Enhanced visible light photocatalytic hydrogen production activity of CuS/ZnS nanoflower spheres†

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A novel visible-light-driven photocatalyst CuS/ZnS with nanoflower architectures has been synthesized by a simple hydrothermal method and a successive cation exchange treatment. The visible light photocatalytic hydrogen production activity was estimated from a mixed Na2S and Na2SO3 aqueous solution. The experimental results reveal that the photocatalytic performance of ZnS nanomaterials can be enhanced dramatically with the deposition of a small percentage of CuS. When loading a 1.97 mol% CuS content, the as-prepared CuS/ZnS sample reaches an optimal hydrogen production rate of 5152 μmol h⁻¹ g⁻¹ under visible light and an apparent quantum efficiency of 26.2% at 420 nm (without the assistance of a Pt co-catalyst). The high photocatalytic performances are attributed to the low energy level provided by the deposited CuS on the ZnS surface, which can be activated under visible light. Furthermore, the interpair electric field (IPEF) existing in ZnS nano-architectures can also promote the efficient separation of the photogenerated charge carriers and thus enhance the hydrogen production activity.

Introduction

As global economy develops, the energy crisis and environmental pollution have become two principal issues for human beings. Hydrogen, a class of clean and renewable energy source, has received extensive attention for its potential substitution for fossil fuels. However, the primary method of hydrogen production is through the consumption of fossil fuels, which is less eco-friendly. Since Honda and Fujishima’s pioneering work of photocatalytic water splitting on TiO2 electrodes, photocatalytic hydrogen production from water splitting has attracted widespread attention because it is an eco-friendly and economical way of producing hydrogen by using solar energy. Consequently, numerous semiconductor photocatalysts were synthesized to investigate the hydrogen production activity by photocatalytic water splitting. Among the investigated photocatalysts, ZnS has been studied extensively for its high hydrogen production activity. The theoretical efficiency of photo-carrier generation of ZnS should be much higher than that of TiO2 because it is a direct band gap semiconductor, leading to a high photocatalytic activity. Some ZnS nanomaterials with special morphologies actually display higher photocatalytic activities than the commercial TiO2. Nonetheless, the relatively wide band gap of ZnS unfortunately only has the capacity to absorb ultraviolet light, which only occupies 4% of the total solar energy, and thus greatly restricts its practical applications. Therefore, numerous attempts have been adopted to make UV-active ZnS-based photocatalysts with visible light activity, for instance through the use of metal ion doping (i.e., Ni2+ and Cu2+) surface sensitization, the preparation of solid solutions, and combination with some narrow band gap semiconductors (such as CdS, Bi2O3, etc.). According to the existing results, a composite of two semiconductors is considered to favour the generation and separation of photoinduced carriers and thus improve the photocatalytic activity. Furthermore, composite semiconductors can expand the absorption scope and enhance the use of solar energy compared to a single semiconductor. On the other hand, in order to reduce the overpotential for hydrogen evolution, a Pt co-catalyst sometimes is still needed for higher activity. Therefore, noble metal-free ZnS-based composites are prospective candidates as hydrogen evolution photocatalysts.

In this work, we have synthesized CuS/ZnS nano-architectures by a simple hydrothermal and cation exchange

†Electronic supplementary information (ESI) available: The EDX pattern of ZC3, the STEM and HAADF images of sample ZC3, the transient photocurrent responses and Nyquist plots of ZC3, ZC10 and ZC0, PL spectra of ZnS samples with different Cu concentration, XRD patterns of CuS and CuS + ZnS, XPS spectra of CuS and CuS + ZnS. See DOI: 10.1039/c5ta02500a
method, and chosen the self-supported ZnS nanoflowers as the carriers for CuS nanoparticle loading. Compared with nanoparticles, the proposed ZnS nanoarchitectures do not easily aggregate and thus the rapid decline of the active surface area during the photocatalytic reaction can be prevented. After loading some CuS nanoparticles, the photocatalytic H2 production activity was found to be substantially improved under visible light. A series of CuS/ZnS samples were extensively characterized and investigated, and the related mechanisms of production activity was found to be substantially improved (IPEF) were presented to interpret the enhancement of H2 production activity by loading CuS.

**Experimental section**

**Preparation of original ZnS microspheres**

All the reagents were of analytical grade from Sinopharm Medicine Company and were used without any further purification. The original ZnS microspheres were prepared by a hydrothermal method as reported in our previous work. In detail, ZnO (0.167 g, 2 mmol) was dissolved in a mixture of NaOH (16 M, 12.875 mL) and Na2S (1 M, 2 mL) (the final concentration of NaOH solution is 14 M after mixing all of them). It was then put into a hydrothermal bomb that was sealed and heated at 230 °C for 12 h. After heat treatment, the bomb was rapidly cooled to room temperature. The white powder was then centrifuged and washed with excess distilled water and ethanol, and finally dried under vacuum at room temperature for 10 hours.

**Preparation of CuS/ZnS nanoarchitecture composites**

CuS/ZnS nanoarchitecture composites were prepared by the cation exchange method. Typically, ZnS nanoarchitectures (0.1 g) were first dispersed into water, ultrasonicated for 10 minutes, then a certain amount of Cu(NO3)2 aqueous solution (1 mM) was added and the mixture was stirred for 60 minutes. The theoretical molar ratios of Cu/Zn, tagged as RCu, were 0, 1, 2, 3, 5 and 10 mol%, and the samples were labeled ZC0, ZC1, ZC2, ZC3, ZC5 and ZC10, respectively. The final samples were washed with distilled water and ethanol, and then dried at 70 °C for 8 h. The simple CuS sample was synthesized by adding a high excess of Cu2+ ions during the preparation process. The sample of ZnS + CuS was synthesized by the physical mixing of simple CuS (molar rate of 3%) and ZnS.

**Characterization**

X-ray diffraction (XRD) analysis was used to determine the crystal structures and phase compositions. The diffraction data were collected using a PANalytical 25 X’Pert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA) at a scan rate of 0.02° 2θ s⁻¹. Scanning electron microscopy (SEM, JEOL, JSM-6700F) analyses were performed to observe the morphology and particle size. Transmission electron microscopy (TEM) was carried out to determine the morphology and structure using a JEOL JEM2010 HRTEM instrument at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed in a Thermo Scientific ESCALAB 250 system with a Mg Kα source. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The Bru- nauer–Emmett–Teller (BET) surface area was analyzed by using a Micrometries ASAP 2020 system, and the pore size distribution was determined by the Barret–Joyner–Halenda (BJH) method in a cylindrical pore model. The fluorescence spectra were measured using a FLS920 fluorescence spectrometer with an excitation wavelength of 325 nm. The diffuse reflectance UV–vis spectra were recorded on a UV-vis spectrophotometer (UV2550, Shimadzu, Japan), and BaSO4 was used as a reflectance standard. The Kubelka–Munk function was further used to analyze the absorption spectra, $K/S = (1 - R)^2/2R$, where K is the absorption coefficient, R is the diffused reflectance, and S is the scattering coefficient.

**Photocatalytic activity**

The photocatalytic hydrogen evolution measurements were carried out in a 100 mL Pyrex flask (sealed with a silicone rubber septum) at ambient temperature and atmospheric pressure. A 350 W xenon arc lamp with a UV-cutoff filter (≤420 nm) was used as a visible light source to trigger the photocatalytic reaction and was positioned 20 cm away from the reactor. The intensity on the focused flask was ca. 180 mW cm⁻². In a typical photocatalytic experiment, 50 mg of catalyst was dispersed under constant stirring in a 80 mL mixed aqueous solution containing 0.35 M Na2S and 0.25 M Na2SO3. The system was bubbled with N2 for 30 min to remove the air inside before irradiation and ensure anaerobic conditions in the reaction system. A 0.4 mL volume of gas was intermittently sampled through the septum, and gas chromatography (GC-14C, Shimadzu, Japan, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column) was used to analyze the produced hydrogen. The apparent quantum efficiency (QE) was tested under the same photocatalytic reaction conditions. Four low-power 420 nm-LEDs (3 W) (Shenzhen LAMPLIC Science Co. Ltd. China) were used as light sources to trigger the photocatalytic reaction, which were positioned 1 cm away from the reactor in four different directions. The focused intensity for each 420 nm-LED was ca. 6.0 mW cm⁻². The QE was calculated according to eqn (1):

$$\text{QE} [%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$

$$= \frac{\text{number of evolved H}_2 \text{molecules} \times 2}{\text{number of incident photons}} \times 100$$

(1)

**Photoelectrochemical measurements**

The photocurrent measurements were completed using an electrochemical instrument (CHI 660D) using a conventional three-electrode system with a Pt wire as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. The light source was a 350 W Xe arc lamp, and the electrolyte was a 0.35 M Na2S and 0.25 M Na2SO3 mixed aqueous solution. The following process was used for the fabrication of the electrode; 10 mg of
the sample was grained with 20 μL of PEDOTPS (Sigma-Aldrich) and 100 μL of water to form a mud. Then the mud was coated on a substrate of 2 × 0.5 cm² ITO glass using the doctor blade method. The as-prepared electrode was dried and treated at 200 °C for 1 hour in a N₂ atmosphere. The photoresponses of the samples with light on and off were measured at 0.0 V. The electrochemical impedance spectra (EIS) data were obtained by using the above three-electrode system, and the parameter was that the frequency range is 0.005–105 Hz with an ac amplitude of 10 mV at 0.5 V.

Results and discussion

Crystal structure and morphology

CuS/ZnS nanoflower architectures were prepared by a hydrothermal method and a cation exchange treatment. The nominal molar ratios of Cu/Zn (R_{Cu}) were 0, 1, 2, 3, 5 and 10 mol%, which were labeled ZC0, ZC1, ZC2, ZC3, ZC5 and ZC10, respectively. The accurate concentrations of Cu²⁺ were detected by inductively coupled plasma atomic emission spectrometry (ICP-AES), and the values were 0.37, 0.94, 1.97, 2.98, and 5.67 mol%, respectively (see Table 1). The initial self-supported ZnS nanoflowers consist of 10–20 nm thick interwoven nanosheets (Fig. 1a and b). Fig. 1c and d show the typical SEM images of ZC3 (the highest hydrogen production activity), and we can find that the initial nanoarchitecture of ZnS has been almost unchanged, however, the microsphere surface has been loaded with nanoparticles, which can be seen from the images. The elements of sample ZC3 are composed of copper, zinc, and sulfur, which are identified by energy-dispersive X-ray spectroscopy (Fig. S1†). Furthermore, these loaded nanoparticles with diameters ca. 10–20 nm can be observed in the TEM image of ZC3 (Fig. 1e). In addition, the lattice fringes can be obviously observed in the HRTEM image (Fig. 1f). From the HRTEM image, the lattice spacing of ca. 0.31 nm can be characterized as a hexagonal ZnS (002) plane, and some small clusters with a lattice spacing of ca. 0.31 nm can be indexed as cubic CuS (103) planes. Further confirmation is shown in Fig. S3,† where the lighter (A) and darker (B) areas can be attributed to CuS and ZnS, respectively. The elemental mapping indicates that area A contains Cu and S (from CuS) and area B contains Zn and S elements (from ZnS). It implies that CuS is loaded on the ZnS surface instead of simply being mixed with ZnS. From the above analysis, it can be concluded that ZnS is closely interconnected with CuS.

The XRD patterns of the CuS/ZnS samples with various Cu concentrations are shown in Fig. 2. It indicates that the phase of all the samples is clarified as ZnS wurtzite, which is the same as our early results.29 Specifically, the diffraction peak at 27.2° can be identified as ZnS wurtzite (100), and the broader peak is composed of the overlapping peaks of sphalerite (111), wurtzite (002) and wurtzite (101). It is worth noting that the XRD detection does not find any CuS phases even when the Cu content is as high as 5.67% (ZC10). Nevertheless, the CuS phase can be clearly observed in sample ZC20 where the content of Cu rises to 10.9% (Fig. S2†). This phenomenon can be attributed to the fact that the CuS particles loaded on the ZnS surface have poorer crystallinity.30 Moreover, with increasing Cu concentration, the intensity of the ZnS diffraction peaks decreases and the peak widths become a little wider, suggesting a decline in crystallinity and particle size.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states of the Cu element. Fig. 3a shows the XPS spectrum of ZC3, in which the peaks of Zn 2p, Cu 2p, O 1s, S 2p and C 1s can be obviously found. Before the catalytic reaction, the binding energies of 932.8 and 953.1 eV in the XPS spectrum of Cu 2p (Fig. 3b) can be indexed as the peaks of Cu 2p_{3/2} and Cu 2p_{1/2} of Cu²⁺ in CuS.31,32 However, the XPS spectrum has changed greatly after three hours of reaction. The binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} show a slight shift to 932.0 and 952.0 eV, respectively, which indicates the existence of Cu⁺.33 From the XPS analysis results, it can be deduced that a small fraction of CuS was reduced to Cu⁺, which is consistent with the results of our early studies.21,22

<table>
<thead>
<tr>
<th>Samples</th>
<th>x</th>
<th>Cu (mol%) [ICP-AES]</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore size (nm)</th>
<th>Activity (μmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC0</td>
<td>0</td>
<td>0</td>
<td>106</td>
<td>0.29</td>
<td>10.8</td>
<td>46</td>
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<tr>
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<td>96</td>
<td>0.27</td>
<td>11.8</td>
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<tr>
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<td>0.94</td>
<td>92</td>
<td>0.24</td>
<td>12.4</td>
<td>2162</td>
</tr>
<tr>
<td>ZC3</td>
<td>3</td>
<td>1.97</td>
<td>85</td>
<td>0.26</td>
<td>12.1</td>
<td>5152</td>
</tr>
<tr>
<td>ZC5</td>
<td>5</td>
<td>2.98</td>
<td>88</td>
<td>0.25</td>
<td>11.4</td>
<td>1348</td>
</tr>
<tr>
<td>ZC10</td>
<td>10</td>
<td>5.67</td>
<td>93</td>
<td>0.25</td>
<td>10.9</td>
<td>723</td>
</tr>
</tbody>
</table>

**Fig. 1** (a and b) SEM of sample ZC0. (c and d) SEM of sample ZC3. (e and f) TEM and HRTEM of sample ZC3.
portion of Cu$^{2+}$ in CuS has been reduced to Cu$_2$S after photocatalytic reaction for 3 h. According to the results of SEM, TEM and XPS, we can derive that the partial reduction of CuS to Cu$_2$S is possibly caused by the charge transfer between ZnS and CuS.

**UV-vis diffuse reflection spectra**

The UV-vis diffuse reflection spectra of samples ZC0, ZC1, ZC2, ZC3, ZC5 and ZC10 are shown in Fig. 4. The absorption edge (lower than 355 nm) is considered to be the intrinsic absorption for sample ZnS. By fitting the Tauc/David-Mott model, the band gap of the sample is determined to be 3.45 eV. With increasing Cu content, the CuS/ZnS samples show an obvious enhancing response in the visible-light region. This enhancement can be ascribed to an increase in CuS content, whose absorption edge ranges from 300 to 800 nm in wavelength (see Fig. 4).35

**BET surface areas and pore size distributions**

Fig. 5 depicts the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves of ZC0 and ZC3 samples. The isotherms of these two samples can be characterized as type IV by using the IUPAC classification, indicating the existence of mesopores.40 The hysteresis loops can be classified as type H3, associated with slit-like pores, which is matched well with the ZnS layered nanostructures from our previous work. The pore-size distributions (inset in Fig. 5) of samples ZC0 and ZC3 show a wide range of pore sizes ranging from 2 to 100 nm, further indicating the presence of mesopores and macropores. Table 1 lists some physicochemical properties of all the samples, such as BET surface areas, average pore sizes and pore volumes. It can be seen from Table 1 that the original ZnS (ZC0) has a higher BET surface area ($S_{BET}$). The $S_{BET}$ of the samples slightly decreases as the content of CuS increases to 3%, and then the $S_{BET}$ increases. The decrease in $S_{BET}$ may be due to the CuS loaded on the ZnS surface, which blocks up the pores. However, the increase in $S_{BET}$ can be attributed to the decrease in crystallinity and particle size, which has been discussed in XRD analysis.

**Photocatalytic performance**

The photocatalytic H$_2$ production performance of the CuS/ZnS samples was estimated from 0.35 M Na$_2$S and 0.25 M Na$_2$SO$_3$ mixed aqueous solutions under visible light irradiation ($\lambda \geq 420$ nm). The experimental data are listed in Table 1 and Fig. 6. The pristine ZnS nanoarchitectures (ZC0) exhibit a weak H$_2$ production activity under visible light, which is caused by the large band gap energy of ZnS. With a small portion of Cu$^{2+}$ taking part in the photocatalytic process, the performance of the ZnS nanoarchitectures has substantially improved. The H$_2$ production rates increase with the increase in Cu content when $R_{Cu} < 1.97\%$, and achieve an optimal value of 5152 $\mu$mol h$^{-1}$ g$_{ZnS}$$^{-1}$ with 26.2% apparent quantum efficiency (QE) at 420 nm (for
The value of Pt/CdS is 2001 μmol h⁻¹ g⁻¹ under the same conditions. However, further increase in Cu content causes a decrease in the photocatalytic performance, and the photocatalytic H₂ production rates of the sample ZC10 drop down to 723 μmol h⁻¹ g⁻¹. This phenomenon may be due to the deposition of an excess of CuS clusters caused by a high Cu²⁺ content, which reduces the active spots on the ZnS surface and efficient light absorption. In addition, an excess of CuS particles could serve as charge recombination centers, then decrease the photocatalytic H₂ production activity. It is noted that simply mixing CuS and ZnS (ZnS + CuS) does not lead to an obvious photocatalytic performance. The reason may be that close interactions are hard to form through simple physical mixing, which is important for electron transfer.

Metal sulfides often demonstrate a decline during the photocatalytic process because of photocorrosion. In order to examine the stability of the as-prepared samples, the time-dependence of the photocatalytic H₂ evolution of sample ZC3 was investigated. As shown in Fig. 7, there is no obvious activity drop after five recycles, suggesting a better stability of the sample during the photocatalytic process.

The excitation and transfer of photogenerated charge carriers in photocatalysts are often qualitatively studied by photoelectrochemical measurements. Fig. S4† shows the transient photocurrent responses of ZC0, ZC3, and ZC10, which were investigated for several on–off cycles under visible light. As seen from the figure, sample ZC3 has the highest transient photocurrent, whereas ZC10 and ZC0 give the medium and minimum intensities, respectively. Therefore, it can be deduced that sample ZC3 has the highest efficiency of photogenerated charge separation, and the conclusion is consistent with the results of the photocatalytic H₂-production tests.

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As mentioned above, in the as-prepared nanoflower architectures, the visible light photocatalytic hydrogen production rate is obviously improved when 1.97% CuS is deposited. The photocatalytic mechanisms are depicted in Fig. 8. First, the original ZnS cannot respond under visible light due to its large band gap energy, and the conduction (CB) and valence (VB) band levels are about −1.01 and 2.42 eV by calculation. Also, the simple CuS exhibits zero photocatalytic activity under visible light. Nevertheless, loading a small portion of CuS on the ZnS surface can lead to the formation of close interactions between CuS and ZnS (see SEM, TEM and UV-vis), which is considered to promote the photogenerated charge separation and then enhances the photocatalytic activity. As shown in Fig. 8, the relatively lower redox-potential position of CuS/Cu₂S (−0.5 V vs. SHE) makes it possible for the photogenerated electrons in the VB of ZnS to easily transfer to CuS under visible light, and leads to the partial reduction of CuS into Cu₂S. These CuS/Cu₂S nanoparticles may serve as electron trips to accelerate the separation and migration of photogenerated electrons. Therefore, it can be concluded that the interfacial charge transfer (IFCT) in the heteronanostructures is beneficial for the photogenerated charge separation and then increases the photocatalytic activity. Second, the as-prepared flower-like ZnS...
microspheres consist of 10–20 nm interwoven nanosheets, with exposed wurtzite ZnS (0001) faces. As shown in Fig. 86, the positive and negative charges are located separately on the Zn and S-terminated plane, which induces a spontaneous polarization across the ZnS nanosheets. The interpolar electric field (IEF) produced by polarization will promote the separation of the photogenerated charges and then hasten them to the ZnS surface. Therefore, the IEF can accelerate the migration of the photogenerated charges and improve the photocatalytic performance. In addition, the nanosheet-like frameworks are believed to have an efficient visible-light-response and cation exchange method. The photocatalytic performance of those nanoarchitectures is remarkably improved with the deposition of CuS. The optimal CuS loading concentration is about 1.97 mol% and the H2 production rate is 5152 μmol h⁻¹ g⁻¹. The corresponding apparent quantum efficiency (QE) reaches 26.2% at 420 nm even without noble metal co-catalyst. Based on the above discussion, the IFCT can be induced under visible light, which may lead to the improvement of both the IFCT and the IEF. Yet the H2 production activity falls rapidly with the continuous rise of the concentration of CuS, because the excess of CuS can prevent light absorption and become the recombination center of photoinduced electrons and holes, leading to the decline of the photocatalytic activity.

Conclusions

In conclusion, we have successfully synthesized CuS/ZnS self-supported nanoflower architectures by a hydrothermal treatment and a cation exchange method. The photocatalytic performance of those nanoarchitectures is remarkably improved with the deposition of CuS. The optimal CuS loading concentration is about 1.97 mol% and the H2 production rate is 5152 μmol h⁻¹ g⁻¹. The corresponding apparent quantum efficiency (QE) reaches 26.2% at 420 nm even without noble metal co-catalyst. Based on the above discussion, the IFCT can be induced under visible light, which may lead to the effective photo-generated charge separation and then enhance the photocatalytic activity. In addition, the IEF existing in ZnS nanoarchitectures can also facilitate the separation of light-induced charges, and promote the hydrogen production. Our results will provide a promising strategy for designing and synthesizing economical and highly efficient visible-light-response photocatalysts.

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Notes and references


