Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Multidirectional-charge-transfer urchin-type Mo-doped W18O49 nanostructures on CdS nanorods for enhanced photocatalytic hydrogen evolution

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Experimental Details

Photocatalytic H_2 production: The photocatalytic H_2 production reactions were evaluated in a 135 mL quartz reactor at ambient conditions. Typically, 1.0 mg of the photo catalyst was dispersed in 15 mL of aqueous solution containing 20% lactic acid (LA), and it act as a sacrificial reagent. Then, the reactor was closed with a gas-tight rubber septum. Prior to irradiation, the suspension was evacuated and outgassing with Argon (Ar) gas for 30 min to remove air. A solar simulator equipped with an AM 1.5 G filter and 150 W Xenon lamp (Abet Technologies) was used as the irradiation source. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low-cost calibrated Si reference cell (ABET technologies). The experiments were repeated in three times to check reproducibility. Every test was carried out as described above for 3 h under irradiation source. The H_2 gas production was analyzed using an off-line gas chromatograph (GC, Young Lin Autochro-3000, model 4900) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column. The generated H_2 gas (100 μL) was collected at the headspace of quartz reactor, and purged into the GC, and evaluated by a calibration plot to 5 % standard gas of H_2.

The apparent quantum efficiency (QE) was calculated by the following equation.

$$\mathrm{QE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\,(\%)$$

$$= \frac{(\text{number of evolved } H_2 \text{ molecules}) \times 2}{\text{number of incident photons}} \times 100\,(\%)$$

Here the QE was measured under the same photocatalytic hydrogen evolution experimental conditions except the irradiation source, here 150 W Xe lamp with 425 nm band pass filter having 7 optical density greater than 4 in the rejection band and slope factor less than 1 %, were used as light sources, instead of the solar stimulator. The output light intensity was measured using 15151 low-cost calibrated Si reference cell (ABET technologies). The liquid level is ~16 cm far from the window of lamp and the illuminated area is 21.24 cm^2.

Photo-electrochemical measurements: Photo-electrochemical studies were obtained in a three-electrode system by CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the irradiation source to produce monochromatic illuminating light. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low cost calibrated Si reference cell (ABET technologies). The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and 0.5 M Na_2SO_4 aqueous solution served as the electrolyte. The measured pH value is 6.72. To prepare the working electrode, the as-synthesized 10 mg of CdS and MWO/CdS nanocomposites were first dispersed into ethanol (450 µL) and 50 µL of Nafion mixtures under soft ultrasonic stirring to get a uniform suspension. The solution containing the catalyst (30 µL) was dropped onto the pretreated indium–tin oxide (ITO) conductor glass substrate, which was then dried in an oven at 80 °C for 3 h. Photoresponses were measured at 0.0 V during on-off cycling of the solar simulator. Electrochemical impedance spectroscopy (EIS) was carried out at open-circuit potential over the frequency range of 105 and 10−1 Hz with an AC voltage magnitude of 5 mV. Moreover, to evaluate the flat-band potential (VFB) of the CdS and MWO/CdS Mott−Schottky plots at a frequency of 1 kHz were measured using a standard potentiostat equipped with an impedance spectra analyzer in the same electrochemical configuration and electrolyte under the dark condition. The measured potentials versus Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale by $E_{NHE}= E_{Ag/AgCl} + 0.197$. The cyclicvoltammograms (CV) were measured with as scanning rate of 10 mV/s using whereas the electrolyte was consisting of 0.1M Na_2SO_4 aqueous solution with 1mM $K_3[Fe(CN)_6]$.[1]

Supporting Figures

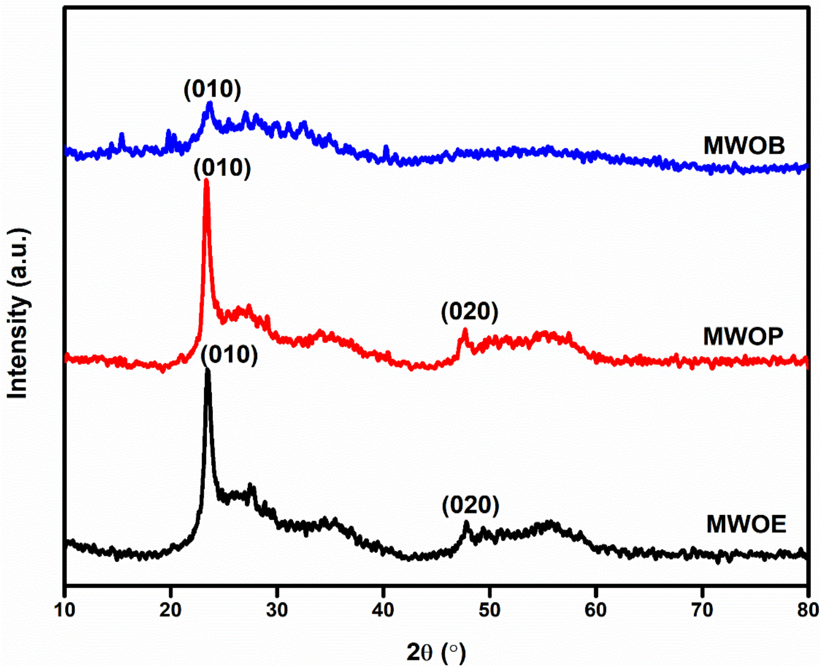

Figure S1. XRD patterns of MWOE, MWOP and MWOB nanocomposites.

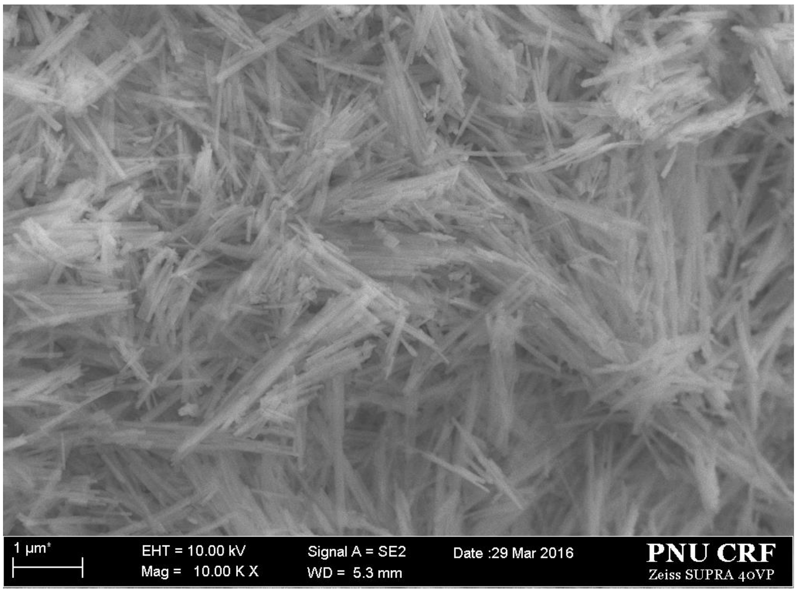

Figure S2. SEM image of CdS nanorods.

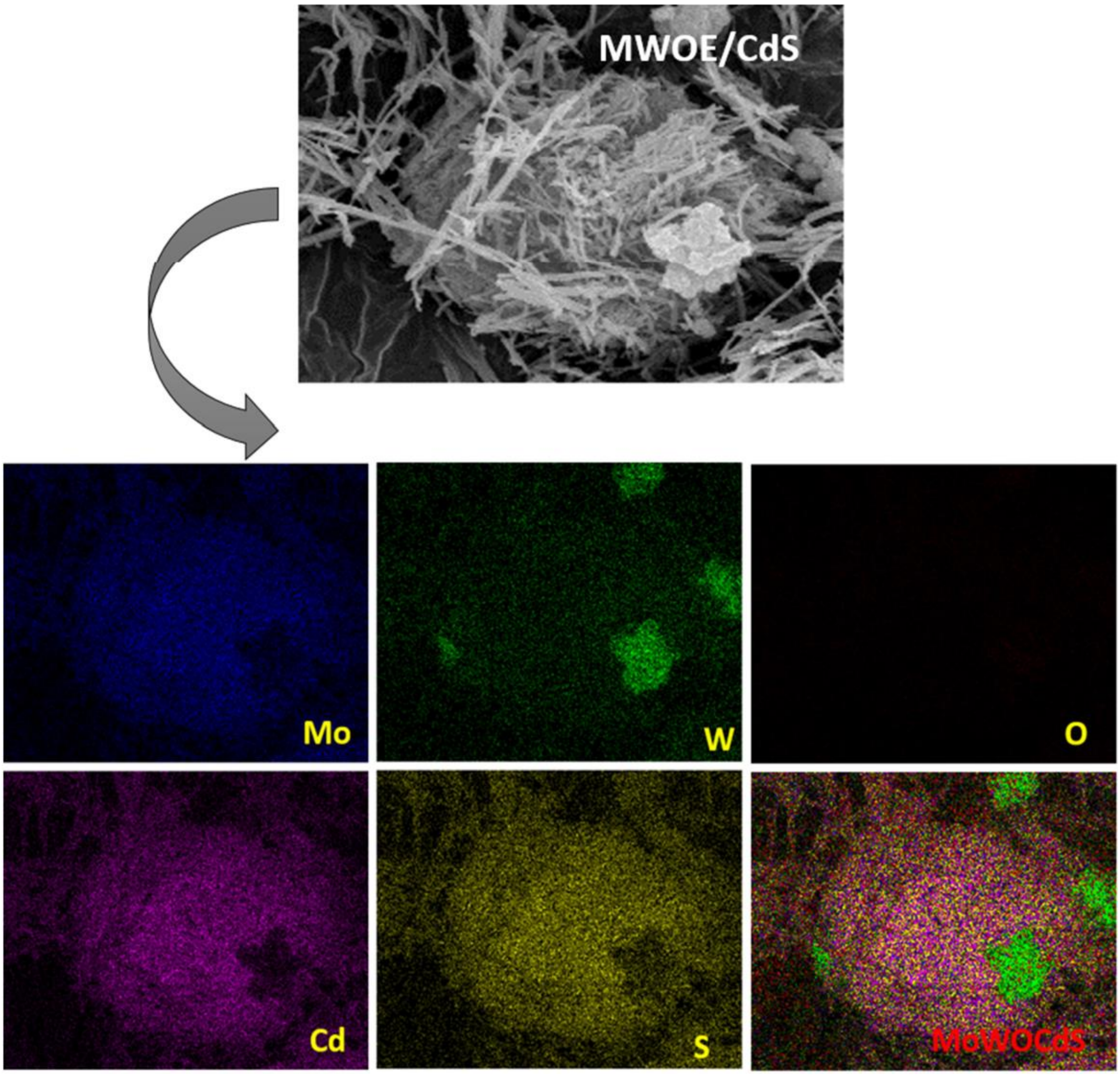

Figure S3. FESEM images and EDS elemental mapping analyses of MWOE/CdS.

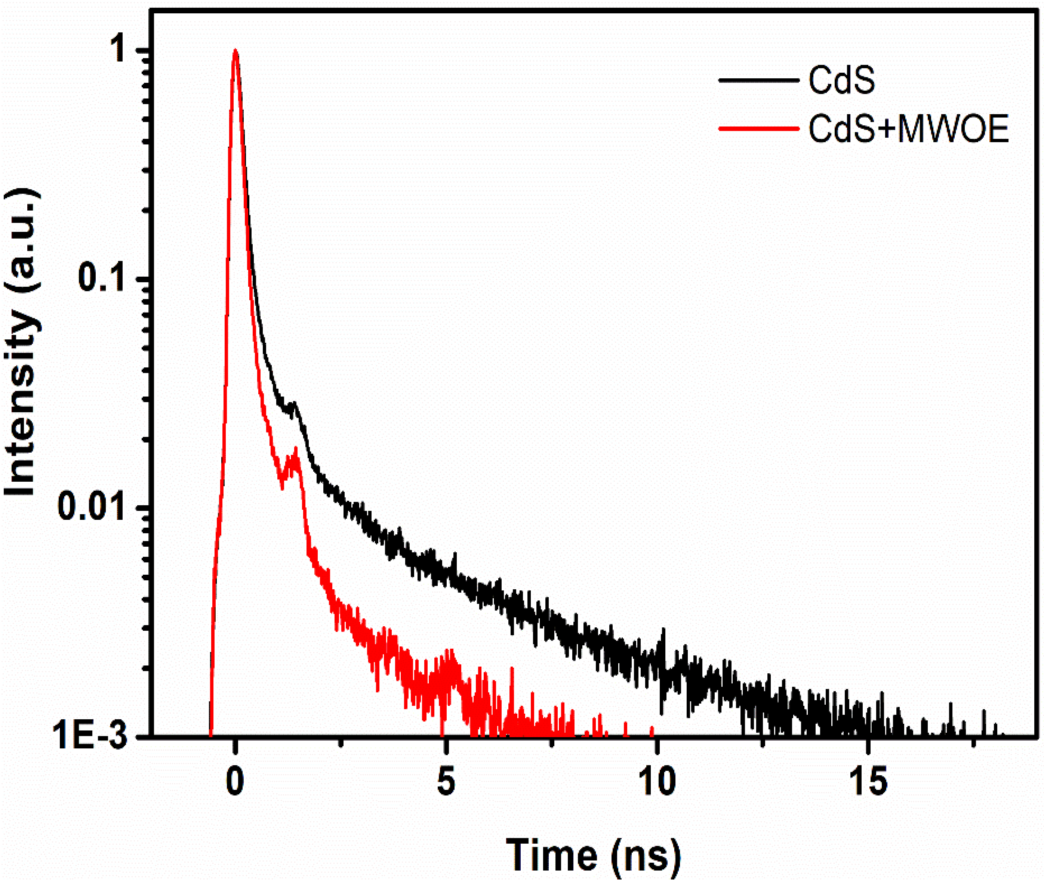

Figure S4. Time-resolved photoluminescence spectra of CdS and MWOE/CdS at 560 nm.

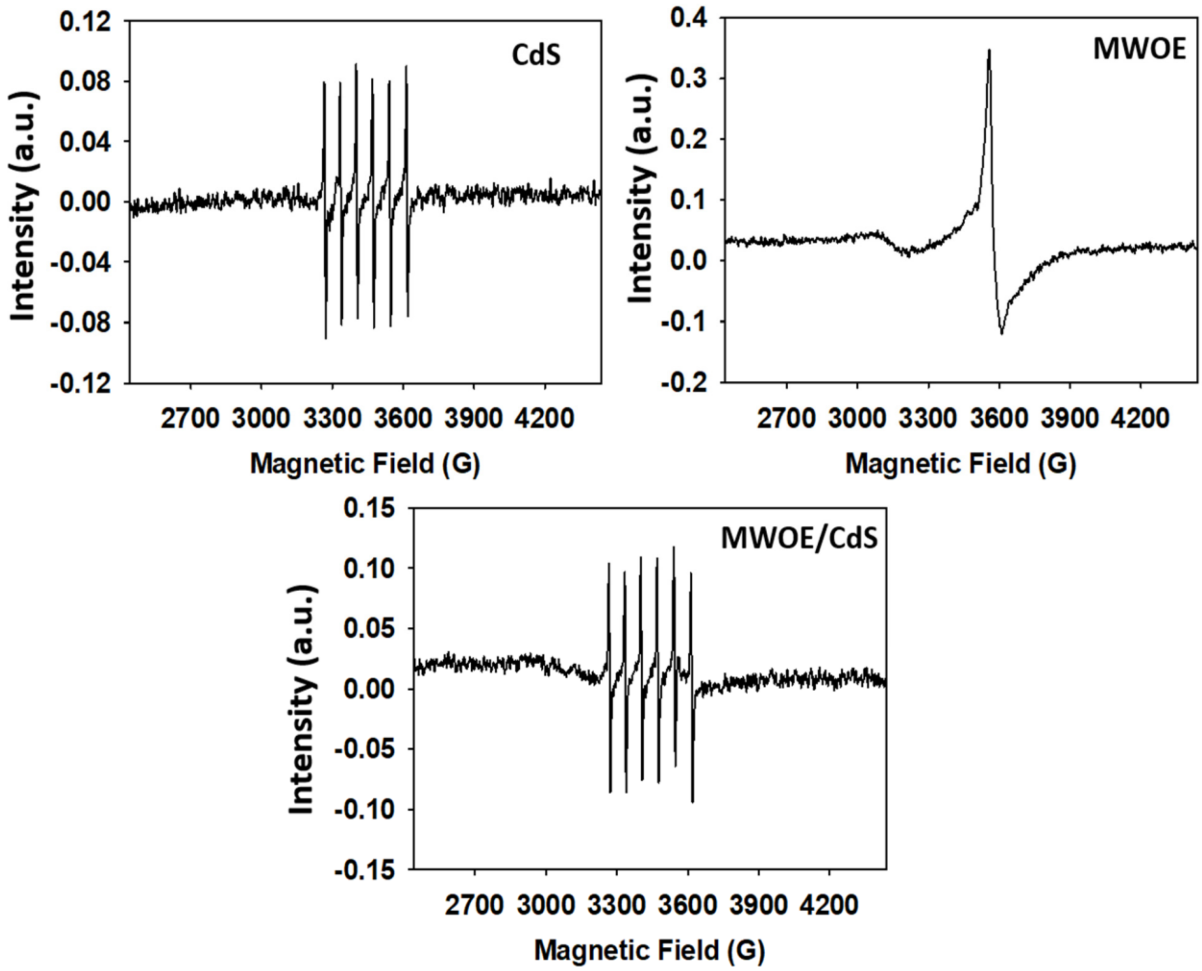

Figure S5. ESR spectra of CdS, MWOE and MWOE/CdS.

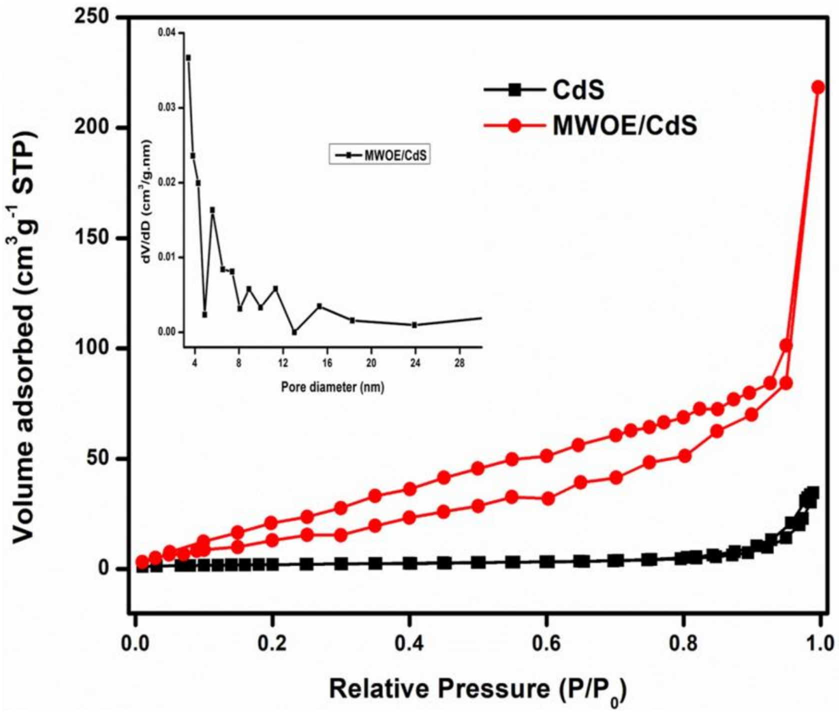

Figure S6. N_2 adsorption/desorption isotherms of CdS and MWOE/CdS and the pore-size distribution of MWOE/CdS nanocomposite.

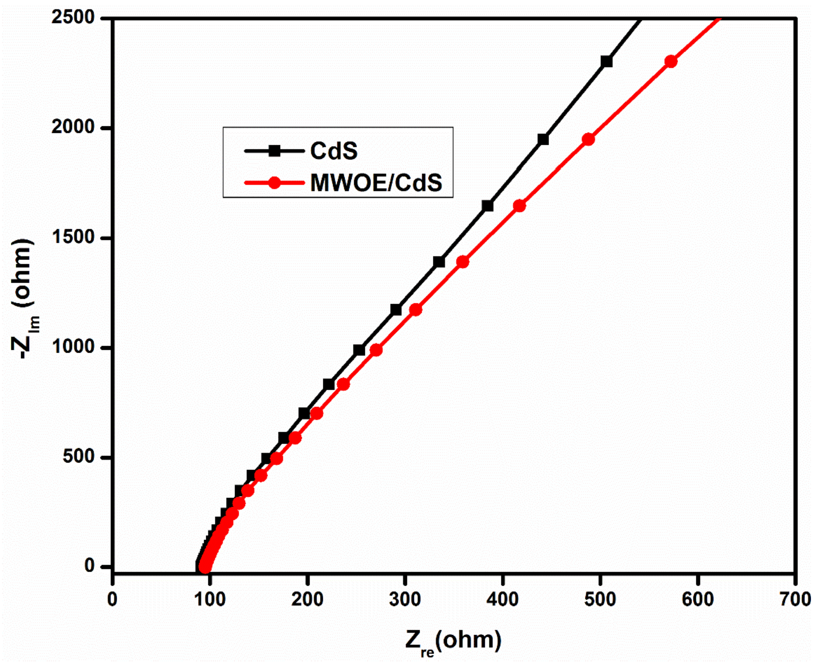

Figure S7. Electrochemical impedance measurements of CdS and MWOE/CdS nanocomposites.

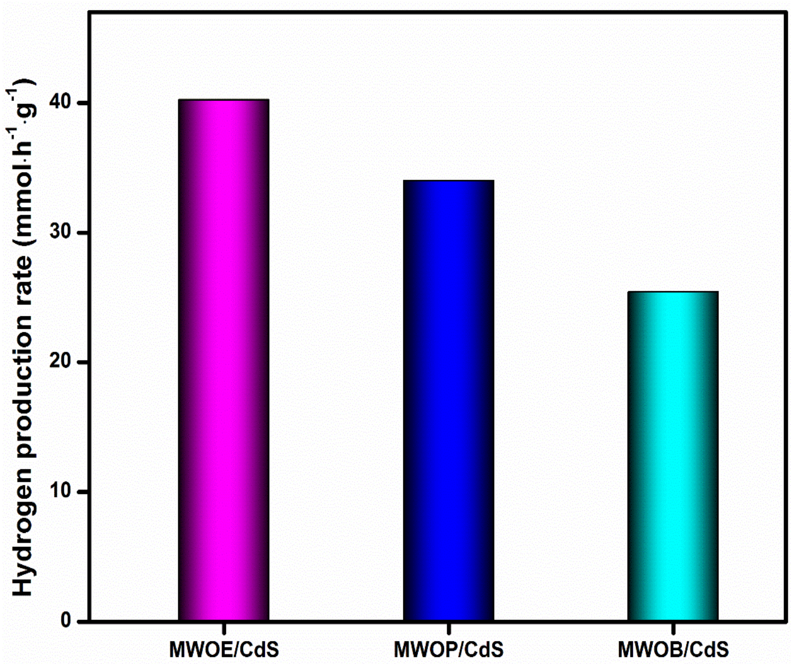

Figure S8. The solvent effect on photocatalytic H_2 production rate.

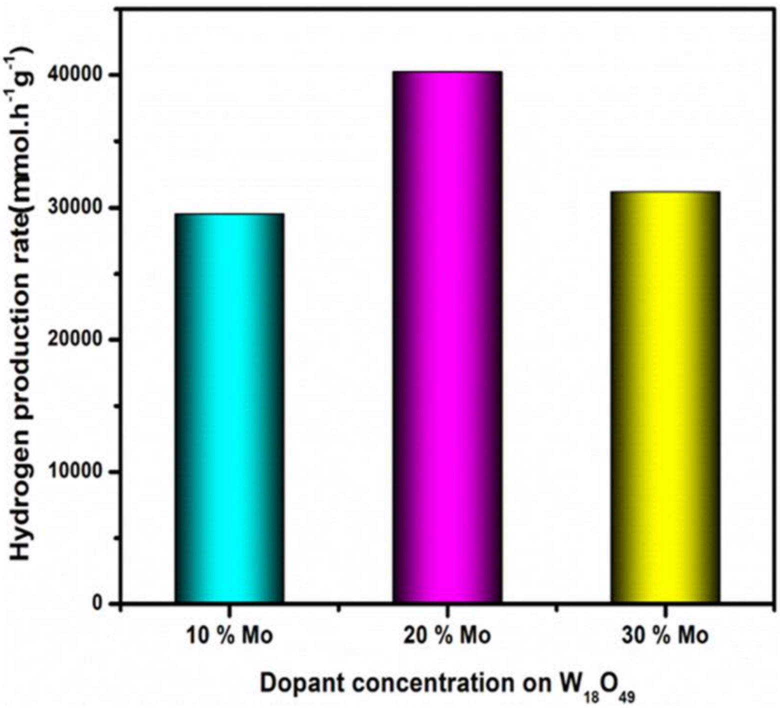

Figure S9. The Mo dopant concentration effect on photocatalytic H_2 production rate.

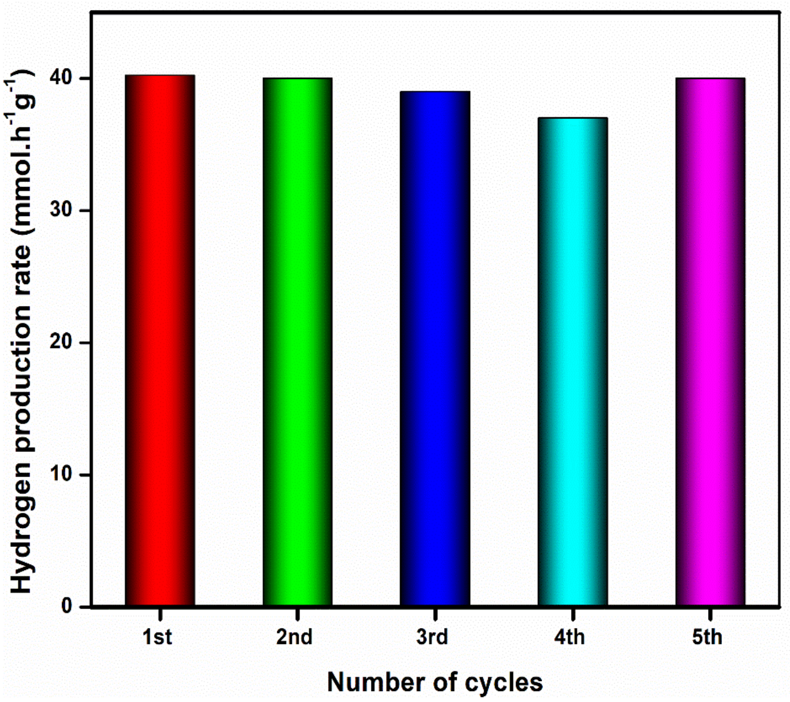

Figure S10. Recycling study of MWOE/CdS nanocomposite**.**

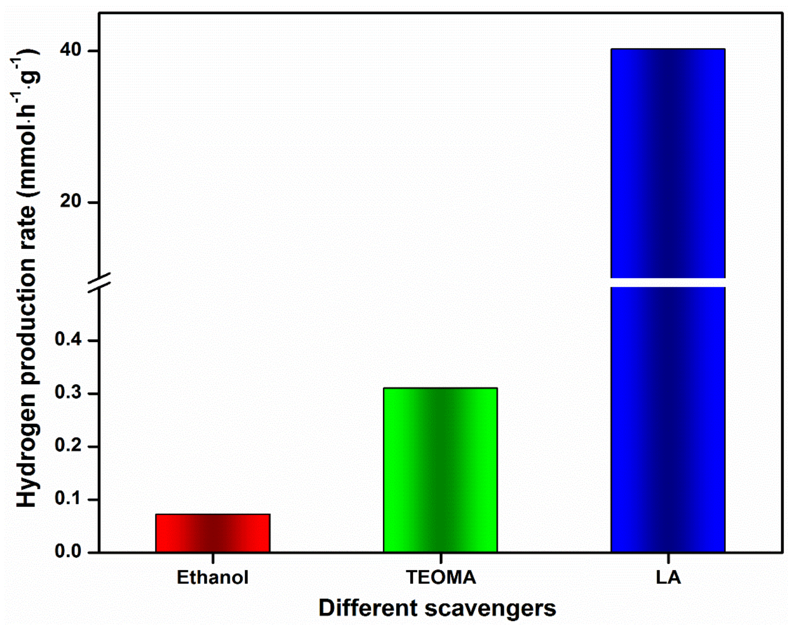

Figure S11. The effect of various scavengers on photocatalytic H_2 production rate.

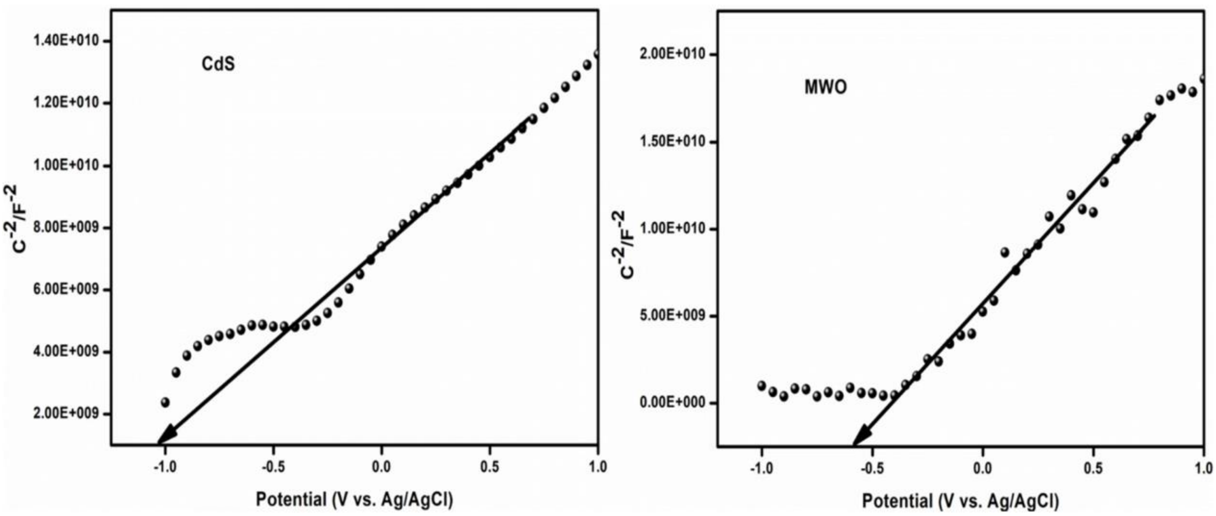

Figure S12. Mott−Schottky plots (Potential vs. $E_{Ag/AgCl}$) of CdS and MWO in 0.5 M Na_2SO_4 electrolyte solution.

Table S1. Comparisons of photocatalytic H_2 production rate for representative W and Mo oxides based photocatalysts.

Photocatalyst	Scavenger	Light source	H_2 production rate ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Reference
Mo-$W_{18}O_{49}$/CdS	**Lactic acid**	**150 W Xe lamp ($\lambda \geq 420$ nm)**	**40,225**	**Present work**
$W_{18}O_{49}$/g-C_3N_4	Triethanolamine	300 W Xe lamp ($\lambda \geq 420$ nm)	738	2
α-MoO_3-WO_3/CdS	Artificial waste water	300 W Xe lamp ($\lambda \geq 420$ nm)	8	3
WO_3/TiO_2	Ethanol	Hg lamp (λ =254 nm)	9,560	4
Cs/WO_3	WO_3:PEG at 1:1 for thin film	250 W Hg lamp (λ=365–550 nm)	3,500	5
WC-CdS	Na_2S/Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	1,370	6
MoO_3-Polymer	Methanol	300 W Hg lamp (λ =420 nm)	350	7
Pt-IrO_2/WO_3	KI solution	Visible light (λ=400–800 nm)	15	8
$CsTaWO_6$/Rh	Methanol	150 W solar (1 sun irradiation)	39	9
Pt/WO_3/CdS/TiO_2	Formic acid	500 W Xe lamp ($\lambda \geq 420$ nm)	1,059	10
CdS/ WO_3	Lactic acid	300 W Xe lamp ($\lambda \geq 420$ nm)	369	11
CdS/Au/WO_3	Na_2S/Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	1,500	12
CdS/Au/U-WO_3	Na_2S/Na_2SO_3	300 W Xe lamp ($\lambda \geq 420$ nm)	1,390	13

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