Supporting Information

Metallic MoO_2 Cocatalyst Significantly Enhanced Visible-Light Photocatalytic Hydrogen Production over $MoO_2/Zn_{0.5}Cd_{0.5}S$ Heterojunction

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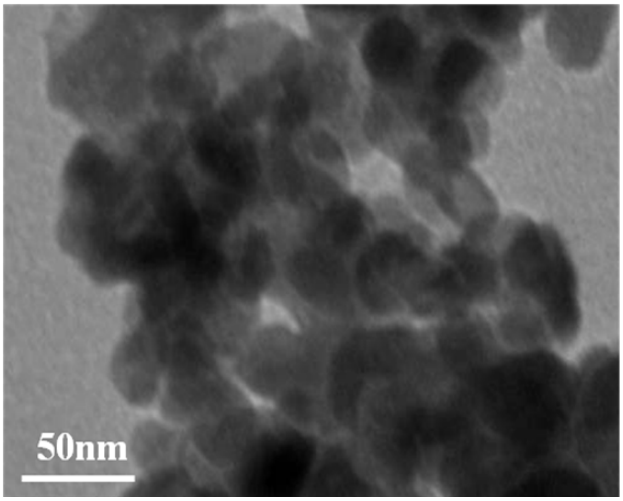

Fig. S1 TEM image of MoO_2 nanoparticles.

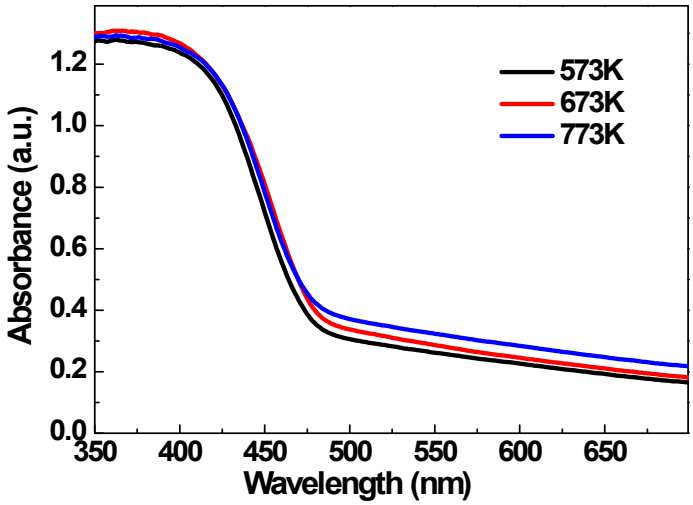

Fig. S2 The UV–vis diffuse reflectance spectra for MoO_2 (2.0 wt %)/$Zn_{0.5}Cd_{0.5}S$ prepared at different temperatures.

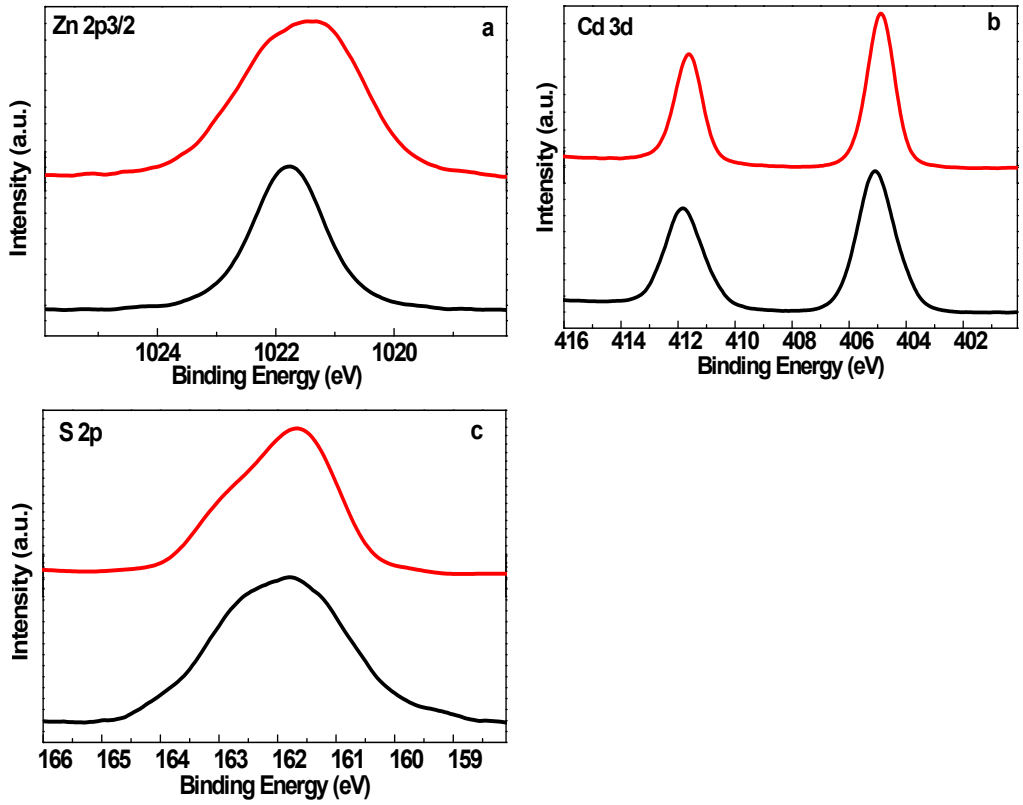

Fig. S3 XPS spectra of samples before (black line) and after loading of MoO_2 (red line) : (a) Zn 2p3/2 XPS spectrum, (b) Cd 3d XPS spectrum, (c) S 2p XPS spectrum.

Table S1 BET surface areas and pore volumes of the samples calcined at the specified temperatures

Treating Temp (K)	573	673	773
Surface Area (m^2/g)	25	21	12
Pore Volume (cm^3/g)	0.196	0.178	0.102

Table S1 shows that the BET surface area and pore volume of the $MoO_2/Zn_{0.5}Cd_{0.5}S$ sample calcined at 773 K are different from those of the sample calcined at 673 and 573 K. The BET surface areas and pore volumes decrease significantly with increasing calcination temperature. It is noted that H_2 evolution rate of MoO_2 (2 wt%)/$Zn_{0.5}Cd_{0.5}S$ hybrid photocatalyst calcined at 573 K (130.3 μmol h^{-1}) is lower than that calcined at 673 K (252.4 μmol h^{-1}) under visible light irradiation (see Fig. 6). This can be explained that the hybrid photocatalyst calcined at 673 K

contain more heterojunction between the MoO_2 and $Zn_{0.5}Cd_{0.5}S$, for efficient charge carrier transfer and separation, high crystallinity for decreasing photogenerated e/h recombination. Further increase of the annealing temperature to 773 K reduced the rate of H_2 evolution to 184.4 μmol h^{-1} for $MoO_2/Zn_{0.5}Cd_{0.5}S$ catalyst, which could be ascribed to the drastic decrease of the surface area and pore volume.

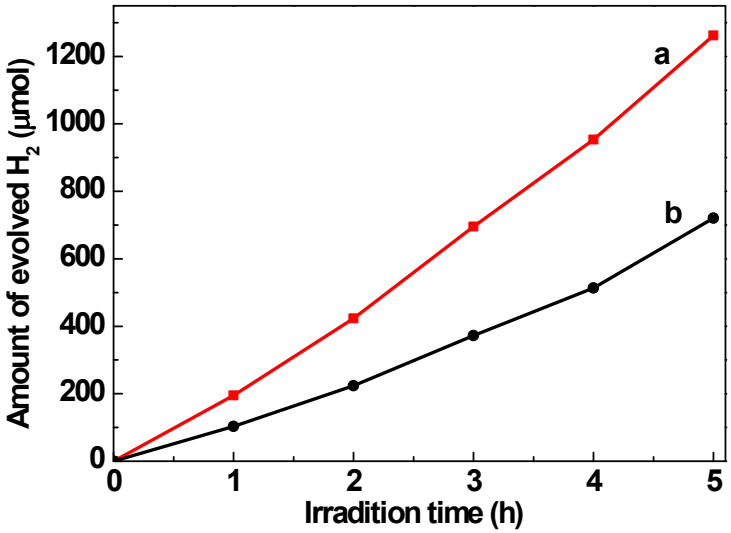

Fig. S4 Time courses of photocatalytic H_2 evolution from water solution on MoO_2 (2 wt%)/$Zn_{0.5}Cd_{0.5}S$ hybrid photocatalyst (a) and Pt (0.5 wt%)/$Zn_{0.5}Cd_{0.5}S$ (b) under visible light irradiation. Reaction conditions: catalyst, 0.1 g; 100 ml aqueous solution containing 0.1 M Na_2S and 0.1 M Na_2SO_3, and light source, 300 W xenon lamp ($\lambda \geq$ 420 nm).

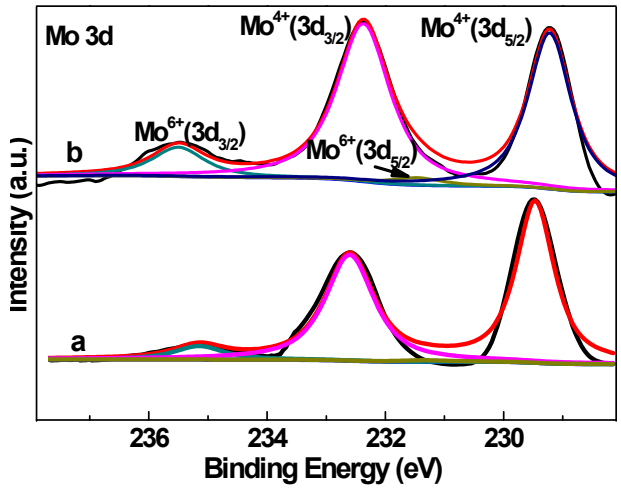

Fig. S5 Mo 3d XPS spectra of MoO_2 (2 wt%)/$Zn_{0.5}Cd_{0.5}S$ before (a) and after (b) photocatalytic reactions.

Table S2 XPS area ratios of chemical states of Mo species for MoO_2 (2 wt%)/$Zn_{0.5}Cd_{0.5}S$ before and after photocatalytic reactions.

Samples	Mo^{4+} area ratio (%)	Mo^{6+} area ratio (%)
$MoO_2/Zn_{0.5}Cd_{0.5}S$ (unused)	93.9%	6.1%
$MoO_2/Zn_{0.5}Cd_{0.5}S$ (used)	91.7%	8.3%

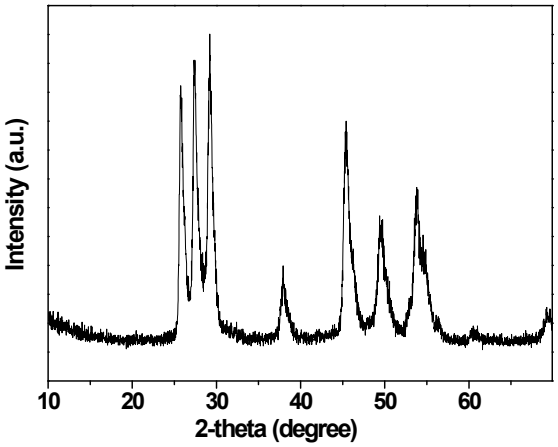

Fig. S6 Powder X-ray diffraction pattern for MoO_2 (2 wt%)/$Zn_{0.5}Cd_{0.5}S$ hybrid after serving as catalysts for a 20 h H_2 evolution.