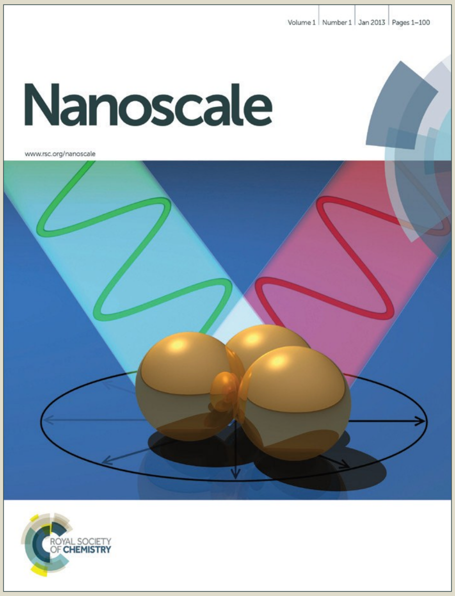

Journal Name

ARTICLE

Exciton Delocalization and Hot Hole Extraction in CdSe QD and CdSe/ZnS Type 1 Core Shell QD Sensitized with Newly Synthesized Thiols

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Abstract

The present work describes ultrafast thermalized and hot hole transfer processes from photo-excited CdSe quantum dot (QD) and CdSe/ZnS core-shell QD (CSQD) to newly synthesized thiols. Three thiols namely 2-Mercapto-N-phenylacetamide (AAT), 3-Mercapto-N-phenylpropanamide (APT) and 3-Mercapto-N-(4 methoxyphenyl) propanamide (ADPT) were synthesized and their interaction with both CdSe QD and CdSe/ZnS CSQD was monitored. Steady state absorption study suggests the exciton delocalization from CdSe QD in presence of the thiols. However the similar features were not observed in presence of ZnS shell over CdSe core, instead a broadening in excitonic peak was observed with both APT and ADPT but not with AAT. This exciton delocalization and broadening in excitonic peak was also confirmed by ultrafast transient absorption studies. Steady state and time resolved emission studies show hole transfer from photo-excited QD and CSQD to the thiols. Signature of hot hole extraction was observed in transient absorption studies which was confirmed by fluorescence upconversion studies. Both hot and thermalized hole transfer rate from CdSe QD and CdSe/ZnS CSQD to the thiols was determined using fluorescence up-conversion technique. Experiments with different ZnS shell thickness have been carried out which suggests that hole transfer is possible till 2.5 monolayer of ZnS shell. To the best of our knowledge we are reporting for the first time extraction of hot hole from CdSe/ZnS type I CSQD by molecular adsorbate.

Introduction

Quantum dots are known to be a good candidate for solar cell application due to their exciting properties such as band-gap tunability[1-5], multiexciton generation (MEG)[6-11], larger extinction coefficient and longer exciton lifetime[12]. Excitation of QD materials with high energy photon generates hot charge carriers. After generation of these hot charge carriers, a number of processes such as carrier multiplication, energy relaxation and Auger recombination are active with each process characterized by its own time constant[13] (Scheme 1). It has been reported that the efficiency of QDSSC can reach to 66% if hot charge carriers[14] can be extracted prior to their cooling. Similarly Nozik[11] and co-workers speculated that efficiency of QDSSC can reach upto 45% through multiple exciton generation and dissociation. However till date the highest photoconversion efficiency of QDSSC is reported to be 8.6%[15], which is much lower as compared to other photovoltaic devices[16] and the expected values as given above. So it's utmost important to understand the facts which are responsible for lowering the efficiency of QDSSC.

It is widely reported in the literature while exciting QD materials with energy more than $2E_g$ (band gap) (Scheme 1, Process 1) generation of multiple excitons[11] (MEG) can be realized (Scheme 1, Process 2). However the main competing process with MEG is the Auger assisted charge recombination process (Scheme 1, Process 3) which leads to the non-radiative recombination of generated exciton. The probability of auger recombination can be reduced if the coupling between electron and hole can be reduced. This can be done either by extracting the electron or hole from photo-excited QD material. It is widely reported in literature that electron[17,18] extraction rate is very fast ~10^{10}-10^{12} S^{-1} however the hole[19,20] extraction rate was found to be slow ~ 10^{8}-10^{9} s^{-1}. This slow hole transfer rate is one of the main reason for less efficiency in QDSSC as it increases

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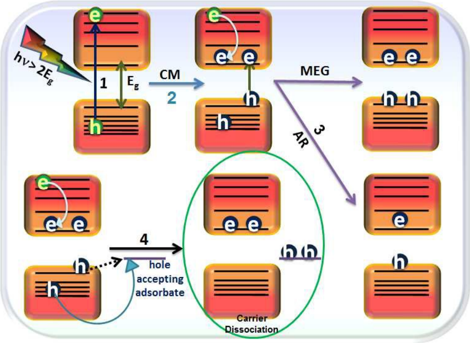
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the recombination probability between photo-generated electron and hole. Therefore it is very important to extract hole at much faster rate. Recently we[21-24] and others[25-27] have reported hole transfer time in QD-molecular adsorbate composite systems in femto second to pico-second time scale. However, till date not many -reports are available on spectroscopic investigation of hole transfer dynamics in QD materials. In addition to this another process can be proposed by which the efficiency of QDSSC can be increased where advantage of CM and hot charge carrier extraction can be combined together as shown in scheme 1. A suitable hole transporting molecule can be used, which can extract the hot hole at a faster rate before its relaxation to band edge level (Scheme 1, process 4). Due to this process both electron – hole recombination probability and hence auger recombination can be reduced drastically which will eventually increase the CM probability. Researchers have demonstrated the hot electron extraction[28-32] from QD materials using different adsorbates in the range of 50 fs-100 ps, however till date no report is available on hot hole extraction except the report by us where we have demostrated the extraction of hot hole from photo-excited CdSe QD to 3-methoxy catechol with time scale of ~250 fs[33]. It has been reported that over coating a wide band gap shell (such as ZnS) on bare CdSe QDs can greatly enhance their photostability[34, 35] and efficiency[36-38] in QDSSC. In literature few reports[39,40] are available which shows that charge carrier extraction is still possible in presence of type I shell over core. However, it will be interesting to see whether hot hole can be extracted in presence of type I shell or not.



Scheme 1: Different processes involved after photo-excitation of QD materials with photon energy > 2Eg. **Process 1:** Generation of hot charge carriers, **Process 2:** Carrier multiplication (CM) followed by multiple exciton generation (MEG), **Process 3:** Non radiative auger recombination, **Process 4:** Charge carrier dissociation in presence of hole accepting adsorbate.

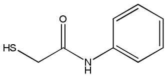
Thiols are known to be good binder for QD surface and many researchers have studied the interaction of thiols with different QDs[41-43]. However very few reports are available in the literature which demonstrates charge carrier extraction from QD to thiols in fast and ultrafast time scale. In the present investigation we have designed and synthesized three thiol molecules (Chart 1) to monitor their interaction and charge carrier dynamics with CdSe QD and CdSe/ZnS type I CSQD. We have used ultrafast transient absorption and fluorescence upconversion techniques to monitor different processes in ultrafast time scale.

Experimental Section:

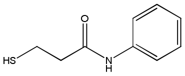
a) Materials: Aniline, anisidine and thioglycolic acid were procured from s.d. fine-chem. ltd. 3-Mercaptopropanoic acid was obtained from Sisco Research Laboratories Ltd. Cadmium oxide (CdO, 99.5%), Zinc acetate ($ZnAc_2$, 99.9%), Selenium (Se,99.99%), Sulpher powder (S, 99.99%), Oleic acid (90%), Tri-octly phosphine (TOP, 90%) and Octadecene (ODE) (90%) was purchased from Aldrich. All the chemicals used as received without further purification. AR grade chloroform and AR methanol were used for precipitation.

b) Synthesis of Mercapto-amides (thiol derivatives)

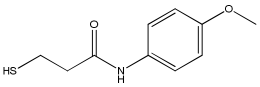
Chart 1: Structure of thiol derivatives



2-Mercapto-N phenylacetamide (AAT) (3a)

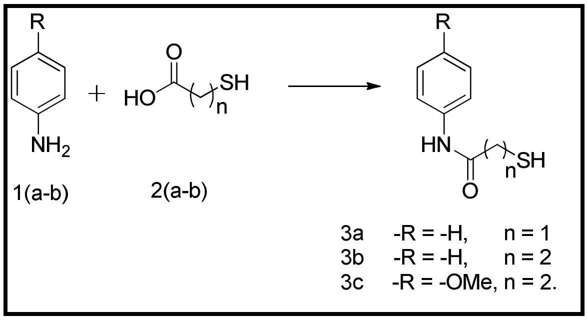


3-Mercapto-N-phenylpropanamide (APT) (3b)



3-Mercapto-N-(4 methoxyphenyl)propanamide (ADPT) (3c)

Reaction scheme:



Mercapto-amides	Aromatic aniline	Mercapto-acids	R	n
3a	1a	2a	H	1
3b	1a	2b	H	2
3c	1b	2b	OMe	2

Procedure: Aromatic amine 1(a-b) was taken in 50mL two necked round bottomed flask with water condenser. To this equimolar quantity of mercapto acid 2(a-b) was added. The mixer was stirred at 130 °C for 3 h. Reaction was monitored on TLC. Reaction mass was cooled to room temperature and slowly added to 20 mL dil. HCl (10%) and stirred well. White solid obtained was filtered and washed with water. It was dried and purified by column chromatography using toluene as eluting system to get 3(a-c).

Characterization: All the synthesized compounds were characterized by melting point, FT-IR spectroscopy, ^1H NMR spectroscopy and mass spectrometry. All melting points were recorded in toluene are uncorrected and are in well accordance with literature values. UV spectrum was obtained on Perkin Elmer Lamda25 instrument using 1,2 Dichloroethane as a solvent. FT-IR spectra were recorded on a Bomem Hartmann and Braun MB-Series FT-IR spectrometer.^1H NMR spectrums were recorded on Varian 300-MHz mercury plus spectrometer, and chemical shifts are expressed in δ ppm using tetramethylsilane (TMS) as an internal standard. Mass spectral data were obtained with a Micromass Q-TOF spectrometer.

All three compounds was characterized using FT-IR spectroscopy, ^1H NMR and mass spectroscopy. In FT-IR spectra of these compounds five different bands at 3263 (NH), 3138 and 3094 (Ar-H), 2569 (SH), 1643 (C=O amide), 1546 and 1489 (C=C aromatic) for AAT, 3297 (NH), 3088 (Ar-H), 2558 (SH), 1658 (C=O amide), 1545 and 1496 (C=C aromatic) for ADPT, 3313 (NH), 3124 and 3011 (Ar-H), 2562 (SH), 1652 (C=O amide), 1531 and 1455 cm^{-1} (C=C aromatic) for APT appears.

^1H NMR spectra of all three thiol derivatives was recorded in DMSO solvent. ^1H NMR spectra of AAT, ADPT and APT shows different peaks at δ (ppm): 2.93 (s,1H, SH), 3.30 (s, 2H, CH_2), 7.06 (t, 1H, Ar-H), 7.32 (t, 2H, Ar-H), 7.5 (d, 2H, Ar-H), 10.06 (s, 1H, NH); δ (ppm): 2.38 (t, 1H, SH), 2.63 (t, 2H, CH_2), 2.75 (q, 2H, CH_2), 7.03 (t, 1H, Ar-H), 7.30 (t, 2H, Ar-H), 7.60 (d, 2H, Ar-H), 9.95 (s, 1H, NH) and δ (ppm):2.36 (t, 1H, SH), 2.59 (t, 2H, CH_2), 2.74 (q, 2H, CH_2), 3.72 (s, 3H, OCH_3), 6.87 (d, 2H, Ar-H), 7.50 (d, 2H, Ar-H), 9.80 (s, 1H, NH) respectively.

All three compounds were also characterized through mass spectrometry to find their m/z ratio. 2-Mercapto-*N*-phenylacetamide (3a). MS: m/z (PCI) 167.3 (M^+) C_8H_9NOS, 3-Mercapto-*N*-phenylpropanamide (3b). MS: m/z (PCI) 182.1 (M+1) $C_9H_{11}NOS$, 3-Mercapto-*N*-(4-methoxyphenyl) propanamide (3c). MS: m/z (PCI) 212.1 (M+1) $C_{10}H_{13}NO_2S$.

c) Synthesis of CdSe QD: Oleic acid capped CdSe QD was synthesized by hot injection route with slight modification. In brief stock cadmium oleate solution was prepared by heating 0.51 g cadmium oxide (4.0 mmol), 3.4ml oleic acid (10.6 mmol), and 11.6 ml octadecene at 180 °C under the flow of Ar gas. Once the solution becomes clear the temperature was increased to 260-270 °C. A stock solution of selenium was prepared by mixing 1.1 ml of TOP (2.5mmol) with 0.16 g of selenium (2 mmol) and 4.4 ml octadecene. This TOPSe solution was quickly injected to the reaction mixture. Rapid color change from yellow to orange to red was observed. Optical absorption spectra were recorded at different time interval to monitor the growth of CdSe QD. Once a desired size was obtained the temperature was decreased and the reaction mixture was allowed to cool. The solution was dissolved in chloroform and then re-precipitated with methanol for 3 times. Size of QD was determined using sizing curve[53] and found to be 3.3 nm.

d) Synthesis of CdSe/ZnS Type-I CSQD: For the preparation of CdSe/ZnS core-shell QD, previously prepared CdSe QD was used as a core. For the preparation of ZnS shell, Zn-oleate was used as Zinc precursor and Sulphur powder as Sulphur precursor. Zn-oleate was prepared by taking 0.109g of Zn-acetate (0.5 mmol) and 0.425 ml oleic acid (1.3 mmol) in 1.5 ml octadecene. This mixture is refluxed at 180 °C into a three-neck round bottom flask in inert atmosphere. This Zn-oleate was added to a 5µmole CdSe QD solution. To prepare the stock sulphur solution, 0.16 g sulphur powder (2 mmol) was reacted with 1.1 ml TOP (2.5mmol) in 4.4 ml octadecene. TOPS was added drop wise to the solution of Zn-oleate in CdSe through a syringe at 180°C. Different amount of Zn and S precursor were added sequentially to get the desired monolayer thickness of ZnS over CdSe core. A colour change from yellow to red to dark red colour solution was obtained after addition of TOPS. The temperature was allowed to fall below 100 °C and the solution was dissolved in chloroform. The prepared CdSe/ZnS core shell QD was re-precipitated with methanol for 3 times.

e) Steady State Optical Absorption and Emission Spectrometer: Steady-state absorption spectra were recorded on a Thermo-Electron model Biomate spectrophotometer. Fluorescence spectra, which were corrected for the wavelength dependence of the instrument sensitivity, were recorded using Hitachi model 4010 Spectrofluorometer.

f) Analytical Technique: Samples were digested in aqua regia to find the thickness of ZnS shell over CdSe core. The digested samples were analysed for Zn and Cd content using 904 BT, Double Beam flame Atomic Absorption Spectrometer (GBC Avanta) which uses Hollow Cathode Lamp as radiation source. The concentration of the analyte was determined by calibration curve method.

g) Time Resolved Emission Spectrometer: Time resolved fluorescence measurements were carried out using a diode laser based spectrofluorimeter from IBH (UK). The instrument works on the principle of time-correlated single photon counting (TCSPC). In the present work, a 374 nm, 406 nm laser pulses were used as the excitation light sources and a TBX4 detection module (IBH) coupled with a special Hamamatsu PMT was used for fluorescence detection.

h) Femtosecond Fluorescence Upconversion: In femtosecond fluorescence up-conversion setup (FOG 100, CDP), FLU was excited at ~400 nm and emission was monitored at 510 nm (emission maxima). The second harmonic (SH) of a mode locked Ti:sapphire laser (CDP Corp., Moscow, Russia, 82.2 MHz repetition rate) pumped by a 5 W DPSS laser was used for excitation. The SH was generated in a type I BBO angle-tuned phase-matched nonlinear crystal with 1 mm thickness. Optical delay between the excitation and the gate pulse was varied using a delay rail (6.6 fs per steps) at the path of the gate pulses. The up-converted signal was measured with a photon counter after passing through a proper band-pass filter and a double monochromator. In all of these measurements, the samples were taken in a rotating cell (0.4 mm path length) to have a better heat dissipation and thus to avoid the photodegradation of the dye. For the measurements of fluorescence transients, polarization of the SH beam was set to the magic angle (54.7°) with respect to the observed horizontally polarized fluorescence signal using Berek wave plate arrangement (CDP Corp., Moscow, Russia). The fluorescence signal from the sample was up-converted in another nonlinear BBO crystal (thickness 0.5 mm) using the Ti:sapphire fundamental beam as the gate pulse. A cross correlation of fundamental and the SH displayed a full width at half-maxima (fwhm) of ~250 fs for the instrument response function (IRF). Femtosecond transients were fitted by convolution analysis using a Gaussian shape for the IRF.

i) Femtosecond Transient absorption Spectrometer: Ultrafast transient absorption measurements were carried out in femtosecond (0.1 ps-4 ns) transient absorption (TA) spectrometer which is based on multi-pass Ti: sapphire laser system (CDP, Moscow, 800 nm, <100 fs, 1.2 mJ/pulse, and 1 kHz repetition rate) and Excipro pump-probe spectrometer (CDP, Moscow). Briefly the pulses of 40 fs duration and 4 nJ energy per pulse at 800 nm obtained from a self-mode-locked Ti-Sapphire laser oscillator (Tissa 50, CDP, Moscow, Russia) were amplified in a multi-pass amplifier pumped by a 20W DPSS laser (Jade-II, Thales Laser, France) to generate 40 fs laser pulses of about 1.2 mJ energy at a repetition rate of 1 kHz. Pump pulse at 400 nm were generated by frequency doubling of the 800 nm pulse at a β-barium borate (BBO) crystal. The spectrometer is coupled with Multi channel detector head, with two 1024-pixels linear image sensors, 200 -1000 nm spectral response (10% of peak), up to 1 kHz readout rep rate. To generate visible probe pulses, about 1 µJ of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. An imaging spectrometer is adapted to the detector head and connected to a computer via serial port with Visible grating 300 –1100 nm spectral range which has 206 nm detection range. The pump beam diameter at the sample is ~350 µm, corresponding to an excitation density of 0.28 $\mu J/cm^2$. A white light continuum (from 450 to 850 nm) was generated by attenuating and focusing ~10 µJ of the 800 nm pulse into a sapphire window and splitting into a probe and reference beam. The probe beam was focused with an Al parabolic reflector onto the sample (with a beam diameter of 150 µm at the sample). The instrument response function (IRF) for 400 nm excitation was obtained by fitting the rise time of the bleach of sodium salt of *meso* tetrakis (4 sulfonatophenyl) porphyrin (TPPS) at 710 nm and found to be 120 fs. The <N>(jσ) was maintained <1 to prevent multiexciton formation due to higher pump intensity. For all spectroscopy measurements, the samples were kept in a 1 mm cuvette and the experimental solutions were circulated to avoid sample bleaching during the course of the experiment. The data analysis and fitting at individual wavelengths were carried out by Lab-View program.

Results and Discussions:

Figure 1A shows the optical absorption spectra of CdSe QD in absence and in presence of different concentrations of AAT. Absorption spectra of pure CdSe QD (Figure 1a) shows the first excitonic peak at 559 nm corresponding to 1S ($1S_e$-$1S_{3/2}$) transition and another peak at 470 nm corresponding to 1P ($1P_e$-$1P_h$) transition[44]. From the sizing curve[45] the diameter of CdSe QD was found to be 3 nm. Optical absorption spectra of CdSe QD in presence of different concentration of AAT shows that no charge transfer complex are formed between them, however interestingly the first excitonic peak (1S) position shifts to the red region of the spectrum with increasing AAT concentration (559 to 564 nm) (Figure 1e). The similar results were found with other two thiols (APT and ADPT) also and shown in supporting information (SI Figure 1). On addition of the thiols, ligand exchange process on QD surface takes place (Figure 1B) which results in mixing of VB orbital of QD with the HOMO of thiol ligands. Due to this mixing hole can delocalize into the ligand shell and a red shift in absorption spectra was observed. To demonstrate exciton delocalization in CdSe/AAT system, we have also plotted change in excitonic radius[45] (ΔR) with an increase in AAT concentration and shown in Figure 1 inset. It is clearly seen from Figure 1 inset that with an increase in AAT concentration an increment in excitonic radius was observed. Similar exciton delocalization and red shift in absorption spectra was also reported earlier by Weiss and coworkers[43] where they have shown that ligand exchange on CdSe QD with phenyldithiocarbate (PTC) ligand can delocalize hole from QD to PTC. It is interesting to note that with all three thiols we got almost similar degree of exciton delocalization despite the difference in molecular structure of the thiols. It suggests that the binding of S^- ion of the thiols to the Cd^{2+} ions on the QD surface is responsible for the exciton delocalization. Since this S^- ion is not in conjugation with the main molecule therefore the charge carriers will be localized only on S^- ion of the thiols. As a result similar degree of exciton delocalization was observed in all the systems.

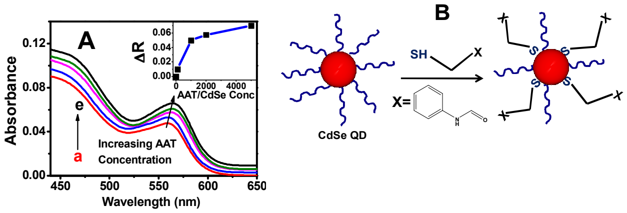


Figure 1A: Steady state optical absorption spectra of CdSe QD with different concentration of AAT (a) Pure QD, (b) QD:AAT= 1:10, (c) QD:AAT= 1:100 (d) QD:AAT= 1:1000, (e) QD:AAT= 1:5000. Inset: change in ΔR value with increase in concentration of AAT. Figure 1B: Schematic diagram of ligand exchange of oleic acid with thiols on QD surface in presence of large concentration of thiols.

Now to monitor the effect of shell on exciton delocalization steady state absorption studies of CdSe/ZnS CSQD has been carried out in absence and in presence of different derivatives of thiol and are shown in Figure 2A. Steady state absorption spectra of CdSe/ZnS CSQD (Figure 2A) shows the presence of 1S and 1P excitons at 570 and 475 nm in contrast to 559 and 470 nm (Figure 1A) for CdSe QD. This red shift in absorption spectra of CSQD as compared to pure core QD has been observed earlier also and assigned to the leaking of charge carriers from core to shell[35,46]. The thickness of ZnS shell over CdSe core is determined to be 1.2 ML using elemental analysis (SI Table 2). Steady state absorption studies of CdSe/ZnS CSQD in presence of all the three thiols show no red shift in absorption spectra (Figure 2A) as observed for CdSe QD (Figure 1A). However, with time the exciton peak becomes broader in case of both ADPT and APT at higher thiol concentration (QD:Thiol = 1:1000) but not in case of AAT (Figure 2A Inset, SI Figure 2). To understand the mechanism of interaction and different behaviour of AAT as compared to both APT and ADPT, we have carried out separate experiments in presence of added Zn^{2+} ions to the CSQD solution with thiols.

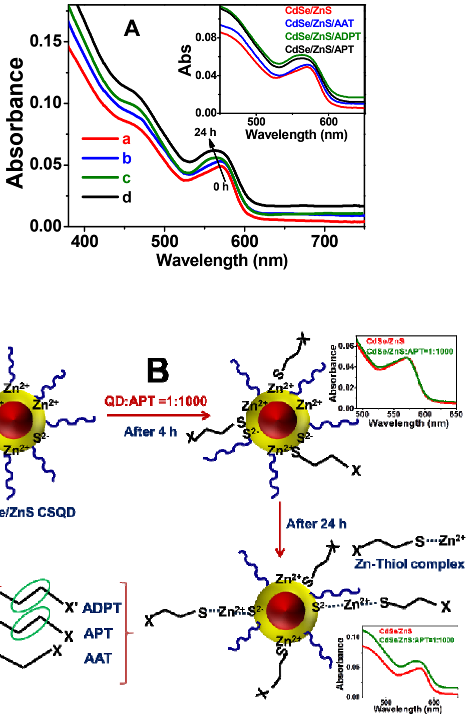


Figure 2A: Steady state optical absorption spectra of CdSe/ZnS (1.2 ML) CSQD at different time in presence of ADPT (ADPT:CdSe/ZnS=1000:1) (a) Pure CSQD, (b) CSQD/ADPT at 4 h, (c) CSQD/ADPT at 16 h, (d) CSQD/ADPT at 24 h Inset: Steady state optical absorption spectra of CSQD after 24 h in presence of all three thiols (Thiol:QD=1000:1). **2B:** Schematic diagram of interaction of thiols with CSQD.

The experiments were carried out as follows. First we have prepared a solution of CSQD with thiols, and then 50 μL of methanol containing 1.5 mg of Zn^{2+} ion was added in the solution. The mixture was sonicated for 1 hr to allow proper mixing of all the constituents. Steady state absorption spectra were recorded at different time and changes in spectra was monitored (Figure 3). Interestingly the absorption spectra of CSQD/thiols in presence of added Zn^{2+} ions at 4 hrs matches with the spectra of CSQD with respective thiols after one day (Figure 3). This observation suggests that the formation of Zn^{2+}/thiol complex and its interaction with CSQD surface is responsible for the change in absorption spectra. When extra added Zn^{2+} ions is present in the system, the formation of Zn^{2+}/thiol complex is fast and consequently change in absorption spectra is observed even in 4 hrs. In case of pure CSQD with thiols, some of the Zn^{2+} ions will be etched from the QD surface but this process is slow and such changes in absorption spectra has been observed only after one day. In both APT and ADPT this Zn^{2+}/thiol complex is able to interact with the CSQD surface thereby changing absorption spectrum while in AAT it is not. This is due to the presence of extra CH_2 group in both APT and ADPT. Due to this extra CH_2 group the steric hindrance for the interaction with CSQD surface will be less. We have also carried out experiment with low concentration of thiols (QD:Thiol = 1:10) where we have not observed such features. This observation suggests that low concentration of thiols is not sufficient for etching of Zn^{2+} ions from the surface and no change in absorption spectra is observed. We have also carried out steady state and time resolved luminescence studies in above systems to further confirm this observation and mechanism of interaction and is shown in SI Figure 3.

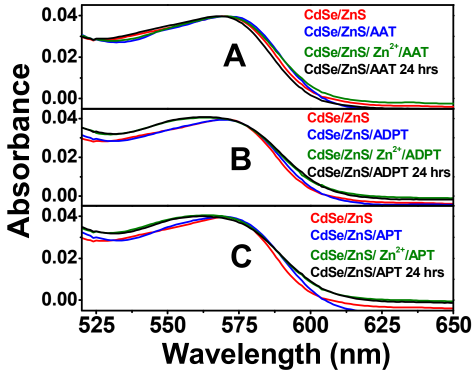


Figure 3: Steady state absorption studies of CdSe/ZnS (1.2 ML) CSQD with (A) AAT, (B) ADPT (C) APT in presence and absence of Zn^{2+} ions and thiols.

Since thiols are known to be good binder[47] as well as good hole transporting molecules we have studied the hole transfer dynamics in CdSe/thiol and CdSe/ZnS/thiol systems. To verify hole transfer processes steady state emission studies have been carried out for both QD and CSQD in absence and in presence of the thiols. Figure 4A and 4B indicate the emission spectra of CdSe QD and CdSe/ZnS CSQD in absence and in presence of AAT, APT and ADPT at the concentration ratio of thiols:QD = 1000:1. The emission peak for CdSe QD appears at 580 nm (ϕ_f = 20%) and for CdSe/ZnS CSQD (ϕ_f = 30%) appears at 590 nm. It is interesting to see that in presence of all the thiols the emission intensity of CdSe QD is drastically reduced (Figure 4A). This quenching in CdSe QD emission cannot be attributed to the energy transfer from photo-excited CdSe QD to the thiols as there is no overlap between optical absorption spectra of the thiols (SI Figure 4) and emission spectra of CdSe QD. Now to confirm that the quenching of CdSe QD emission is due to hole transfer, the redox level of the thiols and QDs were determined. The valence band (VB) ($1S_h$) level of CdSe QDs was reported to be 1.65 V,[17] whereas the conduction band ($1S_e$) was determined to be -0.56 V after adding the bandgap energy to the valence-band energy (E_{BG}=2.21 eV). Redox level of ADPT was determined using differential pulse voltammetry (DPV) studies and found to be 1.56 V vs NHE (SI Figure 5).

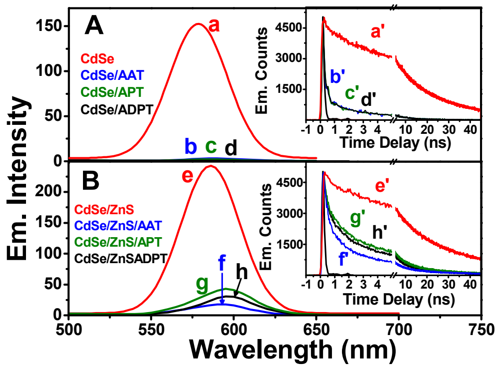


Figure 4: Panel A: Steady state emission spectra of CdSe QD (a) in absence and in presence of the thiols (b) AAT, (c) APT and (d) ADPT. Inset: Time-resolved emission spectra of CdSe QD (a') in absence and in presence of the thiols (b') AAT, (c') APT and (d') ADPT. **Panel B:** Steady state emission spectra of CdSe/ZnS (1.2 ML) CSQD (e) in absence and in presence of thiols (f) AAT, (g) APT and (h) ADPT. Inset: Time-resolved emission spectra of CdSe/ZnS CSQD (e') in absence and in presence of the thiols (f') AAT, (g') APT and (h') ADPT. Concentration ratio for thiol:QD and thiol:CSQD were 1000:1.

The VB level of QD and HOMO of ADPT suggests that the hole transfer from photo-excited CdSe QD to ADPT is thermodynamically favourable process. At this point we would like to mention that the redox level of other two thiols, APT and AAT could not be measured, however keeping in mind that the molecular structure of all three thiols are almost similar, it is expected that redox level of both APT and AAT will be almost similar as that of ADPT and therefore the quenching in emission can be attributed to the hole transfer. Steady state emission studies of CdSe/ZnS CSQD have also been carried out in presence of the thiols and there also an appreciable quenching in emission was observed. In our earlier investigation[23] we have reported emission quenching of CdSe/ZnS CSQD in presence of aurin-tricaboxylic acid (ATC) which has been has been assigned to the hole transfer from CSQD to ATC. Similarly in the present investigation also the quenching in CSQD emission on addition of thiols has been assigned to the hole transfer from CSQD to thiols (Scheme 2). To determine hole transfer dynamics, time resolved emission studies of CdSe QD and CdSe/ZnS CSQD have been carried out in absence and presence of thiols and are shown in Figure 4A and 4B Inset. Emission decay trace of CdSe QD and CdSe/ZnS CSQD can be fitted multi-exponentially with average life time of ~ 10 ns and ~ 15 ns respectively (SI Table 3). However it is interesting to see that in presence of the thiols the emission trace of QD decays with pulse width limited time constant (< 100 ps). Similarly in case of CSQD the emission trace decays very fast with the fastest component of ~ 150 ps (SI Table 3). These observations again confirm the hole transfer process from QD and CSQD to the thiols.

By employing steady state absorption and emission and time-resolved emission studies we have demonstrated the exciton delocalization and hole transfer processes from both QD and CSQD. To further reconfirm hole transfer processes, exciton delocalization and their impact on charge carrier dynamics we have carried out ultrafast transient absorption spectroscopy after exciting the QD samples at 400 nm and monitoring the transients in 460-650 nm regions. Transient absorption spectra of pure CdSe QD shows the presence of two distinct negative absorption bands peaking at 470 nm (1P) and at 558 nm (1S) with a hump at 525nm (2S) (SI Figure 6). Interestingly in presence of the thiols the transient peak appears at 475 nm and at 564 nm respectively (SI Figure 7). This red shift (558 nm to 564 nm) in transient absorption spectrum of QD/thiol confirms the exciton delocalization into the ligand shell. Transient absorption spectra of CSQD also show two transient bleach peaks at 575 (1S) and at 480 nm (1P) (SI Figure 6). However, in presence of both ADPT and APT the exciton peak becomes broader but not with AAT (SI Figure 7). The similar observation was also found in our steady state measurements.

To summarize the above mentioned features we have plotted transient spectrum at 2 ps time delay for both CdSe QD and CdSe/AAT along with their absorption spectra and shown in Figure 5A and 5B respectively. It is interesting to see that in the transient spectra of CdSe/AAT both 1P and 1S excitonic bleach of CdSe QD moves to the red region. Earlier many authors[41, 43] have demonstrated the carrier delocalization using steady state absorption and emission studies. However nobody has established the same through transient absorption spectroscopy and to the best of our knowledge we are confirming it for the first time. We have also plotted the transient spectra of CdSe/ZnS CSQD in presence of the thiols at 2 ps time delay. Interestingly transient bleach due to 1S exciton for CSQD does not change in presence of AAT (Figure 5d) but become broader in presence of both APT (Figure 5e) and ADPT (SI Figure 8) as observed in steady state absorption measurements (Figure 2A). Another interesting observation we made is that in CdSe/thiol system (Figure 5b) the bleach due to 2S excitonic absorption decreases as compared to CdSe QD (Figure 5a). This can be attributed to the extraction of hole from 2S state of QDs (hot state) to the thiols. The similar features were not observed with CSQDs which might be due to the broadening of transient spectra in presence of the thiols.

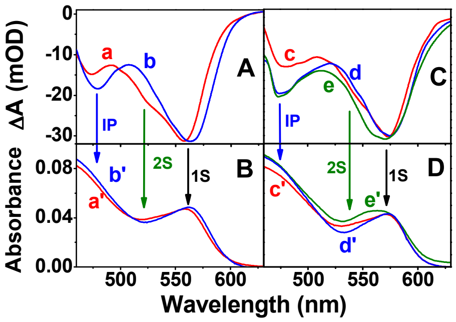


Figure 5: (A) Transient spectra at 2 ps time delay for CdSe QD (a) in absence and (b) in presence of AAT after normalizing the bleach at 558 nm (1S exciton). **(B)** Steady state optical absorption spectra of CdSe QD (a') in absence and (b') in presence of AAT showing different excitonic position. **(C)** Transient spectra at 2 ps time delay for CdSe/ZnS (1.2 ML) CSQD (c) in absence and in presence of (d) AAT and (e) APT after normalizing the bleach at 575 nm (1S exciton). **(D)** Steady state optical absorption spectra of CdSe/ZnS (1.2 ML) CSQD (c') in absence and in presence of (d') AAT and (e') APT showing different excitonic position.

To understand hot hole transfer processes we have monitored the transient bleach recovery kinetics at 2S excitonic position for both CdSe QD and CdSe/ZnS CSQD in absence and in presence the thiols and shown in Figure 6. All the kinetics can be fitted multi-exponentially and are shown in supporting information (SI Table 4). It is interesting to see that the bleach recovery kinetics is faster in presence of the thiols. In our earlier studies[33] we have monitored the transient spectra of CdSe QD in presence of 3-methoxy catechol (3-OCH_3) where a faster bleach recovery at 2S excitonic position was observed as compared to pure CdSe QD. This was attributed to the hot hole transfer reaction from $2S_{3/2}$ state of photo-excited CdSe QD to HOMO of 3-OCH_3. Similarly in the present studies faster bleach recovery kinetics can also be attributed to hot hole transfer from photo-excited CdSe QD and CdSe/ZnS CSQD to the thiols.

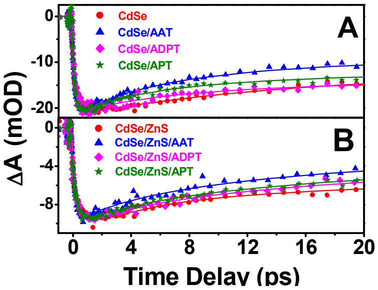


Figure 6: Bleach recovery kinetics of (A) CdSe QD and (B) CdSe/ZnS (1.2 ML) CSQD in absence and in presence of the thiols at 525 nm and 535 nm respectively (2S excitonic position).

As we have mentioned above that the thiols interact with both QDs and CSQDs leading to hole transfer. However the hole transfer rate was too fast to monitor with nanosecond time scale resolution. At the same time signature of hot hole extraction was also observed through ultrafast transient absorption spectroscopy but time scale of hot hole transfer reaction could not be determined due to overlap of different transients in the transient absorption spectra. To determine hole transfer rate (both hot and thermalized) precisely in the above systems femtosecond fluorescence upconversion studies have been carried out by exciting the samples at 400 nm laser light. Figure 7 shows the fluorescence upconversion decay traces of pure CdSe QD at 580 nm and CdSe/ZnS CSQD at 590 nm in absence and in presence of the thiols. In all QD/thiols and CSQD/thiols composite systems, the thiol/QD concentration ratio was kept at approximately 1000:1, where complete quenching of luminescence was observed. It is clearly seen that the emission decay traces of QD/thiols and CSQD/thiols composite systems decay much faster as compared to both pure QDs and CSQD respectively. For CdSe QD the kinetic decay trace at 580 nm can be fitted multi-exponentially with time constants of τ_1 = 3.2 ps (33%), τ_2 = 22.7 ps (45%), and τ_3 = > 1ns (22%), with τ_{avg} = 231.3 ps. However, in presence of ADPT, the kinetic decay trace becomes much faster and can be fitted multi-exponentially with time constants of τ_1 = 0.6 ps (72%), τ_2 = 1.8 ps (20.3%), and τ_3 = 62.6 ps (7.7%), with τ_{avg} = 4.85 ps. It is interesting to see that in presence of all three thiols, the emission decay trace is almost similar with marginal difference in time constants (Table 1) and the average lifetime of CdSe/thiol system is ~50 times faster as compared to that of pure CdSe QD. Now using equation 1 the hole transfer rate constant and hole transfer time has been determined to be $2\text{x}10^{11}$ S^{-1} and ~5 ps respectively.

$$k_{HT} = 1/\tau_{CdSe/thiol} - 1/\tau_{CdSe} = 1/\tau_{HT} \qquad (1)$$

The fluorescence upconversion decay trace of CdSe/ZnS CSQD is also found to decay faster in presence of the thiols suggesting hole transfer reaction from photo-excited CSQD to the thiols. Upconversion decay trace at 590 nm for CdSe/ZnS CSQD can be fitted multi-exponentially with time constants of τ_1 = 26.3 ps (43.2%), τ_2 = 373 ps (21.2%), and τ_3 = > 1ns (35.6%), with τ_{avg} = 385 ps (Table 1). However, in presence of ADPT the kinetic decay trace of CdSe/ZnS CSQD can be fitted multi-exponentially with time constants of τ_1 = 2.5 ps (47%), τ_2 = 31.45 ps (44.2%), and τ_3 = >

100 ps (8.8%), with τ_{avg} = 23.2 ps (Table 1). Using equation 1 the hole transfer rate and hole transfer time is determined to be ~ $4.3X10^{10}$ S^{-1} and ~ 23 ps respectively. With other two thiols also the hole transfer rate is found to be almost similar. This slow hole transfer rate for CdSe/ZnS/thiol composite as compared to CdSe/thiol can be attributed due to the presence of ZnS shell over CdSe core. The presence of a wider band gap material (ZnS) over CdSe core creates an energetic barrier for hole transfer reaction as a result hole transfer rate is found to be slow. It's noteworthy to mention that in both the CdSe QD and CdSe/ZnS CSQD systems hole transfer rate does not change appreciably with the change in molecular structure of the adsorbate.

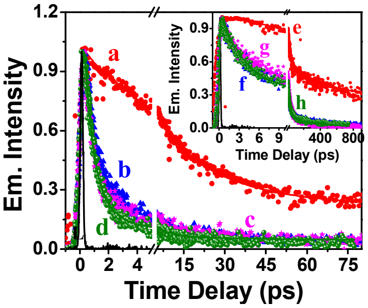


Figure 7: Fluorescence upconversion decay traces of (λ_{ex} - 400 nm) (a) CdSe QD (b) CdSe/AAT (c) CdSe/ADPT (d) CdSe/APT at 580 nm. **Inset** Fluorescence upconversion decay traces of (e) CdSe/ZnS (f) CdSe/ZnS/AAT (g) CdSe/ZnS/ADPT (h) CdSe/ZnS/APT at 590 with 1.2 ML thickness of ZnS. Concentration ratio for both thiols:QD and thiols:CSQD were kept 1000:1.

Table 1: Femtosecond fluorescence upconversion fitting parameters (λ_{ex}-400nm, λ_{em}^{CdSe}-580 nm, $\lambda_{em}^{CdSe/ZnS\ (1.2\ ML)}$ - 590 nm)

	τ_1 (ps)	τ_2 (ps)	τ_3	τ_{avg} (ps)
CdSe	3.2 (33%)	22.7 (45%)	>1 ns (22%)	231.3
CdSe/AAT	0.82 (78.3%)	4.8 (16.3%)	105.6 ps (5.4%)	5.75
CdSe/APT	0.7 (88.2%)	6.6 (7.3%)	100 ps (4.5%)	5.03
CdSe/ADPT	0.6 (72%)	1.8 (20.3%)	62.6 ps (7.7%)	4.85
CdSe/ZnS	26.4 (43.2%)	373 (21.2%)	>1 ns (35.6%)	385
CdSe/ZnS/AAT	2 (50.4%)	20.5 (38.4%)	>100 ps (11.2%)	19.4
CdSe/ZnS/APT	3 (58.7%)	32.3 (33.3%)	>100 ps (8%)	19.3
CdSe/ZnS/ADPT	2.5 (47%)	31.45 (44.2%)	>100 ps (8.8%)	23.2

As we have seen that hole transfer rate is very fast in case of QD/thiol system, this leads us to explore the possibility of hot hole extraction from photo-excited CdSe QD to the thiols. At the same time in our transient absorption studies also we got a signature of hot hole extraction however hot hole extraction time could not be determined. Therefore to explore the hot hole extraction possibility and to determine hot hole transfer rate, fluorescence upconversion studies have been carried out by exciting the samples at 400 nm and monitoring the luminescence at hot exciton position. Luminescence from hot excitonic state is not widely reported due to low quantum yield[48] and ultrafast excitonic decay, however Mondal et.al.[49] and Cho et.al.[50] have reported hot luminescence from QD materials. Recently we have reported[33] hot hole extraction from CdSe QD to 3 methoxy catechols after monitoring 2S luminescence, where the hot hole extraction time is determined to be ~250 fs. Though we had reported hot hole transfer from photo-excited QD to molecular adsorbate, however effect of type I shell on hot hole extraction dynamics was never discussed earlier by us or any other research group.

As we have mentioned above that it is difficult to get hot exciton luminescence from QD materials, in the present investigation also we have not observed any emission band corresponding to 2S excitonic state from both CdSe QD and CdSe/ZnS CSQD. From transient absorption spectra of CdSe QD, 2S excitonic absorption band appears at 525 nm (Figure 5A), so 2S excitonic luminescence band is expected to appear at ~540 nm. Similarly for CdSe/ZnS CSQD 2S excitonic luminescence band is expected to appear at ~550 nm. Figure 8 shows the fluorescence upconversion decay trace of both CdSe QD and CdSe/ZnS CSQD in absence and in presence of different the thiols at 540 nm and 550 nm respectively. It is interesting to see that the emission decay trace at 2S excitonic position decays much faster as compared to that of at 1S excitonic position (Figure 7) for both CdSe QD and CdSe/ZnS CSQD. Emission decay trace of CdSe QD can be fitted multi- exponentially with major component of 600 fs (60%) time constant (Table 2). This faster component can be attributed to relaxation of hole from $2S_{3/2}$ state to $1S_{3/2}$ state or due to radiative and nonradiative recombination of electron in $1S_e$ state and hole in $2S_{3/2}$ state (Scheme 2). In presence of the thiols, this decay becomes much faster as compared to pure QD as shown in Figure 8A. This observation clearly suggests that in presence of thiols additional decay channel is available for photo-generated charge carriers, which is much faster as compared to the relaxation processes of the pure QDs. This faster relaxation channel can be assigned to the hot hole transfer from photo-excited QDs to the thiols (Figure 8A, centre scheme). The emission decay trace of CdSe QD in presence of thiols can be fitted multi-exponentially with major component as 300 fs (>90%) (Table 2). This 300 fs time constant can be attributed to hot hole transfer from photo-excited CdSe QD to the thiols. In our earlier studies in CdSe/catechol systems we have observed that hot hole extraction depends on the electron donating and withdrawing ability of adsorbates[33]. However, interestingly in the present investigation hot hole transfer rate is found to be independent of the molecular structure of the thiols. In our earlier section we have observed exciton delocalization in QD/thiol systems and is also independent of molecular structure of thiol group. Our observation suggest that in the present studies interaction between thiol group and QDs plays a major role and hole delocalization facilitate hot hole extraction and is independent of molecular structure of thiols.

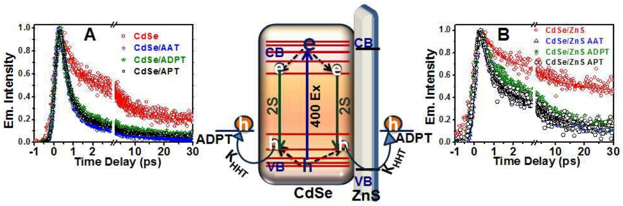


Figure 8: Fluorescence upconversion decay traces of (A) CdSe QD (B) CdSe/ZnS (1.2 ML) CSQD with different thiols at 2S luminescence position (λ_{ex}- 400 nm, λ_{em}- 540 nm for CdSe QD and 550 nm for CdSe/ZnS CSQD)

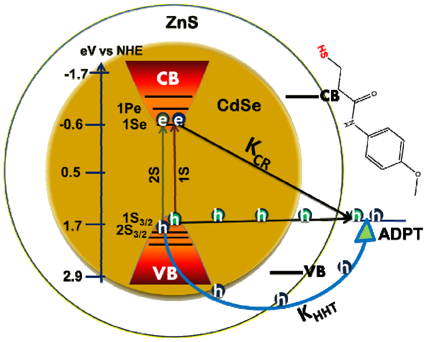
Table 2: Femtosecond fluorescence upconversion fitting parameters (λ_{ex} = 400nm, λ_{em}^{CdSe} = 540 nm, $\lambda_{em}^{CdSe/ZnS\ (1.2\ ML)}$ = 550 nm)

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
CdSe	0.6 (56.1%)	6.6 (28.4%)	>100 ps (15.5%)

CdSe/AAT	0.3 (93.2%)	20.5 (6.8%)	
CdSe/APT	0.3 (92.2%)	20.7 (7%)	
CdSe/ADPT	0.3 (90%)	21.7 (10%)	
CdSe/ZnS	1 (44.3%)	13.1(18.8%)	>1 ns (36.9%)
CdSe/ZnS/AAT	0.5 (62.2%)	6 (26.7%)	>100 ps (11.1%)
CdSe/ZnS/ADPT	0.5 (63%)	6.7 (22.8%)	>100 ps (14.2%)
CdSe/ZnS/APT	0.5 (68.4%)	6.5 (20.5%)	>100 ps (11.1%)

One of the most important aim in the present investigation is to find out whether it is possible to extract hot hole from CdSe QD core even in presence of type 1 shell ZnS over it or not. To find out this fluorescence upconversion decay trace for CSQD was monitored at 2S excitonic position in presence and in absence of the thiols and is shown in Figure 8B. The emission decay trace of CdSe/ZnS CSQD can be fitted multi- exponentially with major component of 1ps (44%) time constant (Table 2). However interestingly in presence of the thiols emission decay traces become faster with the time constant of 500 fs as major component with higher contribution (~65%). This 500 fs time constant can be assigned to the hot hole extraction time from CdSe/ZnS CSQD to the thiols. Due to the presence higher band gap ZnS shell over CdSe core hole transfer is thermodynamically not viable. However we have already mentioned above that leaking of hole is possible from core to thiols. From our experimental observation it is clear that like thermalized hole, hot hole can also leak from CdSe core to the thiol molecules through ZnS shell. This might be due to higher coupling of thiols with QDs which facilitates hot hole extraction. To the best of our knowledge this is the first report on hot hole extraction reaction from type I CSQD by any molecular adsorbate.

As we have observed that both thermalized and hot hole extraction from CdSe QD is possible in presence of 1.2 ML of ZnS shell. This lead us to find out till what thickness of ZnS shell the hole extraction is possible from CdSe core. For this we have synthesized new set of CSQD samples with two different shell thickness, 2.5ML and 4.5ML. We have carried out fluorescence upconversion studies to monitor both hot and thermalized hole transfer processes and is shown in SI Figure 9. The result shows that both hot and thermalized hole extraction is still possible with 2.5 ML of ZnS shell but not with 4.5 ML. This can be due to the high potential energy barrier provided by the thicker shell for hole and hot hole extraction. Our study shows that with 2.5 ML of ZnS shell over CdSe core also, both hot and thermalized hole extraction is possible.



Scheme 2: Energy level diagram of CdSe/ZnS core-shell QD showing different discrete states of both conduction band and valence band. HOMO level of ADPT is also shown. The scheme demonstrate both thermalized and hot hole extraction by ADPT from CdSe QD.

Finally to determine the charge recombination dynamics between electrons in the QDs and hole in the thiols (Scheme 2), bleach recovery kinetics was monitored at 1S excitonic position (560 nm for CdSe QD and at 570 nm for CdSe/ZnS CSQD) for CdSe/Thiol and CdSe/ZnS/Thiol systems using ultrafast transient absorption spectroscopy and are shown in Figure 9. The bleach recovery kinetics for pure CdSe QD and CdSe/ZnS CSQD can be fitted multi-exponentially with time constants of $\tau_1 = 10$ ps (39%), $\tau_2 = 50$ ps (6%), τ_3 =>400 ps (55%) and $\tau_1 = 15$ ps (33.3%), $\tau_2 = 60$ ps (10%), τ_3 =>400 ps (56.7%) respectively (SI Table 5). These dynamics can be attributed to charge recombination between in the conduction band and hole in the valence band of the QDs. Bleach recovery kinetics for both QD and CSQD in presence of thiols was also monitored and is shown in Figure 9. It is interesting to see that although no appreciable change was observed on both hot and thermalized hole transfer dynamics, bleach recovery kinetics in QD/thiols and CSQD/thiols are different for different thiol derivatives depending on the molecular structure of the thiol derivatives (SI Table 4). It is clear from Figure 8 and SI Table 4 that charge recombination dynamics is relatively faster in QD/AAT as compared to that in QD/ADPT for both QD and CSQD. This might be due to the difference in molecular size of AAT and ADPT (Chart 1). As we have mentioned above that thiols interact with QDs through S atom so after the hole transfer, initially the hole will be localized on the S atom of thiols and then it will be delocalized in the benzene ring. Since ADPT have larger molecular structure as compared to AAT, the delocalization of hole should be more in ADPT as compared to that in AAT. This implies that the charge recombination rate will be slower in QD/ADPT and CSQD/ADPT system as compared to that in QD/AAT and CSQD/AAT as we have also observed.

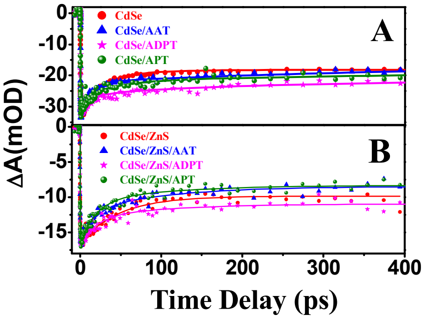


Figure 9: Bleach recovery kinetics of A) CdSe QD and B) CdSe/ZnS (1.2 ML) CSQD in absence and in presence of the thiols. Bleach kinetics was monitored at 560 nm and at 570 nm for CdSe QD and for CdSe/ZnS CSQD respectively.

Conclusion:

To conclude we have demonstrated carrier delocalization, hole transfer and charge recombination dynamics in CdSe QD and CdSe/ZnS (1.2 ML) CSQD in presence of three newly synthesized thiols using femtosecond transient absorption and fluorescence upconversion techniques. Steady state absorption and ultrafast transient absorption studies demonstrate exciton delocalization from CdSe QD to thiols. Similar features were not observed in presence of ZnS layer over CdSe core however a broadening in excitonic absorption was observed for ADPT and APT but not for AAT. Redox energy level of QDs and thiols suggest hole transfer process from photo-excited CdSe QD to the thiols is thermodynamically viable and was confirmed by steady state and time resolved emission studies. Hole transfer from CSQD to the thiols was also observed even in presence of wider band gap ZnS shell over CdSe core which might be due to leaking of hole from core to the thiols. Hole transfer time from photo-excited CdSe QD and CdSe/ZnS CSQD to thiols was determined using fluorescence upconversion technique and was found to be ~5 ps and ~20 ps respectively. Interestingly hot hole transfer was also observed from both CdSe QD and CdSe/ZnS CSQD with a time scale of ~300 fs and ~500 fs respectively. We have carried out experiment with different thickness of ZnS shell where we have observed that both hot and thermalized hole extraction is possible till 2.5 ML of ZnS shell but no hole transfer is observed with 4.5 ML of ZnS shell. To the best of our knowledge for the first time we are reporting hot hole extraction from QD material in presence of a wider band gap material. Our result suggests that extraction of hot hole from photo-excited QDs can minimize the unnecessary heat loss and might reduce the probability of auger recombination which eventually improves carrier multiplication. Hot hole extraction even in presence of type 1 shell suggests that this material can be a probable candidate, both in terms of stability and charge carrier extraction and finally higher efficient quantum dot solar cell can be realized.

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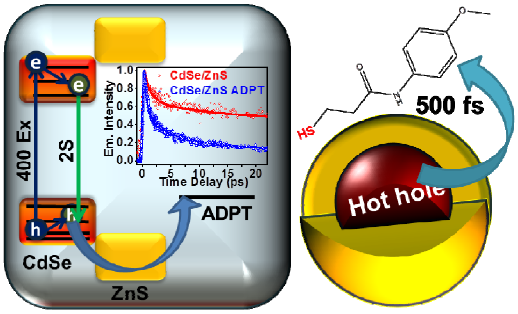

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