

# Interaction of surface plasmons with CdTe quantum dot excitons

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## ABSTRACT

A 5-fold enhancement in the luminescence of CdTe nanocrystal quantum dots (QDs) is observed when they are placed in proximity to a nanostructured Au film deposited by pulsed laser deposition technique. No enhancement is observed with a nanostructured Ag film. The enhancement is due to the interaction of the QDs excitons with the localized surface plasmons (LSP). The Au surface plasmon (SP) frequency is closer to the QDs emission frequency than Ag LSP frequency and this accounts for the differences in observed behavior. As the SP-QD interaction strongly depends on the geometric structure and shape of the metal nanoparticles, a comparison with QDs deposited on a film of Au colloidal nanoparticles is presented. In the case of QDs placed directly on the Au colloids the luminescence quenching is much stronger and with a spacer layer a 3.5-fold enhancement over the bare QDs luminescence is observed.

Keywords: CdTe, quantum dots, nanostructured films, metal nanoparticles, excitons, surface plasmons, photoluminescence.

## 1. INTRODUCTION

The ability to control spontaneous emission (SE) of quantum dots (QDs) can have profound consequences in optoelectronic devices and biological imaging applications. The SE modification of molecule located near a metallic surface, compared to free space emission, has been first experimentally demonstrated by Drexhage et al<sup>1</sup>. Since then, there has been much progress in coupling metal surface plasmons to different radiative systems<sup>2-4</sup>. The effect of a metal surface on the radiative and non-radiative processes of an emitting species on the nanoscale has been theoretically predicted<sup>5</sup> and more recently demonstrated<sup>4,6,7</sup>. Metallic films containing nanoscale surface features can also produce giant enhancement of linear and nonlinear optical responses<sup>8,9</sup>.

Metals support collective oscillations of the conduction electrons, called bulk plasmons, at the plasma frequency ( $\omega_p$ ). Due to momentum conservation considerations surface plasmons of lower frequency cannot be excited on a flat metallic film by electromagnetic radiation of optical frequency. However gratings or surface roughness can provide additional momentum, allowing for the excitation of surface plasmons.<sup>6,10</sup> In our case SPs, of a lower frequency ( $\omega_{sp}$ ), are excited in nanoscale noble metal structures, which exhibit anomalous optical extinction in the visible spectral range due to resonantly driven electron plasma oscillations called localized surface plasmons (LSP).<sup>11</sup>

Spontaneous emission enhancement from QDs in proximity to a rough Au surface, as well Au nanoparticles has been observed,<sup>6,12,13</sup> under conditions where the LSP wavelength is close to the QDs emission wavelength. The SE enhancement was attributed due to the modified and locally enhanced electromagnetic field produced by the metal. In this paper we investigate the LSP-CdTe QD interaction and modification of the emission near nanostructured Au and Ag metal surfaces deposited using a pulsed laser deposition technique (PLD films). The Au and Ag PLD films exhibit LSP wavelengths of 550 and 450 nm respectively, which are near and far from the QDs emission wavelength of 600 nm

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respectively. The size and shape of metal nanoparticles are known to influence the molecule emission properties<sup>5</sup>. The nanostructures produced using PLD are not uniform in size or shape, and therefore it is interesting to make a comparison with a film of Au colloids, with which the size and shape distribution is expected to be smaller.

## 2. EXPERIMENTATION

Water-soluble CdTe QDs are synthesized by using thioglycolic acid as a short-chain stabilizer, details on the growth conditions can be found elsewhere.<sup>14</sup> Thioglycolic acid molecules impart negative charge to the QD surface at slightly alkaline pH, allowing for the fabrication of QDs monolayers on positively charged substrate using a layer-by-layer (LBL) assembly technique<sup>15</sup>. The peak emission wavelength of the CdTe QDs occurs at 600 nm. A KrF (248nm, 26ns) laser is used to ablate rotating targets of Au and Ag in vacuum at a target-substrate distance of 9 cm and at an incident angle of 45 degrees. Films are deposited at a fluence of  $2 \text{ J cm}^{-2}$  for 3 minutes at room temperature. The plasma is monitored using an ion probe and a quartz crystal deposition monitor. The water-soluble negatively charged colloidal Au nanoparticles used have a strong absorption at 530 nm, details on the growth conditions can be found elsewhere.<sup>16</sup>

Using the LBL technique 2 monolayers of CdTe QDs and 3 monolayers of Au colloids deposited using positively charged Polyethyleneimine (PEI) as a counterpart, by dipping sequentially for 20 min in solution. The metal-QD separation dependence of the PL enhancement was studied by depositing, a polymer spacer layer of controlled thickness between the QDs and metal layers. The spacer layer consists of polymer multilayers built up using the same LBL technique. The metal film, deposited on a quartz substrate, is dipped into an aqueous solution of Poly(diallyldimethylammonium chloride) (PDDA) having positive charge and Poly(p-styrolsulfonsaeure natriumsalz) (PSS) having negative charge sequentially for 20 minutes. In between each dip the structure is rinsed with water to remove any loose molecules not ionically bonded to the surface. By repeating these dipping procedures, the multilayer films can be self-assembled up to the required thickness. The polymer thickness is approximately 1.4 nm for 1 layer and 11.7 nm for 9 layers.<sup>17</sup> The QD monolayers form the final layers, after which the samples are vacuum dried for 10 minutes.

A Shimadzu spectrophotometer is used to record the absorption spectra of the metal layers. A Hitachi H-7000 scanning transmission electron microscope (TEM) is used for imaging the metal nanoparticles films. Room temperature photoluminescence (PL) is recorded using a Perkin-Elmer fluorescence spectrometer, with an excitation wavelength of 400 nm.

## 2. RESULTS & DISCUSSION

Figure 1 shows the absorption spectra of the PLD nanostructured Ag and Au films, exhibiting surface plasmon absorption features at 450 and 550 nm respectively, typical of the nanosized metal structures. In order to confirm the nanostructured nature of the PLD films, STEM micrographs of particles deposited for 90 seconds on a polymer coated copper grid are presented in fig. 2. Isolated Ag and Au nanoparticles can be clearly observed. The feature dimensions are typically  $< 10 \text{ nm}$ , with a distribution of  $\sim 30 \%$ .

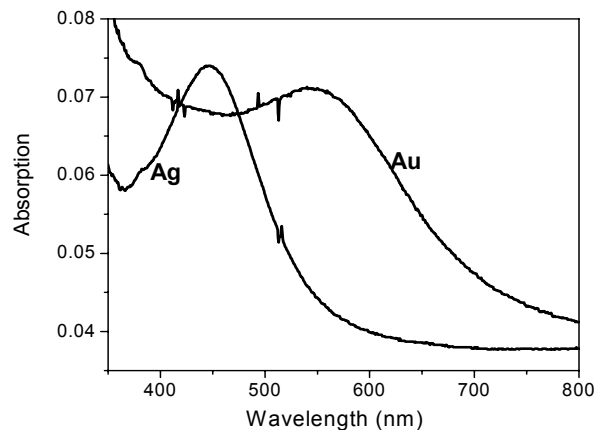


Fig. 1: Absorption spectra of nanostructured Ag and Au films deposited using a pulsed laser deposition technique

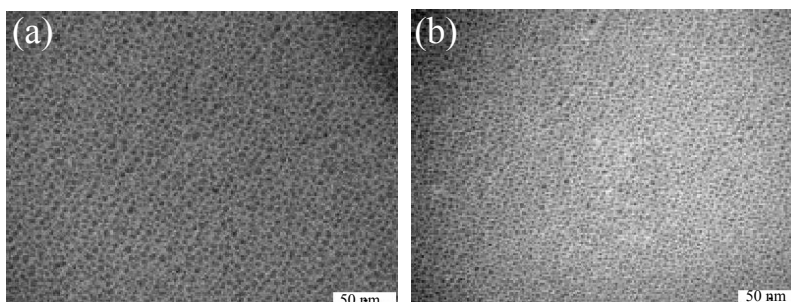


Fig. 2: Scanning Transmission Electron Micrographs of Ag and Au nanoparticles deposited on polymer coated copper grids for 90 seconds using pulsed laser deposition.

Typical photoluminescence (PL) spectra of 2 monolayers of CdTe QDs on a quartz slide and 2 monolayers CdTe QDs separated from the PLD Au films by polymer spacer layers of varying thickness are shown in figure 3. The spectra are labeled according to the number of polyelectrolyte layers forming the spacer. Due to resonance energy transfer between small and large QDs, the PL spectrum of the QD monolayers on the quartz substrate is red shifted to 612 nm, compared to the isolated QDs emission at 600 nm, as measured in solution<sup>18</sup>. In the case of QD monolayers deposited on the PLD Au film separation dependent PL quenching is observed for small metal-QD separations followed by enhancement as the separation increases. The luminescence of QDs is quenched when they are placed directly onto the Au film. Here the dominant mechanism is non-radiative energy transfer from the QDs to the Au film either by inter-band absorption or electron-hole excitation due to strong coulomb interaction<sup>19</sup>.

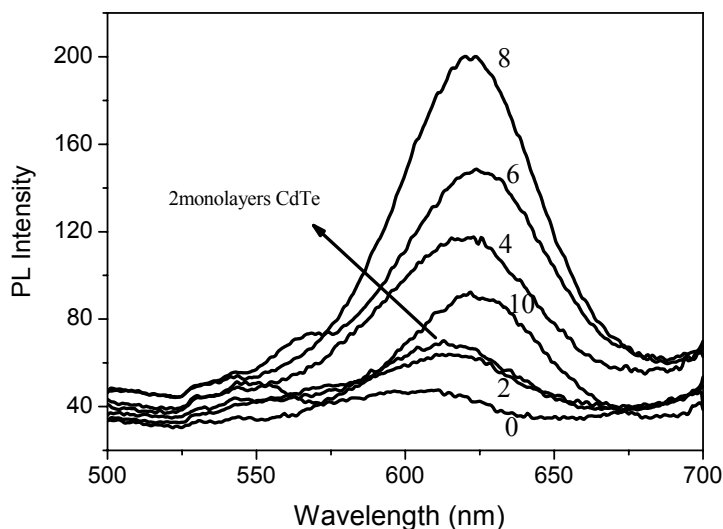


Fig. 3: Room temperature photoluminescence spectra of 2 monolayers of CdTe QDs, and QDs separated by polymer spacer layers from nanostructured Au PLD film. The spectra are labeled according to the number of polyelectrolyte spacer layers that are present between the Au film and the QDs.

With increasing spacer layer thickness between the QDs and Au film this non-radiative energy transfer is suppressed and the PL intensity increases. The PL intensity is seen to be very sensitive to the distance between the QDs and the Au film. A maximum 5-fold enhancement in luminescence has been observed for a spacer thickness of approximately 10 nm (8 spacer layers). This 5-fold enhancement is in comparison to the PL intensity of the CdTe QDs

on the quartz slide in the absence of a metal film. In the calculation of the enhancement factor the background level has been subtracted off all the data sets and the PL baseline has been adjusted to zero. Further increase in the metal-QD separation results in a reduction in the observed PL. Since the SP is an evanescent wave that decays exponentially with distance from the metal surface, QDs can experience strong quantum electrodynamical coupling to an SP modes only when placed within the SP fringing field penetration depth. It was recently reported in case of quantum wells that in this regime an electron-hole pair recombination produce SPs instead of emitting a photon into free space.<sup>2</sup>

We also recorded the PL spectra of QDs on polymer spacer layers of varying thickness in the absence of any metal layer. We have not seen any observable quenching of QDs PL. The absorption spectra of bare polymer layers on a quartz substrate show no increase in the absorption in the visible region with increasing thickness. These observations clearly indicate that there is no strong resonant energy transfer from QDs to polymer spacer layers, or dependence of the QD PL on the polymer layer thickness. Any modification of the QD emission is resulting from the interaction with the metal surface plasmon polariton (SPP) modes.

When the QDs are very close to the metal film a blue shift in PL peak is observed. As the separation between QDs and PLD Au film increases the PL peak red shifts. The spectral shift of the QD emission is likely to be related to the interaction of the QD excitons with metal SPs<sup>6,13</sup>. For example Emedocles et al. showed evidence of spectral shifts resulting from modified exciton diffusion caused by the altered local electric field around QDs<sup>20</sup>.

Figure 4 shows the PL spectra of 2 monolayers of CdTe QDs on a quartz slide and 2 monolayers CdTe QDs separated from the PLD Ag film by 6 and 8 spacer layers. Clearly, there is no enhancement in the PL emission of the QDs, whereas 3.5 and 5-fold enhancement have been observed with Au PLD film at 6 and 8 spacer layers respectively. We attribute the marked difference in the PL behavior of the QDs in proximity to the Au and Ag films to QD-SPP interaction. In the case of the Au film the peak PL emission wavelength (600 nm) is close to the surface plasmon absorption wavelength (550 nm). In contrast the LSP wavelength for Ag film (450 nm) is far from QDs emission wavelength, resulting in no interaction between the QD excitons and surface plasmons. Consequently, in the case of the Au PLD film, the SPP-QD coupling is expected to be stronger and result in an increase in the spontaneous emission. The experimental results indicate that enhancement in spontaneous emission is not only due to the modified and locally enhanced electromagnetic field produced at the QDs by metal surface. It is due to the strong electrodynamic interaction of excitons with metal SPs.

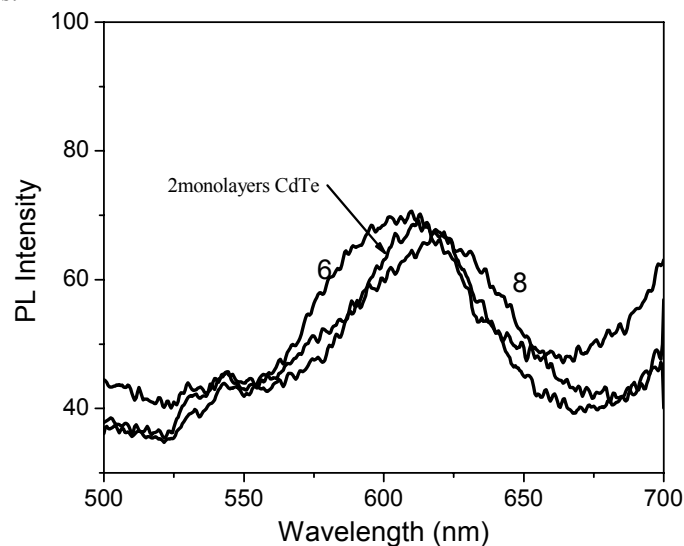


Fig. 4: Room temperature photoluminescence spectra of 2 monolayers of CdTe QDs, and QDs separated by 6 and 8 polymer spacer layers from nanostructured Ag PLD film.

Figure 5 show PL spectra of 2 monolayers of CdTe QDs on a quartz slide and 2 monolayers CdTe QDs separated by polymer spacer layers from 3 monolayers of Au colloids. The spectra are labeled according to the number of polyelectrolyte layers forming the spacer between the Au colloids and the QDs. The metal-QD separation dependent quenching and enhancement of QDs interacting with Au colloids presents a number of differences when compared to the observations for the nanostructured Au film. Firstly there is stronger quenching of the PL for QDs placed directly on the Au colloids. 4 spacer layers are required before the QDs PL has recovered to the level of 2 monolayers deposited directly on a quartz slide. In case of the Au PLD film only 2 layers of polymer spacing were required. Secondly, a maximum 3.5-fold enhancement is observed at 6 spacer layers with Au colloids compared to 5-fold enhancement at 8 spacer layers with PLD Au film.

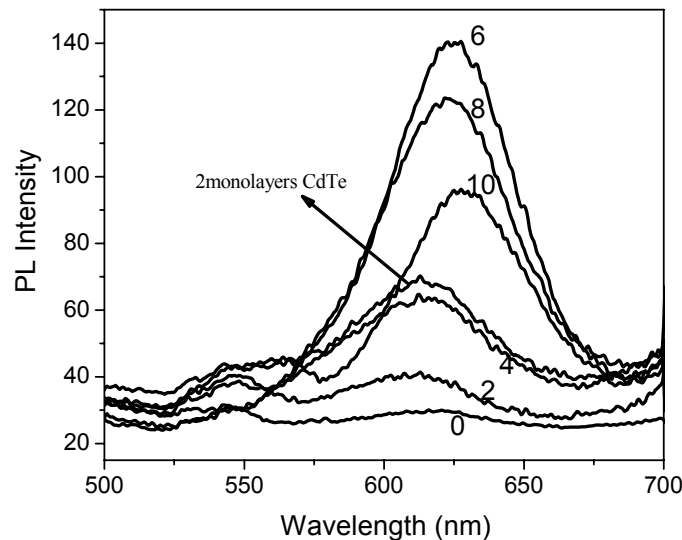


Fig. 5: Room temperature photoluminescence spectra of 2 monolayers of CdTe QDs, and QDs separated by polymer spacer layers from 3 monolayers of Au colloids. The spectra are labeled according to the number of polyelectrolyte spacer layers that are present between the Au colloids and the QDs.

Surface plasmons are electromagnetic modes whose properties can be drastically altered through change of size, shape, or type of surface ligands<sup>21</sup>. Electromagnetic modes of metal particles can influence both radiative and non-radiative processes of the QDs.<sup>5</sup> Consequently QD PL quenching and enhancements, associated with the excitation of SPs are also sensitive to these changes. There are a number of possible contributing factors to the different behavior for the Au PLD and colloidal films. Firstly, the SP absorption peak of the Au colloids occurs at 530 nm, further away from the QD PL peak than in the case of the PLD Au film. Based on the comparison of the Au and Ag PLD films this is expected to result in weaker SP-QD coupling and hence lower enhancement of the QD emission. This is in agreement with the experimental observations on the metal colloid film. The stronger quenching of the QD emission on the Au colloidal film can be interpreted as a stronger dipole-dipole interaction between the Au colloids and the QDs. The radiative rate of the QDs can also influence due to interaction of the exciton dipole field with induced dipole field in Au particles<sup>7</sup>. The quenching is greater than for either of the PLD films, and this likely to be a consequence of the greater overlap in size and shape of the metal colloids and the QDs. Further experiments are required to fully understand these effects.

### 3. CONCLUSIONS

We conclude that the PL enhancement observed in CdTe QDs is due to resonant coupling of the SP and QDs. It is not sufficient to only take account of a modification of electric field around the QDs due to the proximity of the metal surface. The coupling strength can be tuned by varying the relative frequencies of the SP and the QD emission. The maximum enhancement of the spontaneous emission is expected under resonant conditions, and will occur at greater separations from the metal layer. In the case of a Au PLD film we observed a 5-fold enhancement in the QD spontaneous emission under near resonant conditions with a metal-QD separation of  $\sim 10$  nm, whereas no enhancement is observed for the a Ag PLD film. We have seen evidence for a stronger dipole-dipole interaction in the case of QDs

deposited on a Au Colloid film. A 3.5-fold enhancement of the spontaneous emission at a separation of ~8 nm was observed in this case. The strong quenching of QDs emission observed with Au colloids shows the possibility of using in biological fluorescence-based detection systems.

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