Photocatalysts

Outside-In Recrystallization of ZnS–Cu_{1.8}S Hollow Spheres with Interdispersed Lattices for Enhanced Visible Light Solar Hydrogen Generation

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Abstract: For the first time an earth-abundant and nontoxic ZnS–Cu_{1.8}S hybrid photocatalyst has been engineered with well-defined nanosheet hollow structures by a template-engaged method. In contrast to conventional surface coupling and loading, the unique outside-in recrystallization promotes co-precipitation of ZnS and Cu_{1.8}S into homogeneous interdispersed lattices, hence forming a hybrid semiconductor with visible responsive photocatalytic activity. The as-derived

Introduction

The exhaustion of global fossil-fuel resources and growing environmental problems are prompting mankind to move to a green and sustainable lifestyle. Hence, the harvesting of solar energy and conversion to clean and safe energy sources is a key goal for the next generation's energy consumption.^[1,2] Hydrogen (H₂) is a clean energy source with a high fuel value of 484 kJ mol⁻¹, and the combustion product of H₂ is only water, making it an ideal candidate as energy carrier.^[3] Unfortunately, the current large-scale production of H₂ in industry relies on the decomposition and gasification of fossil fuels, which brings new environmental problems, such as the release of the greenhouse gas (carbon dioxide).^[4] Consequently, the relevant research community is paying intense attention to H₂ evolution from water splitting using solar irradiation because of the abundance and inexhaustible availability of solar energy.^[5] However, water splitting is a thermodynamically uphill reaction, which requires a photocatalyst to absorb photons to overcome the Gibbs free energy.^[3]

Light-driven water splitting is initiated when photons carrying energies higher than the bandgap of the host photocatalyst are absorbed. The captured photons generate photon-induced electrons in the conduction band (CB) and holes in the valence band (VB) of the host photocatalyst. Subsequently, the ZnS-Cu_{1.8}S semiconductor alloy is tailored into a hierarchical hollow structure to provide readily accessible porous shells and interior spaces for effective ion transfer/exchange. Notably, this synergistic morphology, interface and crystal lattice engineering, aim towards the design of novel nanocatalysts for various sustainable environmental and energy applications.

separated photoinduced electrons and holes migrate to the surface of the photocatalyst, reducing the protons and oxidizing the hydroxyls, respectively.^[6]

 $\mbox{Oxidation}:\ 2\,\mbox{OH}^- + 4\,\mbox{h}^+ \rightarrow 2\,\mbox{H}^+ + \mbox{O}_2$

 $\mbox{Reduction}:\ 2\,\mbox{H}^+ + 2\,\mbox{e}^- \rightarrow \mbox{H}_2$

In the past few years, various types of active photocatalysts have been explored to achieve the above reactions efficient-ly.^[7-16] However, many photocatalytic materials reported show poor response to visible light, which takes approximately 70% of the total sunlight energy.^[3] Therefore, it is highly desirable to design and fabricate new heterogeneous photocatalysts with higher response to visible light irradiation.

Zinc sulfide (ZnS) is a widely studied semiconductor for water splitting because of its rapid generation of electron-hole pairs.^[17,18] However, ZnS can only absorb UV light due to its large bandgap (3.6 eV), which has inspired various strategies, such as metal-ion doping and loading to increase the visiblelight activity.^[19,20] The developed strategies usually require multiple steps (ZnS preparation and metal-ion doping), leading to the partial sacrifice of architectures during the ion exchange. Also, some researchers are devoted to engineering the band structures of semiconductor solid solutions, such as Zn_xCd_{1-x}S to improve H₂ performance under visible light,^[21,22] but the biological evidence shows that cadmium is toxic and can cause environmental problems, which restricts its practical use in the future.^[23,24] Copper sulfide is a class of semiconductor, containing various phases (e.g., CuS, Cu_{1.8}S, and Cu₂S)^[25] that are responsive to visible light.[26]

In this work, we have fabricated $ZnS-Cu_{1.8}S$ hybrid photocatalyst for the first time with well-defined hierarchical hollow structures by an outside-in recrystallization process. Firstly, in

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the presence of urea, the Zn^{2+} and Cu^{2+} are co-precipitated onto the surface of mesoporous silica (m-SiO₂) nanocolloids (~ 400 nm in diameter), forming the hierarchical Zn-Cu-silicate shell structures. Secondly, the as-grown hierarchical shell structures are transformed into ZnS-Cu_{1.8}S hybrid sulfides with thiourea through a hydrothermal reaction. In this way, the lattices of ZnS and Cu_{1.8}S are engineered to be homogeneously interdispersed. The shell structures are found to be well-preserved after the transformation, which shows the reliability of our synthetic strategy. Meanwhile, the m-SiO₂ cores are hydrothermally eliminated by thiourea, creating a hollow interior in the structure. Interestingly, the shell structures are thickened (from 80 to 100 nm) while particle size is retained after transformation, inferring an outside-in recrystallization process against the dissolution and evacuation of m-SiO₂ cores. The as-fabricated ZnS-Cu₁₈S hollow spheres were characterized and found to possess a large surface area, which aims to provide considerable active sites for the redox reaction during the photocatalytic reaction.

Experimental Section

Synthesis of m-SiO₂

The preparation of m-SiO₂ nanocolloids was based on a modified Stöber method.^[27] Briefly, ethanol (81 mL) and ammonia aqueous solution (24 mL; wt%=25%) were mixed at RT, and then hexade-cyltrimethylammonium bromide (CTAB; 0.2 g) was dissolved in the solution by sonication for 10 min. Under vigorous stirring at RT, tetraethyl orthosilicate (TEOS; 4.2 mL) was injected into the solution and the mixture was stirred for 1 h before the white product was washed with deionized (DI)-water and ethanol several times and collected by centrifugation. The collected m-SiO₂ was dried at 60 °C in an oven for 24 h for further use. The common SiO₂ was prepared with the same conditions but in the absence of CTAB.

Synthesis of m-SiO₂@Zn-Cu-silicate

The as-prepared m-SiO₂ (0.1 g) was dispersed into DI-water (40 mL) by ultrasonication for 20 min, followed by the addition of urea (0.8 g) for the activation of the SiO₂ surface. After sonication for another 10 min, $Zn(NO_3)_2$ (0.5 mL; 0.1 M) and $Cu(NO_3)_2$ (0.8 mL; 0.1 M) were added dropwise to the solution. The mixture was heated at 102 °C in an oven for 12 h. The reaction was allowed to cool naturally and the light-blue product was collected by the rinse–centrifugation process with DI water and ethanol several times. The obtained product was thoroughly dried at 60 °C in an air-flow oven for 24 h for the next-step.

Fabrication of ZnS-Cu_{1.8}S hollow spheres

In order to prepare ZnS–Cu_{1.8}S hollow structures, the as-prepared m-SiO₂@Zn–Cu-silicate (30 mg) was firstly dispersed in DI-water (40 mL) by sonication for 15 min. Later, thiourea (60 mg) was added to the solution and the mixture was sealed in a glass bottle before being heated at 95 °C for 24 h. After the reaction, the glass bottle was allowed to cool naturally, and the black product was collected by the rinse–centrifugation process with DI-water and ethanol several times. The obtained product was dried thoroughly at 60 °C in a vacuum oven for 12 h. In the control experiments, pure ZnS and Cu_{1.8}S, and ZnS–Cu_{1.8}S sulfides by co-precipitation in

the absence of m-SiO₂ were also synthesized. Hollow-sphere samples of ZnS-Cu_{1.8}S, ZnS, Cu_{1.8}S, co-precipitated ZnS-Cu_{1.8}S, physically mixed ZnS-Cu_{1.8}S are denoted as HS-ZS-CS, pure ZS, pure CS, CP-ZS-CS, and PM-ZS-CS, respectively.

Material characterization

All samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL FEG JSM-7001F) equipped with an energy dispersive X-ray spectrometer (EDX), transmission electron microscopy (TEM, Philips FEG CM300) and X-ray diffraction (XRD, Philips X-ray diffractometer, Cu_{Ka}). X-ray photoelectron spectroscopy (XPS), VGSCALAB 220I-XL system equipped with an Mg_{ka} X-ray source was employed to study the elemental compositions. For the texture property measurement, the powder was loaded into a sample cell and degassed at 120°C thoroughly before it was immersed together with a sensor into a Dewar full of liquid nitrogen. The N₂ adsorption and desorption isotherms were measured at 77 K by a Quantachrome NOVA-1200 system. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.05 to 0.3. The pore volume was estimated using desorption isotherm based on the Barrett-Joyner-Halenda (BJH) method. Absorption spectra of the samples were measured with a UV/Vis/NIR spectrophotometer (UV/ Vis, Shimadzu UV-3600).

H₂ evolution measurements

The photocatalytic reactions were conducted in a quartz cylindrical glass tube of 25 mL in volume. The as-prepared photocatalysts (10 mg) were weighed into the glass tube and dispersed in Na₂S/Na₂SO₃ (10 mL) aqueous solution ([Na₂S]=0.35 M, [Na₂SO₃]= 0.25 M) by sonication for 5 min. The glass tube was sealed and purged with argon gas (Ar) for 10 min before the mixture was stirred vigorously. A 300 W xenon arc lamp equipped with a cut-off filter (λ > 400 nm) was used as incident visible light. Gas samples were analyzed using a gas chromatograph (Shimadzu GC2014) to determine the amount of H₂. In addition, the H₂ experiment was carried out under natural sunlight to further study the photocatalytic activity. The quartz tube was ultrasonicated for 10 min before being exposed to sunlight for 15 min without magnetic stirring.

Results and Discussion

Figure 1 shows our synthetic strategy to achieve HS-ZS-CS hybrid materials. Firstly, m-SiO₂ nanocolloids were employed as hard templates to grow uniform Zn–Cu-silicate precursors (ZCSP) to form core-shell structures in the presence of urea, which is illustrated by Figure 1a. Subsequently, the core-shell ZCSP were transformed into hybrid sulfides with thiourea by hydrothermal synthesis, in which the m-SiO₂ cores were eliminated simultaneously, creating hollow interiors (Figure 1b). It should be noted that the uniform growth of ZCSP is facilitated and improved by the introduction of m-SiO₂, as our control experiments have shown that isolated and free-standing nanosheets can be synthesized if conventional SiO₂ cores are used.

The uniform growth of the ZCSP nanosheets onto the m- SiO_2 nanocolloids (Figure 2a) was confirmed by FESEM (Figure 2b). Most of the particles are uniform in size and no aggregation can be observed due to the introduction of m- SiO_2 and fine-tuning of the chemistry process. The formation of core-

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Figure 1. Schematic illustration of the formation process of HS-ZS-CS sample.

shell structures is revealed by the TEM results (Figure 2 c), in which the hierarchical shells (~ 80 nm in thickness) and the m-SiO₂ cores (darker in contrast) can be distinguished clearly. The EDX result shown in Figure 2d confirms the presence of Zn, Cu, Si, O elements (the strong Al peak is contributed by the Al foil substrate). XRD was carried out to determine the crystal structures of the as-synthesized spheres (Figure S1 in the Supporting Information). The star-indexed peaks can be assigned to zinc silicate (Zn₄Si₂O₇(OH)₂·H₂O, JCPDS 05-0555), while the dot-indexed peaks are attributed to copper silicate (JCPDS 03-0219).^[28,29] The appearance of a broad diffraction peak around 25° (indexed by hashtag) reveals the preservation of the silica cores.



Figure 2. a) FESEM image of $m-SiO_2$ nanocolloids; b) FESEM image, c) TEM image, and d) EDX analysis of the as-prepared Zn–Cu-silicate core-shell structures.

After hydrothermal treatment in the presence of thiourea, the as-formed ZCSP core-shell structures were transformed into HS-ZS-CS, while the hierarchical shell structures were well preserved (Figure 3 a). The creation of hollow interiors was affirmed by the TEM images displayed in Figure 3 b and c. Furthermore, it is interesting to note that the shell structures assume a more densely packed nanosheet after transformation as compared to the ZCSP shells. Our detailed observations show that the shells of HS-ZS-CS have thickened (from 80 to 100 nm) while retaining the particle size, owing to the outsidein recrystallization during the transformation process against the dissolution and evacuation of the m-SiO₂ cores. The HR-TEM was taken from the area marked by a rectangle shown in Figure 3 c. The interplanar spacing of 0.28 nm corresponds to Cu_{1.8}S-(200) while the d-spacings of 0.312 and 0.191 nm are assigned to the ZnS-(111) and ZnS-(220), respectively.^[30,31] It is evident from the TEM observations that the lattices of ZnS and Cu_{1.8}S are interdispersed, revealing the atomic-level hybridization of ZnS and Cu_{1.8}S.



Figure 3. a) FESEM image, b), c) TEM images, d) HR-TEM, e) XRD pattern, and f) EDX of the as-fabricated HS-ZS-CS sample.

The crystal phases of the HS-ZS-CS were further examined by XRD as shown in Figure 3d, and except for the star-marked peaks ascribed to Cu_{1.8}S, all the indexed peaks can be assigned to the cubic β -ZnS (JCPDS 05-0566), which is consistent with previous reports.^[30, 32] The EDX performed on the AI substrate was used to determine the chemical composition of the astransformed products (Figure 3 f). The presences of Zn, Cu, and S peaks indicate the formation of zinc sulfide and copper sulfide (Zn/Cu molar ratio of ~5:1). It should also be noted that the silica cores are removed by the alkaline atmosphere created by the hydrolysis of thiourea during the transformation. The emergence of the negligible Si peak in the EDX pattern may be due to the silicate ion residue trapped in the interior cavity of the hollow spheres. XPS was performed to determine the elemental composition of the HS-ZS-CS sample (Figure 4). The XPS survey spectra clearly reveal the peaks of Zn 2p, Cu

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2p, S 2p, O 1s, and C 1s (Figure 4a). The appearance of weak peaks of O and C can be assigned to H₂O, O₂, and CO₂ absorbed on the surface of the sample and adventitious hydrocarbon from the XPS instrument itself.^[26] Figure 4b–d show the typical peaks of Zn 2p, Cu 2p, S 2p, respectively. The binding energies of Zn 2p_{1/2}, Zn 2p_{3/2} are allocated at 1044.7 and 1021.5 eV while that of Cu 2p_{3/2} and Cu 2p_{1/2} are observed at 932.4 and 952.3 eV, respectively.^[33] The absence of satellite line confirmed that Cu⁺ is the only copper species existing in the as-synthesized HS-ZS-CS sample. This is in agreement with the TEM and XRD structural characterizations in which copper is in the form of monovalence. The S 2p core-level spectrum shows two deconvoluted peaks with binding energies of S 2p_{3/2} and S 2p_{1/2} at 161 and 162.2 eV, respectively, which suggest that S is in sulfide state.^[34]

The as-prepared nanosheet spheres are expected to possess a large surface area due to their hollow voids and hierarchical shell structure. Hence the BET specific surface area and pore characteristic measurements were carried out. The N₂ adsorption/desorption measurement of the HS-ZS-CS hybrid sulfides shows a high specific surface area of 196 m²g⁻¹ with a pore size distribution of 1.8 nm (Figure 5a) while the CP-ZS-CS reference sample shows a much lower specific surface area of 40 m²g⁻¹, however, with a larger pore size of 4.2 nm (Figure 5b). It is believed that the larger specific surface area of the hollow spheres may translate to an increase in photocatalytic active sites.

Figure 6a shows the absorption curves of UV/Vis spectra for different photocatalysts. It can be seen that the HS-ZS-CS sample exhibits the highest and extended light absorption as compared to other samples. The increase in light absorption from UV to visible-light range will allow more efficient utilization of the solar spectrum, which is beneficial for photocatalytic reactivity.^[35] Figure 6b shows the H₂-evolution performance of various photocatalytic samples under both UV/Vis and visible-light spectra. Under visible light, a small amount of H₂ can be detected after 2 h for both pure ZnS and Cu_{1.8}S samples, which shows their inactivity in the visible-light range. However, a high evolution rate of 467 μ mol h⁻¹g⁻¹ was obtained for the HS-ZS-CS sample, indicating its high response to visible light. In order to understand the association between the evolution rate and macro/microstructure, the properties of CP-ZS-CS and PM-ZS-CS samples were also compared. The results show that the evolution rate of CP-ZS-CS (101 μ mol h⁻¹g⁻¹) is higher than that of PM-ZS-CS (11.4 μ mol h⁻¹ q⁻¹), but much lower than that of HS-ZS-CS, demonstrating the importance of adopting hierarchical hollow structure for photocatalysis. In addition, we also measured the H₂ performance of all the samples under the UV/Vis range. The pure CS sample still delivers an insignificant evolution rate under UV/Vis range, which suggests that copper sulfide on its own may not be suitable for photocatalysis. On the other hand, the pure ZS sample shows a dramatic increase in evolution rate to 314 μ mol h⁻¹g⁻¹ under UV irradiation as compared to visible light, verifying the good photoactivity of ZnS in the UV range. Furthermore, UV/Vis irradiation increases the H2-evolution rate of HS-ZS-CS to 762 μ mol h⁻¹g⁻¹, which is significantly higher than that of CP-



Figure 4. a) Typical room temperature XPS survey spectrum, and spectra for b) Zn 2p, c) Cu 2p, and d) S 2p of HS-ZS-CS sample.

ZS-CS (405 μ mol h⁻¹ g⁻¹) and PM-ZS-CS (137 μ mol h⁻¹ g⁻¹). It is interesting to note that the H₂-evolution rate of HS-ZS-CS under visible irradiation is even higher than the rates of CP-ZS-CS and PM-ZS-CS under extended UV/Vis irradiation. Such improved performance of the CP-ZS-CS sample may be attributed to the following reasons: 1) homogeneous interdispersion of crystal lattices resulting in a visible responsive hybrid semiconductor alloy; 2) HS-ZS-CS possesses a much higher surface area inferring an increased number of active sites for the photoabsorption; 3) the hollow interiors serve as nanoreactors to facilitate ion transfer/exchange for water molecules, where effective reduction and oxidation at the interface between solid and liquid phases can occur. Moreover, it is noteworthy that the H₂ production rate of 17.6 μ mol h⁻¹ g⁻¹ is measured when HS-ZS-CS is exposed to natural sunlight. This suggests a potential use





Figure 5. BET results of the as-prepared a) HS-ZS-CS, and b) CP-ZS-CS samples.

of this hybrid semiconductor in next-generation photocatalysts even if the production rate is not high at present.

On the basis of the obtained results, a plausible H₂-evolution mechanism for visible-light photocatalysis is proposed in Figure 7. The formation of the hybrid semiconductor alloy is suggested to occur by heterostructuring of a wide-bandgap (ZnS) with a narrow-bandgap semiconductor (CuS) of similar crystal structure.^[36] Both the ZnS and Cu_{1.8}S formed in our hollow spheres are present as cubic phase, which enable effective interdispersion of the crystal lattice. In this work, the bandgap of pure ZS sample is determined to be approximately 3.34 eV based on the Tauc plot, and this bandgap is only active to UV corresponding to a wavelength less than 370 nm. By engineering the lattice structures, the bandgap of the assynthesized hybrid ZnS-Cu_{1.8}S semiconductor can be narrowed to approximately 2.76 eV based on the Tauc plot estimation, making the photocatalyst active to visible light. A recent report also shows a similar blue-shift of the absorption edge by doping Cu²⁺ into porous ZnS nanosheets.^[37] Hence, upon UV/Vis or solely visible-light irradiation, the photons are ab-



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Figure 6. a) UV/Vis spectra of the various photocatalysts, and a) their corresponding H_2 -evolution performance.

sorbed by the hybrid semiconductor alloy hollow spheres, through which electrons are generated in the conduction band and holes are formed in the valence band. The subsequent charge separation and migration processes transfer the electrons and holes from the bulk of the semiconductor to the reaction sites on the photocatalyst surface. Finally, the photoinduced electrons are combined with H^+ to generate H_2 , while the holes left are consumed by the sacrificial reagents.

In summary, this work has demonstrated an efficient synthetic strategy to prepare hierarchical ZnS-Cu_{1.8}S hollow spheres with readily accessible porous nanosheet shells and interior spaces for desirable liquid/gas access and diffusion. The unique outside-in recrystallization is designed to promote in-



Figure 7. Proposed photocatalytic mechanism of the pure ZnS and ZnS– $Cu_{1,8}$ S hybrid sulfides.



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terdispersion of ZnS and Cu_{1.8}S lattices to yield a hybrid semiconductor of visible responsive photocatalyst. The as-prepared ZnS-Cu_{1.8}S hybrid semiconductor exhibited a high H₂-evolution rate under visible light, showing its potential use in the nextgeneration noble-metal free photocatalysts.

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