Supporting Information for the manuscript

Rationally designed dual cocatalysts on $ZnIn_2S_4$ nanoflower for photoredox coupling of benzyl alcohol oxidation with H_2 evolution

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Synthetic procedures and characterization of products

1. Synthesis of $ZnIn_2S_4$ (ZIS)

ZIS was prepared by a hydrothermal method. In a typical procedure, $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol), $InCl_3$ (2 mmol) and CTAB (0.7 mmol) were dissolved in 30 mL of deionized (DI) water by stirring 0.5 h to form a homogeneous transparent solution. Then, excessive sulfur source TAA (8 mmol) was added into the above mixture solution. After being stirred for another 0.5 h, the mixture solution was transferred into a 50 mL Teflon-lined stainless-steel room maintained at 160 ℃ for 16 h. The product is cooled to room temperature in an autoclave and recovered by filtration and washed with deionized (DI) water and absolute ethanol several times, respectively. The final sample was fully dried at 60 ℃ in vacuum.

2. Synthesis of pure GO

GO was synthesized by a modified Hummers' method. In detail, 10 g graphite powder (supplied from Qingdao Zhong tian Company, China) was put into 230 mL concentrated H_2SO_4 under moderate stirring. Then, 30 g $KMnO_4$ was added gradually under stirring and the solution was cold below 5 °C in an ice bath. After that, the solution was heated to 35 °C in a water-bath and kept stirring for 2 h. Then, the mixture was diluted with 500 mL DI water in an ice bath to keep the temperature below 5 °C. Shortly after the further diluted with 1.5 L of DI water, 80 mL 30% H_2O_2 was then added into the mixture. The mixture was centrifuged and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. After that, the mixture was dialyzed for one week and the final GO sample was obtained after full sonication.

3. Synthesis of $ZnIn_2S_4$-GR (ZIS-GR)

ZIS With the exception of adding graphene additional, ZIS-GR was prepared in the same manner as ZIS.

4. Synthesis of $ZnIn_2S_4$-Ni_2P (ZIS-Ni_2P)

ZIS-Ni_2P were prepared by an insitu photochemical deposition strategy. Typically, 60 mg of the prepared ZIS were first dispersed in a 20 mL DI by sufficient sonication, followed by addition of a calculated amount of $Ni(NO_3)_2 \cdot 6H_2O$ and NaH_2PO_2. After using nitrogen (N_2) bubbling for 40 min to eliminate air from the mixture, the yellow suspension was illuminated under visible light ($\lambda > 420$ nm) for 20 min with stirring. After illumination, the precipitate was recovered by filtration and washed three times with deionised water. Finally, sample was fully dried at 60 ℃ in vacuum.

5. Characterizations

The morphological characteristics were tested through scanning electron microscopy SEM (ZEISS Sigma 500 instrument) and transmission electron microscopy TEM (Jeol JEM-2100F instrument). The determination of crystal structures was determined by X-ray diffraction (XRD) with Cu Kα ($\lambda = 0.15406$ nm, Bruker D8). The surface composition of the samples was determined by X-ray photoelectron spectrometer (XPS, Thermo Fisher K-Alpha). The nitrogen adsorption-desorption isotherm of samples was analyzed using ASAP 2020 automatic analyzer.

The photoluminescence of the samples was analyzed by using FLS980 fluorescence spectrometer at the excitation wavelength λ=300 nm. Furthermore, all the electrochemical measurements of the photocurrent, the electrochemical impedance spectra (EIS), the Mott–Schottky (MS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were carried out in the three-electrode cell, in which Ag/AgCl was used as reference electrode, a Pt wire was used as a counter electrode and an indium in oxide (ITO) conductive glass was used with the samples as a working electrode in 0.1 M Na_2SO_4 electrolyte (pH=7.56), all measurements were carried out on CH Instruments CHI-660E electrochemical workstation. The values relative to Ag/AgCl could be directly converted to the values vs NHE to facilitate comparison.

$$E_{NHE} = E_{Ag/AgCl} + 0.059 \times pH + E^{\theta}_{Ag/AgCl} \quad (1)$$

Contact angle measurements were carried out using the static drop method using a Fangrui Instrument Company JCY contact angle meter.

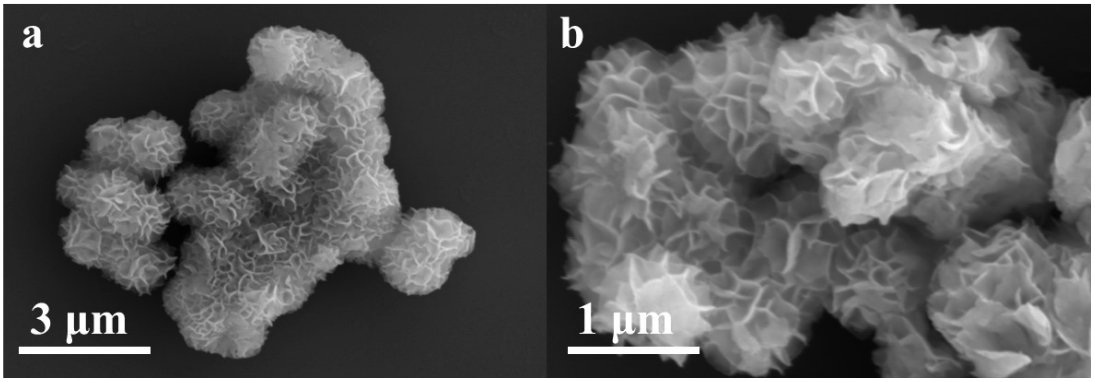

Fig. S1. FESEM images of ZIS-GR (a, b).

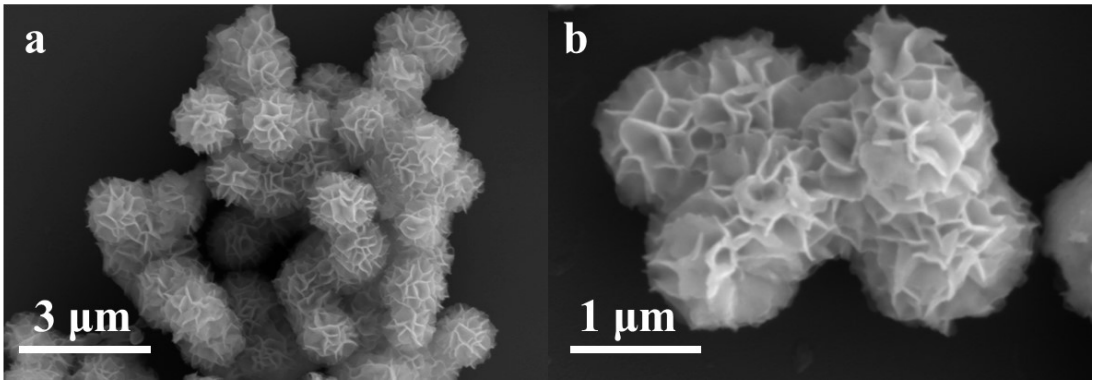

Fig. S2. FESEM images of ZIS-Ni_2P(a, b).

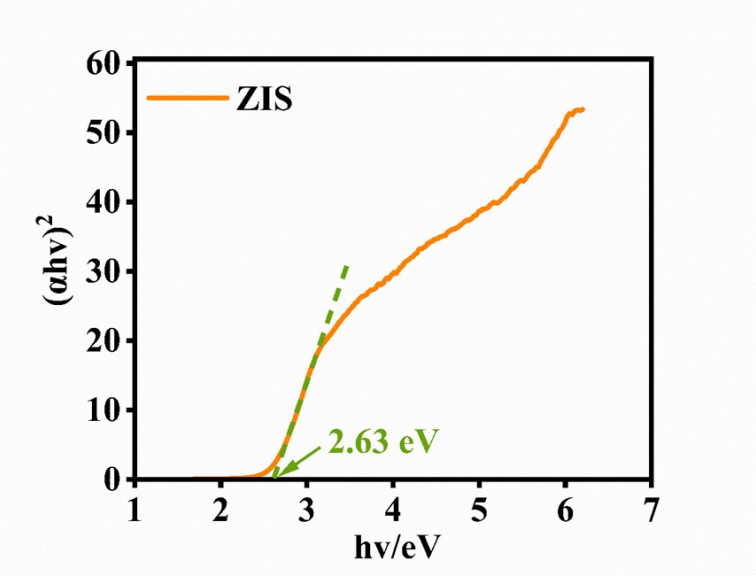

Fig. S3. Tauc plot for optical band gap of blank ZIS.

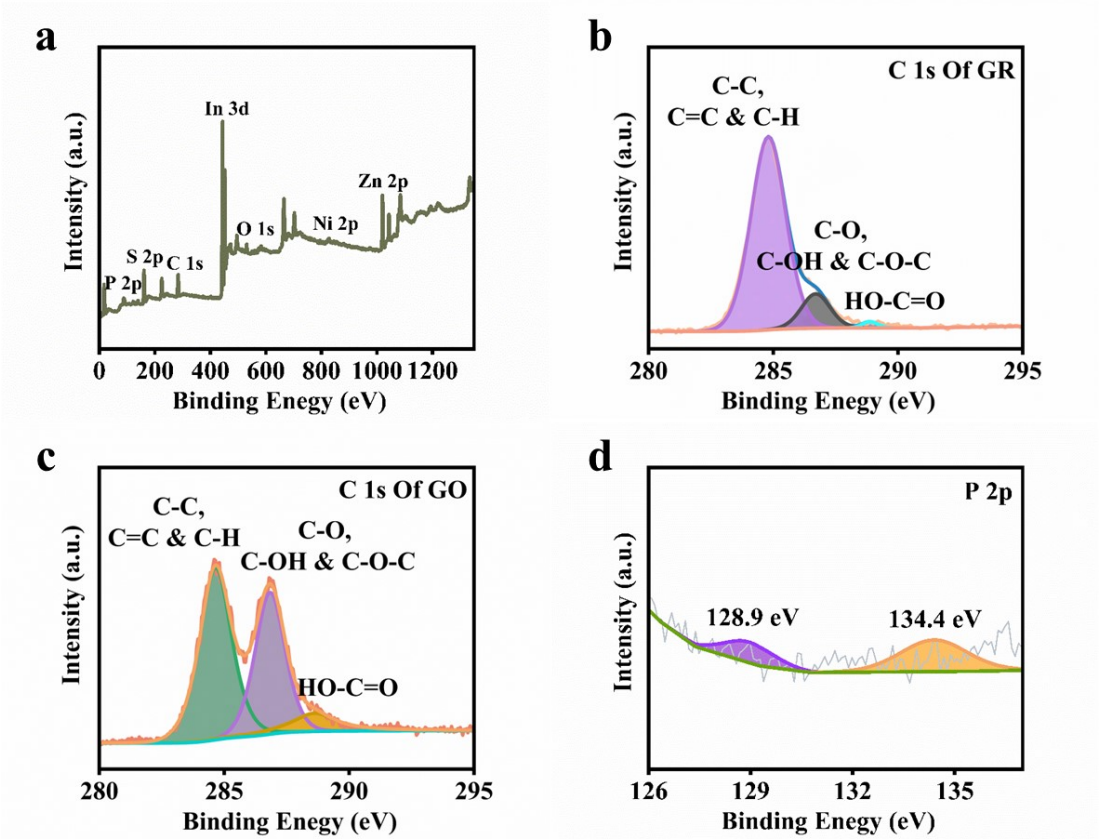

Fig. S4. XPS survey spectrum of ZIS-GR-Ni_2P (a). XPS spectra of C 1s (c) of GR (b). XPS spectra of C 1s (c) of GO (c) and P 2p (d) of ZIS-GR-Ni_2P composite.

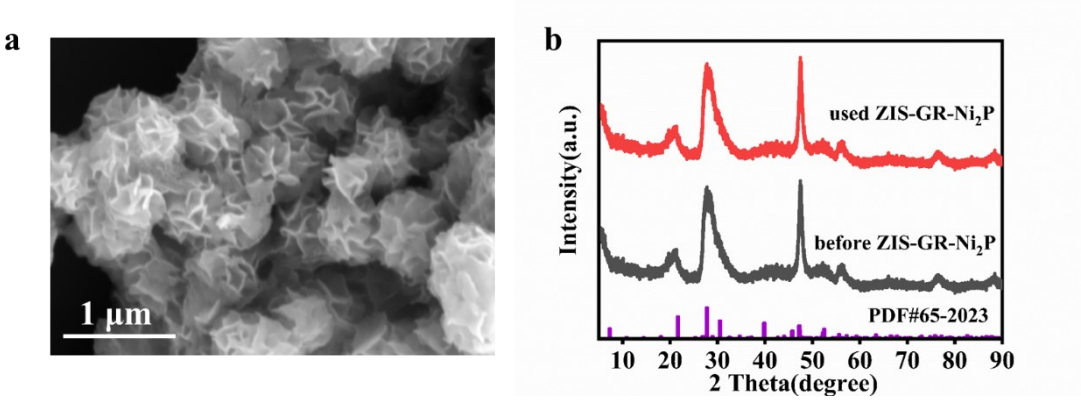

Fig. S5. FESEM images of used ZIS-GR-Ni_2P composites (a). X-ray diffraction (XRD) patterns of fresh and used ZIS-GR-Ni_2P composites (b).

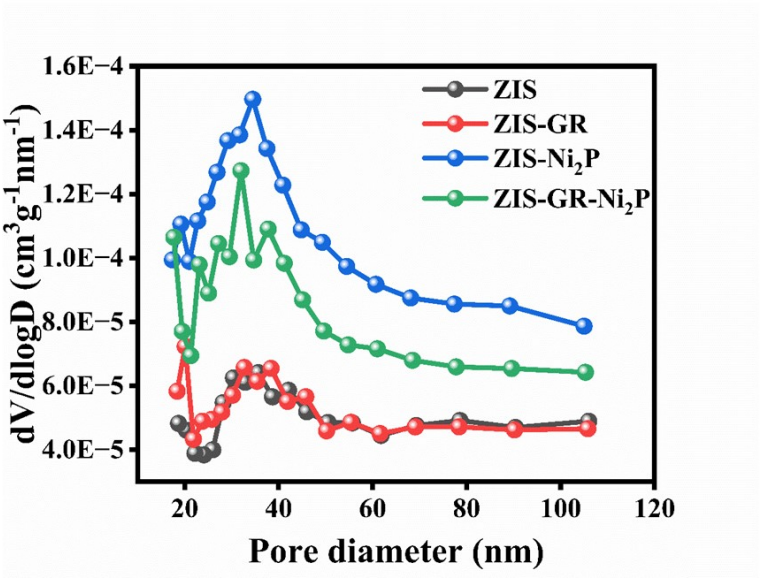

Fig. S6. Pore size distribution of ZIS, ZIS-GR, ZIS-Ni_2P and ZIS-GR-Ni_2P.

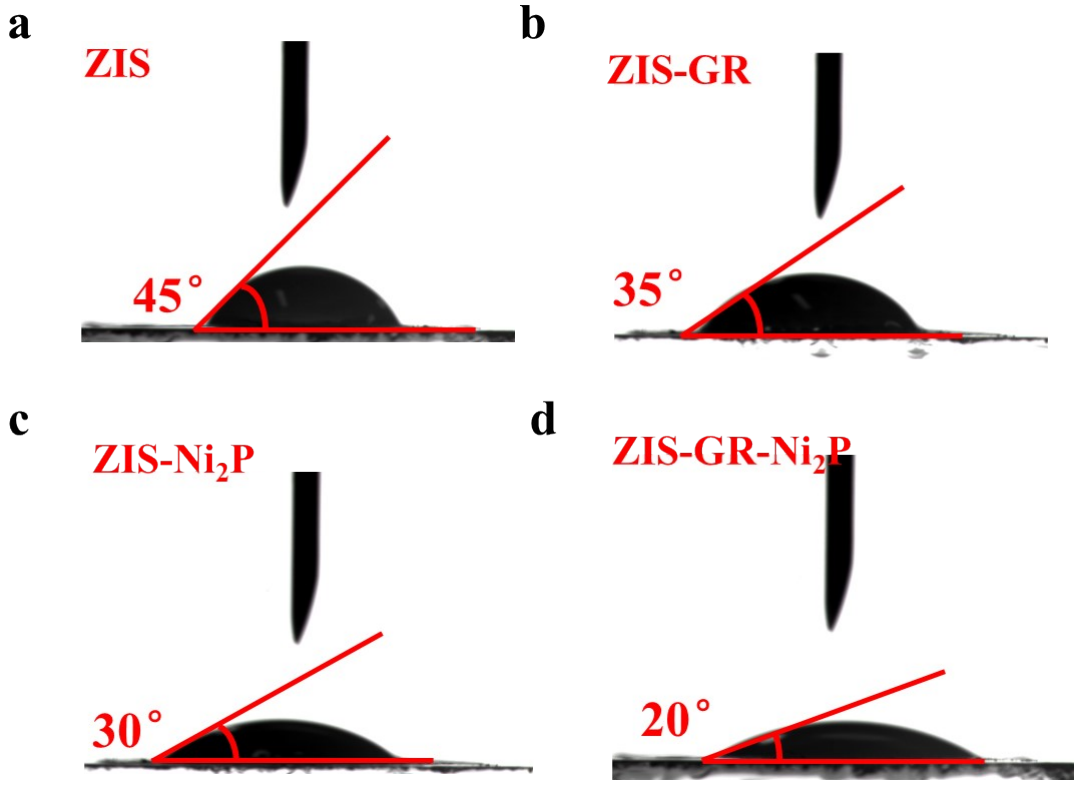

Fig. S7. Schematic diagram of the contact angles of ZIS (a), ZIS-GR (b), ZIS-Ni_2P (c) and ZIS-GR-Ni_2P (d) with droplets.

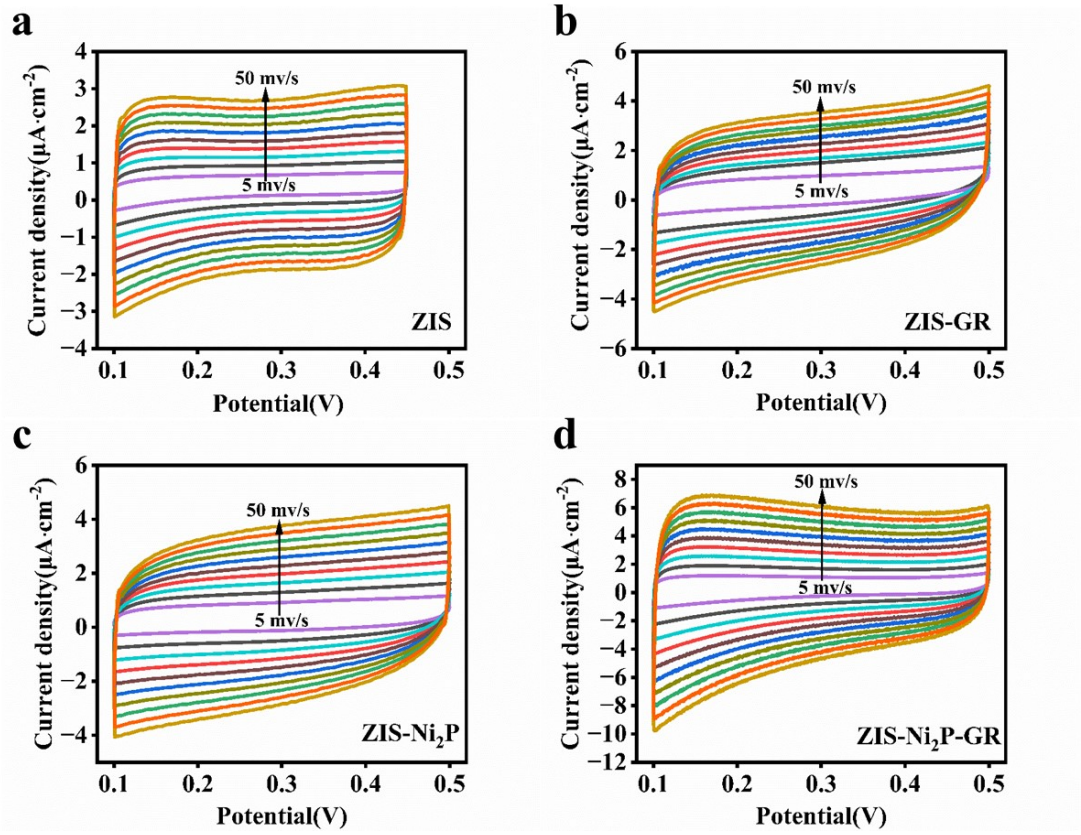

Fig. S8. CV curves of ZIS (a), ZIS-GR (b), ZIS-Ni_2P (c) and ZIS-GR-Ni_2P (d).

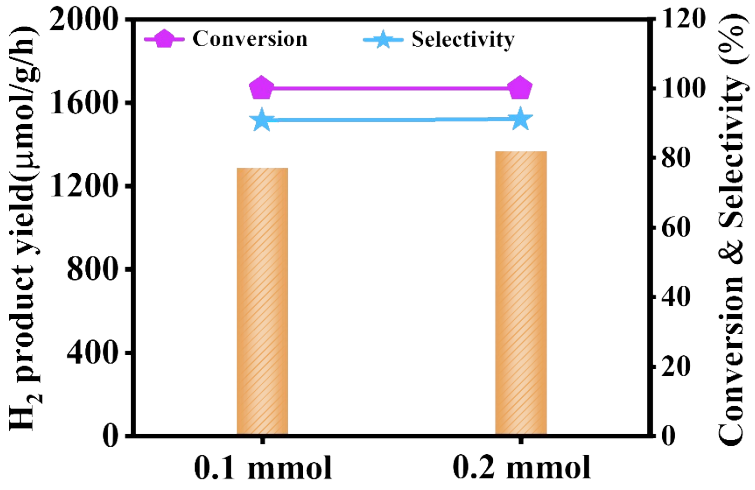

Fig. S9. Results of experiments with different BA concentration over ZIS-GR-Ni_2P.

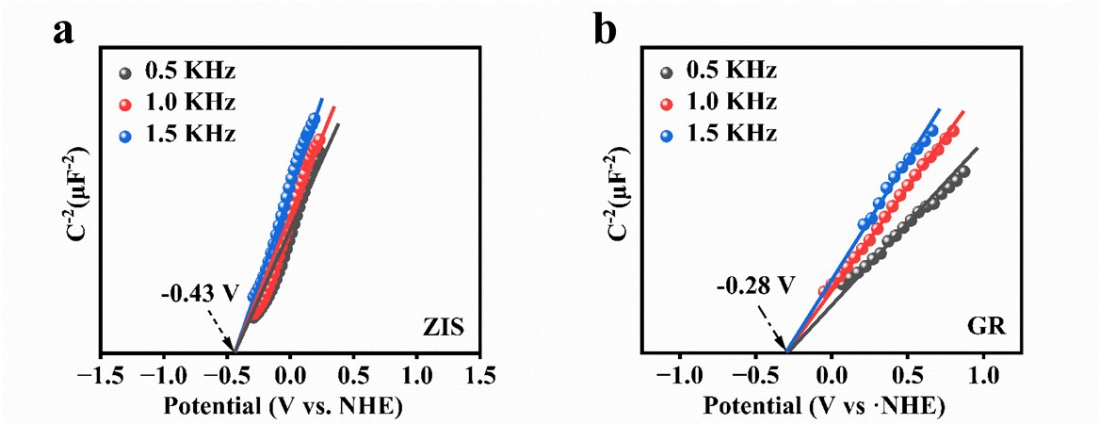

Fig. S10. Mott-Schottky curve of ZIS (a). Mott-Schottky curve of GR (b).

Table S1. Comparison the performance of benzyl alcohol oxidation to benzaldehyde and simultaneous hydrogen production

Catalyst	Conversion /%	Selectivity/ %	H_2 (μmol/g/h)	Light source	Reference
$ZnIn_2S_4$-GR-Ni_2P	100	90.9	1287.8	300 W Xe lamp ($\lambda \geq 420$ nm)	This work
Ni/$Zn_{0.5}Cd_{0.5}S$	40.4	57.7	284.8	300 W Xe lamp ($\lambda \geq 420$ nm)	1
Ni: $ZnIn_2S_4$	97.2	92.8	36.5	300 W Xe lamp ($\lambda \geq 400$ nm)	2
Pt-g-C_3N_4	40	90	51	300 W Xe lamp ($\lambda \geq 400$ nm)	3
$NCNCN_x$-GO-NiP	22.1	100	7.19	AM 1.5 G 100 mW cm^{-2}	4
ZnS-Ni_xS_y	42.1	90.5	176.6	500 W Xe lamp ($\lambda \geq 200$ nm)	5
$ZnCo_2S_4$/$Zn_{0.2}Cd_{0.8}S$	54.3	92.2	45.1	300 W Xe lamp ($\lambda \geq 420$ nm)	6
ZnTi-LDH	61	77	-	300 W Xe lamp ($\lambda \geq 400$ nm)	7
$Zn_3In_2S_6$@10%ZnO	91.3	88.6	-	300 W Xe lamp ($\lambda \geq 400$ nm)	8

Table S2. Summary of the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis results of the samples of ZIS-GR-Ni_2P composite after photocatalytic reaction.

Sample	Zn^{2+} (ppm)	Ni^{2+} (ppm)
ZIS-GR-Ni_2P	1.56	Negligible

Table S3. BET Surface area (SBET), pore diameter (Dp) and pore volume (Vp) of pure ZIS, ZIS-GR, ZIS-Ni_2P, and ZIS-GR-Ni_2P samples.

Samples	BET surface area($m^2 \cdot g^{-1}$)	Pore Volume($cm^3 \cdot g^{-1}$)	Pore Size(nm)
ZIS	8.8303	0.044719	183.7451
ZIS-GR	9.1171	0.046028	201.9414
ZIS-Ni_2P	12.2451	0.061956	202.3882
ZIS-Ni_2P-GR	13.7705	0.063256	202.5736

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