Scientific Report

PLASMON – Exchange Grant – 4920

"Study of the effect of coupling between electronic excitations in J-aggregates and plasmons in metal nanoparticles on the photoluminescence properties of hybrid nanosystems"

1. Purpose of the visit

The main aim of this visit was to strengthen further the collaboration between the Nanomaterials and Spectroscopy 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 and dye nano-aggregates for photonic and sensing applications.

2. Description of the work carried out during the visit

During this visit we carried out the detailed investigation of the factors influencing Rabi effect in photoluminescence spectra of hybrid excitonic/plasmonic nanostructures consisting of a dye molecules in J-aggregate state and gold nanoparticles. Main goal was to investigate how photoluminescence lineshape of coupled nanostructure depends on detuning of plasmonic absorption bands from the excitonic resonance of J-aggregates.

3. Description of the main results obtained

Because the duration of the project have been limited by 1 month (instead of requested 4 months) we were able in this project to investigate only one plasmonic system, namely gold nanorods integrated with J-aggregates of cyanine dyes. The main result is the observation of coupling effect in photoluminescence spectra of exciton/plasmon hybrid system made of gold nanorods covered by the shell of J-aggregates which manifested itself in pronounced splitting of photoluminescence bands. Another main experimental result is the fact that spectral positions of splitted photoluminescence bands do not correspond the spectral positions of bands in absorption spectra of the hybrid system which probably suggest weakening of the coupling strength upon photoluminescence excitation.

3.1 Experimental details

Gold nanorods were synthesized in aqueous solution using cetyltrimethylammonium bromide (CTAB) as the capping and growth regulating agent. The nanorods of the same diameter (around 15 nm) but different lengths, were specifically synthesized to study coupling effects with J-aggregates at spectral positions of absorption bands close to the excitonic resonance, and away from it.

J-aggregates were formed from cyanine dye JC1 (5,5',6,6'-tetrachloro-1,1',3,3'-tetraethyl-imidacarbocyanine iodide) by dissolution of the dye in the deionized water at pH7. Absorption spectra of nanorods with different lengths are shown in Figure 1 in comparison with absorption spectra of J-aggregates.

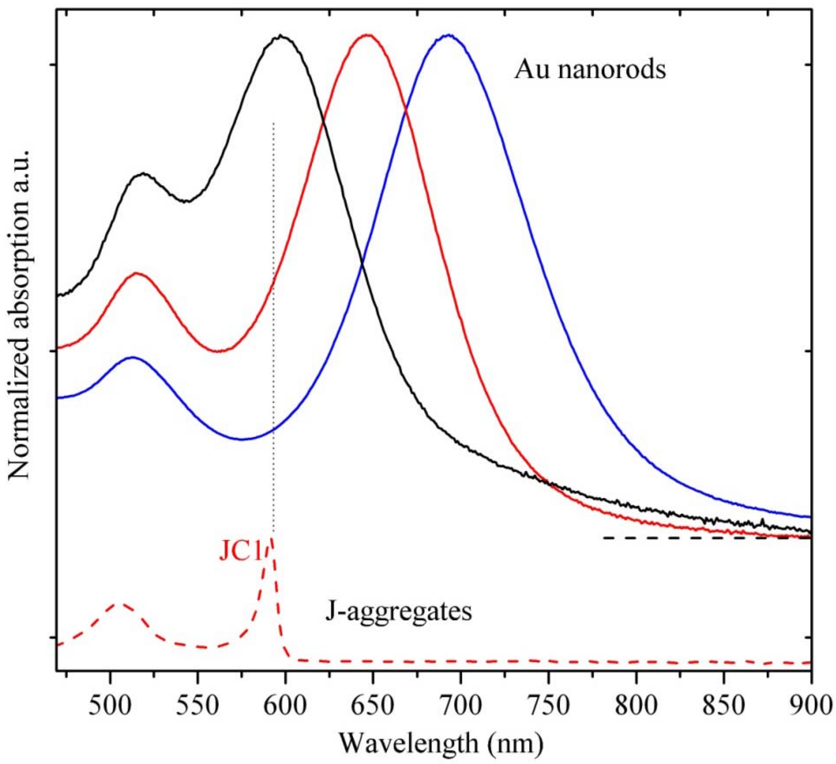

Figure 1. Absorption spectra of Au nanorods with different lengths and absorption spectra of J-aggregates of JC1 cyanine dye.

The reason why this particular dye was chosen was that upon the aggregation J-aggregates of this dye develop very narrow absorption band (centered at 591 nm) which is located very close to the maximum of absorption of the smallest nanorods used in our experiments (Figure 1). This favors the regime of strong plasmon-exciton coupling in the hybrid systems.

3.2 Plasmon-exciton coupling in a hybrid system of gold nanorods and its effect on photoluminescence spectra

Main results of our study are presented in Figure 2. In the hybrid structure of formed from nanorods and J-aggregates, the pronounced dip at 590 nm appears as a result of strong coupling of the excited states of J-aggregates and plasmon modes of the nanorods. Also it is demonstrated that the separation between short-wavelength and long-wavelength peaks in absorption spectra grows with detuning of absorption peaks of gold nanorods with different lengths from excitonic resonance of J-aggregates (Figures 1 and 2).

Along with the changes in the absorption spectrum we also observed some changes in luminescence properties of hybrid J-aggregates/gold nanorods complexes. Figure 2 shows the photoluminescence spectra of plasmon-exciton systems formed from gold nanorods of three different sizes and J-aggregates.

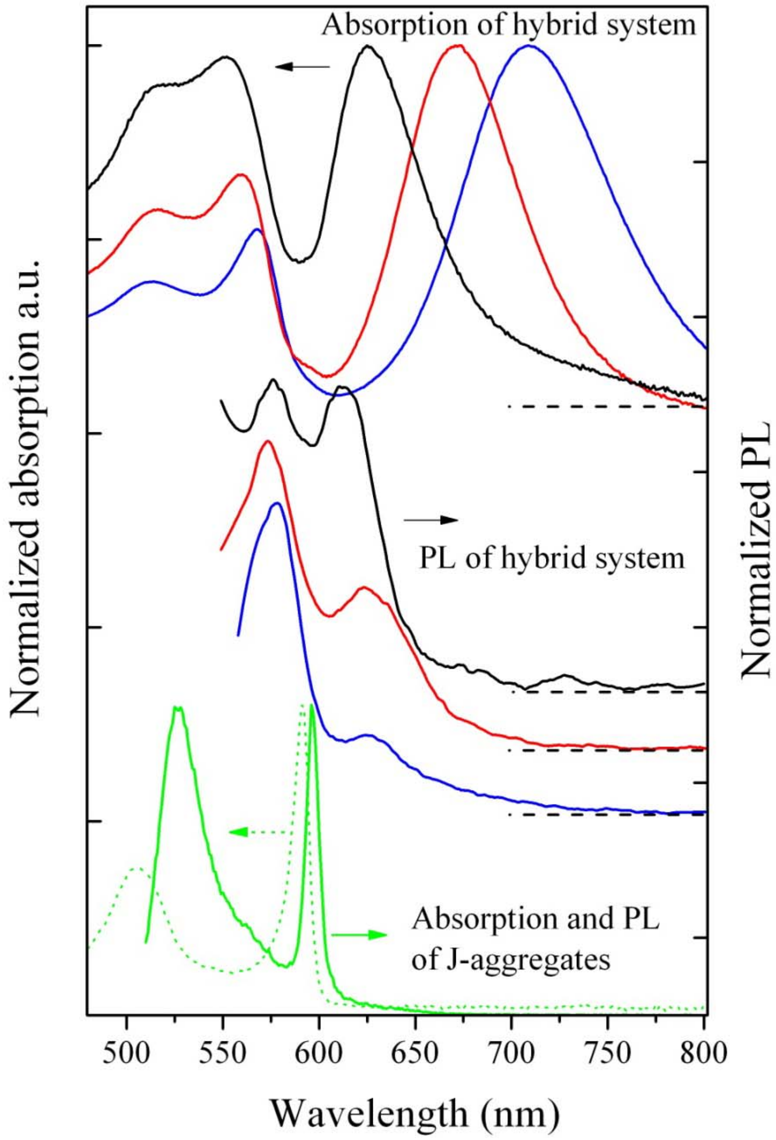

Figure 2. Absorption spectra of hybrid system formed from nanorods of three different lengths and J-aggregates, PL spectra of the same system in comparison with absorption and PL spectra of pure J-aggregates.

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It should be noted that for resonant conditions when absorption of gold nanorods centered at the same wavelength as absorption band of J-aggregates (Figure 1), photoluminescence spectrum of the hybrid system shows two pronounced peaks (Figure 2, black curve). Spectral position of these two bands is very close to the spectral positions of two resonances in absorption spectrum of the hybrid structure (Figure 2, black curves). However for the hybrid systems with bigger detunings from excitonic resonance (red and blue curves in Figures 1 and 2) spectral position of PL bands deviates strongly from positions of peaks in absorption spectra (red and blue curves in Figures 1 and 2). At the present this phenomenon is under close investigation by our two groups. One of the reasons for such a behavior of PL bands might be some weakening of the coupling strength upon excitation of photoluminescence which results in smaller values of Rabi splitting.

4. Future collaboration with host institution

This study allows us to build stronger collaboration between involved research groups for further development of new advanced materials for sensing and other photonics applications. Also there are number of phenomena which have to be put under further tests in order to achieve clear understanding of the effect of coupling between excitons and plasmons in hybrid nanostructures.
One of the next steps might be the investigation of plasmon-exciton coupling effects in photoluminescence spectra of the hybrid systems combined with dark-field microscopy at a single nanoparticle level. This field remains largely unexplored so far.

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.