Supporting information

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1. Materials

Thioacetamide (TAA, 99%, AR) was obtained from Shanghai Macklin Biochemical Co. Ltd, and nickel nitrate hexahydrate (\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 98.5\%) and cobalt nitrate hexahydrate (\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 98.5\%) were received from Tianjin Kemiu Chemical Reagent Co. Ltd. Other reagents such as (\text{CH}_3\text{COO})_2\text{Zn}, \text{InCl}_3, \text{urea} and \text{NH}_4\text{F} were all of analytical grade and used as received without further purification. Ultrapure water was used during whole process.

2. Characterizations

2.1 Physic characterization

The crystal structure and composition of the samples was ascertained by X-ray diffraction (XRD, Rigaku Smartlab) with Cu K\textalpha radiation ($\lambda = 0.154$ nm), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, Kratos AXIS NOVA spectrometer). The morphology of the photocatalyst was examined using transmission electron microscopy (Tecnai G2 F30) and scanning electron microscopy (Carl Zeiss Sigma, SEM). The photoresponse characteristics of the catalysts were measured using a UV-vis spectrophotometer (Shimadzu UV-3600). 4.8\%-\text{NiCo}_2\text{O}_4/\text{ZnIn}_2\text{S}_4 composite was chosen for characterization because it has better activity during H\textsubscript{2} production experiments.

2.2 Photoelectrochemical test

The photoelectric test of the samples was assessed on an electrochemical workstation (CHI660E, ChenHua in Shanghai) using a traditional three-electrode system in 0.5 mol/L Na\textsubscript{2}SO\textsubscript{4} electrolyte. They are divided into two groups, with a platinum wire serving as the counter electrode and a standard calomel electrode (SCE)
serving as the reference electrode. The working electrode is prepared as follows: 3 mg of the samples were dissolved in 4 mL of deionized water following 2 h of ultrasonic treatment. 1 mL of a homogeneous solution was dropped on a piece of 2 cm×3 cm FTO glass, and it dried naturally at room temperature. This work measured the transient photocurrent response (I-t curve, at -0.5 V potential vs. SCE), electrochemical impedance analysis (EIS, frequency ranging from 10-2 to 105 Hz), MS (Mott-Schottky curves, ranging from -0.6 V to 0.8 V vs. SCE), and LSV curve analysis (linear sweep voltammetry curves, ranging from -2.0 to 2.0 V vs SCE.

2.3 Photocatalytic activity test

Photocatalytic H₂ production experiments were carried out in Lab solar III-AG system (Beijing Perfect light Technology Co. Ltd., China). In detail, 10 mg of catalyst and 100 mL of the sacrificial solution (the volume of triethanolamine and water is 1:4) were put into the reactor, the gas in the system was evacuated before the reaction, the temperature was maintained at 30 °C using circulating cooling water, and the light source was a 300 W xenon lamp (350-780 nm), it was placed at a distance of 10 cm from the reaction solution. The amount of produced H₂ was measured using gas chromatography (Tianmei, GC7900) using N₂ as carrier gas.

![Fig.S1 XRD pattern of 4.8%-NiCo₂O₄/ZnIn₂S₄ composite before and after use.](image)
Fig. S2 (a-b) SEM characterization of 4.8%-NiCo$_2$O$_4$/ZnIn$_2$S$_4$ before and after H$_2$ evolution