

Fabrication of highly dispersed Co_3O_4 modified MOFs derived $\text{ZnO}@\text{ZnS}$ porous heterostructure for efficient photocatalytic hydrogen production

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Experimental

Materials

Absolute ethanol, methanol, thioacetamide (CH_3CSNH_2 , TAA), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-Methylimidazole (2-MI) was provided by J&K Co., Ltd. All the reagents were used without further purification.

Preparation of photocatalysts

Synthesis of ZnCo-ZIF and ZnCo-ZIF@ZIF-8

The ZnCo-ZIF was synthesized according to the literature¹. Briefly, 2.0824 g (7.0 mmol) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2910 g (1.0 mmol) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 66.4 mL anhydrous methanol to obtain the Zn-Co-MeOH solution. At the same time, 2.6275 g (32.0 mmol) 2-MI was added to another 66.4 mL anhydrous methanol to give the 2-MI-MeOH solution. Then, the Zn-Co-MeOH solution was poured into the 2-MI-MeOH solution under magnetic stirring. After stirring at room temperature for 20 minutes, it was sealed with plastic wrap and aged for 24 hours. Subsequently, the product was obtained by centrifugation, washed three times with ethanol and dried. The final product was named as ZnCo-ZIF.

To prepare the ZnCo-ZIF@ZIF-8, the obtained ZnCo-ZIF and 2.6275 g (32.0 mmol) 2-MI were added in 100.0 mL of anhydrous methanol. Then the $\text{Zn}(\text{NO}_3)_2$ solution (2.3799 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 22.8 mL of methanol,) was added dropwise into the above solution under stirring. After the addition, the mixture was stirred at room temperature for another 20 minutes, then sealed with plastic wrap and aged for 4 hours. Finally, the ZnCo-ZIF@ZIF-8 was acquired by centrifugation, washed three times with ethanol, and dried in an oven.

ZIF-8 was prepared by a similar method of ZnCo-ZIF without using the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Synthesis of $\text{Co}_3\text{O}_4\text{-ZnO}$ and $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$

The acquired light purple ZnCo-ZIF@ZIF-8 was put into a muffle furnace heating up to 500°C at a heating rate of 2°C/min in air for 3h. After cooling to room temperature, the $\text{Co}_3\text{O}_4\text{-ZnO}$ sample was obtained. The $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$ was prepared by direct sulfurization of $\text{Co}_3\text{O}_4\text{-ZnO}$. 0.2 g $\text{Co}_3\text{O}_4\text{-ZnO}$ sample and 1.0 g thioacetamide (TAA) were dispersed in a round-bottom flask containing 100 mL of water by sonicating, then the reaction was carried out in an oil bath at 75°C for 1 h. The precipitates were collected by centrifugation and washed with deionized water three times, then dried in an oven at 60°C to obtain $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$ sample.

For comparison, ZnO, ZnS, ZnO@ZnS were prepared by this similar method except that $\text{Co}_3\text{O}_4\text{-ZnO}$ was replaced by ZIF-8.

Synthesis of $\text{Co}_3\text{O}_4\text{-ZnO@ZnS/Pt}$

Pt was loaded on the $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$ by the photodeposition method². 0.13 g $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$ sample was dispersed in a mixed solution of 45.0 mL water and 5.0 mL methanol. 330 μL chloroplatinic acid aqueous solution (10 mg/mL) was diluted with 6.0 mL water, and then added dropwise to the $\text{Co}_3\text{O}_4\text{-ZnO@ZnS}$ suspension with stirring under illumination. After the addition,

the photodeposition was further stirred for 45 minutes under the light. Finally, the precipitate was collected by centrifugation and washed 3 times with deionized water, then dried in an oven at 60°C to obtain the Co₃O₄-ZnO@ ZnS/Pt sample.

Material Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Puxi DX-3 diffractometer (operating at 40 kV and 30 mA) with Cu K α radiation. Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microscopy JSM 6701F. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were acquired by a JEOL JEM-2010F. The metal contents were determined by inductively coupled plasma emission spectroscopy (ICP-OES, Agilent-5100). X-ray photoelectron spectroscopy analyzer (XPS, ThermoFischer, ESCALAB 250Xi 12.5 kV) was used to analyze the surface state of the catalysts with Al K α source. Electrochemical impedance spectroscopy (EIS) experiments and Mott-Schottky plot were measured via a Princeton electrochemical workstation (PARSTAT MC 500, America) by a three-electrode system in 0.1 M Na₂SO₄ electrolyte solution. The UV-vis absorption spectra were tested via a UV-vis spectrophotometer using a Halon plate reference (Agilent, Cary 60 UV-Vis). Photoluminescence (PL) spectra were obtained in the spectral range of 200-800 nm under the excitation wavelength of 251 nm with a slit width of 0.5 (Hitachi-F7000). Photocurrent transient responses were recorded at the potential of 0.1 V vs Ag/AgCl in 0.1 M Na₂SO₄ solution (CHI-601). Nitrogen adsorption isotherm was measured on an Autosorb iQ2 analyzer (Quantachrome). The surface area was calculated by the multi-point BET method and the pore diameter was evaluated by the BJH formula.

Photocatalytic H₂ evolution

Photocatalytic water splitting reactions were conducted in a closed glass system (Perfect Light Labsolar-6A) at 15°C. 50 mg of the photocatalyst was dispersed in 100 mL of Na₂S-Na₂SO₃ (35 mM-18 mM) solution. Before starting the test, a vacuum pump was used to remove the air in the system and maintain a vacuum state during the experiment. A 300 W Xe lamp (PLX-300) was used as the light source. The H₂ evolution rate was detected by GC with an interval of 0.5 h (Agilent 8890, with the HP-Plot Molesieve column, TCD, Ar as the carrier).

Apparent quantum efficiency tests

The AQE of photocatalytic water splitting for H₂ generation was calculated from the amount of H₂ produced and the total number of photons participating in the reaction (Eq. 1). 50 mg of catalyst was dispersed in 100 mL of Na₂S-Na₂SO₃ (35 mM-18 mM) solution at a vacuum environment of 15 °C. The incident light source is a 300 W Xe lamp (PLX-300) with a 365 nm band-pass filter. The irradiation range of the incident light is 40.6 cm². The light intensity of the Xe lamp (PLX-300) with a 365 nm band-pass filter is 62.3 mw cm⁻². The AQE was calculated by using the following formula.

$$AQE = \frac{2 \times \text{Number of Hydrogen}}{\text{Number of incident photons}} \times 100\% \quad (\text{Eq.1})$$

$$\text{Number of incident photons} = \frac{IA\lambda}{hc} \quad (\text{Eq.2})$$

Where I is incident light intensity, A is irradiation area, λ is the wavelength of light source, h is Planck constant and c is the speed of light.

Table S1 ICP-OES test results

Sample	Co (wt%)	Pt (wt%)
Co ₃ O ₄ -ZnO	3.18	--
Co ₃ O ₄ -ZnO@ZnS	3.14	--
Co ₃ O ₄ -ZnO@ZnS/Pt	3.09	1.72

Table S2 Fluorescence lifetime of ZnO, ZnS, ZnO@ZnS, Co₃O₄-ZnO, Co₃O₄-ZnO@ZnS and Co₃O₄-ZnO@ZnS/Pt.

Sample	Time
ZnO	1.3345 ns
ZnS	1.7000 ns
ZnO@ZnS	1.7079 ns
Co ₃ O ₄ -ZnO	1.6216 ns
Co ₃ O ₄ -ZnO@ZnS	2.7506 ns
Co ₃ O ₄ -ZnO@ZnS/Pt	3.3361 ns

Table S3 The AQEs of Co₃O₄-ZnO@ZnS and Co₃O₄-ZnO@ZnS/Pt for H₂ generation in 0.35 M Na₂S, Na₂SO₃ solution under 365 nm light irradiation.

365 nm	H ₂ ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	AQE (%)
Co ₃ O ₄ -ZnO@ZnS	41.5	7.01
Co ₃ O ₄ -ZnO@ZnS/Pt	68.6	11.69

Table S4 Comparison of the photocatalytic H₂ evolution rates over different ZnO or ZnS-based materials.

Materials	Experimental condition	H ₂ evolution rate	Reference
ZnO/ZnS Nanorod	Simulated sunlight, 10%, glycerol	384 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[3]
ZnS-ZnO/ZnAl-LDH	UV Pen-Ray, 50%, methanol	1599 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[4]
flower-like ZnO@ZnS	300 W Xenon lamp, 10%, methanol	757.07 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[5]
ZnO/ZnS nanobranches decorated with Cu(OH) ₂ clusters	350 W Xe lamp, 0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	1350 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[6]
ZnS quantum/ZnO sphere/Bi ₄ O ₅ I ₂	300 W Xenon lamp, 20%, methanol	578.4 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[7]
ZnO/ZnS-PdS	125 W He lamp, 5% glycerol	2141.9 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[8]
Ce doped ZnO/ZnS	500 W Hg-Xe arc lamp, 0.1 M Na ₂ S/0.04 M Na ₂ SO ₃	1200 $\mu\text{mol h}^{-1} \text{g}^{-1}$	[9]
Co₃O₄-ZnO@ZnS/Pt	300 W Xe lamp 0.35 M Na₂S/0.18 M Na₂SO₃	3269.3 $\mu\text{mol h}^{-1} \text{g}^{-1}$	This work

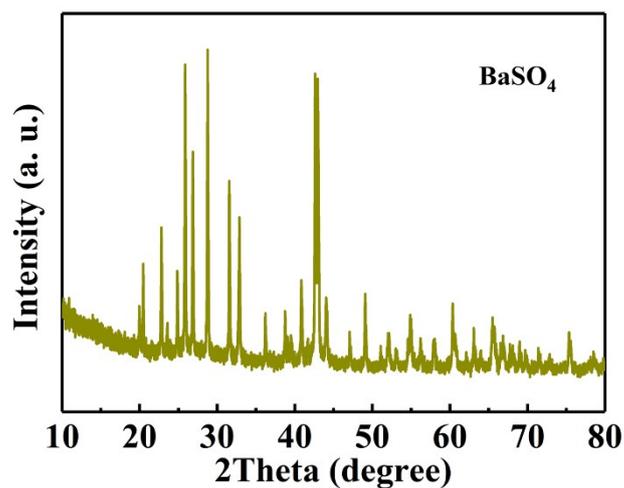


Fig. S1 The PXRD pattern of the white precipitate obtained from the photocatalytic reaction without using the sacrificial agent.

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