

Supporting Information

Remarkable improvement in visible-light induced hydrogen generation by ZnO/Pt/Cd_{1-y}Zn_yS heterostructures through substitution of N and F in ZnO

S. R. Lingampalli and C. N. R. Rao*

New Chemistry Unit, CSIR Centre of Excellence in Chemistry and International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore-560064, India.

E-mail: cnrrao@jncasr.ac.in; Fax: +91-80-2208-2760

Experimental

Materials

Zn(CH₃COO)₂·2H₂O (SD Fine Chem Ltd, India, 99.5 %), Cd(CH₃COO)₂·2H₂O (SD Fine Chem Ltd, India, 99.0 %), KOH (SD Fine Chem Ltd, India, 85.5 %), NaBH₄ (SD Fine Chem Ltd, India, 98 %), H₂PtCl₆ (Sigma-Aldrich, 37.5 % Pt basis), Na₂S·xH₂O (SD Fine Chem Ltd, India), Na₂SO₃ (SD Fine Chem Ltd, India, 97 %), benzyl alcohol (SD Fine Chem Ltd, India, 99 %), methanol (Spectrochem, India, 99.9 %), water (Millipore, 18.2 MΩ.cm), NH₃ gas (Chemix, India, 99.99%), NH₄F (Spectrochem, India, 99%) and acetic acid (Spectrochem, India, 99.8%) are used without any further purification.

Characterization

Transmission electron microscopy (TEM) images were obtained with JEOL-3010 system and FEI TITAN microscope. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Diffraction System using a Cu Kα source (λ= 0.154178 nm). UV-Vis absorption spectra were taken with Perkin Elmer Model Lambda 900 spectrometer. XPS with a MgKα (1253.6 eV) X-ray source was used to determine the composition of the sample.

Synthesis

a. Synthesis of ZnO nanoparticles:

Zinc acetate dihydrate (4mmol) was dissolved in methanol (70 mL) and the solution temperature was raised to 60 °C. Methanolic solution of KOH (8 mmol in 10 mL of methanol) was dropwise added to the zinc acetate solution and the solution was maintained at 60 °C for 2h with stirring at 1500 rpm. After 2 h, 5 mL of H₂O was added and the solution was stirred for 10 min. The product was separated by centrifugation, washed with methanol and dried at room temperature. The dry product of ZnO nanoparticles was ground well and used for further characterization. The average particle size was found to be ~ 10 nm.

b. Co-doping of N and F in ZnO:

ZnO nanoparticles (2 mmol) and NH₄F (40 mmol) were taken in a mortar and were ground well to obtain uniform mixing. This mixture was transferred to a ceramic boat and the boat was placed in a tube at midst of furnace. The sample was heated in presence of ammonia flow, with a ramp rate of 3 °C/min to 100 °C and dwelled for 2 h at 100 °C followed by raise in temperature with a ramp rate of 3 °C/min to 600 °C and dwelled at 600 °C for 3h. The sample was allowed to cool down to room temperature naturally. The resultant bright orange colored N, F co-doped ZnO with intense visible light absorption was collected and calcined at 400 °C for two hours in the air.

c. Formation of heterostructures of ZnO_{1-x}(N,F)_x/Pt/CdS:

ZnO_{1-x}(N,F)_x (~ 0.19 mmol, 15 mg) was taken in a beaker containing water (50 mL) and sonicated for few minutes to form uniform dispersions. To this solution aqueous solution of H₂PtCl₆ (240 uL, 7.4 mM) was added followed by dropwise addition of aqueous solution of dilute NaBH₄ (2 mL, 20 mM). The sample color has become dark due to the deposition of Pt nanoparticles to the ZnO surfaces. The excess ions were removed by centrifugation and the products were re-dispersed in methanol (50 mL) and by sonication for few minutes then the solution was stirred with a rpm of 1500. To this solution, methanolic solutions of cadmium acetate (47 μmol in 10 mL) and sodium sulfide (47 μmol in 10 mL) were added drop wise simultaneously. The solution has turned to bright green color. The solid products of ZnO_{1-x}

$x(\text{N,F})_x/\text{Pt}/\text{CdS}$ were precipitated out from the solution and the product was collected by centrifugation and used for further characterization.

In order to form the solid solutions of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ in these heterostructures, required amount of zinc acetate dihydrate was added to dispersion of $\text{ZnO}_{1-x}(\text{N,F})_x/\text{Pt}$ prior to addition of cadmium acetate and sodium sulfide solutions.

Photocatalytic hydrogen evolution studies

The photocatalytic activity of synthesized samples was evaluated by the generation of hydrogen in the presence of Na_2S , Na_2SO_3 as sacrificial agents under visible light irradiation. In a typical photocatalytic study, 15 mg of the photocatalyst was dispersed in a 75 mL of water containing 0.1 M Na_2S and 0.1 M Na_2SO_3 in a cylindrical quartz cell with flat surfaces being exposed to light. 5 mL of acetic acid and 5 mL of benzyl alcohol mixture was diluted with water to 75 mL, used for photocatalytic evolution of hydrogen. We have not observed any hydrogen evolution under visible light irradiation from the solution of $\text{Na}_2\text{S}-\text{Na}_2\text{SO}_3$ or benzyl alcohol-acetic acid in the absence of the photocatalyst. However $\text{Na}_2\text{S}-\text{Na}_2\text{SO}_3$ alone showed H_2 evolution without photocatalyst under UV- Visible light irradiation. The solution was exposed to light using 450 W Xe arc lamp (working at 400 W) (New Port, 6279NS, Ozone-free) fitted with water (IR) filter (New Port). A 395 nm cut-off filter was employed to remove the UV fraction leaving behind the visible fraction of light (> 395 nm). The H_2 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 Alivisotos¹ 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
395-475	3.9×10^{17}
395-515	6.3×10^{17}

Table S2. Comparison of photocatalytic hydrogen evolution results of the present study with those reported on similar systems in the literature.

Photocatalyst	Amount of catalyst (mg)	Activity (mmolh ⁻¹ g ⁻¹)	AQY (%)	Reference
ZnO/Pt/CdS ^a	15	4 ^c	3	Present work
ZnO _{1-x} (N,F) _x /Pt/CdS ^a	16	12 ^c	10	Present work
ZnO _{1-x} (N,F) _x /Pt/Cd _{0.8} Zn _{0.2} S ^a	-	-	-	Present work
ZnO/Pt/CdS ^b	15	15 ^c	12	Present work
ZnO _{1-x} (N,F) _x /Pt/CdS ^b	16	35 ^c	30	Present work
ZnO _{1-x} (N,F) _x /Pt/Cd _{0.8} Zn _{0.2} S ^b	15	43 ^c	44	Present work
CdS-CdSe-Pt	4	40 ^c	20 ^c	1
CdS/Pt	50	4.4 ^c	13.9 ^c	2
RGO-Zn _x Cd _{1-x} S	50	1.8 ^d	23.4 ^c	3
CdS-Pt	50	24 ^c	51 ^{c,e}	4
CdS/Pt/TiO ₂	40	14.7 ^c	13.9 ^{c,e}	5
CdS-Graphene-Pt	20	56 ^c	22.5 ^{c,e}	6
TiO ₂ -Pt	20	16.7 ^d	-	7
CdS/(Pt-TiO ₂)	12	9 ^c	4.5 ^c	8
TiO ₂ -CdS-Pt	100	4.2 ^c	-	9
Zn _x Cd _{1-x} S	100	11 ^c	30.4 ^c	10
ZnO/CdS/Pt	200	3.9 ^d	3.2 ^d	11
CdS-Zn _{1-x} Cd _x S	50	2.1 ^c (3 ^d)	6.3 ^c	12
ZnO/Pt/CdS ^a	20	11.2 ^c (17.4 ^d)	11.9 ^c (11.1 ^d)	13
ZnO/Pt/CdS ^b	20	31.6 ^c	34.5 ^c	13
ZnO/Pt/Cd _{0.8} Zn _{0.2} S ^a	20	12.5 ^c (31.2 ^d)	18.0 ^c (23.1 ^d)	13
ZnO/Pt/ Cd _{0.8} Zn _{0.2} S ^b	20	36.5 ^c	50.4 ^c	13
ZnO/Pt/CdS _{0.5} Se _{0.5} ^a	20	16.0 ^c (19.0 ^d)	9.3 ^c (8.1 ^d)	13

^a Na₂S and Na₂SO₃ are used as hole scavengers. ^b Benzyl alcohol-acetic acid is used as hole scavenger. ^c Visible irradiation. ^d UV-visible irradiation. ^e Light source for the reaction and for AQY calculations are different. In our experiments a 395 nm cut-off filter was employed to remove the UV fraction from the light leaving behind visible light (> 395 nm).

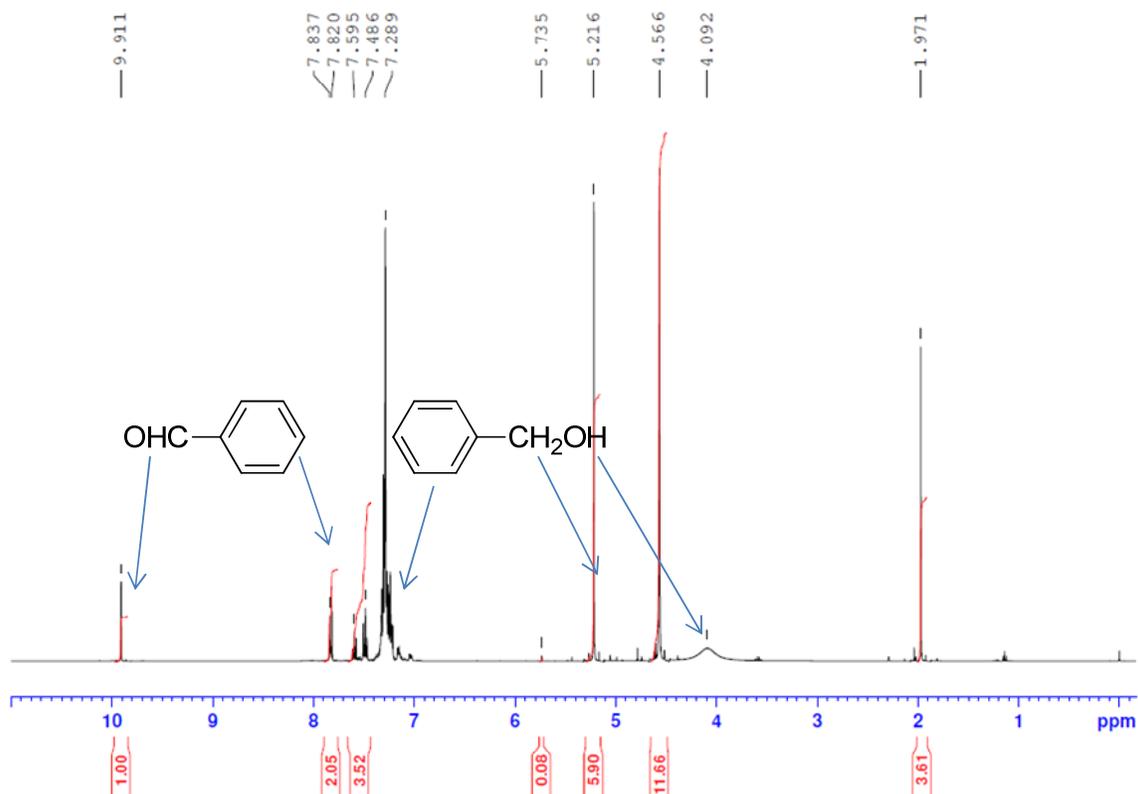


Figure S 1. NMR data of isolated organic phase of the photocatalytic reaction mixture.

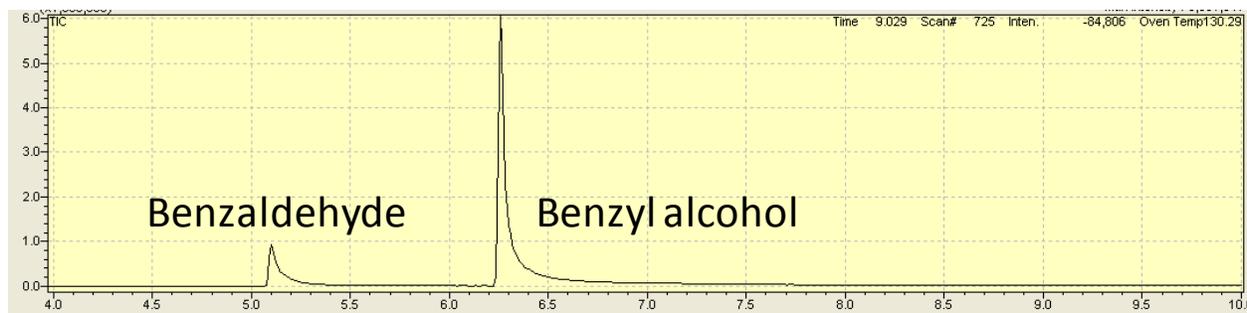


Figure S2. GC-MS data of the isolated part of the organic phase shows the presence of benzaldehyde and benzyl alcohol.

References

1. L. Amirav and A. P. Alivisatos, *J. Phys. Chem. Lett.*, 2010, **1**, 1051-1054.
2. Y. Li, Y. Hu, S. Peng, G. Lu and S. Li, *J. Phys. Chem. C*, 2009, **113**, 9352-9358.
3. J. Zhang, J. Yu, M. Jaroniec and J. R. Gong, *Nano Lett.*, 2012, **12**, 4584-4589.
4. J. Yu, Y. Yu and B. Cheng, *RSC Advances*, 2012, **2**, 11829-11835.
5. L. Qi, J. Yu and M. Jaroniec, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8915-8923.
6. Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. R. Gong, *J. Am. Chem. Soc.*, 2011, **133**, 10878-10884.
7. J. Yu, L. Qi and M. Jaroniec, *J. Phys. Chem. C*, 2010, **114**, 13118-13125.
8. H. Park, W. Choi and M. R. Hoffmann, *J. Mater. Chem.*, 2008, **18**, 2379-2385.
9. J. S. Jang, W. Li, S. H. Oh and J. S. Lee, *Chem. Phys. Lett.*, 2006, **425**, 278-282.
10. Y. Wang, J. Wu, J. Zheng and R. Xu, *Catal. Sci. Technol.*, 2011, **1**, 940-947.
11. X. Wang, G. Liu, Z.-G. Chen, F. Li, L. Wang, G. Q. Lu and H.-M. Cheng, *Chem. Commun.*, 2009, **0**, 3452-3454.
12. J. Yu, J. Zhang and M. Jaroniec, *Green Chem.*, 2010, **12**, 1611-1614.
13. S. R. Lingampalli, U. K. Gautam and C. N. R. Rao, *Energy Environ. Sci.*, 2013, **6**, 3589-3594.