Insight into morphology dependent charge carrier dynamics in ZnSe-CdS nanoheterostructures

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Supporting information

Experimental Section:

Materials required: Cadmium oxide (CdO, 99.5 % trace metal basis), zinc stearate (90 %), elemental selenium (Se, 99.99 % metal basis), oleylamine (technical grade, 70 %), octadecene (ODE, 90 %), trioctylphosphine (TOP, 90 %), trioctylphosphine oxide (TOPO, 90 %), elemental sulphur (99.98 % trace metal basis), oleic acid (OA, 90 %), potassium hydroxide pellets, 3-mercaptopropionic acid (MPA, ≥ 99 %), sodium sulphite (Na2SO3), and 1-bromotetradecane (97 %) were purchased from Sigma-Aldrich. Hexadecylamine (HDA, ≥ 95 %, Merck), sodium sulphide (CDH), and triethylphosphite (spectrochem) were used without further purification. Methanol (Fisher Scientific, 99.85 %) and hexane (Merck, 99.5 %) were
always dried and distilled prior to use. Octadecylphosphonic acid (ODPA) and hexylphosphonic acid (HPA) were purchased from PCI synthesis.

**Synthesis of ZnSe NCs:** ZnSe NCs were synthesized by following the synthetic procedure of Reiss et al.\textsuperscript{1} with some modifications. In this procedure, a mixture of 1 mmol zinc stearate (0.632 g) and 10 mL ODE were vacuum degassed at 120 °C for 1 h. After 1 h, the reaction mixture was heated to 300 °C in an argon atmosphere with continuous stirring and 1 mmol Se in 2.5 mL TOP (0.4 M) was injected at 300 °C and the growth process was monitored by recording UV-Vis absorption spectrum. The reaction was quenched after 15 min by lowering down the reaction temperature. ZnSe NCs were purified thrice by precipitation with an excess of methanol and then redissolved in hexane. The purified ZnSe NCs were dispersed in distilled hexane for further studies.

**Synthesis of ZnSe-CdS nanospheres (NSs):** The stock solution of 0.4 M Cd/OA/ODE and 0.4 M S/ODE were prepared for the growth of the CdS shell on the above-synthesized ZnSe seed by adopting the procedures from the previous report.\textsuperscript{2} ZnSe/CdS DISs NCs were synthesized by following the previous report\textsuperscript{3} with slight modification. In this synthetic procedure, 6 mmol HDA (1.5 g) and 6 mL ODE were loaded in a 25 ml round bottom (RB) flask and heated to 120 °C in an argon atmosphere. The reaction mixture was vacuum degassed for 1 h at 120 °C. Then 1.5 \times 10^{-7} mol of ZnSe NCs in 1 mL hexane (concentration determined by AAS) was added at 120 °C in an argon atmosphere and the temperature of the reaction mixture was increased to 240 °C. At 240 °C, 400 µL of the combined mixture of Cd and S precursor solutions (0.4 M each) was injected very slowly with a speed of 1 mL/h into the above solution for the continuous growth of CdS shell over ZnSe seed. After the addition of precursor solutions, the reaction mixture was annealed for 30 – 40 min to ensure complete coverage of CdS shell as well as passivation of core-shell NCs with ligands which in turn
increased the photoluminescence efficiency. The reaction was quenched and purified thrice by precipitation with an excess of ethanol and dispersed in distilled hexane for further use.

**Synthesis of ZnSe-CdS nanorods (NRs):** ZnSe-CdS NRs were synthesized using seeded growth of ZnSe NCs synthesized above. In a typical procedure, a mixture of 0.47 mmol CdO (60 mg), 0.86 mmol TDPA (288 mg), 0.48 mmol HPA (80 mg), and 7.7 mmol TOPO (3 g) were loaded in a 25 mL RB flask and vacuum degassed for 1 h at 150 °C. Then, the temperature of the reaction mixture was increased to 350 °C in an argon atmosphere with continuous stirring. Once the solution becomes clear, 1.8 mL TOP was injected into the reaction mixture at 350 °C and it was allowed to recover the same temperature again. Afterward, 3.75 mmol S in 1.8 mL TOP which contained 1.5 x 10^{-8} mol (concentration determined by AAS) ZnSe NCs in TOP were injected at 350 °C and the ZnSe-CdS nanorods were allowed to grow at 330 °C for 5 min after injection. The reaction mixture was quenched by removing the heating mantle and purified thrice by precipitation with an excess of ethanol. These purified ZnSe-CdS NRs were dispersed in distilled hexane.

**Synthesis of ZnSe-CdS nanoplates (NPs):** ZnSe-CdS NPs were synthesized using colloidal seeded growth of ZnSe NCs. 0.47 mmol CdO (60 mg), 0.86 mmol TDPA (288 mg), 0.48 mmol HPA (80 mg) and 7.7 mmol TOPO (3 g) were loaded in 25 mL RB flask and vacuum degassed for 1 h at 150 °C. Then, the temperature of the reaction mixture was increased to 350 °C in an argon atmosphere with continuous stirring. Once the solution becomes clear, 2.4 mL oleylamine was injected into it at 350 °C and it was allowed to recover the same temperature again. Afterward, 3.75 mmol S in 2.4 mL oleylamine which contained 1.5 x 10^{-8} mol ZnSe NCs in 1 ml oleylamine were injected at 350 °C and the reaction was continued at 330 °C for 5 min. The reaction mixture was quenched by removing the heating mantle and purified by precipitation with an excess of ethanol. Finally, the purified ZnSe-CdS NPs were dispersed in distilled hexane.
Synthesis of MPA-capped NCs: The hydrophobic ligands such as oleic acid, hexadecylamine, TOP, TOPO, TDPA, and oleylamine on ZnSe and ZnSe-CdS NHSs were exchanged with mercaptopropionic acid (MPA) using the reported method\textsuperscript{6,7} with some modifications. Initially, a mixture of 250 µL MPA in 10 mL methanol was prepared and pH was maintained to 11 using 0.1 M aqueous KOH solution. Then, 2 mL of NCs solution (10 mg/mL) in hexane was mixed with 2 mL of MPA solution in methanol (25 µL/mL). This solution was stirred till it leads to a complete phase transfer of NCs from hexane to methanolic phase. The methanolic phase was separated via a separating funnel and precipitated with acetone. These MPA-capped ZnSe and ZnSe-CdS NHSs were dried in a vacuum oven for their use in photocatalytic hydrogen evolution experiments.

Photocatalytic hydrogen production: The photocatalytic hydrogen production experiments were carried out in a 25 mL round bottom flask, which was connected to the specific outlet for gas collection. In a typical photocatalytic hydrogen production setup, 10 mg photocatalyst was suspended in 20 mL mixed aqueous solution of Na\textsubscript{2}S (0.1 M) and Na\textsubscript{2}SO\textsubscript{3} (0.1 M) in distilled water. It has been observed that pure photocatalyst cannot split water into oxygen and hydrogen owing to fast and undesirable electron-hole recombination. As a result, the sacrificial agent, hole scavenger, is employed to prevent electron-hole recombination. The photogenerated holes irreversibly oxidize the reducing agent instead of water, which in turn increases the hydrogen evolution during photocatalysis by making the photocatalyst electron-rich. It was discovered that Na\textsubscript{2}S solution can yield equimolar concentrations of hydrogen and disulfide ions and that elemental sulfur can be extracted from the disulfide solution. However, elemental sulfur did not aid the creation of hydrogen for the photocatalytic system owing to catalyst deactivation and hence, Na\textsubscript{2}SO\textsubscript{3} solution is added along with Na\textsubscript{2}S solution. It has been hypothesized that sulfite ions (SO\textsubscript{3}\textsuperscript{2-}) had the effect of suppressing S\textsubscript{2}\textsuperscript{2-} creation from Na\textsubscript{2}S, based on the results of irradiating CdS suspensions in electrolyte solutions as stated in the literature.\textsuperscript{8,9} A metal
halide lamp of 150 W was used as a source of visible light which was positioned 15 cm away from the reaction mixture. Before irradiation, the system was purged with inert gas for 30 – 40 min to remove dissolved oxygen. Then, the samples were irradiated using visible light with continuous stirring to keep the photocatalyst in suspension during the experiments, and evolved H₂ content was analyzed volumetrically and confirmed by gas chromatography. To estimate the number of moles of NHSs in the solution, the number of ZnSe and CdS formula units per ZnSe-CdS NHS is calculated using their average size from TEM. The mass of the catalyst added is then divided by the molar mass of one NHS to estimate the moles of NHSs in the solution. Based on these values, the amount of H₂ generation for equal amounts of photocatalysts is calculated and shown in Figure 6a.

Characterization: UV-Vis absorption spectra were acquired on Perkin-Elmer UV-Vis-NIR Lambda 1050 spectrophotometer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer with Ni-filtered Cu-Kα radiation with a step size of 0.02 °. TEM images were recorded on an FEI Tecnai G2 F20 equipped with a field emission gun source at an accelerating voltage of 200 kV. Samples were prepared on 200-mesh carbon-coated Cu grids by dropping NCs solutions dissolved in hexane and allowing the solvent to evaporate. The Energy-dispersive X-Ray spectroscopy (EDX) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were performed with a JEOL JEM-2100F, operated at 200 kV and equipped with a field emission gun. Analysis and evaluation of the data were done with the software Oxford Instruments INCA 300 and the average images (Figure 3, b-e and h-k) of HAADF-STEM images and STEM-EDXS images were created with the software ImageJ. The ZnSe-CdS NRs and ZnSe-CdS NPs solutions were precipitated and centrifuged (3000 G, 10 min). The samples were diluted in a mixture of hexane/chloroform 2:1, precipitated with an excess of ethanol, and centrifuged.
samples were dispersed in chloroform and washed in different steps with a small amount of methanol, acetone, and isopropanol. 10 $\mu$L of each diluted sample were dropped cast on a carbon-covered copper grid (200 mesh). At last, the TEM grids were cleaned 10 - 15 s by Plasma cleaning. The mapping frames are 120 with a total mapping time of 60 min. The produced hydrogen was analyzed using a Nucon gas chromatograph.

**Transient absorption spectroscopy:** Ti: sapphire laser source (800 nm, <100 fs, 1.2 mJ per pulse, and 1 kHz) provided by CDP, Moscow, and Excipro pump-probe spectrometer have been used for femtosecond transient absorption measurements. Briefly, 800 nm seed pulse with 40 fs pulse duration and 4 nJ energy per pulse is generated by a self-mode-locked Ti-sapphire laser oscillator (Tissa 50, CDP, Moscow, Russia). This low energy pulse is amplified to 1.2 mJ with a 1 kHz repetition rate through a multi-pass amplification system pumped by 20 W DPSS laser (Jade-II, Thales Laser, and France). For a second harmonic generation, i.e. to generate the 400 nm pump pulse the 800 nm laser focussed on the $\beta$-barium borate (BBO) window. Visible probe pulse from 450 to 850 nm is created by focussing the 800 nm light onto 3 nm sapphire window crystal. The 0.28 $\mu$J cm$^{-2}$ excitation density pump with $\sim$350 $\mu$m beam diameter is used for TA measurement. The 1 mm rotating sample holder was used to minimize the sample degradation by the exposed pump beam. To prevent multi-exciton generation the used pump fluency was kept very low for maintaining the $N_{eh} < 1$, where $N_{eh}$ is the average number of e–h pairs excited per NC. The Lab-View program was used for data analysis and fitting.
Figure S1: TEM images of ZnSe-CdS nanoplates (NPs).
Figure S2: Very early time transient absorption spectra of ZnSe-CdS nanospheres (NSs), nanoplates (NPs), and nanorods (NRs) for bleach growth.
**Figure S3:** Comparison of TA spectrum of CdS core with ZnSe/CdS nanospheres (NSs), nanoplates (NPs), and nanorods (NRs) at different time scales.

We have performed the same transient absorption measurements on CdS NCs with the nearly same size, and compared with the spectrum of different morphology in the same timescale in Figure S3. We can see the spectrum of heterostructure is quite different from the CdS core one, especially in the red part of the bleach which is quite broader in the case of heterostructure relative to CdS core, confirming the charge-separated state formation in this heterostructure.

**References**


