

Scientific Report

PLASMON – Exchange Grant – 3985

“Enhancement effects in plasmonic nanocavities formed at metal nanowire junctions”

1. Purpose of the visit

The main aim of this visit was to further strengthen collaboration between the Nanophotonics Group at Materials Physics Centre (MPC) in San Sebastian (Spain) and Nanochemistry group at Trinity College Dublin (Ireland) leading by Prof. Y. Gunko in the area of plasmonic noble metal nanostructures, dye nano-aggregates and biomolecules for photonic and sensing applications.

2. Description of the work carried out during the visit

During this visit we investigated the optical enhancement effects in a novel type of hybrid structures that combine crossed silver nanowires with organic dye molecules in a J-aggregate state. Confocal photoluminescence (PL) imaging, PL lifetime imaging and Raman imaging and spectroscopy were used in this work.

3. Description of the main results obtained

The main results are strong enhancement of Raman scattering, photoluminescence enhancement and photoluminescence lifetime modification observed at junction of silver nanowires covered by shell of J-aggregates.

3.1 Experimental details

Silver nanowires were synthesized by the reduction of silver nitrate occurred in the presence of poly(vinyl pyrrolidone) in ethylene glycol at a constant temperature (140 °C) during four hours. 1,1'-Diethyl-2,2'-cyanine iodide (PIC), carrying net positive charge was purchased from Sigma-Aldrich. In order to trigger the formation of J-aggregates we took advantage of electrostatic interaction between anionic polyelectrolyte (Polystyrenesulfonate sodium salt) and cationic dye molecules of PIC with an iodide counter-ion. While the monomeric PIC does not fluoresce, the aggregates exhibit a narrow absorption J-band at 570 nm and strong fluorescence band with Stokes shift between them of only 3nm (Fig. 1). Corresponding PL decay of J-aggregates shows two-peak temporal distribution with the shortest component centered around 315 ps and the longest one grouped around 575 ps (Insert in Fig. 1b).

The procedure of adsorption of J-aggregates on silver nanowires was as follows. First the silver NWs were dissolving in water and then the aqueous solution of J-aggregates was injected. The nanowires originally possessing slightly negative surface charge electrostatically interact with cationic PIC J-aggregates. After 30 minutes of gentle stirring, nanowires were carefully washed in water (by centrifugation) to remove the

excess molecules of the dye and polyelectrolyte not ionically bonded to the surface of NWs. All sample preparation and characterization was carried out at room temperature.

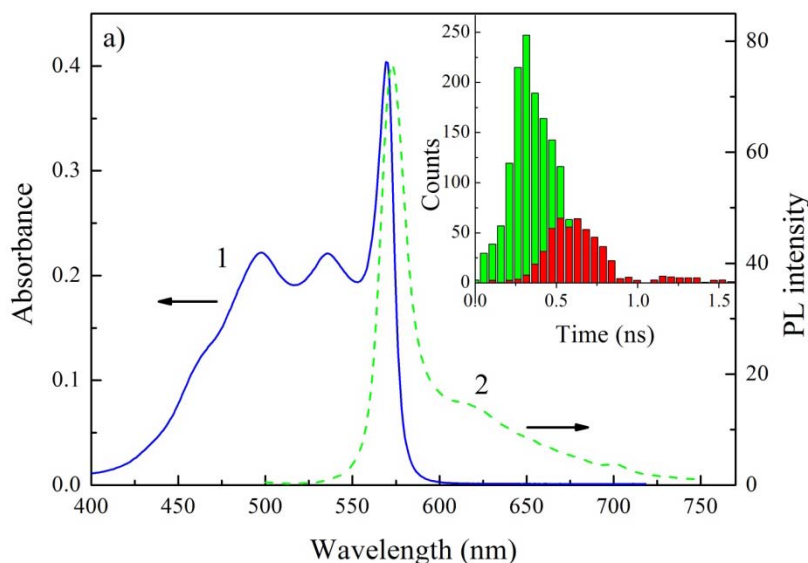


Figure 1. Room-temperature absorption (1) and PL (2) spectra ($\lambda_{\text{exc}} = 485 \text{ nm}$) of J-aggregates formed in aqueous solution of PIC by interaction with polyelectrolyte. Insert: PL lifetime histogram obtained from the same sample ($\lambda_{\text{exc}} = 485 \text{ nm}$, excitation power $0.05 \mu\text{W}$).

Cary 50 and Cary Eclipse (Varian) were used to measure the absorption and PL spectra, respectively. Confocal Raman microscopy setup (RENISHAW) was used to measure micro-PL and Raman spectra, respectively. The time resolved PL decays were measured using Microtime200 fluorescence lifetime imaging microscopy (FLIM) system (PicoQuant).

3.2 Surface Enhanced Raman Scattering (SERS)

Figure 2 displays enhanced Raman spectra and SERS micromapping for selected silver nanowires junction with the strongest central point, which corresponds to the crossed wires junction. We have observed 20-times enhancement of Raman signal from the junction as compared to signal from the ends of individual nanowires.

The spectral positions of all peaks in spectra presented in Fig.2 exactly match the positions of the Raman peaks of PIC J-aggregates reported elsewhere [Guo, C., et al., *J. Phys. Chem. A*, 2002. **106**, 5447 (2002)]. The most pronounced lines (around 1500 cm^{-1}) are associated with the totally symmetrical in-plane deformations of individual phenyl and pyridyl rings, which are constituents of PIC molecule. These deformations give major contribution to the Raman optical activity spectra of PIC J-aggregates and therefore these Raman modes are most pronounced. Multiple lines around 500 cm^{-1} are associated with various (not necessarily totally symmetrical) deformations involving both phenyl and pyridyl rings.

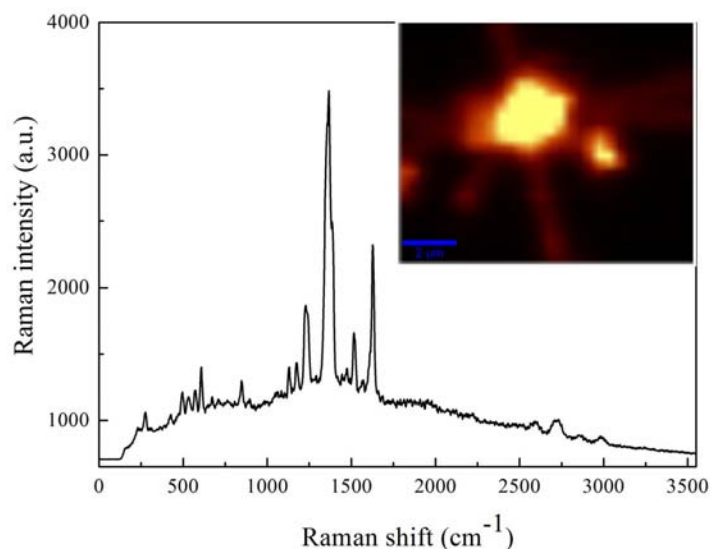


Figure 2. Raman spectrum of Ag nanowires with shell of J-aggregates measured at the crossed nanowire junction. Inset shows Raman image of crossed wires.

3.3 Photoluminescence (PL) enhancement and photoluminescence lifetime modification observed at junction of silver nanowires covered by shell of J-aggregates

Figure 3a demonstrates strong enhancement of PL intensity at the crossed nanowire junction and at the ends of individual wires. Two physical phenomena are assumed to be involved. First, the excitation rate of the J-aggregates is determined by the local electrical field. This field can be strongly enhanced with respect to the incident field by nanogap of nanocavity formed by crossed Ag nanowires at their junction. Second, the emission rate of the J-aggregates is also affected by the metallic nanocavity.

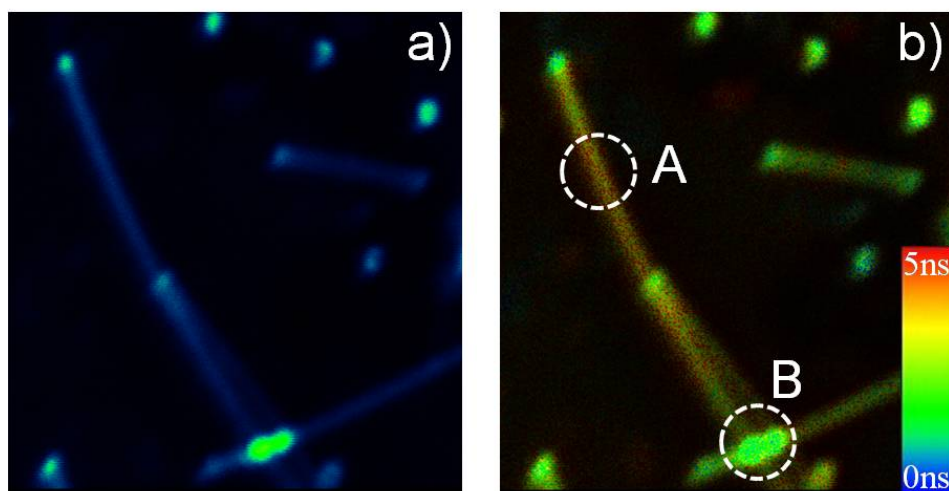


Figure 3. PL intensity (a) and FLIM (b) images of crossed Ag nanowires covered with shell of PIC J-aggregates. Each pixel in the FLIM image gives the lifetime at a particular position in space (x,y), while monitoring the entire PL spectrum.

The latter effect can be monitored by FLIM imaging, that is, maps of two-dimensional in-plane variations of the PL decay times. Indeed, Fig.3b clearly shows that the enhancement in PL intensity at crossed nanowire junction is accompanied by modification of PL lifetime.

To gain a better insight into the modification of lifetimes, the PL dynamics at two different regions (marked as A and B in Fig.3b) were evaluated from the PL lifetime histograms (Fig. 4).

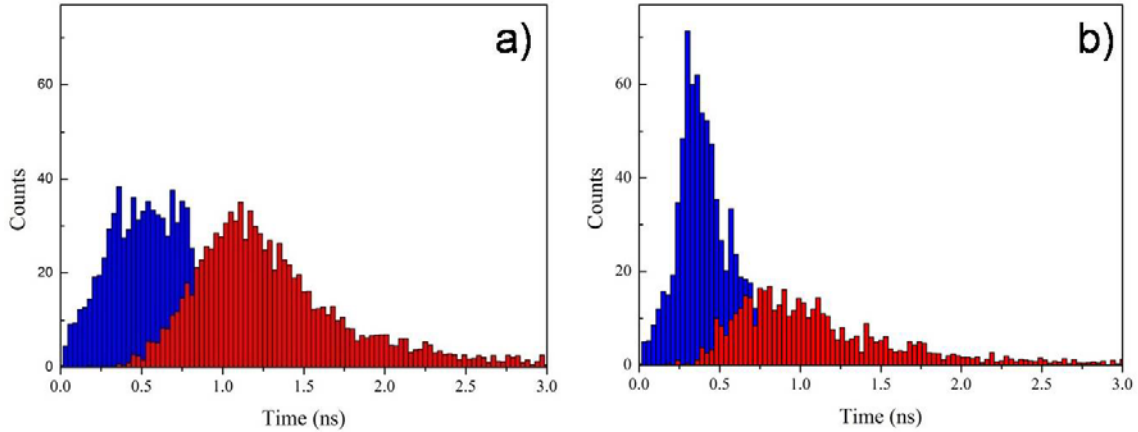


Figure 4. (a) The PL lifetime histogram measured from single nanowire (region A in Fig.2b) and (b) The PL lifetime histogram measured from junction of crossed wires (region B in Fig2b).

In both regions – away from crossed nanowires junction (Fig.4a) and at the junction (Fig.4b) the histograms show lifetime distributions that consist of two maxima. In the first region (Fig.4a) they are two maxima centered at 0.55 and 1.1 ns with values of full-width-at-half-maximum (FWHM) equal to 0.56 and 0.62 ns, respectively. However at the junction (Fig.4b) the first maximum is shifted to 0.37 ns whereas the second maximum now is centered at 0.89 ns. Corresponding FWHM values are also modified. The first peak shows substantial narrowing (FWHM=0.28 ns) whereas the second peak in Fig.4b has FWHM equal to 0.58 ns, which is very close to the FWHM value of the second peak in Fig.4a. If we assume that the second PL lifetime component originates from a distribution of exciton delocalization lengths in the J-aggregates due to structural disorder, it can explain why FWHM of the second peak in the regions A and B remains almost unchanged. We can hardly expect that plasmonic nanostructure can modify spatial arrangement of monomers in J-aggregate structure. The most striking result is strong shortening of PL lifetime associated with first maxima in region B as compared to position of first maximum in the region away from crossed nanowires junction. This result clearly demonstrates possibility to modify spontaneous emission rate of J-aggregates using plasmonic crossbar nanostructures.

4. Future collaboration with host institution

This feasibility study allows us to build stronger collaboration between involved research groups for further development of new advanced materials for sensing and

other photonics applications. One of the next steps might be an investigation of plasmon-exciton coupling in a hybrid system of silver crossbar nanostructures and J-aggregates.

5. Projected publications

We plan to report main results of this work in paper which will soon be submitted for publication in ACS Nano. EFS support will be acknowledged.