

Supporting Information

Hierarchically phase junction CdS in situ growth on the H-Mordenite zeolite for enhanced photocatalytic properties

Teng Du¹, Yifu Zhang¹, Yue Chao¹, Yonglin An¹, Changgong Meng^{1,*}

¹ *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, PR China*

*Corresponding authors. E-mail addresses: E-mail addresses: cgmeng@dlut.edu.cn;

Experimental section

1. Materials

All reagents used in this study were purchased from Aladin Chemical Reagent Co., Ltd, and used without any further purification. Trisodium citrate dihydrate ($C_6H_5Na_3O_7$, 99%), Cadmium Chloride ($CdCl_2$, 99%), Thiourea (CH_4N_2S , 99%), p-Quinone ($C_6H_4O_2$, 98%), Iso-Propyl alcohol (C_3H_8O , 99%), Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 99%), H_2O_2 (30 wt%), Ammonium Hydroxide. H-Mordenite ($SiO_2/Al_2O_3=25$) were ordered from Tianjin Nankai University Catalyst Co., Ltd.

2. Structure and morphology characterization

The phase of the sample was analyzed by X-ray diffraction (XRD) with Cu $K\alpha$ radiation, collecting angle 2θ from 5° to 60° , step size 10° (XRD, Smartlab, Japan). X-ray photoelectron spectroscopy (XPS) measurements with Al $K\alpha$ (Thermo ESCALAB XI+, America)). The room-temperature Raman spectra of samples were recorded on a LabRam HR system from Horiba Jobin Yvon at room temperature using the 532 nm solid laser as the exciting source. Ultraviolet-visible (UV-Vis) spectrophotometer (Cary 300, Agilent, Japan) was used to record the absorbance of MB concentration. The absorbance of the materials were obtained by Ultraviolet-visible diffuse reflectance spectroscopy (V-3900, Hitachi, Japan) and $BaSO_4$ was taken as the blank sample. The fluorescence emission intensity was analyzed by fluorescence spectrometer (Edinburgh Instruments, FS 503030429, Britain). The morphologies and structure of sample were tested by Scanning Electronic microscopy (SEM Nova Nanosem, FEI, America) and Transmission electron microscopy (TEM TF, FEI, America)The nitrogen adsorption-desorption isotherm of the material was measured with a nitrogen adsorption device (3 FLEX, Micromeritics, America). The

photocurrent test was carried out on an electrochemical system (CHI 660 E, Chinstruments, China) using the three-electrode method. The platinum mesh electrode was used as the counter electrode, the saturated calomel electrode (SCE) was used as the reference electrode, and 1 M Na₂SO₄ was used as the electrolyte. Electron spin resonance (ESR) and active substance capture experiments were used to test the active species (Brooke, E 50003030710, China).

3. *Catalytic activity characterization*

The light source was provided by the xenon lamp source system (CEL-HXF 300, Ceavlight, china). The photocatalytic activities of CdS@HMOR were evaluated by Methylene blue (MB, 10 mg/L) degradation under visible-light irradiation (400-780nm). The power density of visible light at the position of reactor was measured to be 7.5 mW/cm². In typical experiment, 0.1 g of catalyst powder was added to the MB (40 ml) aqueous solution in the container. Before irradiation, the suspension was magnetically stirred in a dark place irradiation for 60 min to reach adsorption equilibrium. In the process of MB photodegradation, the samples (5 ml) were extracted every 30 minutes, and the solid particles were separated by centrifugation and analyzed by a ultraviolet spectrophotometer. The absorbance was measured at 664 nm.

4. *Parameter setting of electrochemical impedance spectroscopy test*

Standard three electrode method were used to measure, the sample was used as the working electrode, platinum net electrode as the opposite electrode, saturated calomel electrode (saturated KCl solution) as the reference electrode, Na₂SO₄ (1 mol/l) water solution as electrolyte.

Preparation of working electrode: Clean the 1 cm * 1 cm glass of ITO with acetone, boiled NaOH (0.1 mol/L) and deionized water in turn, then dry it in the oven, press 0.5 cm * 0.5 cm conductive adhesive

on the center of the ITO glass, and finally grind and compact the prepared material on the conductive adhesive.

Figure S1

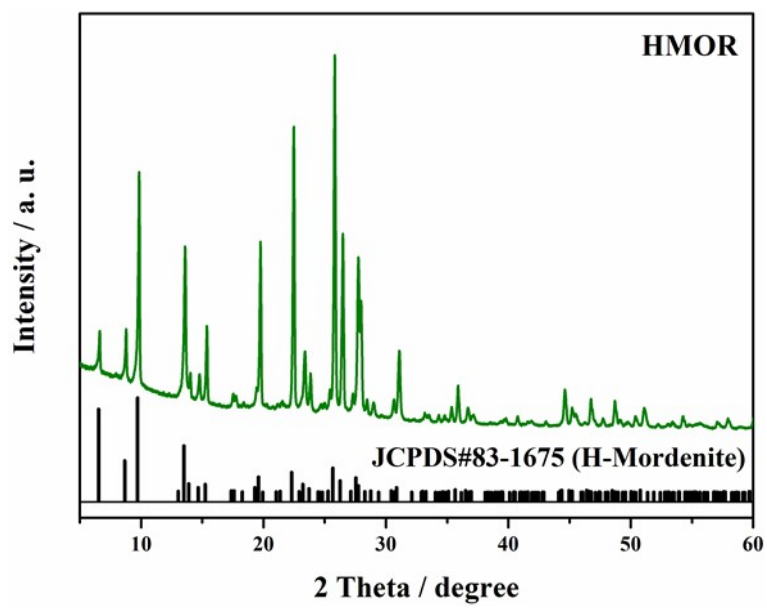


Figure S1. XRD patterns of HMOR

Figure S2

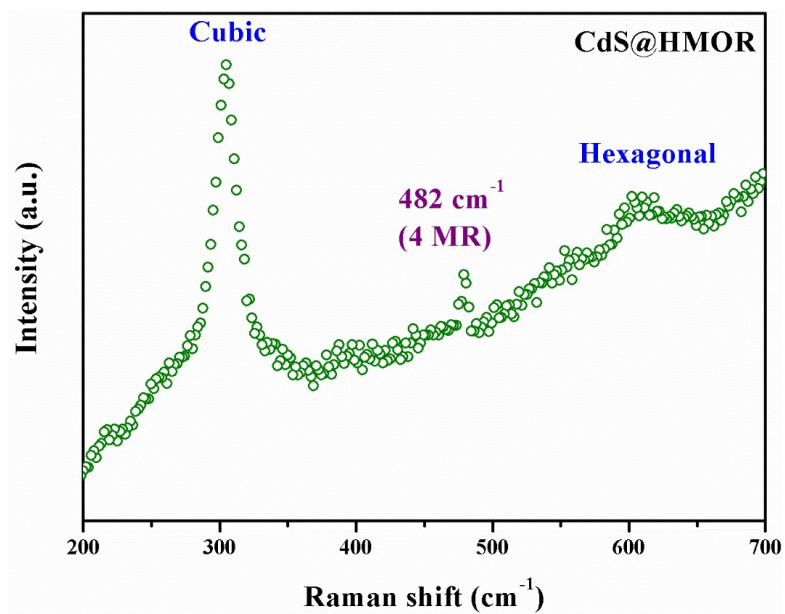


Figure S2. Raman spectrum of pure CdS

Figure S3

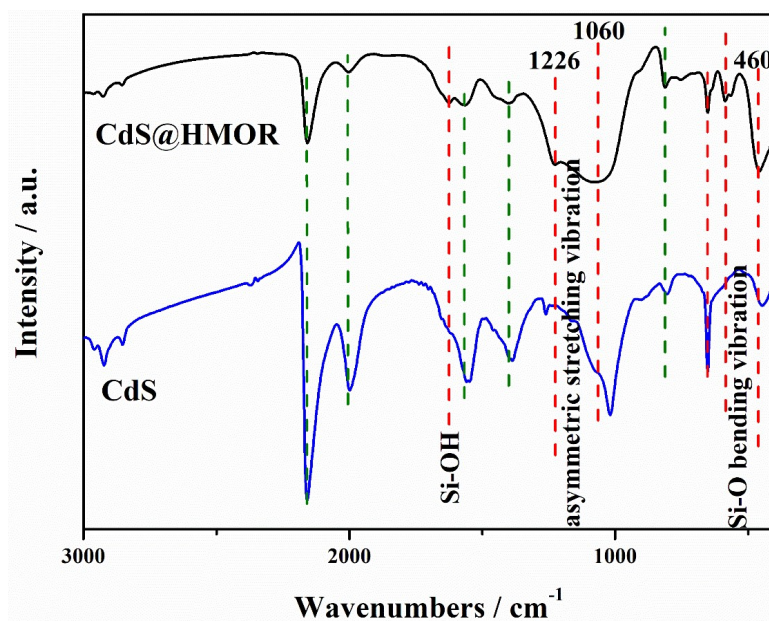


Figure S3. FT-IR spectra of 2 wt % CdS@HMOR and CdS.

Figure S4

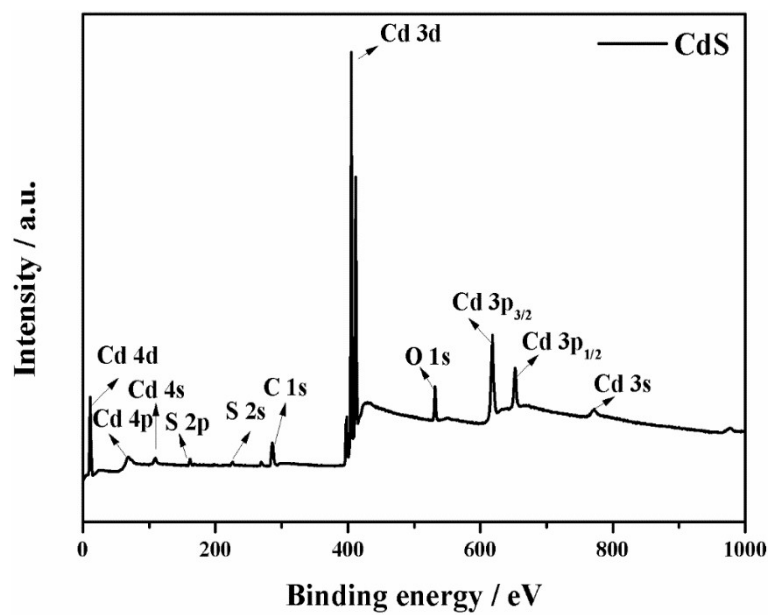


Figure S4. XPS survey spectra of CdS.

Figure S5

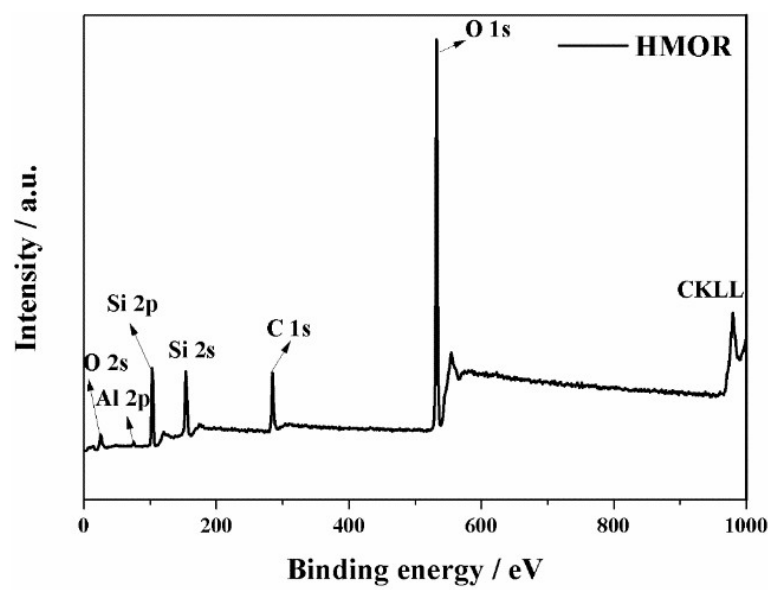


Figure S5. XPS survey spectra of HMOR.

Figure S6

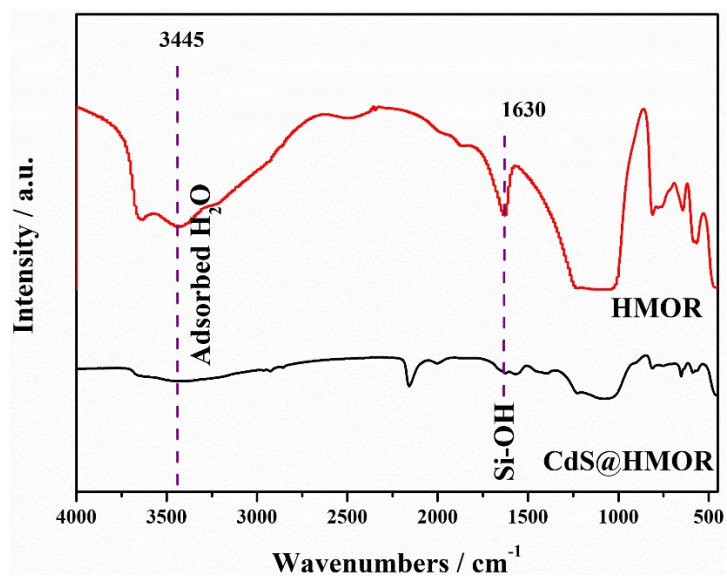


Figure S6. FT-IR spectra of 2 wt % CdS@HMOR and HMOR.

Figure S7

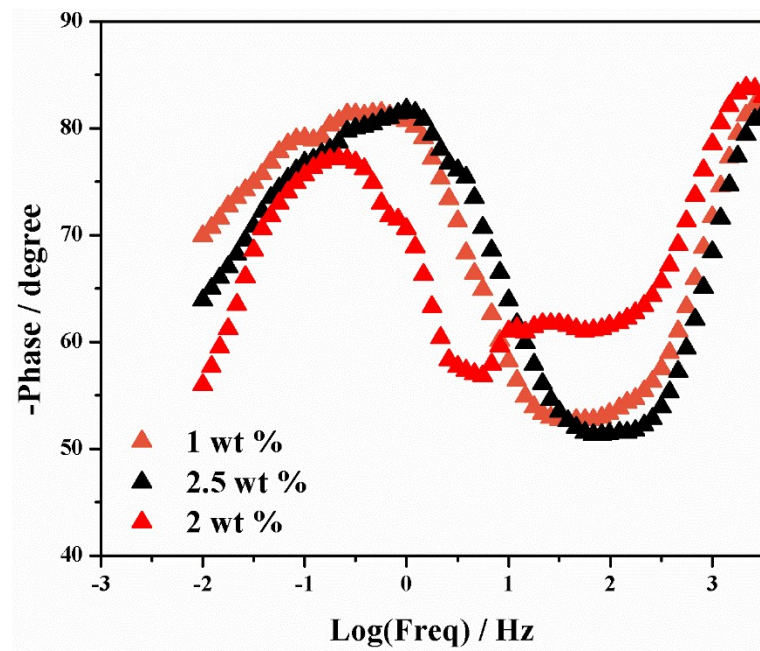


Figure S7. Phase angle plots

Table S1. Comparative degradation activity of photocatalysts reported in this study with 2 wt % CdS@HMOR

E. No.	catalyst	pollutant	light	Time (mins)	Removal efficiency (%)	Ref
1.	TiO ₂ /NaY zeolite (40 mg)	MB (5 mg/l)	UV	200	90	(1)
2.	Ag@CdSe/Zeolite (30 mg)	MB (7.17 mg/l)	visible	40	89.98	(2)
3.	CuO/Zeolite X (0.1 g/l)	MB (10 mg/l)	visible	120	88	(3)
4.	Fe ³⁺ doped TiO ₂ /natural zeolite (1 g/l)	MB (25 mg/l)	visible	90	92 (40 mg/l H ₂ O ₂)	(4)
5.	Ag-ligand modified tungstovandates	MB (5 mg/l)	UV-visible	40	79.5	(5)
6.	Poly (EPE)/f-MWCNT (5 mg/l)	MB (40 ml, 1*10 ⁻⁵ M)	visible	120	67	(6)
7.	TiO ₂ -Mn ₃ O ₄ (10 mg/l)	MB (10 mg/l)	visible	120	96.39 (3 ml H ₂ O ₂)	(7)
8.	MnO _x /WO ₃ (10 mg)	MB (10 mg/l)	visible	60	95 (10 ml H ₂ O ₂)	(8)
This work						
9	2 wt % CdS@HMOR (0.1 g)	MB (10 mg/l)	visible	120	84.15	This work
10	2 wt % CdS@HMOR (0.1 g)	MB (10 mg/l)	visible	120	98.98 (1.5 ml H ₂ O ₂)	

References

- [1] M. Zendehtdel, Z. Kalateh, Z. Mortezaei, photocatalytic activity of the nano-sized TiO₂/NaY zeolite for removal of methylene blue, *J. Nov. Appl. Sci.* 3 (2014) 135-141.
- [2] S. A. Mosavi, A. Ghadi, P. Gharbani, A. Mehrizad, Photocatalytic removal of Methylene Blue using Ag@CdSe/Zeolite nanocomposite under visible light irradiation by Response Surface Methodology, *Mater. Chem. Phys.* 267 (2021) 124696.
- [3] A. Nezamzadeh-Ejhi, M. Karimi-Shamsabadi, Comparison of photocatalytic efficiency of supported CuO onto micro and nano particles of zeolite X in photodecolorization of Methylene blue and Methyl orange aqueous mixture, *Appl. Catal. A: General* 477 (2014) 83–92.
- [4] G. Foura, N. Chouchou, A. Soualah, K. Kouachi, M. Guidotti, D. Robert, Fe-Doped TiO₂ Supported on HY Zeolite for Solar Photocatalytic Treatment of Dye Pollutants, *Catalysts*, 7 (2017) 344.
- [5] R. Zheng, H.X. Zhang, Y.P. Liu, X.X. Wang, Z.G. Han, Ag-ligand modified tungstovanadates and their efficient catalysis degradation properties for methylene blue, *J. Solid State Chem.* 246 (2017) 258-263.
- [6] F.F. Liu, R. Jamal, Y.J. Wang, M.C. Wang, L. Yang, T. Abdiryim, Photodegradation of methylene blue by photocatalyst of D-A-D type polymer/functionalized multi-walled carbon nanotubes composite under visible-light irradiation, *Chemosphere* 168 (2017) 1669-1676.
- [7] J.H. Park, I. Jang, K. Song, S.G. Oh, Surfactants-assisted preparation of TiO₂-Mn oxide composites and their catalytic activities for degradation of organic pollutant, *J. Phys. Chem. Solids*, 74 (2013) 1056–1062.
- [8] M. Amini, B. Pourbadiei, T. P. A. Ruberu, L. K. Woo, Catalytic activity of MnOx/WO₃ nanoparticles: synthesis, structure characterization and oxidative degradation of methylene blue, *New. J. chem.* 38 (2014) 1250-1255.