

Supplementary information

Dual Z scheme ZnS@g C₃N₄@ZnIn₂S₄ heterojunction for enhanced photocatalytic selective oxidation of toluene

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1. Materials and methods

1.1 Experimental drugs and reagents

Toluene (C_7H_8 , 99.0%), Urea (99.0%), melamine ($C_3H_6N_6$, 99.0%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.0%), thioacetamide (TAA, 99.0%), and acetonitrile (MeCN, 99%) were purchased from Aladdin Reagent Company, Shanghai, China. Indium chloride ($InCl_3$, 99.0%) was purchased from Shanghai Shaoyuan Reagent Co. Ltd., Shanghai, China. Hexadecyl trimethyl ammonium Bromide (CTAB, 99.0%), glycerine (99.0%) and nitric acid (HNO_3 , 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Ultra-pure research grade (99.999%) O_2 was purchased from Air Liquide. All chemicals were obtained from commercial sources and were used without further purification otherwise stated.

1.2 Synthesis of catalysts

Synthesis of $ZnIn_2S_4$ (ZC): Dissolved 1 mmol $Zn(NO_3)_2 \cdot 6H_2O$ and 2 mmol $InCl_3$, as well as 500 mg CTAB in 20 mL of water/glycerol (16:4 v/v) to form solution A, stirring at room temperature for 30 minutes; then slowly added 4 mmol TAA to solution A to dissolve the mixed solution evenly and formed solution B. The uniformly dissolved mixture was then transferred to a 50 mL polytetrafluoroethylene reactor and maintained at $80^\circ C$ for 6 hours; After natural cooling to room temperature, a light yellow precipitate was obtained, centrifuge collection, washed with water and ethanol, and finally dried at $60^\circ C$ vacuum for 6 hours. The resulting sample was denoted as ZC.

Synthesis of ZnS: 1 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 1 mmol of TAA were dissolved in 10 mL of deionised water. After ultrasonic dissolution for 10 min, the solution was placed in a water bath at $60^\circ C$ and heated with constant temperature stirring for 4 h. The reaction was carried out in a water bath at $60^\circ C$ for 4 h. The solution was then heated with constant temperature stirring. After the reaction, the white precipitate was washed three times with deionised water and anhydrous ethanol, and then dried in an oven at $60^\circ C$ for 12 h to obtain ZnS nanoparticles.

Synthesis of fragmented g- C_3N_4 (FCN): 6 g of urea was ground with 2 g of melamine for 1 h, put into a 50 mL crucible, covered with a layer of tinfoil,

and roasted in a muffle furnace at 550 °C for 4 h, with a temperature increase rate of 5°C/min. About 1.7 g of product was obtained. The resulting sample was denoted as BCN. 0.50 g of BCN powder was dispersed in 50 mL of distilled water under stirring in a beaker. 0.5 mL of HNO₃ was added with vigorous stirring for 30 min and then transferred to an autoclave and heated at 100°C for 12 h for NO₃⁻ anion intercalation. After being cooled down to room temperature, the NO₃⁻ anion intercalated BCN (NO₃⁻-BCN) was washed with distilled water for several times and dried at 80°C overnight. Finally, NO₃⁻-BCN was calcined in a muffle furnace for 3 h at temperatures of 550°C and denoted as FCN.

Synthesis of ZnS@FCN@ZC: 0.1 g of ZnS and 0.1 g of FCN were added to 16 mL of water and 4 mL of propanetriol, and after stirring for 30 min, the mixture was recorded as Liquid C. In Liquid C, 1 mmol of Zn(NO₃)₂·6H₂O and 2 mmol of InCl₃ were dissolved, as well as 500 mg of CTAB, and the mixture was stirred for 30 min at room temperature, and 4 mmol TAA and continue stirring to dissolve the mixed solution evenly. After 30 min of stirring and mixing, the mixed solution was poured into a 50 mL polytetrafluoroethylene reactor and kept in an oven at 80 °C for 6 h. The reaction was carried out at room temperature. When the reaction time was over, it was naturally cooled to room temperature, centrifuged, washed three times with deionised water and ethanol, and subsequently dried in a vacuum drying oven at 60 °C for 6 hours. The obtained catalyst was noted as ZnS@FCN@ZC. keeping the additions of ZnS and FCN unchanged, and continuing to load different additions of ZC, keeping the molar ratio of each component of ZC unchanged, and naming the molar amount of Zn(NO₃)₂·6H₂O as X mmol, five groups of composite catalysts were obtained as ZnS@FCN@ZC-X (X=0.5, 1, 2, 3, 4), respectively.

ZnS@FCN, FCN@ZC, and ZnS@ZC were prepared in the same way as ZnS@FCN@ZC.

2. Material characterization

The morphology and structure of the catalyst were studied by ZEISS Gemini 300 field emission high-power scanning electron microscope (SEM)

and JEOL JEM-F200 a high-resolution transmission electron microscope (HRTEM). The phase structure of the catalyst was analyzed by D8 Advance X-ray diffractometer (XRD) produced by Bruker, Germany. Fourier transform infrared (FTIR) spectra for examining functional groups were recorded on a Thermo Fisher Scientific instrument. The visible light absorption of the catalyst was studied using a UV-4802S UV-visible spectrometer with a measurement range of 220-1000 nm, using the measurement curve of a pure solid BaSO₄ crystal as the baseline. The surface element composition and state of the catalyst were studied by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, USA) at an operating voltage of 12 kV. The instrument used for EPR testing is the Bruker A300. The steady-state. Photoluminescence spectrum (PL) was recorded on a Varian Cary Eclipse fluorescence spectrophotometer using a laser with an excitation wavelength of 545 nm. Ultraviolet photoelectron (UPS) spectra were acquired on an Escalab 250Xi spectrometer (Thermo Fisher Scientific) using He I (21.22 eV) emission line.

3. Photocatalytic Performance Test

Qualitative analysis of photocatalytic oxidation of toluene: The reaction was carried out in a 15 mL quartz tube with 10 mg of catalyst, 0.1 mmol of substrate toluene, 2 mL of reaction solvent, and 10 minutes of replacement oxygen. The photocatalytic reaction of toluene was placed in a 12 W blue LED lamp under room temperature conditions. The post-reaction products were analysed by Agilent 7890B-5977A GC/MS.

Quantitative analysis of photocatalytic oxidation of toluene: The post-reaction products were analysed by Shimadzu LC-2010A high performance liquid chromatography (HPLC), and the analytes were separated on a column GOLD (250 nm×4.6 mm, particle size of 5 μm); the temperature of the column was kept at 28 °C. The analytes were separated on a GOLD column (250 nm×4.6 mm, particle size of 5 μm). The mobile phases were water and acetonitrile at a flow rate of 0.8 mL·min⁻¹ with an injection volume of 10 μL. The R² values of the standard curves of the substrate and the product were greater than 0.9999. The formula for toluene selective

oxidation reaction is shown below:

$$\text{Conversion rate (\%)} = \frac{\text{moles of toluene reacted}}{\text{moles of substrate}} * 100\%$$

$$\text{Yield (\%)} = \frac{\text{actual yield of the product}}{\text{theoretical yield of the product}} * 100\%$$

$$\text{Conversion rate (mmol g}^{-1} \text{ h}^{-1}) = \frac{\text{moles of toluene reacted}}{\text{amount of catalyst} * \text{reaction time}}$$

$$\text{Selectivity (\%)} = \frac{\text{Yield}}{\text{Conversion rate}} * 100\%$$

4. Electrochemical Performance Test

The working electrode was prepared by coating a 200 μL suspension on the surface of a fluorinated tin oxide glass plate (FTO) and covering 1 cm^2 with a mixture of 5 mg sample and 360 μL ethanol, 600 μL water and 40 μL membrane solution. Electrochemical measurements were performed on a CHI760E electrochemical analyzer using a conventional three-electrode cell including platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The experiment was carried out in 0.5 M Na_2SO_4 electrolyte at room temperature.

5. Figure and Table

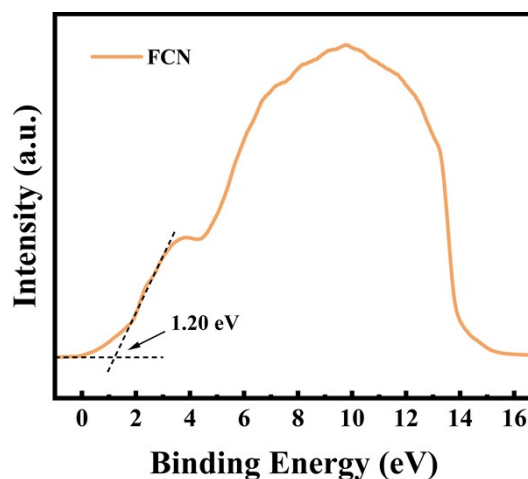


Fig. S1 UPS spectroscopy of FCN

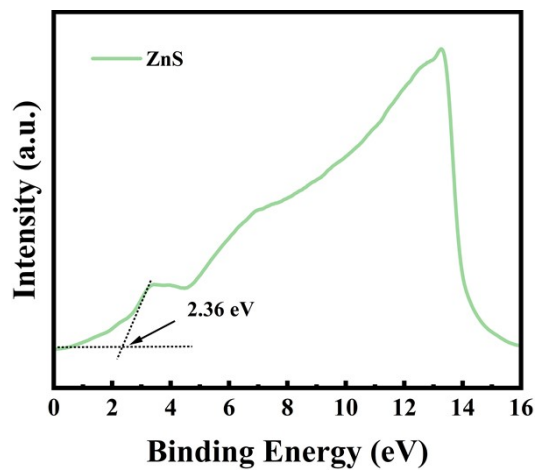


Fig. S2 UPS spectroscopy of ZnS

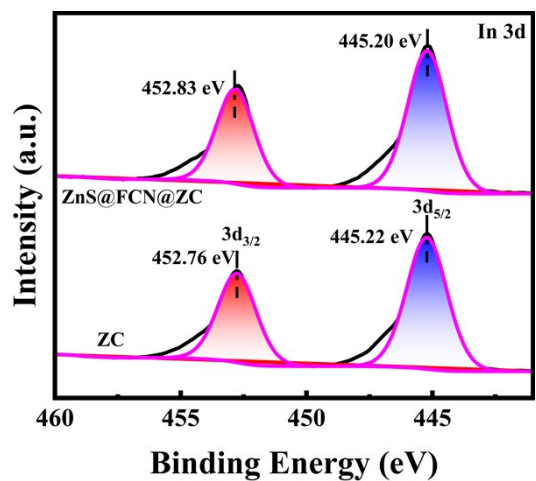


Fig. S3 XPS spectra of In 3d of ZnS@FCN@ZC

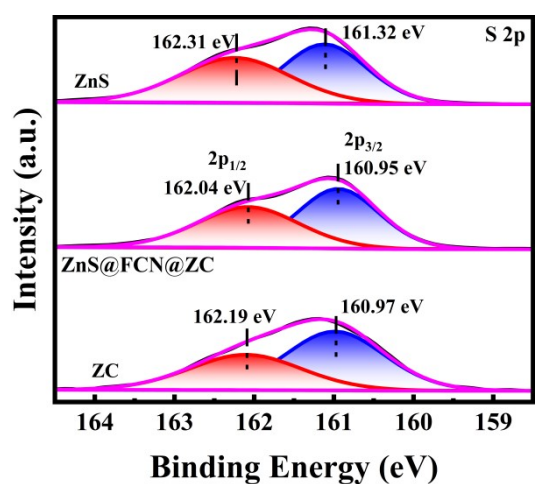


Fig. S4 XPS spectra of S 2p of ZnS@FCN@ZC

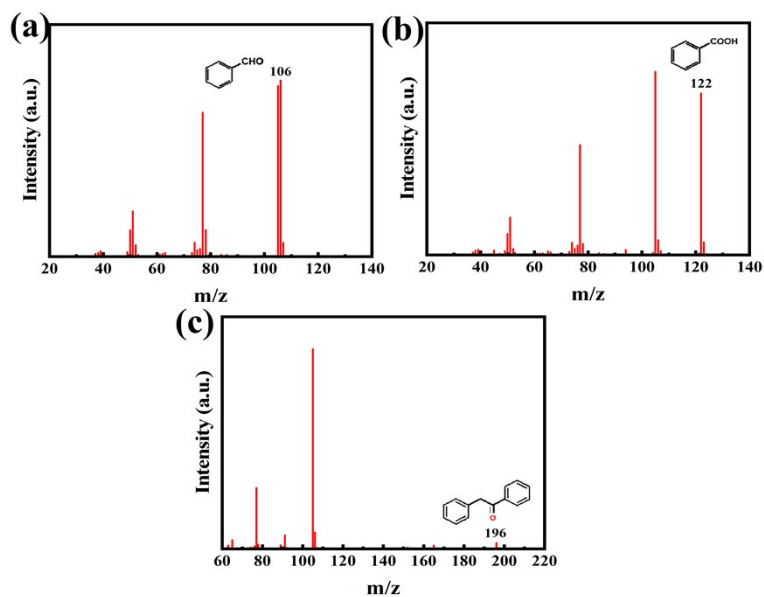


Fig. S5 MS spectra of (a) benzaldehyde; (b) benzoic acid; (c) deoxybenzoin

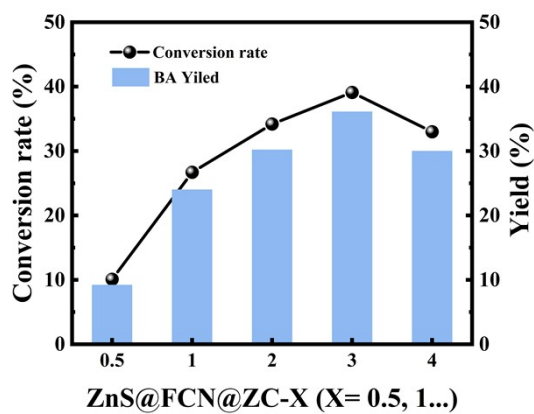


Fig. S6 Performance of different photocatalysts for toluene oxidation

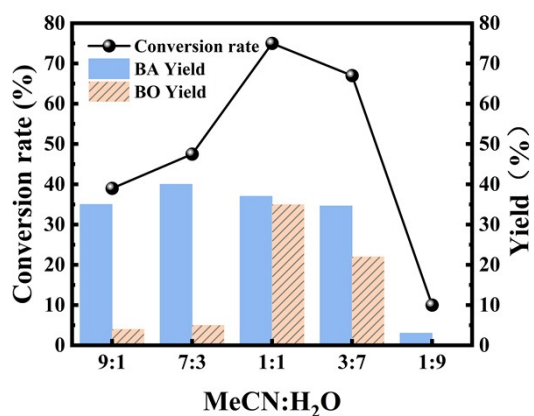


Fig. S7 Performance of different solvents for toluene oxidation

Table S1 Comparison of the performance with different photocatalysts

Photocatalysts	Reaction condition	Toluene Conversion rate ($\text{mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	BA Selectivity (%)	Ref
CdS@C ₃ N ₄	100 mg photocatalyst, 10 mmol toluene, 300 W Xe lamp, room temperature, O ₂ , reaction time:3 h.	0.9	83	[1]
CdIn ₂ S ₄ -CdS-140	10 mg photocatalyst, 47.2 μmol toluene, 1 mL acetonitrile, 300 W Xe lamp, room temperature, O ₂ , reaction time: 6 h.	0.7	99	[2]
ZnS/CdIn ₂ S ₄ -OP	10 mg photocatalyst, 15 μL toluene, 3 mL acetonitrile, 300 W Xe lamp, room temperature, O ₂ .	1.1	98	[3]
Y1/TiO ₂	50 mg of photocatalyst, 0.5 mmol of toluene, 1 atm oxygen, room temperature, 4 h, and 0.91 W cm ⁻² light intensity.	0.9	94	[4]
0.01BOC/TiO ₂	25 mg photocatalyst, 1 mmol toluene, 3 mL of acetonitrile, 500 mW cm ⁻² , 297K, O ₂ , reaction time: 2 h.	1.7	85	[5]
EC-BiOBr	10 mg photocatalyst, 10 μL toluene, 2 mL acetonitrile, 300 W Xe lamp, room temperature, O ₂ .	2.5	66	[6]
Bi ₂ WO ₆ (BT-48)	15 mg photocatalyst, 2.5 mL toluene, 150 W Xe lamp, room temperature, O ₂ , reaction time: 4 h.	7.1	96	[7]
Bi ₂ W _{0.3} Mo _{0.7} O ₆	15 mg of catalyst, 1 mL toluene, 300 W Xe lamp, 15°C, O ₂ balloon, reaction time: 5 h.	1.9	91	[8]
ZnS@FCN@ZC-3	10 mg catalyst, 0.1 mmol toluene, 1 mL H ₂ O and 1 mL of MeCN, 12 W blue LED lamp, room temperature, O ₂ balloon.	21.6	78	This work

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