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Perspective Article

Exfoliated thin Bi_2MoO_6 nanosheets supported on WO_3 electrode for enhanced photoelectrochemical water splitting

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ABSTRACT

Thin Bi_2MoO_6 nanosheets are obtained by a microwave-assisted ultrasonic separation process. After exfoliation, the thinner and uniform nanosheets with a thickness of about 10 nm were obtained. The exfoliated nanosheets would provide many amazing functionalities such as high electron mobility and quantum Hall effects. Therefore, thin Bi_2MoO_6 supported on WO_3 electrode (WO_3/thin Bi_2MoO_6) exhibits facilitated charge separation than pure WO_3 film and the un-exfoliated Bi_2MoO_6 nanosheets supported on WO_3 electrode (WO_3/Bi_2MoO_6). As a result, WO_3/thin Bi_2MoO_6 shows remarkably stable photocurrent density of 2.2 mA/cm^2 at 0.8 V_{SCE} in 0.1 M Na_2SO_4 which is higher than that of that of WO_3 (1.1 mA/cm^2) and WO_3/Bi_2MoO_6 (1.5 mA/cm^2).

1. Introduction

As well known, layered materials endow a diverse and largely untapped source of two-dimensional (2D) systems [1,2] with excellent electronic properties and high specific surface areas that are important for sensing [3,4], catalysis [5–7] and energy storage [8–10] applications. Since the preparation of thinnest graphene [11–14], the exfoliation of layered materials has attracted numerous attentions. As typically, the thinner materials can be achieved by mechanical exfoliation [15–19] and chemical exfoliation [20–24]. Moreover, the microwave assisted exfoliation combined the physical oscillation with thermal chemistry would be more feasible, environmental and effective. Up to now, the exfoliation of layered crystals which stack via van der Waals interactions such as graphene [25] and carbon nitride [26] has been successfully acquired by microwave assisted exfoliation. It turns out that the exfoliated thin two-dimensional materials show high thermal conductivity, superior mechanical and excellent electronic transportation properties. [27]

Bi_2MoO_6 is an aurivillius oxide with layered structure, which has a corner-sharing structure of MoO_6 octahedra sandwiched between $(Bi_2O_2)^{2+}$ layer [28]. Recent studies confirmed that Bi_2MoO_6 possesses efficient visible-light-driven photocatalytic activity for water splitting and degradation of organic contaminants. Various morphologies of Bi_2MoO_6 such as hierarchical flower-like hollow spheres, nanobelts, boxes have been fabricated and exhibited enhanced photocatalytic activities, indicating that the photocatalytic performance is strongly dependent on the morphology and structure [29–31]. However, the low electron-hole separation is still one major limitation of Bi_2MoO_6 for photocatalytic performance and photocurrent generation. More specifically, the poor electron transport appears to be the vital factor affecting the charge separation of Bi_2MoO_6. As reported, the 3D heterojunction of Bi_2MoO_6 with another highly conductive semiconducting oxide have been adopted to compensate the inferior transport properties of Bi_2MoO_6 [32]. However, the exfoliated Bi_2MoO_6 nanosheets have never been reported and applied for the efficient photoelectrochemical property.

Herein, the thin exfoliated Bi_2MoO_6 nanosheets were prepared through a facile microwave process, which possess the thickness of about ten nanometers. Furthermore, as illustrated in Scheme 1, drop the exfoliated Bi_2MoO_6 nanosheets solution on the porous WO_3 film obtained by sol-gel process results in the formation of the hetero-electrodes. Considering that the suitable band between WO_3 (conduction band at 0.41 eV) and Bi_2MoO_6 (conduction band at −0.32 eV), combine these two semiconductors would produce a potential driving force for the electrons shift. Especially, WO_3 served as the electrons collector and facilitated

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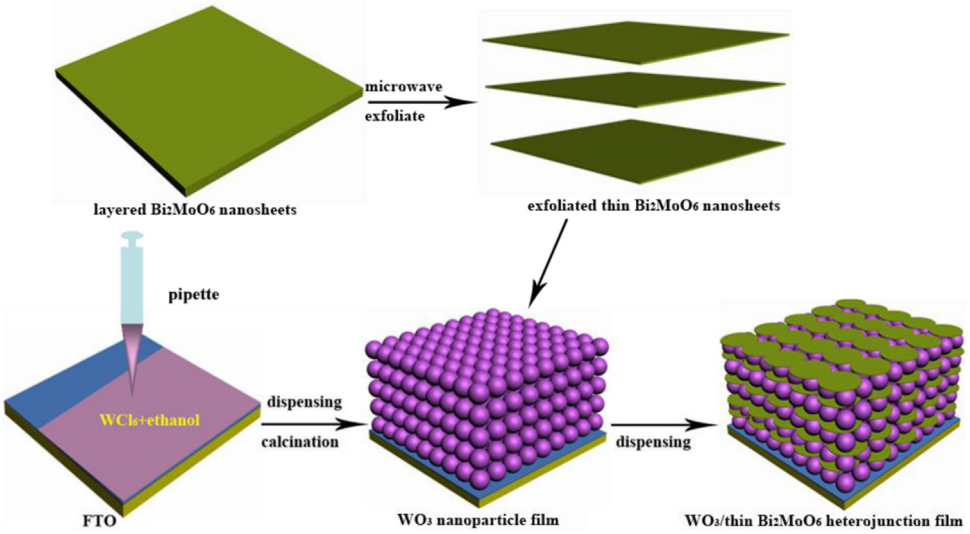

Scheme 1. Schematic illustration of the synthesis process of WO_3/thin Bi_2MoO_6 electrode.

charge separation which contributed to the improved PEC property. In this configuration the thin Bi_2MoO_6 layer is greatly reduced to about ten nanometers, which could significantly facilitate the light absorption and electrons movement. Such hybrid film exhibits a dramatically improved photocurrent density (2.2 mA/cm^2) at 0.8 V versus saturated calomel electrode (SCE), which is higher than that of WO_3 film (1.1 mA/cm^2) and the WO_3/Bi_2MoO_6 film (1.5 mA/cm^2). Moreover, a quantum efficiency of 17% was obtained for wavelength $\lambda = 420$ nm. As expected, the exfoliated Bi_2MoO_6 nanosheets could facilitate not only electrons transfer but also charge separation for the efficient photoelectrochemical (PEC) activity.

The un-exfoliated Bi_2MoO_6 nanosheets and exfoliated thin Bi_2MoO_6 nanosheets were characterized by field-emission scanning electron microscope (FESEM) as shown in Fig. 1. It is obviously that the morphology of Bi_2MoO_6 nanosheets (Fig. 1A) changes after microwave ultrasonic separation as shown as Fig. 1B. The un-treated Bi_2MoO_6 nanosheets present smooth while the edges of thin exfoliated Bi_2MoO_6 nanosheets exhibit curly. The corresponding transmission electron microscope (TEM) images clearly display the nanostructure of these two kinds of nanosheets. Before exfoliation, the nanosheets exhibit accumulated and a thickness of about 20 nm. After exfoliation, the uniformly and well-distributed thinner nanosheets were obtained. More specifically, the thickness of the thin nanosheets is calculated to be about 10 nm which is further confirmed by the high resolution TEM (HRTEM) image (Fig. 1F) derived from the cross-section of thin Bi_2MoO_6 nanosheet. Moreover, a planar spacing of 0.803 nm can be ascribed to the (020) crystal plane of Bi_2MoO_6. In the HRTEM image (Fig. 1D) of un-foliated Bi_2MoO_6 nanosheets, a planar spacing of 0.274 nm corresponds to the (002) crystal plane of Bi_2MoO_6.

Top-view FESEM image in Fig. 2A shows the as-synthesized WO_3 porous nanoparticle film deposited on the conducting substrate. The nanoparticles are interconnected, producing a randomly oriented and porous network of WO_3 nanoparticles. Moreover, the film with thickness of about 1.5 μm is formed as shown in the cross view image (Fig. S1A). Interestingly, depositing of thin Bi_2MoO_6 nanosheet on the WO_3 film leads to the formation of WO_3/thin Bi_2MoO_6 film (Fig. 2B). Fig. S1 B exhibits the cross view of thin Bi_2MoO_6 nanosheet covered WO_3 film. It is obviously that the Bi_2MoO_6 not only disperse on the surface of WO_3 film, but also embed in the WO_3 film. In order to reveal the structure of WO_3/Bi_2MoO_6 and WO_3/Bi_2MoO_6 films, the TEM and HRTEM images are exhibited in Fig. 2C–F. As shown in Fig. 2C, the un-exfoliated nanosheets are stacked on WO_3 particles. However, the thin Bi_2MoO_6 nanosheets attach uniformly to the nanoparticles (Fig. 2E), indicating that the thin exfoliated Bi_2MoO_6 nanosheets show better contact with WO_3 nanoparticles than the un-exfoliated Bi_2MoO_6 nanosheets. The HRTEM image further confirms that the structure of heterojunction film. More specifically, the planar spacing of 0.335 nm and 0.274 nm in the HRTEM image can be ascribed to the (120) plane of WO_3 and (002) plane of Bi_2MoO_6, respectively.

The crystal structures of the pure WO_3 film and hybrid films were investigated by X-ray diffraction (XRD). It confirms the coexistence of monoclinic WO_3 (JCPDS: 20-1324) [33] and orthorhombic Bi_2MoO_6 (JPCDS: 21-0102) in the composite. Except the diffraction peaks devoted to the WO_3, the peaks at 28.3°, 32.6° and 33.1° can be ascribed to (131) (002) and (060) planes of Bi_2MoO_6. Besides, the X-ray photoelectron spectroscopy (XPS) survey of both WO_3/Bi_2MoO_6 and WO_3/thin Bi_2MoO_6 film shows the presence of W, O, Bi and Mo (Fig. 3B). In the fine XPS spectra of W from pure WO_3 film, the binding energy peaks at 35.5 and 37.6 eV (Fig. 3C) were attributable to the W 4f 7/2 and W 4f 5/2 of W^{6+}, respectively. It is worth to note that in the W 4f and O 1s spectra, the binding energies of the hybrid film both show blue-shifts compared with pure WO_3 film, indicating the incorporation of Bi_2MoO_6 into WO_3 [34]. The Bi 4f and Mo 3d exhibit binding energies peaks corresponded to Bi^{3+} and Mo^{6+}, respectively [28]. As shown in Fig. S2, the mapping images of WO_3/thin Bi_2MoO_6 give an overall view of the Bi, Mo, O and W distribution. It is clearly that the Bi_2MoO_6 disperse uniformly and tightly on the WO_3 nanoparticles. Among line scanning curves (Fig. S3), the relatively straight lines of Bi and Mo suggest the uniform distribution of Bi_2MoO_6 on the WO_3 nanoparticles further.

In order to study the PEC activities of electrodes, linear sweep voltammetry (LSV) (Fig. 4A) and transient photocurrent responses (Fig. 4B) were characterized under visible light irradiation. For comparison, the PEC performance of Bi_2MoO_6 nanosheet covered WO_3 electrode was also investigated. The pure porous WO_3 film provides a photocurrent density of 1.1 mA/cm^2 at 0.8 V versus SCE. However, a photocurrent density of 1.5 mA/cm^2 (at 0.8 V_{SCE}) was yield when combining WO_3 film with Bi_2MoO_6 nanosheets. Most important, the thin Bi_2MoO_6 nanosheets modified WO_3 film exhibits the best PEC activity (2.2 mA/cm^2 at 0.8 V_{SCE}) among the three type electrodes, which are two-folds of pure WO_3 film. These results suggest that the exfoliated thin Bi_2MoO_6 nanosheet could dramatically enhance the PEC performance of WO_3 electrode. It is