## Supporting information for

# Fabrication of Cd(II)-MOF-based ternary photocatalytic composite

### materials for H2 production via gel-to-crystal approach

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#### I. Instruments and materials

All the chemicals were obtained from commercial sources (Acros) and used without further purification. Infrared (IR) spectrums were obtained in the 400-4000 cm<sup>-1</sup> range using a Bruker ALPHA FT-IR Spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. <sup>1</sup>H NMR data were collected on a Bruker Avance-300 spectrometer. Chemical shifts are reported in  $\delta$  relative to TMS. All crystal data were obtained by Agilent SuperNova X-Ray single crystal diffractometer. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. UV-Vis spectrums were obtained by UV-Visophotometer (UV 2250, Shimadzu). Thermogravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10 °C/min. XRD pattern was obtained on D8 ADVANCE Xray powder diffractometer (XRPD) with Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope equipped with energy-dispersive X-ray detector (EDS). TEM were performed on JEM-2100 transmission electron microscope equipped with energy-dispersive X-ray detector (EDS). XRD pattern was obtained on D8 ADVANCE X-ray powder diffractometer (XRPD) with Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). UV-Vis spectrums were obtained by UV-Visophotometer (UV 2250, Shimadzu). Mott–Schottky analysis and electrochemical impedance spectra (coated on ITO as working electrode, Pt as counter electrode and NaBF<sub>4</sub> aqueous solution as electrolyte) was measured on the electrochemical analyzer (CHI660D Instruments).

#### II. Characterization of 1-8.





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Fig. S1 Top: The ORTEP figure of 1 and its 3D framework with  $11 \times 11$  Å channels. Bottom: Simulated and measured XRPD patterns of 1. The picture of Cd(II)-MOF (1) crystals are inserted.



Fig. S2 TEM images of 2 to 4 after treated at 90°C for 3 days showing no essential changes happened to their fibrillar structures.



Fig. S3 SEM images of 2 to 4.



Fig. S4 SEM image of 5 and 6.



Element	В	С	Ν	0	F	S	Ti	Cd	Au
Percentage (%)	7.17	9.27	8.66	13.04	25.85	0.38	4.59	13.26	17.78

Fig. S5 EDS spectrum of 7 and the corresponding elemental percentages.





Element	В	С	Ν	0	F	S	Ti	Cd	Au
Percentage (%)	6.01	9.66	7.93	10.66	25.39	0.66	3.54	16.9	19.25

Fig. S6 EDS spectrum of 8 and the corresponding elemental percentages.



Fig. S7 For comparision, photographs of crystals of Cd(II)-MOF (1) (a), intact (b) and broken (c) crystals of CdS@Cd(II)-MOF (9) are shown. (d) TEM image of CdS@Cd(II)-MOF (9). The HRTEM image shows that the size of the CdS cluster is ca. 7-10 nm and the lattice fringes of individual CdS particle with *d* spacing of 0.208 nm assigned to the (220) lattice plane of the cubic CdS. (e) The XRPD patterns of 1 and CdS@Cd(II)-MOF (9). The pictures of 1 and 9 are inserted.



Fig. S8 Left: The XRPD patterns of Cd(II)-MOF (1), Cd(II)-MOF@TiO<sub>2</sub> (10) and TiO<sub>2</sub>. Middle: SEM of Cd(II)-MOF@TiO<sub>2</sub> (10) (inset is the individual microcrystal of 10) and corresponding element mapping. Right: HRTEM image of Cd(II)-MOF@TiO<sub>2</sub> (10). As shown in the HRTEM image, the observed lattice spacing of 0.357 nm is corresponding to the (101) plane of anatase TiO<sub>2</sub> crystal (ca. 10-15 nm).



Fig. S9 EDS spectrum of Cd(II)-MOF@TiO<sub>2</sub> (10) and the corresponding elemental percentages.



**Fig. S10** The XRPD patterns performed on the samples obtained from ZnO,  $CeO_2$  and  $SiO_2$  triggered gel to crystal transformation based on CdS@Cd(II)-MOG. As shown in the figure, only the characteristic peaks related to the corresponding metal oxides were observed in the measured XRPD patterns.



**Fig. S11** Diffuse reflectance spectra of Cd(II)-MOF (1), CdS@Cd(II)-MOF@TiO<sub>2</sub> (7), CdS@Cd(II)-MOF@TiO<sub>2</sub> (8), CdS@Cd(II)-MOF (9), Cd(II)-MOF@TiO<sub>2</sub> (10).

#### III. Synthesis of binary composite materials of 9 and 10

Synthesis of CdS@Cd(II)-MOF (**9**). A aqueous solution of Cd(BF<sub>4</sub>)<sub>2</sub> (80 mg, 0.248 mmol) was added to a MeOH (3 mL) solution of L (46.4 mg, 0.118 mmol) and Na<sub>2</sub>S (10 mg, 0.128 mmol) with a molar ratio of Na<sub>2</sub>S/L/Cd(BF<sub>4</sub>)<sub>2</sub> = 1.1 : 1 : 2.1. The resulting slurry was sealed in an autoclave (10 mL) and incubated at 90°C for 3 days. **9** was obtained as yellow crystals in 45% yield (based on L). IR (KBr pellet cm<sup>-1</sup>): 3357(w), 3075(w), 1606(s), 1478(m), 1402(w), 1228(w), 1057(vs), 795(s), 724(s), 619(m), 494(w). Elemental analysis (%): C 36.98, H 3.52, N 10.45, S 3.92. Synthesis of Cd(II)-MOF@TiO<sub>2</sub> (**10**). An aqueous (2 mL) solution of Cd(BF<sub>4</sub>)<sub>2</sub> (50 mg,

0.155 mmol) was added to a MeOH (3 mL) solution of L (46.4 mg, 0.118 mmol)  $(L/Cd(BF_4)_2 = 1 : 1.3)$ . The resulting slurry was sonicated to a stable gel phase, then the TiO<sub>2</sub> powder (25 mg) was added and mechanically stirred homogeneously. The TiO<sub>2</sub>-containing gel was incubated at 90°C for 20 h and precipitates formed at the bottom of the <sup>6</sup>

solution. The obtained white crystalline solids were successively washed by MeOH and ether, then dried in air to generate **10**. IR (KBr pellet cm<sup>-1</sup>): 3357(w), 3095(w), 1607(vs), 1479(m), 1403(w), 1230(w), 1059(vs), 793(s), 684(m), 441(w). Elemental analysis (%): C 28.16, H 2.00, N 7.91.

#### IV. Typical catalytic experiments

**Typical catalytic procedure**: The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system (Labsolar-IIIAG). photocatalyst (20 mg) was suspended in an aqueous solution (50 mL) of Na<sub>2</sub>SO<sub>3</sub> (0.025 M)/Na<sub>2</sub>S (0.1 M). The suspension was then thoroughly degassed with N<sub>2</sub> for 30 min in the dark to remove the dissolved oxygen and establish the adsorption–desorption equilibrium. A 300 W xenon (PLS-SXE300C, Perfect light Co., Beijing) light source with a UV cut-off filter ( $\lambda > 400$  nm) was used in the experiment. The distance between the light source and the reaction cell is kept at 30 cm. H<sub>2</sub> is detected by an online gas chromatograph (GC-2014C, Shimadzu, TCD, nitrogen as a carrier gas and 5Å molecular sieve column). The reactors were calibrated by injection of known quantities of H<sub>2</sub> into the circulation system after each experiment. No obvious induction time was observed in the experiment benefited from premixing the catalyst and the solution.

**Calculation of quantum efficiency.** The apparent quantum efficiency (QE) was determined under the similar photocatalytic reaction condition except that a 420 nm band-pass filter was used instead of the UV cut off filter. The focused intensity on the flask was ca. 65.0 mW cm<sup>-2</sup>, which was measured by a FZ-A visible light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China) with a wavelength

range of 400 to 1000 nm. The apparent quantum efficiency (QE) was calculated according to the equation given below:

Q. E. (%) = number of reacted electrons / number of incident photons  $\times$  100

= number of evolved H<sub>2</sub> moleclues  $\times$  2 / number of incident photons  $\times$  100



**Fig. S12** Left: Tauc plot of Cd(II)-MOF (1). Right: electrochemical impedance spectra of compounds CdS@Cd(II)-MOF@TiO<sub>2</sub> (7), CdS@Cd(II)-MOF@TiO<sub>2</sub> (8), CdS@Cd(II)-MOF (9), Cd(II)-MOF@TiO<sub>2</sub> (10).



Fig. S13 XRPD of recovered catalysts of 7-10 after irradiation for 8 h.



Fig. S14 <sup>1</sup>H NMR (DMSO- $d^6$ ) of the recovered catalysts (a) CdS@Cd(II)-MOF (9), (b) Cd(II)-MOF@TiO<sub>2</sub> (10), (c) CdS@Cd(II)-MOF@TiO<sub>2</sub> (7), (d) CdS@Cd(II)-MOF@TiO<sub>2</sub> (8).



**Fig. S15** N<sub>2</sub> adsorption isotherms of Cd(II)-MOF-based materials collected at 77 K. Black: 344 m<sup>2</sup> g<sup>-1</sup> (BET) for Cd(II)-MOF (1); Purple: 52 m<sup>2</sup> g<sup>-1</sup> (BET) for CdS@Cd(II)-MOG@TiO<sub>2</sub> (7); Wine: 33 m<sup>2</sup> g<sup>-1</sup> (BET) for CdS@Cd(II)-MOG@TiO<sub>2</sub> (8). Red: 193 m<sup>2</sup> g<sup>-1</sup> (BET) for CdS@Cd(II)-MOF (9); Blue: 71 m<sup>2</sup> g<sup>-1</sup> (BET) for Cd(II)-MOF@TiO<sub>2</sub> (10); Adsorption and desorption branches are shown with filled and empty symbols, respectively.

#### V. Single-Crystal Structure Determination.

Suitable single crystals of **1** was selected and mounted in air onto thin glass fibers. X-ray intensity data of these crystals were measured at 100 K on a Agilent Super Nova CCD-based diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54184$  Å).<sup>1</sup> After determination of crystal

quality and initial tetragonal unit cell parameters, a hemi sphere of frame data was collected. The raw data frames were integrated with CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171. NET) (compiled Aug 2 2013, 16 : 46 : 58).<sup>1</sup> Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The final unit cell parameters are based on the least-squares refinement of 5167 reflections from the data set with  $I > 5\sigma(I)$ . Analysis of the data showed negligible crystal decay during data collection. Systematic absences in the intensity data were consistent with the space groups P4(3)2(1)2. Solution and refinement in P4(3)2(1)2 yielded. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against  $F^2$ , using the SHELXTL software package. All non-hydrogen atoms of the framework were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 1063525. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

# VI. Single-crystal data

Identification code	1				
Empirical formula	$C_{50}H_{44}B_2CdF_8N_{12}O_2$				
Formula weight	1130.99				
Temperature	100.0(2) K				
Wavelength	1.54184 Å				
Crystal system, space group	Tetragonal, P 43 21 2				
Unit cell dimensions	a = 15.9333(6)  Å alpha = 90 deg.				
	b = 15.9333(6) Å beta = 90 deg.				
	c = 21.1312(14)  Å gamma = 90 deg.				
Volume	5364.6(5) Å <sup>3</sup>				
Z, Calculated density	4, 1.400 Mg/m <sup>3</sup>				
Absorption coefficient	3.935 mm <sup>-1</sup>				
F(000)	2296				
Crystal size	0.2000 x 0.1200 x 0.0800 mm				
Theta range for data collection	3.47 to 67.06 deg.				
Reflections collected / unique	14262 / 4716 [R(int) = 0.0345]				
Completeness to theta $= 25.60$	99.7 %				
Data / restraints / parameters	4716 / 48 / 380				
Goodness-of-fit on F <sup>2</sup>	1.043				
Final R indices [I>2sigma(I)]	R1 = 0.0945, WR2 = 0.2324				

**Table S1.** Crystal data and structure refinement for 1.

## **VII. Reference**

(1) CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171.NET) (compiled Aug 2 2013, 16:46:58).