Title: Plasmonic-Enhanced Upconversion Nanocrystals for Organic-Inorganic Hybrid Solar Cells

Context and Problems: Solar cells, photovoltaic devices converting the energy of sunlight into electricity, represent one of the most promising avenues to harvest clean and renewable energy. In the search for cost-effective solar cells, the recently discovered solution-processable hybrid organic-inorganic perovskites are considered as one of the most important candidates. Astonishing photovoltaic performance has been achieved in solar cells based on methylammonium lead trihalide perovskites (MPbX$_3$), with power-conversion efficiency as high as 19%. However, these MPbX$_3$ perovskite solar cells can harvest photons from the visible up to only about 800 nm. More than half of the energy of the solar spectrum (in the near-IR) cannot be absorbed. To harvest near-IR photons, lanthanide-doped fluoride upconversion nanocrystals represent an attractive approach. However, one of the major obstacles lies in the poor absorption and emission efficiency of such nanocrystals. This problem can be overcome if one can concentrate the local electromagnetic field around them by means such as plasmonic nanostructures. Up to now there has been neither report on the application of upconversion nanostructures in perovskite solar cells nor report on plasmonic-enhanced upconversion nanocrystals for solar cells.

Program: This PhD thesis aims to develop plasmonic-enhanced upconversion approaches to extend the spectral sensitivity of hybrid perovskite solar cells to the near-IR. Practically, it will involve the following parts:

1. Design and fabricate a plasmonic metallic-upconversion nanocomposite structure for perovskite solar cells. The nanocrystals will be synthesized through collaboration (M. Mortier, ENS-Chimie Paris) and the nanocomposites will be achieved by the following 3 routes:
   - The application of metallic nanostructured arrays with a wavelength-tunable localized surface plasmon resonance (LSPR) designed to boost the absorption and emission of lanthanide-doped fluoride nanocrystals. Such arrays will be fabricated either by lithographic, template-assisted, or self-assembled molecular linker techniques directly onto the transparent conductive electrode. The nanocrystals can be inserted inside the electron-transporting TiO$_2$ which will be deposited on top of the plasmonic-decorated transparent electrode (Fig. 1).
   - The synthesis of upconversion-nanocrystal-decorated metallic nanoparticles. Following synthetic approaches, we will first synthesize colloidal gold nanorods with a LSPR matching the near-IR absorption of upconversion nanocrystals. We can then physically or chemically link upconversion nanocrystals onto gold or gold/silica core/shell nanorods. The final upconversion/metal composite particles can be inserted into the electron transport layer (TiO$_2$) of the solar cells.
   - A simple combined insertion of both metallic nanoparticles (with or without a silica shell) and upconversion nanocrystals in the electron transport layer (TiO$_2$) of the solar cells.

2. Detailed structural and optical characterizations of the plasmonic-upconversion nanocomposites by SEM, TEM, AFM, transmission/reflection/absorption, photoluminescence, PL decay, and scanning near-field optical microscope (SNOM).

3. Correlation of photovoltaic properties with the structural and optical properties of plasmonic-upconversion nanocomposites. We will complete the solar cell fabrication by applying the state-of-the-art perovskite chemical formula and device architecture (Fig. 1). Photovoltaic characteristics from devices with and without plasmonic-upconversion composites will be compared. Solar cell characteristics, structural and optical properties, SNOM results, and finite-difference time-domain (FDTD) modeling will be correlated together to understand how and which nanocomposite can provide maximum device performance benefits.

In summary, this thesis offers a multidisciplinary training, covering fields including nanophotonics, colloidal chemistry and optoelectronics. Applying the approaches developed in this project, we will be able to design and fabricate advanced device structures to exploit the fascinating upconversion ability of lanthanide-doped fluorides in perovskite solar cells. We expect to provide a proof-of-concept solution allowing perovskite solar cells to surpass their state-of-the-art efficiency with an extended photon-harvest range.
Addendum:

Selected publications of the thesis directors in this field:
(2) A. Vitrey et al. "Parallel collective resonances in arrays of gold nanorods", Nano Lett. 14, 2079-85 (2014);
(3) L. Billot et al. "Near-Field Imaging of Surface Plasmon Polaritons Excited by Chains of Gold Nanodiscs", Plasmonics 8, 1515-1521 (2013);
(5) A. A. Bakulin et al. "Charge trapping dynamics in PbS colloidal quantum dot photovoltaic devices", ACS Nano, 7, 8771-8779 (2013);

Required knowledge of the PhD candidate:
The candidate is required to have a master or equivalent degree on Chemistry, Physics, or Materials Science with strong interest on scientific experiments.