



C'Nano EAST Youth Meeting

June 26th, 2023



Programme & Abstracts

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C'Nano EAST Youth Meeting

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PROGRAMME

Horaire : 14h – 17h

Format : visioconférence

14h00 – Accueil et présentation du C'Nano par Michel VERGNAT (Université de Lorraine – C'Nano EST)

14h15 – Présentations des doctorant.e.s

- DELL'OVA Florian (Université de Bourgogne – ICB)
- DAINONE Pambiang Abel (Université de Lorraine – IJL)
- VERNEUIL Augustin (Université Technologique de Troyes – L2n)
- ZAAROUR Ahmad (Université de Haute-Alsace – IS2M)

15h15 – Présentation des travaux de Konstantin MALCHOW (ICB) lauréat du Prix C'Nano EST :

« Light from electrically driven nanogaps »

15h30 – 15h45 : Pause

15h45 – Présentations des doctorant.e.s

- HERNANDO ABAD Eduardo (Université de Bourgogne – ICB)
- KFOURY Patrick (Université de Lorraine – LCP-A2MC)
- ZALLOUZ Sirine (Université de Haute-Alsace – IS2M)

16h30 – Conférence de Andrey KLYMCHENKO (CNRS-LBP) dans le domaine de la nano-médecine :

« Bright fluorescent polymeric nanoparticles for bioimaging and diagnostics »

17h00 – Clôture par Nadine MILLOT (Université de Bourgogne – C'Nano EST)

ABSTRACTS DISPONIBLES CI-DESSOUS



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Abstract of Konstantin MALCHOW

Bourgogne University & Interdisciplinary Carnot de Bourgogne lab./

ETH Zurich Institute of electromagnetic fields

C'Nano 2022 East PhD Thesis Prize



C'Nano EAST Youth Meeting

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First Name, Family Name: Konstantin MALCHOW

Title : Post-doc

Employer & Thesis Laboratory: Université de Bourgogne & Laboratoire Interdisciplinaire Carnot de Bourgogne/
ETH Zurich Institute of electromagnetic fields

Supervisor(s): Alexandre Bouhelier

Light from electrically driven nanogaps

Abstract

The quest for more energy efficient on-chip transmission has driven the search of small electrically modulable light sources with sizes comparable to current on chip transistors [1]. My thesis is interested in the light emission of a class of very small and surprisingly simple structures: Two metal electrodes separated by a small dielectric gap, see Figure 1. In spite of their simple structure these devices show a variety of different physical behaviors and have been investigated with growing interest in recent years [2]. In my thesis I continue this line of research by presenting different experimental approaches to characterize and analyze their radiation. In my thesis I expand the study of such junctions to larger gaps, adding new emission mechanisms to their arsenal. Larger gaps show an intricate current behavior with a history dependent conductance and light emission triggered by electrochemical dynamics involving field-induced electroluminescent defects.

However also the opposite limit of ultrasmall gaps featuring overbias light emission, characterized by a violation of the standard quantum limit, is still far from being fully understood [3]. I will present second order photon correlation measurements on the nonlinear photoluminescence in metals as a preparatory step to characterize electrically driven overbias emission [4].

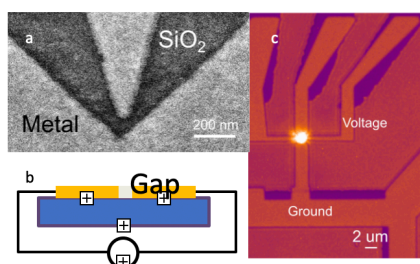


Figure 1 a) SEM image of a pristine metal insulator metal junction sitting on top of a standard glass cover slip. b) A sketch of the horizontal cut together with the electrical connections. c) When driven by an electrical voltage light is emitted in the gap region of the metal insulator metal junction.

[1] D. A. Miller, "Device requirements for optical interconnects to CMOS silicon chips," Optics InfoBase Conference Papers, vol. 97, no. 7, 2010., D. A. Miller, "Attojoule Optoelectronics for Low-Energy Information Processing and Communications," Journal of Lightwave Technology, vol. 35, no. 3, pp. 346–396, 2017, A. H. Atabaki, et al. "Integrating photonics with silicon nanoelectronics for the next generation of systems on a chip," Nature, vol. 556, pp. 349–354, apr 2018. [12] D. A. Miller, "Rationale and challenges for optical interconnects to electronic chips," Proceedings of the IEEE, vol. 88, no. 6, pp. 728–749, 2000.

[2] M. Parzefall and L. Novotny, "Optical antennas driven by quantum tunneling: a key issues review,"

Reports on progress in physics. Physical Society (Great Britain), vol. 82, no. 11, p. 112401, 2019.

[3] M. Buret, et al., "Spontaneous Hot-Electron Light Emission from Electron-Fed Optical Antennas," Nano Letters, vol. 15, no. 9, pp. 5811–5818, 2015, P.-J. Peters et al. , "Quantum Coherent Multielectron Processes in an Atomic Scale Contact," Physical Review Letters, vol. 119, p. 066803, 2017

[4] K. Malchow and A. Bouhelier, "Photon bunching of the nonlinear photoluminescence emitted by plasmonics metals," Journal of the Optical Society of America B, vol. 38, p. 576, feb 2021.

Keywords : tunnel junction; memristors, overbias light emission ; nonlinear photoluminescence; nano-optics; electro-optical antennas



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Abstracts from C'Nano East PhD & Postdoc students



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First Name, Family Name: Florian DELL'OVA

Title PhD student 4th Year

Employer & Laboratory: CNRS & ICB

Supervisor(s): Alexandre BOUHELIER

City: Dijon

Title: Nonlinear photoluminescence from patterned ITO thin films

Abstract

Nonlinear photoluminescence (NPL) is known as a property of noble metals to generate a broad up-converted signal under near-infrared excitation [1]. This broad emission is spanning the whole visible region decaying towards the short wavelength range, see Figure 1. For low laser irradiance, NPL emission is attributed to a nonlinear absorption process, while at large power density, it is the radiative signature of an electron bath brought at temperatures exceeding thousands of degrees [2].

In the realm of nonlinear transparent conductive oxides, indium tin oxide (ITO) is a widely used material [3] sustaining a free-electron system with dispersive properties enabling controllable nonlinear properties notably in the context of epsilon-near-zero material [4]. Here we demonstrate the emergence of NPL emission from ITO-coated glass substrate [5]. The signal shares strong similarities with that commonly detected from noble metals. The emission is activated by the action of a focused Ga ion beam (Ga-FIB) on the surface, which modifies the electronic band structure of the film. An in-depth analysis of the NPL dependency on laser intensity unambiguously unveils the role of a heated electron gas in the emission process.

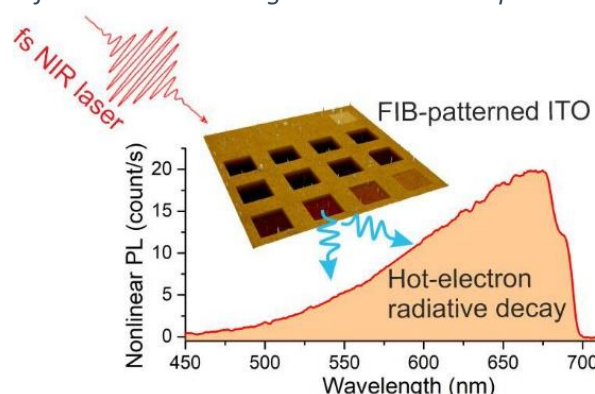


Figure 1: Scheme of NPL emission emerging from Ga-FIB-patterned thin ITO layer under NIR pulsed laser excitation.

1. K. Malchow, and A. Bouhelier, J. Opt. Soc. Am. B 38, 576-583 (2021)
2. L. Roloff, P. Klemm, I. Gronwald, R. Huber, J. M. Lupton, and S. Bange, Nano Lett. 17, 7914–7919 (2017)
3. A. Capretti, Y. Wang, N. Engheta, and L. Dal Negro, ACS Photonics 2, 1584-1591 (2015)
4. G. K. Dalapati, *et al.*, J. Mater. Chem. A 9, 16621–16684 (2021)
5. F. Dell'Ova, *et al.*, ACS Applied Optical Materials 1, 244-25 (2023)

Keywords : Indium Tin Oxide, Nonlinear Photoluminescence, Hot Electrons, Focused Ion Beam.



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First Name, Family Name: Pambiang Abel DAINONE

Title: PhD student 2nd

Employer & Laboratory: Université de Lorraine & IJL

Supervisor(s): Dr Yuan LU and Pr Mathieu STOFFEL

City: Nancy

Electrical switching of circular polarization of spin light emitting diode

Abstract

Direct high-speed modulation of circular polarization (P_c) of coherent light will open the way for new communication technology and offers the possibility to overcome the main bottleneck of the optical telecommunications. An innovative way to modulate the circular polarization of a light source is to inject a spin-polarized current from a ferromagnetic spin-injector and to take advantage of spin-photon polarization conversion in semiconductor to transform spin information into optical polarization information. To realize P_c modulation, one emerging challenge is to electrically modulate the spin-injector magnetization in order to control the output circular polarization. Here, by using spin-orbit torque (SOT) with spin Hall effect to control the spin injector magnetization, we report for the first time to achieve electrical control of the circular polarization of light emitted from a quantum dot-based light emitting diode (LED) at room temperature. The critical switching current is found to be as low as $9 \times 10^6 \text{ A/cm}^2$, which is sufficient low to overcome the LED substrate shutting effect. The standard LED with such kind of SOT injector shows a new record of high circular polarization (40%) at room temperature with zero applied magnetic field. In the SOT spin LED, the circular polarization can be modulated between $\pm 30\%$ at 300K after pulsed current switching injector magnetization. A repetition of more than 60 times do not reveal any degradation at the injector/semiconductor interface. Our achievement will directly contribute the implementation of the new optical telecommunication technology with P_c modulation.

Keywords : Spin injection; Light emitting diodes; spin orbit torque



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First Name, Family Name: Augustin Verneuil
Title: PhD student, 2nd year
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City: Troyes, France
Email: augustin.verneuil@utt.fr

Optimizing the extraction of second-harmonic light from a plasmonic array

Abstract

In recent years, plasmonic metasurfaces have been employed to enhance nonlinear upconversion rates, with the best results being obtained using two surface lattice resonances (SLR) at the fundamental and harmonic wavelengths. However, these designs are often based on sub-wavelength arrays to couple local modes to SLRs, only allowing the 0th diffraction order to be collected.

Here, we report on a periodic, plasmonic metasurface whose pitch can be optimized to allow maximal extraction of the second-harmonic generation (SHG) excited in the telecom wavelength (1550 nm) and emitted by the individual meta-atom. In particular, we found that the SHG from the first horizontal diffraction order can be enhanced about a factor 2 by optimizing the metasurface pitch (see Figure 1a).

We confirmed this by experimentally reconstructing the SHG radiation pattern of a single nanoantenna from different diffraction orders (see Figure 1b) through angular-resolved excitation (see Figure 1c). We obtained excellent agreement with the simulated radiation pattern using the finite elements method. In addition, the emission of a single particle in the Fourier plane was also directly imaged (see Figure 1d), yielding again very good agreement with the simulation.

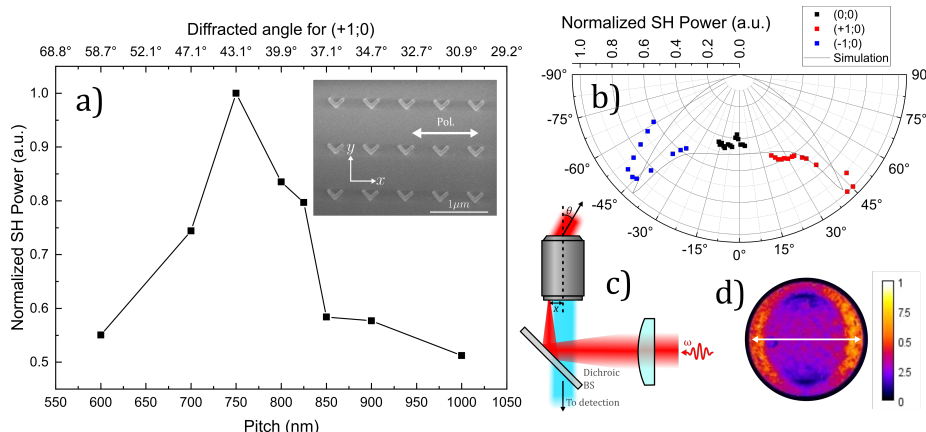


Figure 1: (a) SH power emitted at 775 nm by the metasurface in the (+1;0) diffraction order, measured as a function of the pitch in the x axis. Inset: SEM image of the metasurface, the double arrow represents the incident polarization. (b) Simulated and reconstructed emission pattern in the horizontal axis of the BFP (see cut in fig. 1d). (c) Sketch of the experimental setup for tilted excitation used in fig. 1b: a laser is focused on the back pupil of the objective, giving near collimated excitation. (d) Normalized SH power (a.u.) of a single nanoantenna in Fourier space.

Keywords : Plasmonics, Nonlinear optics, Fourier optics, Optimization



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First Name, Family Name: Ahmad ZAAROUR

Title : PhD student 2nd year

Employer & Laboratory: Universite de Haut Alsace & Institut de Science des Matériaux de Mulhouse (IS2M)

Supervisor(s): Laurent SIMON

City: Mulhouse

Flat band and Lifshitz transition in long-range-ordered supergraphene obtained by Erbium intercalation

We report the observation of a heavily electron-doped graphene up to the Lifshitz transition obtained solely by the intercalation of Erbium atoms [1]. A new long range ordered hexagonal supergraphene has been observed by Scanning Tunneling Microscopy (STM) Fig. 1(a). The ARPES measurements show a strong linear dispersion around K points with a shift of Dirac point energy by about 1.72 eV below the Fermi level Fig. 1(b) (which is the highest doping level ever reported so far) and a wide flat band around the M point Fig. 1(c). The measured Fermi surface indicates that the Lifshitz transition has been reached with an electron density of $5.1 \pm 0.8 \times 10^{14} \text{ cm}^{-2}$ Fig. 1(d). XPS measurements show that the Er atoms are free standing in between the graphene layer and the substrate and keep their metallic character. On the basis of Tight-Binding calculations we propose a theoretical model where diluted ordered Erbium atoms act as impurities under the graphene and induce a local-density-of-states perturbation, as for a kekulé order, which is usually observed for a Fermi level around the Dirac point [2]. We also discuss the possible effects of a spin-orbit coupling on the topology of the Fermi surface and the flattening of the band around M at Lifshitz transition.

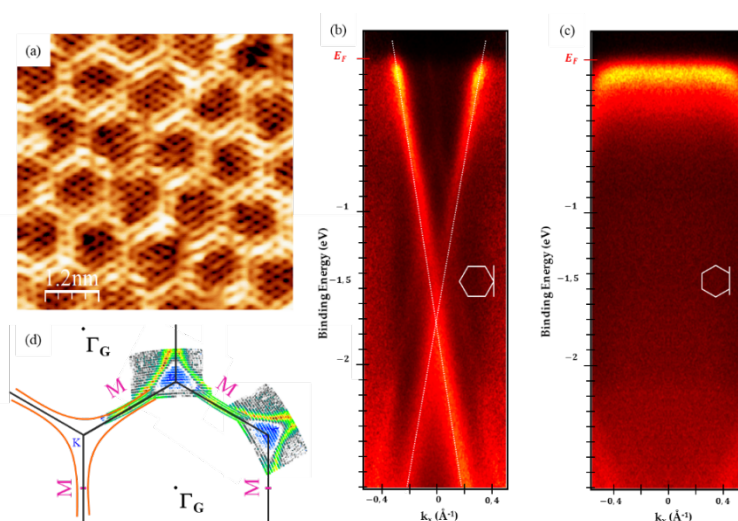


Figure 1: **(a)** Topographic STM image of the (5.75×5.75) R19O-G superstructure; $6 \times 6 \text{ nm}^2$. ARPES measurements of the dispersion band around K point in **(b)** and around M point in **(c)**. **(d)** Fermi surface of the system.

Keywords: Graphene, Intercalation, Flat-band, Lifshitz transition.



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First Name, Family Name: Eduardo HERNANDO ABAD

Title : PhD student 3rd year

Employer & Laboratory: Université de Bourgogne & Laboratoire Interdisciplinaire Carnot de Bourgogne

Supervisor(s): Lucien SAVIOT, Frédéric BOUYER

City: Dijon

Surface modification of mesoporous silica nanoparticles to enhance colloidal stability for theranostic purposes

Abstract

MCM-41 silica nanoparticles (MCM-41-MSNs) are frequently used as a platform for theranostic applications. However, few studies have focused on their colloidal stability despite its tremendous importance considering that MSNs are usually administrated by the IV route. In this study, two approaches to enhance the colloidal stability of MCM-41-MSNs in physiological fluids are proposed: grafting of branched copolymers (MSN-NH₂@C33s) or ultrasmall gold nanoparticles (MSN-NH₂@Au@DTDTPA).

Amino-functionalized MCM-41-MSNs of about 150 nm are obtained by a co-condensation approach using a mixture of TEOS and APTES as silica precursors and CTAB as a template [1]. Grafting of branched polymer (C33s) or ultrasmall gold nanoparticles (Au@DTDTPA) [2] exhibiting carboxylic groups is carried out using coupling agents (EDC/NHS). All the nanosystems are characterized by TEM, STEM, XRD, N₂ physisorption, TGA, Raman and FT-IR. The colloidal stability is evaluated by DLS in physiological fluids.

For both systems, we show that a minimum amount of Au@DTDTPA or C33s grafted onto the MSNs is required to obtain MSN suspensions stable for several days, since pristine MSNs and MSNs physically mixed with Au@DTDTPA or C33s are not stable.

The stable suspensions are used to conduct a preliminary evaluation of the cytotoxicity of MSN-NH₂@C33s and MSN-NH₂@Au@DTDTPA in the presence and absence of an anticancer drug in different cancer cell lines.

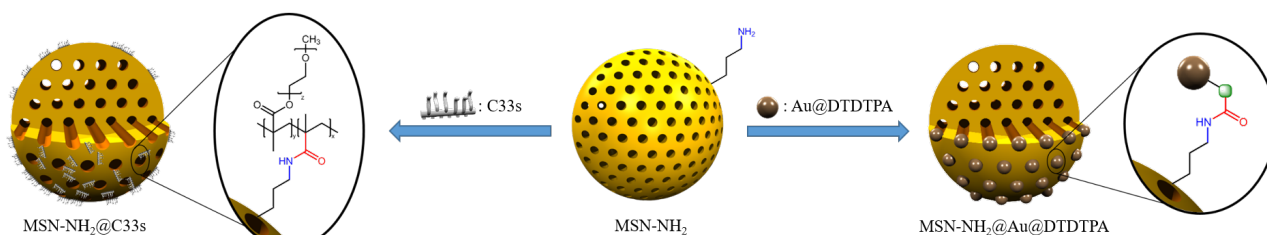


Figure 1. Schematic representation of the nanoassemblies prepared after surface modification by grafting of C33s (left) and by grafting of Au@DTDTPA (right).

[1] M. Varache et al., *Journal of Non-Crystalline Solids*, 2015, 408, 87–97.

[2] P.-J. Debouttière et al., *Adv. Funct. Mater.*, 2006, 16, 2330–2339.

Keywords : mesoporous silica nanoparticules – colloidal stability – grafting – biomedical applications



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First Name, Family Name: Patrick KFOURY

Title : PhD student 2nd year

Employer & Thesis Laboratory: University of Lorraine. Laboratory of Chemistry and Physics & Multi-scale Approach of Complex Media (LCP-A2MC)

Supervisor(s): Yann BATTIE, Nouari CHAOUI, and Aotmane EN NACIRI

City : Metz

Plasmonic nanoparticles growth in polymeric thin films in situ monitored by spectroscopic ellipsometry

Abstract

Silver nanoparticles (Ag NPs) present much more interesting physical properties than their bulk counterparts. Indeed, Ag NPs exhibit plasmon resonances induced by the collective oscillation of their free electrons. The plasmon bands of Ag NPs depend on their size, their shape and their host medium. The growth of metallic NPs in thin films gives rise to nanocomposite materials with interesting optical properties and applications such as sensors, photovoltaic cells, non-linear optical activity-based devices, SERS, and optical filters.

The purpose of this study is to investigate the thermal growth of silver nanoparticles in Poly -vinyl alcohol matrix by in-situ spectroscopic ellipsometry in the visible spectral range. Each spectrum is analyzed with the Shape Distributed Effective Medium Theory (SDEMT) model. This procedure allows the determination of the film thickness, the shape distribution and the volume fraction of the NPs as well as the effective dielectric function of the nanocomposite film during the annealing process. In accordance with transmission electron microscopy measurements, we found the nanoparticles remain almost spherical during the annealing. We show that the films exhibit a plasmon resonance which progressively increases in amplitude during the annealing. Due to the evaporation of the solvent, the film thickness decreases during the annealing. The growth mechanism of silver NPs is elucidated by analyzing the variation of the volume fraction of nanoparticles. We demonstrate that the nanoparticle growth is governed by Oswald's ripening process.

Keywords : Plasmonic Nanoparticles; Spectroscopic Ellipsometry; Polyvinyl Alcohol; SDEMT; Oswald's Ripening



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First Name, Family Name: Sirine ZALLOUZ

Title: Postdoc

Employer & Laboratory: IS2M

Supervisor(s): Jean-Marc LE MEINS, Camélia MATEI GHIMBEU

City: Mulhouse

Optimization of nano-sized Carbon/ FeS_2 electrochemical performance: Impact of ageing in air and in electrolyte

Transition metal sulfides are interesting materials as electrodes for electrochemical supercapacitors owing to their high theoretical specific capacity. In particular, pyrite (FeS_2) is attractive due to its eco-friendly nature and good electronic conductivity. However, the common synthesized materials have large particles size and nanoparticles are seldom reported despite their great potential in electrochemistry. Herein, mesoporous carbon and FeS_2 are combined to provide greater porosity and conductivity with the aim to obtain FeS_2 nanoparticles suitable for supercapacitor application. The hybrid C/FeS_2 materials are prepared via a one-pot synthesis including green biodegradable carbon precursors, cysteine as sulfur source and an iron source, followed by activation and sulfidation. The effect of these thermal treatments at various temperatures and times on the FeS_2 particle size and the hybrid porosity was investigated. The particles of FeS_2 were homogeneously distributed in carbon and show very small size (Figure a). The materials were then used as electrodes in 2-electrode symmetric supercapacitors with 2 M KOH (Figure b). The ageing of FeS_2 nanoparticles during cycling and in air over time (4 months) was studied. Under air, a progressive transformation of FeS_2 in hydrated iron hydroxy sulfate ($\text{Fe}(\text{SO}_4)(\text{OH})\cdot 2\text{H}_2\text{O}$) with a significant morphology modification (particle size increase) is observed. Such compounds proved to be detrimental to the performance, resulting in a drastic decrease in capacitance. Differently, the ageing of FeS_2 during cycling although modifies the particle shape and size, had a positive impact on the performance. A gradual enhancement of electrochemical behavior occurred and could be associated with the formation of a supplementary iron oxyhydroxides (FeOOH) phase.

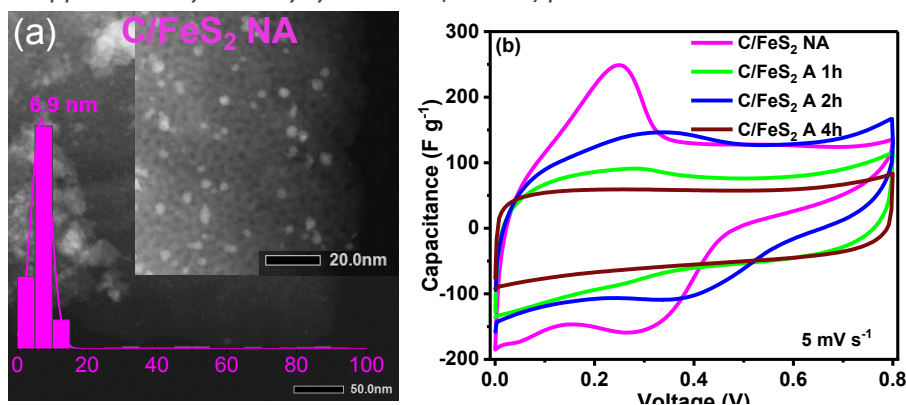


Figure: (a) STEM image of C/FeS_2 NA (non-activated) with the particle size distribution (b) cyclic voltammetry of the different C/FeS_2 materials

Keywords : supercapacitor, carbon composite, FeS_2 , nanoparticles, ageing effect



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Andrey KLYMCHENKO (CNRS-LBP)

**« Bright fluorescent polymeric
nanoparticles for bioimaging and
diagnostics »**



C'Nano EAST Youth Meeting

June 26th, 2023



First Name, Family Name : Andrey KLYMCHENKO

Title : CNRS researcher

Employer & Laboratory: CNRS - LBP

City : Strasbourg

Bright fluorescent polymeric nanoparticles for bioimaging and diagnostics

Abstract

Dye-loaded fluorescent polymeric nanoparticles (NPs) appear as an attractive alternative to inorganic NPs, such as quantum dots (QDots). Controlled small size of NPs can be achieved by nanoprecipitation of specially designing hydrophobic polymers bearing few charged groups. Confining large number of dyes with bulky counterions within small polymeric nanoparticles makes the latter particularly bright and enable phenomenon of giant light-harvesting allowing efficient Förster resonance energy transfer (FRET). Functionalization of these NPs with DNA yields FRET-based color switching nanoprobes for nucleic acids with single-molecule sensitivity and compatibility with RGB camera of a smartphone, important for cancer diagnostics. We also found that the energy transfer between two NPs connected by DNA duplexes does not follow canonical Förster law, allowing efficient long-range FRET at distances up to 20 nm, important for construction of ultrasensitive biosensors. Our NPs enabled detection of microRNA cancer markers as well as SARS-Cov-2 viral RNA. When applied to cells, the small size of NPs was found essential for their free diffusion in cytosol and detection of intracellular RNA. At the animal level, the high brightness of NPs enabled single-particle tracking in the mice brain and visualization of crossing the blood-brain barrier. The developed small dye-loaded polymeric NPs open the route to ultrabright tools for sensing and tracking of biomolecules and cells in biology and medicine.

Keywords : fluorescent polymeric nanoparticles, particle assembly, energy transfer, optical sensing, fluorescence microscopy