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Short communication

Multi-layered mesh-like MoS_2 hierarchical nanostructure fabricated on Ti foil: An efficient noble metal-free photocatalyst for visible-light-driven H_2 evolution from water

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ABSTRACT

In the present work, multi-layered mesh-like MoS_2 hierarchical nanostructure was fabricated on a Ti foil in a hydrothermal process. Meanwhile, photocatalytic H_2 evolution from water over the as-prepared MoS_2 hierarchical nanostructure was investigated under visible irradiation. The results indicate that the as-prepared MoS_2 hierarchical nanostructure consists of the vertically grown few-layers MoS_2 nanosheets. And this three-dimensional mesh-like MoS_2 hierarchical nanostructure possesses high photocatalytic activity for visible-light-driven H_2 evolution from water. A rate of H_2 evolution of approximately 240 μmol g^{-1} h^{-1} was achieved under optimal conditions. Furthermore, the photocatalytic mechanism was preliminarily discussed.

1. Introduction

Nowadays, molybdenum disulfide (MoS_2) invoked increasing research interest due to its excellent electronic and optical properties, layered structure and earth-abundant composition [1–5]. Therein, the particular attention was paid to the application of mono-layer or few-layers MoS_2 nanosheets in hydrogen evolution from water (denoted as HEW). A series of functional materials containing the MoS_2 nanosheets were prepared and widely utilized in HEW [6–9]. The experimental results indicate that the MoS_2 nanosheets are a promising electroactive catalyst in electrochemical hydrogen evolution [10] and an efficient co-catalyst in the photocatalytic hydrogen evolution [11]. Unfortunately, it is not very clear whether the MoS_2 nanosheets alone can serve as an efficient photocatalyst under visible irradiation for HEW or not. Theoretically, the MoS_2 nanosheets hold all requirements for the visible photocatalyst which can be used in solar water splitting [12–14]. In addition, it was reported that the single and few-layers MoS_2 nanosheets are an efficient photocatalyst under visible irradiation for the degradation of dyes in water [15]. Therefore, it is essential to investigate whether the MoS_2 nanosheets alone can be used as a noble metal-free photocatalyst for visible-light-driven HEW.

It is well known that the activity of MoS_2 nanosheets in the H_2 evolution reaction is strongly correlated to the active sulfur atoms on exposed edges [16]. Therefore, a lot of research interest was inspired to avoid stack of MoS_2 nanosheets in the H_2 evolution reaction. And numerous hierarchical nanostructures (denoted as HNSTs) containing MoS_2 nanosheets were designed and fabricated to maximally maintain exposal of the active edge of MoS_2 nanosheets [9,17–19]. Among these HNSTs, the HNSTs fabricated on Ti foil may be proper for the application of MoS_2 nanosheets in the field of photocatalytic H_2 evolution. However, on the one hand, the HNSTs of MoS_2 nanosheets fabricated on Ti foil are usually thin so that the amount of MoS_2 is not enough to efficiently convert light energy into H_2. On another hand, the thicker MoS_2 film may enjoy disadvantages of stack of MoS_2 nanosheets and difficult release of evolved H_2 from the surface of MoS_2 nanosheets. Therefore, it is still a challenge to fabricate HNST of MoS_2 nanosheets which can efficiently power the visible-light-driven HEW.

In the present work, we designed and prepared a multi-layered mesh-like HNST which consists of the vertically grown few-layers MoS_2 nanosheets. This HNST possesses some promising advantages as follows, (1) the mesh-like HNST would enable a large specific surface area and efficient exposal of the active edge of MoS_2 nanosheets; (2) the multi-layered structure would increase the amount of MoS_2 coated on the Ti foil; (3) the internal meshes would result in fast diffusion of sacrificial reagent and timely release of H_2 bubbles; (4) the conductivity of Ti foil might enhance the photo-generated charge separation; (5) the immobilization of MoS_2 nanosheets would lead to convenient separation of photocatalyst from water; (6) the application of the as-prepared HNST in a continuous flow photocatalytic system

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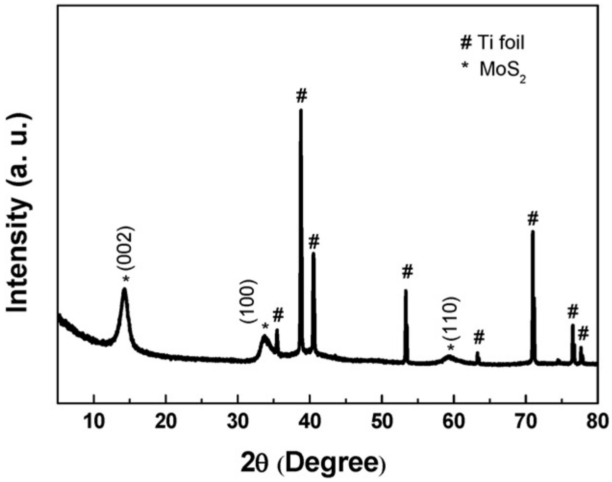

Fig. 1. XRD pattern of MSHNS-Ti.

would become very convenience due to the outstanding flexibility and mechanical strength of Ti foil. Based on these viewpoints above, the photocatalytic activity of the as-prepared MoS_2 HNST was investigated under visible irradiation for HEW. And the photocatalytic mechanism was preliminarily discussed.

2. Experimental

The multi-layered mesh-like MoS_2 HNST (MSHNS-Ti) was fabricated in a facile hydrothermal process. Photocatalytic reaction was carried out in a sealed quartz reactor (inner diameter 49 mm, height 113 mm, available volume 200 mL) at room temperature. A 300 W Xenon lamp equipped with an ultraviolet cut off filter ($\lambda > 420$ nm) was used as a light source. The distance between the lamp and the reactor is 1 cm. In a typical experiment, the Ti foil loaded with MSHNS-Ti was laid in lactic acid aqueous solution (60 mL, 30 vol.%). Next, the reaction solution was deaerated using N_2 for 30 min. Finally, the amount of hydrogen was measured with a gas chromatograph after a certain period of irradiation. The experimental details about the preparation procedure and the description on the instruments are reported in supplementary.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of MSHNS-Ti. As can be seen from Fig. 1, three diffraction peaks appear at 14.4°, 33.6° and 59.3°, corresponding to the (002), (100) and (110) planes of hexagonal MoS_2 (JCPDS No. 37-1492), respectively [20,21]. Moreover, it is also found that there exist seven sharp peaks at 35.5°, 38.8°, 40.5°, 53.3°, 63.2°, 70.9° and 77.7°, which should be ascribed to the Ti substrate (JCPDS No. 44-1294) [22]. Supplementary Fig. S1A and B shows the high-resolution XPS spectra of Mo 3d and S 2p of MSHNS-Ti. From Fig. S1A, we can observe two XPS peaks at 229.5 eV and 232.6 eV, which may be assigned to the Mo 3d5/2 and Mo 3d3/2 signals of MoS_2, respectively [23]. Meanwhile, Fig. S1B exhibits that two obvious XPS peaks appear at 162.3 eV and 163.5 eV, corresponding to the S 2p3/2 peak and the S 2p1/2 peak of MoS_2 [23]. These results confirm that hexagonal MoS_2 can be coated on the Ti foil according to the process described above.

Fig. 2 shows the SEM images, the TEM images and the digital image of MSHNS-Ti. From the digital image of MSHNS-Ti (Fig. 2e), it can be observed that the surface of Ti foil is covered with a layer of the MoS_2 film whose color is black in the sunlight. This MoS_2 film shows good adhesion to the substrate, and it is dense and uniform with the naked eye. Moreover, the film is not destroyed when the Ti foil is bended. The SEM images of MSHNS-Ti (Fig. 2a and b) clearly show that a three-dimensional mesh-like MoS_2 HNST is fabricated on the Ti foil. The HNST prepared is composed of sheet-like subunits, and these sheet-like subunits are vertically aligned to the Ti foil. It is interested that

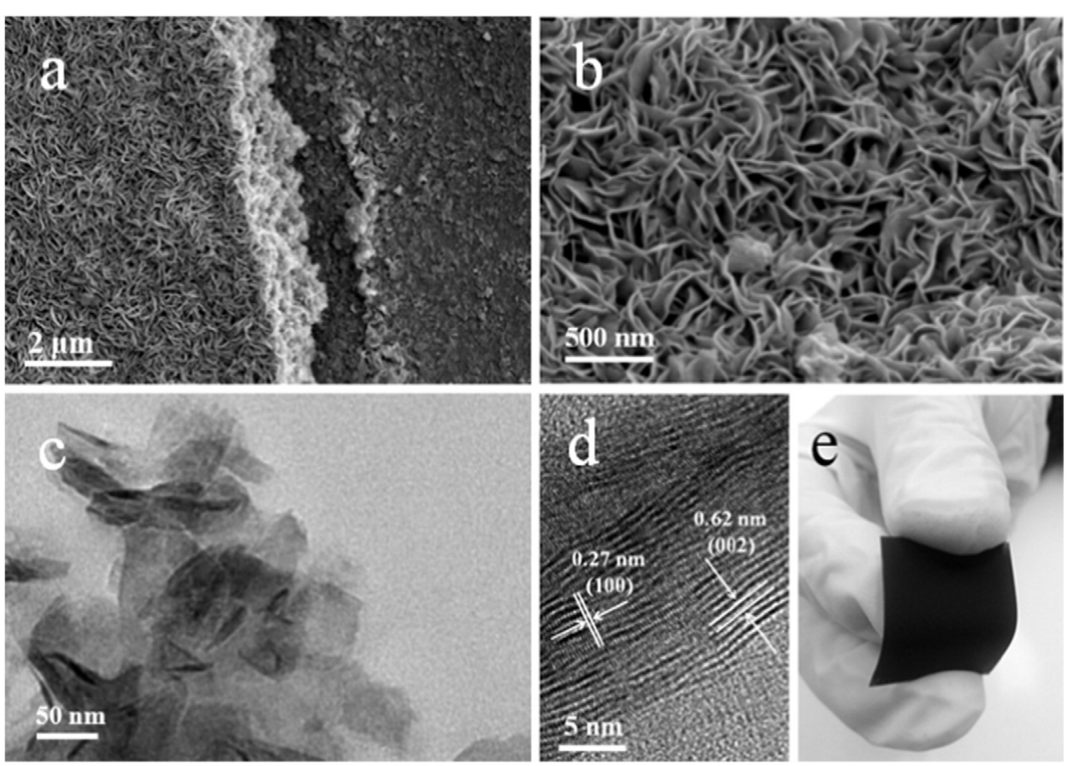

Fig. 2. (a, b) SEM images, (c) TEM image, (d) HRTEM image and (e) digital image of MSHNS-Ti.