Charge Separation in Type II Tunneling Structures of Close-packed CdTe and CdSe Nanocrystals

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ABSTRACT

We report on charge separation between type II aligned CdTe and CdSe nanocrystals. Two types of electrostatically bound nanocrystal structures have been studied: first, clusters of nanocrystals hold together by Ca(II) ions in aqueous solution and, second, thin film structures of nanocrystals created with layer-by-layer deposition in combination with polyelectrolytes. In both types of structures, short interparticle distances of less than 1 nm have been achieved, whereby the isolating organic ligands on the nanocrystal surfaces and/or the polymer monolayers act as tunneling barriers between nanocrystals. We have observed an efficient quenching of photoluminescence and a reduced emission lifetime for CdTe nanocrystals in both types of type II heterostructures. This result is explained by a spatial charge separation of the photoexcited electron−hole pairs due to tunneling of charge carriers through the thin organic layer between CdTe and CdSe nanocrystals. Type II heterostructures demonstrated here may find future applications in photovoltaics.

Semiconductor nanocrystals (NCs) are of increasing interest in science, providing promising concepts for applications in diverse areas, including light-emitting diodes,[1] photodetectors,[2] biosensing,[3] and biolabeling.[4] Very recently, increasing research efforts have been devoted to the new generation solar cells containing NCs as active materials.[5–9] NCs are easy to synthesize with low energy and material consumption;[10,11] they perfectly lend themselves as building blocks in controlled nano assemblies on a molecular scale like spatially ordered structures[12] or colloidal supercrystals.[13] Their optical properties are determined by both the band gap of the bulk material and the quantum confinement effect.[14] The influence of close packing of different types of NCs on the optical and electronic properties of the resulting "artificial solids" is of great interest. Closely packed structures of NCs may be obtained in different ways, including spin-coating,[5] drop casting,[13] and dipping.[8] Previously, preferentially type I aligned NCs were investigated.[15–18] "Type I" refers to the situation where one type of NCs possesses an energetically higher valence band state and an energetically lower conduction band state in relation to the other type of NCs. Type I assemblies of NCs were extensively discussed with respect to Förster resonant energy transfer (FRET),[15–17] culminating in the creation of a cascaded exciton funneling FRET structure inspired by light-harvesting complexes in nature.[18]

Fueled by the worldwide interest in photovoltaics, an increasing research effort in type II aligned nanostructures is perceived.[5,9] A type II band alignment is schematically shown in Figure 1a; bulk materials of CdSe and CdTe present a natural type II band offset, where the valence band and the conduction band of the CdSe are both energetically below the respective bands of CdTe.[19] In several recent publications, type II core/shell or core/shell/shell nanostructures[20,21] and nanorod heterostructures[22–24] have been introduced. An all-inorganic solar cell based on sintered layers of CdTe and CdSe nanorods was demonstrated,[5] with a remarkable value of the external quantum efficiency of 2.9% for a nonoptimized heterostructure. This value can be improved further if a better physical understanding of the charge separation process becomes available, making NC-based solar cells a competitive alternative to widely studied conjugated polymer/C_{60} bulk heterojunctions[25] and dye-sensitized Grätzel-type cells.[26]

In this Letter, we demonstrate quenching and lifetime shortening of the band-edge emission of CdTe NCs in type II hybrid structures of CdTe and CdSe NCs. We attribute both observations to a charge separation by electron tunneling from the CdTe NCs to the CdSe NCs. We denote the samples as tunneling structures because the NC surfaces are passi-
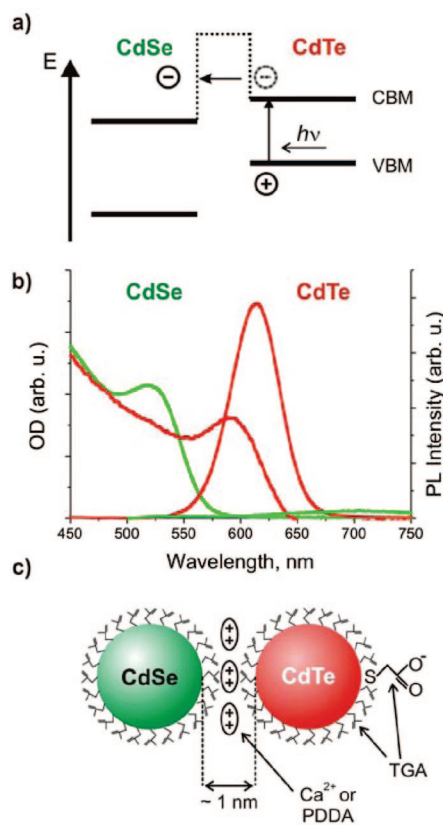
Figure 1. (a) Schematic drawing of a type II alignment for CdTe and CdSe NCs, facilitating charge separation of electrons and holes in different materials. CBM stands for conduction band minima, VBM for valence band maxima. (b) Representative absorption and luminescence spectra of CdTe and CdSe NCs used in this work (refer to text for the exact positions of absorption and emission maxima). (c) Schematic drawing of closely packed CdTe and CdSe NCs coated by negatively charged TGA ligands and held together by electrostatic interactions with positive charged Ca(II) ions (referred to as "clustered samples" in text) or PDDA (referred to as "layered samples" in text).

vated by a ligand shell of isolating organic molecules. The electrical contact between the semiconducting materials is absent and charge carriers have to tunnel through the shell of organic ligands. The band gap of the CdSe NCs used in this work is larger than the band gap of the CdTe NCs, and the absorption spectrum of the CdSe NCs shows only little overlap with the emission spectrum of the CdTe NCs (Figure 1b). Therefore, FRET from CdTe to CdSe NCs can be considered as a very unlikely process. Close packing of NCs was achieved by a controlled clustering of NCs in solution facilitated by electrostatic interactions of negatively charged TGA ligands on the surface of the NCs with positively charged Ca(II) ions. Alternatively, we used the well-documented layer-by-layer assembly technique[27] of poly-electrolytes in combination with NCs.[28] In both cases, the NCs are separated from each other by a narrow (<1 nm) insulating barrier of organic ligands and/or polyelectrolytes. A schematic drawing of two closely packed structures of NCs studied in our work is shown in Figure 1c.

Both CdTe and CdSe NCs are water-soluble particles when capped by thioglycolic acid (TGA) ligands (Figure 1c). We recently reported on CdTe NCs, which show an efficient

band-edge emission with a room temperature quantum efficiency of 40−60%,[11] whereas TGA-capped CdSe NCs[29] typically show no band edge emission and a weak (<0.1% quantum efficiency) broad trap-related emission in the region of 600−850 nm (Figure 1b). We used a stock solution of CdTe NCs of 100 μM concentration, a first extinction maximum (ODMax) at 567 nm, and a particle diameter of 3.1 nm. The stock solution of CdSe NCs was of 500 μM NC concentration, an ODMax at 529 nm, and a diameter of 2.7 nm. The NC concentrations and diameters were calculated from extinction spectra according to refs 11 and 30. Three samples were prepared by addition of CaCl$_2$ into diluted NC solutions: the first solution contained CaCl$_2$ and CdTe NCs (CdTe reference), the second contained CaCl$_2$ and CdSe NCs (CdSe reference), and the third contained CaCl$_2$, CdTe, and CdSe NCs (mixed hybrid clusters). The final concentrations of the components were 100 μM Ca^{2+} in each sample, 0.4 μM CdTe NCs in the CdTe reference and the hybrid sample, and 0.4 μM CdSe NC in the CdSe reference and the hybrid sample. After mixing, all samples were left in darkness for 30 min, followed by optical measurements. Clustering of NCs capped by negatively charged surface ligands induced by addition of positively charged divalent calcium ions led to stable colloidal ag-gregates with sizes on the order of 100 nm as estimated by dynamic light scattering measurements (Zetasizer Nano ZS90, Malvern).

The layer-by-layer assembled samples were grown through alternating deposition of the positively charged polyelectro-lyte poly(diallyldimethylamonium chloride) (PDDA, 1 mg/ mL in a 0.5 M NaCl solution) and negatively charged CdTe NCs (30 μM, ODMax at 583 nm, 3.2 nm diameter) and CdSe NCs (200 μM, ODMax at 519 nm, 2.5 nm diameter). A glass slide precovered with a PDDA−polystyrensulfonate−PDDA film (polystyrensulfonate: 1 mg/mL in a 0.5 M NaCl solution) served as substrate. Dipping times of 15 min in each solution were chosen. The hybrid type II samples were composed of CdTe−(CdSe-CdTe)$_2$−CdSe, alternated with PDDA. Reference samples consisted of six layers of CdTe NCs only or six layers of CdSe NCs only, alternated with PDDA as well. All samples were prepared in darkness in a shaded laboratory space to minimize photodegradation of the NCs.

Figure 2a shows PL spectra of the clustered hybrid CdTe-CdSe ensemble and the two reference samples, where clusters of only one type of NCs are present (reference CdTe and reference CdSe). The reference sample of CdTe-only clusters shows a strong excitonic PL peak at 607 nm, while the reference sample of CdSe-only clusters does not show any detectable PL signal on the scale of this figure. The PL peak in the hybrid CdTe-CdSe NC structure with a maximum at 606 nm is attributed to PL from CdTe NCs; no CdSe-CdTe interband transitions between the conduction band of CdSe NCs and the valence band of the CdTe NCs were detected. We now compare the PL intensities of the CdTe reference sample and the mixed sample. In the mixed sample, CdSe NCs are present and absorb photons, which are therefore not available to excite the CdTe NCs. This effect can be
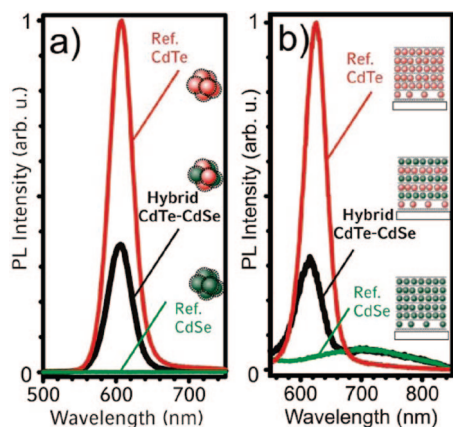
Figure 2. PL spectra of hybrid CdTe-CdSe (black lines) and reference CdTe-only (red lines) and CdSe-only (green lines) samples for clustered (a) and layered (b) structures. All spectra are taken at 400 ± 5 nm excitation wavelength; PL intensities of reference CdTe-only samples in clustered and layered structures are normalized to 1.

Figure 3. Time-resolved PL decays of hybrid CdTe-CdSe (black line) and reference CdTe-only (red line) samples in clustered structures (inset: same decays normalized to maximum). Excitation at 470 ± 10 nm, emission at 605 ± 16 nm, time resolution ca. 1 ns.

quantified by the optical densities of the samples and has been taken into account in Figure 2a. The excitonic PL peak of CdTe NCs in the hybrid sample was quenched by (65 ± 5)%, which we attribute to the charge separation by a tunneling transfer of electrons from the CdTe to the CdSe NCs due to the type II alignment in a close-packed CdTe-CdSe system.

PL spectra of layered samples are shown in Figure 2b. The PL spectra of the reference samples have been divided by 2 in order to take into account that the reference samples consisted of six layers of CdTe NCs or six layers of CdSe NCs, while the mixed sample contained only three layers of each type of NCs. The CdTe NCs in the reference sample show a PL peak at 625 nm. The CdSe NCs in the reference sample show a broad trap emission centered around 700 nm. In comparison with the CdTe emission, it seems as if the CdSe trap emission is stronger in the layered sample (Figure 2b) than in the clustered sample (Figure 2a). However, we note that it is not the CdSe trap emission that gains strength when the NCs are assembled in layers but it is rather the emission of the CdTe NCs that is weakened in the layered samples with respect to the clustered sample. The hybrid CdTe-CdSe sample in Figure 2b shows a PL signal from CdTe NCs at 616 nm, which is quenched by (70 ± 10)% compared to the reference CdTe-only sample (the CdSe trap emissions was subtracted). This behavior is similar to the behavior of clustered hybrid samples where a quenching of (65 ± 5)% was observed (Figure 2a) and is attributed to the charge separation by a tunneling transfer of electrons from the CdTe to the CdSe NCs. The trap emission of CdSe NCs appeares to be the same in the hybrid structure and in the CdSe NC reference. The slight blue-shift of the PL of CdTe NCs in the layered hybrid sample compared to the CdTe reference sample is attributed to degradation processes of NCs like photo-oxidation (similarly observed in corresponding extinction spectra).

Figure 3 presents the temporal evolution of the PL intensity for the hybrid CdTe-CdSe (black line) and the reference
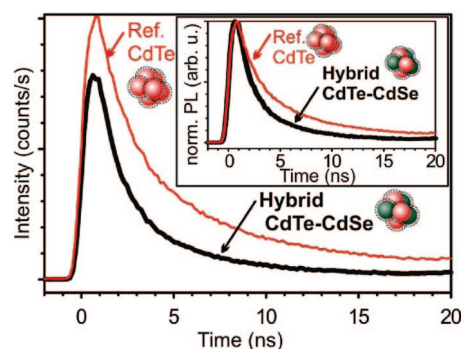
CdTe-only (red line) structures of clustered samples, measured with a time correlated single photon counting setup (TCSPC, PicoQuant FluoTime 200). The count rates for the hybrid sample are well below those of the CdTe-only reference (main graph of Figure 3), indicating a quenching of the CdTe NC emission in the hybrid clusters. A quenching efficiency of (55 ± 5)% deduced from time integrating the data in Figure 3 is in fair agreement with the value of (65 ± 5)% derived from the PL time-integrated measurements in Figure 2. The inset in Figure 3 presents the normalized decays of the CdTe NC reference and the CdTe-CdSe NC hybrid sample. The precise determination of the associated decay time constants is complicated by several reasons. First, the PL decay of colloidal NCs is characterized by a multiexponential behavior, which also involves extrinsic effects such as surface charges. Second, the time resolution of the TCSPC setup is limited to 250 ps in the shortest time window. According to recent studies on type II NC heterostructures, charge transfer processes can happen on a time scale of a few ps.[31] Although limited by the time resolution, the data in Figure 3, where a pronounced decrease in the PL intensity is observed at time zero, provide evidence for a fast (<1 ns) charge transfer process. Moreover, the normalized decays in the inset of Figure 3 demonstrate an additional slower dynamic (few ns) involving the quenching of the PL in the hybrid structure. While we cannot unequivocally assign this long component to a charge transfer process, it is conceivable that in a strongly inhomogeneous assembly, such as the clustered NCs, a distribution of interparticle distances and therefore a distribution of charge transfer rates is present. We exclude that FRET is involved in the slow dynamics because of the well-designed type II alignment where the band gap of the CdSe NCs is larger than the band gap of the CdTe NCs (Figure 1b). However, the quenching of the CdTe PL on the long time scale could eventually involve charge transfer to trap states.

In conclusion, our study demonstrates efficient quenching of excitonic emission of CdTe NCs of about 60% in close-packed structures with CdSe NCs, even in spite of the tunneling barrier between NCs due to isolating organic ligands and/or polymer linker. This quenching is ascribed to a charge separation in the close packed type II tunneling structures. Photodegradation of NCs was found to be pro-

nounced for the hybrid type II layered structures, a process that may be furthered by charge separation creating NC radicals. In future studies, these charges must be transported off the NCs in subsequent steps following the primary step of charge separation. This will lead to type II aligned hybrid assemblies of CdTe and CdSe NCs, which can be used for solar cell applications similar to the one presented by Gur et al.[5] CdTe–CdSe NC hybrids may further be used as a nanoscopic supplier of free charge carriers being able to trigger selective reactions or to create radicals.

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NL080489A