SORBONNE UNIVERSITÉ

CHINA SCHOLARSHIP COUNCIL

Appel à projets
Campagne 2022
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Title of the research project :

Plasmonic nanocrystals: from synthesis to optoelectronic applications

Thesis supervisor (HDR) :

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Research Unit

Name : LPEM (Laboratoire de Physique et d'Etude des Matériaux)

Code *(ex. UMR xxxx)* : UMR 8213

Doctorate School

Thesis supervisor's doctorate school (candidate's futur doctoral school) : ED397

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :

Total: 1,3 (1 (50% 2019-2022); 1 (50% 2018-2022); 1 (30% 2021-2024))

Joint supervisor :

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Research Unit

Name : LPEM (Laboratoire de Physique et d'Etude des Matériaux)

Code *(ex. UMR xxxx)* : UMR 8213

École doctorale

Joint supervisor's doctorate school :
ED397

Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :
Total: 0,5 (1 PhD student (50% supervision, 2019-2022))

Joint supervisor :

Name :

Surname :

Title :

email :

Professional adress :
(site, dresse, bulding, office…)

Research Unit

Name :

Code *(ex. UMR xxxx)* :

École doctorale

Joint supervisor's doctorate school :

Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :

PLASMONIC NANOCRYSTALS:

FROM SYNTHESIS TO OPTOELECTRONIC APPLICATIONS

Advisor Name: Dr. Zhuoying Chen; Dr. Charlotte Tripon-Canseliet

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Surface plasmon resonance (SPR) is an important physical phenomenon that has aroused extensive fundamental and practical interest since their first observation. When an incident light is shone onto a conductive nanostructure, the confined free electrons oscillate collectively with respect to the positively charged nuclei with the same frequency as the radiation. The resonance of such oscillation (termed "localized surface plasmon resonance", LSPR) produces intense and well-defined spectral absorption as well as strong localized electromagnetic near fields. LSPR subsequently decays either radiatively by re-emitting a photon or non-radiatively through Landau damping generating hot carriers on a time scale ranging from 1 to 100 fs after LSPR excitation. Hot carriers, if not extracted through a specific device structure, will then quickly redistribute their energy towards lower energy electrons via electron-electron scattering followed by thermalization with the lattice and heat transferred to the surroundings on a time scale ranging from 100 ps to 10 ns. Plasmonic nanostructures are therefore both hot carrier generators and efficient mediums to convert photons to thermal energy [C. Clavero, *Nat. Photonics*, 8, 95-103 (2014); H. Chen et al. *Chem. Soc. Rev.*, 42, 2679-2724 (2013)].

Specifically, this PhD thesis will involve the following two aspects:

<u>(1) Colloidal synthesis:</u> Colloidal plasmonic nanocrystals (NCs), formed by bottom-up synthesis with rational design, belong to the above-mentioned nanostructures capable to exhibit intense LSPR upon photoexcitation. The magnitude and the optical spectral features of the extinction cross-sections of plasmonic metallic NCs can be fine-tuned by controlling the shape, size, and dielectric environment of the NCs. Their extinction cross-sections are contributed to by two components: absorption cross-sections and scattering cross-sections, with the relative proportion between the two depending on the NC volume for a specific type of NC. For example, by controlling the NC volume (e.g. by controlling NC dimensions) from the synthesis, it is thus possible to have either large NCs favoring scattering (an example shown in **Figure 1c**), or small NCs favoring the absorption (which contributes to the plasmonic antenna effect and the concentration of near-field) (**Fig. 1a**), or medium-size NCs where both effects have similar weights (**Fig. 1b**).

In terms of compositions, here, three different compositions: gold (Au), silver (Ag) and aluminum (Al) are selected to be the main NC compositions under study. Each of them has their advantages and disadvantages. For example, Au and Ag are noble metals and various colloidal methods to synthesize Au and Ag spherical and anisotropic (e.g. rods, nanoprisms) NCs are well-documented in the literature (results from our group shown in **Figure 2**), resulting in rich tuning knobs on the desired LSPR wavelength positions and the scattering/absorption ratio within the optical extinction. For Ag, despites its lower material cost and brighter perspectives for large-scale industrial application, it is in general less stable than Au unless grown with a well-protected surface. We thus plan to explore Ag and core/shell Ag/oxide or Ag/metal in the project. Finally, concerning the system of plasmonic Al, it is by far a less investigated system by comparison to Au and Ag. Much still needs to be done in this system. In comparison to Au and Ag, it exhibits a clear advantage as the most abundant metal in the Earth's crust. Very importantly, plasmonic Al NCs possess a size-tunable LSPR that spans from the UV to visible spectrum (**Fig.1e**). But studies carried out on the colloidal synthesis of Al NCs are, however, less matured than studies done on Au or Ag NCs, with successful methods typically requiring rigorous air and water-free conditions. Concerning this thesis proposal, while large Al NCs (diameter > 50 nm) can be a low-cost alternative to Ag and Au NCs with tunable scattering and absorption properties in the visible spectrum, we are also interested in the visible-transparent but UV-absorbing properties of small Al NCs.

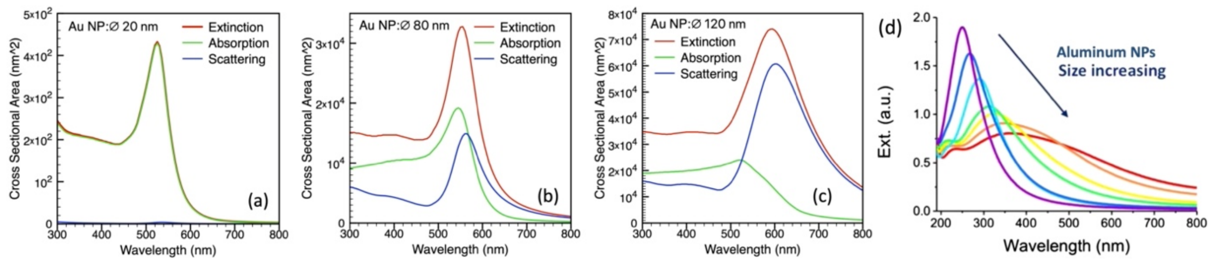

Figure 1. *We performed numerical simulation based on Mie theory on the extinction, absorption and scattering cross-sections of a spherical plasmonic gold NC with a diameter of (c) 20 nm, (d) 80 nm, and (e) 120 nm. (f) Experimental extinction spectra of different size of aluminum (Al) NC aqueous solutions (image (f) taken from S. Yang et al, CCS Chem. 2, 516 (2020)).*

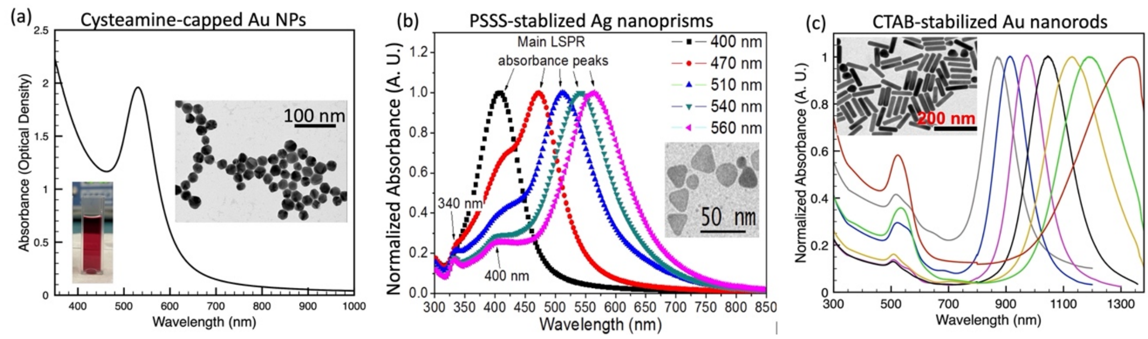

Figure 2. *(a-c) Various plasmonic NCs synthesized by our team in LPEM laboratory: (a) Cysteamine-capped Au NPs; (b) Citrate-stabilized Ag seed NPs (black) and nanoprisms (color) where the morphology and the extinction properties of the nanoprisms can be tuned by adjusting the amount of seeds during growth; (c) CTAB-stabilized Au NRs where their aspect-ratio and the extinction properties can be tuned by adjusting various growth parameters such as seed amount, surfactant type and amount, and the PH values of the growth solution.*

<u>(2) Coupling of plasmonic NCs with optoelectronic devices:</u> The plasmonic NCs synthesized in this thesis will then be inserted rationally into different optoelectronic devices, including photovoltaic (PV) cells, photodetectors (PDs), and microwave photoconductive switches (PCS), on all of which our research teams have experience to fabricate. Different possible types of beneficial mechanisms can be involved when plasmonic NCs are incorporated into these devices: (1) Plasmonic NCs can act as a subwavelength light scattering elements, increasing the optical absorption paths in the photoactive material of the device; (2) Plasmonic NCs can offer an "antenna" effect due to the LSPR excitation, resulting in a concentration of the electromagnetic field in the vicinity of NCs which can not only boost the absorption (and emission) cross-sections of the semiconductor absorber next to them but also alter significantly the carrier lifetime of the semiconductor; (3) Plasmonic NCs, when inserted at a

metal/semiconductor interface, can couple sunlight into surface plasmon polariton (SPP) modes at such an interface, creating more absorption and photocurrent generation events in the photovoltaic material. (4) UV-absorbing and visible-transparent NCs (e.g. Al NCs) can potentially protect the semiconductor from UV-induced degradation. In addition to the above-mentioned four main mechanisms, recent findings also suggest further beneficial mechanisms based on hot-carrier-induced charge transfer and energy transfer under specific device structures. Depending on the exact type of plasmonic NCs synthesized, this thesis will investigate methods to insert them rationally into the above-mentioned optoelectronic devices (PV, PDs, and microwave PCS) aiming for optimized results on *at least two types of devices*. Mechanisms behind device functioning and the origins of the plasmonic enhancements obtained will be investigated in detail.

<u>Role and scientific competence of the supervisors:</u> Z. Chen has a solid and multi-disciplinary scientific background on colloidal synthesis, photovoltaic and photodetection devices based on nanomaterials, their fabrication and characterizations. C. Tripon-Canseilet has extensive experience on plasmonic metamaterials formation and characterization, microwave photoconductive switches fabrication, simulations, and characterizations.

<u>Required background of the PhD candidate:</u> Solid academic background and a Master Degree on chemistry, material science, physics or applied physics. Good speaking & writing skills in English. Passionate in scientific experiments.

<u>A few representative recent publications of the group in the field of this thesis proposal :</u>

- "Flexible and wearable plasmonic-enabled organic/inorganic hybrid photothermoelectric generators", C. Xin, Z. Hu, Z. Fang, M. Chaudhary, H. Xiang , X. Xu, L. Aigouy, Z. Chen, *Materials Today Energy*, accepted and in press (2021)
- "Colloidal upconversion nanocrystals enable low-temperature-grown GaAs photoconductive switch operating at λ= 1.55 µm", H. Xiang, M. Chaudhary, C. Tripon-Canseliet, Z. Chen, *Nanotechnology*, 32, 45, 45LT01 (2021)
- "Reconfigurable Antenna Assembly Having A Metasurface Of Metasurfaces", C. Tripon-canseliet, S. Maci, C. D. Giovampaola, G. Vecchi, *US patent*, no. 17055315 (2021)
- "TiO_2 Nanocolumn Arrays for More Efficient and Stable Perovskite Solar Cells", Z. Hu, J. M. García-Martín, Y. Li, L. Billot, B. Sun, F. Fresno, A. Garcia-Martin, M. U. González, L. Aigouy, Z. Chen, *ACS applied materials & interfaces*, 12, 5, 5979-5989 (2020)
- "Heavy-metal-free flexible hybrid polymer-nanocrystal photodetectors sensitive to 1.5 µm wavelength", H. Xiang, Z. Hu, L. Billot, L. Aigouy, W. Zhang, I. McCulloch, Z. Chen, *ACS applied materials & interfaces*, 11, 45, 42571-42579 (2019)
- "Hybrid plasmonic gold-nanorod–platinum short-wave infrared photodetectors with fast response", H. Xiang, Z. Hu, L. Billot, L. Aigouy, Z. Chen, *Nanoscale*, 11, 39, 18124-18131 (2019)
- "Short-Wave Infrared Sensor by the Photothermal Effect of Colloidal Gold Nanorods", H. Xiang, T. Niu, M. S. Sebag, Z. Hu, X. Xu, L. Billot, L. Aigouy, Z. Chen, *Small*, 14, 16, 1704013 (2018)