Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2019

# **Supporting Information**

Enhanced photocatalytic hydrogen evolution over bimetallic Zeolite Imidazole

Framework encapsulated CdS nanorod

Jia-Hui Zhao, Yan-Ju Wang, Xiu Tang, Yu-Han Li, Fu-Tian Liu,\* Yu-Zhuo Zhang\* and Kui Li\*

School of Materials Science and Engineering, University of Jinan, Jinan 250022, China

Email: mse\_liuft@ujn.edu.cn; zhangyz053@nenu.edu.cn; mse\_lik@ujn.edu.cn.

## **1. Experimental Section:**

**1.1 Chemicals:** The Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, thiourea, 2-Dimethylimidazole (MIM), methanol and ethylenediamine (Shanghai Macklin Biochemical Technology Co., Ltd) are analytical grade and used as received without further purification.

### **1.2 Sample preparation.**

*1.2.1 Synthesis of CdS nanorod:* As show in **Table S1**, suitable contents of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (2 mmol) and thiourea (4 mmol) was dissolved in 20 mL ethylenediamine under ultrasound for 45 minutes. Thereafter, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 18 h. After naturally cooling to room temperature, the intermediate was collected by centrifugation, and washed with deionized water, and dispersed into 120 mL deionized water. Afterwards, the above suspension, which was evenly divided into 25 parts, was transferred into 10 mL autoclaves and heated at 140 °C for 14 h. The purpose was to remove the templating agent ethylenediamine and form CdS nanorods. The final products were rinsed with distilled deionized water and ethanol for two times, respectively, and dried at 70 °C overnight.

*1.2.2 Synthesis of CdS-ZnM-ZIF samples:* The detail fabrication parameters of the CdS-ZnM-ZIFs were summarized in **Table S2** to **S3**. In a typical synthesis, 1 mmol of the above prepared CdS nanorods, various molar quantities of  $Zn(NO_3)_2 \cdot 6H_2O$  and 2-methylimidazole (the molar ratio of 2-methylimidazole to  $Zn(NO_3)_2 \cdot 6H_2O$  was 10:1) mixture were dispersed into 30mL of methanol and stirred at room temperature for 24 h, Then, the products were collected by centrifugation, and washed with ethanol, and dried at 60 °C for overnight. The samples obtained with various molar quantities of  $Zn(NO_3)_2 \cdot 6H_2O$  were labeled as CZx, in which x was the molar ratio of  $Zn(NO_3)_2 \cdot 6H_2O$  in the composites. Additionally, the CdS-ZnM-ZIF samples were synthesized under the similar conditions. Through doping partial Zn with transition metal (Cu, Co and Ni), the CdS-ZnM-ZIF heterostructue were fabricated with different amount of the transition metal, and the corresponding samples were abbreviated as CZMy, with y was the molar ratio of metal + Zn) at%. The CdS + ZIFs samples were prepared by grinding CdS and ZIFs for 15 min, and the ratio of CdS and ZIFs addition was determined by ICP results.

CdS + ZIF CdS + ZIFs s (CdS + ZIFs represents the physical mixture of CdS and ZIFs with the same proportion)

#### 2. Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54060$  Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. The morphology of samples was researched using a scanning electron microscope (SEM, Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDS) for determining the distribution of chemical components. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. The atomic structure of the CdS phase junction was characterized using an ARM-200CF (JEOL, Tokyo, Japan) transmission electron microscope operated at 200 kV and equipped with double spherical aberration (Cs) correctors. Element content analysis was tested on an inductively coupled plasma (ICP) spectroscope (Prodigy, Leeman, America). The UV–Vis absorption and diffused reflectance spectra were recorded using a Cary 5000 UV-Vis spectrometer (Viarian, USA) with  $BaSO_4$  as a reflectance standard. The Xray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 Xi (USA)-ray photoelectron spectrometer using Al as the excitation source. Photoluminescence (PL) emission spectra were measured at room temperature by using a Fluorescence spectrophotometer-5with the excitation wavelength of 350 nm for the oxide. Electrochemical measurements were perfprmed on a CHI 660E Electrochemical Workstation (CH Instruments, Inc. Shanghai). The electrochemical cell was assembled with a conventional three-electrode system, in which a glassy carbon electrode (3mm in diameter), (sheet resistance 20–25  $\Omega$ /square) with a geometrical area of 1.0 ± 0.1 cm<sup>2</sup> as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. Typically, a total of 4 mg of the catalysts were dispersed in 2 ml of 9:1 v/v water/Nafion solution by sonication to form a homogeneous ink. Finally, 5 µl welldispersed catalysts were covered on the glassy carbon electrode and then dried in an ambient environment for measurements. The electrolyte of transient photocurrent responses experiments, Electrochemical impedance spectroscopy (EIS), and Mott-Schottky (MS) was 0.5M Na<sub>2</sub>SO<sub>4</sub> aqueous solution and the electrolyte of linear sweep voltammetry (LSV) was 0.5M KOH solution. EIS was performed at a impressed voltage of -0.3 eV, for voltage ranging from -2.5 V to 2.5 V. MS was measured for a scan voltage ranging from -1 V to 0.5 V. The transient photocurrent responses measurement was performed under full light irradiation. The LSV obtained at a scan rate of 1 mV/s. The Brunauer-Emmett-Teller (BET) specific surface area ( $S_{BET}$ ) of the heterojunction samples analyzed by nitrogen adsorption and water vapor adsorption is investigated by an Autosorb-iQ adsorption apparatus (Quantachrome instruments, USA). All of the prepared samples were degassed at 90 °C for 3 hours prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using adsorption data in the relative pressure  $(P/P_0)$  range of 0.05 – 0.3. A desorption isotherm was used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method, assuming a cylindrical pore model. The nitrogen adsorption volume at a relative pressure  $(P/P_0)$  of 0.972 was used to determine the pore volume and average pore size.

### 3. Photocatalytic Hydrogen Production.

The photocatalytic H<sub>2</sub> production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 420–800 nm, which was positioned 13 cm away from the reaction solution, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was about 200 mW·cm<sup>-2</sup>, which was measured by a FZ-A visible-light radiometer (CEAULight, China). In a typical photocatalytic H<sub>2</sub>-production experiment, 5 mg of the prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing Na<sub>2</sub>S (0.35 M) and Na<sub>2</sub>SO<sub>3</sub> (0.25 M). Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments. H<sub>2</sub> content was analyzed by gas chromatography (GC-7900, CEAULight, China). All glassware was carefully rinsed with deionized water prior to use.

The amount of hydrogen production was calculated according to the hydrogen standard curve (**Table S4** and **Fig. S9**). Typically, the The 100 mL Pyrex flask containing 50 ml of distilled water

was installed on the photocatalytic reaction integrated system by sealing with a silicone rubber diaphragm. The system was evacuated by a vacuum pump for 5 minutes to completely remove dissolved oxygen and ensure that the reactor was in anaerobic conditions. Different amount of hydrogen (1, 2, 3 mL) was injected into the system, and the hydrogen area was tested after an hour. After each cycle, residual gas in the system was removed by a vacuum pump for 5 minutes.

In the catalytic stability test of CdS-ZIFs under visible light irradiation, four consecutive cycles were tested and the time of one cycle was 5 hours. After each cycle, the system was vacuumed renewedly for 5 min to remove the residual gas formed in the last cycle.

# 4. Supporting Tables and Figures

Table S1 The synthetic conditions of CdS nanorods.							
Molar quantities		First solvothermal reaction conditions			Second hydrothermal reaction conditions		
Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Thiourea	Ethylenediamine	Temperatur e	Time	Deionized water	Temperatur e	Time
<mark>2 mmol</mark>	<mark>4 mmol</mark>	20 mL	<mark>180 °C</mark>	<mark>18 h</mark>	<mark>4.8 mL</mark>	140 °C	<mark>14 h</mark>

 Table S2
 The synthetic conditions of CdS-ZIF-8

Samples	CdS	$Zn(NO_3)_2 \cdot 6H_2O$	MIM	Methanol	<mark>Stirring</mark> time	Drying temperature
CdS	1 mmol	0	<mark>0</mark>	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZ0.2	1 mmol	0.2 mmol	2 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZ0.5	1 mmol	<mark>0.5 mmol</mark>	<mark>5mmol</mark>	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZ1	1 mmol	1 mmol	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZ2	1 mmol	2 mmol	20 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZ5	<mark>1 mmol</mark>	<mark>5 mmol</mark>	<mark>50 mmol</mark>	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>

#### Table S3 The synthetic conditions of CdS-ZnM-ZIF

Samples	CdS	M	MIM	Methanol	<mark>Stirring</mark> time	Drying temperature
CZC05	1 mmol	<mark>5</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZCo10	<mark>1 mmol</mark>	<mark>10</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZCo30	<mark>1 mmol</mark>	<mark>30</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZCu5	1 mmol	<mark>5</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZCu10	1 mmol	<mark>10</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZCu30	1 mmol	<mark>30</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZNi10	1 mmol	10	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZNi30	1 mmol	<mark>30</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>
CZNi50	1 mmol	<mark>50</mark>	10 mmol	<mark>30 mL</mark>	<mark>24 h</mark>	<mark>60 °C</mark>

M was the molar ratio of doping metal / (doping metal + Zn) at%, the molar quantity of doping metal and Zn was 1 mmol.



**Fig. S1.** Inductively coupled plasma (ICP) results for the CZx samples prepared with different ZIF-8 content.



Fig. S2. The TEM image of CdS nanorod.



**Fig. S3.** The essential elemental mapping images of (a) CdS-ZnCu-ZIF, (b) CdS-ZnCo-ZIF and (c) CdS-ZIF-8.



Fig. S4. The UV–visible diffuse reflection spectra of the optimal CZx heterostructure.



**Fig. S5.** Effect of (a) Cu, (b) Co and (c) Ni concentration on the UV–visible diffuse reflection spectra of the CZMy samples, respectively.



**Fig. S6.** Plots of  $(\alpha hv)^2$  vs photon energy of the optimal CdS-ZIFs heterostructure.



**Fig. S7.** The corresponding pore size distribution curves of ZIF-8 and the CdS-ZIFs heterostructure samples.



**Fig. S8.** (a) Co 2p high resolution XPS spectra of CdS-ZnCo-ZIF, (b) high resolution Cu 2p XPS spectra of CdS-ZnCu-ZIF, (c) high resolution Ni 2p XPS spectra of CdS-ZnNi-ZIF.

Table S4 The Change of hydrogen production area					
H <sub>2</sub> injection volume (mL)	H <sub>2</sub> production area (mV • S)				
1	72.1819				
2	148.3987				
3	230.0839				



**Fig. S9.** The fitting straight line of the hydrogen injection volume and the hydrogen production area. and corresponding fitting table (insets).



Fig. S10. The comparison results of the photocatalytic hydrogen production activity of CdS-ZIFs and CdS + ZIFs (CdS + ZIFs represents the physical mixture of CdS and ZIFs with the same proportion).



Fig. S11. Effect of (a) Ni, (b) Co and (c) Cu concentration on the transient photocurrent responses

of the CZMy samples, respectively.



Fig. S12. Effect of (a) Cu, (b) Co and (c) Ni concentration on the EIS spectra of the CZMy samples, respectively.



Fig. S13. The electrochemical hydrogen evolution rates of CdS and CdS-ZIFs.