**PLASMON – Exchange Grant – 4942**

**Scientific Report of Exchange Visit (March 1-st – 31-st, 2015)**

**M.I. Vasilevskiy**

**Work title: "Effect of exciton–surface-plasmon interaction on the fluorescence of quantum dot structures grown by self-assembling on plasmonic substrates"**

## 1. Purpose of the visit

The main goal of this visit supported by the ESF Exchange Grant was to strengthen further my collaboration with the Nanomaterials and Spectroscopy Group lead by Prof. Yu. Rakovich at the Materials Physics Centre (MPC) in San Sebastian (Spain), by developing theoretical models relevant to the optical properties of nanosystems composed of quantum dot (QD) based systems and plasmonic structures, such as metallic surfaces, ultrathin conductive films (such as graphene) and nanoparticles (NPs).

## 2. Description of the work carried out during the visit and the results obtained

During this visit we carried out experimental and theoretical research of the light emitting and scattering properties of quantum emitters (QDs or dye molecules) located in the vicinity of a plasmonic substrate.

On the theoretical side, the QD emission decay rate and the probability of the Förster resonant energy transfer (FRET) between two QDs located above a flat plasmonic substrate were calculated. By comparing their spectral dependences it was concluded that, in order to optimize the QD exciton transport by means of plasmon-assisted FRET, the exciton energy should be chosen considerably below the surface plasmon (SP) energy (in the electrostatic limit).

The main experimental result obtained is the observation of surface-enhanced Raman scattering (SERS) in J-aggregates of a cyanine dye deposited on top of fractal-dimension dendrites formed by Ag NPs precipitated on a $TiO_2$ substrate.

Since the duration of the project was limited to 1 month (instead of requested 2 months) we were not able to extend these studies to other potentially interesting systems, including those containing graphene. This research, both experimental and theoretical, will be performed in the near future.

### 2.1 Theoretical results

The effect of a flat interface between two media on the electromagnetic (EM) emission and energy transfer rates for an emitter (for instance, a QD) located at a certain distance from the interface was considered using the Green function formalism. When the second medium is a metal, several contributions to both processes arise that can be associated with: (i) propagating EM waves (so called radiative losses), affected by the

presence of the second medium, (ii) coupling to propagating surface plasmons (SPs), and (iii) Ohmic losses (when the exciton energy is irreversibly transferred to heat via electron scattering in the metal). We found that the relative contribution of the above three mechanisms depends very strongly on the QD distance to the interface ($h$). At very short distances ($\sqrt{\varepsilon}(\omega/c)h<<1$, where $\varepsilon$ is the dielectric constant of the medium where the emitter is embedded, $\omega$ is the photon frequency and $c$ is the velocity of light), the Ohmic losses dominate. This effect decreases with the distance as $h^{-3}$ and is well described by the approximate solution for the EM field using the image dipole method.

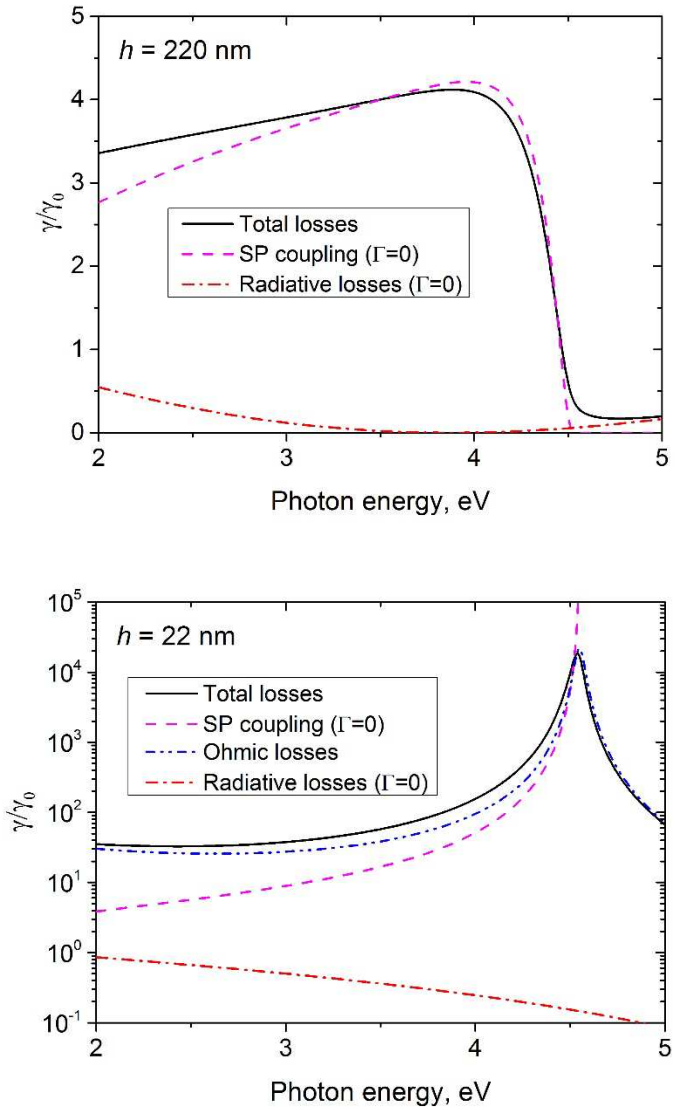



Figure 1. Spectral of dependence of different contributions to the emission decay rate for an emitter located in a dielectric with $\varepsilon = 2$ at two different distances (indicated on the plots) above a flat interface with gold.

However, as the distance to the interface increases, for $\sqrt{\varepsilon}(\omega/c)h \approx 1$, the coupling to SPs becomes the mechanism that determines the QD exciton lifetime (see Fig. 1, lower panel). This effect (overlooked by the image dipole method) decreases with the distance as $\exp\left[-2\sqrt{\varepsilon}(\omega/c)h\right]$, so it vanishes quickly at $\sqrt{\varepsilon}(\omega/c)h > 1$ and the exciton lifetime becomes $\tau = \gamma_0^{-1}/\sqrt{\varepsilon}$, where $\gamma_0$ is the radiative decay rate in vacuum.

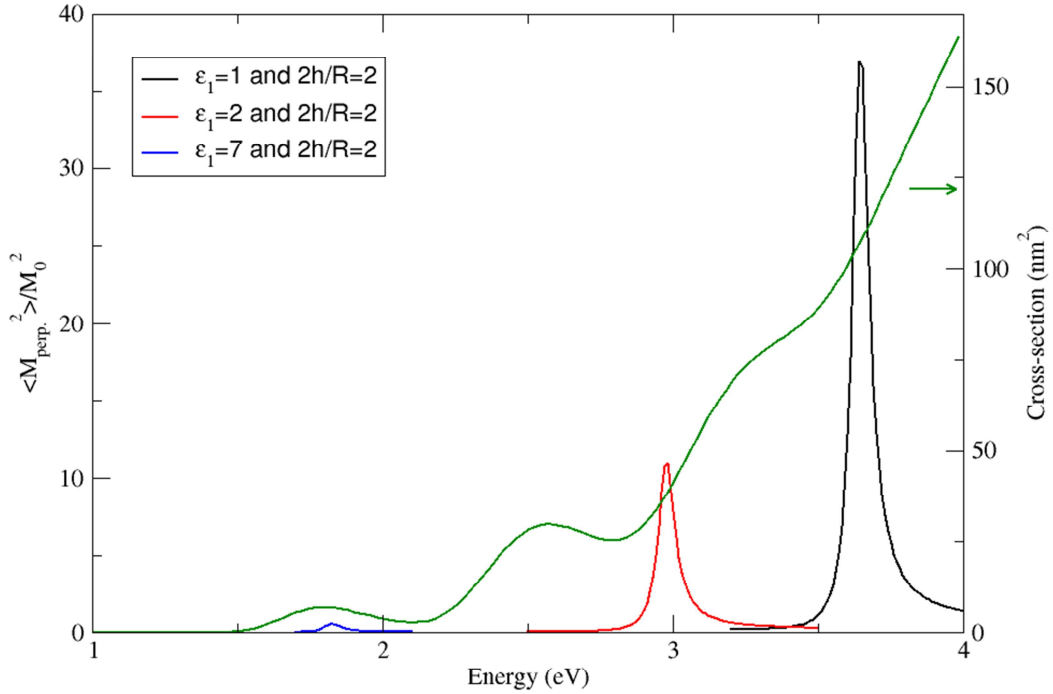



Figure 2. Spectral dependence of the enhancement factor in the vicinity of a metal substrate, for the donor QD perpendicular to the interface, for different values of the dielectric constant of the medium where the QDs are embedded. The peaks are at the corresponding electrostatic SP frequencies. Also shown is the absorption cross-section of an ensemble of CdTe QDs with the radius $3 \pm 0.25$ nm (green curve).

The transition matrix element that determines the FRET probability per unit time between two similar QDs shows very similar trends (for a fixed distance between the dots, $R$). It shows a resonant behavior at the electrostatic SP frequency (determined by the equation $\varepsilon + \mathrm{Re}\,\varepsilon_M = 0$, where $\varepsilon_M$ is the dielectric function of the metal), see Fig. 3. However, so does also the nonradiative decay rate (Fig. 2, lower panel). For $\sqrt{\varepsilon}(\omega/c)h << 1$ and $\sqrt{\varepsilon}(\omega/c)R << 1$ (near field zone), the Ohmic mechanism of the QD-metal interaction dominates. It is clear from the image dipole approximation (valid in this limit) that the effect of the metallic substrate (that enhances the FRET probability) decreases with $R$ faster than $R^{-6}$ (which is the scaling law in vacuum). Therefore this

enhancement does not offer advantages in terms of QD exciton transport because of its very short range and also because of the strong quenching of the QD emission (i.e. resonant enhancement of the nonradiative decay due to the Ohmic losses) in this regime. Still, there might be a chance that the FRET process can compete with the deexcitation (via relaxation towards ground state) for some excited QD exciton states as shown in Fig. 2 where the $\varepsilon = 1$ resonance matches one of the higher exciton states.

If the QDs are located at a higher distance from the interface, such that $\sqrt{\varepsilon}(\omega/c)h \approx 1$, coupling to SPs becomes the dominant mechanism of their interaction with the metal. If the propagation length of the surface plasmons (determined by the imaginary part of their wavevector) is not too short, the FRET probability decays much slower (and also oscillates) with the inter-dot distance, approximately as $J_0^2\left(\sqrt{\varepsilon^2/|\varepsilon + \mathrm{Re}\,\varepsilon_M|}(\omega/c)R\right)$, where $J_0$ is the Bessel function of 0-th order. Therefore it can be interesting for QD exciton transport by means of FRET over larger distances.

For resonant Raman scattering (RRS), when the excitation wavelength matches one of the electronic transitions of the analysed molecule (or an exciton transition in a QD if it is used as a scatterer), the probability is proportional to the EM field enhancement factor squared because it is a second order process. Since the emission quenching is not a problem if one is interested in the RRS measurement, it is advantageous to use double resonance, i.e. achieve the matching between the photons and the SP frequencies. Therefore it is better to use localized SPs (LSPs) in metallic NPs rather than flat metallic surfaces because these resonances have lower frequencies. Moreover, if aggregates of plasmonic NPs are used, one may expect the formation of local zones where the EM field is particularly strong (so called “hot zones”). The effect of the RRS enhancement by the local EM field is known as surface enhanced Raman scattering (SERS). Since LSPs are always lossy, the enhancement factor should decrease as $d^{-6}$ with the distance ( $d$ ) between the scatterer and the nanoparticle or NP aggregate.

### 2.2 Experimental results

Some potentially interesting plasmonic substrates were prepared at the Centre of Physics of Minho University. Composite films of silver and $TiO_2$ were deposited on Si substrate using the magnetron sputtering technique. After annealing in a neutral atmosphere for 1 hour, Ag precipitated on the surface of the film in the form of dendrites with a typical size of a few tens of micrometers. Their fractal dimensionality was estimated at 1.7 – 1.8 (for the planar projection). We believe that the fractal geometry of these aggregates is responsible for their broad SP resonance band, locaterd in the visible spectral range owing to the high dielectric constant of $TiO_2$. Therefore these samples were chosen as a platform to study the exciton-plasmon coupling effects using a well characterized organic emitter.

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. The reason why this particular dye has been chosen is that its J-aggregates develop

a narrow absorption band (centered at 591 nm) which is located within the LSP band of the plasmonic substrates described above. This is expected to favor the regime of strong plasmon-exciton coupling in the hybrid systems consisting of the J-aggregates deposited on top of the fractal Ag dendrites (Fig. 3, top).

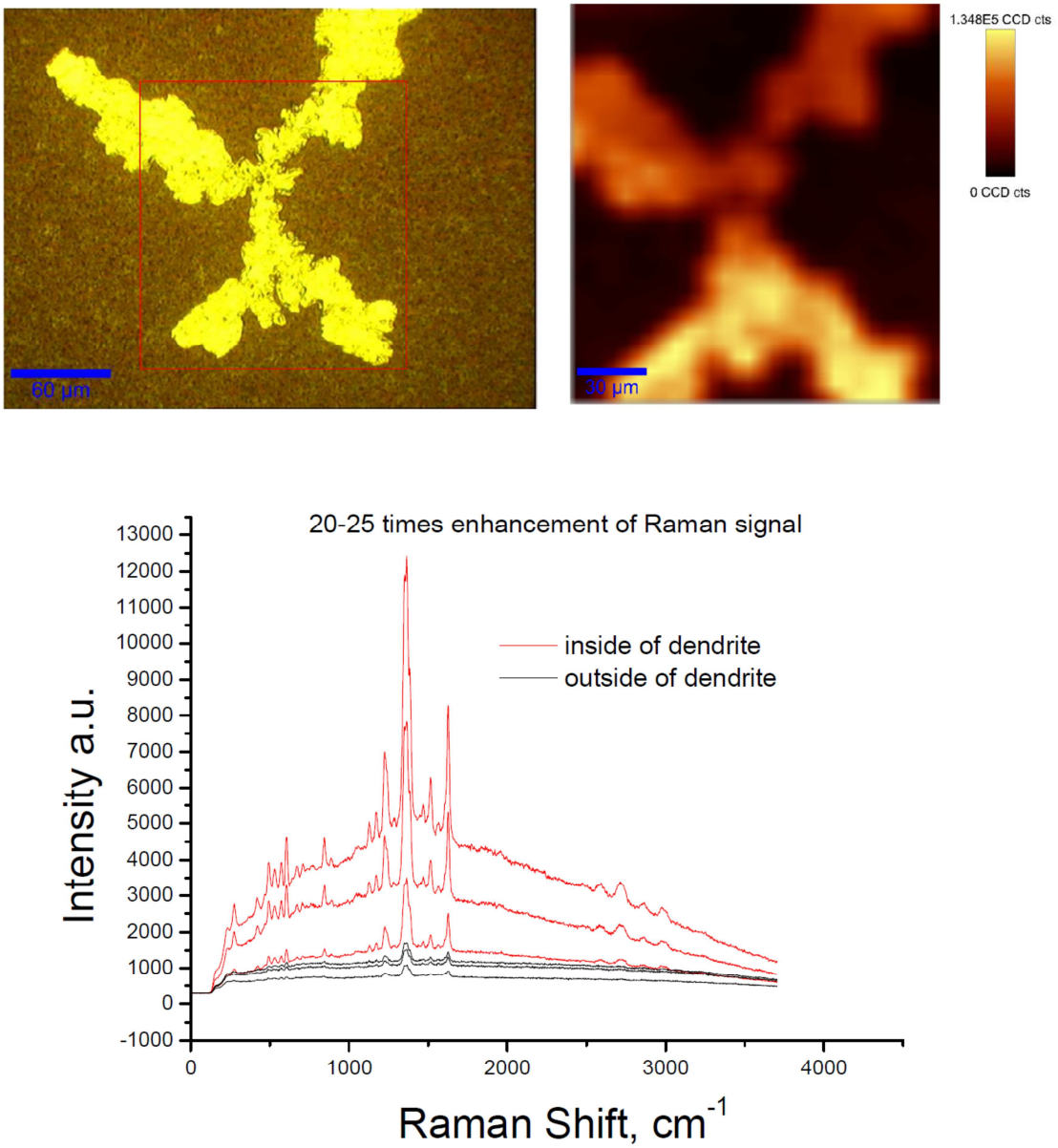



Figure 3. Surface-enhanced Raman scattering spectra of J-aggregates deposited on top of Ag dendrite structure (shown top left). A 20-25 times enhancement of the Raman signal within the dendrite structure is observed, compared to the Raman signal of J-aggregates outside of the dendrite.

So far, only RRS spectroscopy studies have been performed. The main results are shown in Fig. 3. We notice a 20-25 times increase in the RRS intensity from the dendrite region as compared to zones outside the silver agglomerates, for the same concentration of J-aggregates. This is comparable to other plasmonic structures proposed as SERS platforms, such as gold nanorods and nanostars. However, the

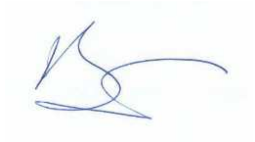
dendrite structures considered here have the potential advantage of broad SP resonance band, which makes them suitable for detection of a range of molecular species with different electron transition energies.

### 3. Future collaboration and projected publications

This study will be continued. On the theoretical side, the emission decay rates and the FRET probability will be calculated and analyzed for emitters located near a thin metallic film, the results will be relevant to graphene. Also, the possibility to consider composite plasmonic substrates (metallic inclusions in a dielectric matrix) and describe them by an effective dielectric function, in order to calculate the abovementioned quantities will be analyzed. Experimentally, beyond completing the study of SERS, the behavior of FRET between QDs and J-aggregates in the vicinity of Ag dendrites will be investigated.
We plan to report the results of this work in one or two papers which will be submitted for publication in a high profile journal. The EFS support will be acknowledged.

### 4. Conference presentation during the visit

Some results of our previous collaboration in the field related to the topic of this visit was presented by Prof. Yu. Rakovich as a keynote talk at the ImagineNano 2015 Conference (March 10-13, Bilbao, Spain), under the title “Upconversion of photoluminescence in II-VI nanocrystals: Feasibility of anti-Stokes cooling” (Book of Abstracts, p. 328).



(Mikhail Vasilevskiy)