

## Supporting information

# Construction of hierarchical $\text{CoP}@ZnIn_2\text{S}_4$ heterojunction for photocatalytic hydrogen evolution

Yuqin Liu <sup>a</sup>, Liyong Ding <sup>b\*</sup>, Qian Xu<sup>c</sup>, Yu Ma <sup>a</sup>, Juncheng Hu <sup>a\*</sup>

<sup>a</sup> Hubei Key Laboratory of Catalysis and Materials Science, School of Chemistry and Materials Science, South-Central Minzu University, Wuhan 430074, China

<sup>b</sup> College of Chemical and Material Engineering, Quzhou University, Quzhou 324000, China

<sup>c</sup> Zhongnan University of Economics and Law, Wuhan 430073, China.

\*Corresponding authors

E-mail: [jchu@mail.scuec.edu.cn](mailto:jchu@mail.scuec.edu.cn); [liyongding1988@163.com](mailto:liyongding1988@163.com)

## 1. Experimental details

### 1.1. Materials

Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 98.5\%$ ), urea ( $\text{CH}_4\text{N}_2\text{O}$ ,  $\geq 99\%$ ), thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ,  $\geq 99\%$ ), sodium hypophosphite monohydrate ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 98%), triethanolamine ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ,  $\geq 99\%$ ) and glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ,  $\geq 99\%$ ) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Zinc chloride ( $\text{ZnCl}_2$ ,  $\geq 98\%$ ) and indium chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ , 99.9%) were supplied from Aladdin Industrial Corporation. All reagents were analytical grade, and deionized (DI) water was utilized throughout the experiments.

### 1.2. Synthesis of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})_{0.11}\text{H}_2\text{O}$ nanoflowers

$\text{Co}(\text{CO}_3)_{0.5}(\text{OH})_{0.11}\text{H}_2\text{O}$  was prepared as follows. Typically, 1 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 4 mmol of urea were dispersed in 40 mL deionized water and stirred at room temperature for 30 min to form a uniform solution. Then the above mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and reacted at 120 °C for 5 h. After cooling to room temperature, the resulting pink product were washed with ethanol for several times, and then collected and dried in vacuum at 60 °C overnight.

### 1.3. Synthesis of CoP nanobunches

$\text{Co}(\text{CO}_3)_{0.5}(\text{OH})_{0.11}\text{H}_2\text{O}$  powder was placed in an aluminum crucible, which was heated to 300 °C with a ramping rate of 2 °C/min and kept at this temperature for 2 h in air. Next, 50 mg of obtained  $\text{Co}_3\text{O}_4$  powder and 500 mg of  $\text{NaH}_2\text{PO}_2$  (mass ratio 1:10) were put into two quartz boats respectively, and put into the tube furnace with sodium hypophosphite monohydrate upstream and heated at a ramping rate of 3 °C/min to 350 °C for 2 h in Ar flow. Finally, CoP black power was collected after cooling to room temperature.

### 1.4. Synthesis of hierarchical $\text{CoP}@Z\text{nIn}_2\text{S}_4$ composite

$\text{CoP}@Z\text{nIn}_2\text{S}_4$  was synthesized by a simple low temperature solvothermal process. In a typical preparation, 5 mg CoP was dispersed into 32 mL water and 8 mL glycerol

by ultrasonication. Then, 175.9 mg  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  and 40.9 mg  $\text{ZnCl}_2$  were added consecutively into the above solution under stirring. After continuous stirring for 2 h, 120.2 mg of thioacetamide was added and stirred for 10 min. Afterward, the obtained mixed solution was subjected to an oil bath at 80 °C under stirring for 2 h. The obtained products were centrifuged and washed completely by ethanol several times, and dried under vacuum at 60 °C overnight. The dark green powders denoted as 5-CoP@ZnIn<sub>2</sub>S<sub>4</sub> (5-CoP@ZIS). The resulting samples containing different CoP loading amounts (e.g. 4 mg, 6 mg, 8 mg and 10 mg) were marked as 4-CoP@ZnIn<sub>2</sub>S<sub>4</sub> (4-CoP@ZIS), 6-CoP@ZnIn<sub>2</sub>S<sub>4</sub> (6-CoP@ZIS), 8-CoP@ZnIn<sub>2</sub>S<sub>4</sub> (8-CoP@ZIS) and 10-CoP@ZnIn<sub>2</sub>S<sub>4</sub> (10-CoP@ZIS) respectively. For comparison, pure ZnIn<sub>2</sub>S<sub>4</sub> (ZIS) was synthesized by the same method without the addition of CoP.

## 2. Characterization

The crystal structure of the as-obtained products was collected by X-ray diffraction (XRD) (Bruker D8 Advance; Cu K $\alpha$  = 1.5404 Å). The 2 $\theta$  range was from 15° to 80° with the 0.05 °/s scanning rate. The samples surface morphology and size were characterized by SU8010 field-emission scanning electron microscopy (FESEM, Hitachi, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were measured on FEI F200X microscope which operated on an accelerating mode of 200 kV. The element chemical state of the resulting products was analyzed by X-ray photoelectron spectroscopy (XPS) (VG Multi lab 2000) and calibrated by C 1s spectrum (binding energy is 284.8 eV). The optical absorption property of the obtained photocatalysts was detected by the UV–Vis diffused reflectance spectra (DRS), which was recorded using a Cary Series UV–Vis–NIR Spectrophotometer (Agilent Technologies) from 200 nm to 800 nm by a diffuse reflectance method using BaSO<sub>4</sub> as reflectance standard. Photoluminescence (PL) spectra were characterized on a Hitachi F-7000 with a 150 W Xe lamp. The transient photocurrent responses, electrochemical impedance spectroscopy (EIS) and Mott–Schottky(M-S) plots were performed on the electrochemical workstation (CHI-760E, CHI Shanghai, Inc.) with a three-electrode system, in which platinum plate as the counter electrode and Ag/AgCl as the reference electrode, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> was

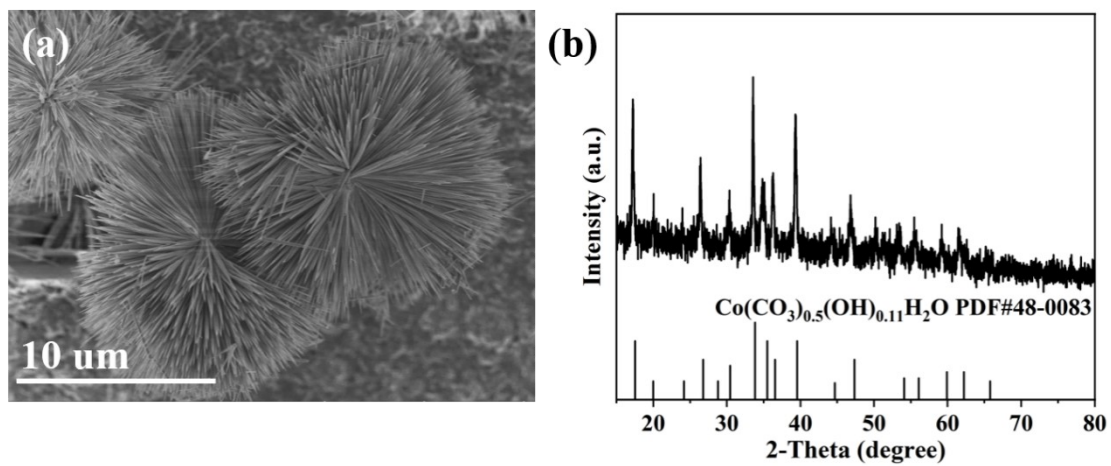
employed as electrolyte solution. The working electrode was prepared as follows: 5 mg of photocatalysts were ultrasonically dispersed in 950  $\mu\text{L}$  anhydrous ethanol and 50  $\mu\text{L}$  Nafion to form a homogeneous solution. Then the homogeneous solution (40  $\mu\text{L}$ ) was coated on a piece of FTO glass with an active area of ca. 1  $\text{cm}^2$  and dried naturally at room temperature. Transient photocurrent test was carried out on the above electrochemical instrument, and the light source (365 nm) was provided by a LED light (LAMPLIC GUV-310) as an accessory to the electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was measured under the open circuit voltage without the light irradiation, and the frequency range was 1-100 kHz with an AC amplitude of 5 mV. The same electrochemical system was also used to determine the flat-band potential of the working electrodes by the Mott-Schottky (MS) method. The frequencies were 500, 1000, and 1500 Hz.

### **3. Photocatalytic H<sub>2</sub> evolution tests**

The photocatalytic H<sub>2</sub> evolution experiments were detected in an online reaction system (nitrogen as a carrier gas, FULI 9790). A 300 W Xenon lamp with AM 1.5G filter was employed to simulate solar illumination. Typically, 20 mg of the as-obtained photocatalyst was dispersed in 100 ml of aqueous solution (containing 10 vol% TEOA as a sacrificial agent), which was placed in a closed quartz reactor and ultrasound for 10min. Prior to light irradiation, purged with nitrogen for 30 min to remove the air. The reactor was equipped with water circulation in the outer interlayer to alleviate the influence brought by the heat from light. During the photocatalytic tests, 0.4 mL of gas was taken out each 30 min by the gas injector, and the concentration of H<sub>2</sub> was monitored by gas chromatography (FULI 9790).

The recycling experiments of photocatalytic H<sub>2</sub> evolution were performed as follows: briefly, 20 mg of the as-obtained photocatalyst was dispersed in 100 ml of aqueous solution (containing 10 vol% TEOA as a sacrificial agent). After every run with 4 h, the photocatalysts were centrifugated and washed by water 2 times, the resultant precipitate was collected and dried at 60 °C in a vacuum oven overnight, and the quartz reactor was degassed and placed with photocatalyst and sacrificial agents as the above photocatalytic H<sub>2</sub> evolution tests. Similarly, the following three runs were

performed with the same procedures.



**Figure S1.** (a) SEM image and (b) XRD pattern of  $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})_{0.11}\text{H}_2\text{O}$ .

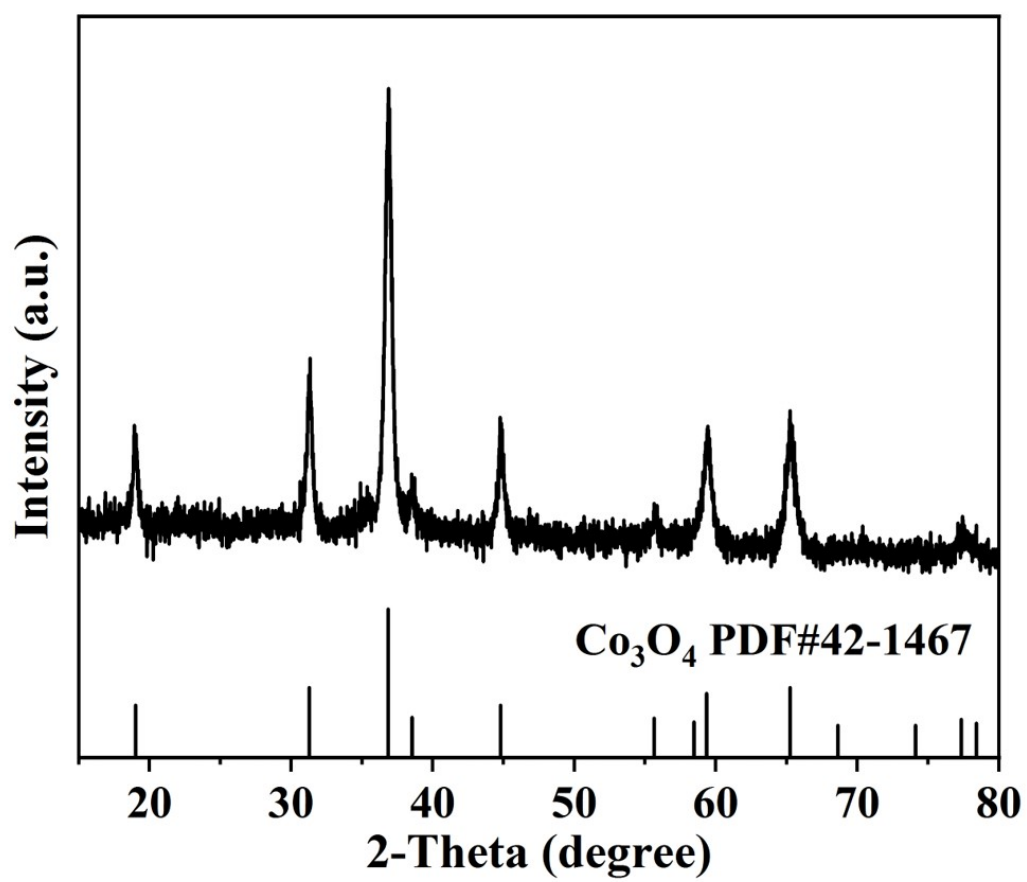
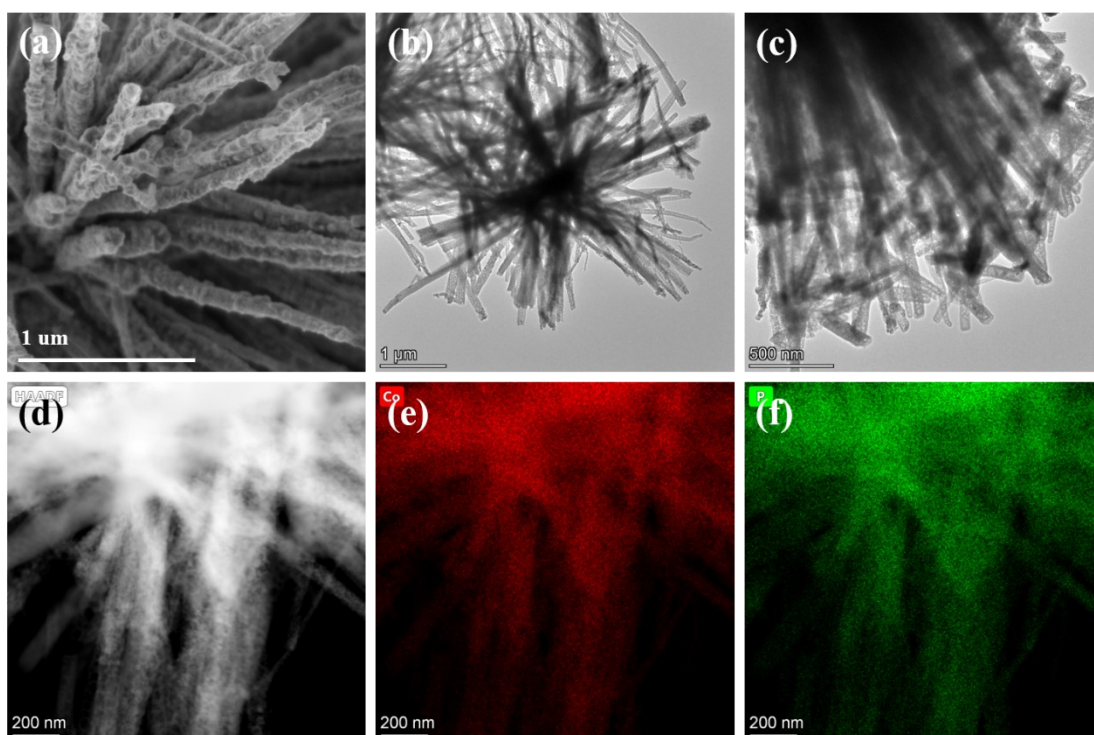
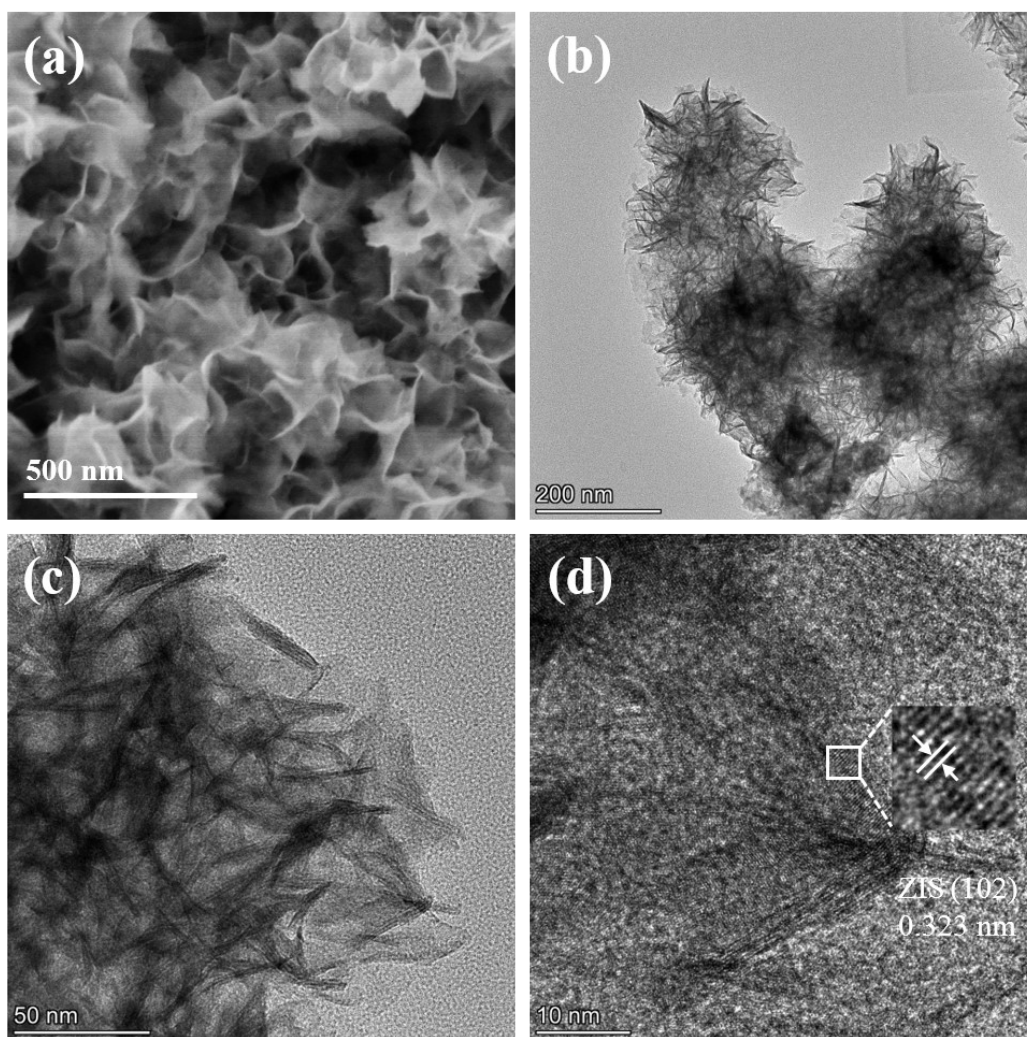


Figure S2. XRD pattern of  $\text{Co}_3\text{O}_4$ .

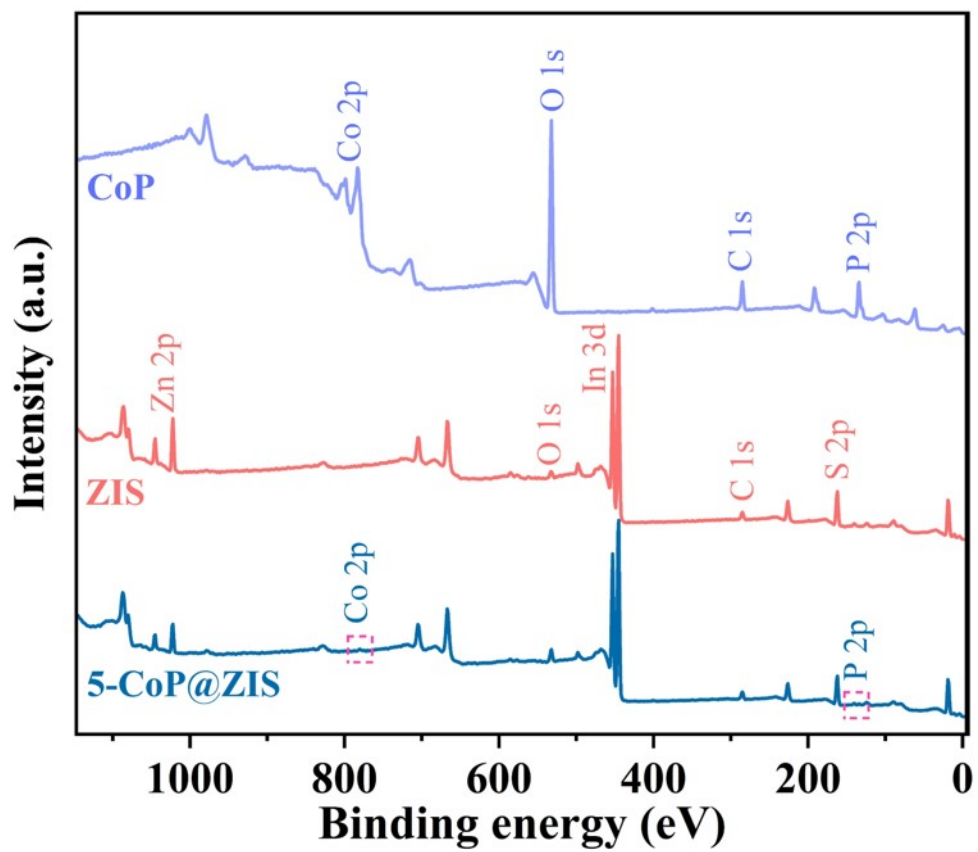


**Figure S3.** (a) SEM, (b-c) TEM, (d) HAADF-STEM, and (e-f) corresponding elemental mapping images of CoP.

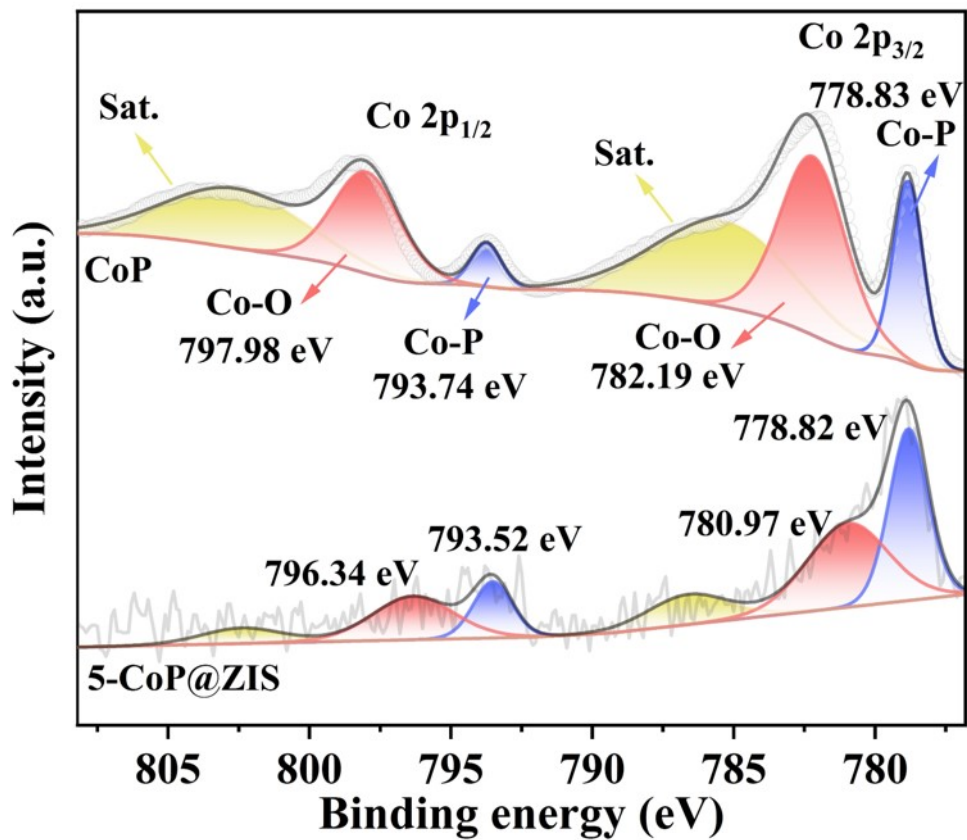


**Figure S4.** (a) SEM, (b-c) TEM, and (d) HRTEM images of pure ZIS.

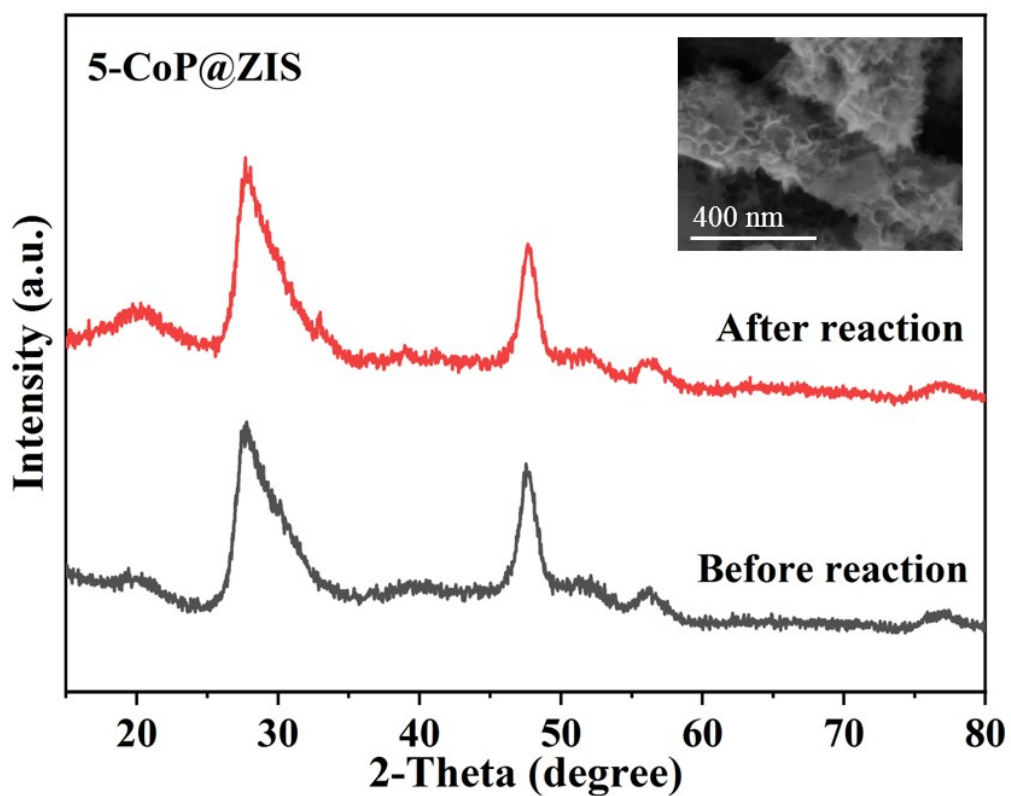




**Figure S5.** The survey XPS spectra of CoP, ZIS and 5-CoP@ZIS.



**Figure S6.** High-resolution XPS spectra of Co 2p of CoP and 5-CoP@ZIS.



**Figure S7.** XRD patterns comparison of fresh and used 5-CoP@ZIS (inside is the SEM image after the photocatalytic reaction).