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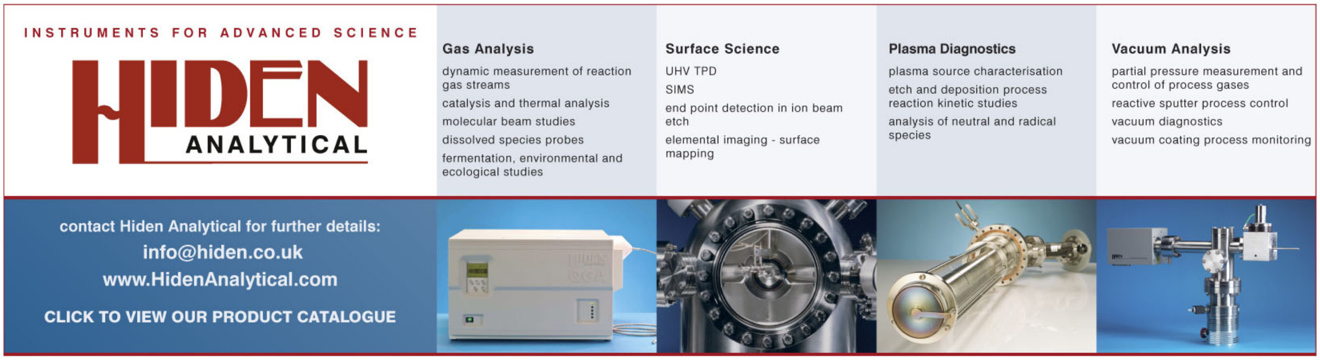

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Efficient energy transfer from hole transporting materials to CdSe-core CdS/ZnCdS/ZnS-multishell quantum dots in type II aligned blend films

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We studied the energy transfer between CdSe core/shell quantum dots (QDs) and hole transporting materials (HTMs) in type II aligned inorganic/organic blend films by using steady-state and time-resolved photoluminescence (PL) spectroscopy. The lengthening and shortening in PL lifetimes of the QDs in HTMs under resonant excitation condition were explained by energy transfer and charge separation processes. Surprisingly, the maximum energy transfer efficiency from 4,4′,4″-Tris (carbazol-9-yl)-triphenylamine (TcTa) to CdSe/CdS/ZnCdS/ZnS core/multishell QDs was determined to be 86% by calculating the excited state lifetime of the TcTa molecules participating in the energy transfer process. © *2011 American Institute of Physics*. [doi:10.1063/1.3633110]

The inorganic/organic composites with quantum dots (QDs) and organic functional molecules have been explored for their applications in light emitting diodes (LEDs)[1–7] and photovoltaic cells[8–10] due to their size-tunable optoelectronic properties and flexible fabrication conditions. In recent years, the most efficient QD-LEDs were fabricated by sandwiching an inorganic QD layer between organic hole and electron transporting materials (HTMs).[2] The electroluminescence is considered to originate from excitons in the QD layer generated by energy transfer or direct charge injection from organic host materials.[2,3,6] However, the energy level alignment at QD/HTM heterojunction interface causes a staggered gap (type II structure), which may result in imbalance of carrier injection and the corresponding charging in the QD layer.[2,6,11] Recently, in a type II aligned CdTe core QD and conjugated polymer hybrid system, Lutich *et al.*[12] found a dominant energy transfer process with a maximum efficiency of 70% although charge separation was presented. Generally, photoluminescence (PL) properties of CdSe QDs can be significantly improved by growing a monoshell (CdS or ZnS) or a multishell (CdS/ZnCdS/ZnS) on a CdSe core.[13,14] The charge separation process between organic molecules and the QDs should be modified by the shell structure of the QD as an energy barrier and a spacer. Therefore, it is hopeful to explore the energy transfer mechanism in type II aligned QD/organic composite nanomaterials to optimize the performance of their optoelectronic devices.

In this letter, we report a study on the energy transfer processes between CdSe core/shell QDs and frequently used HTMs such as N,N′-di(3-methylphenyl)-N,N′-di(phenyl)benzidine (TPD) and 4,4′,4″’-Tris (carbazol-9-yl)-triphenylamine (TcTa) in inorganic/organic blend films using steady-state and time-resolved photoluminescence (TRPL) spectroscopy. The lengthening and shortening in PL lifetimes of the QDs in HTMs are explained in terms of energy transfer and charge separation processes at the QD/HTM interface. Efficient Förster resonance energy transfer (FRET) from HTMs to CdSe/CdS/ZnCdS/ZnS core/multishell QDs is demonstrated.

CdSe QDs with different shell structures were synthesized following Ref. 14. The shell structures, shell layer thicknesses, the PL peak wavelengths, dot diameters, and PL quantum yield of the CdSe core/shell QDs are described as follows: (QD1) CdSe/ZnS(3 ML) (570 nm) (5.0 nm) (40%) and (QD2) CdSe/CdS(2 ML)/ZnCdS (3 ML)/ZnS(2 ML) (615 nm) (8.0 nm) (70%), respectively. The core size was estimated to be about 3.0 nm. The transmission electron microscopy (TEM) images of QDs are shown in the inset of Fig. 1(a). The QD/TPD (TcTa) blend films were deposited on quartz substrates from QD and TPD (TcTa) mixed solutions with a mole ratio of 1/2000-1/3000 by a spin coater with a speed of 1500 rpm. The QD concentration in these blend films was low to avoid aggregation of QDs and the influence of the QD/HTM mole ratio on the energy transfer rate.[15] The QD/PMMA (poly(methyl methacrylate) films were prepared as reference samples. The TRPL spectra were measured by FL920 fluorescence lifetime spectrometer (Edinburgh instruments). The excitation source is a hydrogen flash lamp (nF900) with a pulse width of 1.5 ns and a picosecond pulsed diode laser (EPL-485) with a pulse width of 85 ps. All measurements were carried out at room temperature.

Fig. 1(a) shows absorption and PL spectra of CdSe core/shell QDs and TPD (TcTa) molecules. The spectral overlap of the HTM molecule (donor) PL emission and CdSe core/shell QD (acceptor) absorption is a pre-requisite for FRET.[12,15,17] The molecular structures and energy level alignments of TPD and TcTa are shown in Fig. 1(b). The energy offset between the highest occupied molecular orbital (HOMO) level of TPD and the valence band of CdSe QDs is about 1.0 eV, which is larger than that (0.7 eV) between TcTa and the QDs.[2–5] The energy offset is a driving force for charge separation process at the QD/HTM interface, resulting in exciton dissociation in QDs.[8,11,18] In a previous work,

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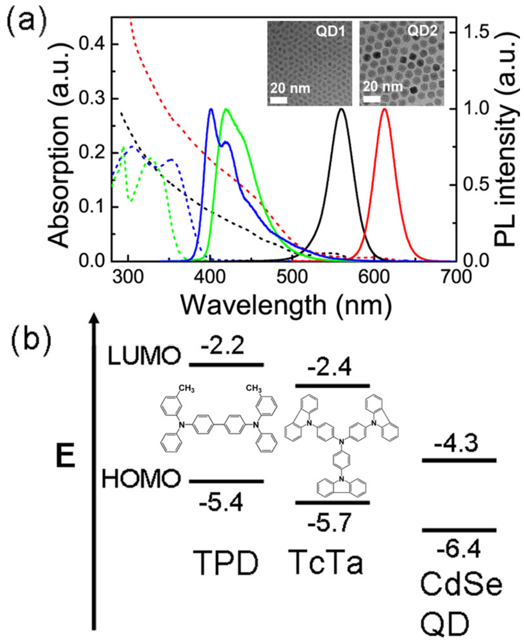

FIG. 1. (Color online) (a) Steady-state absorption (dashed lines) and PL (solid lines) spectra of TPD (blue diamonds), TcTa (green triangles), CdSe/ZnS(3 ML) (QD1, black squares), and CdSe/CdS/ZnCdS/ZnS(7 ML) (QD2, red circles) core/shell QDs, respectively. Inset: TEM images of QD1 and QD2 samples. The scale bar is 20 nm. (b) Molecular structures and energy level alignments of HTMs and QDs relative to vacuum level.

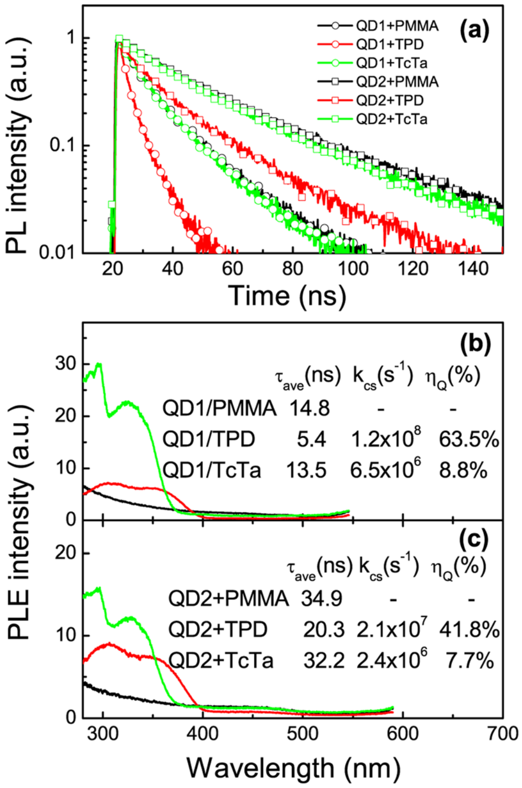

FIG. 2. (Color online) PL decay curves of QD1 (filled) and QD2 (empty) core/shell QDs in PMMA (black squares), TPD (red circles) and TcTa (green triangles) (a), the adjusted PL excitation spectra of QD1 (b), and QD2 (c). Average PL lifetimes of QDs, charge separation rates, and PL quenching efficiencies are given in the inset.

Zhang *et al.*[18] demonstrated that the PL quenching of CdSe core/shell QDs in solution in the presence of hole transporting materials was dependent on the shell structure of QDs.[18] Zhu *et al.*[19] proposed the possible ways of optimizing the charge separation and recombination rates by controlling the thickness and nature of the shell materials.

In order to understand the PL quenching of the QDs in HTMs, PL decays of CdSe core/shell QDs in HTMs were measured under excitation of 485 nm which is below the absorption edge of TPD (TcTa) molecules, avoiding the contribution of energy transfer from the HTMs to the QDs, as seen in Fig. 2(a). A significant shortening in the PL decays of CdSe core/shell QDs embedded in TPD is observed, indicating charge separation is an additional de-excitation pathway for excitation in QDs. The calculated average PL lifetimes, hole transfer rates ($k_{CS} = 1/\tau_{QD\text{-}HTM}\text{-}1/\tau_{QD}$), and quenching efficiencies ($\eta_Q = 1\text{-}\tau_{QD\text{-}HTM}/\tau_{QD}$) for QD1 and QD2 in TPD and TcTa films are summarized in the inset of Fig. 2. It is clearly noted that the charge separation rate in QD/TcTa blend film ($\sim 10^6\ S^{-1}$) is smaller than that in QD/TPD blend film ($10^7 \sim 10^8\ S^{-1}$). From Marcus theory, the difference of nonadiabatic electron transfer rate is dependent on the electronic coupling strength (H_{DA}), the total reorganization energy (λ), and the driving force (ΔG).[19,20]

Figs. 2(b) and 2(c) show the PLE spectra of the CdSe QDs in the HTM or PMMA detecting PL at their emission wavelength. Comparing with the PLE spectrum of the QDs in a QD/PMMA film, the relative enhancement of PLE intensity of the QDs in the QD/HTM blend films is clearly observed at wavelength of the donor absorption, indicating that energy transfer happens from HTM molecules to CdSe core/shell QDs.[12,15] In our experiment, the concentration of QDs in blend films is so low that the majority of HTMs molecules is far away from the QD surface. This means that the HTM molecules participating in energy transfer is a little fraction of all HTM molecules in the films. Thus, the PL decays of the HTMs in the blend films should be almost the same as those of pure HTM films which cover up the information of energy transfer process.[12,15,16] On the other hand, the information about energy transfer dynamics is also provided in the TRPL spectra of acceptor QDs. Fig. 3 shows the PL decays of acceptor CdSe core/mono-shell and core/multi-shell QDs under excitation of 320 nm. The PL lifetimes of pure TPD and TcTa films were determined to be $\tau_{TPD} = 0.6$ and $\tau_{TcTa} = 13.6$ ns as given in the inset of Fig. 3(a). Due to the filling of excited states of the QDs via energy transfer process, the initial rise and final decay processes in the TRPL spectra of CdSe QDs in QD/TcTa blend films become slower than those of a QD/PMMA film.[12,15] However, the PL lifetime of the QDs in TPD is shortened, which is attributed to efficient charge separation and fast energy transfer processes.

From the experimental results, two paths can be considered to be excitation sources of the QDs:[12,15–17] (1) direct excitation of light (320 nm) and (2) energy transfer from the surrounding HTM molecules. Additionally, the charge separation process in the type II aligned hybrid films is also considered to happen at the same time when an exciton is generated in QDs via light excitation or energy transfer, reducing the PL intensity and decay lifetime.

In our measurement system, we can safely compare charge separation and energy transfer processes in QD/TcTa

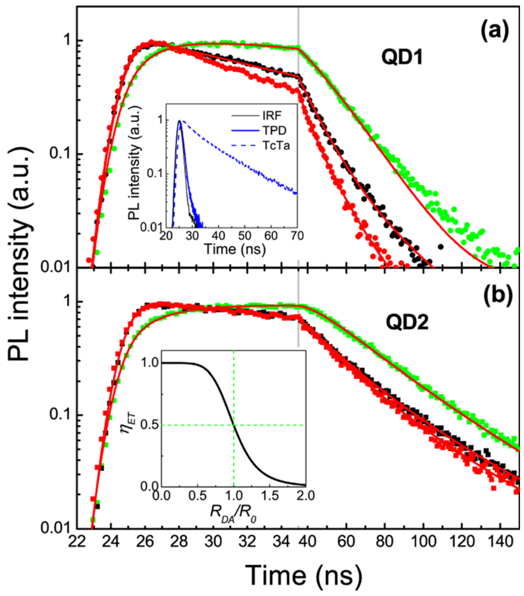

FIG. 3. (Color online) PL decay curves of QD1 (a) and QD2 (b) core/shell QDs in PMMA (black line), TPD (red line), and TcTa (green line). The solid red lines represent the fitting curves. Inset in (a): PL decay curves of pure TPD (blue solid line) and TcTa (blue dashed line) films. The solid black line is instrument response function (IRF). Inset in (b): Dependence of the energy transfer efficiency (η_{ET}) on the distance (R_{DA}).

blend films. The effect of charge separation on the energy transfer in QD/TcTa can be distinguished by a PL decay measurement as seen in Fig. 2. We modeled the time dependent PL decay curves of the QDs in QD/TcTa blend films using the decay parameters of bare QDs in PMMA and introducing additional excitation and de-excitation channels corresponding to energy transfer and charge separation processes.[12,18] We obtained the excited state lifetimes of a TcTa molecule layer around the QD contributed to energy transfer by fitting initial rise processes of PL decay curves of acceptor QDs as seen in Figs. 3(a) and 3(b), respectively. The excited state lifetimes ($\tau_{TcTa\text{-}QD}$) of the surrounding TcTa molecules near the CdSe/ZnS core/shell QDs were determined to be 2.4 ns (70.9%) and 12.1 ns (29.1%). The corresponding energy transfer rate ($k_{ET} = 1/\tau_{TcTa\text{-}QD}\text{-}1/\tau_{TcTa}$) and efficiency ($\eta_{ET} = 1\text{-}\tau_{TcTa\text{-}QD}/\tau_{TcTa}$) were calculated to be 3.4×10^8 s^{-1} and 82.4%, for the short lifetime fraction, and 9.1×10^6 s^{-1} and 11.0% for the long lifetime fraction, respectively.[16] From the Förster theory, the energy transfer rate for an isolated single donor-acceptor pair separated by a distance R_{DA} can be expressed as follows: $k_{ET} = T_D^{-1}(R_0/R_{DA})^6$, where τ_D is the excited state lifetime of a donor without acceptor and R_0 is the Förster radius defined as the critical distance with an energy transfer efficiency of 50%.[16] The dependence of η_{ET} on R_{DA} is shown in inset of Fig. 3(b).[16] Therefore, the TcTa molecules near the QD surface ($R_{DA} < R_0$) with a high energy transfer efficiency (>80%) contributed a large fraction (~70%) of energy for acceptor PL emission. However, the thickness of the CdS/ZnCdS/ZnS(7 ML) multishell is about $2 \times 0.33 + 3 \times 0.32 + 2 \times 0.31 = 2.24$ nm and the ligand (trioctylphosphine oxide (TOPO), octadecylamine (ODA), etc.) shell thickness is about 0.5 nm.[13,14] The excited state lifetimes of the surrounding TcTa molecules near the CdSe/CdS/ZnCdS/ZnS core/multishell QDs were calculated to be to be 1.9 ns (71.8%) and 12.3 ns (28.2%). The corresponding energy transfer rate and efficiency were estimated to 4.5×10^8 s^{-1} and 86.0% for the short lifetime fraction and 7.8×10^6 s^{-1} and 9.6% for the long lifetime fraction, respectively. This indicates that the thick multishell coated CdSe QDs also possess the high energy transfer efficiency of over 80%, which is related to energy transfer from TcTa to ZnCdS and CdS shells.

In conclusion, we have studied the energy transfer process from HTMs to CdSe core/shell QDs in inorganic/organic hybrid nanocomposites. We demonstrated that the energy transfer efficiency from TcTa molecules near the QD surface to thick CdS/ZnCdS/ZnS multishell coated CdSe QDs reached up to 86%, which resulted in a significant enhancement in PL intensity and PL lifetime of the QDs in TcTa. However, PL quenching and the resulting shortening of PL decays observed in the QDs/TPD films were suggested to result from the significant charge separation between QDs and TPD molecules. Therefore, it is expected to improve the performance of CdSe QD-LEDs by optimizing the shell structure and material of the QDs and selecting HTMs.

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