SORBONNE UNIVERSITÉ

Sorbonne Université/China Scholarship Council program 2021

Thesis proposal

Title of the research project: **Mono and bimetallic nanoparticles for modulated plasmonic catalysis properties**

Keywords: mono and bimetallic nanoparticles, chemical synthesis, photocatalysis, optical fluorescence microscopy and spectroscopy

Joint supervision: Adrien GIRARD, Laboratoire MONARIS, Sorbonne Université

Joint PhD (cotutelle): no

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Institution: Sorbonne University

Doctoral school (N°+name): ED 388, chimie physique et chimie analytique de Paris centre

Research laboratory: Laboratory MONARIS (UMR 8233)

Address of the laboratory: Laboratoire MONARIS, Campus Pierre et Marie Curie, 4 place Jussieu, 75005 Paris

Name of the laboratory director: Christophe PETIT

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Subject description (2 pages max):

1) Study context: Plasmonic catalysis is one of the emerging frontiers in catalysis at the nanoscale [1]. In the case of noble metals, such as gold (Au), silver (Ag) and copper (Cu), the localized surface plasmon excitation lies in the visible range, which is relevant for the conversion of solar energy to chemical energy. Additionally, plasmonic catalysis allows new reaction pathways otherwise impossible via conventional, thermal catalysis [2,3,4]. One of the current challenges of plasmonic catalysis is to design new nanomaterials with controlled optical properties and improved catalytic performances. Within this context, this thesis project will be dedicated to the synthesis of innovative plasmonic mono and bimetallic nanocatalysts as well as the characterization of their photo-catalytic activity using optical microscopy and spectroscopy techniques.

2) Details of the proposal

Part 1 : Chemistry. One strategy to improve the catalytic performances of metallic nanocatalysts is to develop bimetallic nanocatalysts consisting of two metallic elements that can exhibit synergistic effects between their physico-chemical properties and increased catalytic activity. We are thus interested both in plasmonic monometallic (Ag, Cu) nanoparticles (NPs) and core-shell Cu@M or ag@M (M=Pt or Pd) bimetallic nanocatalysts. The interest is to combine the important and efficient catalytic activities of Pt or Pd shell surface with the high-energy metallic core capable of enhancing the shell activities through its plasmonic properties. In addition, these bimetallic NPs often exhibit superior catalytic activity due to the modification of the Pt-Pt or Pd-Pd atomic bond distance (i.e. the stress effect). The objectives will focus on the use of monometallic (Ag, Cu) NPs in controlled forms (spheres, cuboctahedron, cube, hexagon) [7,8] (Fig.1) as well as bimetallic core-shell Cu@M or Ag@M NPs (M=Pt or Pd). Depending on the seed morphology and the growth conditions of Pt or Pd layer (temperature, concentration of the reagents, mode of addition of the Pt or Pd precursor), bimetallic nanoparticles with different crystal structures and surface morphologies can be obtained. They will be able to either keep the morphology of the seeds or to evolve towards other morphologies. Once the nanocatalysts will be obtained, their photocatalytic properties will be studied.

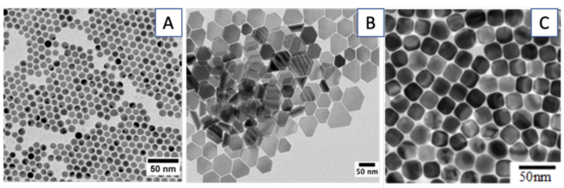

Fig. 1: Copper (A) and silver (B, C) NPs of different shapes obtained by chemical synthesis process developed in MONARIS laboratory

Part 2 : Photo-chemical properties. The plasmon resonance of single nano-objects will be characterized using dark field spectroscopy, see Fig 2 (A) and (B). The thermal catalysis component, due to photo-induced heating, will be monitored at the nano-surface based on NP luminescence nano-thermometry, where the temperature-dependant luminescence of Ag or Cu NPs will be used as an absolute local nano-thermometer. The photocatalitic activity will be first measured using single molecule - single monometallic NP dimers (Ag, Cu) super-resolution fluorescence microscopy *in-operando* during a targeted hot electron-driven fluorogenic chemical reaction, see Fig 2 (C). The nanoparticles will be placed in a microfluidic cell and irradiated by a laser light, while measuring the fluorescence signal of each single fluorescence burst event. Mapping the catalytic activity onto the hot electron emission sites (NP dimers gap) will allow understanding their contribution with respect to the thermal one. Finally, we will investigate how synergetic effects may enhance the photo-catalysic activity of bimetallic (Ag@M or Cu@M) nanocatalysts dimers.

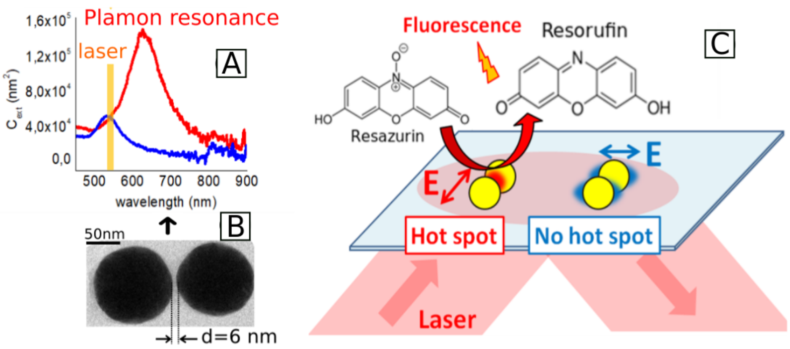

Fig. 2 : (A) Plasmon resonance of a metallic NP dimer in longitudinal (red) and transverse (blue) polarization configuration (B) TEM image of the NP dimer (C) Schematic view of single NP dimer fluorescence experiment.

3) References References :

[1] Christopher P, Xin H and Linic S 2011 Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures Nat. Chem. 3 467–72, [2] Mukherjee, S. *et al.* Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H2 on Au. *Nano Lett.* 13, 240–247 (2013), [3] Mukherjee, S. *et al.* Hot-Electron-Induced Dissociation of H2 on Gold Nanoparticles Supported on SiO2. *J. Am. Chem. Soc.* 136, 64–67 (2014), [4] Hou, B., Shen, L., Shi, H., Kapadia, R. & Cronin, S. B. Hot electron-driven photocatalytic water splitting. *Phys. Chem. Chem. Phys.* 19, 2877–2881 (2017).

4°) Profile of the Applicant (skills/diploma…)

The synthesis of Ag and Cu seeds already developed by MONARIS will assure a fast starting of the project. The PhD student will be focused on the elaboration of the Ag or Cu@M nanocatalysts (from strategies already identified). He will then carry out operando characterizations. The supervising team is interdisciplinary, with chemists and physicists. The applicant should have a master degree in either chemistry or physics. Good basis in material science, chemistry of nanomaterials and their characterizations (MET, XPS, UV-Vis spectroscopy) are welcome.

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