

## Visible Light Assisted Photocatalytic Hydrogen Generation and Organic Dye Degradation by CdS – Metal Oxide hybrids in presence of Graphene Oxide

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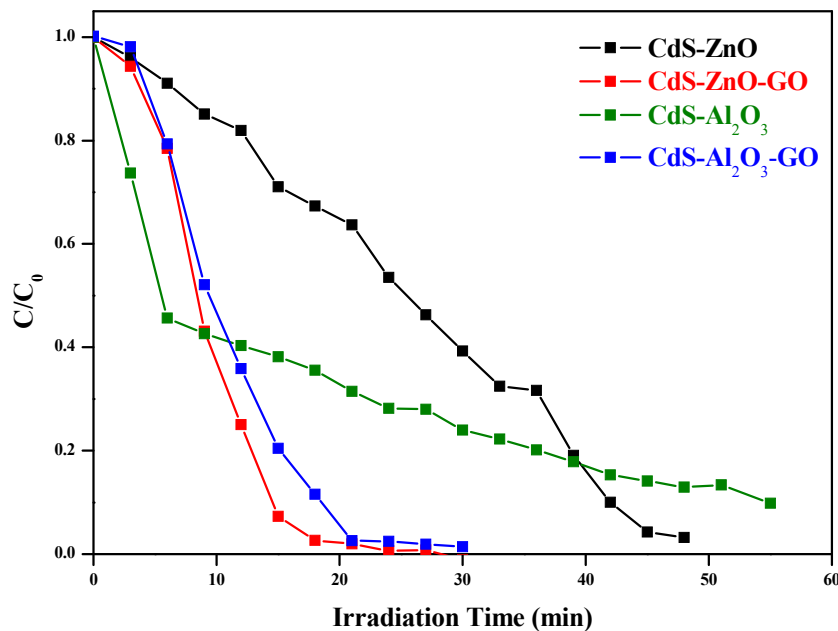
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### Photocatalytic dye degradation experiment

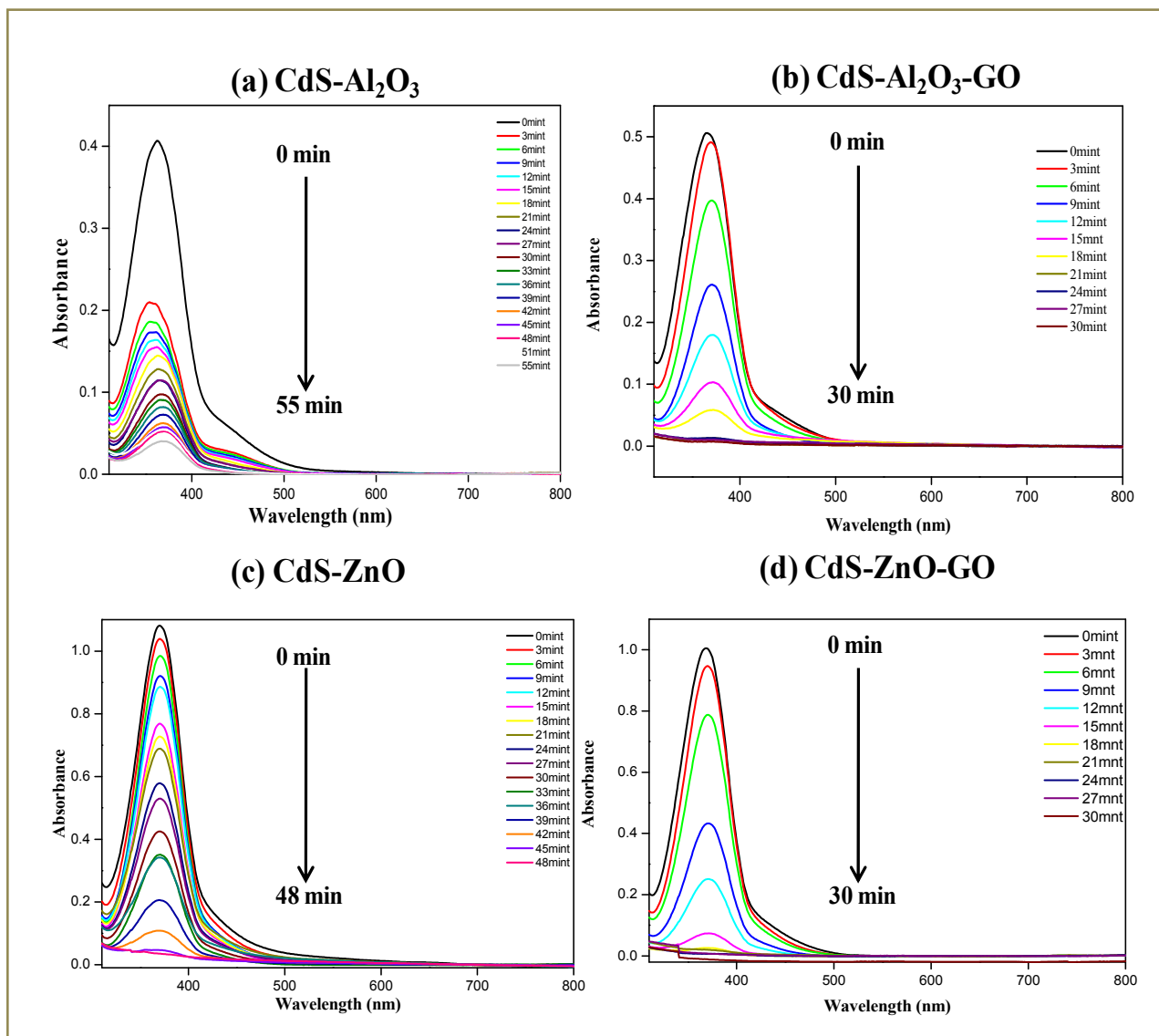
Photocatalytic degradation experiment for CdS NPs, GO, CdS/ZnO/GO and CdS/Al<sub>2</sub>O<sub>3</sub>/GO were performed separately in 100 mL double walled quartz round-bottom flask. In a typical photocatalytic degradation experiment, 50 mL of aqueous methyl orange ( $1 \times 10^{-5}$  M) and 0.2 g photocatalyst samples were loaded into a quartz photoreactor. Prior to irradiation, reaction mixture was stirred for an hour in dark at room temperature to maintain adsorption/desorption equilibrium among the photocatalyst, dye, solubilized oxygen and atmospheric oxygen. During the degradation process, 500-W Phoenix tungsten halogen lamp was placed horizontally 30 cm above the photoreactor. The suspension was stirred during the irradiation to make the solution homogenous. 3 mL of samples were collected every five minutes from the photoreactor and absorption measurements were performed within 200-800 nm after removing the solid catalyst particles by centrifugation. The concentration of the aqueous methyl orange was determined from the absorbance value at 464 nm. Degradation of methyl orange is not observed in the absence of either photocatalyst or light.

### Photocatalytic reduction of Cr(VI) experiment<sup>1</sup>

Photocatalytic reduction of Cr(VI) experiment for CdS/ZnO, CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/ZnO/GO and CdS/Al<sub>2</sub>O<sub>3</sub>/GO were performed separately in 100 mL double walled quartz round-bottom flask. In a typical photocatalytic degradation experiment, 50 mL of aqueous Cr(VI) ( $1.5 \times 10^{-4}$  M) and 0.2 g photocatalyst samples were loaded into a quartz photoreactor. Prior to irradiation, reaction mixture was stirred for an hour in dark at room temperature to reach the adsorption/desorption equilibrium. During the degradation process, 500-W Phoenix tungsten halogen lamp was placed horizontally 30 cm above the photoreactor. The suspension was stirred during the irradiation to make the solution homogenous. 2 mL of samples were collected every three minutes from the photoreactor and absorption measurements were performed within 200-800 nm after removing the solid catalyst particles by centrifugation.



**Figure S1.** Photocatalytic reduction of Cr(VI) by CdS-ZnO, CdS-ZnO-GO, CdS-Al<sub>2</sub>O<sub>3</sub> and CdS-Al<sub>2</sub>O<sub>3</sub>-GO composites.

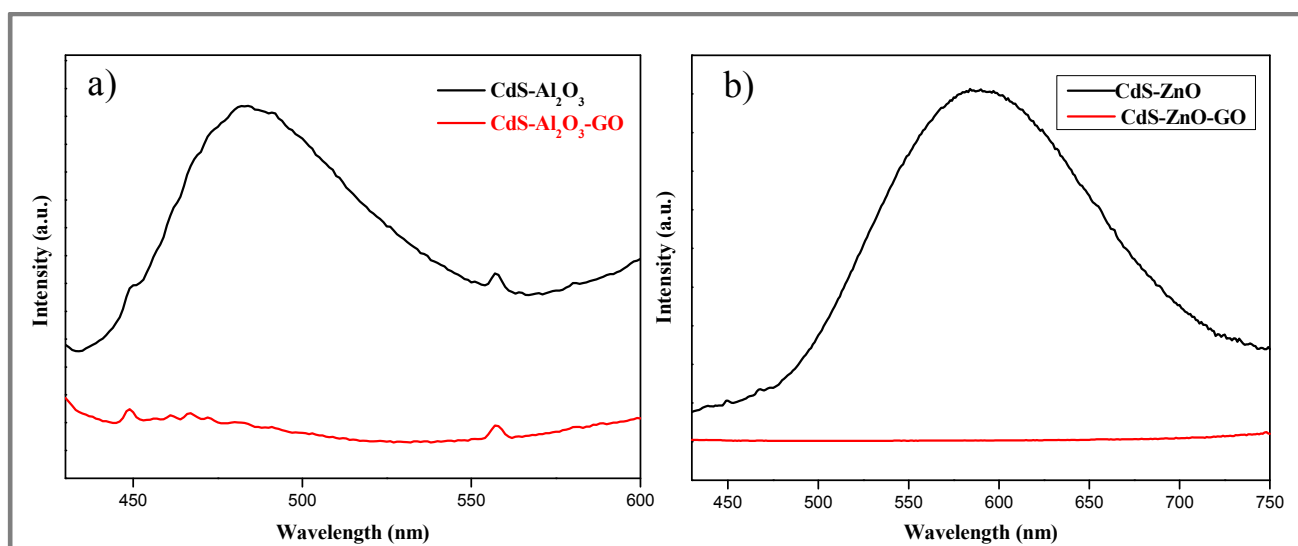


**Figure S2.** UV-Vis absorption spectra of Cr(VI) in presence of as prepared (a) CdS-Al<sub>2</sub>O<sub>3</sub>, (b) CdS-Al<sub>2</sub>O<sub>3</sub>-GO and (c) CdS-ZnO (d) CdS-ZnO-GO respectively.

It was also observed that CdS/Oxide/GO exhibits excellent photocatalytic activity for the reduction of Cr(VI) in water. The dye degradation experiments were performed by using CdS-Al<sub>2</sub>O<sub>3</sub>, CdS-Al<sub>2</sub>O<sub>3</sub>-GO, CdS-ZnO and CdS-ZnO-GO systems. We have found that highest photocatalytic activity was achieved by CdS/ZnO/GO with respect to other photocatalysts

CdS/Al<sub>2</sub>O<sub>3</sub>/GO, CdS-ZnO and CdS-Al<sub>2</sub>O<sub>3</sub>. The reduction efficiencies ( $E_{ff}$ ) for the photocatalysts were calculated based on the initial and final concentration of Cr(VI) in solution.<sup>39</sup> It was found that within 30 min of irradiation, 60.7% and 99.158 % of Cr(VI) reduction was achieved for CdS/ZnO and CdS/ZnO/GO whereas, 76.02% and 98.5% reduction occurred within same period of time in presence of CdS/Al<sub>2</sub>O<sub>3</sub> and CdS/Al<sub>2</sub>O<sub>3</sub>/GO respectively.

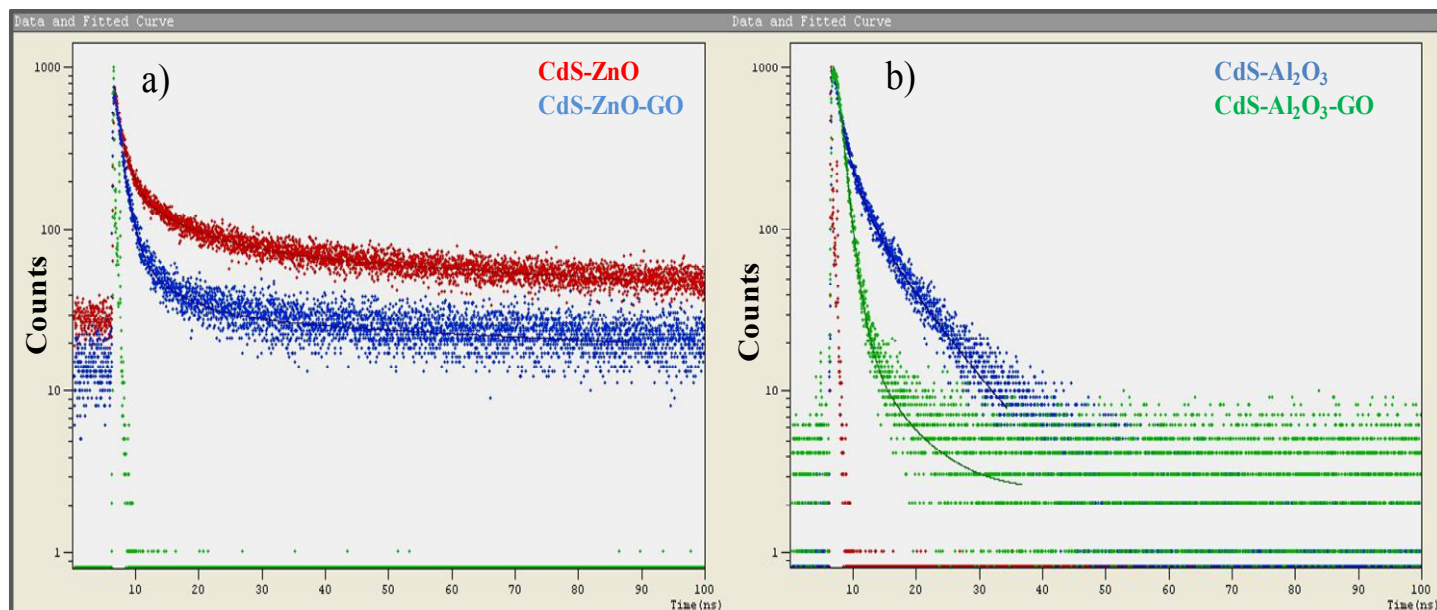
## PL Study



**Figure S3.** Photoluminescence spectra of CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/Al<sub>2</sub>O<sub>3</sub>/GO and CdS/ZnO, CdS/ZnO/GO excited at the wavelength of 410 nm.

Figure S3 shows PL spectra of a) CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/Al<sub>2</sub>O<sub>3</sub>/GO and b) CdS/ZnO, CdS/ZnO/GO excited at the wavelength of 410 nm. Strong emission peaks at about 485 nm and 590 nm are observed for CdS/Al<sub>2</sub>O<sub>3</sub> and CdS/ZnO respectively. Introduction of GO drastically decreases the excitonic PL intensities of CdS-ZnO-GO and CdS-Al<sub>2</sub>O<sub>3</sub>-GO hybrids with respect to CdS-ZnO and CdS-Al<sub>2</sub>O<sub>3</sub>, respectively, which is because of the inhibited recombination of photo-induced electrons and holes in the composites as compared to the hybrids. From these observations we can

conclude that the photoinduced electrons migrate from the semiconductor surface to the graphene oxide nanosheets.<sup>2</sup> This is further supported by the Time Resolved Fluorescence Spectroscopic study. Time-resolved PL measurements of the samples CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/Al<sub>2</sub>O<sub>3</sub>/GO and CdS/ZnO, CdS/ZnO/GO were performed.



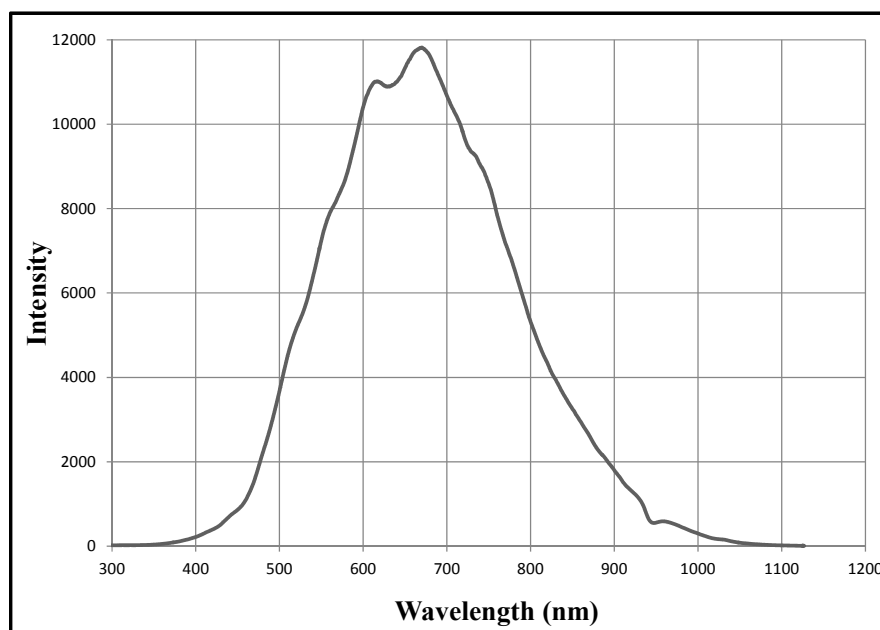
**Figure S4.** Time-resolved PL spectra of CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/Al<sub>2</sub>O<sub>3</sub>/GO and CdS/ZnO, CdS/ZnO/GO excited at the wavelength of 405 nm.

The CdS/Metal Oxide/GO hybrids show significant decrease in the PL lifetime in comparison to their composites which are not coupled with GO. So from this observation we can conclude about the electronic interaction between semiconductor surface and GO.<sup>3</sup> The PL decays of all the samples were fitted with a bi-exponential function to calculate the exciton lifetime. Table S1 represents the details of the excitonic lifetime and fitting parameters for the samples.

Sample	Fitting parameter ( $\chi^2$ )	$\tau_1$ (ns)	$\tau_2$ (ns)
CdS/ZnO	1.031	1.540	14.290
CdS/ZnO/GO	1.015	1.266	10.740
CdS/Al <sub>2</sub> O <sub>3</sub>	1.012	1.588	7.882
CdS/Al <sub>2</sub> O <sub>3</sub> /GO	1.030	1.005	4.266

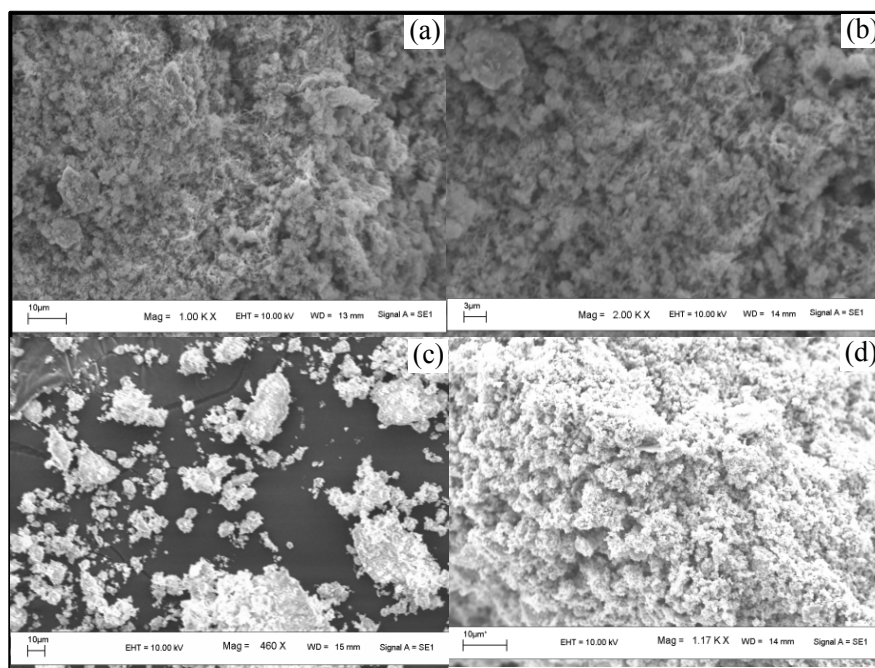
**Table S1.** Picosecond-resolved luminescence transients of various samples CdS/Al<sub>2</sub>O<sub>3</sub>, CdS/Al<sub>2</sub>O<sub>3</sub>/GO and CdS/ZnO, CdS/ZnO/GO were detected with 405 nm excitation.

### Emission Profile of halogen lamp

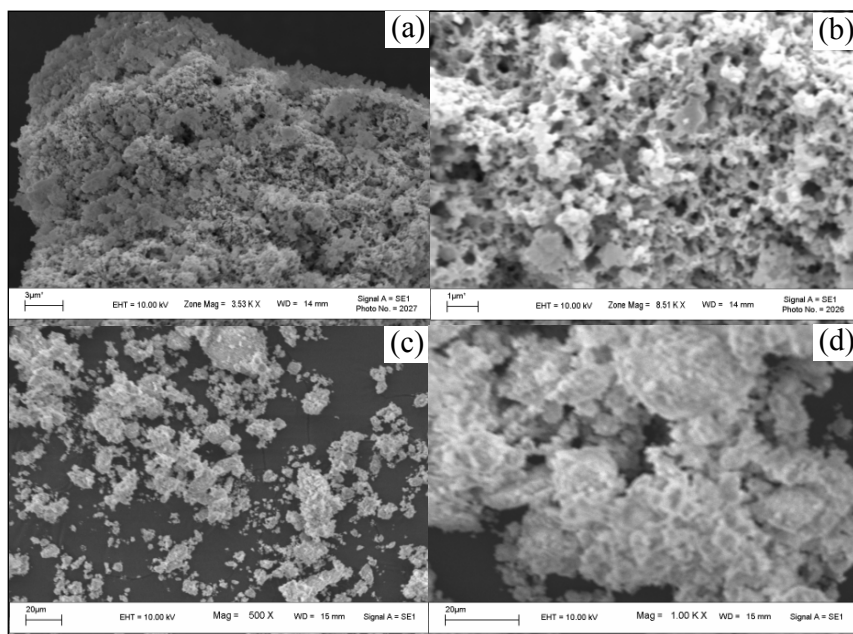


**Figure S5.** Emission spectrum of the 500 W tungsten halogen lamp

### Scanning Electron Microscope Analysis



**Figure S6.** Scanning Electron Microscopic images of (a & b) CdS/Al<sub>2</sub>O<sub>3</sub> whereas (c & d) CdS/Al<sub>2</sub>O<sub>3</sub>/GO at different magnification



**Figure S7.** Scanning Electron Microscopic images of (a & b) CdS/ZnO whereas (c & d) CdS/ZnO/GO at different magnification

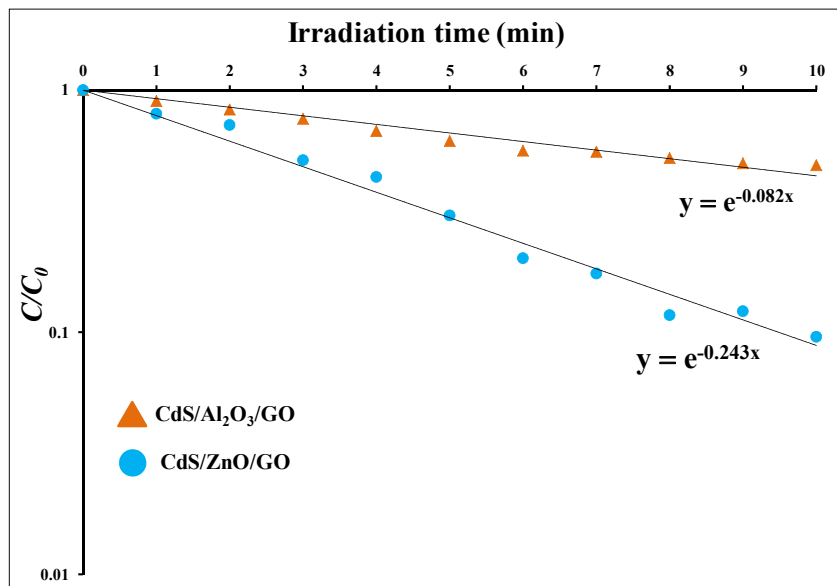
**Table S2.** AQY values of CdS based photocatalysts for hydrogen generation under visible light irradiation

The comparative efficiencies of CdS based photocatalyst reported in literature with CdS/Oxide/GO are shown in Table S2. From Table S2, it is clear that the present CdS/Oxide/GO shows higher AQY than most of the previously reported CdS based photocatalysts.



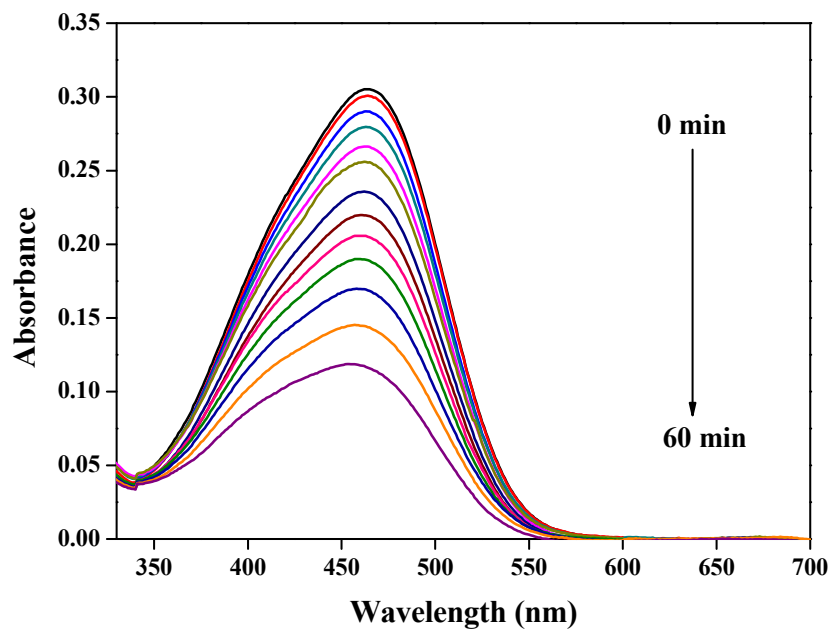
<b>photocatalyst</b>	<b>synthetic method</b>	<b>co-catalyst</b>	<b>AQY* (%)</b>	<b>ref</b>
Mn <sub>1-x</sub> Cd <sub>x</sub> S	hydrothermal	RuO	7	4
Cd <sub>1-x</sub> Zn <sub>x</sub> S (x=0.2)	thermal sulfurization	-	10.23	4
Pt/CdS NWs	chemical deposition	-	3.9	4
CdS/ZnO	two step precipitation	Pt	3.2	5
SrS/CdS	precipitation	Pt	5.83	6
CdS/ZnS	H <sub>2</sub> S thermal sulfurization	-	10.2	4
CdS/ ZTP	-	-	5.84	7
CdS/Graphene	solvothermal	Pt	22.5 (420 nm)	8
CdS/MWCNT	hydrothermal	-	2.16 (420 nm)	9
CdS/KNbO <sub>3</sub>	ion adsorption, precipitation	NiO	8.8	4
Ni/NiO/KNbO <sub>3</sub> /CdS	-	-	4.4	10
CdS-ZnS	-	-	0.60	11
CdS/Ti-MCM-41	ion exchange, sulfurization	Pt	2.6	12
3D CdS/ZnO	hydrothermal	-	15	18
3D CdS/Al <sub>2</sub> O <sub>3</sub>	hydrothermal	-	11	18
CdS	impregnation method	0.2 wt% MoS <sub>2</sub>	7.3 (720 nm)	13,14
NiO/TiO <sub>2</sub>	-	-	0.32	15
3D SrS/CdS	hydrothermal	-	10	16
3D NiO-CdS	hydrothermal	-	6	17
CdS/Al <sub>2</sub> O <sub>3</sub> /GO	hydrothermal	-	14%	
CdS/ZnO/GO	hydrothermal	-	30%	

### Kinetics study of methyl orange degradation by CdS/Oxide/GO at 10 min interval



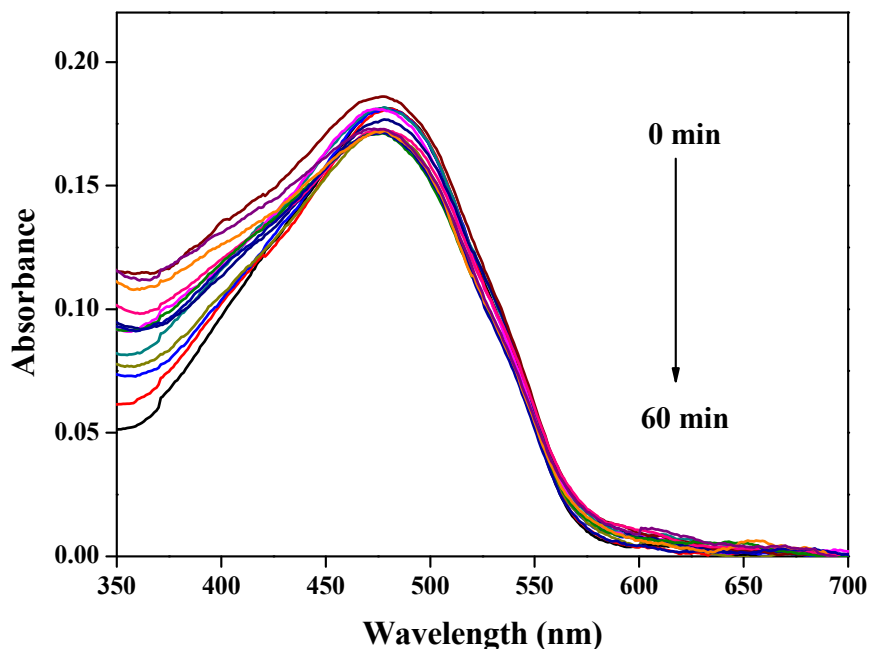
**Figure S8.** Evolution of apparent rate versus irradiation time in the presence of CdS/Al<sub>2</sub>O<sub>3</sub>/GO and CdS/ZnO/GO photocatalyst at 10 min time interval

### UV-Vis absorption spectra of methyl orange in presence of CdS nanoparticles



**Figure S9.** UV-Vis absorption spectra of methyl orange in presence of as prepared CdS nanoparticles

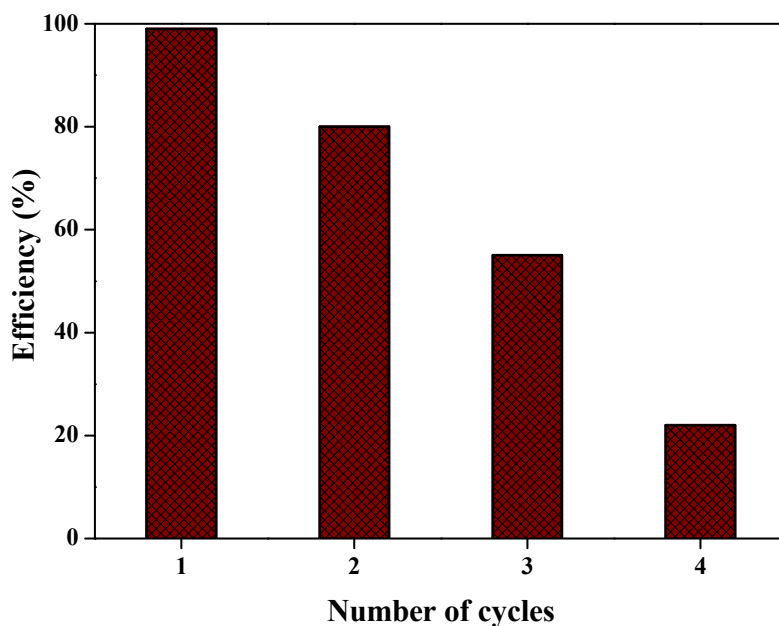
### UV-Vis absorption spectra of methyl orange in presence of graphene oxide



*Figure S10.* UV-vis absorption spectra of methyl orange in presence of as prepared graphene oxide

### Reuse ability of the catalyst for photodegradation of dye

In order to check the reuse ability of the photocatalyst, organic dye degradation experiments were carried out with catalyst CdS/ZnO/GO. It was found that up to third cycle more than 50% degradation of methyl orange was achieved. Therefore, we can conclude that photocatalyst is stable and has not been photocorroded during the photocatalytic degradation of reference dye, which is very important for its practical applications.



**Figure S11.** Four cycles of the degradation of methyl orange by CdS/ZnO/GO hybrid under visible light irradiation

## References

- 1- X. Liu, L. Pan, T. Lv, G. Zhu, Z. Sun and C. Sun, *Chem. Commun.*, 2011, **47**, 11984.
- 2- J. Hou, Z. Wang, W. Kan, S. Jiao, H. Zhu and R. V. Kumar, *J. Mater. Chem.*, 2012, **22**, 7291.
- 3- D. I. Son, B. W. Kwon, D. H. Park, W. S. Seo, Y. Yi, B. Angadi, C. L. Lee and W. K. Choi, *Nature Nanotechnology.*, 2012, **7**, 465.
- 4- X. Chen, S. Shen, L. Guo and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503.
- 5- X. Wang, G. Liu, G. Q. Lu and H.-M. Cheng, *Int. J. Hydrogen Energy*, 2010, **35**, 8199.
- 6- H. Liu, K. Zhang, D. Jing, G. Liu and L. Guo, *Int. J. Hydrogen Energy*, 2010, **35**, 7080.
- 7- K. M. Parida, N. Biswal, D. P. Das and S. Martha, *Int. J. Hydrogen Energy*, 2010, **35**, 5262.
- 8- Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. R. Gong, *J. Am. Chem. Soc.*, 2011, **133**, 10878.
- 9- Y. Chen, L. Wang, G. (Max) Lu, X. Yao and L. Guo, *J. Mater. Chem.*, 2011, **21**, 5134.

- 10-** J. Choi, S. Y. Ryu, W. Balcerski, T. K. Lee and M. R. Hoffmann, *J. Mater. Chem.*, 2008, **18**, 2371.
- 11-** C. Xing, Y. Zhang, W. Yan and L. Guo, *Int. J. Hydrogen Energy*, 2006, **31**, 2018.
- 12-** S. Shen and L. Guo, *Mater. Res. Bull.*, 2008, **43**, 437.
- 13-** X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang and C. Li, *J. Am. Chem. Soc.*, 2008, **130**, 7176.
- 14-** X. Zong, G. Wu, H. Yan, G. Ma, J. Shi, F. Wen, L. Wang and C. Li, *J. Phys. Chem. C*, 2010, **114**, 1963.
- 15-** S. G. Lee, S. Lee and H. I. Lee, *Appl. Catal. A*, 2001, **207**, 173.
- 16-** Z. Khan, T. R. Chetia and M. Qureshi, *Nanoscale*, 2012, **4**, 3543.
- 17-** Z. Khan, M. Khannam, N. Vinothkumar, M. De and M. Qureshi, *J. Mater. Chem.*, 2012, **22**, 12090.
- 18-** D. Barpuzary, Z. Khan, N. Vinothkumar, M. De and M. Qureshi, *J. Phys. Chem. C.*, 2012, **116**, 150.