

Supporting information for

**Phase-dependent photocatalytic H₂ evolution of Copper Zinc Tin
Sulfide under visible light**

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Experimental Details

Chemicals.

Cu(acac)₂, Zn(OAc)₂, Sn(OAc)₄ and 1-dodecanethiol (DDT) were purchased from Alfa and were used as received. All the other reagents were analytical grade.

Synthesis of WZ CZTS nanospindles.

Typically, 1.332 mmol of Cu(acac)₂, 0.915 mmol of Zn(OAc)₂, and 0.75 mmol of Sn(OAc)₄ were sonically dissolved in 25 mL of 1-dodecanethiol (DDT) to produce homogenous precursor solution. Then, the solution was transferred on preheated oil-bath at 235 °C and maintained for 4 hours. After being cooled down room temperature, WZ CZTS were precipitated by ethanol. The particles were washed with 1:1 hexane/ethanol at least 5 times, followed by being dried in vacuum overnight.

Phase-compositional CZTS.

The WZ CZTS nanospindles were first thermally treated at 350°C in air for 3 min. This sample was marked as CZTS350. To obtain the samples with different phase-compositional CZTS, the CZTS350 particles were annealed at 450, 500 and 550 °C for 15 min, respectively, with elemental sulfur in Ar gas. The received samples were marked as CZTS450, CZTS500 and CZTS550.

Characterizations.

The crystallographic phases of the samples were performed on a D8 Advance X-ray powder diffraction (Germany, Bruck), with diffraction angle 2θ ranging from 10 to 90°. Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) were recorded on a JEOL JEM-2010 TEM (Japan) with the accelerating voltage of 200 kV. The ratio of metal elements was analyzed by an Inductively Coupled Plasma-Atomic Emission Spectrometer (Optima DV2100, PerkinElmer, USA). Raman spectrum was performed using a LabRAM-1B confocal laser Raman spectrometer with an excitation wavelength of 632.5 nm. UV-vis spectra were obtained using a

UV-vis spectrometer (Lambda 950, PerkinElmer, USA).

Photocatalytic reactions were conducted at 25 °C in a gas-closed circulation and evacuation system with a Pyrex cell connected to water bath. A 300 W top-irradiated Xenon lamp was used as light source. Prior to the photocatalytic reaction, 0.5 wt % Pt was loaded by photodeposition method in situ, using H_2PtCl_6 as reagent. Approximately 0.040 g CZTS was magnetically stirred in the reaction chamber containing 100 mL of Na_2S ($0.4 \text{ mol}\cdot\text{L}^{-1}$) and Na_2SO_3 ($0.3 \text{ mol}\cdot\text{L}^{-1}$) aqueous solution. The irradiation was visible light ($\lambda \geq 420 \text{ nm}$) using a cut-off filter from 300 W Xenon lamp. The amounts of evolved H_2 were determined using gas chromatography (Agilent 7890A, thermal conductivity detector, and argon carrier).

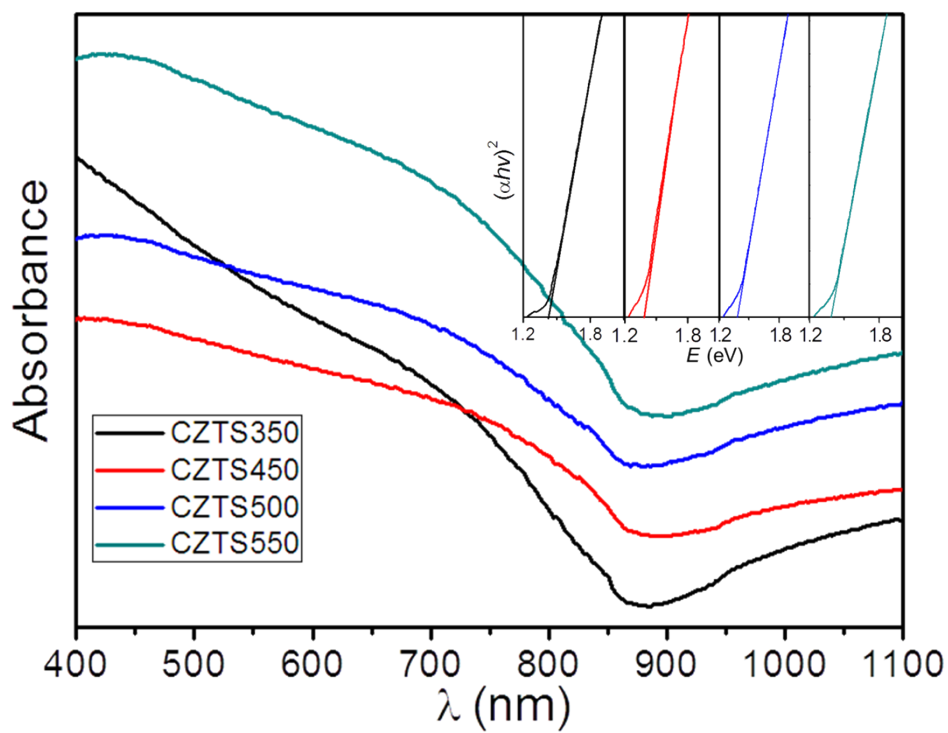


Fig. S1 UV-vis spectra of CZTS samples. The inset is the linear extrapolation of $(\alpha h\nu)^2$ versus photo energy E (eV).

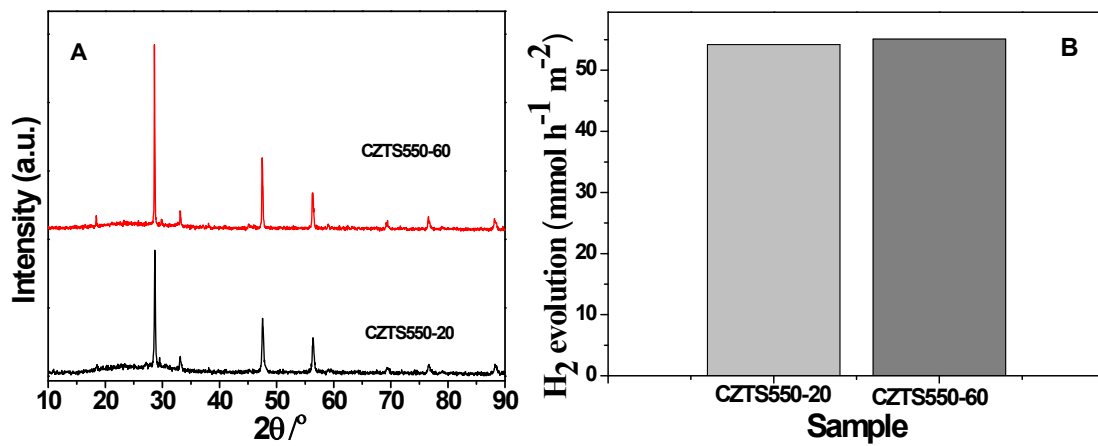


Fig. S2 The XRD patterns (A) and H_2 evolution rates (B) for kesterite CZTS with different crystallinity.

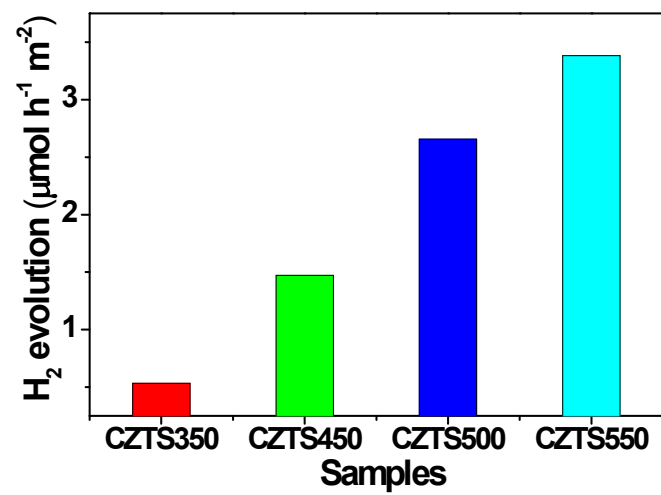


Fig. S3 The normalized H₂ evolution rates of various annealed CZTS to surface area.