Supporting Information

Visible-Light Photocatalytic H₂-Production Activity of CuS/ZnS Porous Nanosheets Based on Photoinduced Interfacial Charge Transfer

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Sample preparation. All the reagents were of analytical grade and were used without further purification. Distilled water was used in all experiments.

Synthesis of ZnS(en)₀.₅ precursor. ZnS(en)₀.₅ nanosheets were prepared by an ethylenediamine assisted solvothermal method according to previous reports.¹⁻⁴ In a typical synthesis, 2 mmol ZnCl₂ and 4 mmol thiourea were dissolved in 60 mL of ethylenediamine under constant stirring. After stirring for 30 min at room temperature, the mixed solution was then transferred to a 100-mL Teflon-lined
autoclave and maintained at 180 °C for 18 h. After that, the precipitate was collected by centrifuge, washed with distilled water and ethanol for three times, and then dried in an oven at 60 °C for 10 h.

**Synthesis of ZnS and CuS/ZnS porous nanosheets.** ZnS and CuS/ZnS porous nanosheets were synthesized by a hydrothermal and cation exchange method using the above prepared ZnS(en)$_{0.5}$ and Cu(NO$_3$)$_2$ as precursors. Typically, ZnS(en)$_{0.5}$ nanosheets (0.1 g) were ultrasonically dispersed in water, and then a certain volume of Cu(NO$_3$)$_2$ aqueous solution (1 mM) was quickly added. The nominal molar ratios of Cu/Zn, which hereafter was designated as $x$, were 0, 0.5, 1, 2, 3 and 5 mol % (see Table S1), and the obtained samples were labeled as CZ0, CZ0.5, CZ1, CZ2, CZ3 and CZ5, respectively. The volume of mixed solution was adjusted to 60 mL with deionized water and stirring for 30 min at room temperature. After that, the suspension was transferred to a 100-mL teflon-lined autoclave and maintained at 140 °C for 12 h. The final products were respectively rinsed three times with distilled water and ethanol, and dried at 60 °C for 10 h. According to the previous reports, ZnS could be transformed into CuS completely by cation exchange reactions with excessive Cu$^{2+}$ ions due to the great difference in solubility products ($K_{sp}$) of ZnS (1.6 x 10$^{-24}$) and CuS (6.3 x 10$^{-36}$). Thus, pure CuS sample was prepared by adding highly excessive Cu$^{2+}$ ions (the molar ratios of Cu/Zn is 50 : 1) in the synthesis procedure. Sample ZnS+CuS was prepared by mechanical mixture of pure CuS and ZnS (i.e. CZ0) with the molar content of CuS equal to 2%. In addition, for comparing, ZnS nanoparticles (NPs) were also prepared using Zn(NO$_3$)$_2$ and thiourea as raw materials by the hydrothermal method. That is, 2 mmol Zn(NO$_3$)$_2$ and 4 mmol thiourea were dissolved in 60 mL of distilled water under constant stirring, and then the mixed solutions were transferred to a 100-mL Teflon-lined autoclave and
maintained at 180 °C for 18 h. CZ2-NPs was also prepared by a hydrothermal and cation exchange method using the above-prepared ZnS nanoparticles and Cu(NO₃)₂ as precursors under the above same experimental conditions and the nominal molar ratio of Cu/Zn is equal to 2 mol %.

**Characterization.** X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (type HZG41B-PC) using Cu Kα radiation at a scan rate of 0.05° 2θ s⁻¹. The crystallite size was calculated using Scherrer formula (d = 0.9λ/Bcosθ, where d, λ, B and θ are crystallite size, Cu Kα wavelength (0.15418 nm), full width at half maximum intensity (FWHM) in radians and Bragg’s diffraction angle, respectively). The chemical compositions of the samples were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Optima 4300 DV spectrometer (Perkin Elmer). X-ray photoelectron spectroscopy (XPS) measurement was performed in an ultrahigh vacuum VG ESCALAB 210 electron spectrometer equipped with a multi-channel detector. The spectra were excited using Mg Kα (1253.6 eV) radiation (operated at 200 W) of a twin anode in the constant analyser energy mode with a pass energy of 30 eV. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Scanning electron microscopy (SEM) was carried out by an S-4800 field emission SEM (FESEM, Hitachi, Japan). Transmission electron microscopy (TEM) analyses were conducted by a JEM-2010 electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface area (SBET) of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). A desorption isotherm was used to determine the pore size distribution by the Barret-Joyner-Halender (BJH) method, assuming a cylindrical pore model. UV-vis diffused reflectance spectra of samples were obtained for the
dry-pressed disk samples using a UV-vis spectrotometer (UV2550, Shimadzu, Japan). BaSO$_4$ was used as a reflectance standard in a UV-vis diffuse reflectance experiment.

**Photocatalytic activity.** The photocatalytic hydrogen evolution experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure, and openings of the flask were sealed with silicone rubber septum. A 350 W xenon arc lamp through a UV-cutoff filter ($\leq 420$ nm), which was positioned 20 cm away from the reactor, was used as a visible light source to trigger the photocatalytic reaction. The focused intensity on the flask was ca. 180 mW/cm$^2$. In a typical photocatalytic experiment, 50 mg of catalyst was dispersed by a constant stirring in 80 mL mixed aqueous solution containing 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$. Before irradiation, the system was bubbled with nitrogen for 30 min to remove the air inside and ensured the reaction system in an anaerobic condition. A 0.4 mL gas was intermittently sampled through the septum, and hydrogen was analyzed by gas chromatograph (GC-14C, Shimadzu, Japan, TCD, nitrogen as a carrier gas and 5Å molecular sieve column). All glassware was carefully rinsed with distilled water prior to use.

The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction condition. Four low-power 420 nm-LED (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China), which were positioned 1 cm away from the reactor in four different directions, were used as light sources to trigger the photocatalytic reaction. The focused intensity for each 420 nm-LED was ca. 6.0 mW/cm$^2$. The QE was calculated according to Eq. (S1):
\[
\text{QE}[^\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\
= \frac{\text{number of evolved H}_2\text{ molecules} \times 2}{\text{number of incident photons}} \times 100
\]

(S1)

**Table S1.** Experimental conditions for the preparation of the samples and the corresponding physicochemical properties

<table>
<thead>
<tr>
<th>Samples</th>
<th>(x)</th>
<th>Cu (mol.%) (ICP-AES)</th>
<th>average crystal size of ZnS (nm)</th>
<th>pore volume (cm(^3) g(^{-1}))</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS(en)(_{0.5})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>16.6</td>
</tr>
<tr>
<td>CZ0</td>
<td>0</td>
<td>0</td>
<td>19.8</td>
<td>0.07</td>
<td>22.0</td>
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<tr>
<td>CZ0.5</td>
<td>0.5</td>
<td>0.38</td>
<td>19.0</td>
<td>0.12</td>
<td>34.5</td>
</tr>
<tr>
<td>CZ1</td>
<td>1</td>
<td>0.59</td>
<td>18.3</td>
<td>0.12</td>
<td>36.7</td>
</tr>
<tr>
<td>CZ2</td>
<td>2</td>
<td>1.12</td>
<td>17.4</td>
<td>0.13</td>
<td>37.5</td>
</tr>
<tr>
<td>CZ3</td>
<td>3</td>
<td>2.03</td>
<td>16.4</td>
<td>0.13</td>
<td>38.9</td>
</tr>
<tr>
<td>CZ5</td>
<td>5</td>
<td>3.91</td>
<td>15.7</td>
<td>0.12</td>
<td>35.4</td>
</tr>
</tbody>
</table>
Figure S1. SEM image (a) and corresponding XRD pattern (b) of ZnS(en)$_{0.5}$ precursor.

The typical morphology of the as-prepared ZnS(en)$_{0.5}$ precursor is shown in the SEM image (Figure S1a), exhibiting a sheet-like structure with rectangle lateral dimensions in the range of 0.3-2 μm. The strong and sharp diffraction peaks in the corresponding XRD pattern (Figure S1b) imply good crystallinity and large particle size of the product, which is in good agreement with that of ZnS(en)$_{0.5}$ reported in literatures.$^{3,4}$ It was reported that lamellar ZnS(en)$_{0.5}$ compound could be converted into ZnS or ZnO nanosheets under heating conditions in vacuum or in air.$^{1-4}$ Nevertheless, a high-temperature heat treatment usually suffers from disadvantages related to high cost and complicated synthetic
procedures. Interestingly, in the present work, hydrothermal method was used instead of high temperature calcinations and pure ZnS porous nanosheets could also be obtained without adding Cu\(^{2+}\) ions. As shown in Figure S3, after the hydrothermal treatment of ZnS(en)\(_{0.5}\) precursor, the sheet structures of prefabricated ZnS(en)\(_{0.5}\) precursor are basically remained and these ZnS porous nanosheets are composed of numerous nanoparticles and the pores are formed between these nanoparticles.

**Figure S2.** XRD patterns of the CZ\(x\) (\(x = 0, 0.5, 1, 2, 3\) and 5 mol %) samples.

**Figure S3.** SEM (a) and TEM (b) images of sample CZ0.
Figure S4. The comparison of photocatalytic H₂-production activity of sample CZ2 under visible-light irradiation (λ ≥ 420 nm) using different hole scavengers: (a) 25%V methanol, (b) 25%V ethanol, (c) 25% glycerol, (d) 25%V lactic acid (e) 0.35 M Na₂S+0.25 M Na₂SO₃

It is well-known that metal sulfide photocatalysts are unstable in the water-oxidation reaction under visible-light because the S²⁻ anions are more susceptible to oxidation than water, thereby causing photocorrosion of the photocatalyst. Furthermore, the common hole scavenger such as methanol and ethanol are excellent fuels themselves. Moreover, as shown in Figure S4, sample CZ2 shows the highest photocatalytic H₂-production activity in the presence of Na₂S/Na₂SO₃ mixture solution as compared with other hole scavengers. Thus, Na₂S/Na₂SO₃ mixture is chosen in this work in order to suppress the photocorrosion of sulfide-based catalysts.
The action spectrum is determined by the apparent quantum efficiencies (QE) of the sample CZ2 under LED light irradiation with different wavelength from 365 nm to 630 nm as shown in Figure S5. The potential of Cu\textsuperscript{2+}/Cu\textsuperscript{+} is 0.16 V (vs. SHE, pH=0), however, in this work Cu(II) is existed as CuS and the solubility products ($K_{sp}$) of CuS is found to be $6.3 \times 10^{-36}$. Thus, according to the Nernst equation, the potential of CuS/Cu\textsubscript{2}S ($\varphi_{\text{CuS/Cu}_2\text{S}}^0$) can be calculated as follow:

$$\varphi_{\text{CuS/Cu}_2\text{S}}^0 = \varphi_{\text{Cu}^{2+}/\text{Cu}^+}^0 + 0.059/2\lg\left(\frac{K_{sp}\text{CuS}}{K_{sp}\text{Cu}_2\text{S}}\right) = -0.5 \text{ V}$$

The interfacial transition energy from the VB of ZnS to CuS/Cu\textsubscript{2}S is determined to be 2.94 eV, thus the maximum excitation wavelength is ca. 420 nm. This result is based on the theory computation; however, such computation is concluded under the standard conditions and also has differences compared with the practical experiments. It should be noted that the other important evidence for the IFCT is absorption...
shoulder from 350-450 nm in UV-vis spectra. Thus, the visible-light (≥ 420 nm) can trigger the photocatalytic reactions and the CuS/ZnS samples do show high H₂-production activity under such experimental conditions. As shown in Figure S5, the sample CZ2 shows high H₂-production efficiency at 365 nm and 420 nm, even at 450 nm the sample also exhibits a considerable activity. Furthermore, using the visible-light (≥ 420 nm) is more meaningful for the solar energy utilization and could eliminate the possibility of the intrinsic bandgap absorption of ZnS. Thus, in this work, we choose visible light (≥ 420 nm) to excite the photocatalyst. On the other hand, as shown in Figure 3a, compared with the UV-Vis spectrum of CZ0, the UV-Vis spectrum of CZ2 shows enhanced absorption in the visible-light region (at wavelength over 400 nm), which are attributed to the absorption of CuS and Cu II d-d transitions. However, no hydrogen can be detected when CuS alone is used as the catalyst, suggesting that pure CuS is not active for photocatalytic H₂-production under the experimental conditions studied. Therefore, associated with the action spectrum (Figure S5) the possibility of optical effects contributing to better performance (such as the extra vis-near IR absorption features due to Cu²⁺ d-d transition and CuS itself) could be eliminated.
Figure S6. Time course of photocatalytic H₂-production over sample CZ2, every three hours the reaction system is bubbled with N₂ for 30 min to remove the H₂ inside; light source: four low-power 420 nm-LED.

The stability of sample CZ2 was confirmed experimentally by recycling this sample (Figure S6). After four recycles, no significant decrease in the H₂-production rate is observed. The mildly declined in the photocatalytic activity could be due to the consumption of the sacrificial reagents (S²⁻, SO₃²⁻), since the concentration of sacrificial reagents affect the performance largely.⁸,⁹ The results indicate that the CuS/ZnS porous nanosheets photocatalysts are highly efficient and stable photocatalysts materials under visible-light irradiation in such experimental conditions.

Cu₂S is just a reaction intermediate in the proposed mechanism. Under visible-light irradiation, the electrons are photoexcitated from VB of ZnS directly to CuS by IFCT and then reduce partial CuS to Cu₂S. CuS nanopatricles could not act as hole scavenger, since the CuS/Cu₂S clusters could act as an electron sink and co-catalyst to reduce H⁺ and release H₂. The holes remained in the VB of ZnS could be
consumed by the sacrificial agents (S\(^2\), SO\(_3\)^{2-}). Meanwhile, the formed Cu\(_2\)S could be oxidized by H\(^+\) and transformed to CuS, because the potential of CuS/Cu\(_2\)S (-0.5 V vs. SHE, pH=0) is much more negative than the potential of H\(^+\)/H\(_2\) (0 V vs. SHE, pH=0) (as shown in equation 3 and 4). However, the reaction rate of equation 3 is faster than that of equation 4, thus when the photocatalytic reaction was stopped, a small amount of Cu\(_2\)S remained in the samples. So, it is not surprising that the XPS results show the presence of Cu\(^+\).

REFERENCES


