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Short communication

Hydrilla derived $ZnIn_2S_4$ photocatalyst with hexagonal-cubic phase junctions: A bio-inspired approach for H_2 evolution

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ABSTRACT

The nature provides inspiration for many special structures due to biological diversity. In this report $ZnIn_2S_4$ with hexagonal-cubic phase junctions was prepared through a bio-inspired approach using hydrilla as a template and can significantly enhance photocatalytic H_2 evolution under visible-light in comparison to those hexagonal or cubic single-phase structures. The enhancement in photocatalytic performance has been shown to be attributed to efficient charge separation and transfer across the hexagonal-cubic phase junction and light harvesting of special hydrilla leaves structure.

1. Introduction

Photocatalytic H_2 production by water splitting has received much attention due to its attractive potential in supplying H_2 using solar energy. However, the number of photocatalysts working under the visible-light region is limited and the light utilization efficiency is still to be improved so far. Therefore, the design of materials that efficiently absorb solar radiation and convert the photon energy into long-lived charge-separated states is of key importance. Formation of heterojunctions (such as p–n junctions) between different materials or phases at nanoscale has been demonstrated to be an effective strategy for promoting interfacial charge transfer and separation [1–3]. The light utilization efficiencies and photocatalytic activities could therefore be enhanced a lot. For example, Zhang et al. found that the photocatalytic activity of TiO_2 can be enhanced up to four times when the phase junction formed between the surface of anatase nanoparticles and rutile particles [4]. Wang et al. reported that Ga_2O_3 with α–β phase junctions can stoichiometrically split water into H_2 and O_2 with significantly enhanced activity [5]. Cui et al. reported a series of sulphides- $K_2La_2Ti_3O_{10}$ composites for highly effective visible-light photocatalysis [6–8]. MoS_2-ternary sulphides [9,10] and MoS_2-TiO_2 2D nanojunction [11] were also developed for solar hydrogen generation.

$ZnIn_2S_4$ is an n-type semiconductor with two distinct polymorphs based on cubic and hexagonal lattices. Previous studies have revealed that both polymorphs of $ZnIn_2S_4$ are active for photocatalytic H_2 generation under visible-light irradiation and show considerable chemical stability [12,13]. Generally, hexagonal $ZnIn_2S_4$ is thermodynamically stable, whereas the cubic polymorph is a high pressure phase. The phase transformation between these two types is not easy. The transformation of 3R polytype hexagonal $ZnIn_2S_4$ to cubic $ZnIn_2S_4$ can occur at 400 °C under a high pressure of 4 MPa. On the contrary, the cubic phase can be transformed back to a hexagonal phase when heated above 500 °C under vacuum or ambient pressure [14]. Recently, Li et al. reported that cubic $ZnIn_2S_4$ nanoparticles and hexagonal $ZnIn_2S_4$ flower-like microspheres were synthesized via a facile hydrothermal method by simply changing the metal precursors [15]. And these two $ZnIn_2S_4$ polymorphs exhibit different band positions, i.e. the CB edge potential of cubic $ZnIn_2S_4$ ($E_{CB} = -1.5$ V and $E_{VB} = 0.9$ V versus NHE) is more negative than that of hexagonal $ZnIn_2S_4$ ($E_{CB} = -1.1$ V and $E_{VB} = 1.5$ V versus NHE) [16]. Thus, it is potential that proper junctions could be formed in presence of hexagonal and cubic phases of $ZnIn_2S_4$ and this may lead to enhanced photocatalytic activity. However, there is no study on the formation of hexagonal-cubic junction of $ZnIn_2S_4$ and its photocatalytic performance, probably because cubic $ZnIn_2S_4$ is a metastable phase.

In biologic system, thermodynamically unstable type can nucleate and stably grow with the existence of organic macromolecules [17,18]. For example, the synthesis of polymorphs of calcium carbonate, which have been studied by many groups [19,20]. Recently, Chen et al. also prepared metastable α-$AgVO_3$ via a facile and bio-inspired route [21]. Thus mediating of $ZnIn_2S_4$ nanocrystalline is more likely to be achieved through a bio-inspired approach. Moreover nature provides inspiration for many special structures due to biological diversity. Biotemplating is

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an effective strategy to obtain morphology controllable materials with structural specialty, complexity, and related unique properties [22].

Usually the aquatic plant leaves are thin and soft with excellent mass transportation and light-harvesting capability. The aquatic plant leaves could provide a template to construct bioinspired hierarchical photocatalyst [23]. On the other hand the photocatalytic H_2 evolution are performed in aquatic solution, where there is low light intensity. Thus the leaf templates are able to focus the light under the water and scatter the light enriched in the artificial leaves, hence boosting the photocatalytic performance [23–25]. *Hydrilla verticillata* (L.f.) Royle, a submersed aquatic weed belonging to the monocot family Hydrocharitaceae (Order Alismatales), is a widely distributed species. The replicas derived from the hydrilla leaves had effective light harvesting ability underwater. However, previous studies have not yet addressed the use of hydrilla as templates to synthesize photocatalytic materials, let alone the achievement of highly photocatalytic activity under solar light.

Herein, we report that $ZnIn_2S_4$ with hexagonal-cubic phase junctions was prepared by a bio-inspired approach. In comparison with those hexagonal or cubic phase structures, this hydrilla template $ZnIn_2S_4$ exhibits dramatically enhanced photocatalytic H_2 evolution rate under visible-light.

2. Experimental

2.1. Preparations

$ZnIn_2S_4$ derived from hydrilla was synthesized via a solvothermal route from the reaction of zinc nitrate, indium nitrate, and thioacetamide (TAA), with ethylene glycol as the solvent. The templates were removed by calcination at 500 °C in H_2S–N_2 mixed gas atmosphere and the product was denoted as $ZnIn_2S_4$-hydrilla. A similar procedure was applied in the preparation of conventional $ZnIn_2S_4$ except that in the absence of hydrilla templates and without calcination. The experimental details of catalysts synthesis were described in detail in Supplementary data.

2.2. Characterizations

Experimental details for the X-ray diffraction (XRD), scanning electron microscopy (SEM) images, transmission electron microscopy (TEM) images, nitrogen adsorption/desorption measurements and UV–Vis diffuse reflectance spectra were described in detail in Supplementary data.

2.3. Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution was tested using a in a glass reaction cell with quartz cover connected to a closed gas circulation. The experimental details for photocatalytic H_2 evolution were described in Supplementary data.

3. Results and discussion

3.1. Characterizations

The XRD pattern of conventional $ZnIn_2S_4$ prepared via a solvothermal route using ethylene glycol as solvent is shown in Fig. 1. The peaks of 2θ values at 21.5°, 27.6°, 30.4°, 39.8°, 47.2°, 52.4° and 55.6° correspond to (006), (102), (104), (108), (110), (116) and (022) crystallographic planes of hexagonal $ZnIn_2S_4$ JCPDS, No. 03-065-2023). No peak attributable to other phases is observed indicating the formation of pure hexagonal $ZnIn_2S_4$. However, in addition to peaks corresponding to hexagonal $ZnIn_2S_4$, $ZnIn_2S_4$-hydrilla shows additional 2θ diffraction peaks at 14.4°, 23.7°, 27.8°, 33.7°, 44.2° and 48.4°, which can be assigned to the (111), (220), (311), (400), (511) and (440) crystallographic planes of cubic $ZnIn_2S_4$ (JCPDS, No. 00-048-1778), implying that biogenic process or calcination at 500 °C partially transform the hexagonal $ZnIn_2S_4$ to cubic one [26]. The proportions of the hexagonal and cubic phases were calculated to be 52.2 and 47.8% from the diffraction peak intensities of the hexagonal (110) plane and the cubic (440) plane. Interestingly, XRD pattern of conventional $ZnIn_2S_4$ without template calcinated under the same conditions showed pure hexagonal phase (in Fig. S1). For the sample of $ZnIn_2S_4$-hydrilla before calcination, the hexagonal phase was formed as shown in Fig. S2. It is suggested that the formation of cubic phase was caused by biogenic process and calcinating.

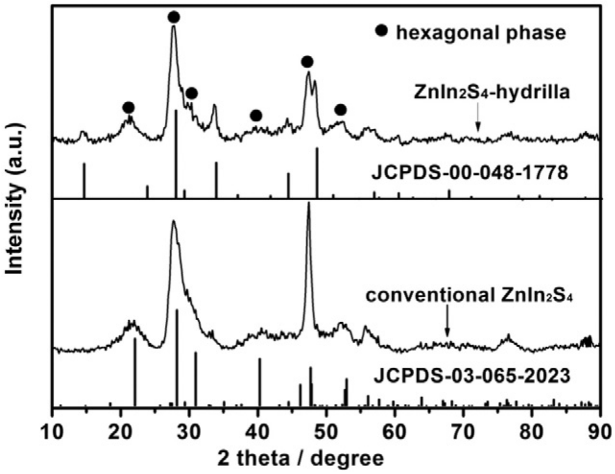

Fig. 1. XRD patterns of conventional $ZnIn_2S_4$ and $ZnIn_2S_4$-hydrilla.

The SEM image of conventional $ZnIn_2S_4$ shows that the sample consists of mono-dispersed microspheres with a dimension in the range of 4–6 μm (Fig. S3a). The formation of such hexagonal $ZnIn_2S_4$ microsphere by a variety of methods has previously been reported in several literatures [27,28]. TEM image shows that each microsphere is comprised of numerous densely packed nanolamella petals (Fig. S3b). The growth tendency of a lamellar structure may be related to the layered feature of hexagonal $ZnIn_2S_4$. Fig. 2a shows that the morphology of hydrilla tissues is retained in $ZnIn_2S_4$-hydrilla on the macroscale. After removal of hydrilla templates by calcination, $ZnIn_2S_4$-hydrilla well replicated the internal spongy cells of aquatic leaves. The spongy mesophyll cells of the aquatic leaves were the primary sites to scatter and absorb light [23–25]. $ZnIn_2S_4$-hydrilla is therefore expected to be active for light absorption and harvesting. An enlarged SEM image in Fig. S3c reveals that $ZnIn_2S_4$-hydrilla is composed of array-like patterns assembled by densely rugate layers. HRTEM image of the composite shows two types of intimately contacted lattice fringes, confirming formation of the phase junction between hexagonal phase and cubic one (Fig. 2c). The lattice spacing of 0.293 nm corresponds to the interplanar distance between adjacent (104) crystallographic planes of hexagonal $ZnIn_2S_4$, while the fringe of $d = 0.375$ nm matches the (220) plane of cubic $ZnIn_2S_4$.

Nitrogen adsorption/desorption isotherms of conventional $ZnIn_2S_4$ and $ZnIn_2S_4$-hydrilla, as well as their corresponding pore size distributions are shown in Fig. S4. The isotherms can be classified as type IV with hysteresis, which are characteristic of mesoporous material. The isotherm of the conventional $ZnIn_2S_4$ is of type IV with a H1 type hysteresis loop, and the pore size distribution consists of a single narrow peak. In contrast, although the isotherm of sample $ZnIn_2S_4$-hydrilla might also be classified as type IV, it has a different line shape and slightly resembles *H*3 type hysteresis loop. The pore size distribution is very broad, which associated with various pore structures of bio-templates [29,30]. The BET surface area for the $ZnIn_2S_4$-hydrilla was 191.9 $m^2 \cdot g^{-1}$, which is larger than that of 161.5 $m^2 \cdot g^{-1}$ for the conventional $ZnIn_2S_4$.