Effect of surface plasmon resonance in TiO₂/Au thin films on the fluorescence of self-assembled CdTe QDs structure

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Abstract. The exceptional properties of localised surface plasmons (LSPs), such as local field enhancement and confinement effects, resonant behavior, make them ideal candidates to control the emission of luminescent nanoparticles. In the present work, we investigated the LSP effect on the steady-state and time-resolved emission properties of quantum dots (QDs) by organizing the dots into self-assembled dendrite structures deposited on plasmonic nanostructures. Self-assembled structures consisting of water-soluble CdTe mono-size QDs, were developed on the surface of co-sputtered TiO₂ thin films doped with Au nanoparticles (NPs) annealed at different temperatures. Their steady-state fluorescence properties were probed by scanning the spatially resolved emission spectra and the energy transfer processes were investigated by the fluorescence lifetime imaging (FLIM) microscopy. Our results indicate that a resonant coupling between excitons confined in QDs and LSPs in Au NPs located beneath the self-assembled structure indeed takes place and results in (i) a shift of the ground state luminescence towards higher energies and onset of emission from excited states in QDs, and (ii) a decrease of the ground state exciton lifetime (fluorescence quenching).

1.Introduction

Surface plasmon resonance (SPR) typically arises in nanostructures of noble metals. Their unique properties such as strong field confinement, resonant behavior and local field enhancement effects make them ideal candidates to control the emission of luminescent nanoparticles (NPs) [1, 2]. Among these NPs, quantum dots (QDs) are highly versatile and suitable for a wide range of applications, due to their single optical properties and tunable emission, as well as high quantum yield (QY) and photostability, making them good energy donors and acceptors [3]. Förster resonant energy transfer (FRET) is an important microscopic mechanism of excitation transport between QDs, which is based on dipole-dipole interactions between energy donors and acceptors [4]. This energy transfer process can be implemented in bio-sensing and light-harvesting applications [5, 6]. It has been demonstrated that the QDs luminescence is either

enhanced or quenched when they interact with localized SPR [7-9]. At the same time, the energy transfer through a SPR-mediated coupling between metal nanostructures and light-emitting nanomaterials can change the luminescence of light-emitting acceptors [9, 10]. Notwithstanding, until now there are only a few experimental reports on SPR effects on FRET, especially for QDs systems [11].

The ability to self-assemble nanostructures into functional devices, where these assembled systems take advantage of the unique properties of the colloidal QDs becomes a new challenge in the field of nanotechnology. However, QD's environment has to be taken into account during their organization into self-assembled structures and under pulsed optical excitation, optimising them for applications. Therefore, the development of a novel material combining QDs and dielectric/plasmonic thin films is of considerable interest.

In this work we investigate the effect of localized SPR, supported by nanocomposites consisting of a dielectric matrix (TiO_2) with embedded Au nanoparticles (NPs), on the steady-state luminescence, its time-resolved kinetics and resonant energy transfer in self-assembled dendrite structures consisting of CdTe mono-size QDs. The results are discussed in view of their relation to surface plasmons localised in gold NPs.

2. Experimental methods

Negatively charged water-soluble CdTe QDs, capped with thioglycolic acid (TGA) were synthetized according a procedure previously reported [12, 13]. CdTe QDs have a maximum photoluminescence emission at 597 nm, Stokes-shifted with respect to the absorption peak associated with the exciton ground state in the dots (see figure 1). From the absorption peak we evaluated an average size of $\approx$ 4 nm, according to the calculated data presented in Ref. [14]. The quantum yield (QY) of colloidal CdTe-TGA was determined using Rhodamine B in ethanol (QY=70%) as a reference, resulting in a value of 36% [15].

Self-assembling technique [16] was used to prepare QDs dendritic structures. First, a diluted solution of QDs was prepared by the addition of sodium hydroxide pH =11, to an aqueous solution of CdTe QDs with an initial concentration of 10-5 mol L-1. Subsequently, aliquots of prepared solution were deposited on the surface of a conventional substrate (glass) and on TiO_2 films doped with Au NPs produced by co-

sputtering and subsequently annealed at different temperatures (see [17] for details of the co-sputtering and annealing regimes) and allowed to dry at room temperature.

A Shimadzu UV-3101PC UV-vis-NIR spectrophotometer was used to record the absorption spectra of TiO_2/Au films and the absorption spectrum of colloidal CdTe QDs in solution. The photoluminescence (PL) spectrum of the QDs solution was recorded using a Fluorolog 3 fluorescence spectrometer with an excitation wavelength of 360 nm provided by a Xenon lamp. These and all other optical measurements were performed under ambient conditions.

Steady state emission of the dendrite samples was investigated by using the Nd:YAG frequency-doubled 532 nm laser line (P_{Laser}=1.5mW at the sample) for excitation and equipped with a motorized sample positioning XY-stage (positioning accuracy better than 1 μm). In particular, the 800^0C annealed sample (the map is shown below) was studied within a square (120×120 μm^2) area representing a typical dendrite. The measurements were performed along 120 parallel lines, each 120 μm long, measuring 120 spectra at each line. Using Witec software tools, the 120×120 spectra were then converted into a "Raman map" of the studied area, which consisted of a single spectrum acquired at each pixel of the area. An appropriate averaging procedure was applied afterwards.

Fluorescence lifetime mapping (FLIM) measurements were recorded using a PicoQuant Micro-time200 time resolved confocal microscope system, equipped with an Olympus IX71 inverted microscope. The samples were excited by a 485 nm picosecond laser pulse (PicoQuant DH485 laser head controlled by Sepia II driver). The system has an overall resolution of 100 ps. Fluorescence lifetime maps were elaborated on a per pixel basis with respect to the logarithm of the emission intensity.

3. Results and discussion

Prior to the QDs deposition, absorption spectroscopy measurements were carried out in order to evaluate the SPR effect in TiO_2/Au films annealed at different temperatures. Figure 1(a), shows the onset of the SPR-related absorption band with the increase of the annealing temperature, caused by the formation of Au NPs. No sign of SPR is seen in the optical spectra of the as-deposited and 200 ºC annealed samples, with only a weak and broad absorption band in the visible range for samples annealed at 400 ºC. In a previous study it was reported that TiO_2/Au films produced by co-sputtering show SPR-related optical response only after annealing at sufficiently high temperatures (above 500ºC), as also can be observed in our figure 1. Torrell et al. [17] demonstrated that high annealing temperatures are required to produce Au NPs inside the dielectric matrix and consequently, the SPR effect on the optical spectra. Such an annealing affects significantly both Au NP's shape and size and also the phase composition of the TiO_2 matrix modifying its dielectric constant.
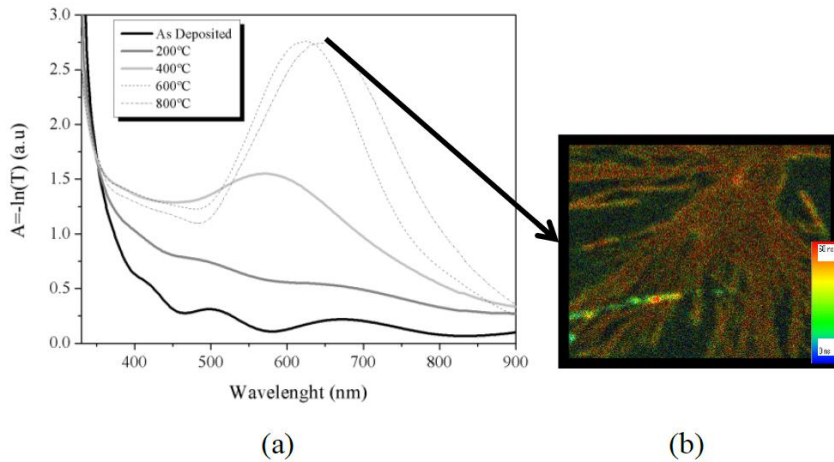

(a)   (b)

Figure 1. (a) Absorption spectra of the TiO2/Au films on SiO2 substrates annealed at different temperatures and (b) QDs structure/TiO2/Au thin film substrate annealed at 800ºC.

The absorption spectrum of a TiO_2/Au thin film annealed at 800ºC is also shown in figure 2, together with the absorption and photoluminescence spectra of colloidal CdTe QDs in solution. As it can be seen from figure 2, the spectra of TiO_2/Au film show a pronounced SPR-related absorption band with a maximum at $\approx$ 650 nm, which encompasses the absorption and emission peaks of the CdTe QDs. Therefore, one can expect a resonant coupling between excitons confined in QDs and surface plasmons in Au NPs. This could open an additional channel of energy transfer between the dots

(QDs1→NP→QDs2) [9, 18], which would enhance the FRET probability. On the other hand, the QDs luminescence can be quenched because surface plasmons are damped and the energy transfer QDs→NP may be irreversible, since the energy is dissipated within the metallic particle [7, 18]. Beyond these dynamical effects, the exciton-plasmon coupling should modify the energy spectrum of the hybrid system and, consequently, its steady-state optical properties, as it has been shown both experimentally [19] and theoretically [20] for structures composed of a QDs monolayer and a silver film.
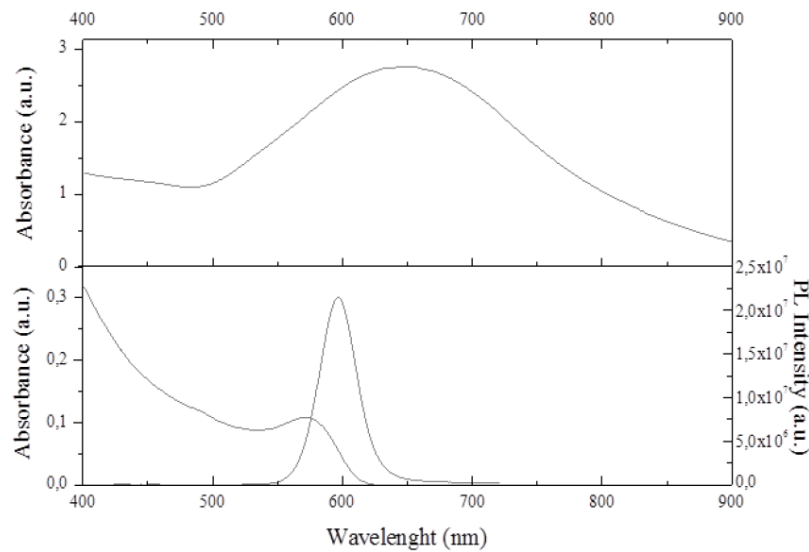

Figure 2. Absorption spectrum of a co-sputtered TiO₂ film doped with Au NPs (top) and absorption and photoluminescence spectra of CdTe QDs in solution (bottom).

To assess the LSP effect on the steady-state photoluminescence spectra of the QDs structures, we performed spatially resolved scanning spectroscopy studies using the Witec Raman alpha300M+ apparatus. By using the Witec tools Cluster and Basis analysis, the emission maps were decomposed into three typical bands (see figure 3) and their relative intensities were compared for different pixels of the map. For QDs samples deposited on "non-plasmonic" substrates (TiO₂/Au film annealed at 200ºC) the spectra (not shown) were composed of almost solely green band corresponding to the QDs ground state emission, similar to the same dots in solution.
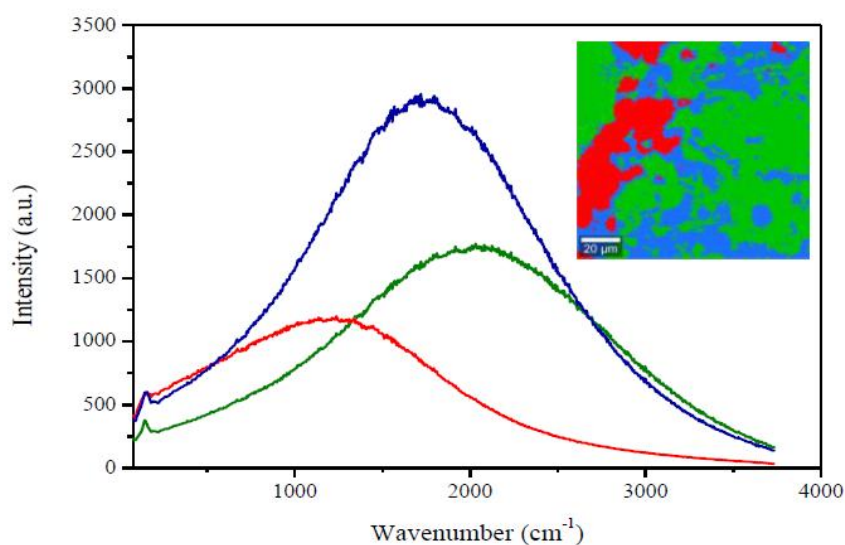
Figure 3. Emission bands for CdTe QDs dendritic structure fabricated on a TiO₂/Au thin film substrate annealed at 800ºC. The wavelengths of the maxima of the red, blue and green bands are 566, 587 and 596 nm, respectively. The small peak at very low wavenumbers is the phonon-related Raman scattering signal from QDs. The inset shows a digital map where the color corresponds to the dominating emission band.

In contrast, the spectra of the dendritic structure developed on the surface of TiO$_2$/Au thin film substrate annealed at 800ºC is inhomogeneous and contain the three emission bands (figure 3). The green band corresponds to the highest wavelength of $\approx$ 596 nm, characteristic of the QDs emission in solution. The blue band is only slightly shifted towards higher photon energies with respect to the former (the shift is $\approx$ 30 meV). The origin of this shift could be the electromagnetic coupling between Au NPs and CdTe QDs since it results in a mode anticrossing and an anti-Stokes shift of the upper coupled mode [19, 20]. Another possible explanation is the formation of QDs molecules with inter-dot-coupled exciton states [21] and/or phonon-assisted (up-converted) emission [22]. Indeed, our analysis indicates that this emission comes mostly from those zones of the self-assembled structure where the QDs density is higher. Then the question about the role of gold NPs arises, namely, whether they can stimulate the aggregation of QDs at the self-assembly stage.

Finally, the "red" band is shifted towards higher energies by more than 100 meV with respect to the "fundamental" emission mode (596 nm). Its origin is not completely clear to us at the moment but it might be an emission owing to the recombination of excited state (possibly 1Se–1S3/2) excitons. Such a "hot" luminescence has sometimes been

observed for resonantly excited QDs [23]. The role of Au NPs here could consist in quenching of the ground state luminescence (see below), which helps revealing the weaker emission owing to the direct recombination of the excited state excitons. We also investigated fluorescence decay kinetics using pulsed laser excitation (λexc =485 nm) and FLIM mapping of the emission from self-assembled dendritic structures on plasmonic and non-plasmonic platforms. FLIM images of the QDs dendritic structures deposited on a conventional substrate and on the surface of a TiO_2/Au thin film annealed at 200ºC and 800ºC are presented in figure 4.
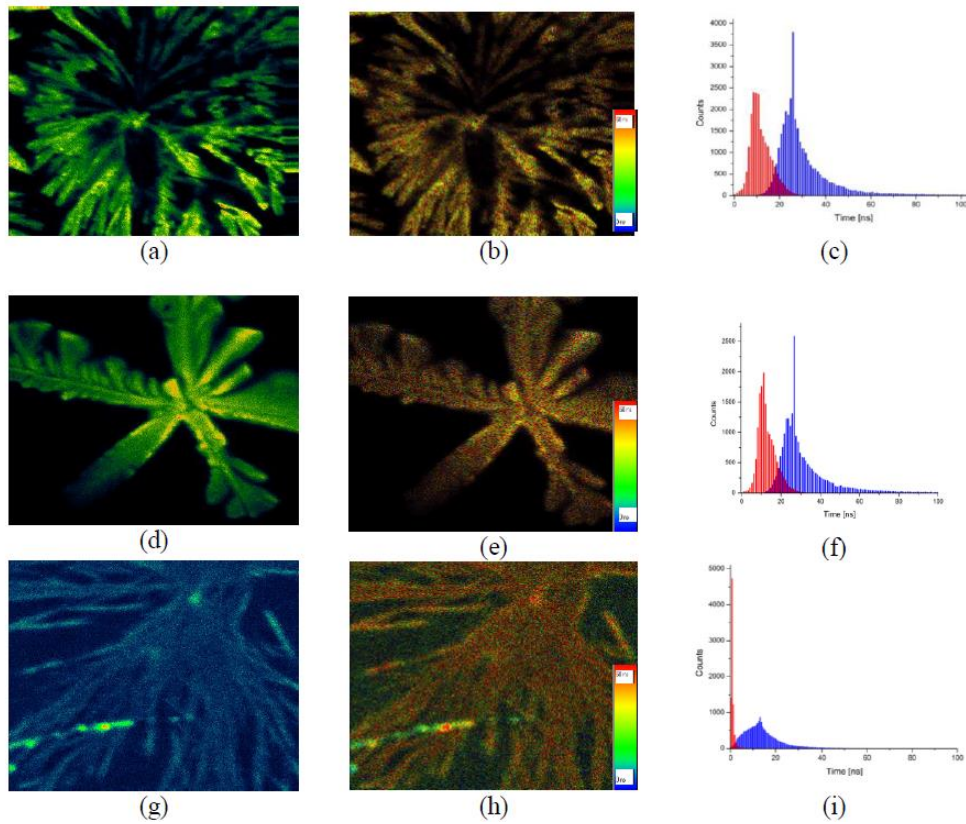

Figure 4. PL intensity (a, d and g) and PL lifetime (b, e and h) maps, for pure CdTe QDs dendrite structures fabricated on glass (a and b) and on the surface of TiO_2/Au thin films annealed at 200 ºC (d and e) and 800 ºC (g and h). The corresponding PL lifetime histograms (c, f and i) were obtained by means of two exponential fitting of the PL decay kinetics at each image spot while scanning over an 82 x 82 μm, 78 x 78 μm and 67 x 67 μm, respectively. The bar heights represent the relative statistical weights of the two components (τ_1, and τ_2, red). The laser excitation wavelength is 485 nm.

According to the results of the analysis performed on the PL decay kinetics, it is possible to distinguish two different time scales with characteristic times $\tau 1$ and $\tau 2$ ($\tau 1 > \tau 2$). These characteristic times are represented by blue and red colors, respectively, in the histograms of figure 4. Presumably $\tau 1$ represents the radiative recombination of a

QDs exciton affected by non-dissipative processes like FRET (it would be just a radiative lifetime for an isolated QDs), while τ2 describes non-radiative dissipation processes. Figure 4 shows that τ1 and τ2 remain unchanged for the QDs dendritic structure on a TiO2/Au substrate annealed at 200 ℃ compared to those fabricated on glass surface. However, for the structure fabricated on the surface of a TiO2/Au film annealed at 800 ℃ τ2 shortens dramatically, meaning that the plasmonic substrate leads to the fast fluorescence quenching. The longer characteristic time ($\tau 1$) is also decreased, which means that it is not just the intrinsic radiative lifetime of a single quantum dot and a more complex analysis involving a continuous distribution of lifetimes would be appropriate [24].

Table 1. Characteristic decay times (τ_1 and τ_2) for QDs structures fabricated on TiO_2/Au substrates annealed at different temperatures.

Sample	Reference	TiO_2/Au 200℃	TiO_2/Au 400℃	TiO_2/Au 600℃	TiO_2/Au 800℃
τ_1	29.3	27.9	21.0	21.0	13.0
τ_2	12.2	12.5	5.3	7.7	0.8

We notice that the decrease of τ1 and τ2 is observed only for TiO_2/Au thin film annealed at 800℃. According to the FLIM maps, a good homogeneity in the lifetime spatial distribution is observed, even though a slightly higher luminescent core, with a longer τ1 is seen for the QDs dendrite on the TiO_2/Au thin film surface annealed at 800 ℃. This observation can be explained by the higher QDs density in the core region. Nevertheless, there is no any pronounced inhomogeneity along the structure in the lifetime map, unlike it was found in our recent study of fractal aggregates of CdTe dots [24]. This indicates that the lifetime is almost independent of the local environment in the self-assembled structure and therefore, energy transfer process does not play an important role within the QDs dendritic structure but rather it takes place in the direction from the dots to the plasmonic substrate. From table 1 we can see that the characteristic time of the slower non-dissipative kinetic processes decreases with the onset of the SPR in the substrate. It can be understood as (plasmon-mediated) exciton energy transfer to larger dots from which it is later emitted at a somewhat different wavelength.

4. Conclusions

In summary, we investigated the effect of SPR supported by nanocomposites consisting of a dielectric matrix (TiO_2) with embedded Au NPs annealed at different temperatures, on the steady-state luminescence and resonant energy transfer in self-assembled structures consisting of CdTe mono-size QDs.Our results indicate that a resonant coupling between excitons confined in QDs and LSPs in Au NPs located beneath the self-assembled structure indeed takes place and results in a shift of the ground state luminescence peak towards higher energies, as well as an onset of a "hot" emission from excited states in QDs. Depending on the morphology, spatial distribution, shape and size of the Au NPs, determined by the annealing temperature, the characteristic fluorescence decays show some SPR-related changes in lifetimes. Indeed, we can conclude that the changes are correlated with the onset of the SPR in the NPs. They possibly include both dissipative quenching of the emission and non-dissipative FRET-type processes. We continue our studies of the microscopic mechanisms operating in these hybrid systems but our results already show the potential of TiO2/Au platforms for environmental sensing applications based on the coupling of localised surface plasmons to the elementary excitations responsible for the light emission, such as QDs excitons.

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