Synergistic effects of Rh-S bond and spatially separated dual cocatalysts on photocatalytic overall water splitting activity of ZnIn2S4 nanosheets under visible light irradiation

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Chemicals

Zinc acetate dihydrate (Aladdin; AR), Indium(III) chloride tetrahydrate (Macklin; AR), Thioacetamide (Macklin; AR), Citric acid (Aladdin; AR), Chromium(III) nitrate nonahydrate (Aladdin; AR), Rhodium Chloride Hydrate (Aladdin; AR)，Ethanol absolute (SCR; AR), Chloroplatinic acid hexahydrate (Aladdin; AR).

Preparation of $ZnIn_2S_4$ loaded with different cocatalysts

The hydrothermal preparation of initial $ZnIn_2S_4$ was obtained according to our reported literature [1].

$ZnIn_2S_4$-Pt-Cr and $ZnIn_2S_4$-Rh-Cr were prepared by loading the cocatalyst onto the initial $ZnIn_2S_4$ by photodeposition method. In general, 100 mL of pure water is mixed with H_2PtCl_6 (1.5wt % Pt) or $RhCl_3$ (1.5wt % Rh), $Cr(NO_3)_3$ (0.5wt % Cr) and photocatalyst (50 mg). Then the suspension was stirred for two hours under vacuum and irradiation with a 300W xenon lamp.

$ZnIn_2S_4$-Pt, $ZnIn_2S_4$-Rh and $ZnIn_2S_4$-Cr were prepared using the above method but only use H_2PtCl_6 (1.5wt % Pt), $RhCl_3$ (1.5wt % Rh) or $Cr(NO_3)_3$ (0.5wt % Cr).

Characterization

The morphologies of the samples were recorded using a high-resolution transmission electron microscope (HRTEM, JEM-2100F) equipped with energy dispersive X-ray spectrometer (EDS). The elemental chemical states of the samples were measured using a X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-

Alpha+), and the binding energies calibrated to the C1s peak at 284.8 eV. The photoluminescence (PL) spectra were measured at room temperature using a fluorescence spectrophotometer (Hitachi F-7000) (excitation wave length: 360 nm). The time-resolved PL (TRPL) decay spectra were recorded using a spectrofluorometer (FLUOROLOG-3-11) with an excitation wavelength of 370 nm.

Photocatalytic overall water splitting activity measurements

Photocatalytic overall water splitting perform were tested on Labsolar-IIIAG system (Perfect Light). $ZnIn_2S_4$ (50 mg) loaded with cocatalyst was added into 100 mL of pure water. A vacuum was applied to remove any dissolved gases before photocatalytic water splitting activity. A 300 W Xenon lamp (Perfect Light, PLX-SXE300) equipped with UV cutoff filter ($\lambda \geq 420$ nm) was used as visible light source.

$$\text{Apparent quantum efficiency (AQE)} = \frac{2 \times moles\ of\ H_2\ production\ per\ hour}{moles\ of\ photon\ flux\ per\ hour} \times 100\%\ (1)$$

A 300 W Xenon lamp with AM 1.5G filter (100 mW cm^{-2}) and 100 mg photocatalyst are used to achieve STH efficiency.

$$\text{STH} = \frac{H_2\ production\ rate\ (mol\ s^{-1}) \times 237KJ\ mol^{-1}}{energy\ flux\ of\ the\ incident\ sunlight\ (W\ m^{-2}) \times irradiated\ area\ (m^2)} \times 100\%\ (2)$$

Photoelectrochemical measurement

In a three-electrode system, photoelectrochemical properties were tested using an electrochemical workstation (CHI-760E). An electrophoretic deposition method was used to prepare the working electrode [1, 2]. The electrophoresis was conducted for five minutes at a constant bias of 10 V. After preparation, the electrode was dried at 100°C in air for one hour. The counter electrode was a platinum foil (10 x 10 mm). The reference electrode was a Hg/HgO electrode. KOH solution (0.1 M, pH = 13) was used as electrolyte.

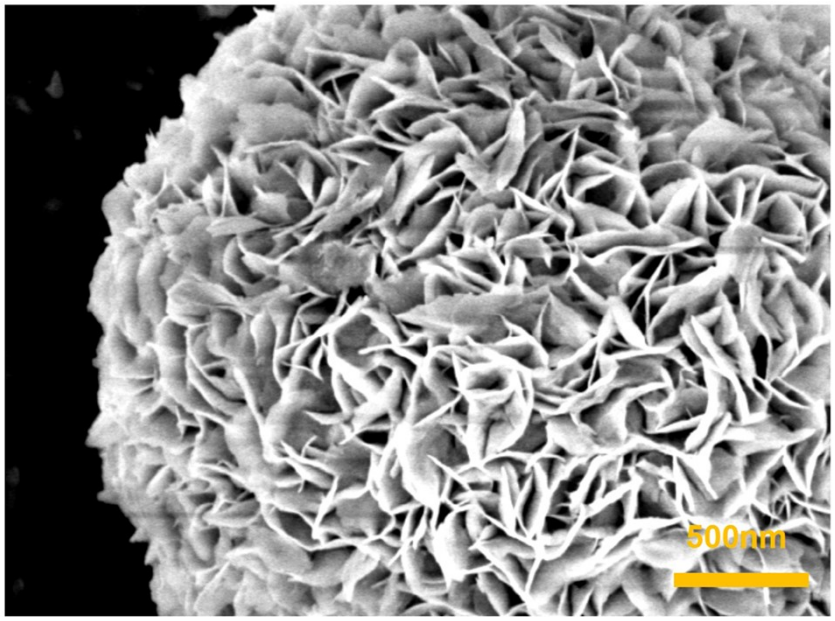

Fig. S1. FESEM image of the $ZnIn_2S_4$.

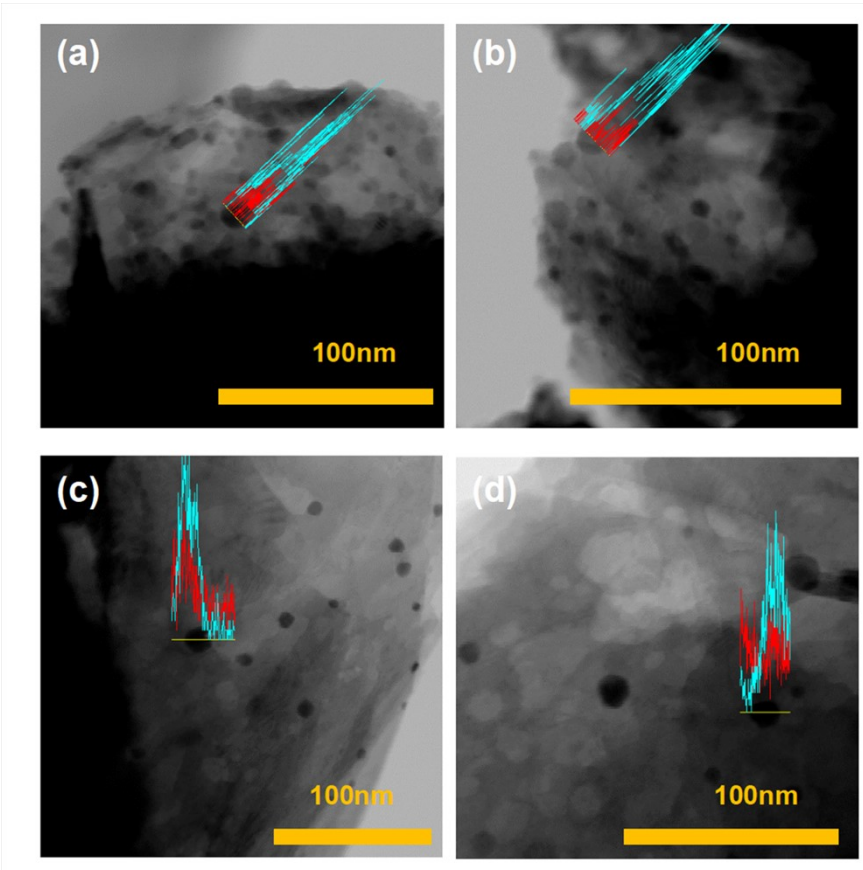

Fig. S2. (a) and (b) Rh (blue lines) and Cr (red lines) EDS line scanning of the $ZnIn_2S_4$-Rh-Cr; (c) and (d) Pt (blue lines) and Cr (red lines) EDS line scanning of the $ZnIn_2S_4$-Pt-Cr;

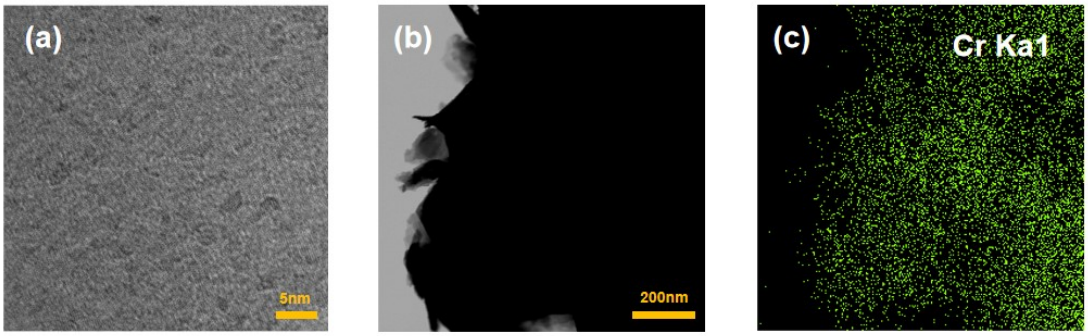

Figure S3. (a) HRTEM images, (b) TEM images and (c) corresponding Cr elemental mapping of the $ZnIn_2S_4$-Cr.

References

1. H. Jing, G. Xu, B. Yao, J. Ren, Y. Wang, Z. Fang, Q. Liang, R. Wu and S. Wei, ACS Appl. Energ. Mater., 2022, 5, 10187-10195.
2. S. Wei, Y. Chen, P. Wu, X. Liu, J. Ren, B. Yao, H. Xu, W. Dou, Y. Wang, R. Wu, Z. Fang and Q. Liang, Appl. Cataly. A-Gen., 2022, 640.