Electronic supplementary information (ESI)

Integrating Mn-ZIF-67 on hollow spherical CdS photocatalysts forming unique interfacial structure for efficient photocatalytic hydrogen evolution and degradation under visible light

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Photocatalytic degradation experiment

A 300 W Xenon lamp with a UV cut-off filter ($\lambda \geq 420$ nm, 700 Mw/cm^2) was used as a simulated visible light source. During photocatalytic degradation experiment, 10 mg of sample powder was placed in Pyrex glass that consists of 50 mL aqueous TC (20 mg/L) solution with magnetic stirring for 5 min. To investigate the adsorption-desorption equilibrium, the mixture solution was magnetic stirred for 60 min in the absence of light prior to the photoreaction. Upon irradiation, 3 mL samples were withdrawn from the suspension every 5 min for up to 60 min. Subsequently, the photocatalysts were removed through a 0.22 μm millipore filter (organic phase) prior to measurement. The obtained supernatant liquid was used to measure the absorption spectra of TC by using UV-vis spectrophotometer.

Table S1. The mixture solution was homogenized by stir vigorously in a 100 mL round-bottom flask. Two metal ion solutions in a quantitative molar ratio (M_1:M_2=8:1) must poured into solution A before ligand solution added, otherwise MOFs will swallow up the CdS nanospheres. Better shape wrapped accompanied by slower dropping speed plus intensive stirring.

Sample Material	Hollow CdS (g)	M_1:$Co(NO_3)_2·6H_2O$ (g)	M_2:$Mn(NO_3)_2·4H_2O$ (g)	2-mim (g)
CdS@Mn-ZIF-67-1 (50%)	0.05	0.0140	0.0020	0.0443
CdS@Mn-ZIF-67-2 (82%)	0.05	0.0232	0.0030	0.0738
CdS@Mn-ZIF-67-3 (100%)	0.05	0.0286	0.0031	0.0909
CdS@Mn-ZIF-67-4 (120%)	0.05	0.0345	0.0040	0.1094

Table S2. Comparison of the TC degradation capacity of CdS@Mn-ZIF-67-1 with other photocatalysts.

Catalyst / mg	V (mL) / C_0 (mg·L^{-1})	Light source (λ > 420 nm)	Time (min)	Result (%)	TOF	Ref.
CdS@Mn-ZIF-67-1 / 10	50 / 20	300 W Xe lamp	60	94.8 %	158.0	This work
NW-Ag / 100	70 / 20	100 W Xe lamp	180	80.0 %	6.2	[30]
Ag_3PO_4/MMO / 50	50 / 40	500 W Xe lamp	90	96.0 %	42.7	[31]
α-Fe_2O_3/d-C_3N_4 / 20	50 / 20	500 W Xe lamp	80	99.1 %	61.9	[32]
CoUiO-66 / 20	100 / 20	300 W Xe lamp	60	94.0 %	156.7	[33]
CInS / 15	50 / 30	300 W Xe lamp	120	100 %	83.3	[34]
$BaTiO_3$/La$(OH)_3$ / 100	100 / 10	350 W Xe lamp	80	100 %	12.5	[35]
γ -In_2Se_3 (EDTA) / 50	50 / 20	300 W Xe lamp	120	91.5 %	15.25	[36]
CdS/Ti_{32}-oxo-cluster / 10	50 / 50	300 W Xe lamp	60	96.3 %	401.3	[37]
$BiVO_4$/g-C_3N_4 / 50	100 / 10	250 W Xe lamp	60	72.3 %	24.1	[38]

Table S3. Comparison of the hydrogen evolution capacity of CdS@Mn-ZIF-67 with other photocatalysts.

Catalyst / mg	Sacrificial agent	Light source (λ > 420 nm)	Time (h)	Result ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Ref.
CdS@Mn-ZIF-67-1 / 100	Na_2SO_3 Na_2S	300 W Xe lamp	4	10462.6	This work
CdS@Mn-ZIF-67-2 / 100				7243.4	
CdS@Mn-ZIF-67-3 / 100				10889.2	
CdS@Mn-ZIF-67-4 / 100				10125.5	
ZIF-67-1@CdS / 50	Lactic acid	300 W Xe lamp	3	4123.1	[26]
ZIF-67-2@CdS / 50				17196.6	
ZIF-67-3@CdS / 50				4542.8	
ZIF-67-4@CdS / 50				3565.4	
CdS/ZIF-67 / 20	Lactic acid	5W LED white light	5	308.0	[24]
Hollow CdS (Pt) / 5	Lactic acid	300 W Xe lamp	4	21654	[25]
Hollow CdS / 5	Lactic acid	300 W Xe lamp	4	3140	[25]
CdS tube / 5	Lactic acid	300 W Xe lamp	4	312.6	[39]
Co_3O_4/CdS/Ni / 20	Lactic acid	5W LED white light	5	5120.0	[40]
CdS/h-TiO_2 / 50	Na_2SO_3 Na_2S	300 W Xe lamp	4	2149.2	[27]
H-CdS@C_3N_4 / 20	Na_2SO_3 Na_2S	300 W Xe lamp	3	4390.0	[28]
CdS@TiO_2@Au / 20	Na_2SO_3 Na_2S	300 W Xe lamp	5	1720.0	[29]
MnOx/CdS/CuS / 25	Na_2SO_3 Na_2S	300 W Xe lamp	6	2425.4	[41]
Laser-CdS / 20	Na_2SO_3 Na_2S	300 W Xe lamp	4	765.5	[42]
g-C_3N_4/CdS / 100	TEOA	300 W Xe lamp	5	716.0	[43]
CDs/g-C_3N_4/MoS_2 / 20	TEOA	300 W Xe lamp	2	517.2	[1]
CdS QDs/CFO@ZFO / 20	Methanol	150 W Xe lamp	1	366.0	[6]

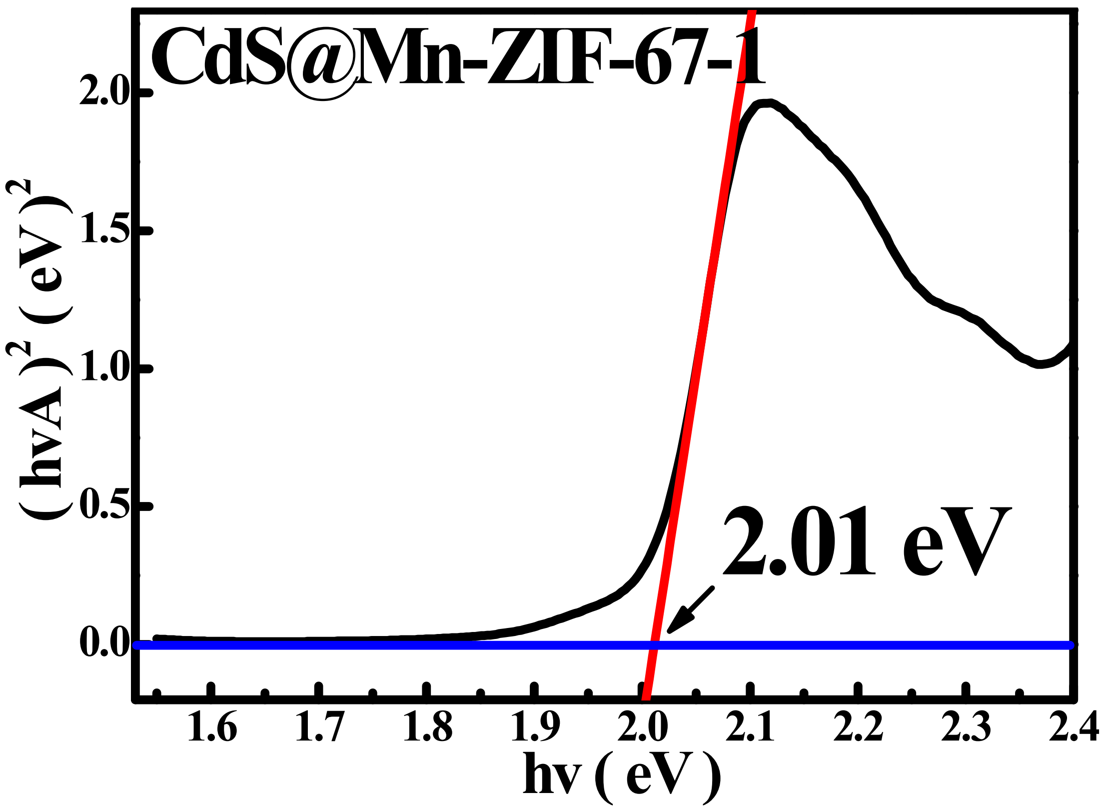

Fig. S1 The band gap energy of photocatalyst CdS@Mn-ZIF-67-1.

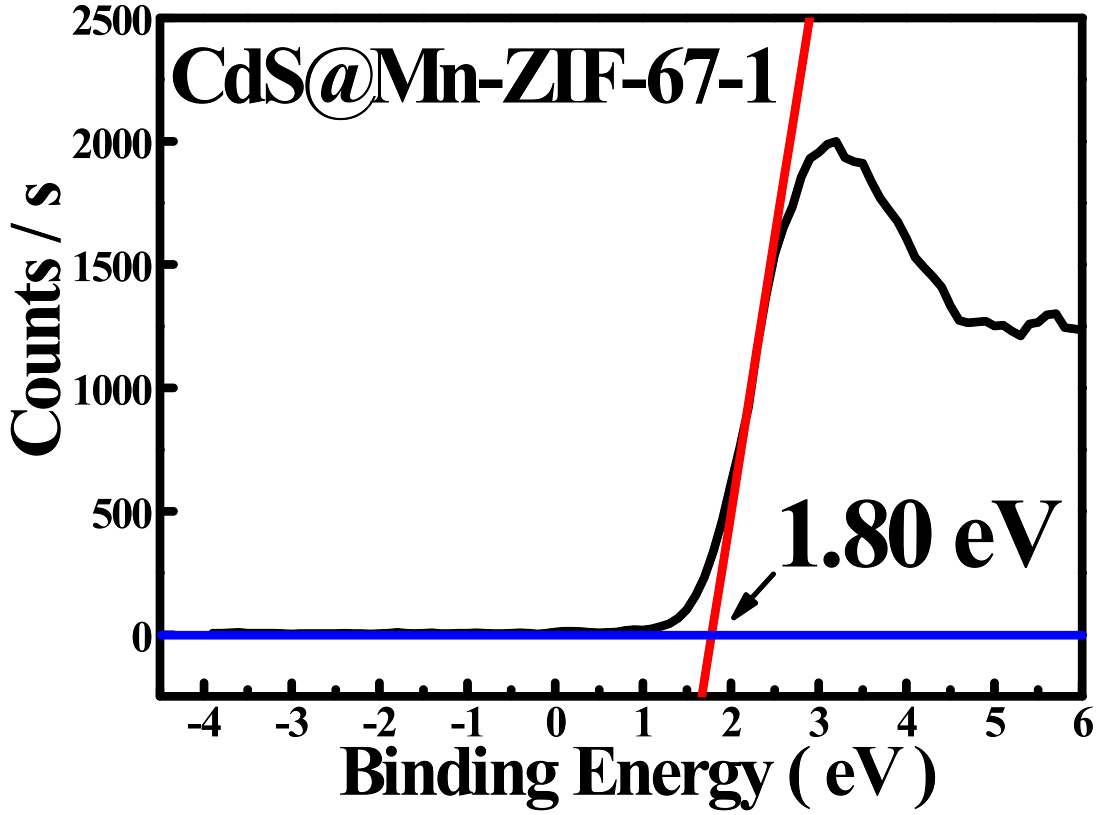

Fig. S2 The valence band position of photocatalyst CdS@Mn-ZIF-67-1.

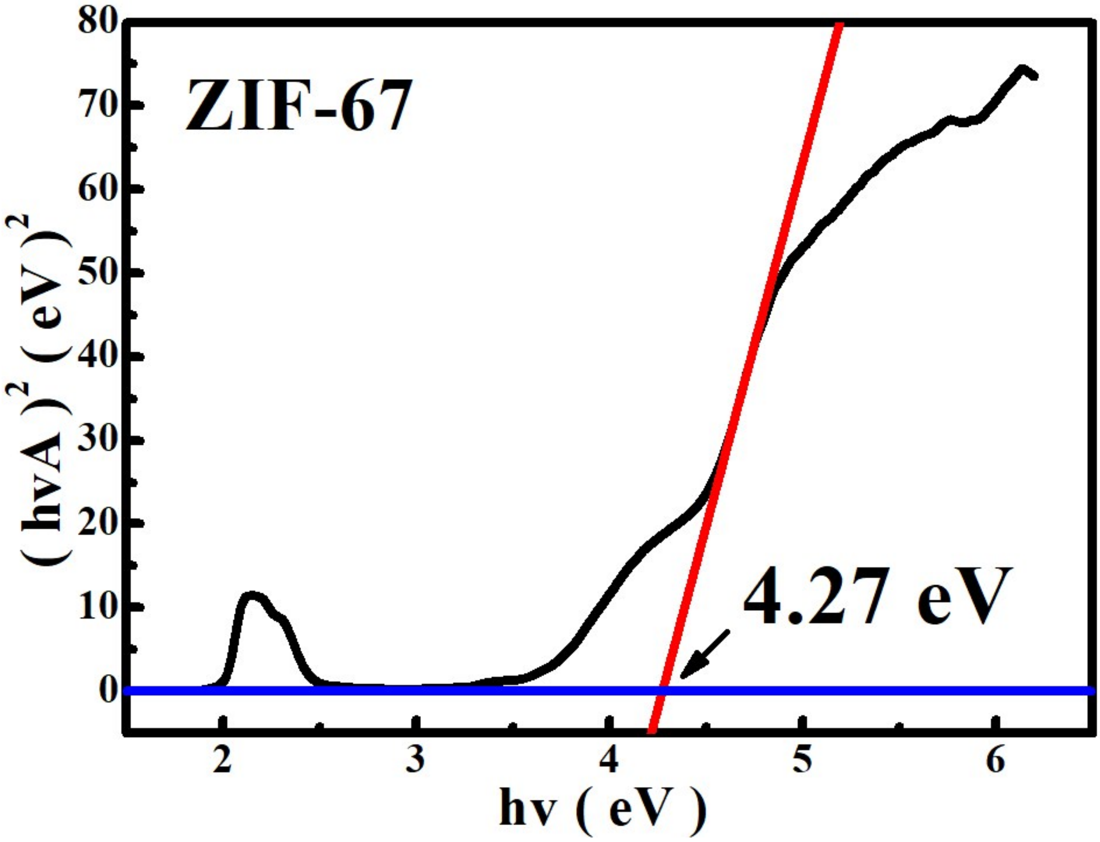

Fig. S3 The band gap energy of pure ZIF-67.

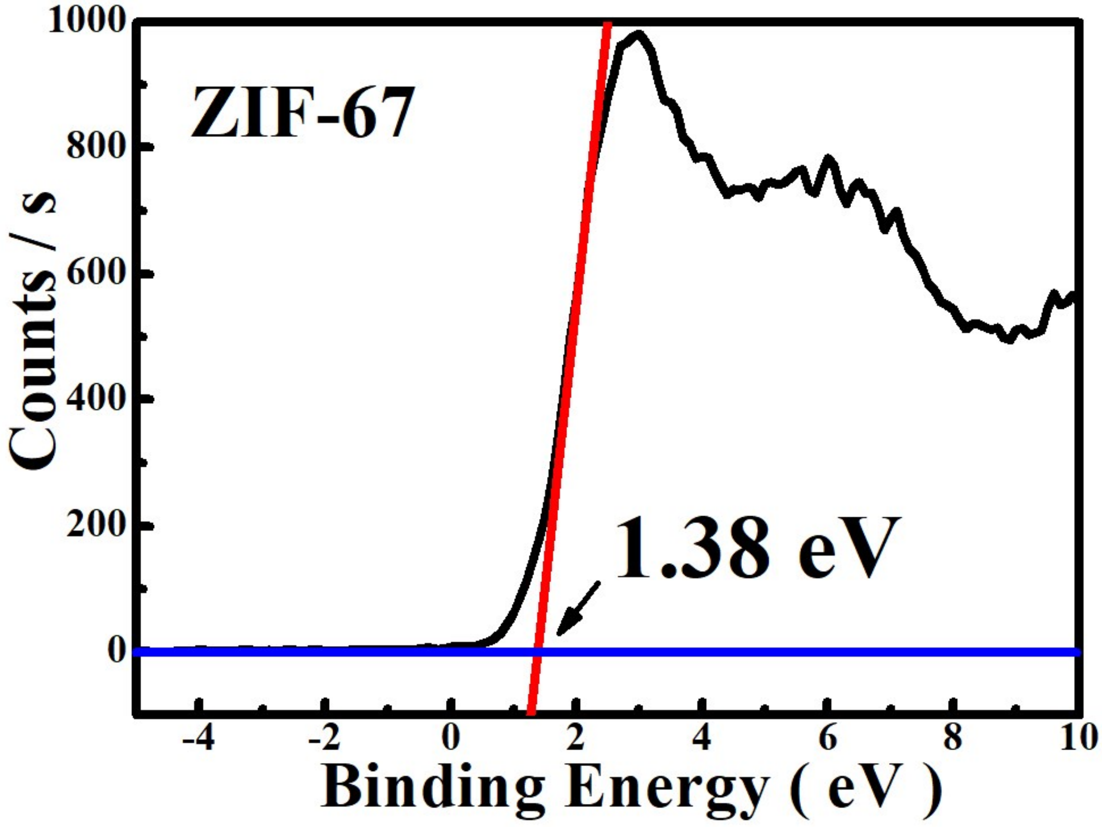

Fig. S4 The valence band position of pure ZIF-67.