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Supporting information

MoP is a Novel, Noble-Metal-Free Cocatalyst for Enhanced Photocatalytic Hydrogen Production in Water under Visible Light

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Experimental section

Materials: All the chemicals, including ammonium molybdate tetrahydrate ([$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$], 99.0 %), citric acid monohydrate ($C_6H_8O_7\cdot H_2O$, 99.5 %), diammonium phosphate ([$(NH_4)_2HPO_4$], 99.0 %), cadmium chloride hemipentahydrate ($CdCl_2\cdot 2.5H_2O$, 99.0 %), thiourea (NH_2CSNH_2, 99.0 %), ethylenediamine ($C_2H_4(NH_2)_2$, 99.0 %), and lactic acid ($C_3H_6O_3$, 85.0 %), were obtained from Aldrich or Alfa and used as received without further purification. Water used throughout all experiments was purified through a Millipore system.

Preparation of MoP

MoP was prepared from the molybdenum precursor by means of temperature programmed reduction (TPR) with linear temperature ramps in flowing hydrogen.[1-2] Specifically, 1.33 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 0.99 g $(NH_4)_2HPO_4$, and 3.17 g of CA as a chelating agent were dissolved in 50 mL deionized water to make the molar ratio of Mo:P:CA = 1:1:2. The solution was kept in an oil bath at 90 °C overnight and further dried at 120 °C until the sample turned into fluffy solid with brown color. The obtained material was ground in an agate mortar, and then calcined at 500 °C for 10 h in a tube furnace to obtain the precursor, which was subsequently reduced in a stream of 3 vol. % H_2/N_2 at 850 °C for 2 h (heating rate 5 $°C\cdot min^{-1}$) and then cooled to room temperature. Finally, the as-synthesized MoP was kept in 2 vol. % O_2/N_2 for 2 h for surface passivation to stabilize it in ambient air.

Preparation of CdS nanorods

A solvothermal synthesis carried out by Jang *et al.* was adopted in this study for the preparation of CdS NRs.[3] 3.69 g (16.2 mmol) $CdCl_2 \cdot 2.5H_2O$ and 3.69 g (48.6 mmol) NH_2CSNH_2 were added into a Teflon-lined, stainless steel autoclave (100 ml) which contained 60 ml ethylenediamine. Then, the autoclave was kept at 160 °C for 48 h. After cooling to room temperature, a yellow precipitate was centrifuged and washed with absolute ethanol and deionized water three times each to remove the residue of organic solvent and then dried at 60 °C for 12 h.

Preparation of MoP/CdS catalysts

A certain amount of MoP and CdS NRs was dispersed in a round-bottomed flask with 5 ml absolute ethanol, and then the suspension was stirred and purged with nitrogen for 10 min to remove air. Subsequently, after sonicating for 60 min to disperse the materials, the suspension was dried at 80 °C with stirring under N_2. The obtained sample was ground in an agate mortar for 30 minutes, and then was calcined at 200 °C for 5 h in a tube furnace under Ar. The mass percentages of MoP in the as-prepared samples were 4 wt %, 6.25 wt %, 9.1 wt %, 12.5 wt %, 16.7 wt %, 20 wt % and 25 wt %. For comparison, pure freshly-prepared CdS NRs was also calcined in a similar process in the absence of MoP.

Computational Methods

All calculations were performed using the periodic density functional theory (DFT) implementation available in the Vienna Ab Initio Simulation Package (VASP)[4] with the GGA-PBE gradient correction for exchange-correlation.[5] The projector augmented wave (PAW) potential[6] and the plane-wave cut-off energy of 350 eV were used. 10 ×

10 × 10 and 10 × 10 × 1 Gamma-centered grids were used for bulk and slab calculation, respectively. The convergence for the total energy and force was set to 1×10^{-5} eV and 0.01 eV/Å, respectively. In addition, the k-point was considered more carefully when calculating different slabs. The (001), (100), and (101) surfaces of MoP were investigated. The vacuum layer was set as 30 Å for all of the slabs. The surface energy is defined as this equation:

$$E(surface) = \{E(slab) - n(\mu_{Mo}) - n(\mu_{P})\}/A$$

Where A is the area of the surface, n is the number of atoms in the slab, μ is the chemical potential of the MoP in ground state, the calculated chemical potential of P and Mo is 5.851eV and 11.818 eV, respectively. The work function of different planes of MoP was also calculated using hybrid functional (HSE06).[7] Compared with the results obtained by HSE06 with GGA, the relative error in these two methods is less than 3%, indicating the work function data of MoP are accurate and reliable.

Photocatalytic hydrogen production

To investigate the photocatalytic activities of MoP/CdS NRs photocatalysts for H_2 production from water, 1.0 mg of as-prepared photocatalysts was added into 50 mL round-bottomed flask which contained 18 mL Millipore water and 2 ml lactic acid (10 %, v/v) as a hole sacrificial agent, followed by bubbling with high purity N_2 to remove oxygen. Visible light irradiation was carried out using a 300 W Xe lamp equipped with a 420 nm cut-off filter for 5 h unless otherwise stated.

In order to determine the apparent quantum yields (AQYs) and long-term H_2 production, 450 nm band-pass filter (±5 nm) was used to replace 420 nm cut-filter. No additional lactic acid was added to the system in the whole illumination process. After the first round in 7 h (cycle 1), N_2 gas was bubbled into the reaction suspension, then followed by the second round irradiation (cycle 2). The reaction suspension for photocatalysis was kept for 1 hour, 16 hours and 9 hours in darkness after the first round (cycle 1), the second round (cycle 2) and the third round (cycle 3), respectively, then high purity N_2 gas was bubbled into the flask to remove the gas inside. Hydrogen gas was measured by gas chromatography (GC, SP-6890, nitrogen as a carrier gas) using a thermal conductivity detector (TCD). The amount of hydrogen was quantified by a calibration plot to the internal CH_4 standard.[8-9] AQY defined by followed equation was measured using a 450 nm band-pass filter:

$$\begin{aligned} AQY(\%) &= \frac{number\ of\ reacted\ electrons}{number\ of\ incident\ photons} \times 100\% \\ &= \frac{number\ of\ evolved\ H_2\ molecules \times 2}{number\ of\ incident\ photons} \times 100\% \end{aligned}$$

Photoelectrochemical measurements.

Photoelectrochemical performance of the samples was studied with a CHI 602E electrochemical work station (Shanghai Chenhua Instrument Co., Ltd, Shanghai, China) in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, an Ag/AgCl as a reference electrode, and Pt wire as the counter electrode. The photoresponses were studied under 300 W Xenon lamp with a UV cut-off filter ($\lambda > 420$ nm). A 0.5 M Na_2SO_4 solution was used as the electrolyte. The working electrodes were prepared by dropping a suspension (15 μL) made of MoP/CdS and CdS (MoP/CdS and CdS, 20 mg/mL) onto the surface of a FTO plate, followed by drying at room temperature. The photocurrents were measured under an applied potential of 0 V (vs. Ag/AgCl).

Characterization

The powder X-ray diffraction (XRD) of as-prepared samples was performed on X-ray diffraction (XRD, D/max-TTR III) with graphite monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min^{-1} from 20 to 80 in 2θ. Transmission electron microscopy (TEM) images and energy-dispersive X-ray analysis (EDX) were obtained with a JEM-2011 electron microscope equipped with a Rontec EDX system. The scanning electron microscopy (SEM) measurements were conducted using a JSM-6700F. The morphologies of the samples were also determined by a high resolution transmission electron microscope (HR-TEM, JEM-2010) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data and the valence state of MoP and MoP/CdS were obtained with an ESCALAB 250 instrument. The UV-vis absorption was performed on a SOLID 3700 UV-vis-NIR spectrophotometer. The BET surface area, and pore size were measured on a Quantachrome Autosorb-iQ system at liquid N_2 temperature, and the outgas temperature was 200 °C.

References

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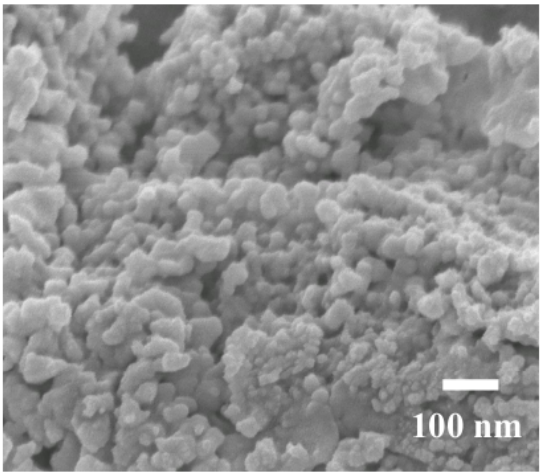

Figure S1. The SEM image of bare MoP.

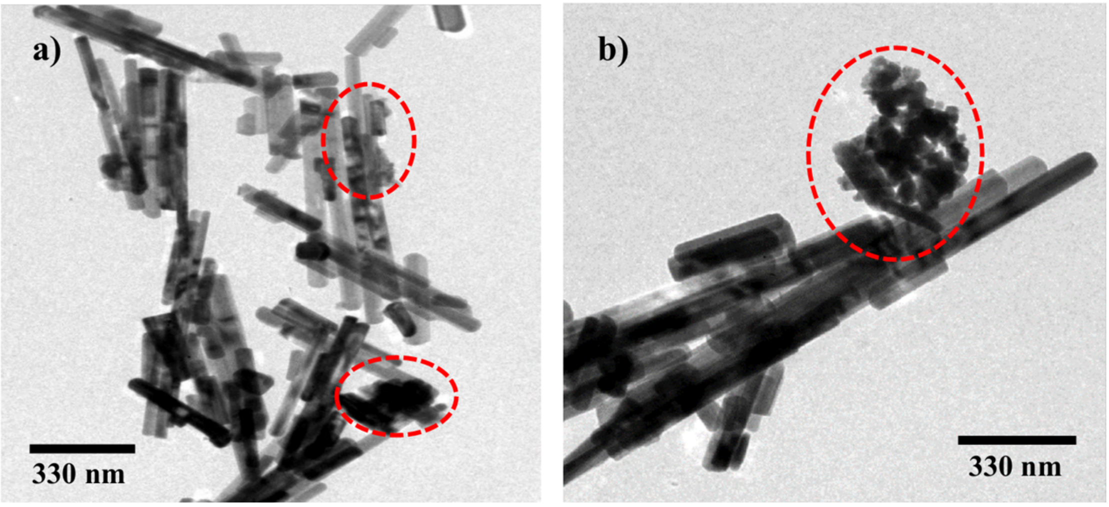

Figure S2. (a) and (b) are the TEM images of 16.7 wt % MoP/CdS NRs.

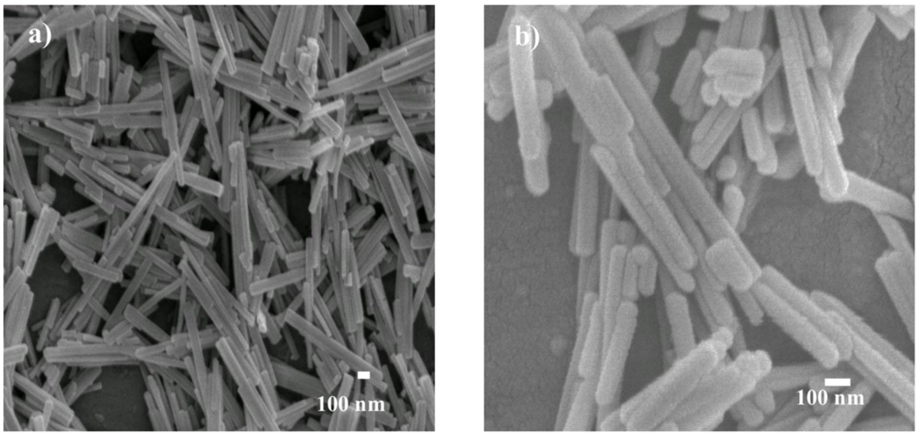

Figure S3. The images of the freshly-prepared CdS NRs (a), and the calcined CdS NRs at 200 °C under Ar atmosphere for 5 h (b).

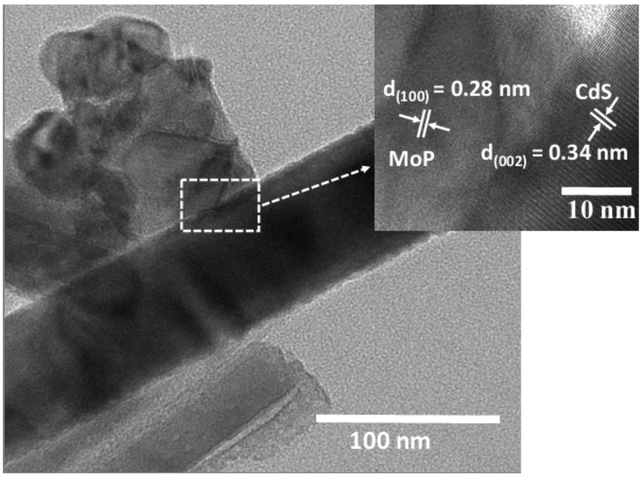

Figure S4. The HR-TEM image of 16.7 wt % MoP/CdS NRs, and the inset image also is shown in Figure 1c.

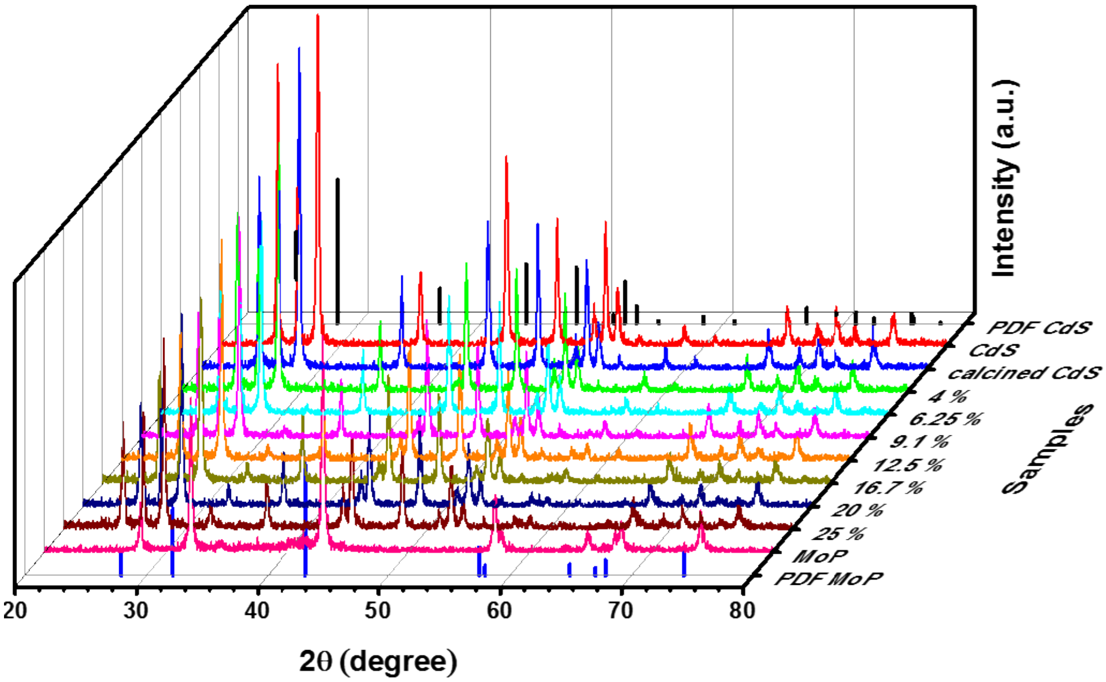

Figure S5. The XRD patterns of MoP/CdS NRs with different contents of MoP.

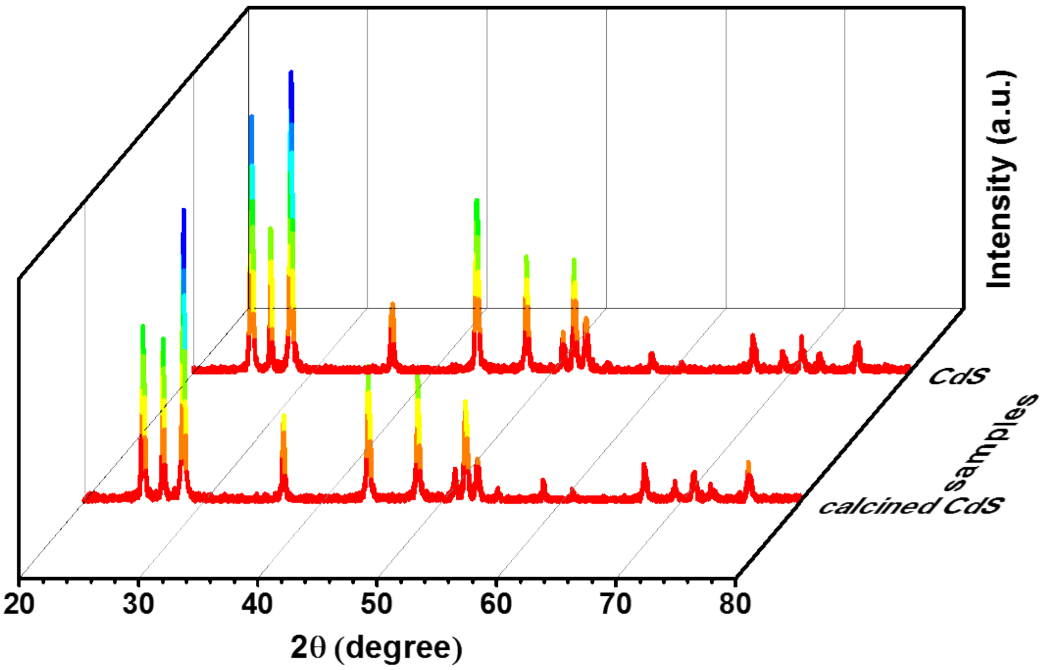

Figure S6. XRD patterns of the freshly-prepared CdS NRs and the calcined CdS NRs.

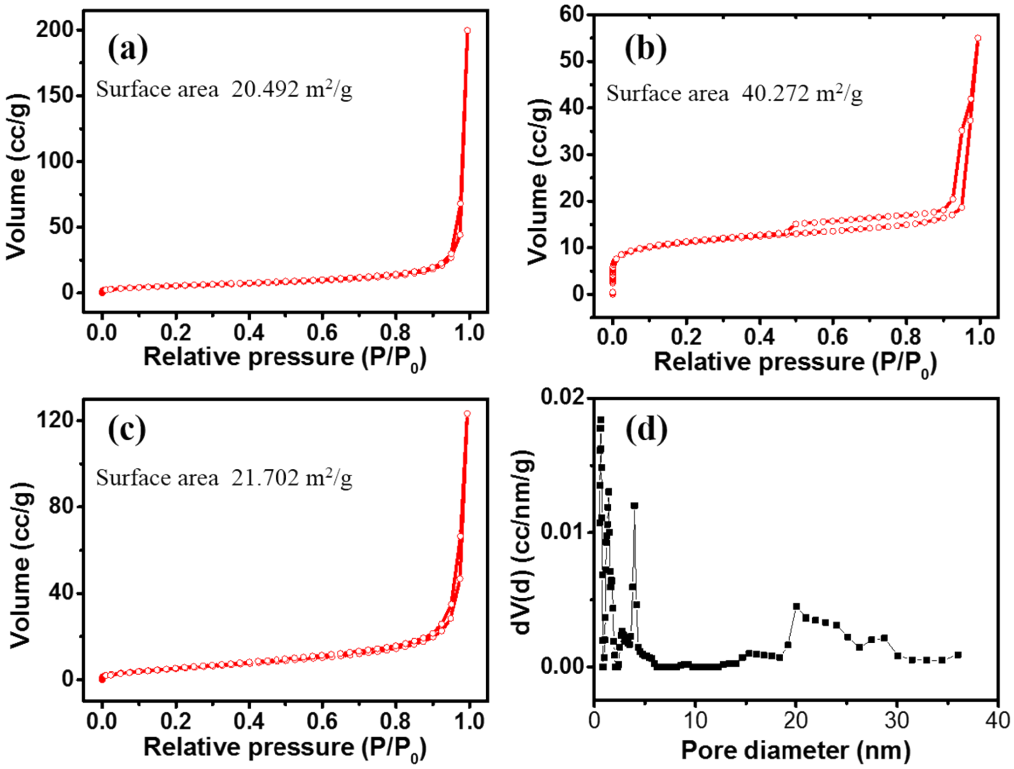

Figure S7. Nitrogen adsorption/desorption isotherm plots of (a) CdS NRs, (b) MoP, (c) 16.7 wt % MoP/CdS NRs (c), and (d) the pore-size distribution curve of MoP.

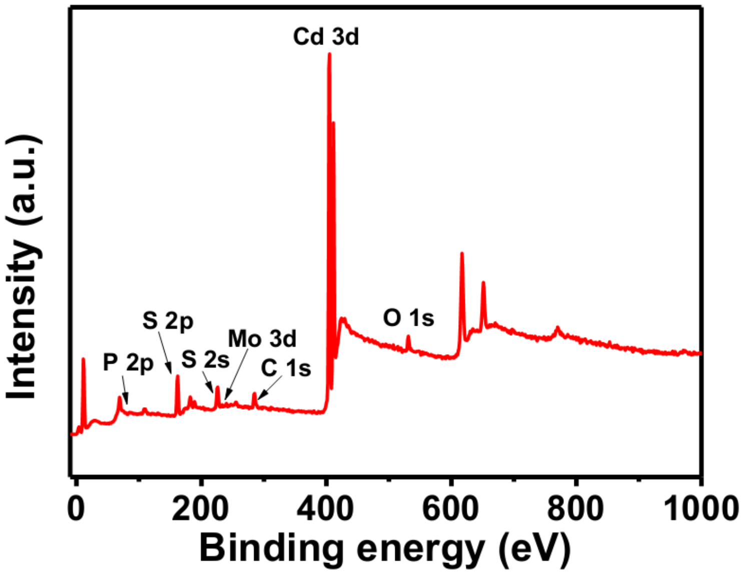

Figure S8. The XPS survey spectrum of 16.7 wt % MoP/CdS NRs before photocatalysis.

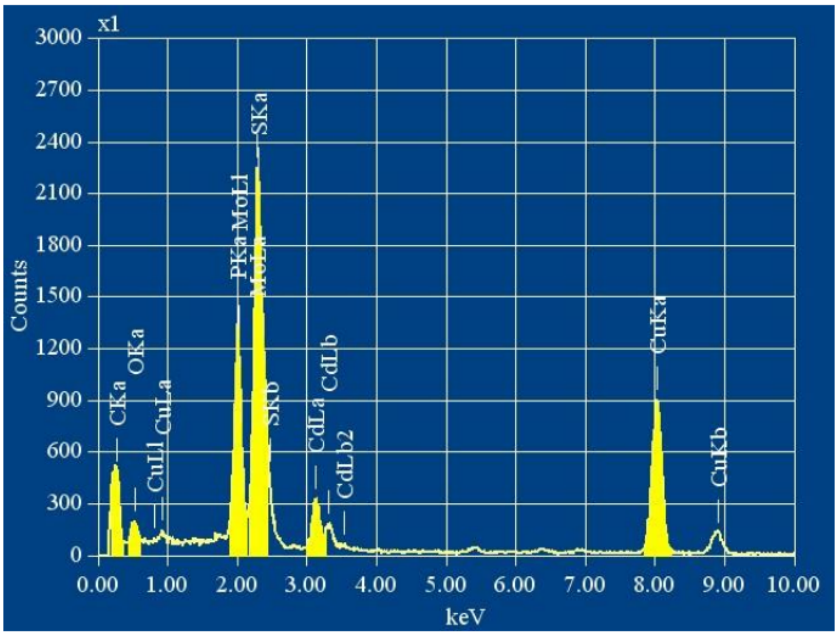

Figure S9. EDX picture of 16.7 wt % MoP/CdS NRs before photocatalysis.

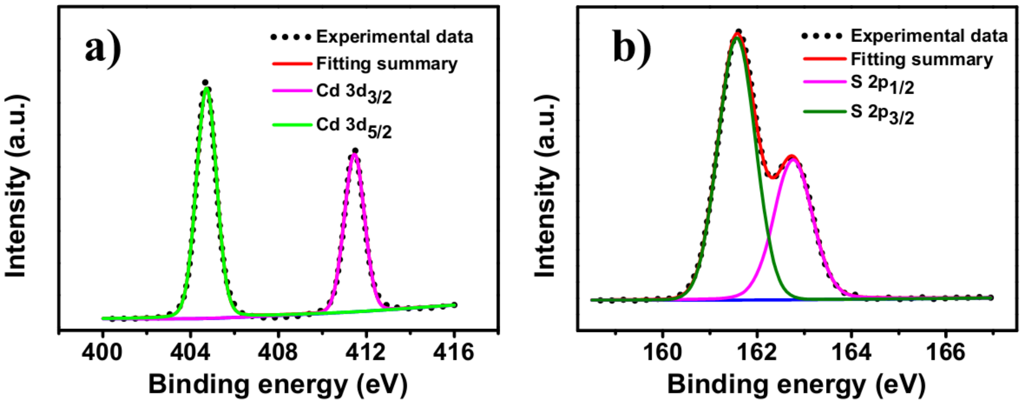

Figure S10. (a) and (b) are the XPS spectra of CdS in 16.7 wt % MoP/CdS before photocatalysis. (a) The XPS spectra of Cd 3d peaks mainly centred at 404.72 eV and 411.45 eV. (b) The XPS spectra of S 2p peaks mianly located at 161.57 eV and 162.76 eV.