CEMES

2020

Highlights

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Summary

Edito

We are happy to send you the fifth edition of the "CEMES Highlights" for the year 2020.

2020 was a very particular year due to the sanitary crisis we all had to face to. CEMES, as many other laboratories, took part in the fight against the COVID pandemic and gave all its stock of gloves, masks, gowns to hospitals, its reserve of alcohol and hydrogen peroxide to synthesize hydroalcoholic gel. We also used our means in 3D printing to fabricate visors, which were sent to the hospitals and clinics staffs in Toulouse area with the help of the CNRS Regional Delegation.

2020 was also the year the CEMES was evaluated by the HCERES committee who visited us during 3 days. We are very happy of the HCERES recommendations for progress and of its conclusions that recognize that *"The CEMES is at the best international level, with tools recognized as unique and scientific (and mainly technical) skills allowing multiple collaborations, partnerships and project funding. Some research topics and the associated results are international in scope, even world firsts".*

Despite the closure of CEMES during the months of lockdown, scientific activities were able to continue. The 2020 release of the CEMES Highlights magazine makes a focus on 10 articles published this year on original scientific advances carried out in our laboratory. The list is far from being exhaustive, and a much more complete overview of our publications can be found in the Open Access HAL collection of CEMES.

2020 also saw the awarding of few CEMES agents distinguished for their work this year, including Florent Houdellier who received the Crystal Medal of the CNRS and Arnaud Arbouet for the creation of the HC-IUMi Joint Laboratory with the Japanese company "Hitachi High Technology" aiming to the co-development between CEMES and HHT of a new ultra-bright pulsed TEM microscope.

These yearly booklets aim also at presenting the different experimental facilities hosted at CEMES and this year we make a focus on the Physical growth and Ion Implantation capacities the laboratory has recently push forward by the acquisition of a new unique UHV sputtering machine equipped with a source of nanoparticles.

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

To finish, 2020 was the last year of the current CEMES management team. Next year, Etienne Snoeck will leave his Director functions and for the following five years, Alain Couret, current deputy director, will become Director of the laboratory assisted by Benedicte Warot-Fonrose as Deputy Director and Muriel Rougalle as General Secretary.

We wish you a fruitful reading of this 2020 publication of the CEMES Highlights.

Etienne Snoeck,
Previous CEMES director (2016-2020)
Alain Couret
Director since 2021, previous Deputy Director
Bénédicte Warot
CEMES Deputy Director since 2021

Édito

Nous sommes heureux de vous envoyer la cinquième édition des « CEMES Highlights » pour l'année 2020.

2020 a été une année très particulière en raison de la crise sanitaire à laquelle nous avons tous dû faire face.
Le CEMES, comme de nombreux autres laboratoires, a participé à la lutte contre la pandémie COVID et a donné tout son stock de gants, masques, blouses aux hôpitaux, sa réserve d'alcool et d'eau oxygénée pour synthétiser du gel hydroalcoolique. Nous avons également utilisé nos moyens en impression 3D pour fabriquer des visières qui ont été envoyées aux personnels des hôpitaux et cliniques de la région toulousaine avec l'aide de la délégation régionale du CNRS.

2020 a également été l'année où le CEMES a été évalué par le comité du HCERES qui nous a rendu visite pendant 3 jours. Nous sommes très heureux des recommandations du comité et de ses conclusions qui reconnaissent que « *Le CEMES est au meilleur niveau international, avec des outils reconnus comme uniques et des compétences scientifiques (et principalement techniques) permettant de multiples collaborations, partenariats et financement de projets. Certains thèmes de recherche et les résultats associés ont une portée internationale, voire représentent des premières mondiales* ».

Malgré la fermeture du CEMES pendant les mois de confinement, les activités scientifiques ont pu se poursuivre. Le numéro de 2020 du magazine CEMES Highlights met en avant 10 articles publiés cette année sur des avancées scientifiques originales réalisées dans notre laboratoire. La liste est loin d'être exhaustive, et un aperçu beaucoup plus complet de nos publications se trouve dans la collection Open Access HAL du CEMES.

2020 a également vu la distinction de quelques agents du CEMES pour leurs travaux, dont Florent Houdellier qui a reçu la médaille de cristal du CNRS et Arnaud Arbouet pour la création du Laboratoire Commun HC-IUMi avec la société japonaise “Hitachi High Technology» visant au co-développement entre le CEMES et HHT d'un nouveau microscope TEM pulsé ultra-brillant.

Nos recueils annuels du CEMES visent aussi à présenter les différentes installations expérimentales disponibles au laboratoire. Cette année, nous nous concentrons sur nos moyens en élaboration du service Croissance physique et Implantation Ionique qui s'est développé plus encore cette année grâce à l'acquisition d'un nouvel équipement UHV de dépôt par pulvérisation cathodique équipé d'une source de nanoparticules.

Un aperçu de nos activités est disponible sur notre site www.cemes.fr, qui détaille les recherches menées dans chacun des 7 groupes de recherche du laboratoire du CEMES.

Pour finir, 2020 fût la dernière année de l'actuelle équipe de direction du CEMES. L'année prochaine, Etienne Snoeck quittera ses fonctions de directeur et pour les cinq années suivantes, Alain Couret, actuel directeur adjoint, deviendra directeur du laboratoire assisté de Bénédicte Warot-Fonrose comme directrice adjointe et Muriel Rougalle comme secrétaire générale.

Nous vous souhaitons bonne lecture de ce numéro.
2020 des Faits-Marquants du CEMES

Etienne Snœck,
Précédent Directeur du CEMES (2016-2020)
Alain Couret,
Directeur du CEMES depuis 2021, précédent Directeur adjoint
Bénédicte Warot-Fonrose,
Directrice adjointe du CEMES depuis 2021

COVID-19 :
CEMES mobilized against the coronavirus epidemic

▸ Donation of equipment to the Toulouse University Hospital: Together with most of the CNRS Délégation Occitanie-Ouest laboratories, CEMES mobilized against the covid-19 pandemic and responded to the call from the Toulouse Hospitals. CEMES donated all its stocks of gloves, surgical masks, overcoats, protectives glasses to contribute to the efforts against the pandemic and protect healthcare workers.

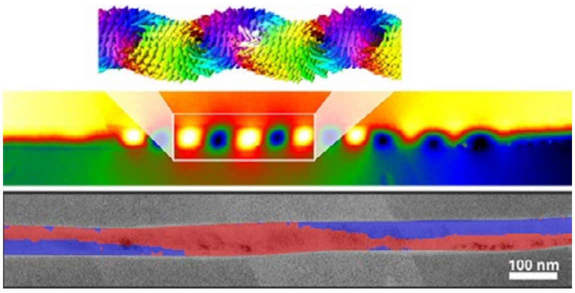
▸ 1,000 visor helmets produced every week for hospitals in Toulouse: From the end of March 2020, the CEMES and LNCMI-T laboratories (National Laboratory of Intense Magnetic Fields of Toulouse) developed and offered anti-virus protective visor masks validated by the Toulouse hospital. A vast manufacturing operation made it possible to distribute more than 7,000 visor helmets to Toulouse health establishments between April and May 2020. This operation and the weekly collection were coordinated by the Regional Delegation CNRS Occitanie Ouest (DR14),

▸ Two models of visor masks have been proposed. After conditioning tests, the teams from the Rangueil University Hospital selected the so-called "CHU" model, considered safer and more comfortable, the visor of which is made of a 200 μm transparent A4 plastic sheet.

▸ The CNRS and La Dépêche du Midi newspapers echoed and welcomed this voluntary initiative by the technical teams of the laboratories.

Effects of structural inhomogeneity in CoNi nanowires on its magnetic configurations

Exotic Transverse-Vortex Magnetic Configurations in CoNi Nanowires
I.M. Andersen, L.A. Rodriguez, C. Bran, C. Marcelot, S. Joulie, T. Hungria, M. Vazquez, C. Gatel and E. Snoeck
ACS Nano, 2019



TEM image of a CoNi nanowire with fcc and hcp grains, marked by false colors (blue and red, respectively), and phase image retrieved from electron holography. The outlined region has a magnetic configuration consisting of a chain of vortex-like transversal states, as evidenced by micromagnetic simulations.

Due to magnetostatic energy, the magnetization in magnetic nanowires (NWs) often aligns along the NWs axis. However, in hexagonal close packed NWs whose "c" direction is oriented perpendicular to the NW axis, the magnetocrystalline anisotropy may be strong enough to compete with the large shape anisotropy. In this study, we have found a chain of transversal vortex-like magnetic structures in a hexagonal close packed grain of a CoNi nanowire whose close-packed direction is oriented perpendicular to the nanowire axis.

The magnetic configurations of cylindrical Co-rich CoNi nanowires have been quantitatively studied at the nanoscale by electron holography and correlated to structural and chemical properties locally at the same positions of the sample. The nanowires display a mixture of crystal grains of both face-centered cubic (fcc) and hexagonal close packed (hcp) crystal structures, with grain boundaries oriented parallel to the nanowire axis direction. Study by electron holography reveal the existence of a complex magnetic configuration that is characterized by two very different types of magnetic configurations coexisting within a single nanowire: a chain of periodical vortices separating small transverse domains in regions with mainly hcp grains with easy axis orientation perpendicular to the nanowire axis, and a more longitudinal magnetic configuration parallel to the nanowire axis in regions fcc grains. The experimental results have been compared to micromagnetic simulations, which has confirmed that the vortex chain is formed within a hcp phase of the Co-rich CoNi nanowire.

Deviations in the local chemical composition are at the origin of these magnetic configuration changes. Variations in the chemical composition lead to a change of the crystalline orientation and/or crystal structure, and give rise to a change in magnetic anisotropies.

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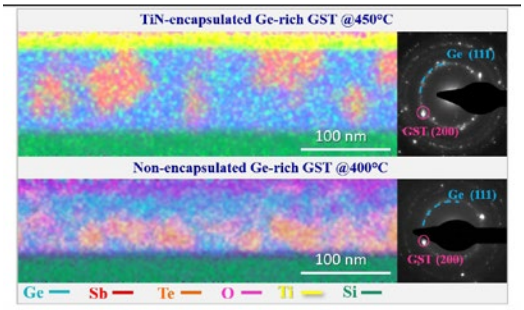
Degradation of phase change memories

Effects of surface oxidation on the crystallization characteristics of Ge-rich Ge-Sb-Te alloys thin films
M. Agati et al.
Applied Surface Science 518 (2020) 146227

Phase change memories (PCMs) appear today as the memories of the future, fast, energy efficient, and integrable in matrices located immediately close to processors, as required for big data processing (1). A PCM cell most often consists of a thin layer of Ge-Sb-Te alloy (GST) sandwiched between two electrodes. Electric current pulses and Joule-induced heating are used to thermally switch the PCM from the RESET state (low electrical conductivity in the amorphous phase) to the SET state (highly conductive in the crystalline phase) and vice versa, via crystallization or quenching after melting, respectively.



It has been repeatedly reported that the voluntary or accidental oxidation of layers of alloys of the Ge-Te or Ge-Sb-Te type greatly degrades their physical characteristics and, consequently, the performance of the devices using them. The crystallization temperature of the layers is greatly reduced, thereby reducing the stability of the RESET state. We have studied in detail the impact of prolonged exposure to air of layers of Ge-rich GST alloys, on the characteristics of the crystallization of such layers deposited homogeneously in the amorphous phase.

When these layers are encapsulated after deposition, their crystallization takes place from 380 °C via the separation of the chemical Ge and GST phases, the homogeneous crystallization of Ge, and finally the crystallization of the Ge2Sb2Te5 phase (2, 3). When the surface comes into contact with air, it oxidizes to a few nanometers thick. This oxidation is highly selective, mainly affecting Ge and, to a lesser extent, Sb. The “in-situ” TEM shows that Germanium crystallizes, not homogeneously in the layer, but heterogeneously, from the surface to the depth of the layer, and at a lower temperature, around 330 °C. These observations, as well as the evidence of the strong chemical redistributions which occur during crystallization, show that the oxidation has the effect of providing seeds for crystallization, probably in the form of Sb2O3, which then allow the subsequent heterogeneous crystallization of Ge.

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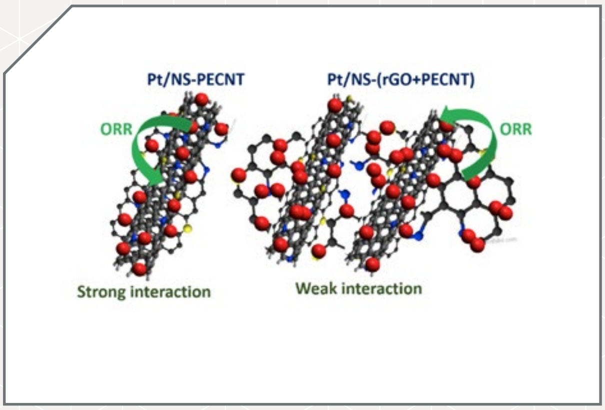
Improved oxygen reduction reaction in fuel cell through

Optimizing metal-support interphase for efficient fuel cell oxygen reduction reaction catalyst,
I D. Nechiyil, M. Seshadhri Garapati, R. Chandrabhan Shende, S. Joulié, D. Neumeyer, R. Bacsa, P. Puech, S. Ramaprabhu, W. Bacsa
Journal of Colloid and Interface Science 561 (2020) 439-448

Proton exchange membrane fuel cells (PEMFC) are promising green technology alternatives. The high cost resulting from the use of Pt-based electrocatalysts and stability issues are bottlenecks in commercialization of PEMFC. Oxygen reduction reaction (ORR) reaction kinetics is much slower than the hydrogen oxidation reaction (HOR) occurring at the anode, which implies high amount of catalyst loading at the cathode side. Efforts are being made to reduce Pt loading either by alloying or by appropriately tailoring and doping the support material. Using a support material with high degree of graphitization like carbon nanotubes/graphene composite materials have the advantage to present a good thermal stability and electrochemically conductivity and to be electrochemically stable. We reported, a hybrid 1D-2D carbonaceous material comprising multiwall carbon nanotubes (MWCNTs) and few-layer graphene (FLG) as support for Pt catalyst in PEMFCs, where graphene is expected to compensate for the relatively low electrochemical surface area of MWCNTs. Our results show using Raman spectroscopy, transmission electron microscopy (STEM-EDS) and XPS that a strong interfacial bonding between the catalyst particle and the support is crucial to prevent degradation of the catalyst material using. We demonstrate that the in-situformed co-doped 1D-2D support leads to a higher performance when compared to similar hybrid supports obtained by adding reduced graphene oxide (rGO) to co-doped CNTs.



Schematic of exfoliated carbon nanotubes doped with nitrogen and sulfur with and without reduced graphen oxide

We have used a modified hybrid support consisting of unzipped carbon nanotubes and N and S co-doped MWCNTs to develop a high performance electrocatalyst for the ORR in PEMFC. By comparing four different supports, we found that a strong interaction between the catalyst nanoparticles and the support material is crucial for ORR activity so as to increase performance and durability of PEMFC. Fuel cell measurements show that Pt/NS PECNTleads to high power density of 642 mW/cm2, which is30% higher than that observed when combining with reduced graphene oxide.

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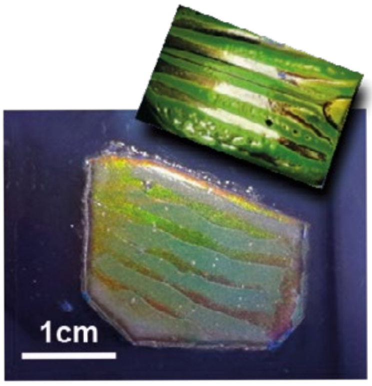
Biomimetic design of patterned insect carapaces

Biomimetic design of Iridescent Insect Cuticles with Tailored, Self-Organized Cholesteric Patterns

A. Scarangella, V. Soldan and M. Mitov, Nature Communications, 11, 4108 (2020)

▸ Carbon 145, 10-22 (2019)

The accurate replication of patterns found in the carapaces of many insects is extremely difficult since discontinuous patterns and colors must coexist in a single layer within continuous structures.



Biomimetic sample with a piece of carapace.

We approach this problem of the high-fidelity capture of the structural complexity observed in nature by focusing on iridescent carapaces with a complex twisted organization of chitin fibers. At the micrometer and submicrometre scale, the helical pitch and orientation of the helical structure depend on the position in 3D, and the formation of periodic patterns is required at 2D. We used liquid crystal oligomers to mimic biological liquid crystals. Geometric constraints are met by controlling the thermal diffusion in a bilayer subjected to local changes in the molecular anchoring conditions.

We attempted to reproduce the textural, structural and color properties at several length scales. The imaging of cross-sections of materials by transmission electron microscopy was performed at the Center for Integrative Biology in Toulouse (CNRS, University Paul-Sabatier).

We made optimal use of resources, in the spirit of eco-design. By means of a single sequence based on self-organization, precise control of a single-piece sample structure composed of different colored patterns with the same unique pitch gradient was enabled.

A multicriterion comparison reveals a very high level of biomimicry.

Proof-of-concept prototypes of optical tags in cryptography are presented. The functionalities of biological and synthetic materials are both relevant to communication and camouflage.

The present design involves a high versatility of chiral patterns unreached by the current manufacturing techniques such as metallic layer vacuum deposition, template embossing or lithograph

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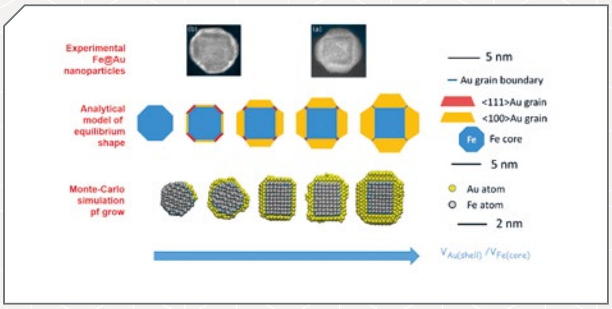
Core-shell nanoparticles with evolving forms

Equilibrium shape of core(Fe)-shell(Au) nanoparticles as a function of the metals volume ratio,
A. Ponchet, S. Combettes, P. Benzo, N. Tarrat, M. J. Casanove and M. Benoit,
‣ J. Appl. Phys. 128, 055307 (2020)

How interface properties control the equilibrium shape of core–shell Fe–Au and Fe–Ag nanoparticles
S. Combettes, J. Lam, P. Benzo, A. Ponchet, M. J. Casanove, F. Calvo and M. Benoit
‣ Nanoscale 12, 18079 (2020)

Nano-objects associating a noble metal such as gold (Au) or silver (Ag) and a magnetic metal such as iron (Fe) combine the optical and magnetic properties of both metals and have enhanced magneto-plasmonic properties. Thus, Fe-Au nanoparticles have potential applications in plasmonics, catalysis and in the biomedical field.



Evolution of the morphology as a function of the shell (Au)/core (Fe) volume ratio, observed experimentally (top), predicted by an analytical model (middle) and modeled by Monte-Carlo methods (bottom).

We have observed an astonishing evolution of the morphology of Fe-Au core-shell nanoparticles elaborated by a UHV technique. The core (iron) and the shell (gold) have the same polyhedral shape when the thickness of the shell is of the order of 2 to 3 monolayers, then the nanoparticles adopt a regular but more complex shape based on gold pyramids epitaxied on an iron cube when the volume of gold is greater than that of iron .

These morphologies cannot be predicted intuitively, as iron crystallizes in the bcc phase while the noble metal is fcc. Through an original approach combining experimental analysis, analytical modeling and numerical simulations, we have been able to elucidate this evolution as a function of the volume ratio between the two metals.

We have developed an analytical model using DFT calculations of surface and interface energies as data. This model, adapted to epitaxy on a nano-substrate of variable shape and experimental size (2 nm and more), investigates the competition between three driving forces: wetting, gold surface energy minimization, and interface energy minimization. These driving forces compete or cooperate according to the shell/core volume ratio and to the core size, leading to the different observed equilibrium morphologies.

On the other hand, we have developed Fe-Au interaction potentials whose parameters reproduce these driving forces computed by DFT, which allowed us to simulate the shell growth on iron cores of predefined shapes (polyhedron or cube). Although the sizes that can be modelled (of the order of 1 nm) are smaller than the experimental ones, the obtained shell morphologies are very similar to the experimental ones. Furthermore, this approach allows us to predict that for the Fe-Ag couple, other equilibrium shapes will be obtained.

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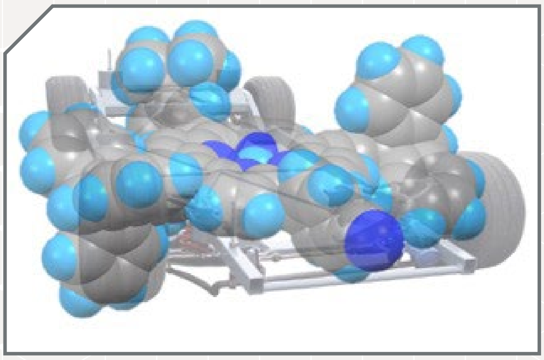
"Blue Buggy", the last generation nanocar ready for the next nano Grand Prix

A dipolar nanocar based on a porphyrin backbone
T. Nishino, C. Martin, H. Takeuchi, F. Lim, K. Yasuhara, Y. Gisbert, S. Abid, N. Saffon-Merceron, C. Kammerer, G. Rapenne,
Chem. Eur. J. 2020, 26, 12010-12018. (Hot paper)

After the first Nanocar Race organized in spring 2017, we designed at CEMES a new family of molecules to behave as cars in the nanoworld. Two years later, we are reporting the result in a publication presenting the synthesis of 9 dipolar nanocars achieved in Japan. The result is amazing. In every flask, about 100 mg of a blue powder stick to the walls. These are the Franco-Japanese racing cars that sleep wisely in the garage waiting for the next Grand Prix in 2021. The design of the molecules has been long thought. To hope to win the race, you have to be fast but you need also to keep the control. The design is then a compromise between opposite requirements. The nanocar is made up of 150 atoms (chemical formula C85H59N5Zn) andconsists of three components. A planar chassis made from porphyrin, a fragment already used in nature for many processes like oxygen transportation (hemoglobin) or photosynthesis (chlorophyl). Long of 2 nm and surrounded by two wheels to minimize contact with the ground and two legs which are able to donate or accept electron making the nanocar dipolar. Ultimately, the presence of a zinc atom could allow transportation of small molecules on the car body. A perspective of this research will be to transport reactants or drugs from one place to another place.



Chemical structure of the Nanocar qualified.

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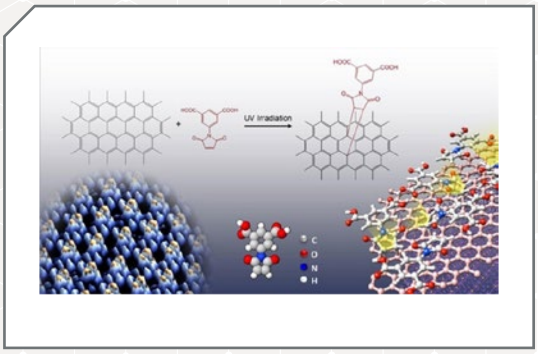
Controlled functionalization of graphene

Long-range ordered and atomic-scale control of graphene hybridizationby photocycloaddition

M. Yu, CC Liu, C. Mattioli, H. Sang, G. Shi, W. Huang, K. Shen, Z. Li, P. Ding, P. Guan, S. Wang, Y. Sun, J. Hu, A. Gourdon, L. Kantorovich, F. Besenbacher, M. Chen, Fei Song, F. Rosei, and X.

Nature Chemistry (2020)

The controlled functionalization of graphene is a subject of major interest because it should open the door to the modification of the electronic properties of this 2D material, for example by opening a gap, or to add functionalities (chemical, optical, biochemical) provided by the anchored molecule. However, this grafting is difficult because graphene is a poorly reactive material, except at its defects. A solution to this problem is to use cycloaddition reactions between the double bond activated of a molecule (a dienophile) and one or two "double bonds" (ene or diene) of graphene in the Kékulé representation. We showed in 2017 [Ref 2] that the formation of these covalent bonds with graphene locally disturbed the electronic properties of graphene. However, this grafting was randomly distributed on the surface and the article concluded by suggesting a possibility of controlling the organization of these reactive sites on the surface using supramolecular self-assembly. This second hedge has just been crossed in the frame of an international cooperation involving four other countries, China, Denmark, Canada and the United Kingdom. In these experiments, the maleimide molecule is functionalized with a phenyl-3,5-dicarboxylic group. After sublimation under ultra-high vacuum on a graphene surface on Cu (111) or on mica, the molecules organize themselves in a very ordered six-fold fashion on the surface to form hexagons held by hydrogen bonds between the carboxylic acid functions. These supramolecular structures, which do not involve covalent bonds between the molecules and graphene, are relatively fragile. The reaction can then be photochemically activated by ultraviolet irradiation. Here again, it leads to [2 + 2] or [2 + 4] cycloadditions but in a totally controlled geometry over areas of several hundred square nanometers.



Controlled functionalization of graphene

The molecules are then covalently linked and this robust grafting confers a great thermal stability to the system. The electronic properties of these modified surfaces have been studied by tunneling microscopy and numerous surface spectroscopic techniques and we have been able to show the opening of a gap of around 170 meV in the irradiated areas.

This result opens the way to prospects for local control of the electronic structure of functionalized graphene, for example using masks during the irradiation phase.

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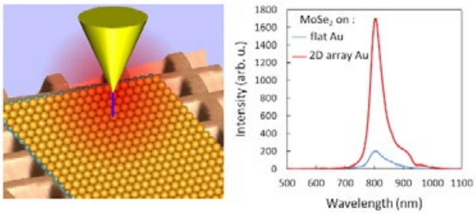
STM in the spotlight!

Plasmonic-Induced Luminescence of MoSe2 Monolayers in a Scanning Tunneling Microscope, R. Péchou, S. Jia, J. Rigor, O. Guillermet, G. Seine, J. Lou, N. Large, A. Mlayah, R. Coratger.

R. Péchou, S. Jia, J. Rigor, O. Guillermet, G. Seine, J. Lou, N. Large, A. Mlayah, R. Coratger.

▸ ACS Photonics 2020

Integrated optics is a promising way for improving information transmission speed. In the race toward miniaturization, near-field techniques allow to overcome the fundamental barrier of diffraction. In this general context, a transverse team bringing together researchers from three different CEMES groups (NeO, SINanO and GNS) has developped an original experimental setup enabling the study of fundamental light emission mechanisms at unprecedented spatial and spectral resolution scales.



Light emission excited by tunneling electrons in a STM allows for studying fundamental luminescence mechanisms at the nanometer scale. This technique has been used to study the luminescence intensity enhancement of MoSe2 monolayers deposited on nanostructured plasmonic substrates.

This so-called STM-induced light emission technique has been applied to the study of the luminescence of MoSe2monolayers deposited on metallic substrates (collaboration with Rice University, Houston and University of Texas, San Antonio). Specific spectral signatures of both the substrate and the MoSe2 monolayer luminescence have been identified. They reveal two distinct fundamental light emission mechanisms: radiative decay of tip-surface gap plasmon modes in the case of a metallic substrate, and electron-hole recombinations in the case of the MoSe2monolayer. Photonic maps show at a nanometer resolution scale that the MoSe2 luminescence emission rate is increased by minority charge carriers creation in the semiconducting monolayer, and allow for a detailed description of the light emission mechanism.

The use of plasmonic substrates to support the MoSe2 monolayers gives birth to a strong coupling between excitons confined in the monolayer, and plasmon modes excited on the substrate surface by tunneling electrons. Substrate morphology appears thus to be a key parameter to tune or de-tune the spectral overlap of these fundamental excitations to modulate this coupling, and in fine the monolayer light emission rate. By using a nanostructured gold substrate, we demonstrate an enhancement by an order of magnitude of light emission intensity of the MoSe2monolayer, compared to the one observed with a flat substrate. This original approach paves the way to novel spectroscopy and imaging techniques for addressing the photon emission from localized emitters such as quantum dots, or molecules.

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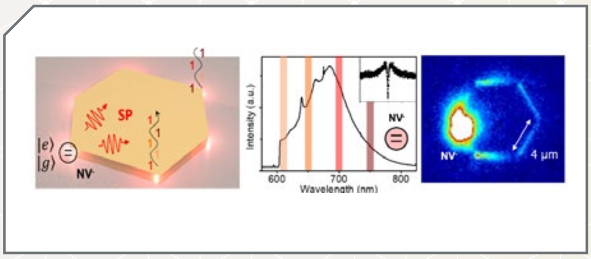
Spectral sorting of single plasmons in a 2D crystalline cavity

Single plasmon spatial and spectral sorting on a crystalline two-dimensional plasmonic platform
U. Kumar, S. Bolisetty, C. Girard, R. Mezzenga, E. Dujardin and A. Cuche.
‣ Nanoscale 12, 13414 (2020)

With the emergence of quantum technologies for information processing, a major stake is the handling and the control of the quantum properties of light at the nanoscale in planar structures. In this context, metallic nanostructures allowing for the conversion of single photons in single surface plasmons (collective oscillations of electrons), offer very promising opportunities. So far, experimental demonstrations have been limited to punctual or unidimensional nanostructures, mainly fabricated by physical processes, where plasmons often undergo high scattering losses that limit their use for actual applications.

Researchers from CEMES (NeO and GNS groups), with the contribution of colleagues from ETH Zürich (Switzerland), have used an ultrathin cavity made of crystalline gold coupled to a single quantum nanosource emitting photons in a wide spectral window in the visible (600-800 nm), aiming at demonstrating a spatial and spectral filtering of the single plasmons that propagate in the structure over several micrometers.



The photons emitted one by one and randomly between $600 < \lambda < 800$ nm by a single NV colored center hosted by a nanodiamond positioned in the direct vicinity of the metallic structure are transferred in the near field to the continuum of available plasmon modes of the cavity. By imaging their propagation as a function of the wavelength, the authors have shown that the two-dimensional distribution of the signal in the hexagonal cavity is driven by the dissipation related to absorption losses.

In a second step, the gold crystalline platelet has been carved by a focused ion beam (FIB) with the inclusion of a plasmonic Bragg mirror optimized at a given wavelength. This periodic structure has provided a new channel for the wavelength-dependent redistribution of the optical signal within the hexagonal cavity. The observations of this "single plasmon sieve" effect have been numerically confirmed by using the formalism of the Green Dyadic function with the simulation of the plasmonic transmittance of the signal emitted by a localized dipolar source.

The results obtained with this hybrid system, made of a single photon nanosource and a plasmonic 2D cavity, are a first step demonstrating the potential of platelets in crystalline gold for the development of more complex multi-inputs/outputs circuits for information processing with for instance the optical interconnexion between several quantum nanosources in a planar architecture.

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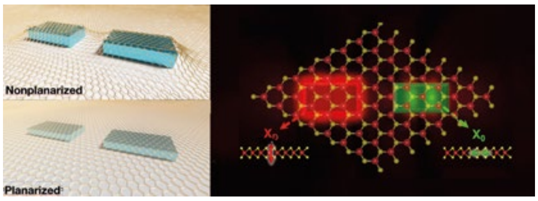
Towards nanoscale efficient light sources

Unveiling the Optical Emission Channels of Monolayer Semiconductors Coupled to Silicon Nanoantennas.
J. M. Poumirol et al., ACS Photonics 7
ACS Photonics 7 (11), 3106-3115 (2020)

The development of quantum technologies needs miniaturized light sources, based on quantum emitters such as monolayers (ML) of transition metal dichalcogenides (TMD) transferred on optically resonant dielectric nanostructures acting as nanoantennas. Such hybrid systems, aimed at controlling both the optical emission rate and the emission pattern, allow tuning parameters such as the geometry, size and environment of the nanostructures, and measuring their impact on the TMD ML optoelectronic properties. Researchers from CEMES, in collaboration with other French and Japanese groups have used different TMD (WSe2, MoSe2) transferred on silicon nanostructures (Si-NS) produced by patterning techniques. The Si-NS have the shape of two pillars of submicron size separated by a gap (30-300 nm). The TMD directly transferred on the samples adapts to the shape of the nanopillars. For comparison, a second type of Si-NS was fabricated, with the gap between the Si-NS is filled with SiO2, yielding to a flat ML lying at the sample surface.



TMD layer placed on Si nanoantennas (ACS Photonics cover, left). Spatially resolved emission in WSe2 layer on nonplanarized sample (right)

For both configurations, referred to as nonplanarized and planarized respectively, the photoluminescence (PL) mapping resulted in enhanced photon emission of the TMD ML above the nanopillars. They also allowed distinguishing the different mechanisms governing the light emission of the TMD/NS systems:

- For planarized samples, the neutral exciton characterized by a dipole oscillating in the TMD plane is observed. Both its emission rate and emission pattern are modified by the Si-NS characteristics. This allows extracting the optical influence of the nanoantenna on the emission of WSe2 and MoSe2.

- For nonplanarized samples, both antenna and strain effects can be investigated. At the edges and in the gap of the Si-NS, either WSe2 or MoSe2 experiences large tensile strain, at the origin of a decrease of the band gap energy of the TMD, thus of the local PL enhancement.

- For WSe2 on nonplanarized Si-NS, an important additional contribution to emission arises attributed to the dark exciton, corresponding to an out-of-plane oscillating dipole. For flat WSe2 ML (including the planarized sample case), the contribution of this exciton is negligible (hence its name “dark”). In present case, the vertical parts of the WSe2 ML along the Si-NS edges offer the best geometry for dark exciton detection, further improved by the antenna effect.

- These results yield to a better understanding of the mechanisms governing light emission in TMD/Si-NS systems. The light emission can be tailored by optimizing independently the nanoantenna design, the TMD material and its strain level.

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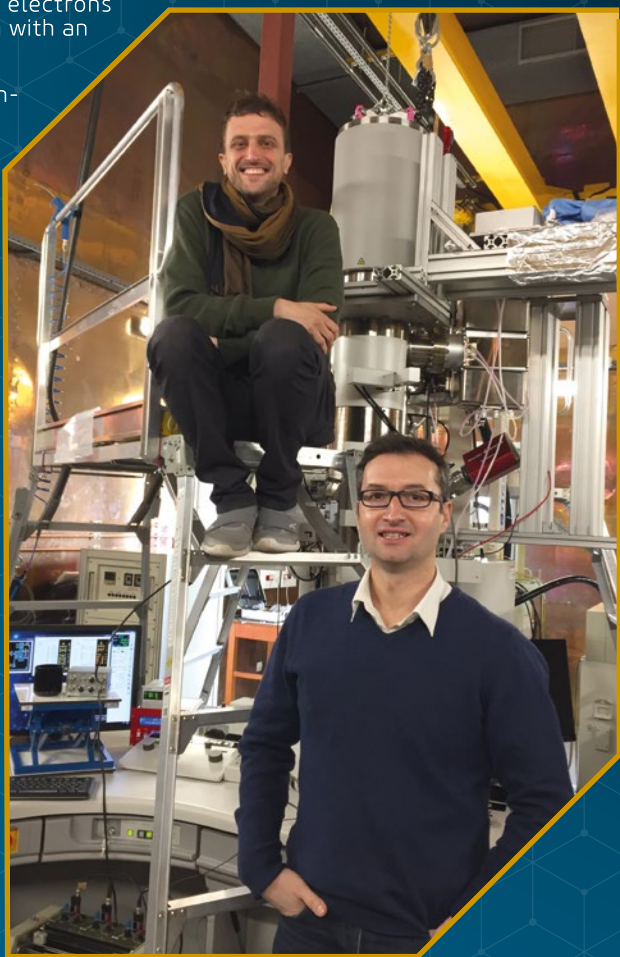
The creation of the joint CNRS-Hitachi laboratory rewarded by the 2020 Outstanding Partnership trophy

TROPHÉES
DE LA VALORISATION
DE LA RECHERCHE

On December 8, Arnaud Arbouet and Florent Houdellier from CEMES received the 2020 Outstanding Partnership trophy from Toulouse Tech Transfer, an entity whose vocation is to promote business innovation by exploiting the results of public research.

This 2020 prize rewards years of cooperation between these two CEMES scientists who have developed new applications of transmission electron microscopy (TEM) and the company Hitachi High Technologies (HHT) which saw in the work of these researchers new potential to be incorporated into its future microscopes.

TEM offers excellent spatial resolution which makes it possible to "see" atoms, but has low temporal resolution: in short, TEM makes it possible to study physical phenomena at the atomic scale at a given instant, but not to follow their evolution over time. The instrument developed by Arnaud Arbouet and Florent Houdellier overcomes this limit with a new electron gun allowing the generation of ultra-short pulses of electrons thanks to ingenious coupling of the beam with an ultra-fast laser.



The Japanese group's interest in this invention is the result of relationships that began in 2009 with CEMES and it was in July 2018 that the bond of trust forged over the years and the scientific and technological complementarity of the two entities materialized through the creation within CEMES of an original structure: a joint CNRS-HHT laboratory, the HC-IUMi (Hitachi-CNRS Infrastructure for Ultrafast Microscopy). It is this unique and fruitful partnership experience that has just been rewarded.

The construction of the ultra-fast TEM is progressing and currently at HC-IUMi the electron source of the future microscope is being modified in order to stabilize the high accelerating voltage of the electrons (300 kV), which is higher than on the prototype which enabled to validate the concept.

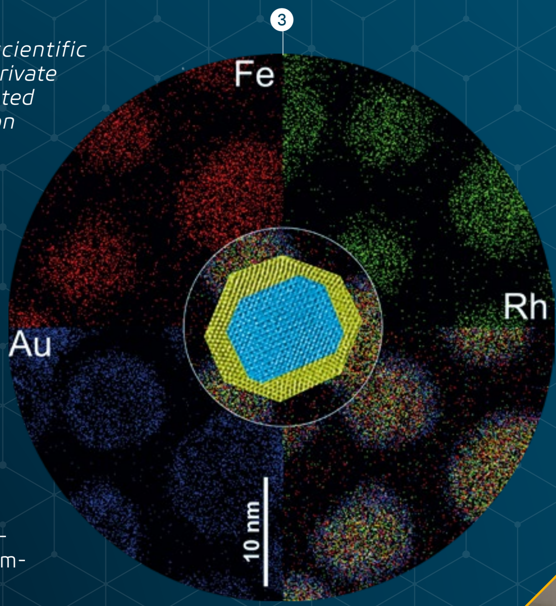
Florent Houdellier is the 2020 laureate of the CNRS crystal medal *

The prize rewards the methodological and instrumental developments Florent Houdellier leads in the field of TEM with remarkable success which gives him international visibility. Florent Houdellier first successfully developped an original electron source for cold field emission (C-FEG) using carbon nano-cones synthesized in the group of Marc Monthioux at CEMES. After this first success, he tackled another project, jointly with Arnaud Arbouet of the NeO group, which aimed at the construction of the first coherent TEM with pulsed femtosecond source allowing to perform experiments resolved in time in pump-probe mode. This second highly challenging project was a success that contributes the skills and quality of F. Houdellier's instrumental developments to be known beyond the borders of Europe. In particular, he was the 2019 winner of the prestigious "Ernst Ruska" prize from the German microscopy society.)

** The crystal medal is handed out to engineers, technicians, and administrative staff whose creativity, expertise, and sense of innovation have contributed, alongside researchers, to the advancement of knowledge and the excellence of French research.*

Ion implantation and thin films/nanoparticles growth facilities at CEMES

The Implantation and Growth platform in CEMES is open to all the scientific community including researchers from both academic laboratories and private companies. It aims at providing expertise, tools and instruments dedicated to nanotechnology and nanomaterials: ion implantion and deposition allow to synthesize nanoparticles (embedded in a matrix or deposited on a free surface), to deposit thin and ultra thin films, to irradiate them and to generate controlled defects in materials.



Experimental techniques

- Implantation: the ion implanter is a Varian one retrofitted in 2015 with a specificity: An Ultra Low Energy (ULE) stage designed and fabricated by CEMES engineers and researchers that allows implantation in an especially wide ions energy range of 0.6 keV to 200 keV. This unique machine for ULE-Ion Beam Synthesis (IBS) allows synthesizing semiconducting and metallic nanocrystals into dielectric thin layers. The choice of the Ultra-Low Energy (<5keV) aims to obtain nanocrystals at a well-controlled depth close to the free surface and/or embedded in thin layers.

  In the field of innovative semiconductor devices, the ion implantation is used at CEMES to change the properties of specific materials by inducing deformations and stress or by creating controlled defects. The ion implanter is also used here to irradiate thin films in order to modify their magnetic properties.

- Growth: The platform provides two UHV sputtering machines, a Plassys and a Mantis: both are equipped with sources dedicated to the atomically controlled growth of thin and ultrathin films. To generate and control original properties in the developed nanostructures, the new Mantis equipment, acquired in the frame of the CPER NANOMAT (2015-2020), is also equipped with a very innovative source allowing the synthesis of nanoparticles in the gas phase, with well controlled size, composition and morphology, and their deposition on various substrates. This equipment also includes analysis technical as an in situ RHEED, an ellipsometer, a Residual Gas Analyzer (RGA),a pyrometer and a Quartz Microbalance.

  In addition to these synthesis techniques, facilities are available to perform high temperature annealing processes up to 1250°C: Rapid thermal Annealing (Annealsys) and Conventional furnace (Carbolite).

People skills

- *Development of custom experimental setups/process related to ion implantation, deposition or synthesis of nanoparticles.*
- *Expertise and Technical support to the users of the platform.*

1 — *Sputtering device Mantis*

2 — *Plasma in the UHV Mantis chamber*

3 — *Three metalic nanocrystals FeRh, FeRh@Au embedded in dielectrics*

4 — *AFM image of the blistering of silicon after sequential H and He ion implantations though a stencil mask*

5 — *Ion implanter equiped with a Ultra Low Energy (ULE) module*

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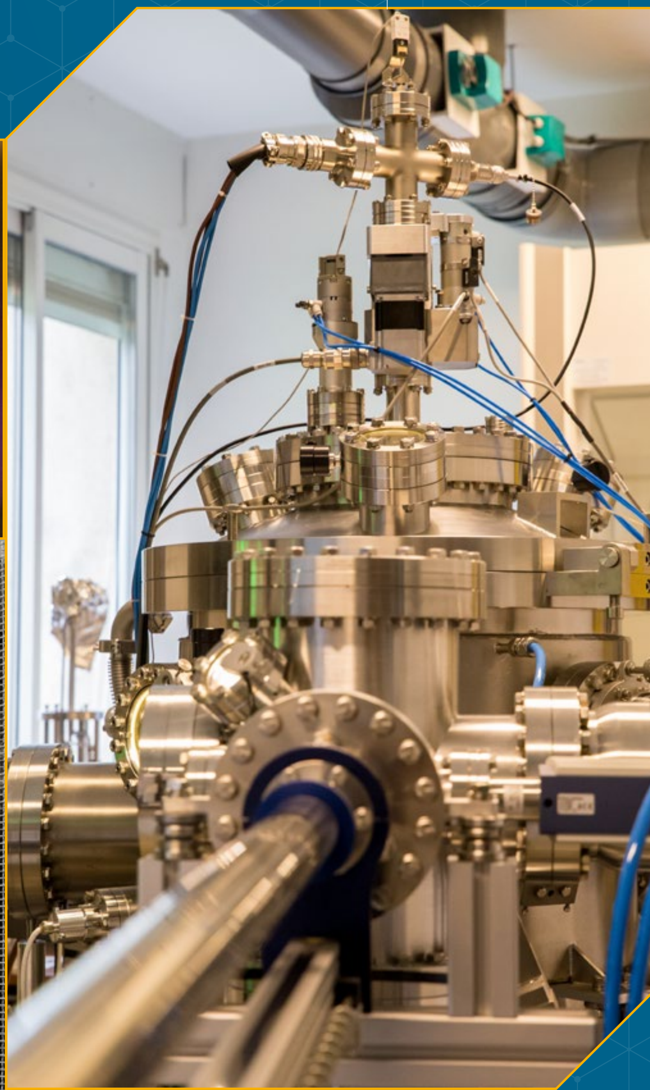

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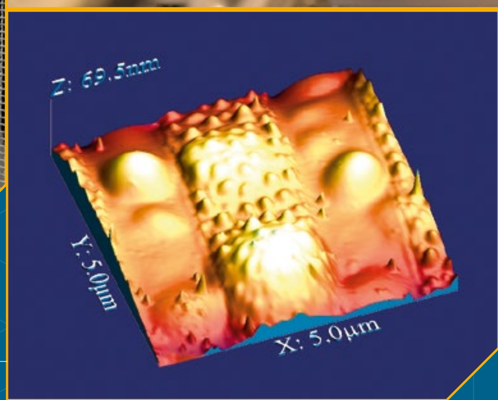

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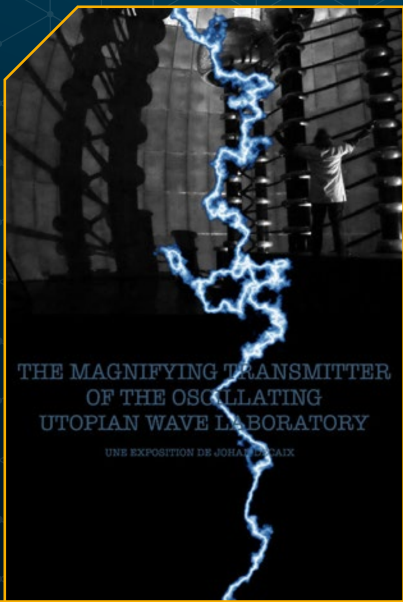
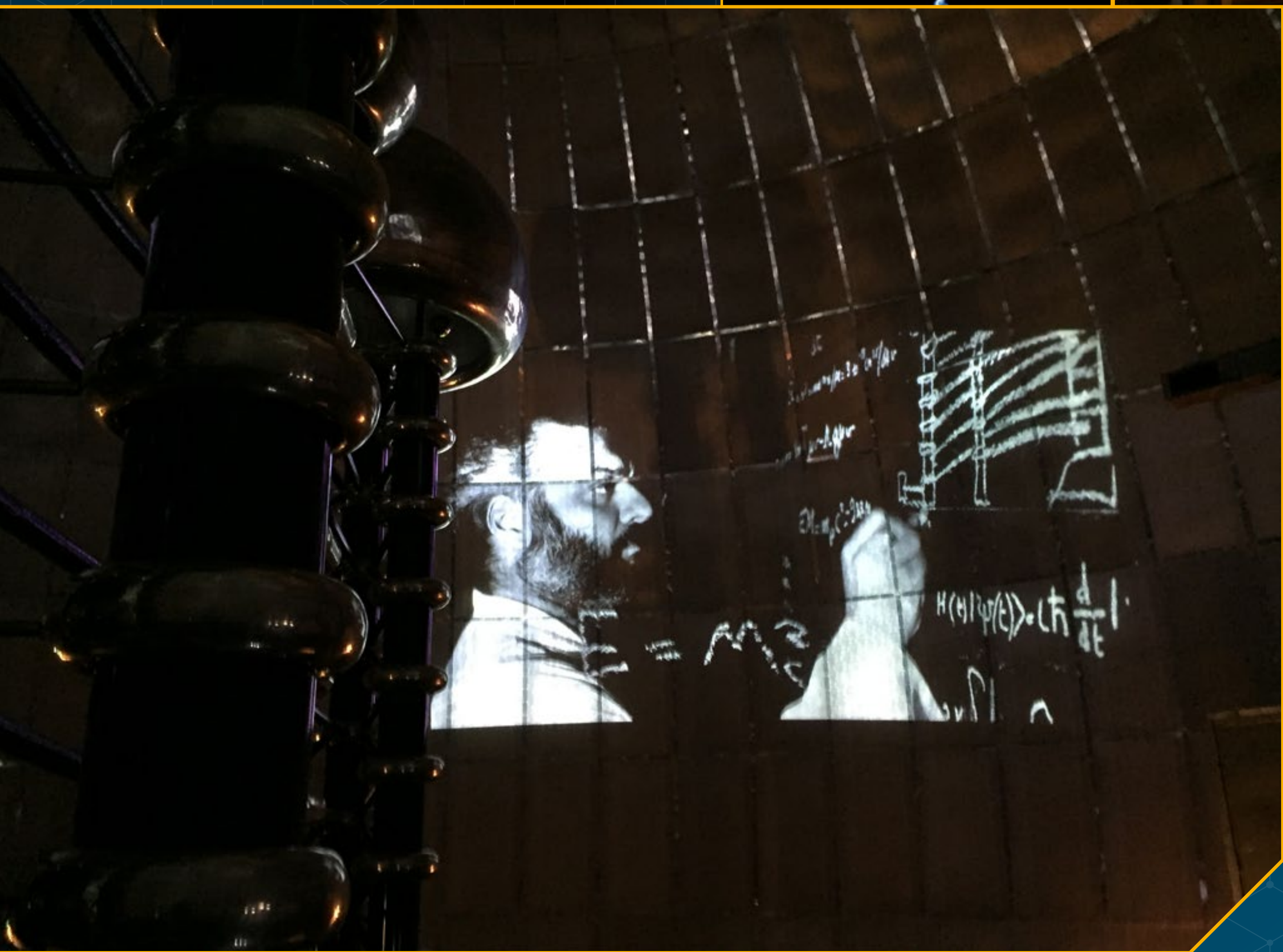

THE MAGNIFYING TRANSMITTER
OF THE OSCILLATING
UTOPIAN WAVE LABORATORY



"The magnifying transmitter of the oscillating utopian wave laboratory": an exposition of the artist Johan Decaix at CEMES

CEMES and the contemporary art museum "Musée des Abattoirs" in Toulouse decided to start a partnership. With the help of the CNRS Regional Delegation, we organized an artist residency at CEMES followed by an exhibition of the work of the selected artist in the famous "La Boule" building.

The "Fond Régional d'Art Contemporain" (FRAC) Midi Pyrénées selected the artist Johan Decaix who thus stayed in the laboratory for 2 weeks to exchange with CEMES scientists and carry out his work in the laboratory. The result of this work was presented in the exposition "The magnifying transmitter of the oscillating utopian wave laboratory ". The installation initially planned for April 2020 was moved to October of this year and received the visit of more than 250 visitors during the six weeks of the exhibition.

This exhibition is the result of a partnership between the "FRAC - Musée des Abattoirs" in Toulouse and the CEMES / CNRS laboratory and was part of the "Fête de la science 2020".

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