Surface plasmon enhanced Förster resonance energy transfer between the CdTe quantum dots

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Förster resonance energy transfer (FRET) between CdTe quantum dots (QDs) at nanoscale proximity to gold nanoparticle (Au NP) layers is investigated experimentally. We have observed the enhancement in the acceptor QDs' photoluminescence lifetime intensities. The decrease in donor QDs' exciton lifetime from 5.74 to 2.06 ns, accompanied by an increase in acceptor QDs' exciton lifetime from 3.38 to 7.52 ns, provided evidence for enhanced FRET between the QDs near Au NPs. The Au NPs' surface plasmon dipole fields are assisted to overcome the weak electronic coupling between the emitting (donor) and absorbing (acceptor) transition exciton dipoles in the homogeneous medium. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2981209]

The Förster resonance energy transfer (FRET) process is an important energy transfer mechanism at the nanoscale distance for transportation of excitation energy between the two chemical species.[1] The FRET process between semiconductor colloidal nanocrystallites or quantum dots (QDs) has been investigated in closely packed mixed layers and in separated donor and acceptor layers.[2] A cascaded FRET in artificial solids formed by layers of QDs has also been demonstrated.[3] Efforts to improve the FRET process have been focused on structures with reduced donor-acceptor QDs' separation, improved spectral overlap of the donor emission and acceptor absorption spectra, and increased packing density of the layers.[4]

Metal nanoparticles (NPs) have been used to modify some of the fundamental optical processes such as Raman scattering[5] and radiative processes[6] in chemical species in a characteristic way. In this letter, we present the experimental evidence for the enhanced FRET between the CdTe QDs at nanoscale proximity to Au NPs, motivated by the previous theoretical studies, which indicated the potential to accelerate the FRET process between the donor and acceptor molecules[7] and QDs (Ref. 8) near metal NPs.

Water-soluble CdTe QDs (Ref. 9) having peak emissions at wavelengths of 525 and 600 nm and water-soluble Au NPs (Ref. 10) having a size of ∼7−8 nm are synthesized according to the reported procedure. The superstructures consisting of nanoscale-thin Au NPs/dielectric spacer/mixed QDs' layers are prepared using a layer-by-layer electrostatic self-assembly technique.[11] 3 monolayers of Au NPs are deposited on a quartz substrate using polyethyleneimine as a counterpart. As a second step, polyelectrolyte (PE) bilayers comprised of 4, 6, 8, 10, 12, 14, and 16 spacer layers are self-assembled on top of the Au NP layers for studying the distance dependence of the FRET process. Each bilayer thickness is approximately 1.4 nm.[12] As a final step, a monolayer of mixed CdTe QDs having donors and acceptors is deposited on top of the Au NPs' trilayer/PE bilayers. Finally,

the samples are vacuum dried for 10 min. Further details of the sample preparation can be found elsewhere.[13] Donor and acceptors concentrations in the mixed QD solution prior to the deposition are selected so that the donors and acceptors from mixed monolayer would exhibit equal steady state photoluminescence (PL) intensities, when we deposited on the quartz substrates with no Au NP layers.[14] The shortest possible distance from the center of donor to the center of an acceptor dot is around ∼4 nm, after considering the diameters of the dots and the capped ligand chain lengths.

Shimadzu spectrophotometer and PerkinElmer fluorescence spectrometer are used for recording the absorption and PL spectra (excitation wavelength of 400 nm), respectively. The time-resolved PL decays are measured using a Pico-Quant Microtime200 confocal microscope system. Samples are excited with 480 nm picosecond pulses, generated by a PicoQuant LDH-480 laser diode. PL lifetime images are recorded by raster scanning a sample area (80×80 μm²) over the focused spot of the incident laser, with a total integration time of 2.81 min. From lifetime images, the decay curves are generated using the SYMPHO time analysis software (Pico-Quant). Lifetime decays are reconvoluted using nonlinear least squares analysis (FluoFit, PicoQuant). Broadband filters at 500 and 600 nm are used in PL lifetime measurements to collect the emission from the donor and acceptor QDs, respectively.

Figure 1 shows the absorption spectra of Au NPs (absorption maximum at ∼565 nm) and acceptor QDs, and also the PL emission spectra for donor (∼525 nm) and acceptor (∼600 nm) QDs. The Au NPs' surface plasmon (SP) absorption has a strong overlap with the donor QDs' emission spectrum and the acceptor QDs' absorption spectrum. Figure 2(a) shows the acceptor QDs' PL lifetime intensities obtained from the raster scanned lifetime images for an area of 80×80 μm² of the mixed QDs on the Au NP layers with 10, 12, 14, and 16 PE spacer layers, and on the quartz substrate (for a reference). The distance dependent acceptor QDs' PL lifetime intensities are also shown in the figure as an inset. The dotted line is a reference one, which is the acceptor QDs' intensity from the mixed dots, when they are on the

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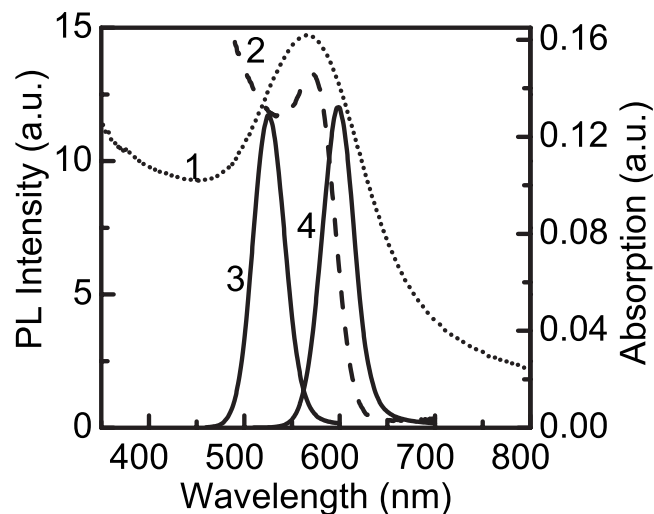
FIG. 1. Absorption spectra for 3 ML of Au NPs exhibiting the SP resonance at 565 nm (1) and for the acceptor CdTe QDs in solution (2). PL spectra for donor (3) and acceptor (4) CdTe QDs in solution.

quartz substrate. From the figure it is clear that there is an enhancement in the PL lifetime intensities of acceptor QDs when the mixed QDs are in close proximity to the Au NP layers. Position dependence of the acceptor QDs' PL lifetime intensities from the layers of Au NPs qualitatively reflects the vertical or evanescent nature of the Au NPs' SP dipole fields.[6] When the layer of mixed QDs is in very close to the Au NPs, i.e., up to eight PE bilayers, the acceptor QDs' intensities are quenched due to the nonradiative energy transfer from the QDs to the Au NPs. Here, we note that the pure monolayer of acceptor QDs' PL lifetime intensities with the Au NPs is not shown the distance dependence. So, the enhanced acceptor QDs' PL lifetime intensities when they are with donor QDs can be attributed due to the accelerated
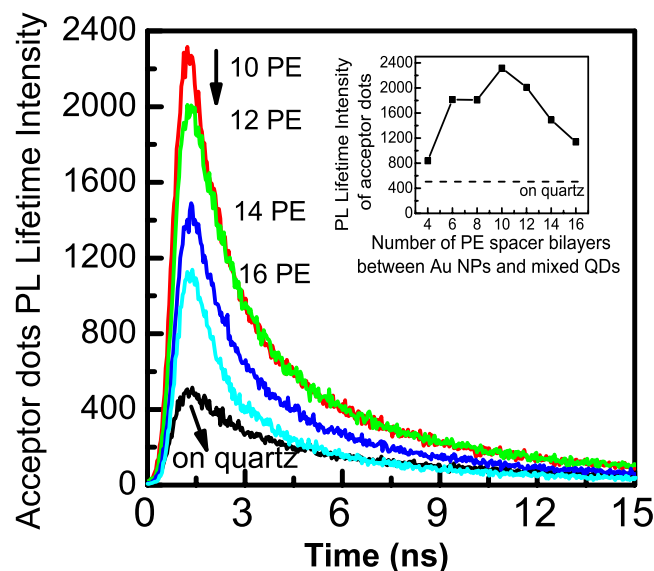

FIG. 2. (Color online) Acceptor QDs' PL lifetime intensities obtained from the raster scanned lifetime images with an area of $80 \times 80~\mu m^2$ from a mixed donor-acceptor CdTe QDs layer while on the quartz substrate, and while on the Au NP layers with 10, 12, 14, and 16 PDDA/PSS polyelectrolyte spacer layers. The inset also shows the distance dependent acceptor QDs' PL lifetime intensities from mixed QDs while on the Au NPs. The dotted line is a reference one, which is the acceptor QDs' intensity from the mixed QDs, while on the quartz substrate.
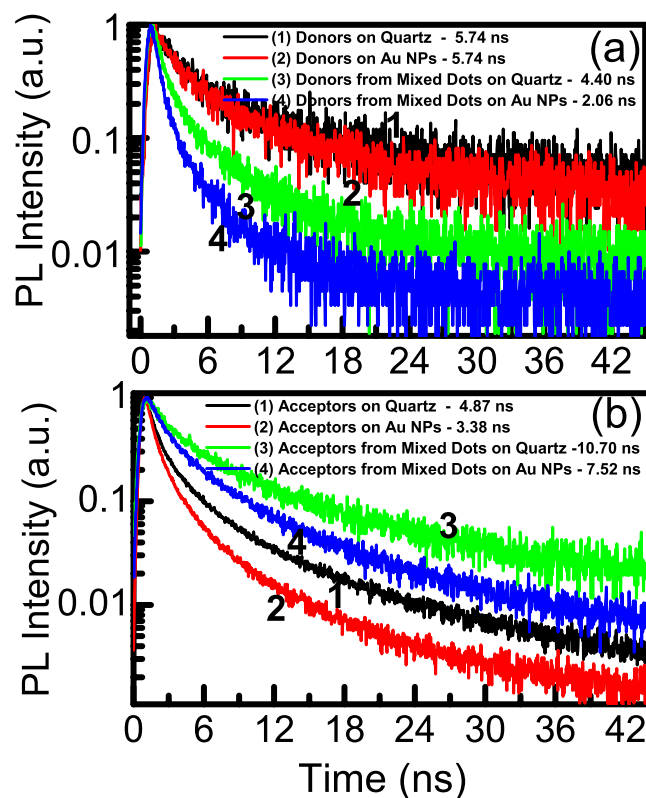

FIG. 3. (Color online) PL decays for (a) the donor and (b) the acceptor CdTe QDs. The decays are labeled 1–4 and the average lifetimes are given in the legend: (1) pure donor or acceptor QDs' monolayer on the quartz substrate, (2) pure donor or acceptor QDs' monolayer on the Au NPs with ten PE spacer layers, (3) mixed QDs' monolayer on the quartz substrate, and (4) mixed QDs' monolayer on the Au NPs with ten PE spacer layers.

FRET process from the neighboring donor QDs.

In the FRET process, along with the enhancement in the acceptor QDs' PL intensities with Au NPs, one should also expect a modified emission rate from the acceptor and donor QDs after the nonradiative energy transfer from donors to acceptors. Figures 3(a) and 3(b) show the PL decays for the donor and acceptor QD, respectively. The measured samples are donor-only, acceptor-only, and the mixed donor-acceptor QD monolayers on the Au NP layers with ten PE spacer layers underneath and also on the quartz substrate. The average lifetimes for pure monolayers of donor and acceptor QDs on the quartz are 5.74 and 4.87 ns, respectively, while on Au NPs, the values are 5.74 and 3.38 ns, respectively. In the case of mixed monolayer of QDs on quartz, the donor QDs' lifetime decreased from 5.74 ns (for pure monolayer of donors) to 4.40 ns and the acceptor QDs' lifetime increased from 4.87 (for pure monolayer of acceptors) to 10.70 ns. The FRET rate, i.e., the de-excitation of donor and the simultaneous excitation of acceptor is faster than the radiative rate of the emitter. This causes an increase in the donor decay rate with reduced PL lifetime and an increase in the acceptor lifetime, which is a clear signature of the FRET process.[2–4] When the layer of mixed QDs is in proximity to the Au NPs, the donor lifetime decreased further from 4.40 ns (on quartz) to 2.06 ns and the acceptor lifetime is modified from 10.70 (on quartz) to 7.52 ns. The average lifetime values of donor and acceptor dots are also shown to be distance dependent.[14] Further modification of exciton decay average lifetimes with the Au NPs gives an additional

evidence for the enhanced FRET rate from the donor to acceptor QDs.

The FRET process between the atoms/molecules fundamentally arises from the emitting and absorbing transition dipole near fields.[1] The FRET rate depends on the dipole moments of emitting and absorbing transition dipoles, the spectral overlap integral, the refractive index of the medium, and the distance between donor and acceptor dipoles.[1] In our case, the donor-acceptor distances in a mixed QD layer are not influenced by the incorporation of Au NPs underneath. The enhanced FRET process between the donor and acceptor QDs can be due to the modified exciton dipole moments with the introduced Au NPs' SP medium.[7,8] As shown in Fig. 1, the Au NP absorption spectrum has a clear overlap with the donor emission and acceptor absorption spectra, so the emitting and absorbing transition dipoles are in resonance with the Au NPs' SP dipole fields. The SP dipole fields are larger and more intense than the QD exciton dipole fields; these SP dipole fields seem to induce the exciton dipoles efficiently. The modified exciton dipole near fields with SP fields may extend spatially beyond their neighbors with an increased coordination number for the FRET process. Wuister *et al.*[15] showed the temperature dependent FRET rates between the CdTe QDs, and it is explained by the influence of exciton dipole moments. The introduced SP electromagnetic medium might also provide the additional channel or the frequency-dependent permittivity for propagating the "virtual photon," which basically mediates the FRET process between the donor and the acceptor.[1]

The enhanced FRET process between the QDs with the Au NPs compared to homogeneous medium (on quartz) may be due to the compensation for or the overcoming of a few of the following factors. (1) The energetically favored or optically resonant donor-acceptor pairs may not occur due to the random distribution of donor and acceptor QDs in the mixed layer. (2) Defect related states from surface atoms and stabilized molecules, which are not of electronic perfection at the interface, might also hinder the resonant coupling between the QDs. (3) The spin-orbit splitting, phonon confinement, and surface states, all vary with the size of the QDs,[16] which can create a weak or incoherent electronic coupling between different sizes of the QDs. (4) Stabilized organic molecules on the surface of QDs and also the center-to-center distances between the donor and acceptor QDs may also keep the spacing greater than the Förster critical distance ($<$10 nm). The decrease of $\sim$0.5 nm spacing between the donor and acceptor QDs reduced the nonradiative energy transfer time from $\sim$250 to $\sim$50 ps, which is very much close to the theoretically estimated value of $\sim$38 ps.[4] (5) In the case of QDs compared to atoms/molecules, the resonant coupling can be attained by the energy matching of either pure electronic states or the phonon/surface related states, and at the same time the exciton dipole fields might also be weak due to its spread of a few a.u. compared to the atomic/molecular dipole

fields.[17] (6) Due to the phonon and surface related states of QDs, the intraband relaxation is also equally important compared to interband relaxation in the decay process.[18] The global Stoke shifts (the difference between the intense lowest 1s absorption peak and the PL peak maximum) for the donor and acceptor QDs in our case are 40 nm (195 meV) and 28 nm (100 meV), respectively, which is an indication of the involvement of either surface or phonon related states in the decay process.

In conclusion, we have demonstrated the enhanced FRET process between CdTe QDs placed in close proximity to the layers of Au NPs. The modified interaction between the donor and acceptor QD dipoles is attributed to the influence of the strong SP dipole field of Au NPs. The possibility to enhance the FRET process through SP interactions can lead to improvements in many QD based photonics and biological applications at nanoscale distances. For example, artificial solids for energy funneling and light harvesting devices can be designed to exploit this effect.

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