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Rapid communication

MOF-derived In_2S_3 nanorods for photocatalytic removal of dye and antibiotics

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ABSTRACT

The idea of sulfidation of metal-organic frameworks (MOFs) has provided a prospective routing to synthesize metal sulfides, which has all kinds of shapes here. Herein, the invaginated hexagonal In_2S_3 nanorods with hollow structure were successfully fabricated by sulfidation of In-MOF (MIL-68-In) precursor. The obtained In_2S_3–8h exhibits high catalytic performance for the photodegradation of tetracycline hydrochloride (TC) and methyl orange (MO). The advantageous crystallinity and optical property have effectively promoted more an efficient separation of photo-induced electron–hole pairs, resulting in the enhanced photocatalytic activity. In this work, we put forward a new strategy, which aims to synthesize the traditional semiconductor photocatalysts by sulfidation of MOFs for eliminating environmental pollutions.

With the mass increasing production and the widespread application, the practical dyes and antibiotics will lead a significant environmental pollutions and a harsh health-risk. Especially, due to amounts of antibiotics enter to the ecosystem, antibiotic-resistant pathogens have emerged and spread all over the world, which make the removal of antibiotic great significance [1–3]. Current wastewater treatment technology (such as adsorption, biological treatment, the membrane process, *etc.*) cannot extensively remove pollutants from waste water [4,5], hence low-cost and efficiently technology is needed. Visible light photodegradation is the lowcost and environmental, which has been widely concerned as a possible treatment technology [6,7].

Semiconductor-based photocatalyst is efficient and available material, which provides a feasible channel to deal with the issues environmental and energy [8]. Owing to its outstanding photosensitivity and valuable electronic property, metal sulfides, such as In_2S_3, are studied by extensively science researchers in the world [9]. In_2S_3 with various morphologies, dimensions and architectures including nanosheets [10], nanotubes [11], microspheres [12], pyramid-like [13] and nanocrystals [14], have been widely reported in photodegradation, water splitting and CO_2 reduction.

Metal-organic frameworks (MOFs) are a fascinating kind of porous coordination materials, which have adjustable pore diameter and multitudinous functional sites due to abundant metal ions and/or metal-containing clusters, and organic ligands [15a–c]. MOFs exhibited a series of interesting application in catalysis [16,17], gas storage [18], separation [19] and chemical sensing [20] etc. As known, MOFs have been regarded as potential templates or sacrificial agents to build porous nanostructures of metal sulfides for extensive applications after the thermal treatment [11,21–25]. By this sulfidation process, metal sulfides can be easily converted to form maintaining the geometric shape of the pure MOFs [22,25]. And the transfer of pollutant molecules will be greatly increased due to the porosity and ordered structure of metal sulfides. Meanwhile, these geometric shapes can also prevent the aggregation of photocatalyst so that it can exhibit higher photocatalytic activity in the photocatalytic degradation process. Thus, different metal sulfides with desirable metallic elements and shapes could be synthesized by thermal treatment appropriate MOFs precursor under suitable experimental conditions.

A proof-of-concept application, beginning with an In-based MOF (MIL-68-In) hexagonal prism as the sacrificial agent, a liquid phase sulfidation process was designed to synthesized In_2S_3 nanorods. The optimized In_2S_3 nanorods exhibit prominent activity and excellent stability for tetracycline hydrochloride (TC) and methyl orange (MO) removal. Furthermore, the plausible mechanism for the photodegradation of MO over In_2S_3–8h was also discussed.

The MIL-68-In precursor was synthesized by solvothermal means from $In(NO_3)_3{\cdot}6H_2O$ and 1,4-benzenedicarboxylic acid (H_2BDC) (see SI). The typical SEM image of MIL-68-In is presented in Fig. 1a. It can

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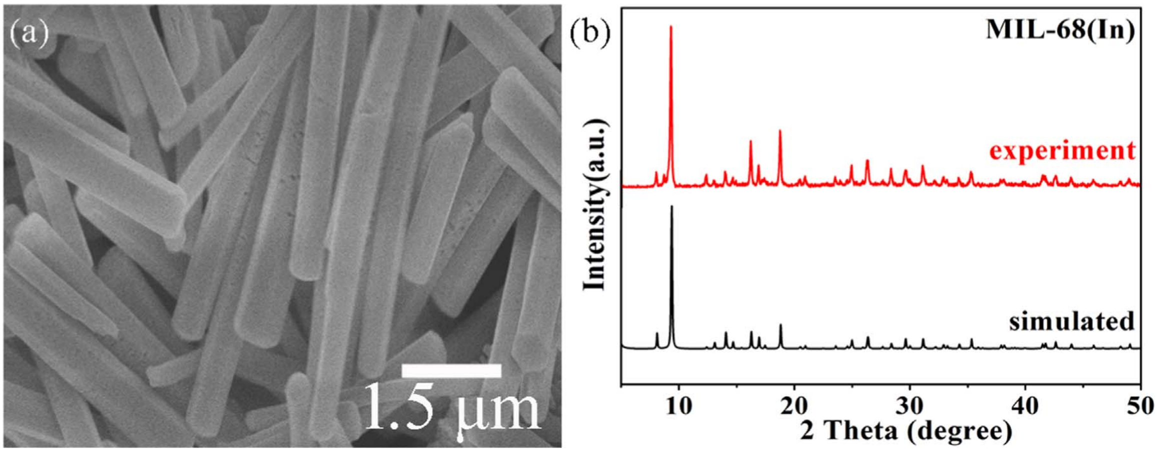

Fig. 1. (a) SEM images and (b) XRD patterns of the MIL-68-In.

be clearly observed that the synthesized sample is consist of homogeneous hexagonal prisms. In addition, the structures of MIL-68-In are confirmed by XRD results as illustrated in Fig. 1b. All of the diffraction pattern are distinctly point to the known bulk phase of MIL-68-In [26]. Therefore, combining the XRD and SEM analysis, it can be demonstrated that the MIL-68-In was synthesized successfully.

The MIL-68-In derived In_2S_3 nanorods were sulfided with thioacetamide (TAA) as sulfur source under solvothermal conditions (see SI). As shown in Fig. 2a, The peaks of In_2S_3–8h located at $2\theta = 27.5°$, 33.2° and 47.7° can be well matched to the (311), (400) and (440) crystal planes, indicating that the pure cubic In_2S_3 phase structure (β-In_2S_3, JCPDS 65–0459) was obtained by sulfidation process of the MIL-68 (In) directly. The crystalline phases of the In_2S_3 with different reaction time were also investigated by XRD (Fig. S1). For comparison, the In_2S_3–8h has optimal crystallinity, which further confirmed that too much or too little reaction time could deteriorate the texture of the catalysts. In addition, EDS spectrum (Fig. 2b) also indicates that the In_2S_3–8h is consist of In and S element. The atomic number ratio of In to S is 1.27, indicating that In_2S_3 is successfully synthetized. In the EDS measurement, A small number of C, O, Al and Si elements are attributed to the silicon wafer substrate. The morphology of samples was exhibited from SEM (Fig. S2 and Fig. 2c). The different reaction time of In_2S_3 samples express a invaginated hexagonal nanorod-like structure after sulfidation treatment. The typical TEM image of In_2S_3–8h is shown in Fig. 2d. It is shown that TAA is an effective way to promote the sulfidation process of MIL-68-In so that it can form compact nanorods structure. In order to investigate whether there are some organic precursors in the nanorods, we analyze FT-IR spectrum of different samples in the Fig. S3. It could be found that there

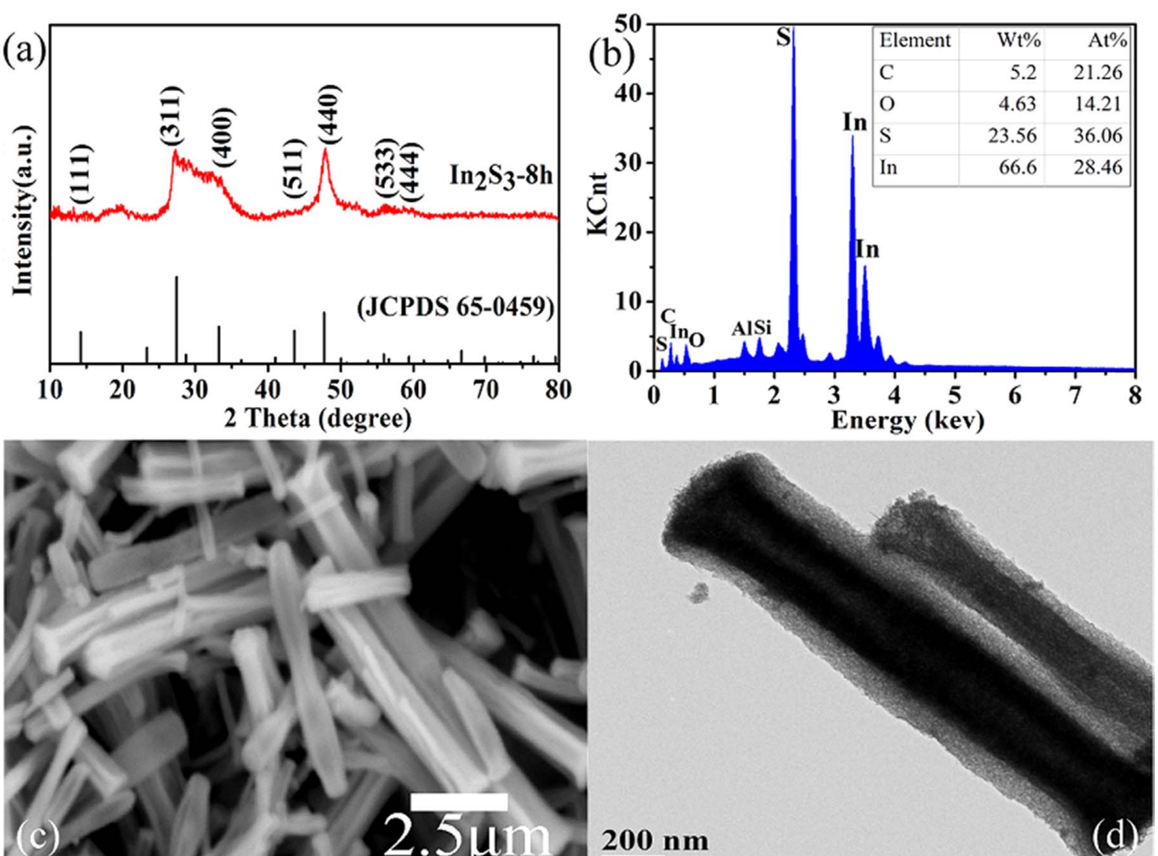

Fig. 2. (a) XRD patterns, (b) EDS analysis, (c) SEM and (d) TEM image of In_2S_3–8h sample.