

Highly efficient photocatalytic hydrogen generation by solution-processed ZnO/Pt/CdS, ZnO/Pt/Cd_{1-x}Zn_xS and ZnO/Pt/CdS_{1-x}Se_x hybrid nanostructures

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Supporting Information

Experimental Section

Synthesis of ZnO/CdS

In a typical synthesis procedure, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (4 mmol) was added to methanol (70 mL) in a 100 mL 3 neck RBF and the temperature was raised to 60 °C. After a few minutes methanolic solution of KOH (500 mg in 10 mL) was added drop wise to the reaction solution and the stirring was continued for 2h at 60 °C. The color of the solution become turbid at the initial stages and become colorless in 30 min. In 2h the solution slowly turned to white color (The particles size also depends on the size of the magnetic bead and rpm of stirring). As formed ZnO nanoparticles were precipitated out by addition of water and excess zinc ions were removed by centrifugation. In order to form CdS layer of particles, the 10mL of cadmium acetate (0.8 mmol) and 10 mL of sodium sulfide (0.8 mmol) methanolic solutions were added drop wise simultaneously. Stirring was continued for 30 min. Products were separated by centrifugation and washed with $\text{H}_2\text{O}/\text{MeOH}$ mixture and dried at 60 °C overnight. Significant amount of color change was found from the wet sample to dry solution. The dry product was grinded and as obtained powder was used for further characterization and studies.

Synthesis of ZnO/Pt

For loading of platinum nanocrystals, 2.3 mL of (8.66 mM) H_2PtCl_6 aqueous solution was added drop-wise to the preformed ZnO nanocrystals dispersed in a fresh methanolic solution, followed by 0.5 mL of NaBH_4 (40mM) aqueous solution. The solution was stirred for 10 min. The solution color became black due to the formation of platinum on ZnO nanoparticles. Excess zinc ions were removed by centrifugation and the solid product was separated and used for further synthesis without allowing it to dry.

Synthesis of ZnO/Pt/CdS

ZnO/Pt nanoparticles obtained in earlier described procedure were redispersed in methanol and temperature was raised to 60 °C. In order to form CdS layer of particles, the 10 mL of cadmium acetate (0.8 mmol) and 10 mL sodium sulfide (0.8 mmol) methanolic solutions were added drop wise simultaneously. Stirring was continued for 30 min more. Products were

separated by centrifugation and washed with H₂O/MeOH mixture and dried at 60 °C overnight. Significant amount of color change was found from the wet sample to dry solution. The dry product was grinded and as obtained powder was used for further characterization and studies.

Synthesis of ZnO /CdS /Pt

ZnO/CdS were synthesized in a similar manner that described earlier and dispersed in 70 mL methanol. For loading of platinum nanocrystals, 2.3 mL of (8.66 mM) H₂PtCl₆ aqueous solution was added drop-wise to the preformed ZnO/CdS nanocrystals dispersed in a fresh methanolic solution, followed by 0.5 mL of NaBH₄ (40 mM) aqueous solution. The products were washed and centrifuged and dried at 60 °C. The dry product was grinded and as obtained powder was used for further characterization and studies.

Synthesis of ZnO/Pt/Cd_{0.8}Zn_{0.2}S

ZnO/Pt nanoparticles were redispersed in methanol and temperature was raised to 60 °C. In order to form Cd_{0.8}Zn_{0.2}S layer of particles, required amount of zinc acetate (0.2 mmol) was added to the solution and the 10mL of cadmium acetate (0.8 mmol) and 10 mL of sodium sulfide (1 mmol) methanolic solutions were added drop wise simultaneously. Stirring was continued for 30 min more. Products were separated by centrifugation and washed with H₂O/MeOH mixture and dried at 60 °C overnight. Significant amount of color change was found from the wet sample to dry solution. The dry product was grinded and as obtained powder was used for further characterization and studies.

Synthesis of ZnO /Pt/CdS_{0.5}Se_{0.5}

ZnO/Pt nanoparticles were redispersed in methanol and temperature was raised to 60 °C. In order to form CdS_{0.5}Se_{0.5} layer of particles, required amount of 10 mL of sodium selenosulfate (40 mM), 10 mL of cadmium acetate (0.8 mmol) and 10 mL of sodium sulfide (0.4 mmol) methanolic solutions were added drop wise simultaneously. Stirring was continued for 30 min more. Products were separated by centrifugation and washed with H₂O/MeOH mixture and dried at 60 °C overnight. Significant amount of color change was found from the wet sample to dry solution. The dry product was grinded and as obtained powder was used for further characterization and studies.

Characterization

Transmission electron microscopy (TEM) images were obtained with JEOL-3010 system and FEI TITAN microscope. Specimens for TEM and HRTEM measurements were prepared via drop casting a drop of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Diffraction System using a Cu K α source ($\lambda = 0.154178$ nm). UV-Vis absorption spectra were taken with Perkin Elmer Model Lambda 900 spectrometer. Photoluminescence measurements were carried out with a Horiba Jobin Yvon Spectrometer (iHR 320) at room temperature.

Photocatalytic Measurements

The photocatalytic activity of synthesized samples was evaluated by the generation of hydrogen in the presence of Na₂S, Na₂SO₃ as sacrificial agents under visible and UV-Visible light irradiation. In a typical photocatalytic study, 20 mg of the photocatalyst was dispersed in a 75 mL of water containing 0.1 M Na₂S and 0.1 M Na₂SO₃ in a cylindrical quartz cell with flat surfaces being exposed to light. The solution was purged with argon for 30 min prior to activity tests to remove dissolved oxygen and to maintain inert atmosphere. The solution was exposed to light using 450 W Xe arc lamp (working at 400 W) (New Port, 6279NS, Ozone-free) fitted with water filter (New Port). Activity tests at a particular wavelength were obtained by using band pass filters with FWHM 70 nm (New Port) (400,450,500 nm). The H₂ evolved was quantified using gas chromatography (Perkin Elmer, Clarus 580 GC) equipped with TCD detector. The photon flux is measured using irradiance meter (New Port) and estimated values are presented in Table S1. The apparent quantum yield (AQY) was estimated as follows.

$$\text{Apparent Quantum Yield (AQY)} = \left(\frac{2R}{I} \right) * 100$$

Where, R is the rate of evolution hydrogen, and I is rate of incident photons.

Similar values are obtained for photon flux in the study of Amirov and Alivisatos^[1] which is 3.0×10^{17} Photons / s.

Table S1: Number of incident photons estimated at different wavelength ranges.

Range/nm	Incident photons (I)
	Photons / s
200-475	8.1×10^{17}
200-515	10.5×10^{17}
395-475	3.9×10^{17}
395-515	6.3×10^{17}
400	2.3×10^{17}
450	2.2×10^{17}
500	3.2×10^{17}

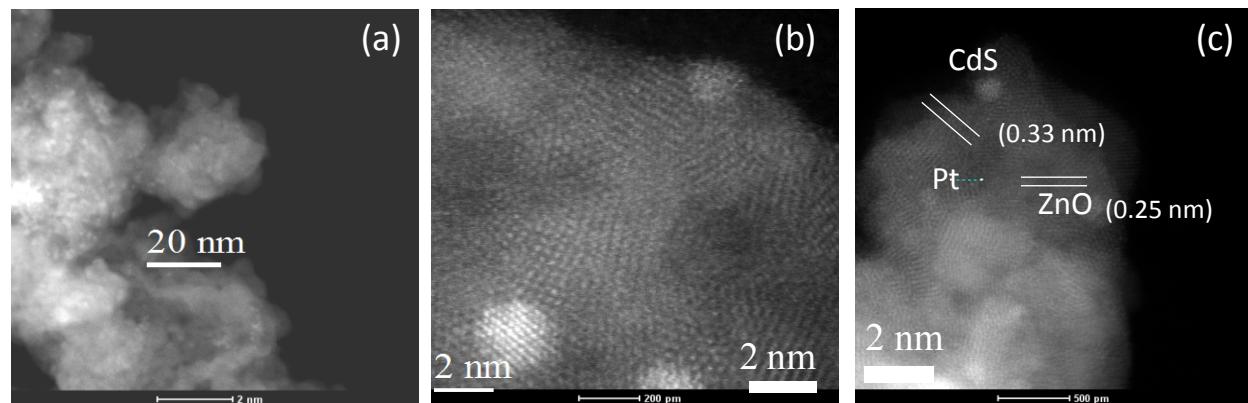


Figure S1 . (a) STEM and (b) HRSTEM images of the ZnO/Pt/Cd_{0.8}Zn_{0.2}S

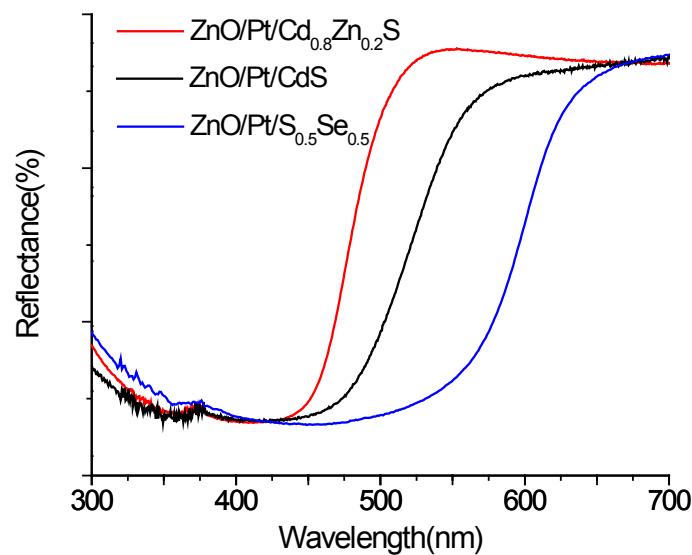


Figure S2. Comparison of diffuse reflectance spectra of ZnO/Pt/CdS , ZnO/Pt/Cd_{0.8}Zn_{0.2}S and ZnO/Pt/CdS_{0.5}Se_{0.5}.

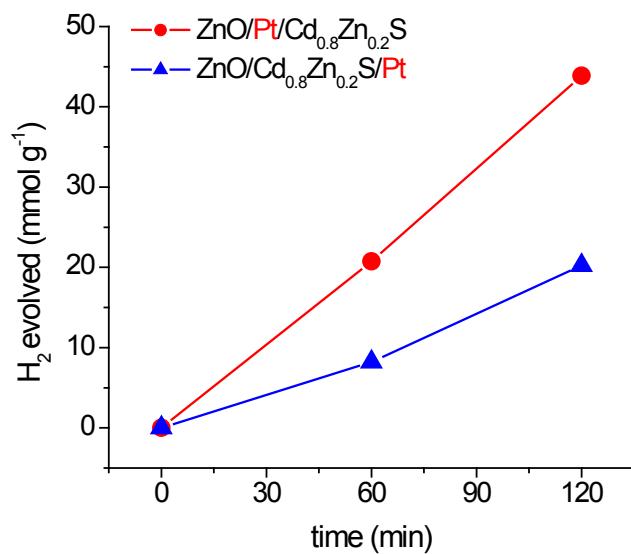


Figure S3. Comparison of photocatalytic activity of ZnO/Pt/Cd_{0.8}Zn_{0.2}S and ZnO/Cd_{0.8}Zn_{0.2}S/Pt.

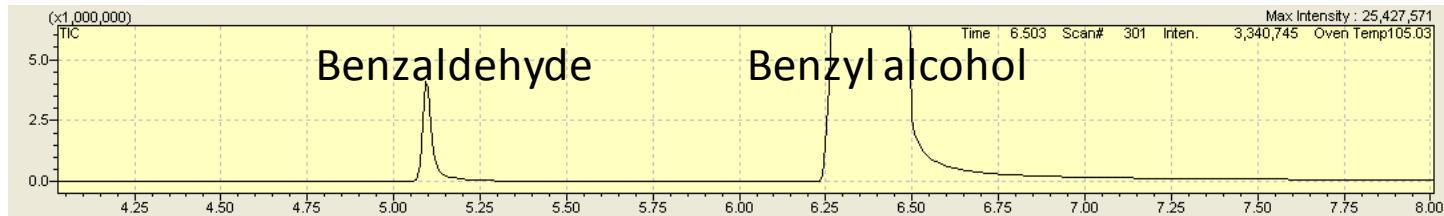


Figure S4. GC-MS data for the aliquot of reaction medium obtained during photocatalytic hydrogen evolution in presence of benzyl alcohol. Benzaldehyde is the only product obtained in the reaction medium.

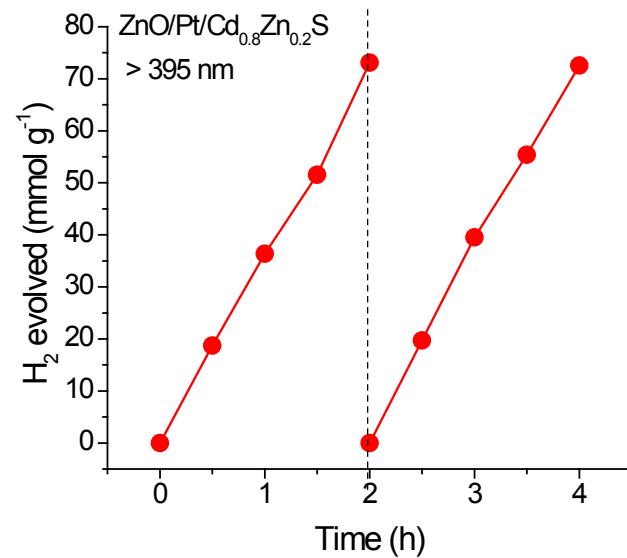


Figure S5. Recyclability of visible light ($\lambda > 395$ nm) activity of H_2 evolution with $ZnO/Pt/Cd_{0.8}Zn_{0.2}S$ when benzyl alcohol is used as hole scavenger.

References

- [1] L. Amirav, A. P. Alivisatos, *J. Phys. Chem. Lett.* **2010**, *1*, 1051.