

Supporting Information

Significantly enhanced photocatalytic hydrogen evolution under visible light over CdS embedded on metal organic frameworks

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Synthesis

MIL-101: A modified hydrothermal procedure reported by Férey [14a] was used to synthesize MIL-101. In a typical synthesis, chromium nitrate onahydrate (2.40 g), terephthalic acid (0.99 g), HF (0.3 mL) and H₂O (30 mL) were mixed in a Teflon liner and kept at 210 °C for 6 h. After cooling, the product in the solution was filtered off to remove excessive reactants, washed with distilled water and absolute ethyl alcohol. The purification of the rude product was carried out in two steps: Suspended and stirred in N, N-dimethylformamide overnight and then treated in ethyl alcohol at 90 °C for 12 h. After washing with ethyl alcohol and drying in air at 90 °C, the pure MIL-101 was obtained.

MOF-5: MOF-5 was synthesized starting from the same organic ligands (terephthalic acid) like MIL-101 but the metal center is Zn. In a 250 mL glass flask, 1.29 g of terephthalic acid, 6.07 g of zinc nitrate hexahydrate were dissolved in 150 mL of N,N-dimethylformamide and heated up to 130 °C for 4 h. The reaction product was cooled down to room temperature and filtered off, washed with absolute ethyl alcohol. The product was then purified in trichloromethane for 2 h, washed with acetone and dried at 90 °C overnight under a reduced pressure.

Pure CdS: 1.85 g of cadmium acetate dehydrate was dispersed in 40 mL of dimethyl sulfoxide. After vigorous stirring, the suspension was transferred into a Teflon-lined

autoclave and held at 180 °C for 12 h. After that, the precipitates from the mixture were filtered and rinsed with acetone, ethanol several times to remove the residue of dimethyl sulfoxide. The final product was dried at 90 °C.

CdS-embedded MOFs: Decorations of CdS clusters on MOFs were carried out using the same method for pure CdS preparation. The difference is introduction of MOFs in the first step. A varying amount of MOFs and Cd(Ac)₂·2H₂O were dispersed in 40 mL of dimethylsulfoxide (DMSO). The suspension was transferred into a Teflon-lined autoclave and held at 453 K for 12 h after mixing. After that, the precipitates from the mixture were filtered and rinsed with acetone, ethanol several times to remove the residue of DMSO. The final product was dried at 353 K. The nominal weight ratios of MOFs to CdS were 0, 5% 10% 20% and 50%, respectively.

Characterizations

Wide angle X-ray powder diffraction (XRD) experiments were conducted on a Rigaku TTRAX III spectrometer with Cu K α radiation from 3° to 60°. HR-TEM micrographs were obtained using a JEM-2100 microscope equipped with an energy dispersive X-ray analysis system EDX INCA from Oxford Instruments. Pore size distributions, BET surface areas and pore volumes were measured by the nitrogen adsorption/desorption measurements using a Micromeritics Tristar II Surface area and porosity analyzer. UV-Vis diffuse reflectance spectra were measured on a Shimadzu UV-2401PC photometer from 200 nm to 800 nm.

Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution by water splitting was performed in a glass reaction cell with quartz cover connected to a closed gas circulation and the gas circulation was swept by high purity N₂ before illumination. 20 mg photocatalyst was dispersed in 100 mL of 10 vol % lactic acid aqueous solution. Prior to photoreaction, a certain amount of H₂PtCl₆ aqueous solution was dripped into the system to load 0.5 wt % Pt through a photochemical reduction deposition method. Then the suspension was exposed to a 300W Xe lamp equipped with an optical filter ($\lambda > 420\text{nm}$) to cut off the light in the ultraviolet region. The reaction solution was stirred continuously and cooled to room temperature by a flow of tap water. The amount of hydrogen evolved was determined at an interval of 1 h with online gas chromatography.

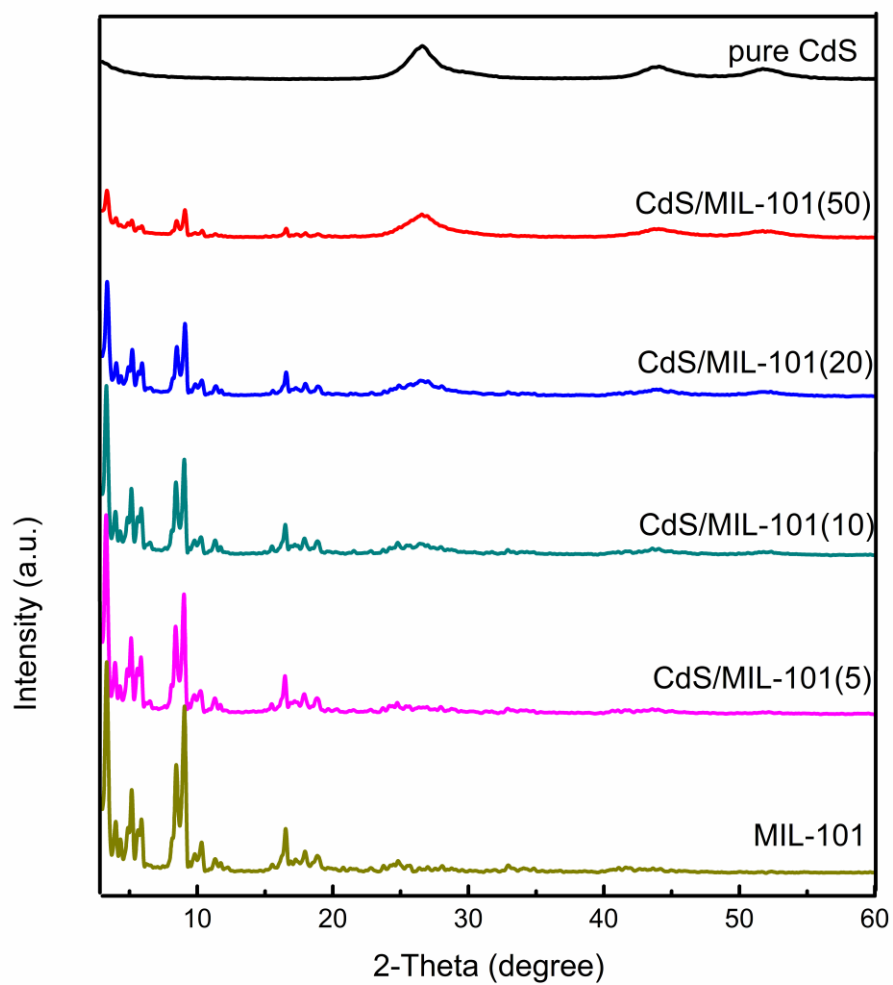


Fig. S1. XRD patterns of pure MIL-101, MIL-101 embedded with different weight ratios of CdS and pure CdS.

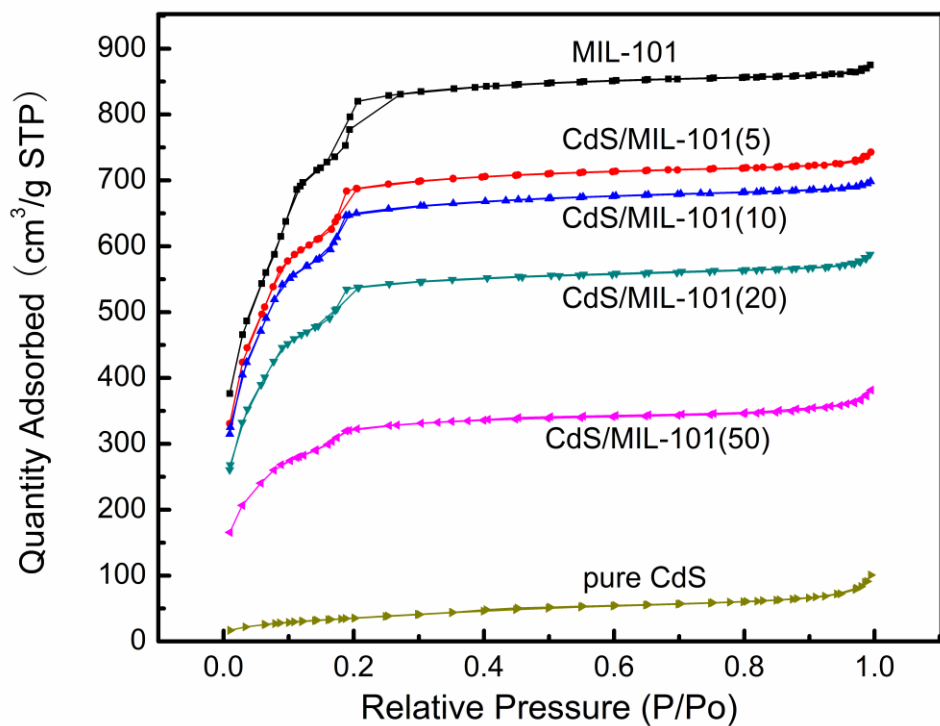


Fig. S2. N₂ adsorption/desorption isotherms of pure MIL-101, MIL-101 embedded with different weight ratios of CdS and pure CdS.

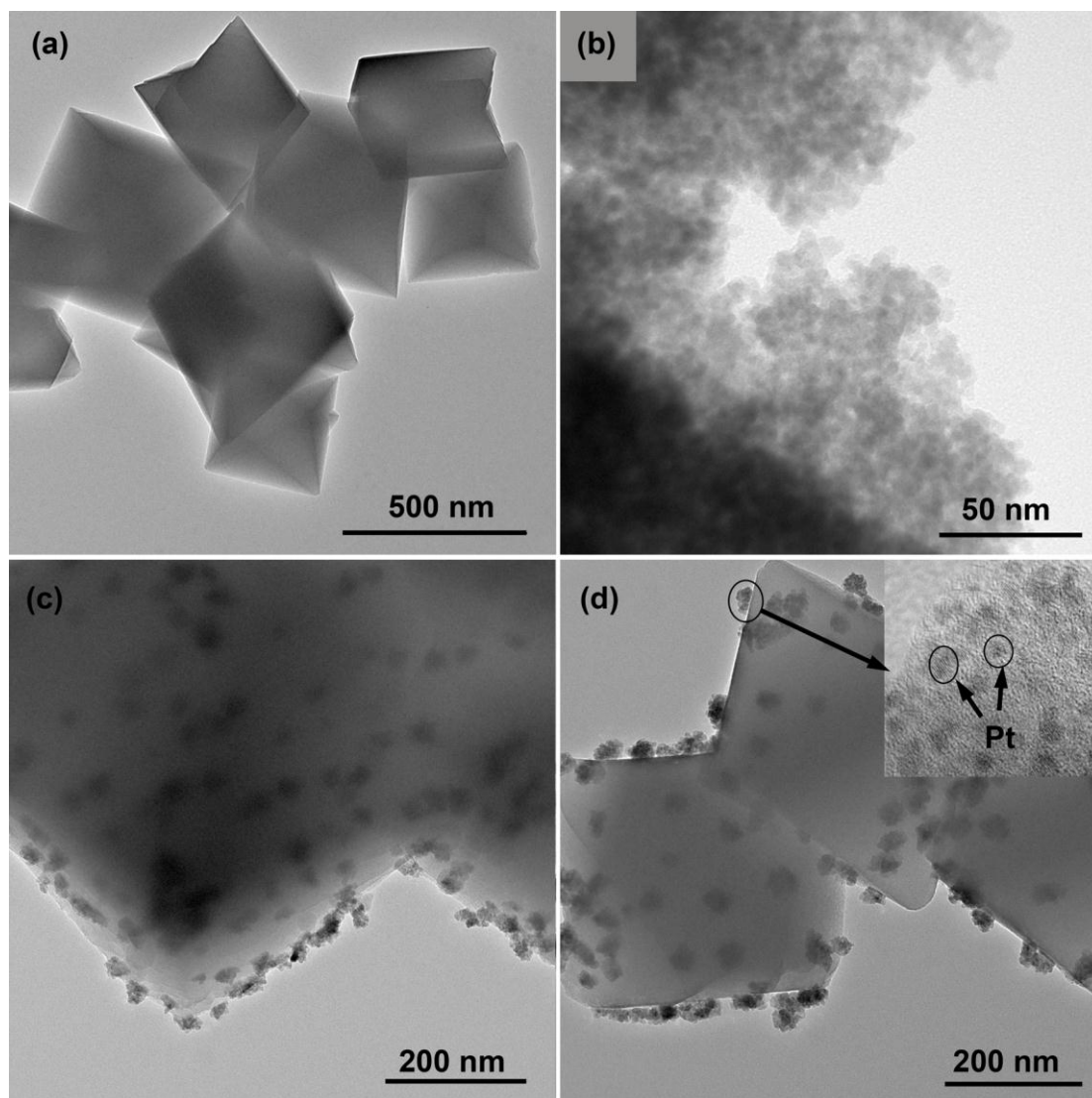


Fig. S3. TEM images of (a) pure MIL-101, (b) pure CdS, (c) fresh CdS/MIL-101 and (d) Pt@CdS/MIL-101 (after photoreaction, inset shows photo-deposited Pt).

Fig. S3b shows that the pure CdS is composed of crystals with a size of about 5 nm and the crystals are highly aggregated. Due to the in-situ photo-reduction process of Pt, fresh CdS/MIL-101 has no Pt particles deposited on (Fig. S3c) and when it underwent photoreaction, Pt particles were loaded (Fig. S3d), it is therefore denoted as Pt@CdS/MIL-101.

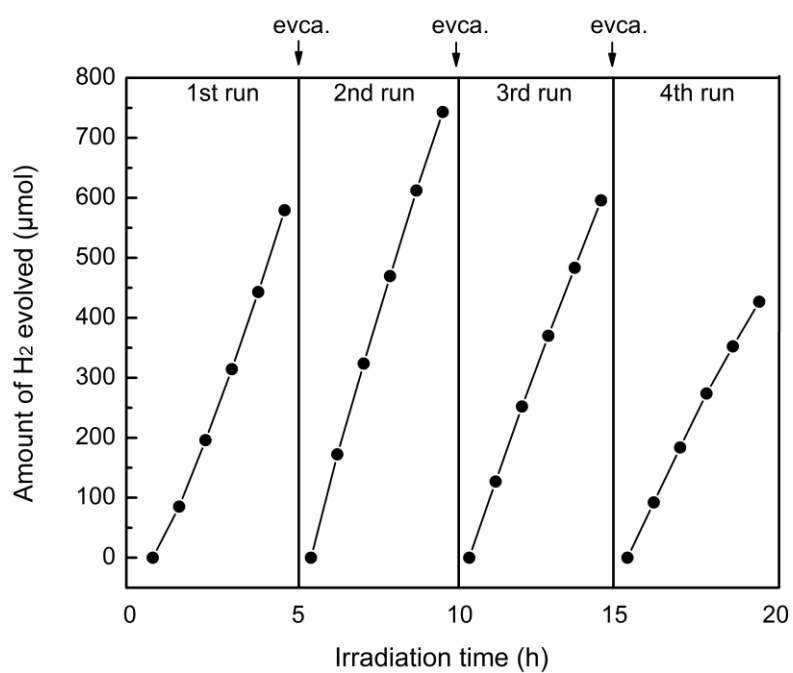


Fig. S4. H₂ production over CdS/MIL-101(10) under visible-light (0.5 wt% Pt deposited).

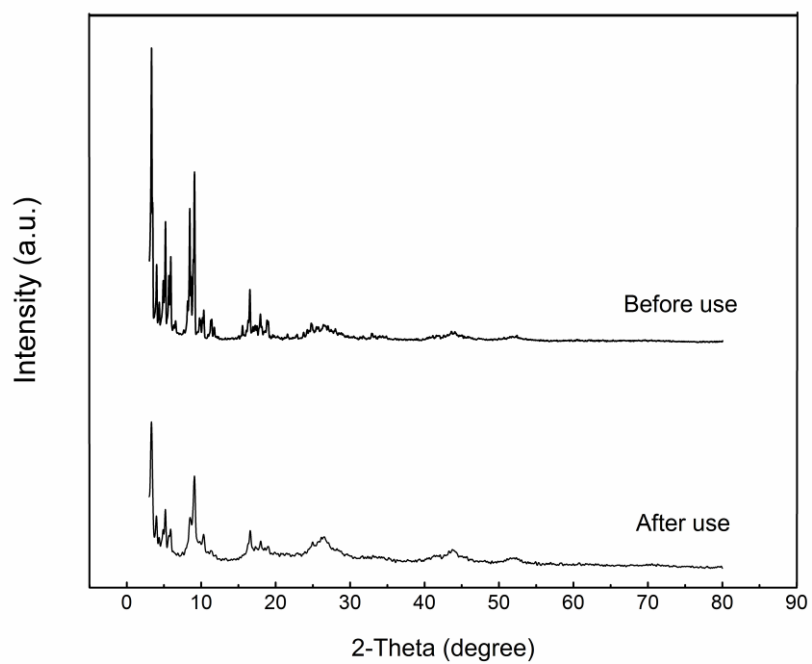


Fig. S5. XRD patterns of CdS/MIL-101(10) (before use and after use).

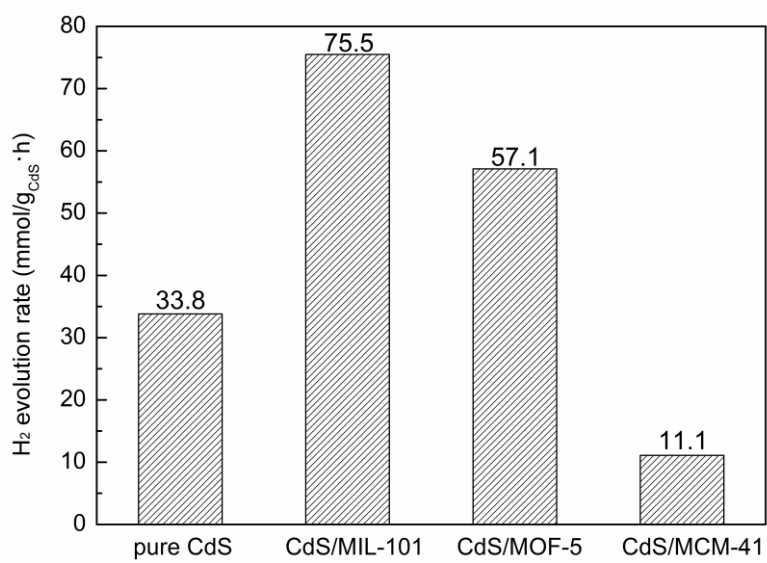


Fig. S6. H₂ production rates of bare CdS and CdS embedded on different frameworks (20mg catalyst, 0.5 wt% Pt loaded).

Table S1. Surface areas, pore volumes, pore sizes of MOF-5 and CdS embedded

MOF-5.

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Activity ($\text{mmol}/\text{g}_{\text{CdS}}\cdot\text{h}$)
MOF-5	787.24	0.36	1.8	-
CdS/MOF-5	71.14	0.13	7.3	57.1