Electronic Supplementary Information

Efficient Visible Light-Driven H_2 Production in Water by CdS/CdSe Core/Shell Nanocrystals and Ordinary Nickel-Sulfur Complex

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Materials. Cadmium oxide (CdO, 99.998%), Sulfur (99.5%, powder, 100 mesh), Trioctylphosphin (TOP, tech. 90%), 1-Octadecene (ODE, tech. 90%), Trifluoroacetic acid (TFA, 99%), $NiCl_2 \cdot 6H_2O$ (99.9998%) and Oleic acid (OA, tech. 90%) were purchased from Alfa Aesar. Selenium (99.5%, 100 mesh), Octadecylamine (ODA, 90%), Potassium hydroxide (KOH, ≥85%), and 3-Mercaptopropionic acid (3-MPA, ≥99%) were purchased from Aldrich. L-Ascorbic acid (AA, reagent grade, 99%) was obtained from Vetec. Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, ≥98%), Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, ≥98%), Acetonitrile (99.5%) and Formamide (≥99.0%) were purchased from Xilong Chemicals. Hydrochloric acid (HCl, 36~38%), Potassium nitrate (KNO_3, ≥99.0%) and Sodium hydroxide (NaOH, ≥96%) were purchased from Beijing Chemicals. All chemicals were used as received without any further purification.

Synthesis of CdSe and CdS Core Nanocrystals (NCs). The synthesis was performed according to the reported procedure with a slight modification.[1] For CdSe core NCs, the mixture of 0.2 mmol of CdO, 0.6 mmol of OA, and 4 mL of ODE in a 25 mL three-neck flask was heated to obtain a colorless clear solution. After that, the solution was cooled down to 160 ºC, and then, 0.7 g of ODA was added into the flask. Under nitrogen flow, the system was heated to 240 ºC. At this temperature, 1 mL of selenium ODE solution composed of 0.1 mmol of selenium and 0.11 mmol of TOP were quickly injected and maintained at 240 ºC for 10 min to obtain the CdSe NCs of about 3.8 nm with the absorption peak at ~ 584 nm.[2] For CdS core NCs, the mixture of 0.1 mmol of CdO, 1.8 mmol of OA, and 4.4 mL of ODE in a 25 mL three-neck flask was heated to obtain a colorless clear solution. Under nitrogen flow, the system was heated to 260 ºC and then 1 mL of sulfur ODE solution containing 0.05 mmol sulfur was injected and the reaction solution was kept at 230 ºC for 7 min to obtain the 3.9 nm CdS NCs with the absorption peak at ~ 414 nm.[2] For both CdSe and CdS core NCs stock solutions, they were allowed to cool down to room temperature and then subjected to the same purification procedure[2] to remove the side products and unreacted precursors. The purified CdSe and CdS NCs were finally dispersed in hexane. The concentration of CdSe and CdS core NCs was determined by Beer's law using the reported extinction coefficients, respectively.[2]

Synthesis of CdSe/CdS and CdS/CdSe Core/Shell NCs. The synthesis was performed using the typical successive ion layer adsorption and reaction, known as SILAR, method. For CdSe/CdS core/shell NCs, the purified CdSe core NCs (3.8 nm, 2.88×10^{-7} mol of particles) in hexane was added into a 25 mL of three-neck flask containing 1.5 g ODA and 5.0 g ODE. The system was then pumped at room temperature using a mechanical pump to remove hexane and at 100 ºC for further 10 min to remove the residual air. Next, the system was switched to the nitrogen flow and heated to 240 ºC for the injections. The first injection was 0.48 mL of the Cd injection solution (0.2 M), and the following amounts of the subsequent injection solutions were calculated using the reported method.[23] After the stock solution was cooled down to room temperature, the final product was diluted by hexane followed by adding acetone to precipitate the NCs. The precipitated NCs was further dispersed in chloroform and precipitated again with acetone to remove excess amines and unreacted reagents. Finally, the purified CdSe/CdS core/shell NCs were dispersed into chloroform for further use. For CdS/CdSe core/shell NCs, the mole of purified CdS core particles used is 7.47×10^{-8} mol, the first injection was 0.33 mL of the Cd injection solution (0.2 M), and the injection and growth temperature was 230 and 260 ºC, respectively. The synthesis and post treatment procedure were the same as that of CdSe/CdS core/shell NCs. The cadmium injection solution (0.2 M) was prepared by dissolving 1.62 g of CdO in 14 mL of OA and 11 mL of ODE at 230 ºC. The sulfur injection solution (0.2 M) was prepared by dissolving sulfur in ODE at 160 ºC. The selenium injection solution (0.2 M) was prepared by dissolving selenium in ODE at 260 ºC.

Organic Ligand Exchange of NCs with S^{2-} and OH^- Ions. The ligand exchange process was performed according to the previous reported procedure with a slight modification.[3] For ligand exchange using S^{2-} ions, 3.74 nmol of purified CdS/CdSe (or CdSe/CdS) core/shell NCs in toluene was mixed with 1 mL of Na_2S solution (5 mg mL^{-1} in formamide, FA). The mixed solution was stirred at ambient temperature for ~ 10 min to complete the transfer of the NCs from toluene to FA phase. The FA phase containing NCs was then separated and 2 mL of acetonitrile was added to precipitate the NCs. The precipitated NCs was dispersed in water and precipitated again by adding 0.4 mL of 6 M NaOH solution. The precipitation was then washed with deionized water for three times to remove unreacted reagents including unbonded S^{2-}. For ligand exchange using OH^- ions, the fresh stock solution of KOH was firstly prepared by dissolving 112 mg of KOH into 0.33 mL of FA, then 3.74 nmol of CdS/CdSe core/shell NCs in toluene was added into 1 mL of FA followed by adding 20 μL of KOH stock solution, and the mixed solution was then stirred at ambient temperature for ~ 15 min to complete the transfer process. The post treatment was the same as that of NCs capped with S^{2-} ions.

Characterizations. TEM, high-resolution TEM (HRTEM), and elemental mapping measurements were carried out by using a FEI TECNAI F20 EM with an accelerating voltage of 200 kV equipped with an energy dispersive spectrometer. TEM samples were prepared by placing a drop of the QD solution on a carbon-coated copper grid and drying under ambient conditions. The UV-Vis extinction spectra were obtained on a Cary 500 UV-Vis-NIR spectrometer. The fluorescence emission spectra were performed on a Fluoromax-4 Spectrofluorometer (HORIBA Jobin YVON, INc NJ, USA) at room temperature. XPS measurements were recorded on a Thermo VG Scientific ESCALAB 250 spectrometer using monochromatized Al Kα excitation. X-ray diffraction (XRD) patterns were recorded by a D8 ADVANCE (BRUKER) diffractometer with Cu Kα radiation (λ=1.54056 Å) in the range of 15-60° (2θ). Infrared spectra were carried out on a VERTEX 70 Fourier transform infrared (FTIR) spectrometer (Bruker). Inductively coupled plasma-atomic emission spectrometer and mass spectrometer (ICP-AES/MS) (icap 6000 series, icp spectrometer, Thermo Scientific) was used to determine the composition of CdS/CdSe core/shell NCs capped with S^{2-} after 20 h illumination of visible light. Cyclic voltammograms were performed on the three-electrode systems by using a CHI 660E electrochemical workstation. Ag/AgCl (3M KCl) and Pt wire are used as the reference and counter electrode, respectively. A glassy carbon (GC) electrode is used as the working electrode.

Before using, it was polished using 1.0 and 0.05 μm alumina slurries sequentially and followed by rinse and sonication in DI-water for 5 min. Potentials finally were converted to NHE. ESI-MS measurement was performed using a Waters Quattro Premier XE mass spectrometer.

Hydrogen Evolution Studies. The experiments were carried out on an airtight inner gas circulation system connected with a gas chromatography (Shimadzu GC-2014c, with a 5 A molecular sieve column and a TCD detector) that could realize the online quantitative detection of H_2. The experimental solution containing semiconductor NCs, Ni-S* and AA was fixed to 50 mL and kept in the dark before use. The pH of the solution was adjusted by adding HCl or NaOH solution and measured using a pH meter (PB-10, Sartorius). The temperature of the solution was maintained at 8°C during the experiments. The solution was illuminated from the top of the reaction cell by using a 300 W Xeon lamp Xeon lamp equipped with the filter of λ > 420 nm or single-pass filters of λ= 420, 435, 450, 475, 500, 520 and 550 nm.

Calculation of the Amount of Bonded-S^{2-} Ions on the Surface of CdS/CdSe Core/shell NCs. Before calculation, several assumptions have to be made: 1. CdS/CdSe core/shell NCs is a standard spherical particle; 2. S^{2-} ions are homogeneously dispersed on the surface of NCs; 3. S^{2-} ion is in a standard sphere either. Based on these assumptions, the number of S^{2-} ions on a single CdS/CdSe nanocrystal ($n_{S^{2-}}$) is calculated by dividing the surface area of CdS/CdSe particle ($S_{CdS/CdSe}$) by the cross sectional area of S^{2-} ion ($S'_{S^{2-}}$).

$$S_{CdS/CdSe} = 4 * \pi * (r_{CdS/CdSe})^2 = 4 * 3.14 * (2.75 \times 10^{-9} m)^2 \cong 9.5 \times 10^{-17} m^2$$

$$S'_{S^{2-}} = \pi * (r_{S^{2-}})^2 = 3.14 * (1.84 \times 10^{-10} m)^2 \cong 1.06 \times 10^{-19} m^2$$

Where $r_{CdS/CdSe} = 2.75\ nm$ is the averaged radius of CdS/CdSe core/shell NCs; whereas $r_{S^{2-}} = 0.184\ nm$ is the radius of S^{2-} ion.[4]

Thus, $n_{S^{2-}} = S_{CdS/CdSe}/S'_{S^{2-}} = 9.5 \times 10^{-17} m^2/1.06 \times 10^{-19} m^2 = 8.96 \times 10^2$, since the mole amount of CdS/CdSe core/shell NCs for hydrogen evolution experiment is 3.74 nmol, the total mole amount of S^{2-} ions is ~ 3.4 μmol, equal to ~ 68 μM of S^{2-} ions per batch reaction solution.

Calculation of Quantum Yield (Φ) of H_2 Generation of the System under the Illumination at 520 nm. The calculation was performed according to the reported method.[5,6] The light absorbed by the NCs was calculated by the light power difference between the solution without and with CdS/CdSe core/shell NCs (0.075 μM), while keeping other conditions the same (100 μM Ni^{2+}, 100 μM 3-MPA and 0.8 M AA at pH 5.2). The power of the light was measured by the FZ-A power meter (Photoelectric Instrument Factory of Beijing Normal University). The quantum yield (Φ) is calculated by the following equation:

$$p = \frac{c \times h \times n}{\lambda \times t} \quad (1)$$

$$q_p = \frac{n}{t} \quad (2)$$

$$\emptyset = \frac{2 \times k}{q_p} \times 100\% \quad (3)$$

Where c is the speed of the light (m/s); h is the Planck's constant (J·s); n is the number of photons; λ is 520 nm; t is the time (s); q_p is the photo-flux; k is the average generation rate of hydrogen (mol/s) calculated from the amount of hydrogen generated from 5h of light illumination.

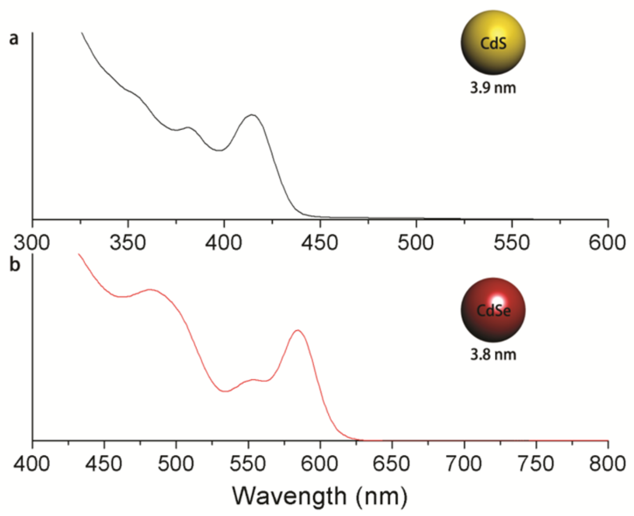

Figure S1. **a**, and **b**, UV-Vis spectrum of the CdS and CdSe core NCs, respectively. The core size of CdS and CdSe was determined by the first exciton absorption peak as indicated in **a** and **b**.[2]

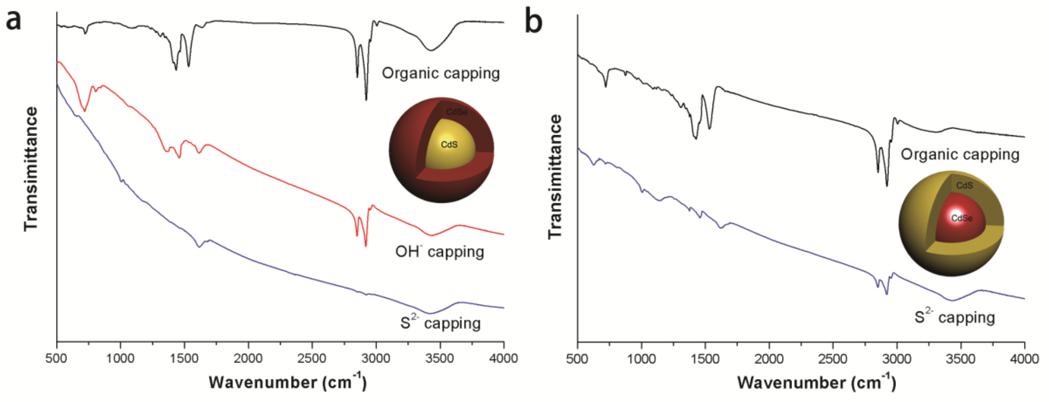

Figure S2. **a**, FTIR spectra of the CdS/CdSe core/shell NCs before and after ligand exchange using OH^- and S^{2-} ions. It is seen that for the S^{2-} capping NCs, the bands at 2851 and 2922 cm^{-1} corresponding to C-H stretching in the organic ligand have almost disappeared, demonstrating the high efficiency of ligand exchange using S^{2-} ions; while for the OH^- capping NCs, the bands at 2851 and 2922 cm^{-1} are still existed, indicating that the organic ligands are not completely removed. **b**, FTIR spectra of the CdSe/CdS core/shell NCs before and after ligand exchange using S^{2-} ions. The results indicate that there are still some organic ligands left after ligand exchange.

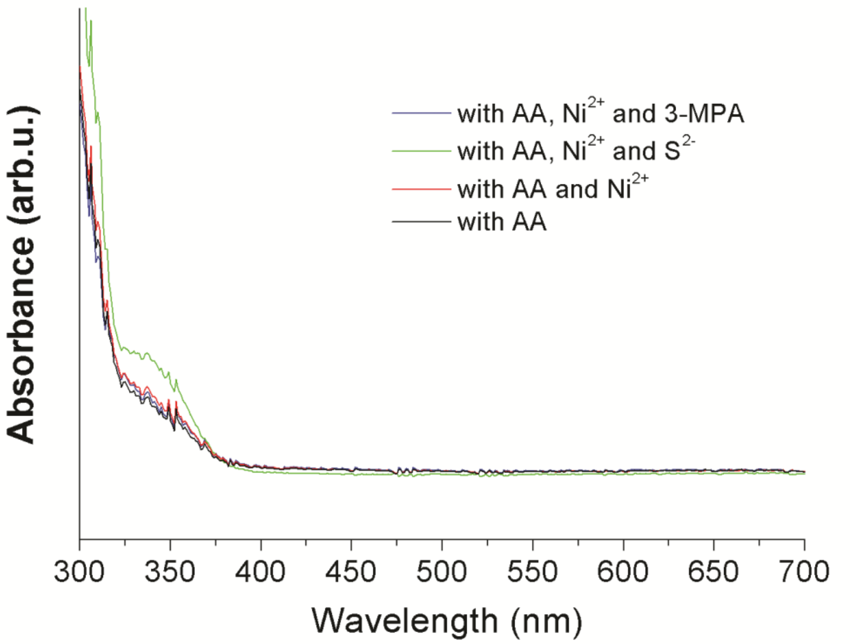

Figure S3. UV-Vis spectra of the QDs-free solution with pH at 5.2 under different conditions, the concentration of AA, Ni^{2+}, S^{2-} and 3-MPA are 0.8 M, 100 μM, 100 μM, and 100 μM, respectively.

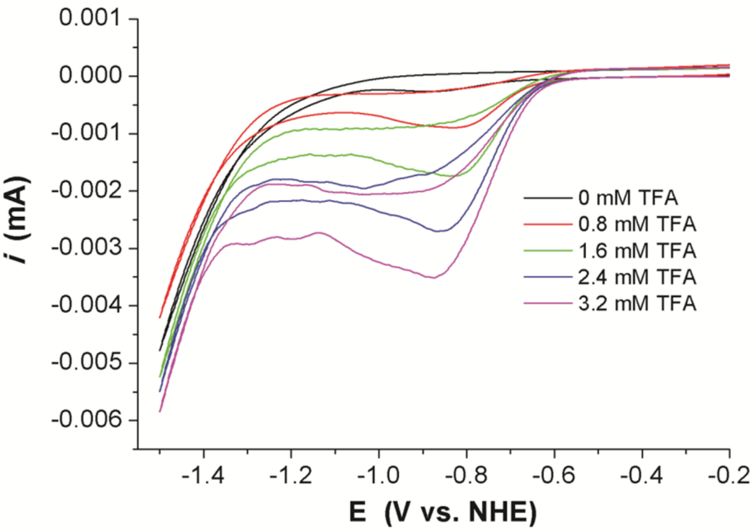

Figure S4. Cyclic voltammograms of the aqueous solution containing Ni^{2+} (100 μM), 3-MPA (200 μM), and KNO_3 (0.1 M) with the addition of different concentration of TFA. The scan rate is 100 mV/s.

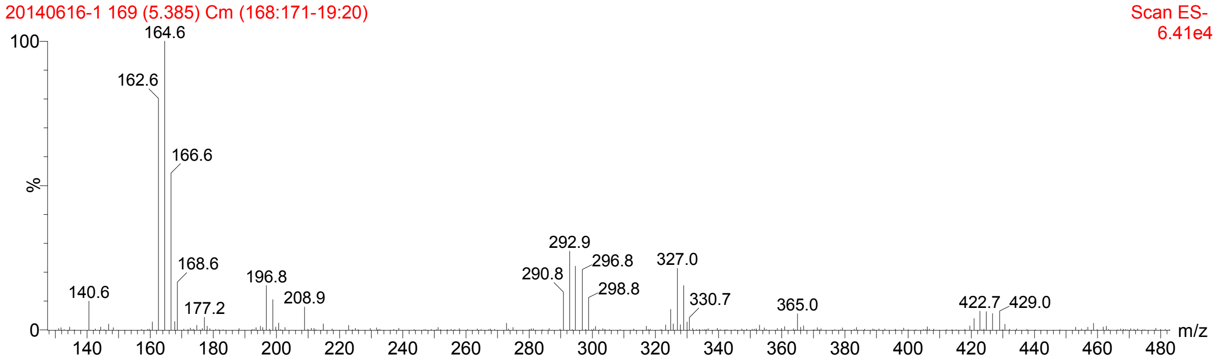

Figure S5. ESI mass spectrum of the aqueous solution containing Ni^{2+} ions and 3-MPA with the molar ratio of 1:2.

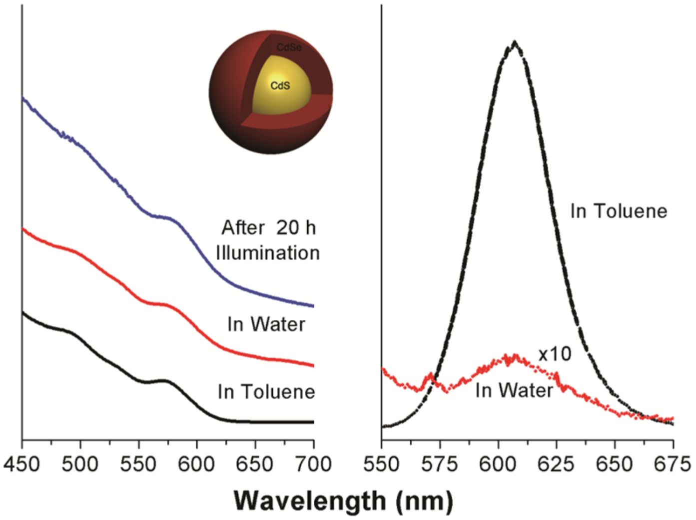

Figure S6. Left panel, UV-Vis spectra of the CdS/CdSe core/shell NCs in toluene with organic ligands, in water capping with S^{2-} ions, and in water after 20 h illumination of visible light ($\lambda > 420$ nm), respectively. The results indicate that after the ligand exchange using S^{2-} ions and further 20 h successive illumination for hydrogen evolution experiment, no obvious change of UV-Vis spectra has been observed demonstrating the good stability of the CdS/CdSe core/shell NCs during the experiment. **Right panel**, PL spectra of the CdS/CdSe core/shell NCs in toluene with organic ligands and in water capping with S^{2-} ions, respectively. The results show that after the ligand exchange of organic ligands using S^{2-}, the PL intensity is greatly decreased, which is assumed to be caused by the non-radiative recombination traps introduced by S^{2-} ligands.[7]

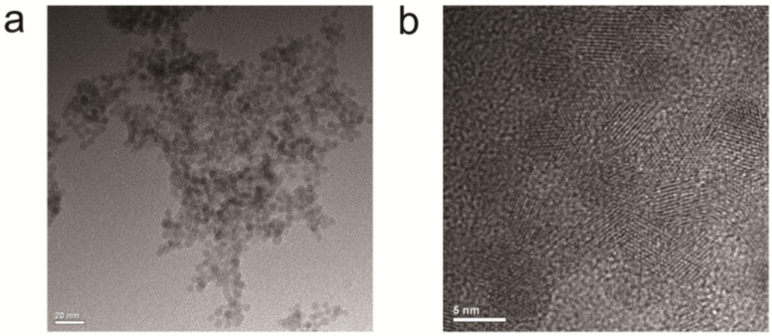

Figure S7. a, TEM and **b**, HRTEM images of the CdS/CdSe core/shell NCs after 20 h successive illumination for hydrogen evolution experiment. The result indicates that no obvious change of both size and the crystallinity of the NCs are observed, demonstrating good stability of the NCs, which is consistent with the UV-Vis results.

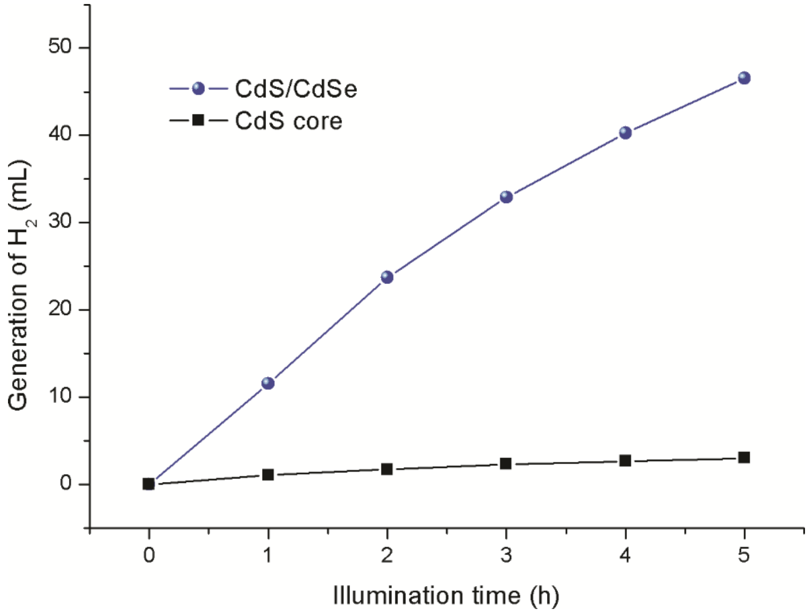

Figure S8. The generation of H_2 of CdS core (black square) and CdS/CdSe core/shell (blue ball) QDs-based HPA system under the illumination of light (> 420 nm) with the conditions of 0.075 μM QDs, 100 μM Ni^{2+}, 100 μM 3-MPA and 0.8 M AA at pH 5.2 versus illumination time.

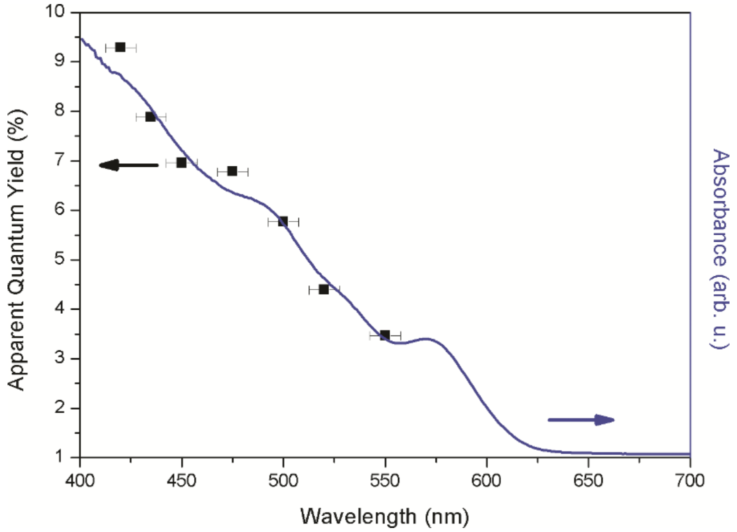

Figure S9. The wavelength dependence of incident light on the apparent quantum yield of the S^{2-} ion-capped CdS/CdSe core/shell QDs-based HPA system; and the UV-Vis spectrum of the CdS/CdSe core/shell QDs in toluene.

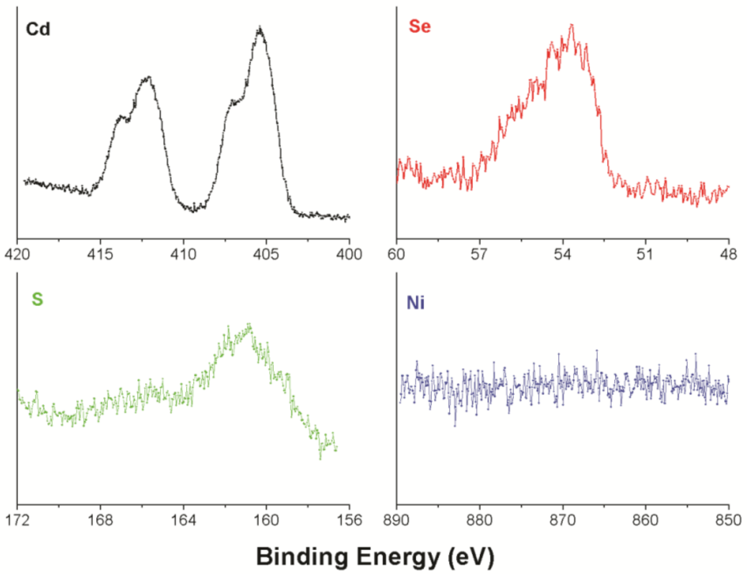

Figure S10. Cd 3d, Se 3d, S 2p and Ni 2p XPS spectra of the CdS/CdSe core/shell NCs, respectively, after the H_2 evolution experiment with the illumination at 520 nm.

ICP data

Elements	Atomic ratio (%)
Cd	**48.67**
Se	**30.09**
S	**21.24**
Ni	**N/A**

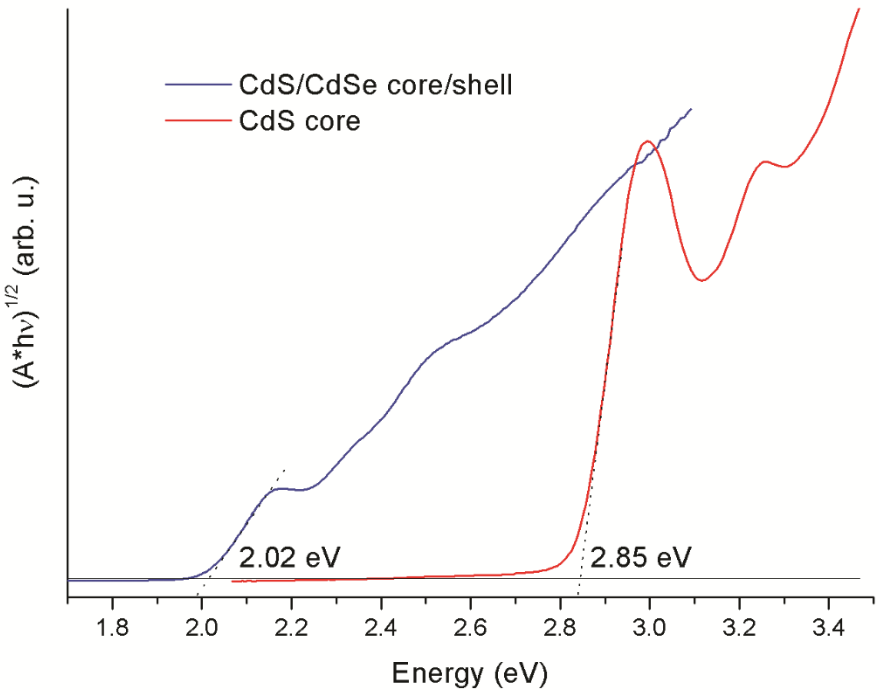

Figure S11. Tauc plots of CdS core and CdS/CdSe core/shell QDs.

REFERENCES

1. J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson and X. Peng, *J. Am. Chem. Soc.,* 2003, **125**, 12567.
2. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854.
3. A. Nag, M. V. Kovalenko, J.-S. Lee, W. Liu, B. Spokoyny and D. V. Talapin, *J. Am. Chem. Soc.*, 2011, **133**, 10612.
4. R. Shannon, *Acta Cryst.*, 1976, **32**, 751.
5. A. Das, Z. Han,M. G. Haghighi and R. Eisenberg, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 16716.
6. Z. Han, F. Qiu, R. Eisenberg,P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321.
7. A. Nag, D. S. Chung, D. S. Dolzhnikov, N. M. Dimitrijevic, S. Chattopadhyay, T. Shibata and D. V. Talapin, *J. Am. Chem. Soc.*, 2012, **134**, 13604.