

Supporting Information

Enhanced Visible Light Photocatalytic Hydrogen Production Activity of CuS/ZnS Nanoflowers Spheres

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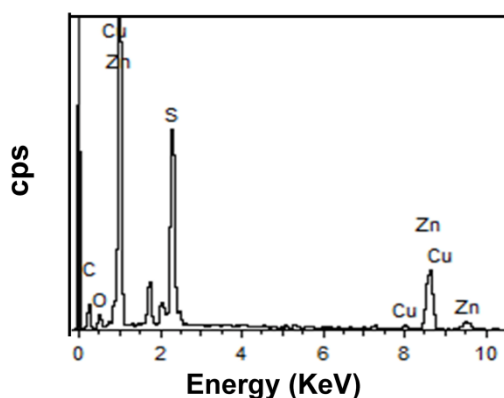


Figure S1. EDX pattern of ZC3 sample

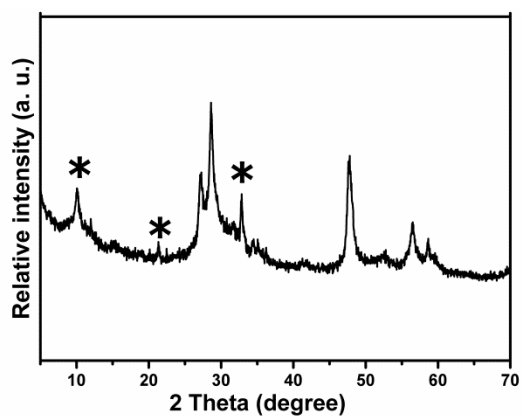


Figure S2. XRD pattern of ZC20 sample (the CuS/ZnS samples with $R_{Cu}(\text{mol}\%)=10.9$). The peaks located at * can be indexed as CuS phase.

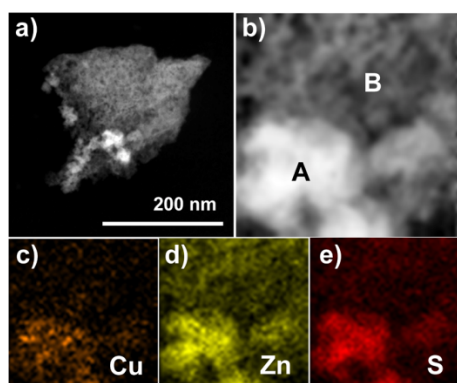


Figure S3. (a and b) STEM and HAADF images of sample ZC3. (c, d and e) the elemental mapping images of Cu, Zn and S.

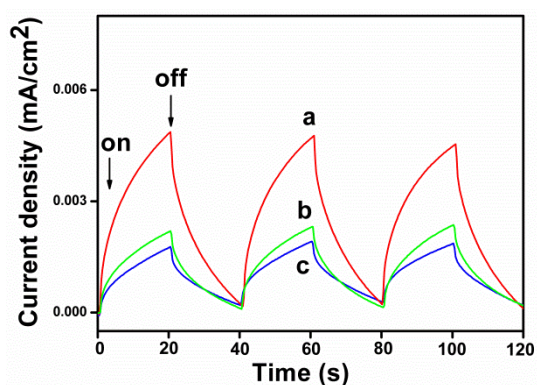


Figure S4. Transient photocurrent responses of ZC3 (a), ZC10 (b), and ZC0 (c) in 0.35 M Na_2S + 0.25 M Na_2SO_3 mixed aqueous solution under visible-light irradiation at 0.0 V using Ag/AgCl as a reference electrode.

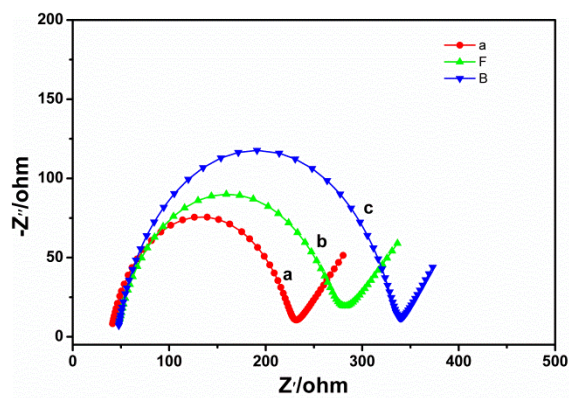


Figure S5. Nyquist plots of ZC3 (a), ZC10 (b), and ZC0 (c) electrodes in 0.35 M Na_2S + 0.25 M Na_2SO_3 aqueous solution under visible-light irradiation.

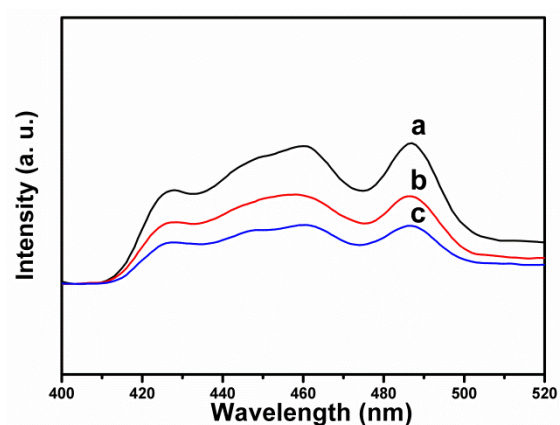


Figure S6. PL spectra of ZnS sample with different Cu concentration (a) 0%, (b) 3%, (c) 10%.

The PL spectra of ZnS sample with different Cu concentration were shown in Figure S6. Three peaks at 425, 464 and 490 nm can be observed in ZnS PL spectra. The peak at 425 nm can be assigned to sulfur vacancies, and the emission band at about 464 nm is a result from the dangling sulfur bonds at the interface of ZnS grains.¹ The peak at 490 nm can be attributed to radiative recombination involving defect states in the ZnS nanocrystals.² The fluorescence intensity of sample decreases with the increase of Cu concentration, and the reason may be as follow. First, too much Cu^{2+} serves as impurities in the reaction, leading to concentration quenching. Second, Cu^{2+} has high thermal diffusivity, and the more CuS deposited on the surface of grain with the increase of Cu concentration, which causes a large number of surface states. These

surface states will capture more electrons or holes, and hinder the radiative recombination of the electron hole pairs in the crystal, resulting in the decline of the fluorescence intensity.

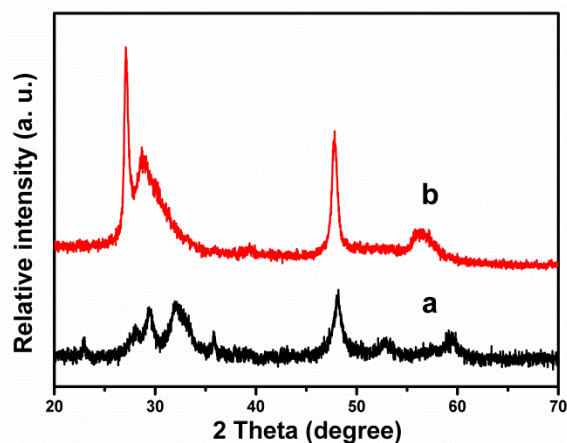


Figure S7. XRD patterns of (a) CuS, (b) CuS+ZnS (simply mixing 3% CuS and ZnS).

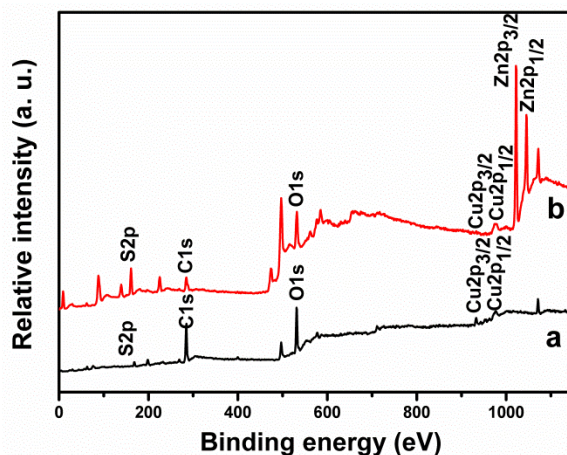


Figure S8. XPS spectra of (a) CuS, (b) CuS+ZnS.

The XRD patterns of sample CuS and CuS+ZnS were shown in Figure S7. It can be seen that the XRD pattern of CuS is well indexed to CuS Hexagonal phase [space group: P63/mmc (194)]. The CuS phase is not detected by XRD (Figure S7b), and the reason may be that the content of CuS is too little to be detected.

The XPS spectra of sample CuS and CuS+ZnS are shown in Figure S8. For sample CuS (Figure S8a), the binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} peaks at 932.5 and 952.5 eV can be indexed as Cu²⁺ in CuS. From Figure S8b, the two strong peaks at 1022.5 and 1045.4 eV are, respectively, assigned to the binding energies of Zn 2p_{3/2}

and Zn $2p_{1/2}$, suggesting the existence of Zn^{2+} .

Reference

- 1 S. Wageh, S. L. Zhao, X. R. Xu, *J. Cryst. Growth*, 2003, **255**, 332-337.
- 2 T. T. Q. Hoa, N. D. The, S. McVitie, N. Hoang Nam, L. V. Vu, T. D. Canh, N. N. Long, *Opt. Mater.*, 2011, **33**, 308–314.