Influence of Localised Surface Plasmons on Energy Transfer between Quantum Dots

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ABSTRACT

The effects of surface plasmons (SPs) on Förster resonant energy transfer (FRET) in colloidal quantum dot (QD) structures have been investigated. CdTe QDs of two different sizes acted as donors and acceptors in a mixed donor-acceptor monolayer on top of a gold nanoparticle layer and an acceptor-gold-donor sandwich structure. The structures were prepared by a layer-by-layer technique and characterized by absorption and photoluminescence (PL) spectroscopy as well as time-resolved PL measurements. For the case of the mixed QD monolayer a recovery of the acceptor emission is observed when increasing the acceptor-gold separation. The reduction of the donor lifetime indicates that the FRET process is enhanced by 30%.

In the sandwich structure a clear modification of the FRET distance dependence towards a typical SP influenced dependence on the QD-gold separation is observed. The maximum acceptor QD emission occurs at approximately 12 nm from the intermediate gold layer, corresponding to a donor-acceptor separation at which no FRET is observed in structures without gold. By varying the gold concentration the acceptor PL enhancement can be increased and an absolute enhancement of 25% compared to structures without gold is achieved.

Keywords: Localized surface plasmon resonance, Förster resonant energy transfer, nanocrystal quantum dots, spectral overlap, optical spectroscopy, time-resolved PL decays.

1. INTRODUCTION

Förster resonant energy transfer (FRET) is a mechanism based on dipole-dipole interactions between energy donors and acceptors [1]. This energy transfer process can be implemented in sensing and light harvesting structures [2]. Colloidal quantum dots (QDs) possess unique optical properties and their tuneable emission, as well as high quantum yields and photostability, make them good energy donors and acceptors [3]. However, the influence of properties such as QD size [4] and the inhomogeneous broadening of the QD ensemble [5] have to be taken into account when analyzing FRET in QD structures and optimizing it for applications. It has been predicted that the interaction with localized surface plasmons (SPs) can result in enhanced FRET [6]. The resulting higher FRET efficiency, faster FRET rate or larger interaction distance could consequently improve the performance of light-harvesting devices and increase the sensitivity of nano-sensors. To-date there have only been a few experimental reports on SP effects on FRET and, in particular for QD systems [7].

We investigate the effect of SPs, supported by gold nanoparticles (NPs), on FRET in two different structures with colloidal CdTe QDs of two different sizes acting as energy donors and acceptors. The dependence of the FRET process on the QD-gold NP distance as well as the variation of the quantum dot / gold NP concentrations in layered donor-gold-acceptor structure will be discussed and compared with the case of a mixed donor-acceptor monolayer deposited on top of a gold NP layer.

2. EXPERIMENTAL METHODS

Negatively charged CdTe quantum dots (QDs), stabilized by thioglycolic acid in aqueous solution [8], of two different sizes, 2.7 and 3.5 nm, acted as donor and acceptor QDs in the FRET structures. The donor and acceptor QDs emitted at 547 nm and 610 nm, respectively (Fig. 1a). The gold metal NPs, with a diameter of approximately 7 nm, show a surface plasmon resonance at 520 nm in solution. As can be seen in Fig. 1a this SP resonance occurs in the wavelength region where the donor emission and acceptor absorption overlap and the metal nanoparticles should therefore be able to modify the FRET process between the donor and acceptor QDs.

A layer-by-layer electrostatic self-assembly technique [9] was used to prepare structures with either mixed donor / acceptor QD monolayers or separated monodispersed donor and acceptor QD layers. The mixed QD monolayer was deposited on top of three gold NP layers separated by a polyelectrolyte spacer layer with a thickness tuneable in 7 nm steps. In the separated donor-acceptor layer structure a single gold NP layer was introduced between the donor and acceptor QD layers. Polyelectrolyte layers, with thicknesses adjusted in 3 nm steps, acted as QD-gold spacers. Samples with monodispersed donor or acceptor QDs on gold with different gold concentrations and QD-gold separations were also prepared for reference.

The absorption spectra of the QD structures were measured using a double beam UV-Vis Recording Spectrometer (Shimadzu UV-2401 PC). The steady-state photoluminescence (PL) spectra were recorded with a Perkin-Elmer LS 55 fluorescence spectrometer using an excitation wavelength of 400 nm. A PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution was used to measure the time-resolved PL decays of the QD structures. Picosecond pulses at 470 nm were provided by a LDH-480 laser head controlled by a PDL-800B driver (PicoQuant). The measurements were carried out over areas of 80 by 80 µm (150 by 150 pixels) with integration times of 4 ms per pixel and repetition rates of 10 or 5 MHz, depending on the length of the decay. Broad band filters (FWHM: 70 ± 5 nm) centred at 500 nm, 550 nm, 600 nm and 650 nm were used to measure the decays in different spectral regions of the QD emission.

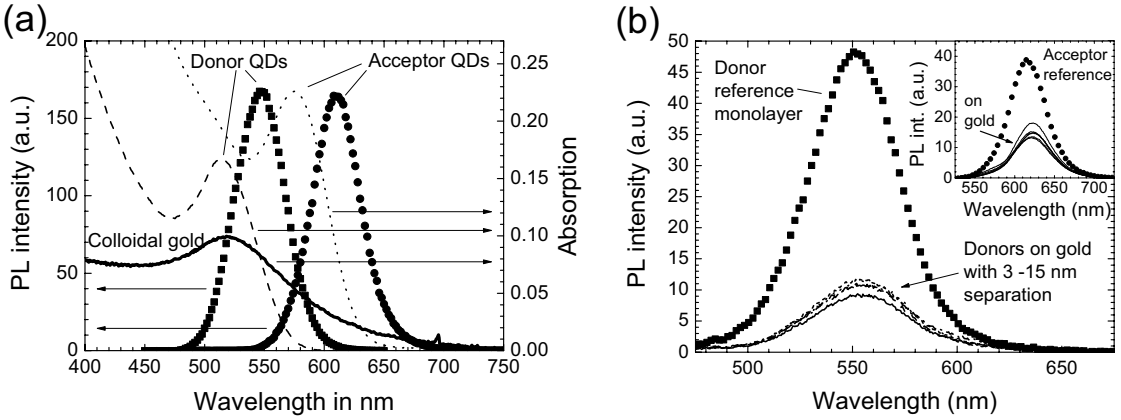

Figure 1: (a) Photoluminescence (PL) spectra (symbols) and absorption spectra (broken lines) for the donor and acceptor QD solutions. The absorption spectrum of the colloidal gold nanoparticle solution is included as a solid line. (b) PL spectra of the donor reference monolayer (squares) and donor monolayers on top of a gold nanoparticle layer for a donor concentration of 3.7×10^{17} m^{-2} and separations between 3 and 15 nm. The inset shows the respective spectra for acceptor layers at a concentration of 0.47×10^{17} m^{-2} for 3 to 18 nm separations.

3. RESULTS AND DISCUSSION

The investigation of SP enhanced FRET is complicated by the fact that the SPs not only modify the FRET process but also the optical properties of the QDs by themselves, through SP enhanced / quenched QD photoluminescence [10]. Therefore, it is critical to carefully characterize FRET in the QD structure without gold NPs as well as SP effects on the individual donor and acceptor layers, before investigating the effect of the SPs on FRET. We are going to briefly discuss the modification of the optical properties of the monodispersed donor and acceptor QD layers in proximity of a gold NP layer, followed by the presentation of the influence of SPs on the energy transfer between donor and acceptor QDs in a mixed monolayer and in a separated layer structure.

3.1 SP effects on monodispersed QD layers

Firstly, the effect of a gold nanoparticle layer on the individual donor and acceptor QD emission is analyzed and the spectral data is shown in Fig. 1b. Time-resolved PL data was also investigated. As can be seen in Fig. 1b, the donor emission decreased in proximity to the gold NPs due to interaction with the SPs. A range of gold-QD separations were studied for reference but no significant distance dependence was observed on this scale. The same quenching effect is observed for the acceptor QDs deposited on top of a gold NP layer (inset of Fig. 1b). No direct SP enhanced PL is observed for either donor or acceptor QDs at any separation or gold concentration investigated. This is important to note as this excludes a SP induced donor PL enhancement as the origin of an increased energy transfer to the acceptor QDs.

3.2 SP influence on FRET in mixed QD monolayer

In Figure 2a the spectra of a mixed donor / acceptor monolayer reference sample and mixed QD monolayers on top of gold layers for three different spacer thicknesses are shown. Varying the thickness of the spacer layer, a distance dependence typical for interactions with SPs is observed for the acceptor PL. The overall luminescence of the samples is quenched due to the high gold concentration, however with increasing QD-gold separation the acceptor luminescence increases up to the spacer layer thickness of 70 nm and starts to decrease again for larger separations (data not shown). In Figure 2b the time-resolved donor decays at a QD-gold NP separation of 70 nm for a pure acceptor and a mixed donor-acceptor monolayer are shown along with that for the reference samples without gold NPs. The FRET efficiency calculated from the relative donor lifetime decrease, $1 - \tau_{mix}/\tau_{pure}$, is 43% in the mixed QD monolayer reference and increases to 56% for the mixed monolayer on

gold. This suggests that the FRET efficiency is increased by 30% on gold NPs compared to the efficiency calculated for the monolayer references.

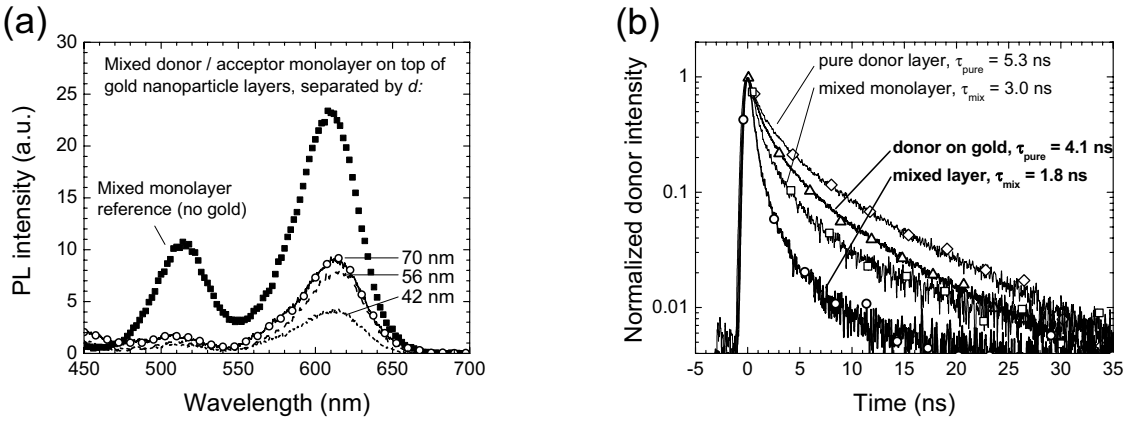

Figure 2: (a) Photoluminescence (PL) spectra of mixed donor / acceptor QD monolayers on top of three gold nanoparticle layers for three different gold-QD separations (lines) and the reference structure without gold nanoparticles (squares). (b) Time-resolved donor PL decays for a pure donor reference layer (diamonds), a donor monolayer on gold (triangles), the mixed donor / acceptor reference (squares) and a mixed monolayer on gold (circles) for a QD-gold separation of 70 nm.

3.3 SP modification of FRET in separate layer structure

In a separated acceptor-donor layer structure the FRET efficiency and the acceptor enhancement decrease with layer separation in good agreement with FRET theory [11], indicating that FRET is the main energy transfer mechanism responsible for the acceptor enhancement.

After the deposition of the gold NPs on top of the acceptor layer, the acceptor luminescence is fully quenched (data not shown). In the full acceptor-gold-donor sandwich structure the distance between the acceptor QD layer and the gold NP layer is varied and it can be seen in Fig. 3a that some of the acceptor emission can be recovered for acceptor-gold separations of 9 nm and for a separation of approximately 12 to 15 nm a maximum in acceptor PL intensity achieved.

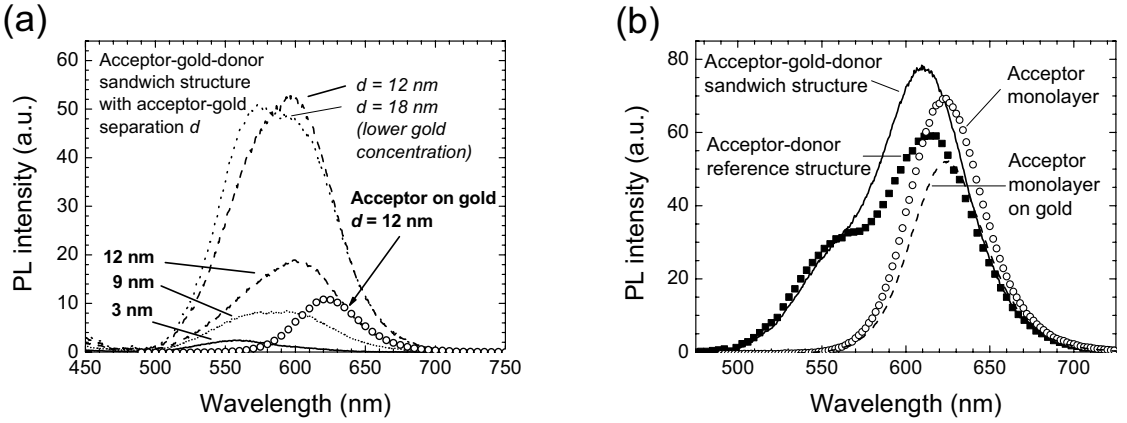

Figure 3: (a) Photoluminescence (PL) spectra of the acceptor-gold-donor sandwich structure (lines) for acceptor-gold separations varying from 3 to 18 nm, the spectrum for an acceptor monolayer on gold (open circles) is shown for reference at a separation of 12 nm. (b) PL spectra of an acceptor monolayer reference (open circles), an acceptor monolayer on gold (dashed line), a donor / acceptor reference structure with a donor-acceptor separation of 21 nm (filled squares) and an acceptor-gold-donor sandwich structure for low gold concentrations and acceptor-gold separations of 12 nm (acceptor concentration adjusted to 0.62 10^{17} m^{-2}).

This distance dependence for the acceptor-gold-donor sandwich structure, as presented by the spectral data in Fig. 3a, is strongly modified compared to the decrease of the acceptor PL with increasing donor-acceptor separation observed for FRET in an acceptor-donor structure without gold NPs, but it is very similar to that previously reported for SP enhanced QD emission [10]. However, as discussed above, in this case the structures with only acceptor and gold layers show PL quenching, indicating that the enhanced acceptor emission in the presence of the donor layer cannot be attributed to direct SP enhancement of the acceptor emission but is instead

resulting from energy transfer from the donor layer. Furthermore, in a sample without the intermediate gold layer no enhancement of the acceptor emission by FRET is observed for the same acceptor-donor separation (see Fig. 3b). Therefore, the data indicates that the enhancement of the acceptor PL in the completed sandwich structure is due to SP mediated energy transfer. This is further confirmed by a study of the gold concentration dependence which shows that the acceptor PL can be further increased. The spectrum for an acceptor-gold-donor sandwich structure, at an acceptor-gold separation of 12 nm, along with all reference structures are shown in Fig. 3b for a low gold concentration. It can be clearly seen that at a similar acceptor-donor separation no enhanced acceptor PL is observed in structures without gold. The acceptor PL in the full sandwich structure is not only enhanced by approximately 50% with respect to the acceptor monolayer on gold, but also shows that an absolute PL enhancement of 25% compared to the acceptor-donor reference structure can be achieved by introducing gold NPs at the right position between the donor and acceptor layers.

4. CONCLUSION

The effect of SPs on FRET has been studied in a mixed donor/acceptor monolayer on gold and in an acceptor-gold-donor sandwich structure. In both cases a strong dependence on the QD-gold NP separation has been observed, whereas for monodispersed donor and acceptor reference samples on gold there is little distance dependence of the emission quenching over the range studied. In the mixed monolayer, the donor lifetime decrease suggests that the FRET efficiency is enhanced by 30% in proximity to the gold NPs.

For the sandwich structure an enhancement of the acceptor emission with respect to a reference without the donor QD layer has been observed and is attributed to SP enhanced energy transfer. This interpretation is supported by a characteristic SP distance dependence that shows a strong modification of the FRET distance dependence measured in the QD structure without gold NPs. By varying the gold NP concentration an overall acceptor PL emission enhancement is observed at a donor-acceptor separation much larger than the typical distances over which FRET occurs in structures without gold NPs.

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