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Fabrication of CdS Frame-in-Cage Particles for Efficient Photocatalytic Hydrogen Generation under Visible-Light Irradiation

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Abstract

The design of advanced structures for semiconductor photocatalysts is an effective approach to enhance their performance towards solar-to-chemical energy conversion. Hollow and frame-like structures show advantageous features for photocatalytic reactions with enlarged surface area, shortened charge transfer distance, promoted light absorption ability, and enhanced mass transfer capability. Here we develop a facile two-step sulfidation strategy to fabricate unique CdS frame-in-cage particles for photocatalytic hydrogen generation. Cd-based Prussian blue analog (Cd-PBA) cubes are first converted to Cd-PBA cube-in-CdS cage particles, which are further transformed to CdS frame-in-cage particles. Benefiting from the novel frame-in-cage structure, the obtained CdS photocatalyst exhibits high activity under visible-light irradiation with the hydrogen generation rate of $13.6 \text{ mmol h}^{-1} \text{ g}^{-1}$, which is much enhanced compared with those of the CdS cubes and CdS cages.

Keywords: Prussian blue analogs; frames; cages; CdS; H₂ generation.

Hydrogen (H_2) is one of the most important clean energy carriers widely applied in many areas such as industrial reactions, fuel cells and aviation.^[1] Traditional methods for the production of H_2 include natural gas reforming^[2] and coal gasification,^[3] which consume fossil fuels and produce carbon dioxide as a by-product. It is essential to develop approaches to generate H_2 fuel from renewable energy sources.^[4] Photocatalytic water splitting is considered as a promising strategy, which utilizes the inexhaustible, universal and clean solar energy.^[5,6] To construct efficient photocatalytic water splitting systems that meet the demands of practical applications, it is important to design photocatalysts with high activity, low cost and good stability.^[7,8]

Semiconductor photocatalysts must meet several criteria, including suitable band structure, high charge conductivity and good reactivity, to achieve high performance towards solar water splitting.^[9] Although metal oxides such as TiO_2 , ZnO and $SrTiO_3$ have been widely studied for the photocatalytic water reduction reaction, their activities are still not satisfactory mainly because they can only absorb ultraviolet light as a result of their large band gaps.^[10,11] Some oxide photocatalysts also suffer from the relatively poor charge conductivity and the serious recombination of photogenerated charge carriers.^[12,13] Considering all these points, more efforts have been devoted to transition metal sulfide photocatalysts, among which CdS shows outstanding properties.^[14,15] CdS possesses a band gap of about 2.4 eV and can utilize a large fraction of the visible-light irradiation.^[16,17] Moreover, CdS has a much more negative conduction band minimum than the redox potential of the water reduction reaction, which provides a large overpotential for the fast reaction kinetics.^[18,19] Therefore, rational design of advanced structures for CdS photocatalysts would be an effective approach to realize high-efficiency photocatalytic water reduction.^[20]

Hollow-structured photocatalysts show distinct advantages for solar energy conversion reactions.^[21] Large surface areas and abundant active sites would be provided by hollow structures to promote the

photocatalytic reactions.^[22] Besides, the thin shells could reduce the distance for the transfer of photogenerated charge carriers.^[23] The light scattering effect can be enhanced in hollow structures, which would lead to enhanced light absorption capability. Most recently, frame-like structures also exhibit similar advantageous features for photocatalytic reactions.^[24] Moreover, frame-like structures can also enhance the mass transfer processes during photocatalytic reactions. Therefore, combining the merits of hollow structures and frame-like structures may lead to high photocatalytic performance.

Synthetic methods based on Prussian blue analogs (PBAs) have been proved effective for the fabrication of hollow and frame-like structures.^[25,26] The intrinsic open frameworks and tunable compositions of PBAs provide great flexibility for the design of photocatalysts with desired features.^[27,28] Herein, we have developed a facile two-step sulfidation approach to fabricate CdS frame-in-cage particles for photocatalytic H₂ generation (**Figure 1a**). Specifically, Cd-based PBA (Cd-PBA) cubes are first synthesized through a conventional solution reaction at room temperature (see the Supporting Information for the experimental details).^[25,29] As shown in the field-emission scanning electron microscopy (FESEM) images, the obtained particles possess a well-defined cubic structure with an average particle size of about 1.4 μm (Figure 1b,c). The solid nature of the Cd-PBA cubes can be revealed by the transmission electron microscopy (TEM) image (Figure 1d). The sharp diffraction peaks at 2θ of 16.6° , 23.5° and 33.5° in the X-ray diffraction (XRD) pattern confirm the formation of the Cd-PBA (Supporting Information, Figure S1a).^[29] Energy-dispersive X-ray (EDX) spectrum of the sample indicates the existence of Cd, Co, C and N elements, which verifies the successful synthesis of the Cd-PBA cubes (Supporting Information, Figure S1b).

Subsequently, the as-prepared Cd-PBA cubes are converted to Cd-PBA cube-in-CdS cage particles through a sulfidation reaction. The reaction is conducted at room temperature with thioacetamide as the sulfidation reagent. This method can be easily conducted and shows good control over the sulfidation

process by simply adjusting the amount of the sulfidation reagent. The crystalline structure of Cd-PBA is preserved as shown in the XRD pattern of the obtained sample (Supporting Information, Figure S2a), indicating that the Cd-PBA cubes are not fully transformed. However, diffraction peaks of CdS are not observed possibly due to the relatively small amount and low crystallinity of the CdS formed. As revealed by the EDX spectrum, the sample contains S in addition to the Cd, Co, C and N elements, which is expected as a result of the partial conversion of Cd-PBA to CdS. FESEM images indicate that the cubic structure of Cd-PBA is inherited with slight deformation on the surfaces (**Figure 2a,b**). The observation of one broken particle shows that the formed structure consists of a solid cubic core covered by a thin-shell cage (Figure 2c). The formation of the cube-in-cage structure can be further proved by the TEM images (Figure 2d-f). Concave surfaces of the particles can be observed, suggesting the shrinking of the solid cubic cores during the sulfidation reaction (Figure 2d,e). At the same time, there is a clear gap between the core and shell, which indicates the formation of the cube-in-cage structure (Figure 2f). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image clearly shows the cube-in-cage structure, while the corresponding elemental mapping images further prove that the cubic core is CdS-PBA and the thin-shell cage is CdS (Figure 2g). In this sulfidation process, the alkaline environment in the solution would etch the Cd-PBA cubes. Since the surface of the Cd-PBA cubes is covered and protected by the polyvinylpyrrolidone (PVP) surfactant introduced during the synthesis, the etching process could initiate at the subsurface with the outward diffusion of ions.^[30] Simultaneously, Cd²⁺ cations at the surface tend to be first sulfurized to generate CdS cages. As a result, the Cd-PBA cubes are converted to Cd-PBA cube-in-CdS cage particles through the sulfidation reaction.

A secondary sulfidation reaction is conducted to transform Cd-PBA cube-in-CdS cage particles to CdS frame-in-cage particles. XRD pattern of the sample shows diffraction peaks at 2θ of 26.5°, 44.1° and 51.9°, confirming the formation of CdS (Supporting Information, Figure S3a).^[31] As shown in the EDX

spectrum (Supporting Information, Figure S3b), only Cd and S elements exist in the sample with the atomic ratio of approximately 1:1. FESEM images reveal that the obtained sample possesses a cubic morphology with convex surfaces (**Figure 3a,b**). The observation of one broken particle shows the formation of a frame-like structure in the core (Figure 3c). TEM images further demonstrate the formation of the well-defined frame-in-cage structure (Figure 3d,e). The thicknesses of the frames and the cages are about 250 nm and 100 nm, respectively (Figure 3f,g). Moreover, the frames and cages are composed by nanosized particles, which could ensure that photoinduced electrons and holes can easily reach the surface and participate in the redox reactions. The lattice spacing of 0.336 nm in the high-resolution TEM (HRTEM) image corresponds to the (111) plane of CdS (Figure 3h), which is in accordance with the result of the XRD characterization. As shown in the HAADF-STEM and elemental mapping images of a CdS frame-in-cage particle, Cd and S elements distribute uniformly in the frame and cage (Figure 3i). In this second-step sulfidation process, the surface of the Cd-PBA cubes inside the CdS cages is not protected. Thus, the etching process would initiate from the surface of the Cd-PBA cubes along with the sulfidation reaction, forming CdS frames inside the CdS cages.^[28] At the same time, the diffused ions would accumulate and react at the CdS cages to increase the thickness of the shells. Finally, CdS frame-in-cage particles are obtained.

To reveal the merits of the CdS frame-in-cage particles as the photocatalyst for H₂ generation, two control samples (CdS cubes and CdS cages) are also fabricated (Supporting Information, Figure S4-S7). The photocatalytic H₂ generation reactions are evaluated in a cocatalyst-free system under visible-light irradiation ($\lambda \geq 400$ nm) with Na₂S and Na₂SO₃ as the effective hole scavengers (Supporting Information, Table S1). The CdS cubes exhibit a H₂ generation rate of 9.5 mmol h⁻¹ g⁻¹, while the CdS cages show an enhanced H₂ generation rate of 11.3 mmol h⁻¹ g⁻¹ (**Figure 4a**). These results indicate that the construction of hollow structures is effective for promoting the activity. The CdS frame-in-cage particles possess the

highest H₂ generation rate of 13.6 mmol h⁻¹ g⁻¹ among the samples, which reveals the advantages of the complex frame-in-cage structure for photocatalytic reactions. To prove that the H₂ is generated by the photocatalytic process, control experiments without irradiation or photocatalyst are conducted. No H₂ is detected in these experiments (Supporting Information, Table S1), suggesting both the solar irradiation and photocatalyst are essential for the H₂ generation. Furthermore, the photocatalytic H₂ generation rate of CdS frame-in-cage particles depends strongly on the wavelength of the incident light and follows the trend of the light absorption spectrum of the photocatalyst (Figure 4b). This phenomenon indicates that the water reduction reaction is indeed triggered by the light excitation of the photocatalyst.^[32] The H₂ generation rate of CdS frame-in-cage particles increases almost linearly with the proceeding of the reaction for 30 h (Figure 4c), showing the high performance and long-term durability. The slight decrease of the activity after 20 h might be caused by the consumption of the hole scavengers and partial self-oxidation of CdS by the photogenerated holes. Cycling photocatalytic tests with a duration of 3 h for each cycle are conducted (Figure 4d). No apparent decrease of the activity is observed. Moreover, the crystalline structure and composition of the CdS frame-in-cage particles are almost unchanged after the cycling tests (Supporting Information, Figure S8), indicating the high stability of the photocatalyst. The frame-in-cage structure is also maintained after the cycling tests (Supporting Information, Figure S9), which reveals the structural robustness of the sample. The apparent quantum efficiency (AQE) of the CdS frame-in-cage particles is about 3.2% at 400 nm, which is higher than those of some representative CdS photocatalysts.^[16,33,34] The photocatalytic performance of CdS frame-in-cage particles compares favorably to that of some CdS photocatalysts reported recently for solar water splitting (Supporting Information, Table S2), but it is still not as good as the CdS-based photocatalysts with cocatalysts or heterostructures.^[32,35-38]

To gain more insights into the high photocatalytic performance of the CdS frame-in-cage particles, different characterizations are performed. The diffuse reflectance ultra-violet-visible (UV-vis) spectrum of the CdS frame-in-cage particles shows a slightly red-shifted absorption edge compared with the other samples (Supporting Information, Figure S10a). This result indicates that the CdS frame-in-cage particles possess a reduced band gap as reflected by the Tauc plots and can utilize a larger fraction of the solar spectrum (Supporting Information, Figure S10b). Mott-Schottky plots of the samples are collected to further investigate the band structures (Supporting Information, Figure S11). CdS frame-in-cage particles show a more negative flat band position than the CdS cubes and cages. As the flat band potential of an n-type semiconductor is close to the conduction band, the CdS frame-in-cage particles might have a higher driving force to attain better photocatalytic performance. Moreover, the CdS frame-in-cage particles exhibit an enhanced transient photocurrent (Supporting Information, Figure S12a), which could be attributed to the promoted generation and separation of charge carriers. This point can be further proved by the photoluminescence (PL) spectra (Supporting Information, Figure S12b). The relatively low intensity of the PL spectrum indicates that the recombination of electrons and holes could be prohibited in the CdS frame-in-cage particles. The results of electrochemical impedance spectroscopy (EIS) characterizations reveal that the CdS frame-in-cage particles have a lower charge-transfer resistance than those of the CdS cubes and cages (Supporting Information, Figure S12c). The enhanced charge separation in the CdS frame-in-cage particles may be ascribed to the reduced charge transfer distance in the thin-shelled topology of the complex hollow structure. On the other hand, the CdS frame-in-cage particles have a larger electrochemically active surface area (ECSA) than the other samples, which can provide more active sites to promote the photocatalytic activity (Supporting Information, Figure S13).

In summary, novel CdS frame-in-cage particles have been fabricated through a two-step sulfidation strategy. The first sulfidation reaction converts uniform Cd-based Prussian blue analog (Cd-PBA) cubes to Cd-PBA cube-in-CdS cage particles, which are further transformed to CdS frame-in-cage particles through the second sulfidation step. The synthesis of the Cd-PBA precursors and the sulfidation reactions are conducted under mild conditions at room temperature. Owing to the structural advantages, the CdS frame-in-cage particles exhibit enhanced photocatalytic activity towards H₂ generation under visible-light irradiation, comparing with CdS cubes and CdS cages. The developed synthetic strategy may provide new inspirations for the design and construction of high-performance photocatalysts with advanced structures for solar-to-chemical energy conversion.

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Figures and Captions

Figure 1. (a) Schematic illustration of the two-step sulfidation approach for the fabrication of CdS frame-in-cage particles. (b,c) FESEM and (d) TEM images of Cd-PBA cubes.

Figure 2. (a-c) FESEM and (d-f) TEM images of Cd-PBA cube-in-CdS cage particles. (g) HAADF-STEM image of a Cd-PBA cube-in-CdS cage particle and elemental mapping images for N, Co, Cd, and S with the overlay image of the mapping images.

Figure 3. (a-c) FESEM, (d-g) TEM and (h) HRTEM images of CdS frame-in-cage particles. (i) HAADF-STEM image of a CdS frame-in-cage particle and elemental mapping images for Cd and S with the overlay image of the mapping images.

Figure 4. (a) Photocatalytic H_2 generation rates of CdS cubes, CdS cages and CdS frame-in-cage particles under visible-light irradiation. (b) Wavelength-dependent H_2 generation rates and light absorption spectrum of CdS frame-in-cage particles. (c) Time-yield plot of CdS frame-in-cage particles. (d) Cycling tests of CdS frame-in-cage particles.

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CdS frame-in-cage particles are fabricated through a two-step sulfidation approach. With the advantages of the novel hollow structure, the CdS frame-in-cage particles exhibit enhanced photocatalytic activity towards H₂ generation compared with CdS cubes and CdS cages.