

Electronic Supplementary Information

Photocatalytic cascade reactions and dye degradation over CdS- metal-organic framework hybrids

*Shu-Rong Li, Feng-Di Ren, Lin Wang and Yu-Zhen Chen**

College of Chemistry and Chemical Engineering, Qingdao University, Qingdao,
Shandong 266071, P. R. China.

*To whom correspondence should be addressed.

E-mail: chenzhen1738@163.com

Materials and Characterization

All chemicals were from commercial and used without further purification: 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$, TCI Shanghai, >98%), tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Sinopharm Chemical Reagent Co., Ltd., >98%), cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Rhawn chemical reagent, AR), thioacetamide (TAA, Sinopharm Chemical Reagent Co., Ltd., AR), N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR), acetic acid (CH_3COOH , Sinopharm Chemical Reagent Co., Ltd., AR), methanol (CH_3OH , Sinopharm Chemical Reagent Co., Ltd., AR), ethanol ($\text{C}_2\text{H}_5\text{OH}$, Sinopharm Chemical Reagent Co., Ltd., AR), benzyl alcohol ($\text{C}_7\text{H}_8\text{O}$, Sinopharm Chemical Reagent Co., Ltd., AR), malononitrile ($\text{C}_3\text{H}_2\text{N}_2$, Sinopharm Chemical Reagent Co., Ltd., AR), acetonitrile ($\text{C}_2\text{H}_3\text{N}$, Sinopharm Chemical Reagent Co., Ltd., AR), terephthalic acid (H_2BDC , Sinopharm Chemical Reagent Co., Ltd., AR), Chromic nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd., AR), hydrogen fluoride (HF, Sinopharm Chemical Reagent Co., Ltd., AR), ammonium fluoride (NH_4F , Sinopharm Chemical Reagent Co., Ltd., AR), methyl violet (MV, Sinopharm Chemical Reagent Co., Ltd., BS), safranin T (Energy Chemical, AR) and coomassie brilliant blue R 250 (Energy Chemical, AR). Power X-ray diffractions (PXRD) were carried out on a Rigaku Saturn 70 diffractometer at 113 K with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. Scanning electron microscopy (SEM) images were acquired on JEOL JSM-7800F

at an acceleration voltage of 10 kV. The transmission electron microscopy (TEM) was acquired on JEOL-2010 with an electron acceleration energy of 200 kV. At least three measurements were made on each sample to obtain the values of contact angle. The UV-Vis diffuse reflectance spectrum (UV-Vis DRS) were measured using BaSO₄ as a reference on a PerkinElmer Lamda-950 spectrophotometer. The light irradiation experiments were carried out by using Perfect Light PLS-SXE 300 Xe lamp (420-780 nm). Catalytic reaction products were analyzed and identified by gas chromatography (GC, Panna A91 Plus). UV-Vis absorption spectra for the degradation of dyes were measured on a PerkinElmer Lamda-950 spectrophotometer. The contents of CdS in samples were analyzed by an Agilent ICP-OES 730 inductively coupled plasma atomic emission spectrometer (ICP-AES). The photocurrent test and the Mott-Schottky measurements were carried out with a Zahner Zennium electrochemical workstation by a conventional three-electrode cell, containing a graphite rod (counter electrode) and Ag/AgCl electrode (reference electrode).

Sample Preparation.

Preparation of NH₂-MIL-125. NH₂-MIL-125 was synthesized according to a previous literature procedure with some modifications.¹ Typically, 1.087 g of NH₂-BDC were dissolved in a solution containing DMF (24.3 mL) and CH₃OH (2.7 mL), 0.52 mL of Ti(OC₄H₉)₄ and 1 mL of CH₃COOH were added in turn to the above solution. The mixture was stirred for 30 min at room temperature and then was transferred to a Teflon-lined autoclave followed by heated at 150 °C for 24 h. After that, the yellow solid powder was collected by centrifugation, washed with DMF and MeOH respectively, and dried at 80 °C.

Preparation of MIL-101. Typically, 0.83 g of terephthalic acid and 2 g of Chromic nitrate nonahydrate were added to the 24 mL of deionized (DI) water containing 0.14 mL of HF. The mixture was heated at 200 °C for 8 h to obtain the product. Crude MIL-101(Cr) was further purified in deionized water under stirring for 24 h at 130 °C and then kept refluxing and stirring in ethyl alcohol for 24 h at 90 °C. Subsequently, the green powder was adequately washed with hot ethanol, and further activated with ammonium fluoride aqueous solution (1 mg/mL) at 80 °C.

Preparation of CdS. 27.8 mg of Cd(CH₃COO)₂ · 2H₂O was dissolved in 10 mL C₂H₅OH, which was sonicated for 30 min and then heated at 80 °C for 10 min. After adding 20 mg of TAA, the mixture was kept heating at 80 °C for 30 min followed by washed with C₂H₅OH for several times and finally dried at 80 °C.

Preparation of CdS/NH₂-MIL-125. CdS/NH₂-MIL-125 was synthesized according to a reported procedure with simple modifications.² In a typical project, 100 mg of NH₂-MIL-125 was dissolved in 10 mL of C₂H₅OH, and then 27.8 mg of Cd(CH₃COO)₂ · 2H₂O was added. The mixture was sonicated for 30 min followed by heated at 80 °C for 10 min. After that, 20 mg of TAA were added into above mixture, which was heated at 80 °C for 30 min. The obtained solid was fully washed with C₂H₅OH for several times and dried at 80 °C.

Preparation of CdS@MIL-101. CdS@MIL-101 was synthesized using a literature method with some modifications.² In a typical procedure, 100 mg of MIL-101 was dissolved in 10 mL C₂H₅OH, and then a certain amount of Cd(CH₃COO)₂ · 2H₂O was added. The mixture was sonicated for 30 min followed by heated at 80 °C for 10 min. After that, a certain amount of TAA was added into the mixture, which was heated at 80 °C for 30 min. The solid was washed with C₂H₅OH several times and finally dried at 80 °C.

Catalytic performance evaluation for CdS/NH₂-MIL-125, CdS and NH₂-MIL-125 catalyst toward one-pot cascade reaction between benzyl alcohol and malononitrile: The photocatalytic activity of CdS/NH₂-MIL-125, CdS and NH₂-MIL-125 was evaluated by the one-pot cascade reaction between benzyl alcohol and malononitrile under visible-light irradiation from a xenon lamp ($\lambda \geq 420$). 100 mg of CdS/NH₂-MIL-125 or CdS or NH₂-MIL-125 were dispersed into 5 mL of acetonitrile, and then 5 μ L of benzyl alcohol and 20 μ L of malononitrile were added into the

suspensions. The mixture was stirred at 80 °C under visible-light irradiation. The reaction process was analyzed by GC.

Catalytic performance evaluation for CdS@MIL-101 composites, CdS and MIL-101 toward one-pot cascade reaction between benzyl alcohol and aniline: The photocatalytic performance of CdS@MIL-101, CdS and MIL-101 was evaluated by a one-pot cascade reaction between benzyl alcohol and aniline under visible-light irradiation from a xenon lamp ($\lambda \geq 420$). A certain amount of CdS@MIL-101 or CdS or MIL-101 were dispersed into 10 mL of toluene, then 5 μ L of benzyl alcohol and 5 μ L of aniline were added into the suspensions. The mixture was stirred at O₂ atmosphere and under visible-light irradiation, after reaction, then centrifuged at 12000 rpm to remove catalysts and the solution was analyzed by GC.

Photocatalytic performance evaluation for CdS/NH₂-MIL-125, CdS@MIL-101 and CdS catalyst toward dye degradation: The photocatalytic degradation experiments were performed in a round bottom flask under the visible light illumination ($\lambda \geq 420$). For the dye degradation research, 25 mg·L⁻¹ of methyl violet, safranin T and coomassie brilliant blue R250 were investigated. A 20 mL solution in presence of dye was put in the round bottom flask followed by adding 10 mg of catalysts. The suspensions were stirred at room temperature in the dark for 40 minutes to reach an adsorption/desorption equilibrium. Then the solution was exposed to xenon lamp at room temperature, and the residual concentration of dye was monitored using a UV-Vis spectrometer.

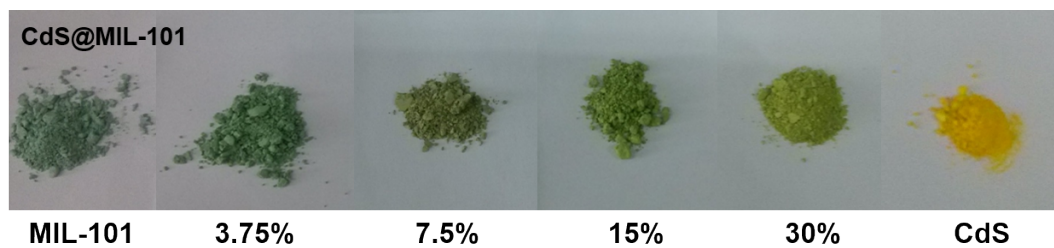


Fig. S1 Gradually varied colors of MIL-101, CdS and CdS@MIL-101 with different CdS contents.

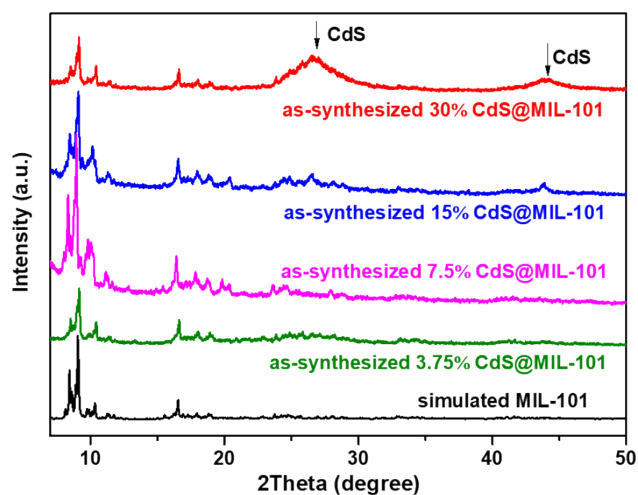


Fig. S2 PXRD patterns of simulated MIL-101 and as-synthesized CdS@MIL-101 catalysts.

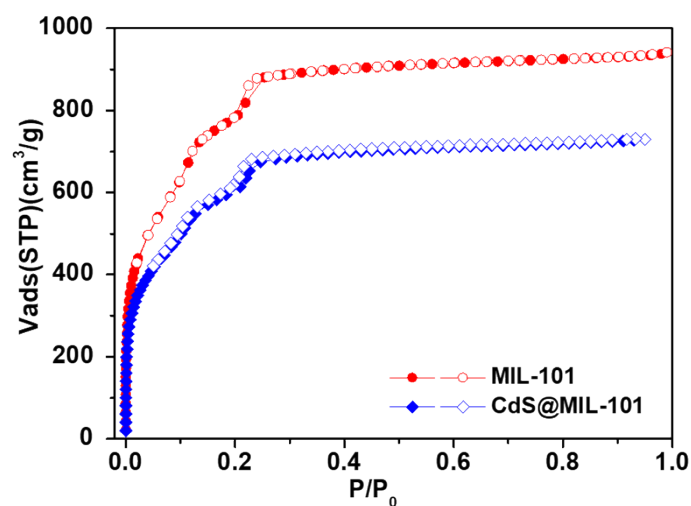


Fig. S3 N₂ sorption isotherms of MIL-101 and CdS@MIL-101 at 77 K.

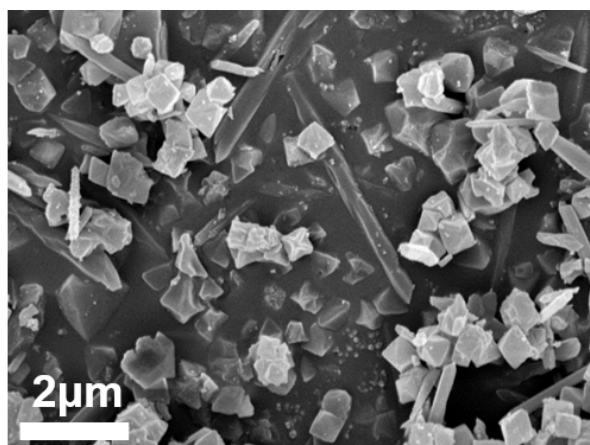


Fig. S4 SEM image of 7.5 wt% CdS@MIL-101.

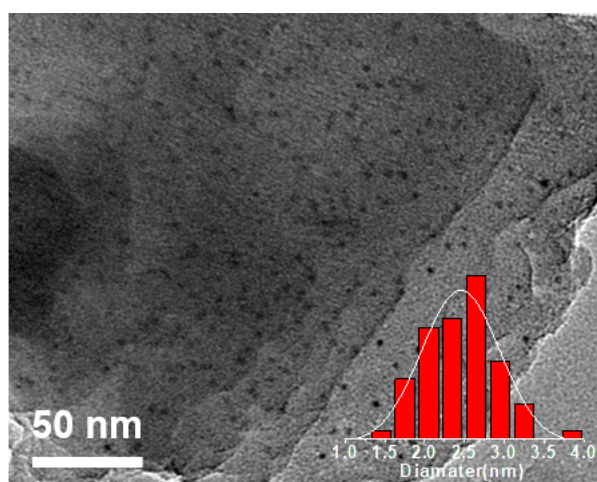


Fig. S5 TEM image of 7.5 wt% CdS@MIL-101 and the corresponding size distribution of CdS NPs.

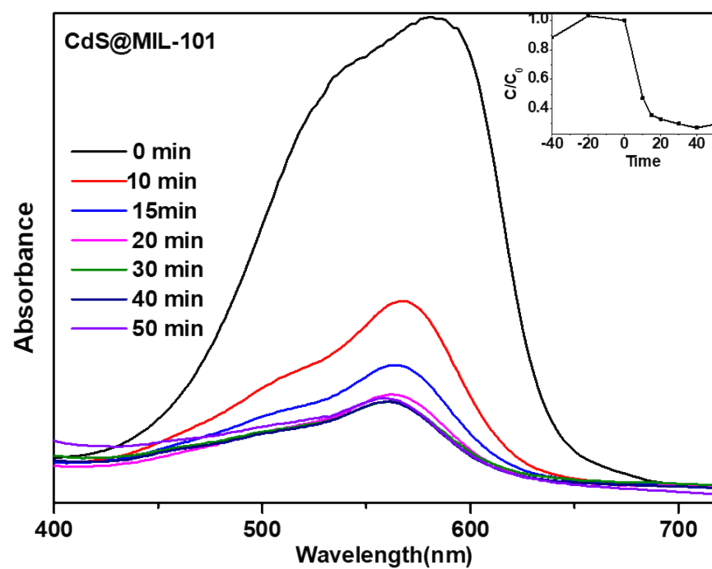


Fig. S6 The UV-Vis absorption spectra for methyl violet degradation using 15 wt% CdS@MIL-101 catalyst.

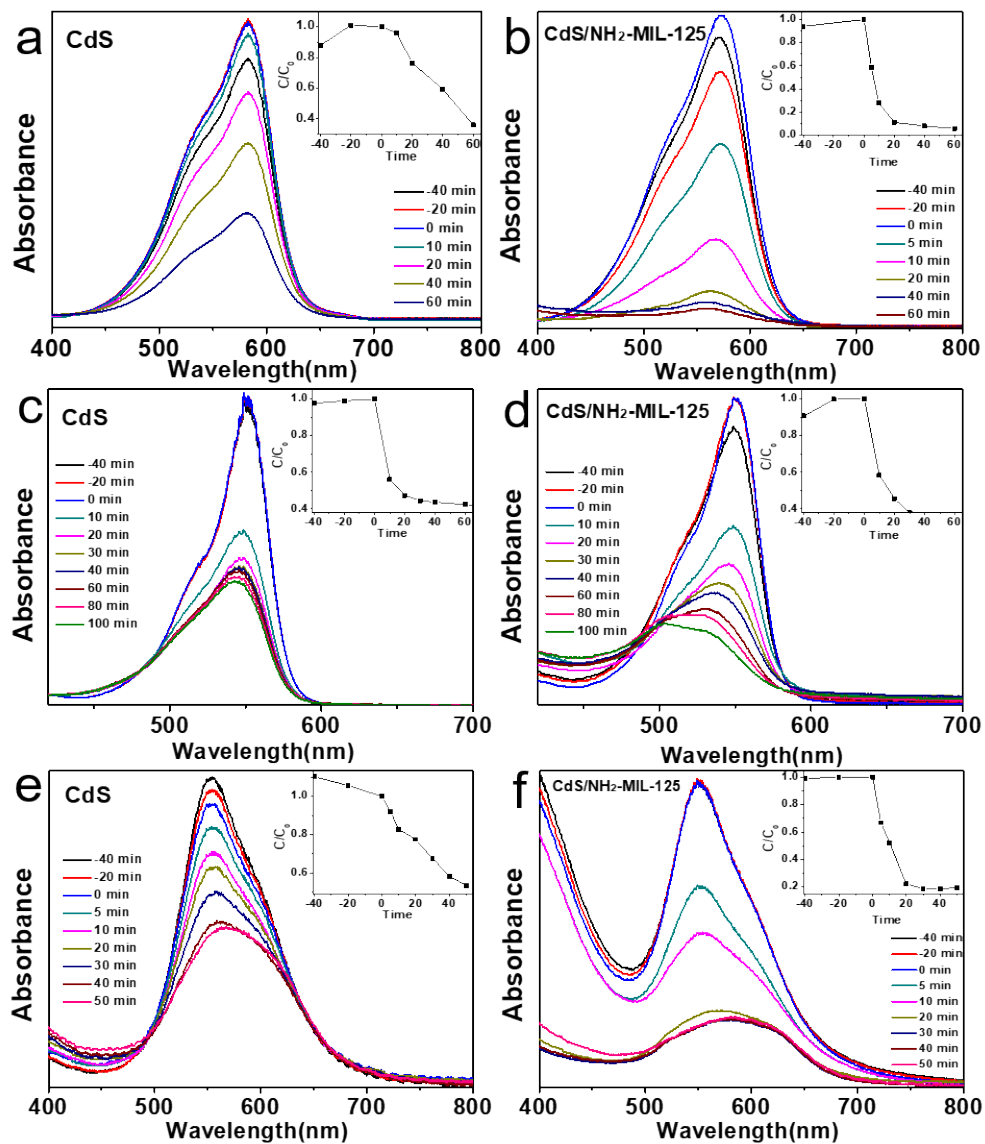


Fig. S7 The UV-Vis absorption spectra for methyl violet (a,b), safranin T (c,d), brilliant blue R250 (e,f) degradation using CdS and CdS/NH₂-MIL-125 as catalysts.

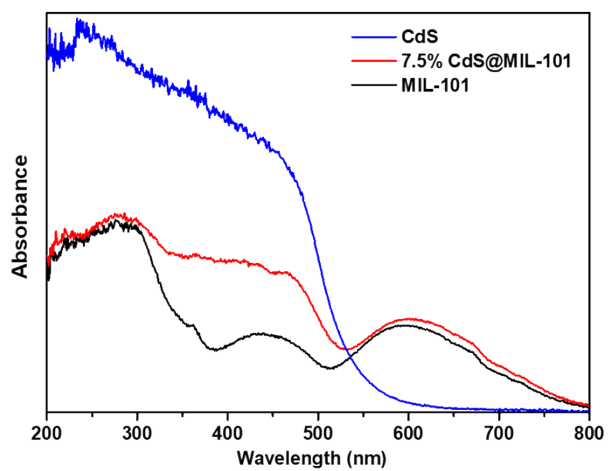


Fig. S8 UV-Vis DRS of MIL-101, 7.5 wt% CdS@MIL-101 and CdS.

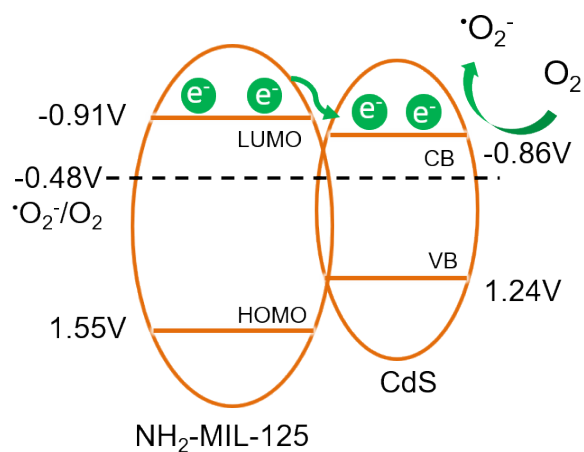


Fig. S9 Schematic illustration of the charge transfer from MOF to CdS.

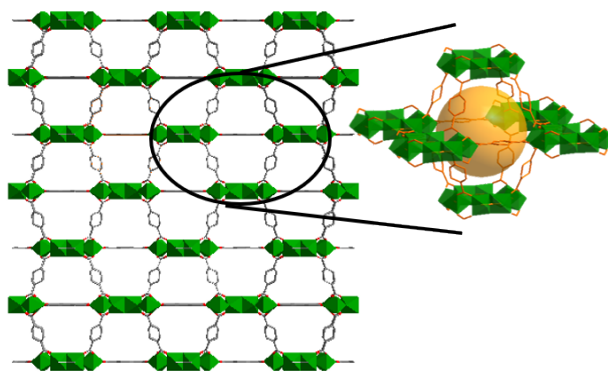


Fig. S10 View of the 3D network of NH₂-MIL-125 featuring through the b-axis.

Table S1 The inductively coupled plasma mass spectrometry (ICP-MS) results for CdS/NH₂-MIL-125 and CdS@MIL-101.

Sample	Substance	Content (wt%)
30 wt% CdS/NH ₂ -MIL-125	CdS	30.5
15 wt% CdS/NH ₂ -MIL-125	CdS	15.3
7.5 wt% CdS/NH ₂ -MIL-125	CdS	7.6
30 wt% CdS@MIL-101	CdS	30.8
15 wt% CdS@MIL-101	CdS	15.9
7.5 wt% CdS@MIL-101	CdS	8.0
3.75 wt% CdS@MIL-101	CdS	3.9

Table S2 A comparison of different catalysts for the one-pot cascade reaction between benzyl alcohol and malononitrile.

Catalyst (amount of catalyst)	Reaction Time (h)	Reaction Conditions	Con./Yield(%)	Refs.
CdS/NH ₂ -MIL-125 (100 mg, CdS-15 wt%)	24	CH ₃ CN, air, $\lambda \geq 420$ nm, 80°C	Con. 97	This work
Zr-MOF-NH ₂ (100 mg)	48	p-xylene, UV-light, 90°C	Yield 91	3
NH ₂ -MIL-101(Fe) (20 mg)	40	trifluorotoluene/acetonitrile, O ₂ , $\lambda \geq 420$ nm	Yield 72	4
Au@Cu(II)-MOF (3 mol% Au)	23	first step: toluene, 110°C; second step: methanol, R.T.	Con. 99	5
g-C ₃ N ₄ /FeWO ₄ (40 mg)	14	CH ₃ CN, R.T., O ₂	Yield 88	6
ompg-C ₃ N ₄ /Co ²⁺ (80 mg)	18	CH ₃ CN, visible light, air; first step: R.T., second step: 80 °C	Yield 78	7

References

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