Supporting Information

Functionalized ZIF-67@CdS for photocatalytic oxidation of benzyl alcohol coupled with hydrogen production

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Materials and methods

Materials and methods

CdS, ZIF-67, ZIF-67-MBI, CdS@ZIF-67 are synthesized according to our previous work.

Synthesis of ZIF-67: Dissolve 6 mmol of cobalt nitrate hexahydrate in 100 mL methanol to form solution A; dissolve 24 mmol of 2-MI in another 100 mL methanol to form solution B; then slowly add solution B to solution A, stir at room temperature for 1 hour, centrifuge collection, wash with methanol for 3 times, and finally dry at 60℃ in a vacuum for 6 hours.

Synthesis of ZIF-67-MBI: 50 mg of ZIF-6 was ultrasonically dispersed in 15 mL of methanol to form solution A, and 100 mg of 2-merhydryl benzimidazole was ultrasonically dispersed in another 15 mL of methanol to form solution B. Then solution B was slowly dropped into solution A, magnetic stirring for 1 hour, centrifugal collection, methanol washing 3 times, and finally vacuum drying at 60℃ for 6 hours. The resulting sample is denoted as ZIF-67-MBI.

Synthesis of CdS: Add 5 mmol of cadmium nitrate and 15 mmol of sodium sulfide to a beaker of 40 mL of distilled water and stir for 10 minutes. The mixture was then transferred to a 100 mL polytetrafluoroethylene reactor and kept at 160 °C for 12 hours. After cooling, wash with distilled water and anhydrous ethanol, and dry at 60 ℃ to obtain CdS.

Synthesis of CdS@ZIF-67: Take 500 mg of the synthesized CdS and disperse it in 25 mL of methanol solution, and record it as solution A. Take 2 g PVP and disperse it in another 25 mL of methanol, denoted as solution B. B was added to A, stirred for 12 hours, centrifuged, washed with methanol, and finally dispersed PVP treated CdS in 25 mL of methanol for use. 2 mmol of cobalt nitrate was ultrasonically dispersed in 25 mL of methanol, and then 10 mL PVP-treated CdS methanol solution was added to it, stirring at room temperature for 0.5 hours, and recorded as solution A. Another 8 mmol 2-

methylimidazole was ultrasonically dispersed in 25 mL of methanol, denoted as solution B. Add B slowly to A, stir continuously for 1 hour, stand for 3 hours, centrifuge, wash with methanol, and dry at 60℃. The resulting product is denoted as CdS@ZIF-67.

Material characterization

The morphology of the catalyst was studied by field emission high-power scanning electron microscope (SEM) of SU8010 made by Hitachi. The phase structure of the catalyst was analyzed by D8 Advance X-ray diffractometer (XRD) manufactured by Bruker, Germany. The test target was copper target, the scanning range was 5-90°, and the scanning speed was 10°/min. Through the UV-4802S Ultraviolet–visible spectrometer (UV-vis) to study the visible light absorption of the catalyst, the test range is 200-1100 nm, with pure solid $BaSO_4$ crystal measured curve as the baseline, The measured reflectance profiles were then converted into UV-visible diffuse reflectance absorption profiles by Kubellka-Munk formula. The surface area and pore structure of the catalysts were studied by Nova 2000E N_2 adsorption instrument made by Quantachrome.

Photocatalytic Performance Test

The photocatalytic activity of the catalyst was studied by photocatalytic oxidation of benzyl alcohol coupled with hydrogen evolution. 10 mg catalyst, a certain amount of benzyl alcohol, and 10 mL distilled water were added to a 20 mL photoreaction bottle and magnetically stirred at room temperature. The temperature is controlled by condensate. Seal the reaction bottle with a rubber diaphragm and pass argon gas for 10 minutes before the reaction to remove air from the bottle. The photocatalytic reaction is carried out in a 300 W xenon lamp ($\lambda \geq 420$ nm) equipped with a long-pass filter. Gas chromatograph (SHIMADZU GC-2014 C) was used to detect the collected gas. The thermal

conductivity detector (TCD, 5A molecular sieve column) was used. The column diameter was 2 m × 4 mm, and the carrier gas was argon. 100 μL was extracted each time with a microinjection needle, and hydrogen was detected by a gas chromatograph. Analysis of liquid products by Shimadzu LC-2010A high performance liquid chromatograph, PDA detector, including binary pump and automatic sample injector. The analytes were separated on the GOLD column (250 nm × 4.6 mm, particle size 5 μm). Column temperature is maintained at 35 °C. The mobile phase consisted of water and acetonitrile, the flow rate was 0.8 $mL \cdot min^{-1}$, and the sample size was 10 μL.The conversion rate of benzyl was calculated as:

$$Conversion\ \% = [(C_0 - C_{benzyl})/C_0] \times 100\% \quad (1)$$

Electrochemical Performance Test

The working electrode was prepared by coating a 200 μL suspension on the surface of a fluorinated tin oxide glass plate (FTO) and covering 1 cm^2 with a mixture of 5 mg sample and 360 μL ethanol, 600 μL water and 40 μL membrane solution. Electrochemical measurements were performed on a CHI760E electrochemical analyzer using a conventional three-electrode cell including platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode is the above prepared electrode, the reference electrode is Ag/AgCl electrode immersed in saturated KCl, and the counter electrode is platinum filament electrode. The experiment was carried out in 0.5 M Na_2SO_4 electrolyte at room temperature.

BET of sample

Table. S1 Physical characteristics of all samples

Sample	S_{BET} (cm^2/g)	V_{total}(cm^3/g)	D_{avg}(nm)
ZIF-67	1893	0.78	1.64
ZIF-67-MBI	1785	0.88	1.94
CdS@ZIF-67	635	0.37	2.35
CdS@ZIF-67-MBI	488	0.32	2.49

SEM of sample

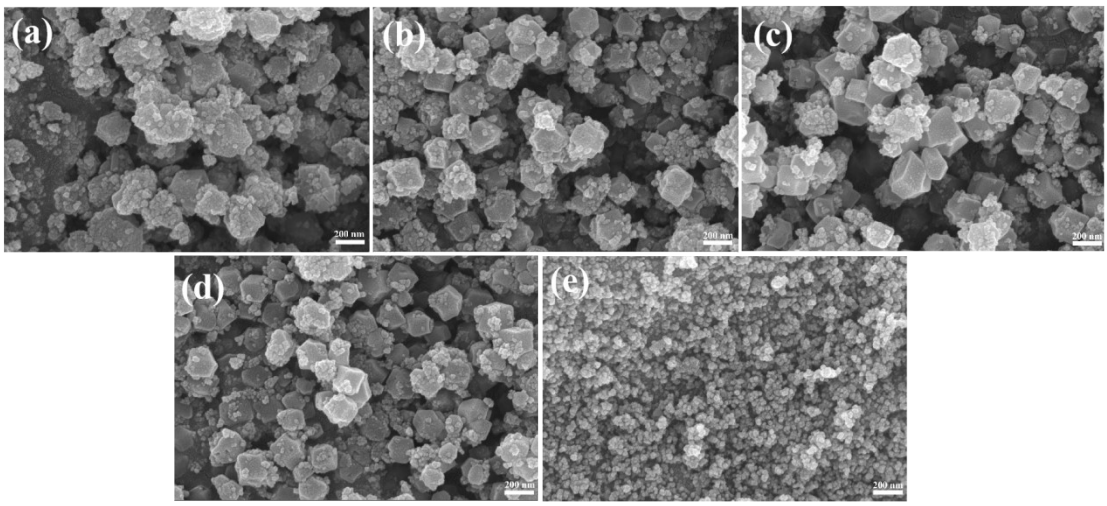

Fig. S1 SEM images of (a) CdS@ZIF-67-MBI-1; (b) CdS@ZIF-67-MBI-2; (c) CdS@ZIF-67-MBI-3; (d) CdS@ZIF-67-MBI-5; (e) CdS

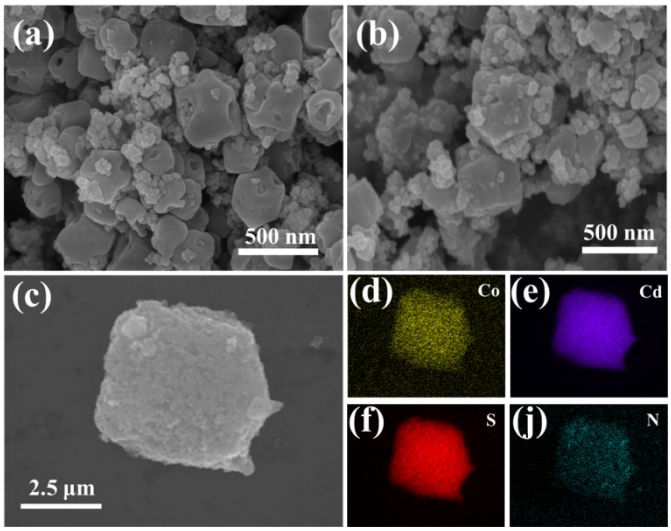

Fig. S2 (a-b) SEM images; (c-j) Element mapping of CdS@ZIF-67-MBI-5 after five cycles

Transient photocurrent response

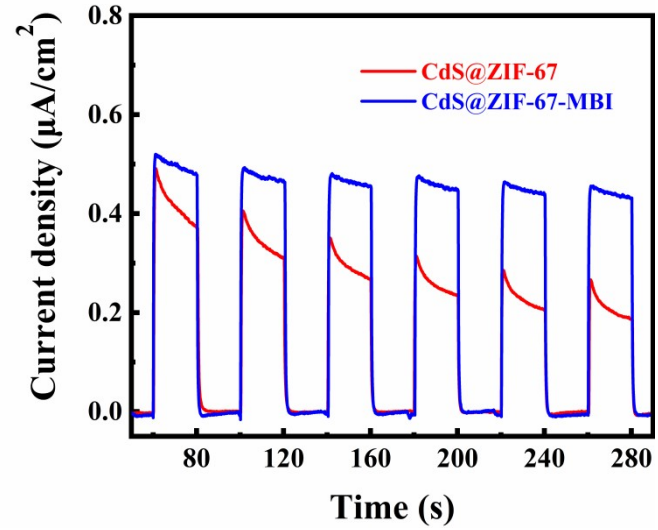

Fig. S3 Transient photocurrent response

Bandgap diagram of ZIF-67-MBI

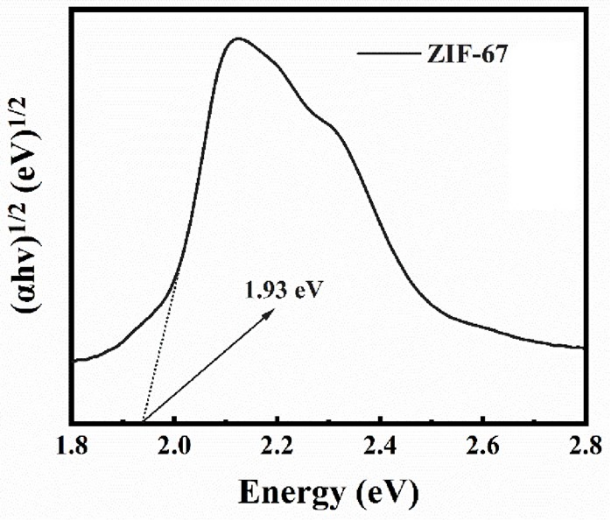

Fig. S4 bandgap diagram of ZIF-67-MBI

Bandgap diagram of CdS

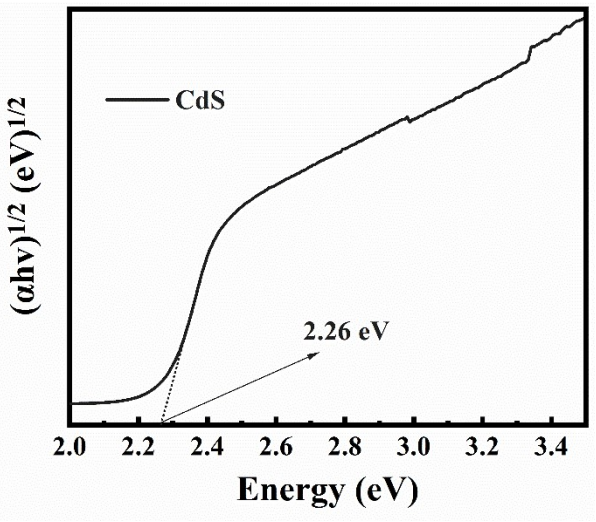

Fig. S5 bandgap diagram of CdS

LC test result

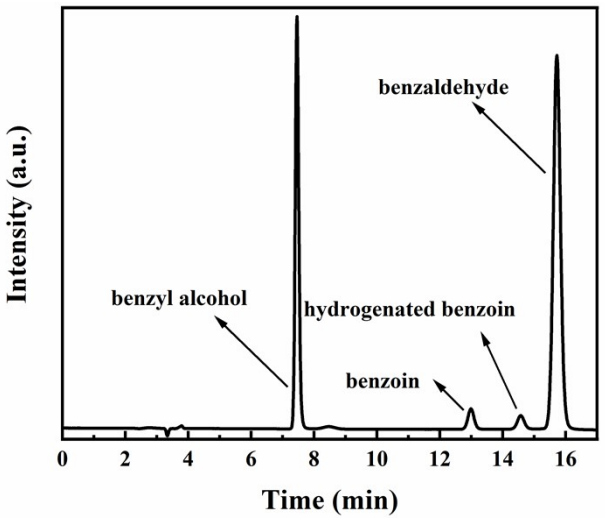

Fig. S6 LC chromatogram of Photocatalytic oxidation of benzyl alcohol coupled hydrogen evolution

GC-MC test result

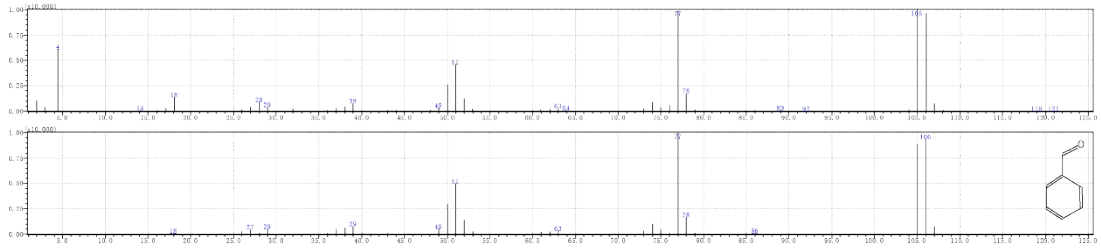

Fig. S7 GC-MC test results for benzaldehyde

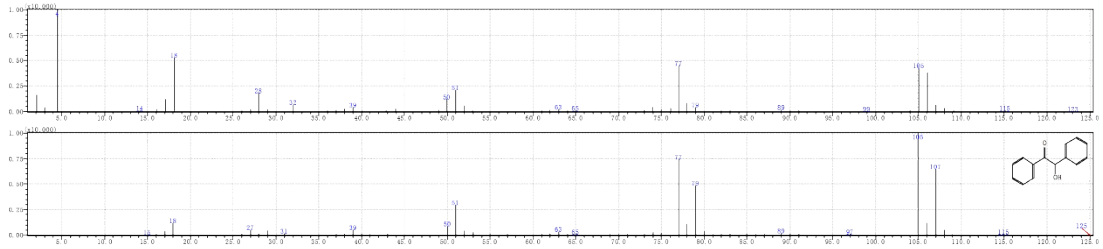

Fig. S8 GC-MC results of Benzoin

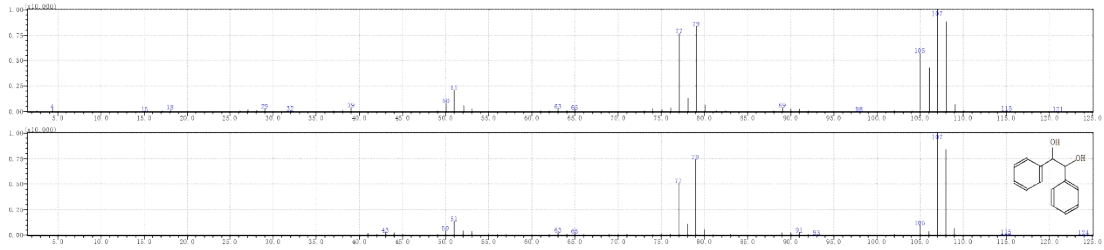

Fig. S9 GC-MC results of hydrogenated benzoin

XRD of sample

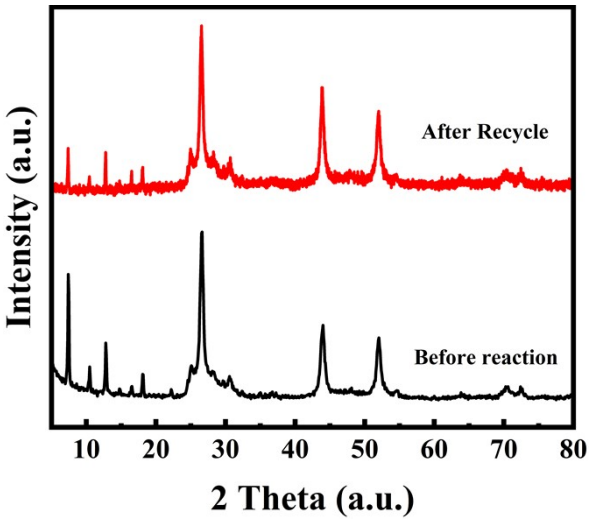

Fig. S10 XRD patterns of CdS@ZIF-67-MBI-5 after five cycles