Supporting Information

Single Crystalline Cu_2ZnSnS_4 Nanosheet Arrays for Efficient Photochemical Hydrogen Generation

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Part 1. Characterization of CuCl film

CuCl film was grown on a FTO substrate by physical vapor deposition. Figure S1a shows that the film consists of a lot of large grains. The XRD pattern (Figure S1b) confirms that the phase of the raw material is unchanged after high temperature processing.

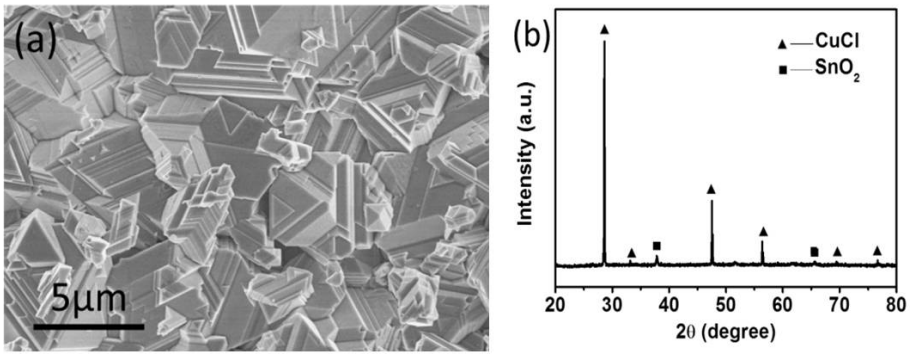


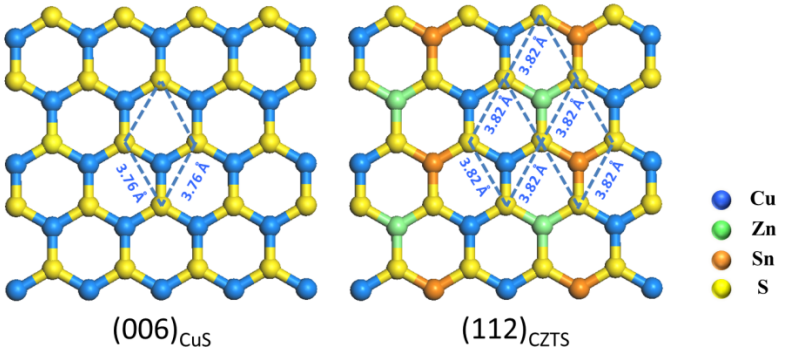
Figure S1. Characterization of CuClfilm. (a) and (b) are top-view SEM image and XRD spectrum of CuCl film on a conductive glass substrate, respectively.

Part 2.The structure analysis of CuS and CZTS

The lattices of CuS and CZTS matched very well, with the discrepancies between {110} CuS (d=1.89Å) and {220} CZTS (d=1.91Å) less than 2%. The S atomic arrangements in (006)CuS and (112) CZTS are similar. As shown in Scheme S1, The S atomic arrangement in (006)CuS is comprised of parallelograms with 3.76Å in side length and 60°in angle. And S atoms in (112) CZTS are structurally arranged in three types of quadrangles with the same side lengths and angles. The lattice match and similarity of S atomic arrangements facilitate the epitaxial

growth of CZTS nanosheet (NS) with (112) facets preferentially exposed on the (006) facets of CuS NS via a cation exchange process.The conversion mechanism can be expressed as the following:

$$4CuS + Zn^{2+} + Sn^{2+} + 2H \rightarrow Cu_2ZnSnS_4 + 2Cu^{+} + 2H^{+} \qquad (S1)$$



Scheme S1. S atomic arrangements in (006) CuS and (112) CZTS.

Part3. Synthesis and Characterization of CuSNSAs

As shown in Scheme 2a, Cu atoms in the parent CuCl fim react with the sulfer vapor to form crystal nuclei. It is believed that the CuS crystal nuclei preferentially grow on the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes and more slowly on the (0001) plane. Thus, NS morpholgy formed with exposed (0001) plane with low surface energy.[S1] Figure S2a is an enlarged SEM image of CuS NS, showing the thickness of CuS NS is approximately 30 nm.Figure S2b is a EDS spectrum ofCuS NSs, which indicates an Cu/S atomic ratio of 48:52.

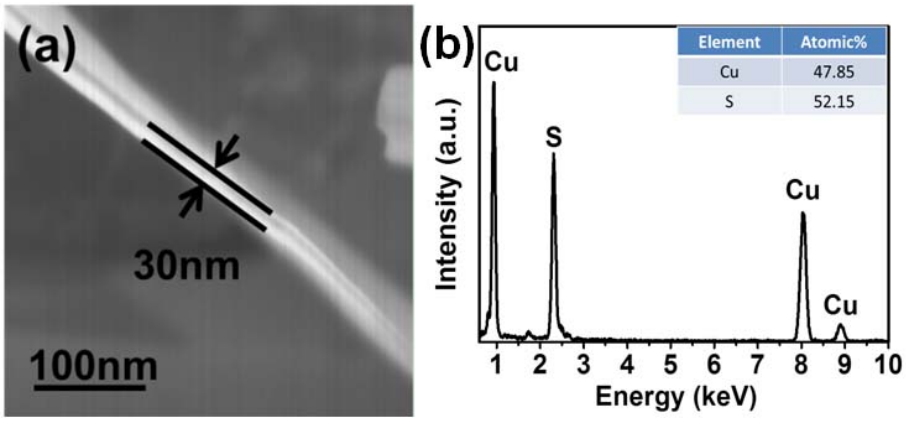


Figure S2. (a) SEM image of a CuS NS, showing the thickness of CuS NS is approximately

30 nm, (b) EDS spectrum obtained from CuS NSs.

Part 4.Characterization of CZTS NSs

The spatial distribution of Cu, Zn, Sn, and S elements isobtained from the STEM-EDS elemental mapping. Figure 4cshows the darkfield image of a single CZTS NS. And Figure S3b-3e are the elemental map ofS, Cu, Zn and Se, respectively, showing uniform distribution of all compositional elements in the NS. The quantitative analysis of the EDS data (Figure S3f) suggests the composition of the NS is close to the stoichiometry of Cu_2ZnSnS_4 (Cu/Zn/Sn/S ~ 2.0/1.0/1.0/3.9).

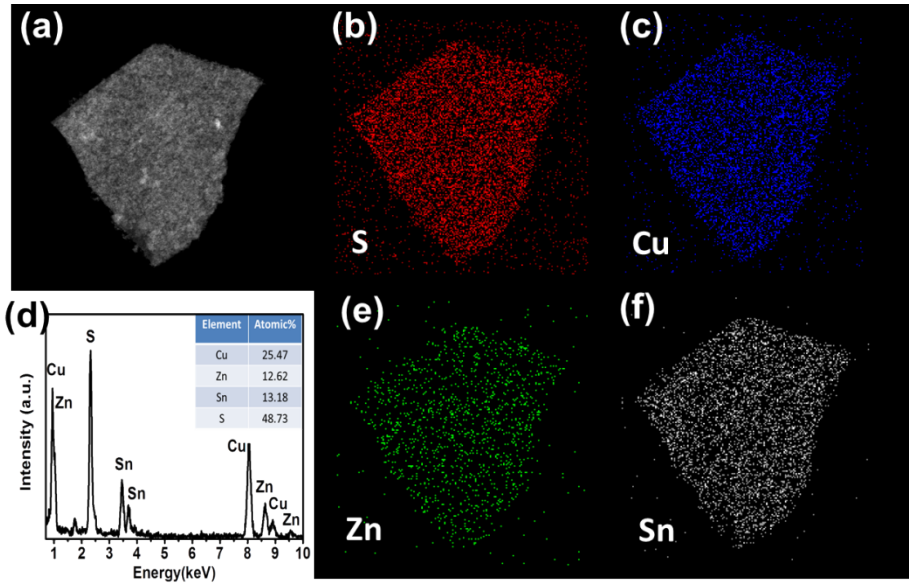


Figure S3. STEM-EDS elemental map and EDS of a single CZTS NS.

Raman spectrum was further used to verify the structure information of CZTS NSs. The intense peak at 332 cm^{-1} (FigureS4) is the characteristic peak of CZTS and close to the reported values.[S2-S4] No other characteristic peaks of impurities were observed, such as $Cu_{2-x}S$ (475 cm^{-1}), ZnS (351 cm^{-1} and 274 cm^{-1}), Cu_3SnS_4 (318,348 and 295 cm^{-1}).[S5] This result excluded the presence of other binary or ternary impurity phases, and confirmed the composition of nanosheetarrays by only CZTS.

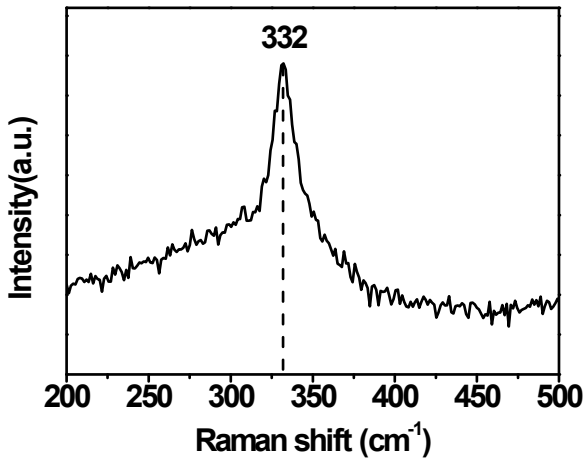


Figure S4. Raman spectrum of the as-synthesized CZTS NSs.

The direct optical band gap, 1.43 eV,of CZTS NSs was calculatedfrom the UV−vis spectrum (Figure S5) by the extrapolation of the linear region of a plot of $(\alpha hv)^2$versusenergy, whereαrepresents the absorption coefficient andhvisthe photon energy.

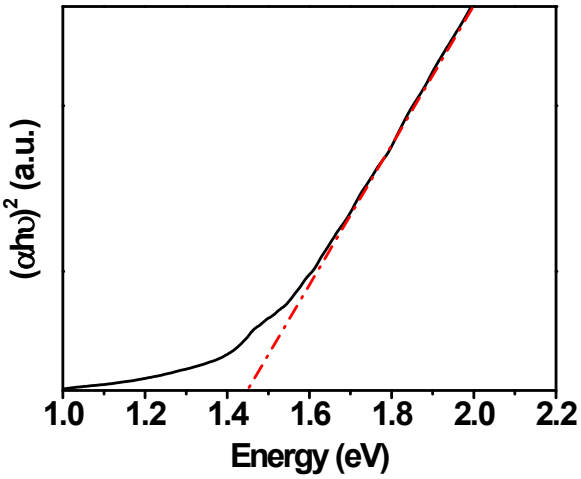


Figure S5. The plots of $(\alpha hv)^2$ versus $hv$for the CZTS NSs.

Moreover, the specific surface area of CZTS NSs were estimated based on atomic absorption analysis. We dissolved 1.88 cm^2 CZTS NSAs into concentrated nitric acid, and the weight of Cu element is measured as 0.23 mg. Then, the weight of CZTS NSAs on per cm^2FTO substrate was calculated as 42 mg.Thus, the surface area of CZTS NSs on per cm^2FTO substrate was calculated using the following equation,

$$S_{CZTS} = \frac{m_{CZTS}}{\rho_{CZTS} d_{CZTS}} \times 2 \qquad \text{(S2)}$$

where m_{CZTS} is the weight of CZTS NSAs on per cm^2 FTO substrate, ρ_{CZTS} is the density of CZTS with the value of 4.56 g/cm^3, and d_{CZTS} is thickness of CZTS NSs determined to be about 35 nm by AFM characterization shown in Figure 2c. Hence, S_{CZTS} is calculated as 22.6 m^2/g.

Part 5.Characterization of CZTS film

The CZTS film was synthesized according to the method describing in the experimental section. The synthesized CZTS film was characterized by SEM and XRD. As seen in Figure S6a, the surface of as-synthesized film is flat and smooth. The side-view SEM image (Figure S6b) shows that the thickness of the film was about 1 μm. The XRD pattern (Figure S6c) exhibits diffraction peaks corresponding to the CZTS, in addition to diffraction peaks of SnO_2, which ascribing to the FTO substrate.

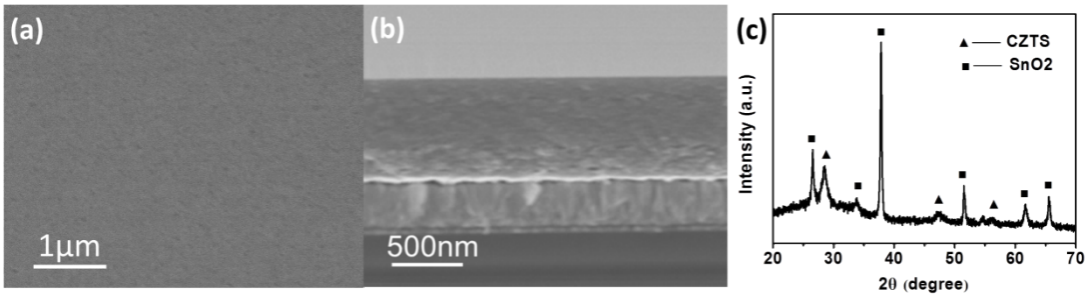


Figure S6. Characterization of CZTS film. (a) and (b) are top-view and side-view SEM images of CZTS film on a conductive glass substrate, respectively. (c) XRD spectrum of the CZTS film.

Part 6. Mott-Schottky analysis

The acceptor density, N_A, was calculated from the slopes of the Mott-Schottky plots (Figure S7) by the following equation,

$$\frac{dC^{-2}}{dV} = \frac{-2}{q\varepsilon_0\varepsilon_r N_A A^2} \qquad \text{(S3)}$$

where A is the surface area of the measured sample, ε_r is the dielectric constant of CZTS with the value of 7.0. The acceptor concentration N_A is obtained as 3.68×10^{20} $cm^{-3}$from the provided Mott-Schottky plot.

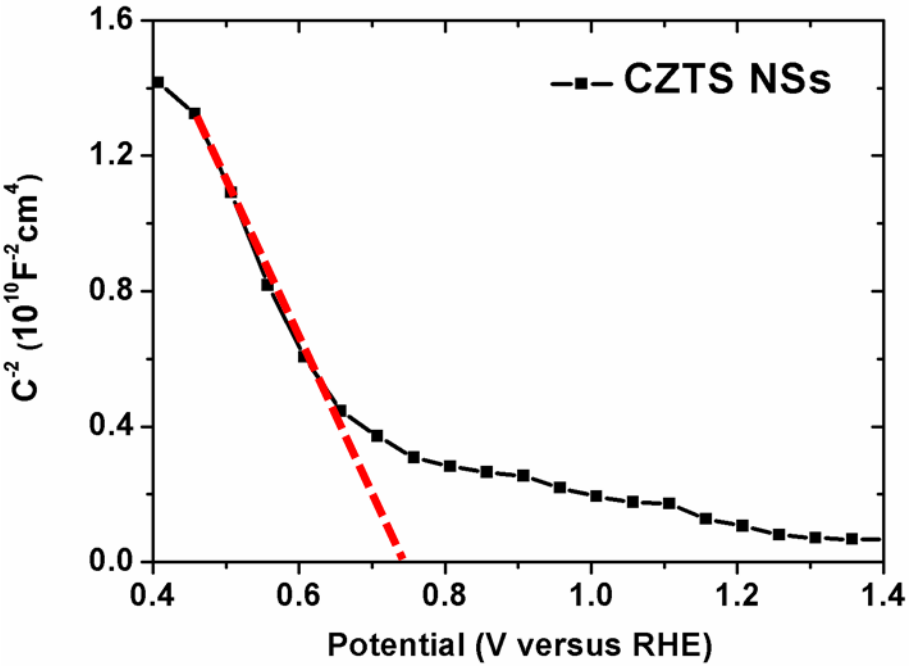


Figure S7. Mott-Schottky plot of CZTS, and the flat-band potential is obtained from the intercept of the extrapolated line.

Part 7. The experimental reflectance spectra of the CZTS film and NSAs structure

Figure S8 shows the reflectance spectra of CZTS film and NSAs. As seen, the reflectance intensity of CZTS film is higher than that of NSAs during the whole detectedwavelength range.

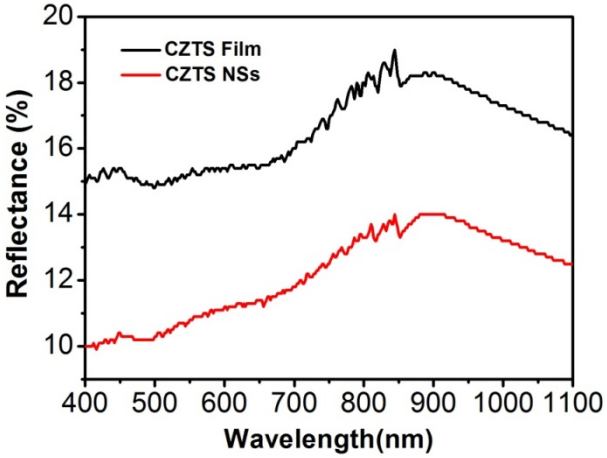


Figure S8. The reflectance spectra of CZTS film and NSAs.

Part 8. FDTD Simulation

All the FDTD simulations were carried out using a commercial software, Lumerical.Total simulation time is 1000 fs, and time step forevery calculation is 0.02fs. The 2-D models used in simulation are shown in **Figure S9**, and the boundary conditions in *x* and *y* directions are periodic and perfectly matched layer (PML), respectively.The electric field distribution is simulated by calculating the electric field intensity per unit volume. To simulate the absorption spectrum, several 2-D power monitors are located at the boundaries to measure the amount of power flowing into and out of the samples. The total absorption corresponds to the difference between these values. The simulation of absorption profile is based on the formula: $Pabs = -Pabs|E|^2 imag(\varepsilon)$, where Pabs represents the power absorption per unit volume, ω is the angular frequency, $|E|$ is the electric field intensity and $imag(\varepsilon)$ is the imaginary part of the permittivity.

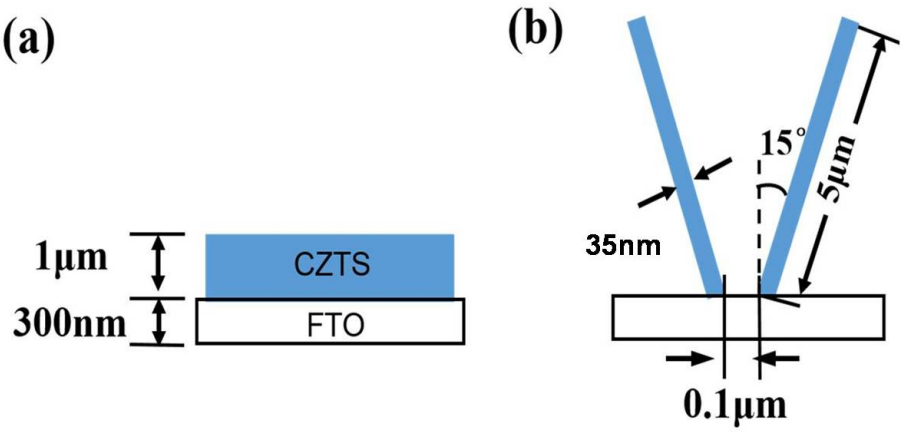


Figure S9. Simulatedgeometrical models of (a) CZTS film and (b) CZTS NSAsarraysamples.

Supplementary References

[S1] K. J. Wang, G. D. Li, J. X. Li, Q. Wang, J. S. Chen, *Cryst. Growth Des.***2007**, *7*, 2265-2267.

[S2] Z. H.Su,C.Yan,D.Tang,K. W.Sun,Z. L.Han,F. Y.Liu,Y. Q.Lai,J.Li,Y. X. Liu, *Crystengcomm* **2012**, *14*, 782-785.

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[S4] X.Xin,M.He,W.Han,J.Jung,Z. Lin, *Angew. Chem. Int. Ed.***2011**, *50*, 11739-42.

[S5] W. H.Zhou,Y. L.Zhou,J.Feng,J. W.Zhang,S. X.Wu,X. C.Guo, X.Cao, *Chem. Phys. Lett.***2012**, *546*, 115-119.