Charge carrier dynamics in CdTe/ZnTe core/shell nanocrystals for photovoltaic applications[§]

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Abstract. CdTe/ZnTe type-II core/shell nanocrystals were synthesized and characterized by the red-shift in the UV-Vis absorption and emission spectra along with the increase in both emission quantum yield and lifetime. The charge carrier dynamics was investigated through ultrafast transient absorption spectroscopy revealing the excited state carrier distribution and the dynamics through which the carriers decay. Upon laser pulse excitation the transient absorption spectrum was characterized by a broad ground state bleach signal in the core/shell nanocrystals in accord with the absorption spectra. Slower electron cooling was found in the core/shell nanocrystals compared to the CdTe core due to the type-II band-alignment that decouples the electron from hole preventing Auger-assisted electron cooling process. The recombination was found to be much slower in the core/shell nanocrystals due to the better surface passivation provided by the ZnTe shell eliminating the surface trapping process. The low band-gap CdTe based nanocrystals with a charge separated state are a viable candidate for photovoltaic applications and finally, we have investigated the potentiality of the synthesized nanocrystals as sensitizers in quantum dot solar cells.

Keywords. Ultrafast spectroscopy; solar energy conversion; Quasi type II core shell, electron transfer.

1. Introduction

Semiconducting nanocrystals (NCs) or quantum dots (QDs) are fundamentally interesting due to their quantum confined nature and have tremendous application potential in solar cells, light emitting devices, biological imaging, lasers and photocatalysis.^{1–12} In this regard, core/shell NCs offers more flexibility in terms of charge carrier confinement as the charge carrier localization can be tuned by varying the core and shell materials. For example, in the type-I structure both electron and hole are confined in the core whereas in type-II structure the electron and hole are spatially separated due to staggered band alignment between the core and shell.^{13–15} Due to this electron–hole decoupling, the type-II nanocrystal systems have long radiative lifetimes and are better candidates for photovoltaic devices.^{14,16–19}

CdTe based NCs with bulk band-gap of 1.7 eV are promising candidates for solar cell applications.²⁰ Earlier we have investigated the carrier dynamics in CdTe/ZnTe NCs synthesized in the aqueous phase at low temperatures having a high density of surface trap states.²¹ However, for photovoltaic applications we need high-quality NCs having less trap density. Herein we have investigated the ultrafast exciton dynamics utilizing transient absorption (TA) spectroscopy in CdTe/ZnTe core/shell NCs synthesized through high-temperature hot injection method. These NCs have higher quantum yield and photoluminescence lifetime compared to the CdTe core implying their superior optoelectronic properties. In TA experiments, the core/shell NCs showed signatures of charge separation due to the type-II nature where the electron and hole are spatially decoupled from each other. Significantly, the recombination was found to be much slower in the core/shell NCs in accord with the improved surface passivation. As a proof-of-concept, we fabricated sensitized solar cell devices with the NCs synthesized. For CdTe/ZnTe NCs the power conversion efficiency (PCE) was found to be 1.35% whereas pure CdTe had negligible PCE

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[§]Dedicated to Professor M V George on the occasion of his 90th Birth Anniversary.

due to instability in polysulfide electrolyte.²² Therefore, the improved surface passivation provided by ZnTe and the charge separated state help to attain better PCE in the core/shell CdTe/ZnTe NCs.

2. Experimental

2.1 Materials

Cadmium oxide (CdO, 99.5%), tellurium (Te, 99.99%), sulfur powder (99.99%), zinc acetate (ZnAc₂, 99.9%), octadecene (90%) oleic acid (90%), tri-octyl phosphine (TOP, 90%), cadmium nitrate tetrahydrate (Cd(NO₃)₂ · 4H₂O), sodium sulfide (Na₂S), zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O), potassium chloride (KCl), potassium hydroxide (KOH) and mercaptopropionic acid (MPA) were obtained from Sigma-Aldrich and used as received. TiO₂ transparent (DSL 18NR-T) and scattering (WER2-O) were purchased from Dyesol. AR grade chloroform, acetone, methanol and de-ionized (DI) water were used for cleaning the nanocrystals.

2.2 Synthesis of CdTe and CdTe/ZnTe nanocrystals

CdTe NCs were synthesized through a high-temperature hot injection method as reported earlier.^{23,24} As a summary, 2 mmol of CdO, 8 mmol of oleic acid and 10 mL of 1-octadecene were loaded in a three-necked flask and heated to 260 °C under nitrogen until the solution becomes colorless indicating the formation of cadmium oleate. The Te-TOP precursor (1 mmol) in 2 mL octadecene was rapidly injected into the mixture and the NCs were grown at 240 °C. The reaction mixture was cooled to room temperature and the CdTe NCs were cleaned with methanol twice and dispersed in chloroform. The ZnTe shell was grown through successive ionic layer adsorption and reaction (SILAR) technique as described previously.^{23,25} Briefly, the shell was grown layer-by-layer (where one monolayer, ML is around 0.32 nm) through alternate injection of Zn-oleate and Te-TOP at an interval of 10 min. 2ML of the shell was grown on the CdTe core.

2.3 Determination of quantum yield

The photoluminescence quantum yield (PLQY) was determined through a relative method using standard dye as a reference.

$$QY_{\text{Sample}} = \frac{PL_{\text{Sample}}}{PL_{\text{Reference}}} \times \frac{Abs_{\text{Reference}}}{Abs_{\text{Sample}}} \times \left(\frac{\eta_{\text{Reference}}}{\eta_{\text{Sample}}} \right)^2 \times QY_{\text{Reference}}$$

Here, PL_{sample} and PL_{reference} are the areas under the emission spectra; Abs_{sample} and Abs_{reference} are the absorbance at the excitation wavelength (525 nm) of the sample and reference respectively. η is the refractive index of the solvent.

The absorbance was kept below 0.1 during quantum yield measurement.

2.4 Photoluminescence lifetime measurements

The photoluminescence lifetime was measured through time-correlated single photon counting (TCSPC) method after exciting the nanocrystals with 445 nm diode laser in IBH (UK) instrument.

2.5 Ultrafast transient absorption measurements

The NCs dispersed in chloroform were excited with 400 nm pump beam and the excited state dynamics was probed in the visible region. The output (800 nm, 5 nJ, 50 fs, 88 MHz) from a mode-locked Ti:sapphire oscillator (Tissa 50, CDP, Moscow, Russia) was amplified in a multipass amplifier to obtain 50 fs pulses with 1 kHz repetition rate having 1 mJ energy per pulse. The pump beam of 400 nm was generated from a β -barium borate (BBO) crystal after frequency doubling. The broadband probe beam was generated after focusing the 800 nm laser on a sapphire crystal. The number of exciton per NC was kept < 1 to avoid multi-excitonic effects. The NC sample was kept in a rotating cell to avoid sample damage from the pump laser. The data (spectrum and kinetics) was collected through Excipro software and the multiexponential fitting of the kinetic traces was performed in Lab-view software. Details of the experimental set-up are provided in our earlier publications.^{26,27}

2.6 Solar cell fabrication and characterization

The quantum dot sensitized solar cells were prepared following reported procedures with required modifications.^{28–34} The process will be described briefly here. The oleic acid capped NCs were phase transferred to the aqueous phase with mercaptopropionic acid for sensitization of the TiO₂ photoanodes. The TiO₂ photoanodes were prepared through doctor blade technique, first by putting transparent TiO₂ followed by baking at 450 °C for 30 min. Then a scattering TiO₂ layer was put through baking at 450 °C for another 30 min. The MPA-capped NCs were drop-casted on the TiO₂ photoanode and kept for 6 h before washing with de-ionized water. On this 4 layers of CdS and 2 layers of ZnS was put through SILAR technique. For counter electrode, Cu₂Se was utilized.³⁵ The NC sensitized TiO₂ photoanode was combined with the Cu₂Se counter electrode and polysulfide (S²⁻/S_n²⁻) electrolyte and assembled with two binder clips. The current density–voltage (J–V) curves were obtained under 1Sun intensity (100 mW/cm²) in a solar simulator (Peccell, PEC-L01) combined with Keithley 2400 as a source meter. The 1Sun intensity was confirmed using a standard photodiode. The power conversion efficiency (η) was measured as

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}}$$

where J_{SC} is the short circuit current density, V_{OC} is the open circuit voltage, FF is the fill factor and P_{in} the input power (100 mW/cm^2). The incident photon to current conversion efficiency (IPCE) spectra was obtained from the set up provided by Peccell (PEC-S20).

3. Results and Discussion

CdTe/ZnTe core/shell NCs represent a type-II system due to staggered band alignment between the CdTe core and ZnTe shell. Therefore, the electron will be localized in the CdTe core whereas the hole will be in the ZnTe shell making a spatially decoupled system.

The CdTe NC core synthesized through high-temperature hot injection method as described in the experimental section were of $\sim 4.5 \text{ nm}$ size as determined from the absorption maxima ($\sim 655 \text{ nm}$).³⁶ The ZnTe shell of 2 ML was grown through SILAR technique. Figure 1 depicts the UV-vis absorption spectra of both the CdTe core and CdTe/ZnTe core/shell NCs where both the absorption and photoluminescence (PL) maxima has red-shifted after deposition of the shell indicating the formation of the core/shell structure. The broad absorption spectra with indistinct excitonic features also indicate type-II structure formation.^{13,17} The PL quantum yield has increased from 6% to 20% in accord with the PL lifetime which increased from 21 ns to 28.4 ns upon ZnTe shell deposition. For CdTe, the PL lifetime was bi-exponential with 2.34 ns (27%) and 28 ns (73%) components. The first component is due to radiative recombination whereas the second component

is due to shallow trap mediated recombination process.^{25,37} In the core/shell NCs the bi-exponential PL decay components are 3.4 ns (22%) and 35.3 ns (78%), respectively. The radiative component has a longer lifetime implying better surface passivation provided by the ZnTe shell.

Figure 1(B) shows the transmission electron micrographs (TEM) of CdTe/ZnTe NCs. The size of the core/shell NCs is $\sim 5.78 \text{ nm}$ which is close to 2ML of ZnTe shell growth.

To ascertain the effect of better passivation and charge separation we have performed ultrafast transient absorption measurements after exciting the NCs with 400 nm pump and monitoring the excited state dynamics throughout the visible range. In the case of CdTe, the transient absorption spectra are characterized by a bleach centered around 655 nm which can be attributed to the ground state 1S bleach ($1S_e - 1S_{3/2}$) as shown in Figure 2. The bleach signal can have a contribution from both electron and hole. However, for II–VI semiconductors the contribution of the hole can be neglected due to the high density of hole states as the effective mass of a hole is much higher than the electron.³⁸ Therefore, the bleach signal provides information about the electron dynamics.³⁹

As we are exciting the NC with 400 nm laser which is higher in energy than the 1S transition in CdTe hot electron is created in the conduction band. This hot electron circumvents the phonon-bottleneck through an Auger-assisted mechanism by transferring its excess energy to valence band hole.^{40,41} This electron cooling process can be identified from the 1S bleach growth which signifies

Figure 1. (A) UV-Vis absorption spectra (a, b) and photoluminescence spectra (a', b') of (a, a') CdTe and (b, b') CdTe/ZnTe NCs. (Inset) Photoluminescence decay traces of (a'') CdTe and (b'') CdTe/ZnSe NCs. L denotes the lamp profile. (B) Transmission electron micrograph of CdTe/ZnTe nanocrystals.

Figure 2. Transient absorption spectra of (A) CdTe and (B) CdTe/ZnSe NCs upon 400 nm pump excitation.

Figure 3. Ground state bleach recovery kinetics of (a) CdTe and (b) CdTe/ZnTe NCs. The solid lines are fitted data.

population of the $1S$ state. The subsequent depopulation through trapping and recombination can be interpreted from bleach recovery kinetics.⁴² The ground state bleach recovery kinetics of the NCs have been compared in Figure 3. For CdTe, the bleach growth has a pulse width limited <100 ps (75%) and 0.65 ps (25%) growth component as well as 5 ps (85%) and 50 ps (15%) recovery components. The 0.65 ps component can be attributed to electron cooling to the $1S_e$ state.^{23,43,44}

For the CdTe/ZnTe NCs there is broad bleach starting from 650 nm as depicted in figure 2. However, due to stimulated emission from the NC, the TA spectral shape is obscured beyond 720 nm. Here, the bleach growth dynamics can be fitted with a pulse width limited <100 fs (45%) and 1.6 ps (55%). Therefore, we observe much slower bleach growth implying slower

Figure 4. (A) Current density (J - V) and (B) IPCE spectrum of CdTe/ZnTe NCs.

electron cooling compared to pure CdTe NCs. This can be attributed to electron-hole decoupling due to the type-II nature of the system. The Auger-assisted energy transfer depends on the electron-hole wave function overlap.^{40,41} In CdTe/ZnTe NCs the hole moves from the CdTe core to the ZnTe shell due to the staggered band alignment decreasing the overlap. On the other hand, the bleach recovery components can be fitted with 4.5 ps (60%), 50 ps (30%) and >400 ps (10%). Therefore, the excitons are longer lived in the core/shell NCs due to the surface passivation provided by the ZnTe shell.

We have tested the potentiality of the core/shell CdTe/ZnTe NCs as sensitizer material in quantum dot solar cells. The details of the device fabrication protocol have been provided in the experimental section. The NC sensitized TiO_2 photoanodes were assembled with the Cu_2Se counter electrode and polysulfide electrolyte for solar cell characterization through J - V and IPCE measurements. The CdTe NCs have a tendency to degrade in presence of polysulfide electrolyte and the PCE was found to be negligible. On the other hand, for CdTe/ZnTe NCs, we have obtained $1.35 \pm 0.05\%$ PCE with short circuit current (J_{SC}) 5.56 mA/cm^2 , open circuit voltage (V_{OC}) 0.49V and fill factor (FF) 49% as represented in Figure 4. The IPCE spectra also show broad photoresponse up to 750 nm in accord with absorption spectra. This implies that the core/shell NCs are stable in presence of the polysulfide electrolyte due to surface passivation provided by the ZnTe shell. Moreover, the extended absorption and charge separation due to type-II structure makes CdTe/ZnTe as a promising material for solar cell applications.

4. Conclusions

CdTe/ZnTe core/shell NCs having type-II band alignment were synthesized through high-temperature colloidal method. The steady state absorption and emission are red shifted in the core/shell structure with an

increase in both the PLQY and PL lifetime due to the formation of the type-II structure. The ultrafast transient absorption spectroscopic measurements revealed signatures of charge separation as the electron cooling slowed down due to the electron-hole decoupling. The recombination was also slower in the core/shell NC depicting the importance of surface passivation by ZnTe. Finally, CdTe/ZnTe NCs-sensitized solar cell devices were fabricated with 1.35% efficiency and a broad photo-response in the IPCE spectra attracting further research to optimize the photovoltaic performance.

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