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This study investigates the dependence of Förster resonance energy transfer (FRET) on donor-acceptor (D/A) concentration ratios in mixed-size CdTe quantum dots (QDs) films by using photoluminescence (PL) and time-resolved PL spectroscopy. Experimental results indicate that an increasing donor concentration significantly quenches the emission intensity and lifetime in donor QDs and enhances that in acceptor QDs, providing clear evidence of increased FRET efficiency. When D/A ratio exceeds 6, however, the emission intensity and the lifetime of acceptors start to decline, reflecting a decreasing FRET efficiency because of a markedly declining availability of acceptor QDs. © *2009 American Institute of Physics.* [doi:10.1063/1.3242371]

Research on colloidal quantum dots (QDs), or semiconductor nanocrystals, has increased rapidly due to their unique and interesting optical properties, including size-dependent spectral tunability, high quantum efficiency, and superior photostability.[1] In highly diluted systems, the optical properties and time responses are determined by the isolated (single) QDs. However, an increasing QDs concentration or close packing of QDs causes the Förster resonance energy transfer (FRET) induced by dipole-dipole interactions between proximal QDs to dominate emission properties.[2,3] Because of the sensitive spatial and spectral dependence of FRET, FRET-related studies on colloidal QDs have gained considerable interest recently in biology and optoelectronics.[4–12] Although efforts to increase FRET efficiency have focused on structures with reduced interdots separation, the effect of donor/acceptor (D/A) concentration ratios on FRET has seldom been addressed. The availability of donor QDs per acceptor, which can be tuned by varying their ratios, markedly influences the probability of direct FRET between nearest-neighbor QDs. Kagan *et al.*[13] demonstrated the electronic energy transfer from small (donor, 82%) to large (acceptor, 18%) CdSe QDs in thin solid films. Mayilo *et al.*[14] found that FRET toward acceptors in CdTe clusters increased the acceptor PL intensity with an increasing amount of donors. Nizamoglu *et al.*[15] recently observed an increase of quantum efficiency in CdSe QDs using FRET when the donor concentration is about 2.4 times that of the acceptor. Therefore, thorough study the dependence of FRET on D/A concentration ratios is important and of great interest. In this letter, FRET process and efficiency in mixed-size CdTe QDs films are studied systematically as a function of D/A ratios (where the ratio varies from 1 to 9) based on use of photoluminescence (PL) and time-resolved PL (TRPL) spectroscopy.

Nominally monodisperse CdTe QDs were synthesized in an aqueous solution as described elsewhere.[16] The water-soluble CdTe QDs used in this study were surface capped with mercaptopropionic acid (MPA). MPA-capped CdTe QDs with diameters of 3.4 and 5.1 nm, as estimated from the sizing curve of Ref. 16, function as donors and acceptors, respectively. For mixed-size samples 33, 99, 165, 198, 231, 264, and 297 nmol of donor QDs and 33 nmol of acceptor QDs were mixed in 3 mL of de-ionized water. The D/A molar or molar concentration ratios varied as 1, 3, 5, 6, 7, 8, and 9, corresponding to an incremental increase in the amount of donors in the mixtures. Samples of the only donors and acceptors were also prepared as references. Prior to the formation of closely packed CdTe QDs films, nominally monodisperse and mixed-size QDs were separately dropped cast onto a clean glass slide. Following solvent evaporation, QDs deposited on glass substrates and formed densely packed films. Room-temperature absorption spectra were recorded in air using a Cary 50 spectrometer (Varian). PL and TRPL were excited by a 300 ps pulsed laser diode (405 nm/2.5 MHz) at room temperature. The PL and TRPL signals were dispersed using an iHR550 single-grating 0.55 m spectrometer and detected, respectively, using a LN_2-cooled charge-coupled device and a high-speed photomultiplier tube. The decay traces were recorded using a time-correlated single photon counting approach (Time-Harp, PicoQuant).

Figure 1(a) shows the absorption and the PL spectra of the only donor (3.4 nm) and only acceptor (5.1 nm) CdTe QDs in an aqueous solution. The only donor and only acceptor QDs provide red and near-infrared emissions centered at around 615 and 720 nm, respectively. The emission spectrum of only donors and the absorption spectrum of only acceptors indicate sufficient spectral overlap. Figure 1(b) presents the PL spectra of the only donor, only acceptor, and mixed-size (D/A=1) CdTe QDs in closely packed films. Clearly, an energy redshift occurs for the films as compared with that in water. The energy redshift in nominally monodisperse CdTe QDs films can be ascribed to the FRET between adjacent QDs of slightly different size within the entire ensemble.[17] The magnitude of energy redshift depends on the PL linewidth of the sample.

Figure 1(b) indicates that, for the densely packed CdTe QDs film (D/A=1), the PL intensity at donor emissions de-

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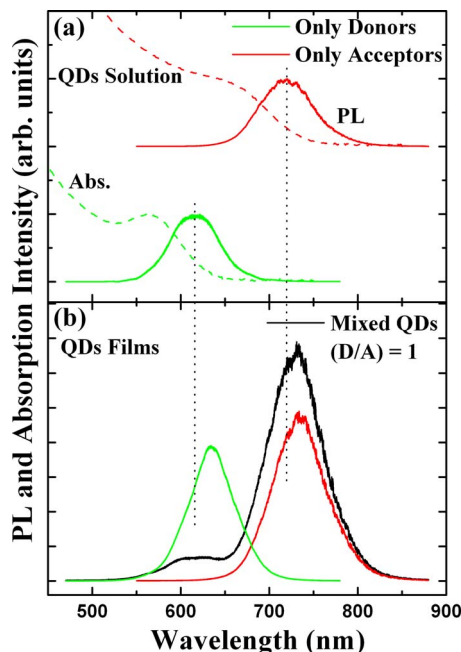
FIG. 1. (Color online) (a) Absorption and PL spectra of only donor (3.4 nm) and only acceptor (5.1 nm) CdTe QDs in water. (b) PL spectra of only donor, only acceptor, and mixed-size (D/A=1) QDs films.

FIG. 3. (Color online) TRPL spectra of mixed-size CdTe QDs films with various D/A ratios monitored (a) at the donor peak emission (635 nm) and (b) at the acceptor peak emission (734 nm). The inset in (a) shows PL lifetime (at 635 nm) of donors in the mixed film vs D/A ratios. The dashed line denotes the lifetime of only donor QDs film.

creases and that at acceptor emissions enhances with respect to the emissions intensity of only donors and only acceptors. The integrated PL intensity of acceptors in the mixed film (D/A=1) is increased by about 1.5 times that of its initial value of the only acceptors film. Above results provide evidence of nonradiative energy transfer from donor to acceptor QDs. Figure 2 displays the dependence of PL spectra on D/A concentration ratios. According to this figure, increasing the ratio from 1 to 6 significantly enhances the PL intensity of acceptors due to the availability of additional donor QDs per acceptor. Moreover, the PL intensity of donors in the mixed film strongly reduces when compared with that of only donors. The integrated PL intensity of acceptors in the mixed film (D/A=6) is about 7.5 times higher than that of only acceptors film. For comparison, the inset of Fig. 2 shows the PL spectra of mixed-size CdTe QDs in water for various D/A concentration ratios. In contrast with mixed-size CdTe QDs films, the emission intensity of donors in mixed-size QDs

solutions monotonically increases with an increasing donor concentration. This phenomenon is attributed to that the interdot distances between donors and acceptors in mixed QDs solutions exceed the Förster critical distance (<10 nm). Consequently, the FRET process between donors and acceptors in mixed QDs solution can be neglected. The above observations imply that the quantum efficiency of acceptor QDs in mixed films can be easily controlled by tuning the concentration of donor QDs.

To verify the dependence of FRET on D/A concentration ratios, the TRPL measurements were performed. Figures 3(a) and 3(b) display the TRPL spectra for mixed-size CdTe QDs films of various D/A concentration ratios monitored at the donor and acceptor peak emission, respectively. Increasing the ratio to nearly 6 decreases the PL lifetime of donors in the mixed film (τ_{DM}) and increases that of acceptors in the mixed film (τ_{AM}). Furthermore, in Fig. 3(b) the lifetime curves of acceptors in the mixed films (D/A=3 and 6) exhibit prolonged excitation during the initial few nanoseconds. The phenomenon becomes even more pronounced upon recording of the long-wavelength emissions and can be attributed to the feeding effect from the trapped excitations.[8] These experimental findings along with the PL results (Fig. 2) provide strong evidence of FRET. The radiative energy transfer via photon reabsorption, which does not quench the lifetime from donor QDs, can be ruled out.

The dynamics of energy transfer can be further depicted by the TRPL image and the temporal evolution of PL spectra for mixed-size CdTe QDs film (D/A=6). In Fig. 4, within the initial few nanoseconds after excitation, donor emissions dominate the PL spectrum. The emission intensity of donors is about five times higher than that of acceptors. As time passes, the emission intensity of donors (acceptors) sharply falls (enhances). Additionally, the PL maximum of the mixed QDs shifts dramatically toward the acceptor emission. Beyond 10.0 ns, the emission from acceptors dominates the entire spectrum (as shown in the inset of Fig. 4), revealing the suppression of an additional energy transfer. However, further increasing the amount of donor QDs (D/A>6), the emission intensity of acceptors starts to decline and that of donors starts to increase. Additionally, τ_{DM} increases along with a decreasing τ_{AM} as the ratio exceeds 6. These phenomena imply the quenching of FRET efficiency, which could be
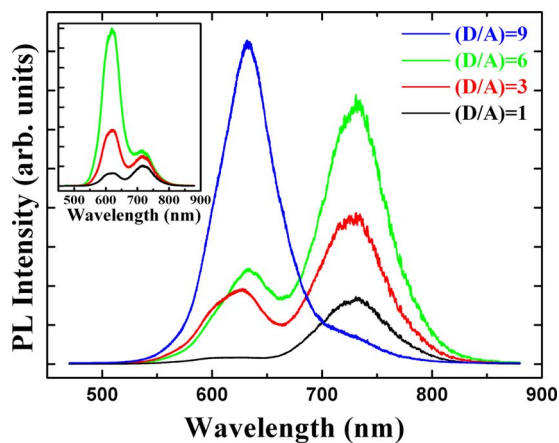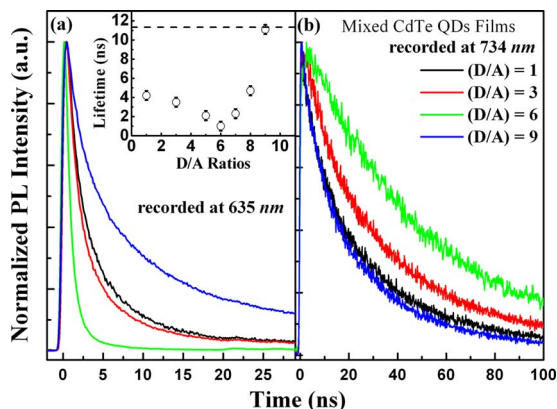

FIG. 2. (Color online) PL spectra of mixed-size CdTe QDs films (D/A=1, 3, 6, and 9). The inset shows PL spectra of mixed-size QDs (D/A=1, 3, and 6) in water.
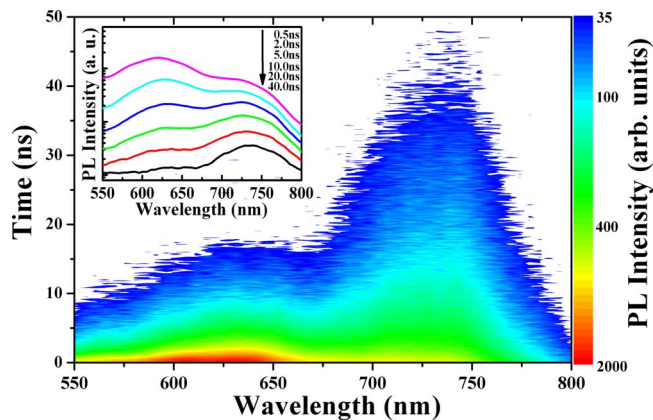
FIG. 4. (Color online) TRPL image of mixed-size CdTe QDs film (D/A =6). The inset shows the temporal evolution of PL spectra.

attributed to the decreasing amount of available acceptor QDs per donor. In other words, donor QDs dominate the FRET process and the entire PL spectrum from the mixed films, as shown in Fig. 2 (D/A=9). When the ratio exceeds 9, τ_{DM} in the mixed films returns to that of only donor QDs film ($\tau_D \sim 11.3$ ns). The inset of Fig. 3(a) summarizes the dependence of τ_{DM} as a function of D/A ratios. The kink in the inset reflects a situation in which the time constant changes maximally around D/A=6, in which each acceptor QD is surrounded on average by six donor QDs. Further quantitative analysis is performed by computing the FRET efficiency based on the TRPL measurements by using the following equation:[18]

$$\eta_{FRET} = 1 - \tau_{DM}/\tau_D. \qquad (1)$$

Increasing the ratio from 1 to 6, the FRET efficiency is enhanced from 63% to 91%. Efficiency, as estimated from the relative integrated PL intensity, provides similar results.

In summary, this study investigated FRET in mixed-size CdTe QDs films as a function of D/A concentration ratios. Increasing the amount of donors initially increases the emission intensity of acceptors, followed by a monotonical decline. When the D/A ratio approaches 6, FRET efficiency reaches 91% and the emission intensity of acceptors in the

mixed film is around 7.5 times higher than that of only acceptors film. The enhancement in both the quantum efficiency and FRET efficiency of mixed-size CdTe QDs films is crucial for hybrid organic/inorganic semiconductor nanostructures and for realizing efficient light emitting devices.

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