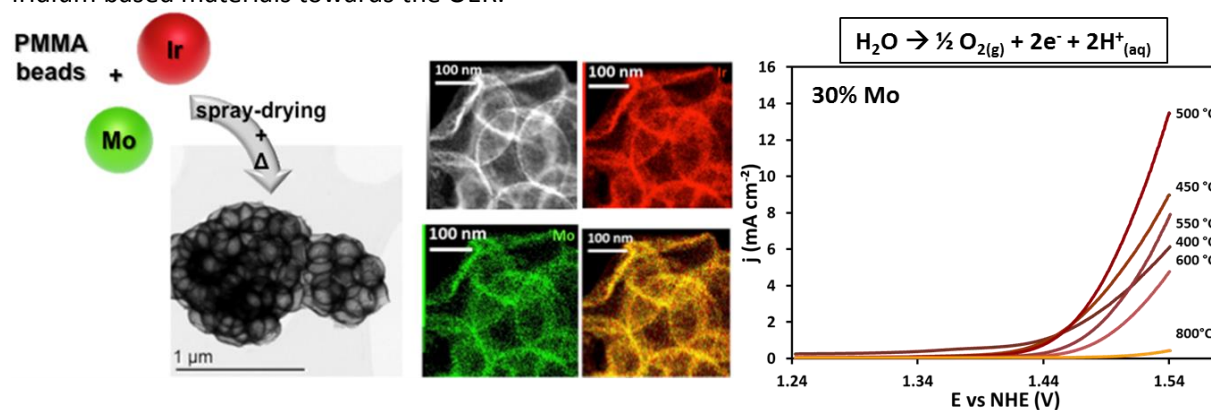


Figure 1: from left to right, SEM images of Ir_{0.7}Mo_{0.3}O₂ calcined at 550 °C, STEM-EDX analysis of Ir_{0.7}Mo_{0.3}O₂ calcined at 550 °C and histogram of activity at 1.5 V for different composition of mixed oxide refer to IrO₂

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Thematic Session: Nanomaterials for Energy

Keywords: Microsupercapacitors, 3D electrodes, Powering microsystems

3D MnO₂/Ni Network as Electrode Material for High Areal Energy Microsupercapacitors

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With the development of various technologies including electrical micro-systems and wireless technology, the question of miniaturization of energy storage devices arises. Microsupercapacitors^[1,2] (MSCs) based on pseudocapacitive electrodes seem to be the best candidates to provide a good autonomy for such small systems thanks to their unlimited life-cycle. Unfortunately, the low technological readiness level of the MSC limits the large-scale deployment of smart miniaturized systems and the energy density value still too low to reach this goal. One attractive solution to improve the areal energy density of MSCs is to significantly enhance the specific surface of the electrode material thanks to high aspect ratio micro/nanostructured scaffold. So, in the frame of this study, dynamic hydrogen bubble templating (DHBT)-assisted electrodeposition method of Ni electrodes was used to prepare highly porous films^[3]. The Ni foams provide a scaffold with 3D architecture based on dendritic nanowalls (3D Ni current collector). Electrodeposited Manganese dioxide (MnO₂) films was investigated in this study as electrode material^[4,5]. To fully fill the porosity created by 3D Ni foam and make a conformal deposit, pulsed electrodeposition of MnO₂ was carried out in 0.14M MnSO₄ electrolyte. First electrochemical measurements in liquid electrolyte (1M Na₂SO₄) between 0 and 0.8 V vs Ag/AgCl of 3D MnO₂/Ni electrode show a promising specific capacitance of 1.5 F cm⁻² at 2 mV s⁻¹. These results demonstrated a high performance of 3D MnO₂/Ni electrode due to the well fabricated porous Ni network providing higher 3D surface area than that of the flat MnO₂/Ni electrode.

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Thematic Session: Nanomaterials for Energy

Keywords: Bimetallic nanoparticles, ligand exchange, electro-catalysis, oxygen evolution reaction.

Ni-Fe oxide electro-catalysts for the Oxygen Evolution Reaction

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The development of renewable energy is one of the biggest challenges for humanity in this century as relying on conventional energy sources such as oil, coal,... leads to serious increases in environmental and health problems[1]. In this context, hydrogen is expected to play an important role as it can be used as a clean fuel[2]and can be obtained by water splitting. In brief, water splitting is a chemical process comprising two half reactions: a hydrogen evolution reaction (HER) and an oxygen evolution reaction (OER) (Scheme 1a). The OER is considered as a critical step for the production of hydrogen by water splitting since it is a kinetically sluggish multistep proton-coupled electron transfer[3]. Therefore, many efforts have been focused on the development of new and efficient catalysts for OER[4]. As one of the most promising catalysts for OER, Ni-Fe based nanomaterials have been the subject of intense investigation in the past decade due to their chemical abundance and well adapted oxidation potential[5]. Herein, we present an organometallic approach to synthesize NiFe-based nanocatalysts for OER. First, NiFe core-shell nanoparticles (NPs) were synthesized in an organic solvent using a hydrophobic stabilizing ligand to better control their size, morphology and structure then the NiFe NPs were transferred from organic to aqueous phase through a ligand exchange process with amino phosphonic acid to allow these NPs to act as OER catalysts. The final NiFeOx NPs were characterized by TEM, FT-IR, XPS... and their catalytic activity for OER in KOH 1M has been studied (Scheme 1b).

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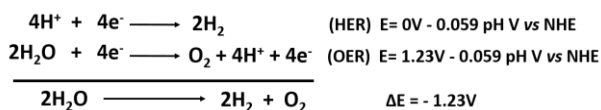
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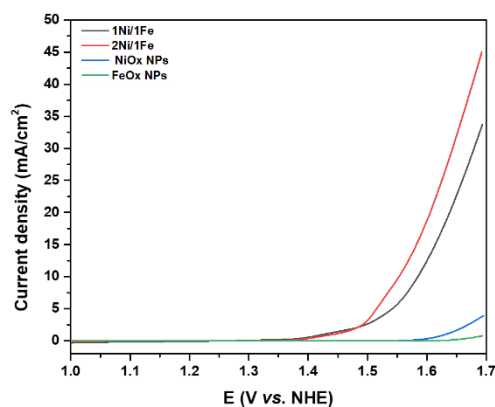
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a)



b)



Scheme 1

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Thursday, November 25th

Session Nanomaterials for Energy

10:20 – 10:50 Keynote

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Abstracts

Keynote Speakers



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Biography

Evelyne Martin is Research Director at the ICube laboratory in Strasbourg. Her interest lies in the modeling of phenomena related to nanotechnologies by atomic-scale simulations. She is currently studying heat conduction at the nanoscale for applications in the thermal management of devices and for thermoelectricity. She is the main developer of the approach-to-equilibrium molecular dynamics (AEMD) methodology aimed at studying thermal transport on atomic trajectories substantially shorter than in earlier molecular dynamics methods. This approach was originally applied to silicon nanostructures described by interatomic potentials. AEMD is currently used to investigate heat propagation in amorphous materials and through molecular layers by resorting to first-principles molecular dynamics (DFT-based) simulations. Evelyne Martin has authored more than 50 articles in peer-reviewed international journals. She is currently coordinator of two ANR projects in the field of thermal properties.

ATOMISTIC MODELING OF HEAT PROPAGATION IN NANOMATERIALS

In the present talk, I will report on the use of first-principles molecular dynamics (FPMD) to model heat propagation in nanomaterials. FPMD enables the calculation of atomic trajectories accounting for the electronic structure, obtained from density-functional theory (DFT). Therefore, FPMD can handle bonding situations quantitatively inaccessible to interatomic potentials, such as organic/inorganic interfaces or network-forming disordered materials. Despite the computational cost required by DFT, FPMD has been fruitfully applied to study thermal properties by resorting to the approach-to-equilibrium molecular dynamics (AEMD) strategy [1]. AEMD aims at studying thermal transport by exploiting affordable time trajectories corresponding to transient regimes. After a presentation of the methodology, I will focus on two applications. The first one is an interfacial molecular layer in between heat reservoirs. The thermal resistance of the layer is obtained under the verified assumption that the heat transport is driven by the transfer at the interface. The thermal resistance has two contributions, the first one corresponding to the bond between the molecules and the reservoirs, and the second attributed to heat conduction in the diffusive regime along the molecular chains [2]. Then, I will consider amorphous materials and the search for propagative modes in these systems. To this purpose, the thermal conductivity of two glasses, GeTe_4 [3] and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [4] (a standard material for non-volatile phase-change memories), has been determined as a function of the length in the direction of the heat transport. Our results are substantiated by an extrapolation at large sizes in quantitative agreement with experiments. The length dependence is a compelling evidence of the existence of propagative modes, expected to extend up to 30-50 nm, well above extended range order. Our results have profound implications on the reduction of thermal conductivity at the nanoscale and the thermal management of relevant devices.

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Keywords: thermal properties; first-principles molecular dynamics; transients; molecular layer; disordered materials.

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Thematic Session: Nanomaterials for Energy

Keywords: electron-phonon interaction, hot carrier relaxation, density functional theory

Ultrafast dynamics of hot carriers in bulk semiconductors and in accumulation layer: energy relaxation and screening effects.

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Electron-phonon coupling determines the charge transport properties in pure materials as well as the relaxation dynamics of photoexcited carriers. The rapid development of the computational methods based on density functional theory, on the one hand, and of the time- energy- and momentum- resolved spectroscopy, on the other hand, allows today an unprecedentedly detailed insight into the role of the electron-phonon coupling [1]. Recently, a computational method, based on density functional theory and on interpolation of the electron-phonon matrix elements in Wannier space allowed us to successfully interpret the dynamics of hot electron relaxation in bulk GaAs, in excellent agreement with time- and angle- resolved photoemission experiments [2].

In this work, we will present our recent results, both experimental and theoretical, on hot electron relaxation in silicon. Numerous additional experiments were performed with respect to the previous work of [3], and a new interpretation of the measured relaxation times is provided, based on our *ab initio* calculations and on the concept of hot electron ensembles proposed recently in [4].

Moreover, we will present our recent results, both experimental and theoretical, on the hot electron relaxation in InSe. InSe is a quasi-2D material which was shown recently to have potential interest for optoelectronics. In this work, we will discuss our new results on the relaxation dynamics and screening of the electron-phonon interaction in doped InSe [5].

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Thematic Session: Nanomaterials for Energy

Keywords: near-field thermal radiation, thermophotovoltaics.

Low-energy bandgap thermophotovoltaic cells for harnessing near-field thermal photons

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To date, the champion thermophotovoltaic (TPV) cells have an efficiency in the range 24-29% [1-2]. They are all made of InGaAs with an energy bandgap of 0.6 or 0.74 eV and convert thermal radiation from emitters at temperatures larger than 1000 °C. For medium-grade heat sources (<700 °C), cells with a lower energy bandgap (e.g. 0.36 eV with InAs) are required in order to efficiently collect the infrared photons. Since it is currently challenging to build large temperature differences between bodies separated by sub-micrometric distances, the requirement of a low-energy bandgap cell is stringent for near-field thermophotovoltaic converters.

This communication reports on the specific design [3], fabrication and characterization [4] of micron-sized indium antimonide TPV cells (energy bandgap of 0.23 eV at 77 K) for proving that photovoltaic conversion of near-field thermal photons can be efficient [5]. The fabricated cells exhibit excellent performances in the dark, under far-field and near-field illuminations, with record efficiency (~15-20%) and electrical power densities (0.75 W cm⁻²). In the near field, the key parameters of the cell are its illuminated area, the doping of the p-layer and the thickness of the substrate. Experimental results suggest that 2D simulations of radiation transfer and electrical transport would probably help improving further the performances of the thermophotovoltaic cells for harnessing near-field thermal photons.

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Acknowledgments: Financial support by the French National Research Agency (ANR) under grant No. ANR-16-CE05-0013 and partial funding by the French "Investment for the Future" program (EquipEx EXTRA ANR-11-EQPX-0016 and IDEXLYON ANR-16-IDEX-0005) and by the Occitanie region are acknowledged.

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Thematic Session: (Nanomaterials for Energy)

Keywords: (Molecular Dynamic simulation, Nanoinclusion, Disorder, thermal conductivity, diffusive transport)

Influence of silicon nanoinclusions shape and interconnection on thermal conductivity in an amorphous Si matrix

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Energy harvesting devices require materials with fine tailored properties, for instance thermoelectric generation involves materials with a good electrical conductivity and a low thermal conductivity. Amorphous materials have the lowest thermal conductivity however their electrical conductivity is very poor. The conduction of electrons can be improved by including crystalline nanoparticles embedded in the amorphous matrix. However, the nanoparticles will also impact the thermal conductivity. This is the object of this study. For this an amorphous matrix with an array of nanoparticles with different shapes has been studied, going from a spherical nanoparticle up to a percolating network of nanoparticles forming a nanowire mesh. If the impact of spherical nanoparticle on amorphous crystalline nanocomposite is already well documented [1] the influence of their shape and eventual interconnection is less studied. In the continuity of the work of Tlili et al. [1], the thermal conductivity is divided in the propagative part and the diffusive part thanks to a wave packet analysis. This showed that eventhough, the mean free path of phonons is greatly impacted by the nanoparticles shape and interconnection, the diffusive part of the thermal conductivity remains unaffected, the diffusivity being reduced only when the nanoparticles are replaces by pores. These results are discussed in terms of the vibrational properties of the nanoparticles and physical insights of the phenomena will be presented.

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[1]Tlili, Ameni, et al. "Enhancement and anticipation of the Ioffe-Regel crossover in amorphous/nanocrystalline composites." *Nanoscale* 11.44 (2019): 21502-21512.

Acknowledgment:

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Thematic Session: Nanomaterials for Energy

Keywords: radiative sky cooling, solar cells, simulation, nanophotonics, thermal radiation

Radiative sky cooling of solar cells: fundamental modelling and cooling potential of single-junction devices

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Abstract (**no longer than 250 words** (or 18 lines max. incl. figure), Calibri 11, single line spacing, black) Photovoltaic (PV) solar cells are designed to efficiently absorb solar photons but convert only a limited proportion of them into electricity. The remaining energy is converted into heat, which in turn, heats solar modules up to 50-60 °C under real operating conditions [1], which is detrimental to their power conversion efficiency and lifetime. In recent years, there has been a growing interest in the so-called radiative sky cooling (RSC) strategy. This approach consists in optimizing the thermal radiation of cells or modules - with the help of photonic structures - by taking advantage of the atmospheric transparency in the 8-13 μm range [2, 3]. Although some preliminary studies on the subject predict cooling of more than 13°C on silicon wafers [4], they remain insufficient to fully assess the potential of this technique for various technologies.

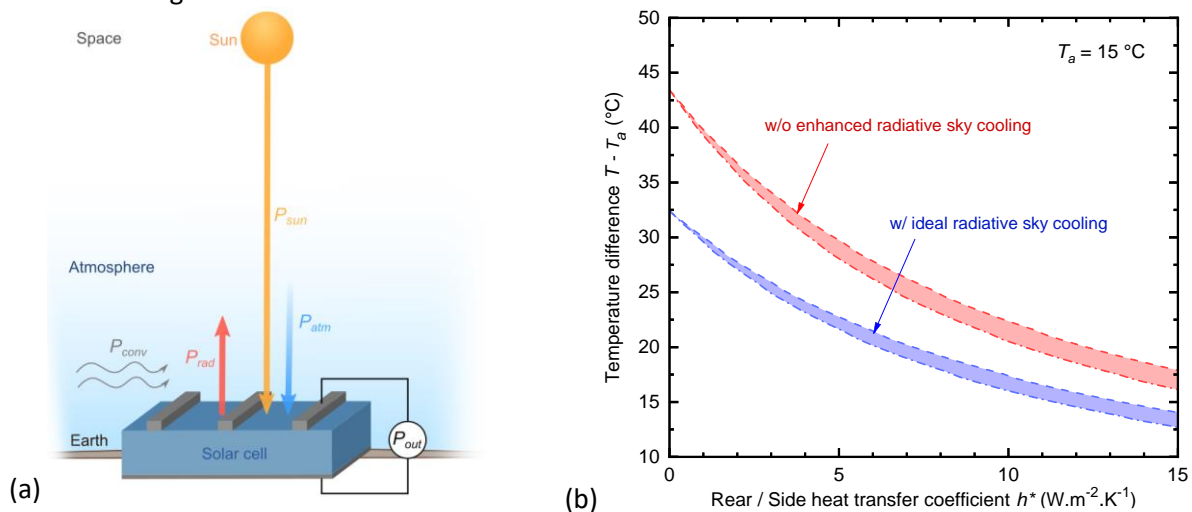


Fig 1 : (a) Main heat sinks and heat sources of the model and (b) Temperature of a simulated silicon cell with (blue) / without (red) optimization of its RSC, as a function of the rear-side heat exchange coefficient h^* (ambient temperature $T_a=15$ °C, 1000 W/m² solar irradiance, no wind)

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In this work, we study the RSC of single-junction PV cells from a general perspective. Based on a thermodynamic approach, a physical and numerical model has been developed to quantify the influence of the main environmental parameters (solar irradiance, ambient temperature, wind speed, cloud cover) and the physical properties of the cell on its temperature and electrical performance. The latter couples a Shockley-Queisser model with a heat balance (Fig. 1a). Our simulations first allowed us to determine the ideal optical properties for RSC of solar cells, and then to estimate the benefit of RSC under various scenarios. Among other things, our results show that the achievable cooling is important even for devices with already good thermal management (Fig. 1b).

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Acknowledgment:

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Thematic Session: Nanomaterials for Energy

Keywords: Nanowires, III-V semiconductors, MBE, Photovoltaics

MBE-grown GaAs/GaN_P nanowire arrays on Silicon for tandem solar cells

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The direct growth of high structural quality III-V nanowires (NWs) on mismatched substrates such as Si, represents an elegant way to fabricate a cost-effective III-V on Si tandem solar cell. In principle, III-V NW based top cells with an optimal bandgap of 1.7 eV can be directly grown on a Si bottom cell and efficiencies exceeding 33% at AM1.5G have been predicted for such architecture [1]. The success of this strategy relies on the precise control of the NWs growth on Si(111), their crystal structure, doping, junction formation, passivation and opportune contacts. At present, state-of-the-art NW solar cells are based on gold catalysed axial GaAs homo-junctions grown on GaAs(111)B by MOCVD with an efficiency of 15.3% [2]. Ga-catalyzed GaAs NWs solar cells directly grown on Si(111) stay behind, with efficiencies of 7.58% for axial homo-junction [3] and 4.1% for radial homo-junctions [4].

In this work, self-catalyzed core-shell GaAs NWs are grown by MBE on a patterned silicon substrate into radial homo- or hetero-junction designs. The optimization of key processing steps ensures a perfect selective growth and a high yield of vertical NWs (>95%, Figures a and b). Following from optoelectrical characterization of encapsulated and contacted NWs, the heterojunction devices demonstrated an energy conversion efficiency of 3.7% under AM1.5G illumination, along with a V_{OC} of 0.65 V, higher than the reported state-of-the-art GaAs NW core-shell junctions [4]. To assess the intrinsic quality of the NWs, the quasi-Fermi level splitting of as-grown NW arrays was determined using hyperspectral imaging. Under a 1 sun illumination, we find values up to 0.92 eV, representing the maximum achievable V_{OC} . It confirms the NWs high crystalline quality and indicates a considerable scope for improvement in device processing.

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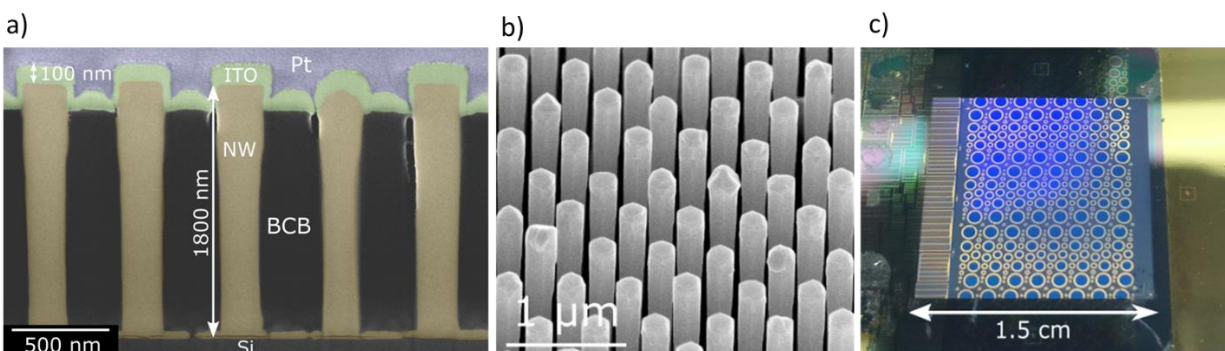


Figure: **a)** Cross-section of a fully contacted core-shell solar cell, viewed by SEM with a 45° tilt (colorized). The Pt layer present at the top is not part of the device but was locally deposited for protection during the FIB cross-section. **b)** As-grown GaAs nanowire array viewed by SEM with a 45° tilt. **c)** Image of a fully processed 1.5 × 1.5 cm NW array, in the center of a 2'' Si wafer. Each circle is an ITO and Ti/Au contact which delimits an individual diode.

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Acknowledgment:

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Thursday, November 25th

Session Nanomaterials for Energy

14:00 – 15:10 Keynote

Abstracts

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Thematic Session: Nanomaterials for energy

Keywords: photocatalytic hydrogen production, HER, water splitting, Au/TiO₂ nanostructures, plasmonic effects, Schottky barrier

On the UV-visible light synergetic mechanisms in hybrid Au/TiO₂ nanostructures achieving photo-reduction of water

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This work elucidates the synergetic effects of UV and visible light irradiation on the photocatalytic activity of nanostructures composed of TiO₂ films and Au nanoparticles. New insights in the processes that drive water decomposition were obtained by varying the position of the NPs on top and at different depths inside the semiconductor. A full structural, chemical, optical, photocatalytic and photoelectrochemical characterization supported by Electric Field Simulation was performed. Systems with Au NPs embedded revealed a 100 % enhancement on the Hydrogen Evolution Reaction (HER) under UV+Visible light compared to the net production obtained only under UV or vis light. This emphasizes that the water-splitting reaction occurs on the TiO₂ surface rather than on the metal. Importantly, almost no hydrogen was produced under visible light exposure, leading to the conclusion that plasmon generated hot electron-holes play a marginal role in the HER. Moreover, the plasmonic NPs create an intense electric field in the semiconductor vicinity (visible light contribution) that promotes the generation of the photo-excited charges in TiO₂ (UV light contribution); this mechanism couples with the Schottky barrier formed between Au/TiO₂ that serves as an effective electron trap where charges are unable to flow back. This process prevents recombination and extends charge lifetime. Furthermore, this study highlights the positive impact of the semiconductor crystallinity surrounding the metal particles and the importance of a surface free of oxygen vacancies, whose presence can inhibit the water decomposition.

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Thematic Session: Nanomaterial for Energy

Keywords: nanocrystal photocatalyst, photo-degradation, thermal condition, charge compensation

Nb/Ta, N co-doped TiO₂ nanoparticles for broad spectrum solar light activation photocatalysis

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TiO₂ nanocrystal photocatalyst co-doped with Nb and N (Nb,N:TiO₂) were synthesized via a sol-gel method followed by a post thermal nitridation in ammonia atmosphere. The structure and composition of prepared materials were characterized by combination of X-ray diffraction (XRD), scanning/transmission electron microscopy (SEM/TEM), UV-vis diffuse reflectance spectroscopy, and X-ray photoelectron (XPS). Further measurement conducted by Electron paramagnetic resonance (EPR) and reversed double-beam photoacoustic spectroscopy (RDB-PAS) revealed the electronic band structure of synthesized materials. The photocatalytic performance of Nb,N:TiO₂ was evaluated by conducting the photo-degradation of methylene blue (MB) solution under the irradiation of UV light or visible light and compared with TiO₂ and N doped TiO₂. Specific thermal condition of nitridation was found to significantly differentiate the photocatalytic activity of Nb,N:TiO₂. The result shows that proper thermal condition for N incorporation can elevate the level of charge compensation between Nb⁵⁺ and N³⁻, leading to negligible formation of bulk defects and therefore strongly enhance the photocatalytic activity. However, over-intensive thermal condition of nitridation caused the generation of Ti³⁺ and oxygen vacancy in the bulk acting as charge recombination center, resulting in the significant deterioration of photocatalytic performance. This study has emphasized the importance of understanding the complexity of the charge compensation scheme in the co-doped system, and that various defects can be introduced depending on the synthesis conditions. The photocatalytic performances in the UV and visible solar region then depend not only on the amount of cation and anion introduced, but also from the crystallographic nature of these introduced dopant in the lattice.

Thematic Session: Nanomaterials for Energy

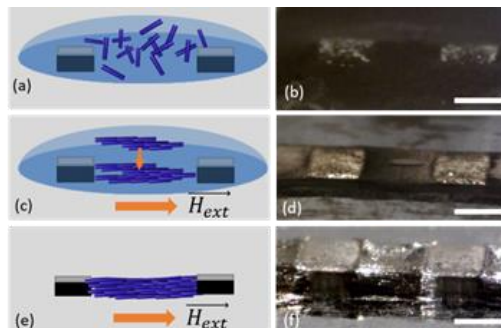
Keywords: Permanent magnet, magnetophoresis, nanorod, MEMS, energy harvester

Fabrication of nanostructured permanent magnet by magnetophoresis for MEMS applications

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Permanent magnets (PM) play a key role for different microelectronic devices as optical isolator, energy harvesters or for Micro-Electro Mechanical Systems (MEMS) actuators. Among the different approaches to realize a hard magnetic layer, the sputtering method¹ offers high performances, but only on thin film ($t < 50 \mu\text{m}$) while thicker films are obtained via electrodeposition² or embedded magnetic powder³ but with limited performances. In order to obtain a process leading to a PM at a submillimeter scale which can be integrated into MEMS fabrication, we developed a new bottom-up process combining capillary forces and magnetophoresis. Co nanorods (NRs) are synthesized via a liquid phase process. Colloidal NRs suspension is deposited on a Si substrate patterned with two Ni blocks facing each other. A dense and parallel assembly of NRs is obtained between the Ni blocks after alignment under a magnetic field and solvent evaporation (Figure). This material exhibits PM properties with in plane magnetization, a remanent induction of 0.3 T and a coercivity of 200 kA/m. The stray field is propagated on a long-range thanks to the energy product (14 kJ/m^3) and large thickness ($150 \mu\text{m}$) of the PM. These properties allow the actuation of a MEMS cantilever via the Lorentz force. As a perspective, the development of out of plane PM is under investigation for energy harvester applications.



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Thematic Session: Nanomaterials for energy

Keywords: ferroelastic domains, GeTe, in situ characterization

Growth, structure and dynamics of ferroelastic domains in GeTe thin films on Si(111)

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Semiconducting group IV–VI chalcogenides, particularly PbTe, SnTe, and GeTe, are well-known thermoelectrics for mid-temperature range applications (500–800 K). An effective strategy for boosting thermoelectric performance involves minimizing electron scattering while maximizing heat-carrying phonon scattering on many length scales. Recently GeTe-based materials have made significant improvements ($zT \approx 1.8$ [1]). In particular, a significant reduction of the thermal conductivity can be obtained through multiscale architecturing. In that respect GeTe is known to undergo a phase transition from cubic to rhombohedral crystal structure and it has been proposed to engineer ferroelastic domain walls to improve the thermoelectric properties [2] by lowering the thermal conductivity.

Epitaxial GeTe thin films are grown on Si(111) by molecular beam epitaxy (MBE) in ultra-high vacuum. Despite a significant lattice mismatch of 8.5% between Si(111) and GeTe(111), the intermediate deposition of one atomic layer of Sb and the formation of the $\sqrt{3} \times \sqrt{3}$ -Si(111)-Sb surface reconstruction favor a single crystalline growth [3]. Transmission Electron Microscopy (TEM) and 3D reciprocal space maps obtained by X-ray diffraction show that the GeTe films are made of one major ferroelectric domain and additional secondary needle shape ferroelastic domains (70° domain wall). By *in situ* low energy electron microscopy (LEEM) we show that these ferroelastic domains are unstable under thermal annealing and disappear at 500-550 K by a progressive size shrinking and reappear by cooling at 420-450 K. This study contributes to a better understanding of the structure, morphology and dynamics of ferroelastic domains in GeTe thin films on Si(111).

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Acknowledgment: This work has been supported by the ANR grant HOLOLEEM (ANR-15-CE09-0012)