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2018

Highlights

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Summary

Edito

You have in your hands the third edition of the “CEMES Highlights”. This year 2018 has been very exciting for the CEMES in particular with the official opening in July at the French embassy in Tokyo of a joint laboratory between CEMES-CNRS and Hitachi High Technologies (HHT). The HC-IUMi lab, namely the Hitachi-CNRS Infrastructure for Ultrafast Microscopy, aims at developing a coherent time-resolved electron microscope by combining the recent developments at CEMES of high brightness pulsed electron sources triggered by a femtosecond laser carried out in CEMES and the HHT expertise in advanced electron microscopes. The HC-IUMi lab will be located at the CEMES campus where a new HHT microscope will be transferred from Japan in March next year.

2018 was also a successful year for two European projects: “ORQUID” (ERA-NET QuantTERA) that will explore the possibility of using single organic molecules as the interface between three quanta, i.e. photons, electrons, phonons, for new hybrid technologies of quantum devices and "ESTEEM3" (Integrated Infrastructure H2020) that is the continuation of the ESTEEM (FP6) and ESTEEM2 (FP7) projects with an enlarged European consortium and whose aim is to provide access for the academic and industrial research community in materials science to the most powerful TEM techniques available at the nanoscale.

Several CEMES members have been distinguished for their work this year including Marc Legros who received the CNRS Silver Medal, André Gourdon awarded with a “Stars of Europe” from the French Ministry for Research and Education for the European project PAMS that he leaded, Christian Joachim, the Sciences prize of the Academy of Occitania, Andrej Jancarik, the Alfred Bader (Sigma-Aldrich) prize for his PhD, and Patrick Calupitan the C’Nano thesis prize under the category “Interdisciplinary research” for his PhD.

The 2018 issue of the CEMES Highlights magazine presents 10 short articles dedicated to the particularly important published scientific advances made this year in our laboratory. The list is far from being exhaustive, and a much more complete overview of our publications can now be found in the Open Access HAL collection of CEMES.

An overview of our activities can be found on our website www.cemes.fr, which details the research work of each of the 7 research groups of the CEMES laboratory.

This booklet also highlights a specific activity in CEMES and this year it makes a focus on the advanced facilities in Optical Spectroscopy that the laboratory has been recently developing and is offering to the wider scientific and industrial communities.

We wish you an interesting reading of this 2018 issue of the CEMES Highlights

Etienne Snoeck, Alain Couret
CEMES director and deputy director

Édito

Vous avez entre les mains la troisième édition des "Faits Marquants du CEMES". Cette année 2018 a été très enthousiasmante pour le laboratoire, notamment avec la création officielle en juillet à l'ambassade de France à Tokyo d'un laboratoire commun entre le CEMES-CNRS et Hitachi High Technologies (HHT).
Le laboratoire HC-IUMi, pour "Hitachi-CNRS Infrastructure for Ultrafast Microscopy", vise à développer un microscope électronique cohérent résolu en temps, combinant les récents développements menés au CEMES de sources d'électrons pulsées de haute brillance, assistées par un laser femtoseconde et la technologie HHT dans le développement de microscopes électroniques avancés. Le laboratoire HC-IUMi sera situé sur le campus du CEMES où un nouveau microscope HHT sera transféré du Japon en mars prochain.

2018 a également été une année fructueuse pour deux projets européens: "ORQUID" (ERA-NET QuantTERA) qui explorera la possibilité d'utiliser des molécules organiques uniques comme interface entre trois quanta, i.e. les photons, les électrons, les phonons, pour le développement de nouvelles technologies hybrides de dispositifs quantiques et "ESTEEM3" (Integrated Infrastructure H2020), qui est le prolongement des projets ESTEEM (FP6) et ESTEEM2 (FP7) avec un consortium européen élargi et qui offre l'accès à des chercheurs universitaires et industriels en science des matériaux aux techniques avancées de microscopie électronique à l'échelle nanométrique.

Cette année, plusieurs membres du CEMES ont été salués pour leur travail. Marc Legros a reçu la médaille d'argent du CNRS, André Gourdon récompensé par le prix "Stars of Europe" du ministère français de la Recherche et de l'Education pour le projet européen PAMS qu'il a coordonné, Christian Joachim, a reçu le prix Sciences de l'Académie d'Occitanie, Andrej Jancarik, le prix Alfred Bader (Sigma-Aldrich) pour son doctorat, et Patrick Calupitan le prix de thèse C'Nano dans la catégorie "Recherche interdisciplinaire" pour son travail de thèse.

Ce recueil des faits marquants 2018 du CEMES présente 10 courts articles spécialement écrits pour décrire les avancées scientifiques particulièrement importantes publiées cette année par notre laboratoire. La liste est loin d'être exhaustive et un aperçu beaucoup plus complet de nos publications figure désormais dans la collection Open Access HAL du CEMES que nous avons finalisée cette année.

Un aperçu beaucoup plus complet de nos activités est disponible sur notre site www.cemes.fr, qui détaille les travaux de recherche du laboratoire.

Nous souhaitons profiter de la publication de cette brochure pour présenter les différents équipements et développements instrumentaux menés dans les différents services techniques du laboratoire. Cette année l'accent est mis sur les équipements du service de Spectroscopie Optique récemment développés au CEMES et ouverts à l'ensemble des communautés scientifiques et industrielles.

Nous vous souhaitons une bonne lecture de cette brochure 2018 des " Faits Marquants du CEMES "

Etienne Snoeck, Alain Couret
Directeur et directeur adjoint du CEMES

Copper approaches by carbon nanotube fibers

The role of iodine and chlorosulfonic acid

Charged iodide in chains behind the highly efficient iodine doping in carbon nanotubes

Ahmed Zubair, Damien Tristant, Chunyang Nie, Dmitri E. Tsentalovich, Robert J. Headrick, Matteo Pasquali, Junichiro Kono, Vincent Meunier, Emmanuel Flahaut, Marc Monthioux, Iann C. Gerber, and Pascal Puech

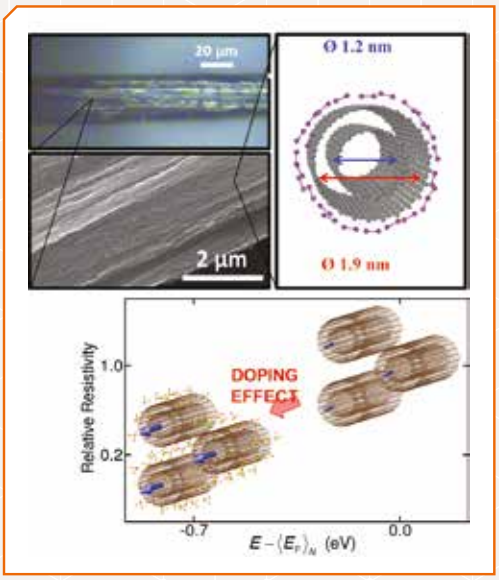
Phys. Rev. Materials 1, 064002, 2017
https://doi.org/10.1103/PhysRevMaterials.1.064002

Enlightening the ultrahigh electrical conductivities of doped double-wall carbon nanotube fibers by Raman spectroscopy and first-principles calculations

Damien Tristant, Ahmed Zubair, Pascal Puech, Frédéric Neumayer, Sébastien Moyano, Robert J. Headrick, Dmitri E. Tsentalovich, Colin C. Young, Iann C. Gerber, Matteo Pasquali, Junichiro Kono, and Jean Leotin

Nanoscale 8, 19668-19676, 2016
DOI:10.1039/C6NR04647A

When double-wall carbon nanotubes are combined with iodine and chlorosulfonic acid, the charge transfer increases the conductivity by a factor of 7. The doping species move the Fermi level up to 1.1eV while not changing the average electronic mean free path at 30 nm. Works combining both optical and transport experiments, and simulations reveal the underlying mechanism.



Fiber of doped double-wall carbon nanotubes

Conductance increase proportionally to the activation of electronic channels through doping (Fermi level shift) in double wall carbon nanotube fibers

Two strategies are possible to obtain high electrical conductivity values in carbon nanotube (CNT) fibers: (1) increasing the electronic mean free path and (2) increasing the number of electronic conduction channels in each NTC by moving the Fermi level through charge transfer.

Chlorosulfonic acid (CSA) is a true solvent of CNT. If, during CNT fiber synthesis, a part of CSA remains in the material, a charge transfer thus occurs and leads to an up-shift of the Fermi level of 0.7 eV. The consequence is an increase of the conductivity by a factor of 5 compared to a system composed of pure CNT only. Similar effects can be obtained in pure CNT fiber impregnate with iodine

At high currents, the CNT fibers are heated by Joule effect and the chemical species (iodine or CSA) evaporate. The pure (dedoped) NTC fibers are then obtained allowing the evaluation of the conductivity gain.

The Raman signals from both the inner and outer tubes of the double-wall CNT allow measuring the charge transfer and, in the case of high doping, to convert it into the Fermi level up-shift. Moreover, it was possible to go further in the analysis in terms of average free path: a value of about 30 nm was obtained independent of the Fermi level position.

Quantum calculations were then carried out to systems typically composed of 500 atoms to explain through iodine chains and charged species how such high doping level is possible.

These works involving synthesis, optical and electrical characterizations, and numerical simulation were carried out within the framework of three PhD projects and have combined the specific fields of expertise of three French laboratories in Toulouse: CEMES, LPCNO and CIRIMAT and two groups in United States: Rensselaer and Rice Universities.

Contact

Dr Pascal Puech ✉ Pascal.Puech@cemes.fr

Controlling the charge of gold nano-islands by NC-AFM

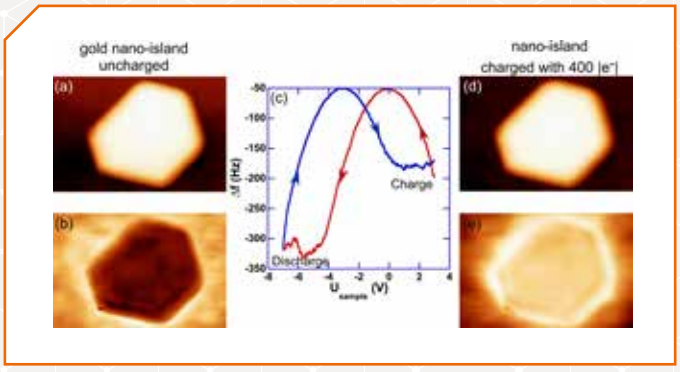
On the road towards voltage nano sources...

Controlling the electric charge of gold nanoplatelets on an insulator by field emission nc-AFM

Bulent BARIS, Mohanad ALCHAAR, Janak PRASAD, Sébastien GAUTHIER, Erik DUJARDIN, and David MARTROU

Applied Physics Letters, 112, 113101 (2018)
https://doi.org/10.1063/1.5020350

Gold nano-islands deposited on an insulating substrate (SiO_2) have been electrically charged using a non contact atomic force microscope (NC-AFM). Charge injection is performed by field emission from the tip to the nano-island or reversely. The simulation of this charging mechanism shows that the injected charge is controllable at the single electron level.



Topography and Kelvin potential image of an Au nano-island on SiO2 before (a,b) and after (d,e) charging.
(c) Δf(V) curves measured on a nano-island showing the charging effect.
The forward blue curve is recorded before the backward red one

Flat metallic islands on an insulating substrate can be used as electron reservoirs to contact a molecule or a graphene nanoribbon in a planar geometry for molecular electronics applications. The challenge is then to control and to stabilize the charge on a metallic nanocrystal for a time long enough to perform in-plane operations. This challenge was taken up using the tip of a nc-AFM microscope to control the charging of 2D Au nano-islands synthesized ex-situ and deposited on a SiO_2 insulating substrate. We image the platelets in the nc-AFM mode and characterize their charge state by Kelvin Probe Force Microscopy (KPFM) (see the figure). Our results demonstrate that the charge of the metallic island can be controlled by electron field emission to or from the tip of a nc-AFM by monitoring Δf(V) spectroscopy curves, as shown in figure (c). The procedure works for both polarities, electrons being emitted by the tip to the nano-island or reversely. As shown by an analytical model and complementary numerical simulations, the rise of the island's potential upon charging leads to a constant charging current and tip-island electric field. Our measurements suggest that this method can be used to set the island potential within a 10 mV precision, corresponding to the transfer of a single electron. This degree of control is achieved thanks to the increased stability and sensitivity provided by the UHV environment. The procedure is robust and opens the way to original experiments, such as establishing a bias at the extremities of a molecule connected between two islands or exploring locally the charge leaking mechanisms across an insulating layer.

Contact

Dr David Martrou ✉ dmartrou@cemes.fr

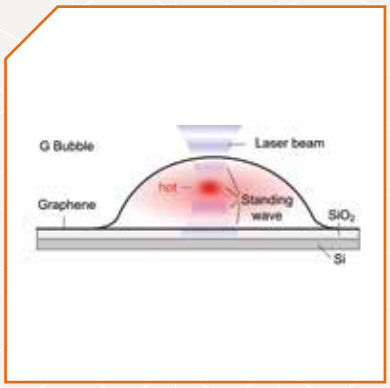
Probing heat flow in large graphene bubbles

Raman spectral band oscillations in large graphene bubbles

Yuan Huang, Xiao Wang, Xu Zhang, Xianjue Chen, Baowen Li, Bin Wang, Ming Huang, Chongyang Zhu, Xuewei Zhang, Wolfgang S. Bacsa, Feng Ding, and Rodney S. Ruoff

Phys. Rev. Lett. 120, 186104 (2018).

It is shown that with a single laser beam, it is possible to measure the temperature distribution of a tiny graphene bubble and to control its temperature. At the same time we learned about the thermal conductivity of graphene and learned how well graphene is attached to the substrate. Temperature variations were identified from the observed spectral shifts.



Schematic of graphene bubble on 'interference substrate' with optical standing wave. The red spot indicates where the bubble gets heated most.

The highly elastic and flexible nature of graphene allows the creation of stable large bubbles on its surface (several micrometers wide and one micrometer high) in a more or less controlled fashion. Such bubbles might serve as micro-lenses or be used to control the morphology of graphene on surfaces or to chemically functionalize graphene on selected regions.

When graphene is illuminated with a laser beam, incident and reflected beams overlap forming an optical standing wave on the surface. While the large graphene bubble is not disturbed much by the standing wave, increasing the laser power has the effect of selectively heating the graphene bubble at the interference maxima of the standing optical wave. Such local changes in temperature can be detected by following the spectral shifts in the vibrational spectrum of graphene, where oscillations in shift and intensity of a spectral peak are recorded when scanning the laser spot across the graphene bubble.

By comparing the experimentally observed spectral shifts with those calculated using a theoretical diffusion model, taking into account curvature and the heat flow in graphene, we discover that the recorded temperature distribution over the bubble depends both on the thermal conductivity of graphene and the adhesion at the edge of the graphene bubble. The highest heating effect is seen in the center region of the bubble, furthest from the bubble boundary. Obtained results confirm the high thermal conductivity of graphene previously measured, demonstrate the excellent adhesion around the perimeter of the graphene bubble and provide new perspectives on how to heat graphene bubbles on specific locations.

Contacts

Dr. Wolfgang Bacsa ✉ Wolfgang.Bacsa@cemes.fr
Dr. Pascal Puech ✉ Pascal.Puech@cemes.fr

Giant reconstruction at the surface of silicon carbide

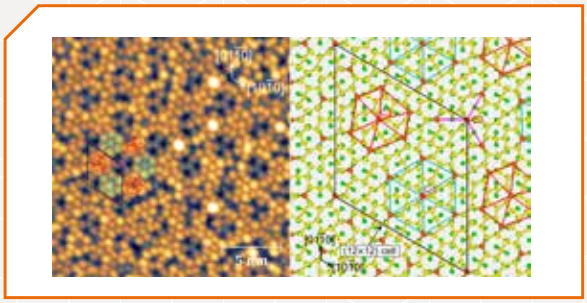
The missing link based on a new type of silicon

Giant (12×12) and (4×8) reconstructions of the 6H-SiC(0001) surface obtained by progressive enrichment in Si atoms

David Martrou, Thomas Leoni, Florian Chaumeton, Fabien Castanié, Sébastien Gauthier, and Xavier Bouju

Phys. Rev. B 97, 081302(R) (2018)

The gradual enrichment of the 6H-SiC (0001) surface with silicon atoms revealed two new reconstructions: a giant (12×12) and a (4×8) reconstruction. From STM images, an atomic model was constructed by introducing a new type of silicon in bridge between Si atoms of the SiC surface. These Si-bridge atoms also allowed to model two other reconstructions observed by other teams.



(left) STM image of the giant (12×12) reconstruction obtained on the 6H-SiC (0001) surface after deposition of 1 monolayer of Si. (right) Atomic model of the (12×12) reconstruction optimized by molecular dynamics. The Si atoms of the (0001) SiC surface are in green, those of the first layer in yellow, and those in orange are at the top of the pyramids observed in STM image.

Hexagonal 6H (0001) silicon carbide is used in power microelectronics for its high bandgap energy (3 eV), and in the field of single-photon sources due to these surface states. In both cases, knowledge of surface reconstructions is essential to obtain the best components. Numerous studies based on the sublimation of an excess of silicon allow to discover different reconstructions, among which the (√3×√3)-R30° and the (3×3) have a known atomic structures, with 1/3 and 13/9 of silicon monolayers. Using a silicon enrichment procedure of the 6H-SiC (0001) surface, we discovered two other intermediate reconstructions: the giant (12×12) and the (4×8). From the position of the surface atoms observed in scanning tunneling microscopy, we have constructed atomic models by introducing a new type of silicon atoms. These so-called Si-bridge atoms are bonded to two silicon atoms of the terminal plane of the 6H-SiC(0001) crystal. They allow to make the link between reconstruction (√3×√3)-R30° and the following reconstructions such as (12×12) and (4×8). Atomic models were validated using molecular dynamics simulations with Tersoff potentials. These simulations showed the stability of the (12×12) up to 600 °C, and the (4×8) up to 900 °C, in good agreement with the experimental observations. In addition, these Si-bridge atoms are at the basis to model two other reconstructions observed experimentally by other teams: the (2√3×2√3)-R30° and the (2√3×2√13). The analysis of silicon coverage rates and symmetry elements allowed us to generate a table with the six reconstructions known to date, and to present an unambiguous way of discerning them in situ by electron diffraction.

Contact

Dr. David Martrou ✉ dmartrou@cemes.fr

Unraveling original aspects of gold nanoparticles

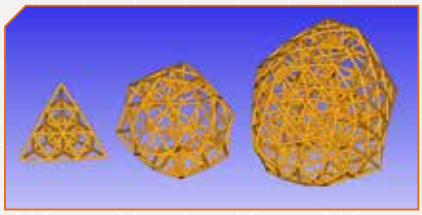
The interplay of charge and size effects on structure and melting

Au_{147} nanoparticles: ordered or amorphous?
N. Tarrat, M. Rapacioli and F. Spiegelman
‣ J. Chem. Phys., 2018, 148, 204398. Editor's Pick!

Melting of the Au_{20} gold cluster: does charge matter?
M. Rapacioli, N. Tarrat and F. Spiegelman
‣ J. Phys. Chem. A, 2018, 122, 4092. Editor's Choice!

Surface-charge dependent orientation of water at the interface of a gold electrode: a cluster study
G. Fazio, G. Seifert, M. Rapacioli, N. Tarrat and J-O. Joswig
‣ J. Phys. Chem., 2018, 232, 1583.

Density-Functional Tight-Binding Approach for Metal Clusters, Surfaces and Bulk: Application to Silver and Gold
J. Cuny, N. Tarrat, F. Spiegelman, A. Huguenot, M. Rapacioli
‣ J. Phys. Condens. Matter, 2018, 30, 303001. Invited Review!



Lowest-energy isomers localized by means of a global optimization procedure (Parallel-Tempering Molecular Dynamics at the DFTB level without pre-screening combined with a DFT refinement): Au_{20}, Au_{55} and Au_{147}

Adapting an approximate quantum method, we modelled gold nanoparticles. The identification and structural analysis of low-energy isomers in the range 55-147 show a predominance for amorphous character. Original structuration is found: occurrence of cavities or core-shell like organization (disordered core/regular surface). We also evidence on Au_{20} that, while varying the charge does not change the equilibrium structure, it strongly affects the melting temperature.

Gold nanoparticles (NPs) have deserved a lot of attention motivated by their unique properties that make them materials of choice in numerous applications. The generic simulation methods to deal with nano-objects can roughly be classified into three schemes: (i) wavefunction methods for small clusters (ii) DFT for intermediate sizes and (iii) force fields or potentials for large NPs. At the frontier between (ii) and (iii), approximate quantum methods have emerged. Among them, the Density Functional based Tight Binding (DFTB) approach allows for an explicit treatment of the electronic structure while reducing the computational cost thanks to the use of parametrized integrals and a minimal valence basis set. DFTB can thus tackle problems requiring an explicit description of the electronic structure even for large systems. We adjusted and benchmarked DFTB for gold. We showed that this method is satisfactory in reproducing essential small cluster properties (low-energy isomers structures, 2D–3D structural transition and its dependency upon charge) and energetic ordering of medium-size isomers. By running global optimization on Au_{20}, Au_{55} and Au_{147} systems using a Parallel-Tempering Molecular Dynamics algorithm at the DFTB level combined with a DFT refinement, we reported for the first time Au_{55} low-energy isomers exhibiting cavities below their external shell and we showed that Au_{147} amorphous geometries are relevant low energy candidates, likely to contribute in finite temperature dynamics and thermodynamics. Concerning the dependence of the properties upon charge, we highlighted on the magic cluster Au_{20} that, for such a size, a single charge strongly affects the melting temperature. Finally, taking into account the surrounding solvent, we have demonstrated the applicability of DFTB to study the structural/dynamical properties of gold/water interfaces. These studies build the bases for further investigations on gold NPs embedded in organic media with a quantum level of theory.

This highlight reports a joint CEMES-LCPQ/IRSAMC research work.

Contact

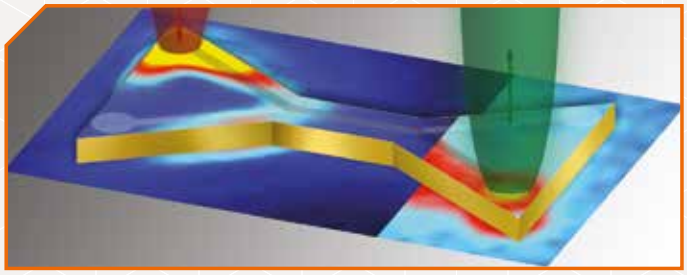
Dr. Nathalie Tarrat ✉ nathalie.tarrat@cemes.fr

Transmission and routing through plasmonic eigenstates

Designing Plasmonic Eigenstates for Optical Signal Transmission in Planar Channel Devices
U. Kumar, S. Viarbitskaya, A. Cuche, C. Girard, S. Bolisetty, R. Mezzenga, G. Colas des Francs, A. Bouhelier and E. Dujardin.
ACS Photonics 2018, 5, 2328-2335. DOI 10.1021/acsphotonics.8b00137

Ultracompact plasmonic devices ensuring optical routing from one chosen entry port to one determined output port are designed from 2D gold crystals. The nonlinear information is transmitted by delocalized cavity modes over > 2 microns and is commuted by 20 dB upon turning the incident polarization. This collaborative work (CEMES, ICB Dijon, ETH Zürich) within the ANR project PlaCoRe opens a way to new electrooptical information processing architectures.

Fast information processing technologies currently exploit all-optical and optoelectronic signal transmission and routing (i.e. selection of a specific signal pathway). At the nanoscale, circuitry based on conversion of photons into surface plasmons (collective oscillations of electrons) offers very promising solutions, yet transmission using propagating plasmons along narrow waveguides often results in signal loss.



Plasmonic modes in 2D gold cavities are designed to route non-linear signal from one input port to one output port and to modulate the transmitted power with the exciting polarization.
© CEMES-CNRS

Researchers in CEMES, in collaboration with colleagues from the ICB lab in Dijon (France) and from ETH Zürich (Switzerland), have conceived, carved and tested ultrathin and compact devices out of 2D gold crystals which are able to transmit nonlinear plasmo-optical signal from one precise input location to a determined and localized output port from which the signal can be collected.
To create the efficient multi input/output signal transmission and routing device, the shape and optical response of 2D mesoscale gold resonators are engineered to sustain plasmon resonances exhibiting a complex plasmonic modal landscape with both delocalized extension and strong spatial modulation.

The experimental results are confirmed numerically using a dedicated near-field SP transmittance code with a realistic polarized Gaussian excitation. This modal design approach contributes to the emerging strategies to embed active information processing functions into pure or hybrid plasmonic structures. This work demonstrates the potential of modal engineering in pure plasmonic systems toward information processing, which could be used to create new computing architectures for classical and quantum optical technology.

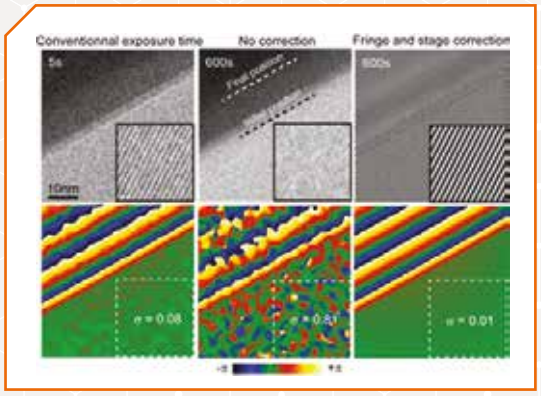
This work was funded as part of the ANR project PlaCoRe (ANR-13-BS10-0007)

Contact
Dr. Erik Dujardin ✉ Erik.Dujardin@cemes.fr

Unlimited acquisition time in electron holography

Unlimited acquisition time in electron holography by automated feedback control of transmission electron microscope
C. Gatel, J. Dupuy, F. Houdellier and M.J. Hÿtch
Applied Physic Letters 113, 133102 (2018);
doi: 10.1063/1.5050906

The signal-to-noise ratio of measurements by electron holography could be considerably improved if longer exposure times were possible. However exposure times were limited to a few seconds by instabilities in experimental conditions during acquisition. We show that by implementing advanced automation, routine exposure times of several tens of mins can be obtained without the need for image stacks.



Holograms and phase images comparison between a conventional exposure time of 5s, 600s of exposure time without and with correction thanks to a feedback with the transmission electron microscope.

The signal-to-noise ratio of measurements by electron holography could be considerably improved if longer exposure times were possible: increasing the number of electrons contributing to the hologram improves the counting statistics. However, instrumental instabilities causing drift in the hologram fringes and specimen position make acquisition times of above a few seconds counterproductive. The current approach then is to acquire image stacks of holograms, with short exposure times, followed by numerical realignment through sophisticated post-processing. The associated data storage and manipulation make in-situ and tomography experiments extremely cumbersome. Here, we implement dynamic automation of electron holography experiments to overcome these problems. Real-time drift measurement and feedback control of the instrument allows single holograms to be acquired with exposure times of 30 minutes or more. The positions of the hologram fringes and the specimen are corrected in real-time by feedback control of the microscope deflectors and specimen stage. Indeed, there are no longer any limitations from instrumental instabilities, only those imposed by the specimen itself. Furthermore, automation allows the implementation of sophisticated phase reconstruction techniques based on precise control of the experimental conditions. Smart acquisition of electron holograms preludes future computer-controlled electron microscopy capabilities. Apart from the necessity of a fast camera and microscope control protocols, the approach presented here is based on software routines and should therefore be widely applicable.

This work was supported by the French National Research Agency under the project IODA (ANR-17-CE24-0), the "Investissement d'Avenir" program reference No. ANR-10-EQPX-38-01 and No. 11-IDEX-0002, the "Conseil Regional Midi-Pyrénées", the European FEDER for financial support within the CPER program. This work was also supported by the international associated laboratory M²OZART.

Contacts

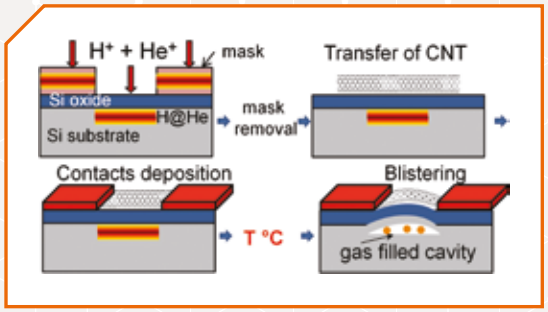
Dr. Christophe Gatel gatel@cemes.fr
Dr. Martin Hytch martin.hytch@cemes.fr

Bottom-up approach for stress transfer to CNTs

A bottom-up approach for controlled deformation of carbon nanotubes through blistering of supporting substrate surface.
V. S. Prudkovskiy, F. Iacovella, K. P. Katin, M. M. Maslov, and N. Cherkashin.
Nanotechnology 29 (36), 365304 (2018). https://doi.org/10.1088/1361-6528/aacc5d

Impact of He and H relative depth distributions on the result of sequential He^+ and H^+ ion implantation and annealing in silicon.
N. Cherkashin, N. Daghbouj, G. Seine, A. Claverie.
J. of Appl. Phys. 123 (16), 161556 (2018).

Researchers from the CEMES-CNRS and the University of Crete (Greece) propose a new bottom-up method for the stress transfer to carbon nanotubes over large surfaces allowing to manipulate in an appropriate way their band structure and consequently to develop modern and efficient HF semiconductor devices. The method is potentially compatible with high end technological application.



Bottom-up method for the stress transfer to carbon nanotubes (CNTs) over large surfaces allowing to manipulate their band structure: 1) H^+ and He^+ ions implantation in supporting wafer; 2) CNTs deposition and structuring; 3) blistering under thermal annealing inducing CNTs deformation.

The extreme mobility of charge carriers, ballistic transport and compatibility with CMOSs (complementary metal-oxide-semiconductor) makes carbon nanotubes (CNTs) promising candidates for replacing the silicon channel in HF transistors. However, metallic CNTs are zero bandgap materials that limits their use in HF nanoelectronics. Early theoretical and experimental work predicted and confirmed the band gap opening in deformed metallic CNTs.The development of a controlled and repetitive deformation of the CNTs would make it possible to appropriately manipulate their band structure and consequently to develop modern and efficient HF semiconductor devices. However, there is an essential breach between existing laboratory scale methods applied for deformation of low-dimensional materials and the needs of large-scale production. In this work, we have proposed a bottom-up method for the transfer of stress to these materials, which is potentially compatible with high end technological application. The CNTs deposited and nanostructured on the flat surface of an oxidized silicon wafer, which has been preliminary implanted with H^+ and He^+ ions, are anisotropically deformed over blisters produced after thermal annealing. The blisters appeared beneath the surface after the thermally activated formation of micro-cracks filled with gas and elastically relaxed through the deformation of the surface. The deformation of the CNTs is manipulated at the local scale (<1µm) by modifying the height/radius ratio of the blisters imposed by the implantation and annealing conditions. Using resonant Raman spectroscopy, we demonstrate that the CNTs attached by contacts at their ends deform over blisters up to a strain of 0.15 ± 0.03%, which is in good agreement with the value calculated from the blisters' dimensions. This approach can become a powerful tool for the elaboration of other 1D and 2D materials with predetermined optical or electrical properties.

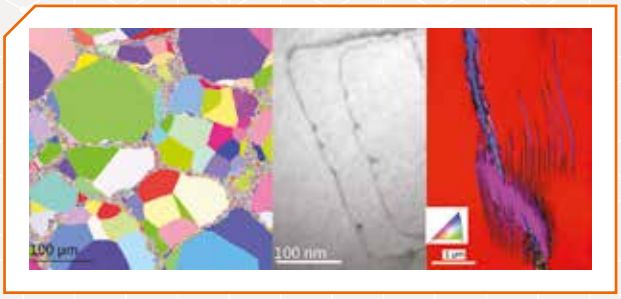
Contact

Dr. Nikolay Cherkashin ✉ nikolay.cherkashin@cemes.fr

Towards a better understanding of the deformation in harmonic Ti-Nb-Zr alloys

Conventional vs Harmonic-structured β-Ti-25Nb-25Zr alloys: a comparative study of deformation mechanisms.
F. Mompiou, D. Tingaud, Y. Chang, B. Gault, G. Dirras
Acta Materialia, Volume 161, December 2018, Pages 420-430, https://doi.org/10.1016/j.actamat.2018.09.032

Harmonic alloys constitute a new class of heterogeneous materials with a grain size gradient. Processed by powder metallurgy, they demonstrate enhanced mechanical properties compared to their conventional counterparts. Using mechanical testing and transmission electron microscopy observations, especially in-situ, we show, in the biomedical Ti-Nb-Zr alloy, that the elementary deformation mechanisms are different in conventional and harmonic alloys. These findings inform both on the hardening and the ductility of this alloy.



From left to right:

An EBSD orientation map showing the core/shell microstructure of a TiNbZr "harmonic" alloy.

A TEM image showing a screw dislocation pinned by obstacles during in-situ straining.

A TEM-orientation map highlighting the presence of both thin martensite laths (pink) and twins (blue) observed during in-situ straining

In the context of more demanding metallic materials for structural applications, a new concept has been settled to develop original heterogeneous microstructures with grain size gradient, called “harmonic”. This approach exploits mechanical milling and sintering methods to form a multimodal microstructure composed of a matrix core of large grains embedded in an ultra-fine grained interconnected shell. These alloys show enhanced mechanical strength while keeping a good ductility, two rather antagonist properties. Within the framework of the ANR project HighS-Ti (LSPM, IJL PPRIME, CEMES), the harmonic design has been applied to Ti alloys and especially to a beta Ti-Nb-Zr alloy. These type of alloy are indeed excellent candidates for implant materials as they present a stiffness comparable to the bone, insuring a good mechanical biocompatibility.

The elementary deformation mechanisms have been studied both after mechanical tests and in-situ in a transmission electron microscope (TEM), in conventional and harmonic microstructures. We show that the deformation mechanisms are quite different : the harmonic one deforms by dislocations, gliding from the core and pilling up against the shell, before being transmitted. In the conventional alloy, besides dislocation glide, the deformation is accommodated by bands composed of several unusual twins for bcc alloys. By combining automated orientation mapping in TEM and straining experiments, we were able to show that twinning occurs after the formation of a martensite phase. The sequence of twinning and phase transformation leads to bands with the same morphology as the ones observed post-mortem. This indicates that twinning is probably a consequence of martensite relaxation. In both case, we show that the initial hardening is controlled by the pinning of gliding dislocations on clusters of solute atoms. Stress measurements at dislocation scale were found comparable to the ones performed during macroscopic mechanical tests. The difference in mechanical behavior between the two microstructures can be attributed to both the existence of chemical heterogeneities arising from the material processing and the existence of strain redistribution mechanisms in the shell of the harmonic structure.

Contact

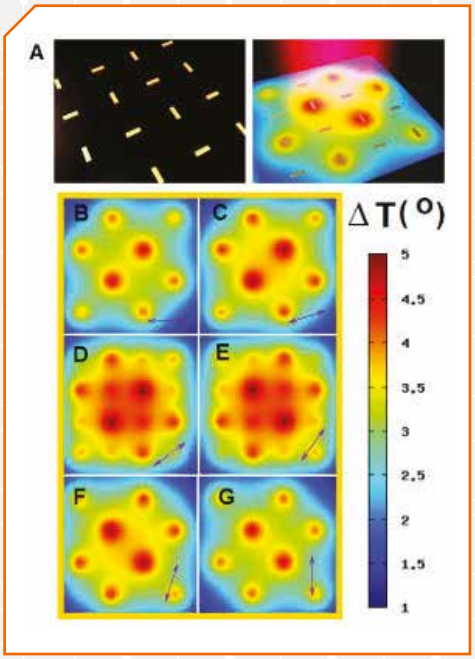
Dr. Frédéric Mompiou ✉ mompiou@cemes.fr

Thermoplasmonics metasurfaces for the control of nano-scale heat sources

Designing thermoplasmonic properties of metallic metasurfaces
Ch Girard, P R Wiecha, A Cuche and E Dujardin
‣ J. Opt. 20 (2018) 075004.

Local field enhancement and thermoplasmonics in multimodal aluminum structures
P R Wiecha, M-M Mennemanteuil, D Khlopin, J Martin, A Arbouet, D Gérard, A Bouhelier, J Plain, and A Cuche.
‣ Phys. Rev. B 96 (2017) 035440.

Thermoplasmonics is a new domain of Plasmonics in which the dissipative effects of the metal are exploited. Researchers from CEMES have shown that the combination of a self-consistent Green Dyadic method, equations of heat transport, and an advanced evolutionary multi-objective algorithm, allows to calculate not only the temperature distribution in the vicinity of a nanostructure, but also the design and optimization of new planar thermoplasmonic meta-surfaces.



(a) Schematic view of a thermoplasmonic metasurface. (b-g) Maps of the rise in temperature close to a network of gold nano-rods lying on a silica surface. Through the transverse and longitudinal plasmon modes of each rod, the laser polarization allows to tune the amount and distribution of generated heat.

During the last ten years, several theoretical and experimental studies have demonstrated that localized plasmon resonances of metal particles can be used to stimulate local and wavelength-dependent nano-sources of heat. For instance, by measuring the resistivity of a nearby conducting nanowire, it is now possible to map the variations of temperature associated to these resonances. In general, the amount of dissipated energy is proportional to the intensity of the local electromagnetic field, inside the particle. Dissipation is therefore strongly dependent on its form, shape and material, as well as on the wavelength.

Very recently, we generalized this type of study to complex ensembles of small particles, regularly arranged on dielectric substrates, extending the concept of meta-surfaces to thermoplasmonics. Usually, optical meta-surfaces are composed of many refractive or diffractive meta-units. The accumulated phase of light propagating along the elements is shaping the wavefront in a pre-defined way. In the case of thermoplasmonics, these nano-elements are metallic structures of sub-wavelength size on a substrate, which are capable to create three-dimensional temperature gradients. In properly designed meta-surfaces, the gradients can be controlled for instance by the polarization of the incident light. These new geometries have been studied and optimized by combining for the first time a fully self-consistent approach, based on Green's dyadic functions, Fourier or Laplace heat-transport equations, and a bio-inspired advanced evolutionary multi-objective algorithm. It allows to optimize the geometry of each single meta-unit, and to calculate the local intensity of electromagnetic field and deduce the induced temperature distribution and gradients inside and in the vicinity of metal-particle assemblies. This new simulation technique allowed us to design meta-surfaces which are capable to generate sub-micrometer heat flux profiles. The flux direction can be furthermore remote-controlled thanks to the polarization and the wavelength of the illuminating laser.

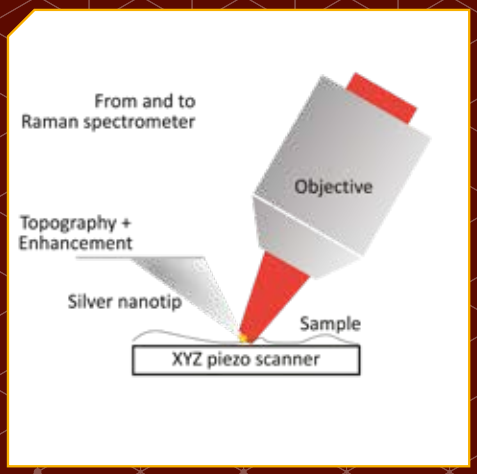
Contacts

Dr. Christian Girard ✉ christian.girard@cemes.fr
Dr. Aurélien Cuche ✉ aurelien.cuche@cemes.fr

Optical Spectroscopy platform

The Optical Spectroscopy Platform (OSP) at CEMES is an open platform available for the global scientific community: for academic researchers within or outside CEMES and also for private companies. OSP aims at providing expertise, tools and instruments dedicated to uncover optical properties of materials in relation to their electronic and/or atomic structure both at the nanometer and femto- to millisecond level.

In the last few years the OSP has bought and developed new sets of experiments toward spatially and temporally resolved studies. Here is a review of new setups as well as the current experimental capabilities in OSP.



TERS : Tip Enhanced Raman Spectrometer principle. Raman spectrometer and AFM microscope in one instrument. This provides both the sample topography and the spatially resolved Raman/fluorescence spectrum on the scale of the AFM tip, that is about 20nm.

Experimental techniques:

▸Optical Raman spectroscopy (or fluorescence spectroscopy) with excitation from the near UV (340nm) to the near IR (1000nm). Options include spatial lateral resolution (~λ/2 resolution), low frequency detection (down to 4cm^{-1}), low/high temperature and eventually sub-wavelength lateral resolution (~20nm) using our TERS setup (see figure).

▸Temporal dynamic from the femtosecond to the millisecond range. Based on femtosecond pump-probe techniques, photon time arrival counting or temporal intensity correlations (down to single photon signal level), the temporal evolution of nanometric system can be studied. Options include spatial lateral resolution (~λ/2 resolution), non-linear excitation, lateral propagation effects (excitation on one area of the sample and detection on another area), absorption, reflection...

▸Ultrashort transmission electron microscopy: femtosecond temporal resolution and atomic spatial resolution. Optical excitation of a sample probed with electron imaging, spectral gain or loss and cathodo-luminescence. (See HC-IUMI highlight)

OSP People Skills:

▸Development of custom experimental setups/prototypes related to optics and spectroscopy (ex: Metheor academic/industry project for temperature sensing, Fourier Transform spectrometer in the IR specific to local needs...)

▸Development of custom software products for human-machine interfacing. For instance, PyMoDAQ project (http:\\pymodaq.cnrs.fr), Metheor project interface...

Computer interface and set of tools to develop and control data acquisition in a lab.

Spectrometers

Name	Options/Features	Lasers	Gratings
T64000 Horiba/Jobin Yvon	▸ Simple/triple monochromator ▸ Cartography	▸ Kr [406-676] nm ▸ DPSS @ 488 nm ▸ Ar [364-515] nm	▸ 2400 l/mm ▸ 1800 l/mm ▸ 150 l/mm
Visible Dilor	▸ Simple/triple mono. ▸ Cartography	▸ Ar [457-514] nm ▸ Ti:Sa [700-850] nm	▸ 1800 l/mm ▸ 600 l/mm ▸ 150 l/mm
UV Dilor	▸ Triple mono. ▸ Cartography	▸ Ar [275-364] nm	▸ 2400 l/mm
Xplora Horiba/Jobin Yvon	▸ Simple mono. ▸ Cartography	▸ DPSS @532 nm ▸ Diode @ 638 nm ▸ Diode @ 785 nm	▸ 2400 l/mm ▸ 1800 l/mm ▸ 600 l/mm ▸ 300 l/mm
LabRAM Horiba/Jobin Yvon	▸ Simple mono ▸ AFM (TERS) coupling ▸ Cartography	▸ DPSS @532nm ▸ He:Ne @ 632nm	▸ 1800 l/mm ▸ 300 l/mm

Other Setups

Name	Options/Features	Lasers	Gratings
Fluorescence Lifetime Imaging Microscope	▸ Photon counting ▸ Time tagging ▸ Cartography	▸ Diode @405nm ▸ DPSS @ 515nm ▸ Diode @638nm	▸ Spectral information in parallel (Shamrock Andor spectrometer)
Micro-photoreflectance	▸ Cartography micrometer range	▸ Diode @405nm ▸ Diode @638nm ▸ White light	▸ Analog spectral information from scanning monochromator (lock-in detection)
Femtosecond setup	▸ Pump-probe ▸ Non-linear spectroscopy ▸ Cartography	▸ Femtosecond oscillator Chameleon Coherent [680-1080]nm ▸ Second harmonic generation	▸ Spectral information in parallel (Shamrock Andor spectrometer)
Quantum plasmonics	▸ Photon counting ▸ Time tagging ▸ Correlation ▸ Cartography	▸ DPSS @532 nm ▸ Diode @405nm ▸ Diode @ 638 nm ▸ Diode @ 785 nm	▸ Spectral information in parallel (Shamrock Andor spectrometer)

OSP contact

Dr. Sébastien Weber, research engineer in charge of the platform
✉ sebastien.weber@cemes.fr

2nd July 2018

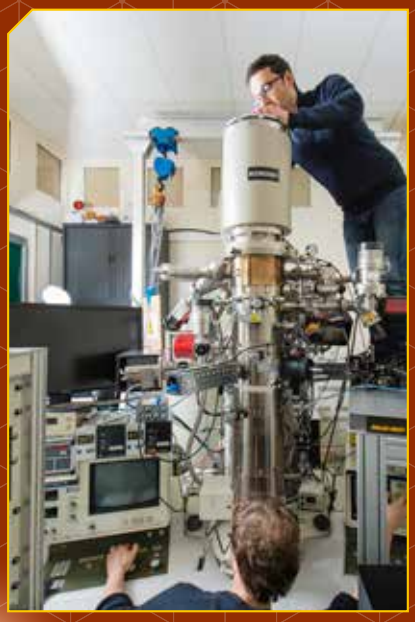
Launch of a joint international laboratory between the CNRS and Hitachi High Technologies Corporation

HC-IUMI

Hitachi - CNRS Infrastructure for Ultrafast Microscopy

French researchers and Japanese engineers have joined forces to develop a new electron microscope that can scan the properties of matter on very small scales of time and space. The Centre d'élaboration de matériaux et d'études structurales (CEMES) of the CNRS and the Hitachi High Technologies Corporation (HHT) have formalized the creation of a joint laboratory on July 2, 2018, the first between the CNRS and a foreign company.

The relations between CEMES and HHT began in 2009, when the laboratory was seeking to acquire a new transmission electron microscope (TEM) that can conduct experiments that are impossible for conventional instruments. In order to better respond to the needs of researchers, HHT engineers modified one of their products and developed a truly novel "electron optical platform". The two partners built on this experience by pursuing their relations, initially through a collaboration agreement aiming to pursue the valorization of this instrument.



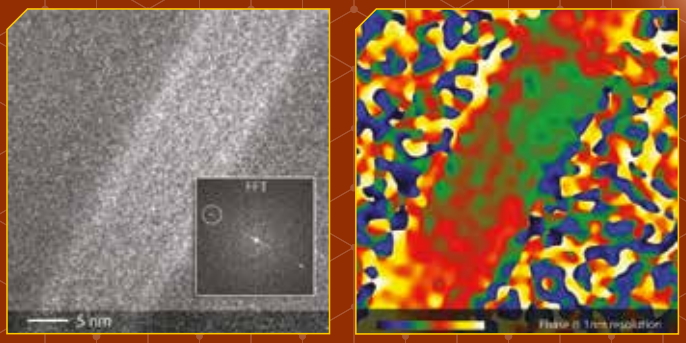
CEMES researchers handling the prototype of the ultrafast coherent FemtoTEM microscope. © Cyril FRESILLON/CEMES/CNRS Photothèque

At the same time, a CEMES team [1] developed a one-of-a-kind coherent [2] source of ultrafast electrons that they successfully tested on a previous generation HHT microscope, making this prototype the first ultrafast coherent TEM. With HHT engineers seeking to collaborate on this new technology and CEMES researchers to continue this research on a more modern microscope, the two partners subsequently decided to establish a joint laboratory, which has been confirmed by the signing of an agreement on July 2 at the French Embassy in Tokyo. While the CNRS already has a number of international joint units bringing together foreign academics and private companies, this is the first international joint laboratory between the CNRS and a foreign company on its own.

The collaboration will revolve around the transfer of the coherent electron source to a cutting-edge model loaned by HHT in connection with this new partnership. CEMES teams will thus enjoy one of the world's most high-performance instruments to conduct their experiments, and Japanese engineers will enjoy the expertise of French researchers in the field of ultrafast microscopy.

The FemtoTEM project, which made possible the development of the first prototype of this technology, combines TEM and ultrafast lasers. TEM offers excellent spatial resolution as well as low temporal resolution: in short, the TEM enables the study of physical phenomena on the atomic scale at a given instant, rather than following their evolution over time. The CEMES instrument frees itself of this limitation through a new electron gun that can generate ultrashort pulses thanks to its coupling with an ultrafast laser. Using a coherent pulsed source like this one enables the study of physical phenomena - such as the dynamics of electrical or magnetic fields, or stress within nanomaterials - over durations on the order of the femtosecond [3], all while observing on the sub-nanometric [4] scale.

Thanks to the joint laboratory between CEMES and HHT, the FemtoTEM technology could be integrated in a modern TEM with new forms of imaging, offering research teams a much more accurate instrument to successfully complete these unique types of studies.



Images obtained using the prototype of the ultrafast coherent FemtoTEM microscope.

Left: illustration of the interference (or electron hologram) of the femtosecond pulsed electron beam.

Right: Map of the phase of the femtosecond electron beam, taken from the hologram with a resolution of 1nm.

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Notes

1. *Supported financially by the CNRS's Institute of Physics and the ANR.*
2. *With a coherent source, the electron beam that enables the viewing of objects in the microscope carries the same quantity of energy and travels on the same trajectory. This excellent coherence is necessary for imaging structures and fields.*
3. *A femtosecond (fs) equals 0.000000000000001 = 10^{-15} seconds.*
4. *A nanometer (nm) equals 0.000000001 = 10^{-9} meters.*

Contacts

Joint laboratory Director: Dr. Florent Houdellier florent.houdellier@cemes.fr
FemtoTEM Manager: Dr. Arnaud Arbouet arnaud.arbouet@cemes.fr

15th March 2018

Agreement signed between CEMES-CNRS and NAra Institute of Science and Technology (NAIST)

CNRS and the japanese University Nara Institute of Science and Technology (NAIST) have decided to renew for three more years their partnership through the contiuation of the NAIST satelite in the Center of elaboration of materials et structural studies (CEMES-CNRS) where a franco-japanese team is developing new molecules with the goal to trigger controled movements on a surface via cascade electron transfers.

NAIST, a japanese university of excellence specialized in sciences, has been selected by the japanese governement as one of the 22 research universities in Japan (among about 500 universities). In this respect, an important budget is dedicated to increase its research capacity through internationalization of its teaching and its research. In this context, it was decided to establish a research satelite of NAIST in CEMES.

Contact

Prof. Gwénaël Rapenne rapenne@cemes.fr

CEMES members awards

Marc Legros

Senior researcher in Materials Physics, Marc Legros received the CNRS Silver Medal.
M. Legros is specialized in the study of dislocation movement and its implications for the transport of chemical species in solid matter. He has developed unique in-situ experiments in electron microscopy for this purpose.
© Photo Patrick Dumas

André Gourdon

Awarded with a Star of Europe for his coordination of the PAMS european project dedicated to the transition from microcomputing to nanocomputing.

Since 2013, the *Étoiles de l'Europe* (Stars of Europe) award has shined a light on European initiatives launched by French scientists. Rewarding both scientific expertise and the capacity to coordinate large international teams, this prize is given each year to twelve researchers and their respective projects.

Andrej Jancarik

Andrej Jancarik, post-doc in the CEMES-GNS group awarded with the Alfred Bader (Sigma-Aldrich) prize.
Dr. Alfred Bader, organic chemist who founded the Aldrich compagny, the largest manufactury and supplier of specialty chemicals for research purpose(now Sigma-Aldrich), created this award in 1994 to supports young scientists (Bader Award for Organic Chemistry and Bader Award for bioorganic chemistry).

Christian Joachim

The 2018 Sciences Prize of the Academy of Occitania is awarded to Christian Joachim, Research Director at CEMES, Physicist of Molecular Machines.
© Photo Florence AT

Patrick Calupitan

Patrick Calupitan received C'Nano thesis prize 2018 under the category "Interdisciplinary research" for his work performed in CEMES during his PhD.
His research consisted of synthesizing new photochromic molecules designed to be deposited on surfaces and studying them with a scanning tunneling microscope (STM) under low-temperature ultra-high-vacuum conditions (LT-UHV).

NEW open archive for CEMES

HAL collection for CEMES

Since June 2018 all scientific publications, research works and thesis since 2014 are in open-access on the HAL-CEMES website at : https://hal.archives-ouvertes.fr/CEMES/

HAL is a French multidisciplinary open archive which provides an international visibility to research works and enables people to link them to arXiv, a repository of electronic preprints and scientific papers in the fields of science

Successful European projects

Quantera Project ORQUID

ERA-NET Cofund in Quantum Technologies • From 2018 to 2021

ORQUID will explore the new possibility of using single organic molecules as the interface between three quanta – photons, electrons, phonons. First, single molecules will interact with light in waveguides and cavities to generate and detect single photons, providing immediate impact in quantum photonics. Second, single molecules will detect single moving charges in nano-electronic circuits to provide quantum coherent information exchange between these charges and the external world. Third, molecules embedded in nanomechanical devices and two-dimensional materials will measure nanoscale forces and displacements, which are keys to developing mechanical quantum systems and understanding nanomachinery. By developing these three interfaces on a common platform, the project aims at creating a versatile hybrid system, a major advance in the technology of quantum devices.

https://www.quantera.eu/
http://cerbero.fisica.unifi.it/joomla/index.php/about-us

Contacts

Dr. André Gourdon ✉ andre.gourdon@cemes.fr
Dr. Claire Kammerer ✉ claire.kammerer@cemes.fr

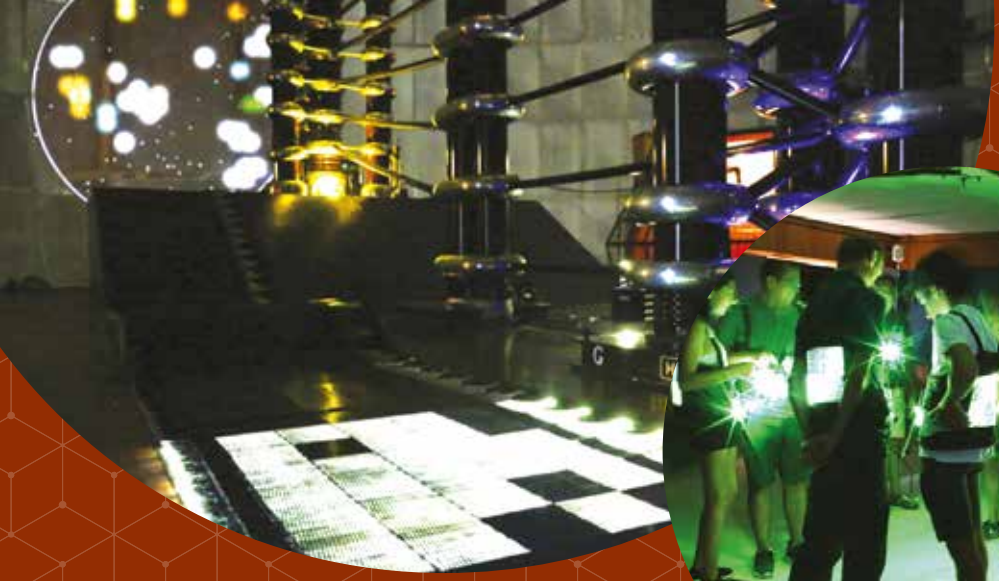
Esteem 3

H2020 Integrated Infrastructure (INFRA-IA) Project • Jan. 2019 to Dec. 2022

ESTEEM3 “Enabling Science and Technology through European Electron Microscopy” is the continuation of the ESTEEM (2005-2011 / FP6) and ESTEEM2 (2012-2016 / FP7) projects with an enlarged European consortium of 15 academic partners and 5 companies.
ESTEEM3 aims to provide access for the academic and industrial research community in materials science to the most powerful TEM techniques available at the nanoscale. It also will carry out Joint Research Activities (JRA) on selected areas in TEM techniques and issues (imaging, diffraction, métrology, spectroscopy, in-situ TEM, data treatment and microscope automation) and specific applications i.e. material for ICT, material for Energy, material for Health, and material for Transport.

Contact

Dr. Etienne Snoeck ✉ snoeck@cemes.fr



Exhibition held as part of the ESOF 2018 event

European Science Open Forum - ESOF from 7th to 15th of July

"Retina-pictonique" exhibition presented works by the artists Sultra & Barthelemy. The artists presented some of their works exploring the relations between local and global, the qualities of self-organization and emergence. The exhibition was associated to conferences on the relation between science and art and took place in "la Boule" of the old electron microscope. " Rectina-pictonique " welcame about 150 visitors from Toulouse area.

RETINA PICTONIQUE

Science Festival 2018
Open days at CEMES

Friday 12th and Saturday 13th October 2018

120 students and more than 500 people visited the CEMES during our open days: a great success for this edition of the Science Festival!

Visitors could choose from 10 workshops including one for children, as well as a plenary lecture. Most stayed no less than two hours in the laboratory and could see electron microscopes or spectrometers, exchange with researchers and visit the famous historical electric generator!

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Editors
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N. Tarrat

Communication
E. Prévots

CEMES

CEMES-CNRS

29, rue Jeanne Marvig

BP 94347

31055 Toulouse

Cedex 4

France

www.cemes.fr

@CEMES_CNRS