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In-situ construction of hierarchical CdS/MoS_2 microboxes for enhanced visible-light photocatalytic H_2 production

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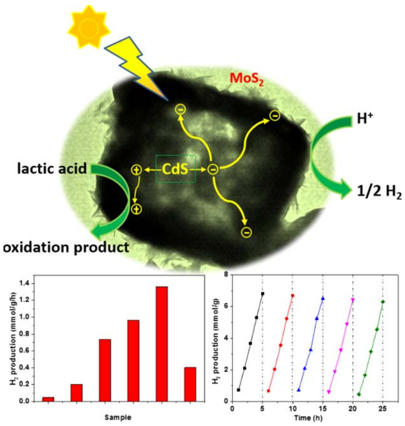
HIGHLIGHTS

- CdS/MoS_2 heterostructures with a unique microbox morphology were fabricated.
- This microarchitecture is beneficial to promote electron transfer and separation.
- An excellent photocatalytic H_2 evolution rate of 1.36 mmol/g/h was achieved.
- The apparent quantum efficiency is as high as 14.5% at 420 nm.

GRAPHICAL ABSTRACT

CdS/MoS_2 heterostructure with a unique hollow microbox morphology have been successfully constructed for high performance visible-light-driven water splitting into H_2.



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ABSTRACT

Exploration of highly active and noble-metal-free photocatalysts for high-efficiency photocatalytic water splitting is of great importance. Herein, a facile and effective in-situ hydrothermal method has been developed for preparation of CdS/MoS_2 heterostructures with a unique hollow microbox morphology for visible-light-driven water splitting into H_2. The influence of MoS_2 is systematically investigated in terms of optical properties and photocatalytic activity of the CdS/MoS_2 microboxes by varying the concentration of sodium molybdate. Under visible-light irradiation ($\lambda \geq 420$ nm), the CdS/MoS_2 microboxes exhibit superior photocatalytic H_2 evolution activity (1.36 mmol/g/h) compared to pure CdS microboxes (0.04 mmol/g/h), corresponding to an apparent quantum yield of 14.5% at 420 nm. Photocatalytic mechanism study proves that the MoS_2 nanosheets can serve as a co-catalyst and electron acceptor, for the effective promotion of electron transfer and separation of photogenerated charge carriers from CdS to further stimulate the surface H_2 evolution kinetics. Furthermore, the well-defined interior voids, low density and shell permeability of the hierarchical CdS/MoS_2 microboxes also contribute to the improvement of the photocatalytic performance.

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1. Introduction

With the rapid growth of global energy demand, the depletion of fossil fuels and serious environmental pollution make the development of clean and renewable energy increasingly urgent [1–3]. Hydrogen, one of the most potential clean energy alternative has attracted great attention recently, which can be produced from water splitting by solar irradiation [4–6]. It is generally known that the n-type CdS semiconductor with narrow band gap ($E_g = 2.43\,eV$) and a more negative conduction band than the reduction potential of H_2O/H_2 ($-0.9\,V$ vs. NHE, pH = 7), has proven to be one of the most promising photocatalyst in visible-light hydrogen evolution [7–9]. Unfortunately, there are two significant drawbacks preventing its further applications. One is the ultrafast recombination of photo-generated charge carriers, which strongly reduces the overall quantum efficiency [10–12]. The other one is photocorrosion caused by strong self-oxidation of CdS by photo-excited holes, leading to low photocatalytic activity and short lifetime of CdS photocatalysts [13]. Therefore, modification of CdS with suitable cocatalysts is a main consideration in photocatalyst to prompt separation and migration of the photogenerated electrons and holes to further increase the photocatalytic activity and cycle stability.

The formation of p-n junction is favorable for the transportation of photoinduced electrons and holes owing to the inner electric field, which can efficiently suppress the recombination of the electrons and holes and further greatly improve the photocatalytic activity [14,15]. Compared to the commonly-used noble metal cocatalysts (Pt, Au and Pd), layered transition-metal dichalcogenides (such as MoS_2 and WS_2) can be produced in an affordable and scalable manner. It was also reported that MoS_2 and WS_2 show p-type properties are promising for the construction of p-n-junction nanohybrid photocatalysts with CdS semiconductor to improve the separation of photoinduced electrons and holes, eventually leading to efficient hydrogen production [16–19]. Especially for MoS_2, a 2D layered material with a typical graphene-like structure, when combined with semiconductors it can provide effective surface active sites to promote the surface catalytic reaction, suppress recombination of photo-generated electrons and holes, and prevent the occurrence of counter reaction between active species and product [20,21]. Furthermore, MoS_2 can share S^{2-} when compositing with sulfide semiconductors to reduce the lattice mismatch and defect states at the interfaces [22]. To date, several reports have demonstrated the various structures of CdS/MoS_2 p-n-junctions with enhanced photocatalytic hydrogen performance under visible light irradiation. For example, a novel symmetric MoS_2-tipped CdS nanowires reported by Zhang et al. exhibited superior photocatalytic H_2 evolution activity (12.6 mmol/g/h) compared to Pt/CdS NWs (2.6 mmol/g/h) [23]. Chen et al. reported a facile one-pot wet-chemical method to fabricate MS_2-CdS (M = W or Mo) nanocrystals, where the photocatalytic performances of WS_2-CdS and MoS_2-CdS nanohybrids towards the hydrogen production under visible light irradiation ($> 420\,nm$) are about 16 and 12 times that of pure CdS, respectively [24]. Therefore, MoS_2 is a potential material both as p-type semiconductor and cocatalyst when combined with CdS in photocatalytic hydrogen evolution.

Hierarchical hollow micro-nanostructures are of great interest in many fields due to the large void space cavities, low density, large specific surface area and shell permeability [25–28]. In the present study, hierarchical CdS/MoS_2 heterostructures constructed by ultrathin MoS_2 nanosheets coating porous CdS microboxes were fabricated using a facile in-situ strategy for the first time. During the growth of MoS_2 nanosheets, $CdCO_3$ microcube templates are converted to CdS microboxes. The novel CdS/MoS_2 microboxes exhibit a quantum efficiency as high as 14.5% ($\lambda_{ex} = 420\,nm$) and highly activity (1.36 mmol/g/h) as well as excellent stability in water splitting under visible-light illumination. The improved photocatalytic performance of the CdS/MoS_2 heterojunction was attributed to in-situ growth of MoS_2 show intimate interfacial contact between p-n junction and the unique hierarchical hollow structures. Moreover, MoS_2 mainly acts as a cocatalyst that promotes the electron transfer from CdS. This work also offers a versatile approach for fabricating other hybrid hollow nanostructures for different applications.

2. Experimental

2.1. Chemicals

All chemicals are analytical grade and used without further purification. Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), sodium bicarbonate ($NaHCO_3$), polyvinylpyrrolidone, molybdate ($Na_2MoO_4{\cdot}2H_2O$), thiourea, lactic acid and sodium sulfate (Na_2SO_4) were purchased from Aladdin (China).

2.2. Synthesis

2.2.1. Synthesis of $CdCO_3$ microcubes

The $CdCO_3$ microcubes were synthesized by a simple precipitation process according to the literature [29]. In a typical procedure, 0.5 mmol of $CdCl_2{\cdot}2.5H_2O$ and 1 g of polyvinylpyrrolidone (PVP) were dissolved in 20 mL of deionized water to form a clear solution. Subsequently, 20 mL of 0.05 M $NaHCO_3$ solution was added into the above solution under vigorous stirring. After continuously stirring for 2 h, a milky solution was obtained and the $CdCO_3$ microcubes were collected by centrifugation and washed with deionized water and ethanol for three times.

2.2.2. Synthesis of CdS/MoS_2 core-shell microboxes

0.3 g of the $CdCO_3$ microcubes were dispersed into 20 mL of deionized water by ultrasonication for 60 min. Then 0.3 g of sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$) and 0.05 g of thiourea were added into the $CdCO_3$ dispersion under ultrasonication for 10 min. Subsequently, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and kept at 220 °C for 24 h. The final product was collected by centrifugation and washed with distilled water and ethanol for 3 times and kept at 60 °C for further characterization. The detailed synthesis is schematically demonstrated in Fig. 1. For comparison, composites prepared with different amount of $Na_2MoO_4{\cdot}2H_2O$ (0.05 g, 0.1 g, 0.2 g, 0.3 g and 0.47 g) were assigned sample codes as CM-5, CM-9, CM-16, CM-33 and CM-40, respectively. The number represents the weight percentage of MoS_2 in the composites. The pure CdS were also prepared without adding sodium molybdate for comparison. The reactions involved in the formation of CdS/MoS_2 core-shell microboxes can be described as follows [30]. First, thiourea reacts with H_2O to release H_2S [Eq. (1)],

$$CS(NH_2)_2 + 2H_2\,O \rightarrow CO_2 + 2NH_3 + H_2S \tag{1}$$

Then, H_2S reacts quickly with Na_2MoO_4 at the surface of the $CdCO_3$ microcubes to produce MoS_2 nanosheets [Eqs. (24)].

$$MoO_4^{2-} + 4S^{2-} + 4H_2\,O \rightarrow MoS_4^{2-} + 8OH^- \tag{2}$$

$$MoS_4^{2-} + 2H^+ \rightarrow H_2\,S + MoS_3 \tag{3}$$

$$MoS_3 \rightarrow S + MoS_2 \tag{4}$$

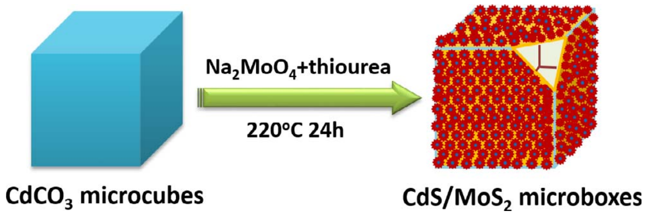

Fig. 1. Schematic illustration of the in-situ formation process of the CdS/MoS_2 microboxes.