

Electronic Supplementary Information

Efficient photocatalytic conversion of xylose to co-produce xylonic acid and CO via dual S-scheme heterojunction photocatalyst between carbon nitride and CuInS₂ quantum dots sensitized ZnIn₂S₄

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Abbreviations

High performance liquid chromatography (HPLC); Scanning electron microscopy (SEM); Transmission electron microscopy (TEM); Energy dispersive spectroscopy (EDS); Energy dispersive X-ray spectroscopy (EDX); High-resolution transmission electron microscopy (HR-TEM); Selected area electron diffraction (SAED); X-ray diffraction (XRD); X-ray photoelectron spectroscopy (XPS); Ultraviolet-visible diffusion reflectance spectroscopy (UV-vis DRS); Valence band (VB); Conduction band (CB); Flat band potential (E_{fb}); Normal hydrogen electrode (NHE); Ultraviolet photoelectron spectroscopy (UPS); Electrochemical impedance spectroscopy (EIS); Electron spin resonance (ESR); 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO); 5,5-dimethyl-1-pyrroline N-oxide (DMPO); 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (TEMPONE).

Characterization

TEM were recorded on JEM-2100 CXII and SEM were explored on Hitachi-4800. The powder XRD patterns were measured with a Bruker D8 Focus diffractometer (CuK α radiation, $\lambda = 0.15418$ nm) in the θ - 2θ mode. XPS analysis was performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated AlK α X-ray source (1486.6 eV). UV-vis DRS was achieved on a Hitachi U3900 spectrophotometer by using BaSO $_4$ as the reference. PL spectrum was measured by an Edinburgh FLS-920 spectrometer. Time-resolved photoluminescence (TRPL) spectra were acquired using

a FLE1000 fluorescence lifetime spectrophotometer (Edinburgh Instruments, U.K.) at an excitation wavelength of 375 nm. Electron spin-resonance spectroscopy was used to study molecules and materials with unpaired electrons, and DMPO was chosen as a spin trap for the detection of hydroxyl radical ($\cdot\text{OH}$) and superoxide ($\cdot\text{O}_2^-$), TEMPO was applied to characterize electrons and holes, while TEMPONE was used to detect singlet oxygen. UPS was measured by using a He (21.20 eV) as monochromatic discharge light source and a VG Scienta R4000 analyzer. A sample bias of -5 V was applied to observe the secondary electron cut-off (SECO).

Photoelectrochemical measurements

Electrochemical measurements were carried out on a CHI760E electrochemical workstation with a standard three-electrodes system. Among them, a Pt wire was used as the counter electrode, and the reference electrode was the saturated Ag/AgCl. The cleaned F-doped tin oxide glass was used as the working electrode. Typically, 5 mg of corresponding photocatalyst and 20 μL of Nafion (5%) were added into 980 μL of ethanol to form a homogeneous slurry. The homogeneous slurry was ultrasonicated for 30 min and then coated on the FTO glass (area 1 cm \times 1 cm). The obtained system was dried at 150 $^\circ\text{C}$ for 60 min. The supporting electrolyte was Na_2SO_4 solution (0.5 M) with the pH value of 6.8. The incident visible light source was Xe lamp (300 W). The photocurrent-time was investigated in the irradiation of Xe lamp at a bias potential of 0.5 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was detected by an AC voltage amplitude of 10 mV at -0.3 V versus Ag/AgCl over the frequency range

from 100,000 Hz to 1 Hz. The Mott-Schottky was studied in the electrolyte of Na₂SO₄ (0.5 M), and the frequency of the AC potential was set as 500, 800, and 1000 Hz, respectively, as well as the amplitude was 10 mV.

Products analysis

CO was analyzed by gas chromatography (GC-7900, Ar carrier gas, molecular sieve 5 Å column, external event) equipped with a flame ionization detector (FID). Sampler temperature was 110 °C. Column temperature was 60 °C. Detector temperature was 200 °C.

After the reaction, the samples were filtrated with a Millipore filter (0.22 µm) and analyzed by HPLC with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 µm). Concentrations of lactic acid was measured by Waters 2414 RI detector. The mobile phase was 5 mmol H₂SO₄ at a flow rate of 0.5 mL/min. The temperature of column was set at 55 °C and the total time to finish the product analysis was set at 30 min.

$$\text{Conversion (\%)} = \frac{\text{Moles of carbon in feedstock consumed}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

$$\text{Product yield (\%)} = \frac{\text{Moles of carbon in organic acid}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

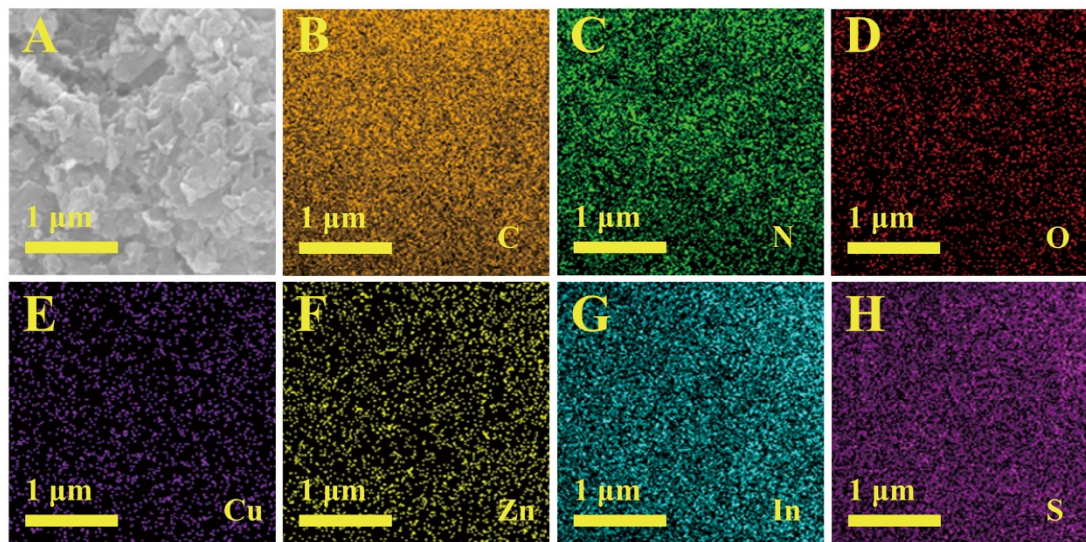


Fig. S1 SEM image (A) and corresponding EDS mappings of C-*s*-ZIS/CN: C (B); N (C); O (D); Cu (E); Zn (F); In (G) and S (H).

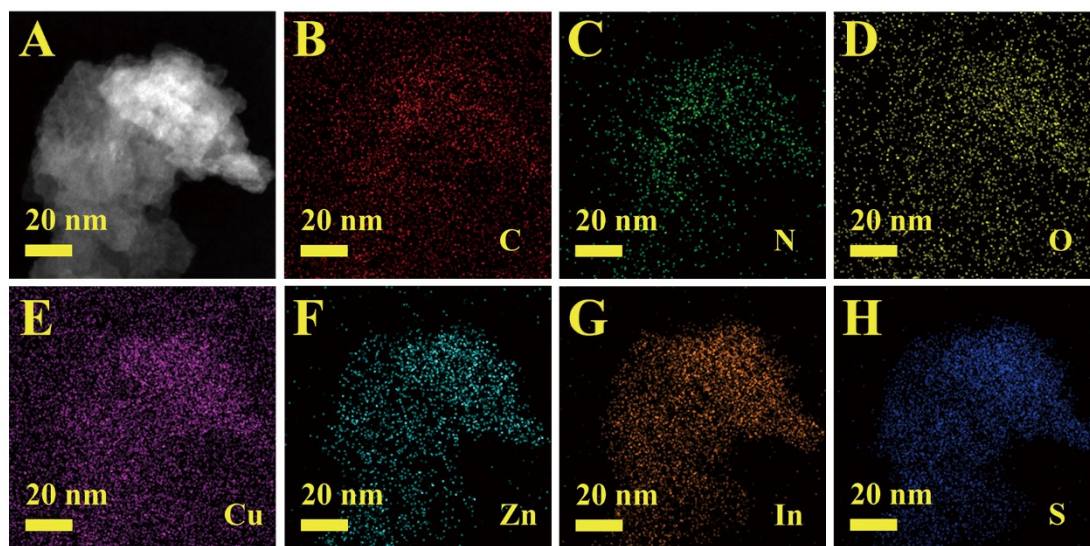


Fig. S2 TEM image (A) and corresponding EDX mappings of C-*s*-ZIS/CN: C (B); N (C); O (D); Cu (E); Zn (F); In (G) and S (H).

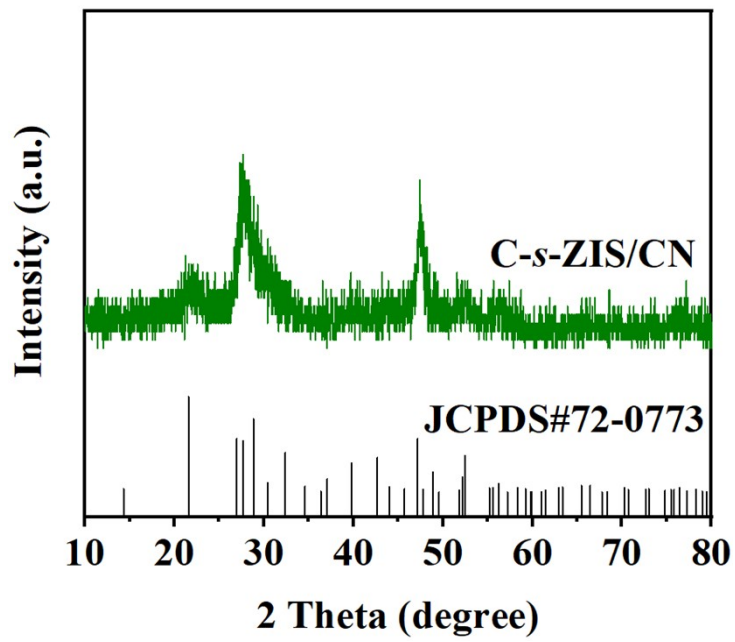


Fig. S3 XRD pattern of C-s-ZIS/CN.

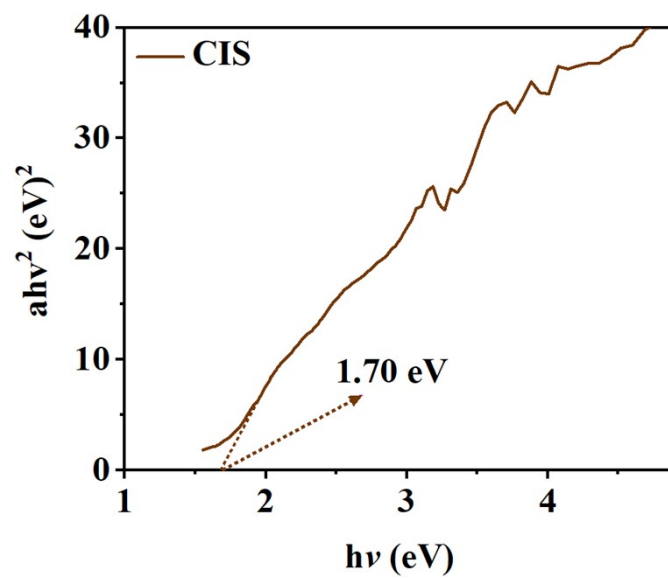


Fig. S4 Tauc plot of CIS.

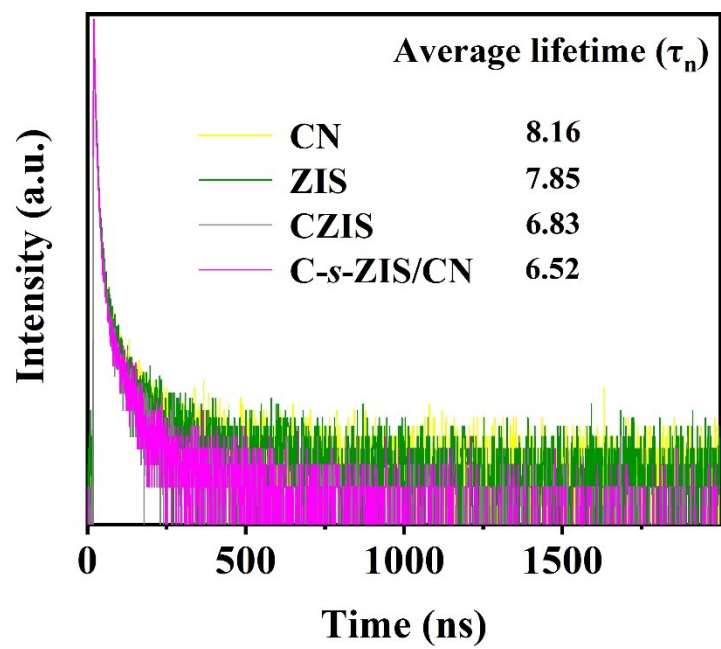


Fig. S5 TRPL spectra of prepared photocatalysts.

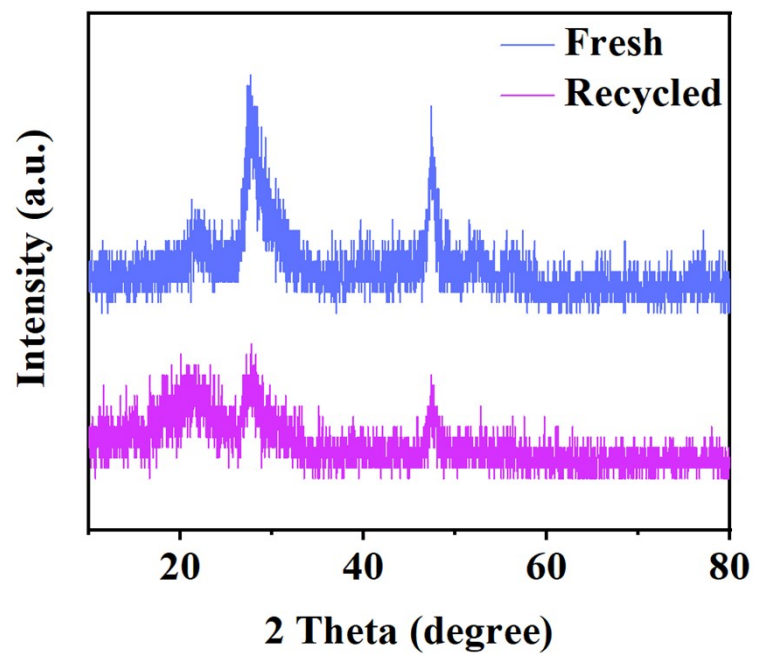


Fig. S6 XRD patterns of fresh and recycled C-*s*-ZIS/CN.