Quantum efficiency enhancement in nanocrystals using nonradiative energy transfer with optimized donor-acceptor ratio for hybrid LEDs

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The quantum efficiency enhancement in nanocrystal solids is critically important for their efficient use as luminophors on color-conversion light emitting diodes (LEDs). For this purpose, we investigate energy gradient mixture of nanocrystal solids for recycling their trapped excitons by varying their donor-acceptor nanocrystal ratios and study the resulting quantum efficiency enhancement as a function of the donor-acceptor ratio in the solid film for hybrid LEDs. We achieve a maximum quantum efficiency enhancement of 17% in these nanocrystal solids when the donor-acceptor ratio is 1:1, demonstrating their highly modified time-resolved photoluminescence decays to reveal the kinetics of strong energy transfer between them. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3141516]

Semiconductor nanocrystal (NC) quantum dots exhibit attractive properties for use in hybrid white light emitting diodes (LEDs). They strongly absorb incident blue/UV light and emit with cooperative downconversion at the desired long wavelengths in the visible upon excitation at the short wavelengths. For example, red-emitting NCs achieve a high photon conversion efficiency of 52.8%, which is larger than the reported level of red phosphors for converting blue into red.[1,2] Furthermore, NCs feature widely tunable emission across the visible spectral range by quantum confinement effect.[3] They also provide us with the ability to easily and uniformly deposit them in solid films employing simple techniques (e.g., spin casting and dip coating). As a result, NC based solid state lighting devices have made important progress in device research in recent years.[4–8] However, these NC emitters suffer from the problem of relatively reduced quantum efficiency in film with respect to their high quantum efficiency in solution.[9] To address this problem, the recycling of trapped excitons into the quantum dots by using nonradiative energy transfer (ET), which is also known as Förster resonance energy transfer, provides a possible solution to enhance the quantum efficiency of these NC solid films. Although Förster ET for colloidal NC emitters are investigated in various studies,[10–18] the dependence of quantum efficiency enhancement on the donor-acceptor variation in the solid film and its optimization have not been investigated for hybrid LEDs to date.

In this letter, we study the optimal donor-acceptor colloidal NC ratio for their quantum efficiency enhancement in the solid film for white LED applications. For that we use carefully selected energy gradient mixtures of CdSe/ZnS core/shell NCs (emitting at 500 and 550 nm) for strong nonradiative ET between them. We investigate the resulting quantum efficiency enhancement of these NC solids with their varied donor-acceptor ratios in film, e.g., 16:1, 4:1, 1:1, 1:4, and 1:16. All of these energy gradient structures exhibit quantum efficiency enhancement with respect to the cases of only donor and only acceptor control groups. Here the observed quantum efficiency increase stems from the ability of transferring excitation energy of some of the excitons trapped in the midgap states through nonradiative ET. We observe that the mixed donor and acceptor NCs achieve a maximum quantum efficiency enhancement of 17% when the donor-acceptor ratio is 1:1, implying that ET is optimized when there is one donor NC for each acceptor NC on the average.

For investigating the quantum efficiency enhancement, we use a xenon halogen lamp in a monochromator as the excitation light source and an integrating sphere for collecting the total emission from the NC solids. For time-resolved spectroscopy measurements, we use a laser head at an emission wavelength of 375 nm and a photon multiplier tube as the detector with a calibrated time resolution of 16 ps. For the numerical analysis of the experimental data, we deconvolute the instrumental response function. In our hybrid system, we use cyan-emitting CdSe/ZnS core/shell NCs as the donors and green-emitting NCs as the acceptors for nonradiative ET. Our cyan-emitting NCs have a concentration of 171 nmol/ml in toluene and their diameters are around 3.2 nm with a size dispersion of <5%; our green-emitting NCs have a concentration of 70 nmol/ml in toluene and their diameters are around 3.4 nm with a size dispersion of <5%.[19] Their molecular weights are 85 and 100 $\mu g/nmol$ for cyan- and green-emitting NCs, respectively, and they exhibit an in-solution quantum efficiency of >50%. After mixing the NC solutions for appropriate donor-acceptor ratios, we prepare the hybrid NC samples by drop casting on quartz substrates and postbake them around 50 °C to remove excess solvent toluene from the films.

Figure 1 presents the quantum efficiency enhancement of these NC solids as a function of varying donor-acceptor ratios in film with respect to the control groups. In Fig. 1, we also show the control group samples of only cyan- and only green-emitting NCs as the base line; these points are presented at the far edges of the plot in Fig. 1 for visualization purposes. Using green- and cyan-emitting NCs in any combination as the donor-acceptor pairs, we experimentally ob-

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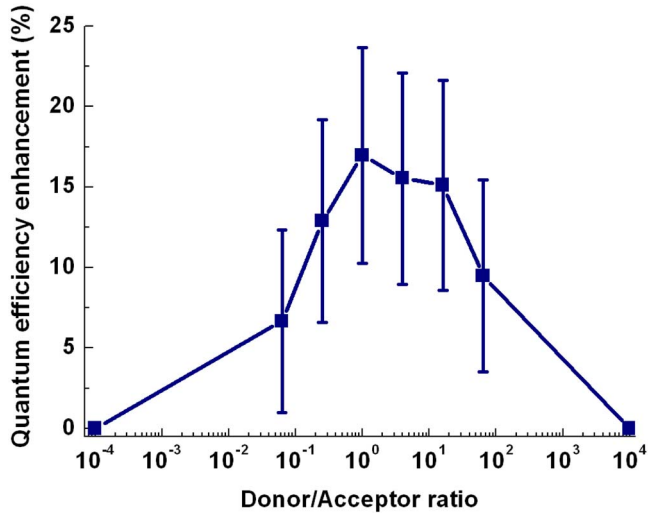
FIG. 1. (Color online) NC donor-acceptor ratio dependent quantum efficiency enhancement of the donor-acceptor hybrid solid films consisting of cyan- and green-emitting CdSe/ZnS core/shell NCs.
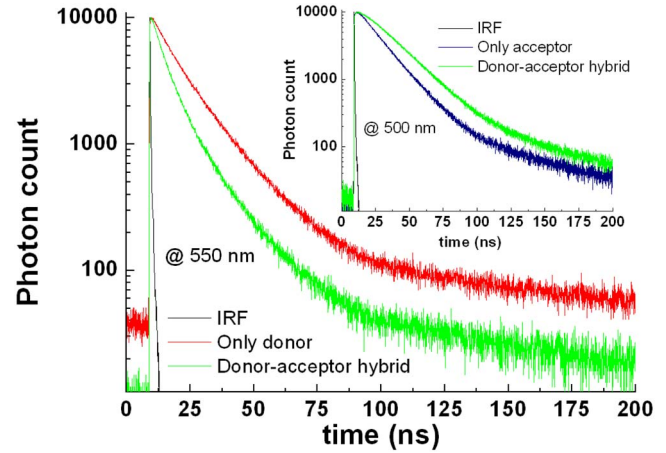

FIG. 2. (Color online) Time-resolved PL kinetics of the only acceptor NC solids and the donor-acceptor hybrid NC solids with 1:1 ratio at the acceptor emission wavelength of 550 nm. Time-resolved PL kinetics of the only donor NC solids and the donor-acceptor hybrid NC solids with 1:1 ratio at the donor emission wavelength of 500 nm are given in the inset.

serve that the quantum efficiency is effectively enhanced in all samples for any donor-acceptor ratio with respect to the control groups.

It is normally expected to be impossible for the overall efficiency of the hybrid donor-acceptor NC film to exceed that of only donors or that of only acceptors as shown in Eq. (1), where the quantum efficiency of the hybrid NC film (QE_{hybrid}) is expressed as a weighted sum of the acceptor and the donor efficiencies (QE_A and QE_D). Given Eq. (1), QE_{hybrid} is required to lie between QE_A and QE_D (when $\tau_{ET} \ll \tau_D$ or $\tau_{ET} \gg \tau_D$ corresponding to the far ends of the possible QE_{hybrid} range, respectively). However, we observe in the experiments that QE_{hybrid} exceeds QE_A and QE_D. This is attributed to the recycling of trapped excitons, as also discussed in the previous works in Refs. 14 and 15. Following the optical absorption process, the electron and hole pairs rapidly relax to the conduction and valance band ground states (in hundreds of femtoseconds). However, due to the surface defects, there also exist additional midgap trap energy states. Some of these excitons thus end up with being trapped in these defect states, mostly making nonradiative recombination. Using nonradiative ET, though, these trapped excitons may also be transferred, possibly contributing to spontaneous emission in addition to the interband excitons. As a result of such recycling of these trapped excitons, the PL of the hybrid films is increased,

$$QE_{hybrid} = QE_A(1 + \tau_{ET}/\tau_D)^{-1} + QE_D(1 + \tau_D/\tau_{ET})^{-1}. \quad (1)$$

Starting the emission enhancement investigation with a donor-acceptor ratio of 1:16, the quantum efficiency is found to be increased by 6.6% with respect to the control groups. As we increase the donor-acceptor ratio from 1:16 to 1:1, this enhancement increases correspondingly from 6.6% to 17.0%. As we further increase the donor-acceptor ratio beyond 1:1, however, the enhancement begins to decrease from 17.0% to 9.5%. When the number of acceptors (donors) significantly exceeds the number of donors (acceptors) in the limiting cases, the number of donors (acceptors) becomes insignificant. Thus, the ET behavior converges the case of only acceptors (donors). This explains the experimental observations of decreasing enhancement before and after 1:1 ratio. As a result, for hybrid LEDs the donor-acceptor ratio of

1:1 is found to be optimum for the maximum possible quantum efficiency enhancement observed in these NC emitters.

For investigation of modified PL kinetics, we present the hybrid sample with the donor-acceptor ratio of 1:1 that reveals the highest in-film emission enhancement among other combinations. Figure 2 shows the time-resolved PL of the hybrid donor-acceptor sample and the only cyan-emitting donor NC solids, both at the donor peak emission wavelength of 500 nm. In Fig. 2, the PL decay of the hybrid sample at 500 nm drops faster with respect to the only cyan-emitting donors because these donor dots in the hybrid sample quench as a result of their excitation energy transferred to the acceptor dots in the hybrid sample. On the other hand, the inset of Fig. 2 reveals the time-resolved PL of the hybrid sample and the only green-emitting acceptor NC solids, this time both at the acceptor peak emission wavelength of 550 nm. In contrast, in the inset, the decay of the hybrid sample at 550 nm slows down with respect to the only green-emitting acceptors because these acceptor dots are fed with the transferred energy from the donor dots in the hybrid sample.

We numerically analyze our PL decay curves in Fig. 2 using a multiexponential model fit. The resulting fitting parameters are summarized in Table I. Here the first lifetime (i.e., τ_1) is the interband recombination of the NCs, which is expectedly on the order of tens of nanoseconds.[16] This recombination lifetime component is found to be 13.7 ns for cyan-emitting dots and 17.4 ns for green-emitting dots. In addition to this interband recombination, the numerical analysis also returns another decay lifetime (i.e., τ_2). This lifetime component exhibits a rather slow decay. It is 63.8 ns for cyan-emitting dots and 103.6 ns for green-emitting dots. This long decay component is weak, exhibiting amplitudes less than 3% of the amplitude of τ_1 for all cases. We therefore attribute this slow and weak decay component to the environmental effects that may potentially be caused by ligands of the NCs in the close vicinity of each other in their close-packed film.[20] Furthermore, for the hybrid sample the numerical analysis gives a third lifetime component (i.e., τ_3), both at the peak emission wavelengths of the donors and the acceptors (at 500 and 550 nm). The numerical analysis reveals that this third component is an additional decay pathway for the small dots serving as the donors and that this is

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TABLE I. The fitting parameters of time-resolved spectra presented in Figs. 2(a) and 2(b). (A_n and τ_n are the amplitudes and decay time constants, for $n=1$, 2, and 3, respectively; τ_{av} and τ_{amp_av} are the intensity and amplitude weighted average decay time constants.)

	Only donor NCs (at 500 nm)	Donor:acceptor 1:1 (at 500 nm)	Only acceptor NCs (at 550 nm)	Donor:acceptor 1:1 (at 550 nm)
A_1 (counts)	11 245	3831	11 941	37 212
τ_1 (ns)	13.7	13.7	17.4	17.4
A_2 (counts)	326	109	189	314.2
τ_2 (ns)	63.8	63.8	103.6	103.6
A_3 (counts)	⋯	8790	⋯	−26 375
τ_3 (ns)	⋯	4.4	⋯	14.1
τ_{av} (ns)	19.6	13.6	24.9	30.7
τ_{amp_av} (ns)	15.1	7.7	18.9	28.9

an energy increase for the large dots serving as the acceptors in the hybrid sample (because the analysis returns negative amplitude associated with this component, as presented in Table I).

To further analyze the ET from cyan-emitting dots to green-emitting dots, we calculate the intensity averaged lifetime components using Eq. (2) (where A_i and τ_i refer to the amplitudes and their associated lifetimes, respectively). The intensity weighted average decay time constant for the cyan-emitting dots at 500 nm decreases from 19.6 to 13.6 ns because of the exciton migration from cyan-emitting NCs to green-emitting NCs. On the other hand, the intensity weighted average decay time constant of green-emitting dots at 550 nm is found to increase from 24.9 to 30.7 ns with respect to only green-emitting dots as a result of the ET. Using Eq. (3) we calculate the amplitude weighted average lifetime of the hybrid NCs sample ($\tau_{amp\_av\_DA}$) and the only cyan-emitting NC case ($\tau_{amp\_av\_D}$) at 550 nm. Furthermore, by using Eq. (4), we determine the efficiency of the ET. As a result, the efficiency of the nonradiative ET in the hybrid NCs achieves a relatively high level of 48%. Here the third decay term for the donors due to the ET quenching is calculated to be 4.4 ns. However, the lifetime of this component for the acceptors because of the exciton migration is computed to be 14.1 ns, which is slower than the quenching lifetime. Since the trap states have energy lower than the interband gap, the overlap of the optical absorption of green-emitting dots with the trapped states is lower because the absorption of NCs increases toward shorter wavelengths. As a result, the rate of energy enhancement decreases and thus the ET lifetime increases,

$$\tau_{av} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}, \tag{2}$$

$$\tau_{amp\_av} = \frac{\sum_i A_i \tau_i}{\sum_i A_i}, \tag{3}$$

$$\eta_{ET} = 1 - \frac{\tau_{amp\_av\_DA}}{\tau_{amp\_av\_D}}. \tag{4}$$

In conclusion, we presented blended nanocrystal energy gradient structures for recycling of trapped excitons and exhibited a maximum quantum efficiency enhancement of 17% when the donor-acceptor ratio is 1:1. The quantum efficiency enhancement of integrated nanocrystals is important for achieving efficient LEDs.

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