Carbon 114 (2017) 591–600

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Bi_2MoO_6 nanosheet array modified with ultrathin graphitic carbon nitride for high photoelectrochemical performance

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A R T I C L E I N F O

Article history:
Received 23 August 2016
Received in revised form
5 December 2016
Accepted 15 December 2016
Available online 22 December 2016

Keywords:
Bi_2MoO_6 nanosheet array
Graphitic carbon nitride
Co-catalyst
Charge separation
Photoelectrochemical property

A B S T R A C T

We report a facile method to fabricate Bi_2MoO_6 nanosheet array exposed with {010} facets for the highly improved photoelectrochemical (PEC) property related to water oxidation. The nanosheet array film would provide large surface area, low resistance and exposed oxygen atoms, facilitating the electrons transport and charge separation. More importantly, the optimized Bi_2MoO_6 nanosheet array yields a photocurrent density of 220 μA/cm2, which is more than two orders of magnitude higher than that of conventional Bi_2MoO_6 particles (1.8 μA/cm^2). Additionally, the nanosheet arrays were modified with ultrathin graphitic carbon nitride (g-C_3N_4) nanolayers as co-catalyst to enhance the photoelectrochemical activity. As expected, this unique photoanode yields a photocurrent density of 520 μA/cm^2 at +0.8 V (versus SCE) under visible light irradiation, which is 2.3 times higher than the pure Bi_2MoO_6 nanosheet film. The origin of enhanced photoelectrochemical activity of the co-catalyst modified film may be due to the large surface area, oriented electrons transport pathways and improved charge separation. These demonstrations clearly reveal that the rationally fabricating of high photoactive nanosheet array and coating ultrathin cocatalysts may serve an alternate strategy toward the development of highly efficient photoanodes for water splitting.

1. Introduction

Solar energy represents one of the most abundant renewable natural energy but still least harvest resource [1,2]. Recently, photoelectrochemical water splitting by semiconductor photocatalysts has been considered as an effective route to convert solar energy directly into hydrogen for future renewable energy applications [3,4]. Most importantly, the two dimensional (2D) nanosheet array has attracted numerous attention ascribed to the enhanced photoelectrochemical activity [5–7]. Simultaneously, high orientation will provide uniform pathways for efficient charge transfer and separation. Moreover, the high surface-to-volume ratios and open-edge geometry of the nanosheet array would improve the solar conversion efficiency. Bismuth molybdate (Bi_2MoO_6), as an excellent photocatalyst, has attracted much attention for photoelectrochemical water oxidation due to its moderate bandgap (2.6 eV) and appropriate band edge positions [8–10]. However, the photocurrent density was still limited ascribed to low mobility of carriers, slow water oxidation kinetics and high electron-hole recombination rates compared to other semiconductors of interest such as TiO_2 and WO_3 [11–13]. To address these issues, the 2D Bi_2MoO_6 nanosheet array was synthesized and studied. As typically, the surface reactivity of inorganic semiconductor has been widely considered to be dominated by their surface chemistry, whose effect plays a critical role for the synthesis of single crystals with high reactivities [14–18]. Moreover, the intrinsic surface atomic structures could be tailored by rational fabrication of crystal with selected facets exposed. The controlled fabrication of intentionally-exposed high-energy crystal planes not only provide a way for the enhanced photocatalytic and photoelectric performance, but also offer a strategy to investigate the relationships between the crystal facets and the photoactive properties. As reported, anatase TiO_2 with {001} facets exposed demonstrated promoted photoelectric activity [19–23] and $BiVO_4$ nanoplates with {010} faces exposed

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http://dx.doi.org/10.1016/j.carbon.2016.12.043

[24–26] exhibited enhanced photoelectric and photocatalytic performance. However, the facet-dependent photoelectric water splitting performance of Bi_2MoO_6 has not been studied.

Except for synthesizing Bi_2MoO_6 as nanostructured films, the surface modification with oxygen evolution cocatalysts has been frequently employed to promote the holes transfer and supress surface charge recombination for improving water oxidation. At present, depositing p-type VIII metal (Fe, Co, Ni) oxide or (oxy) hydroxide, extensively utilized as electrocatalysts for water oxidation, has been proved to be an effective approach to accelerate the surface charge separation as well as minimize the kinetic over potential [27–32]. More specifically, the photogenerated holes could be extracted from the bulk and stored in the p-type cocatalysts for suppressing electron-hole recombination. Although these p-type VIII metal cocatalysts could effectively enhance the PEC properties of photoanodes, but the metallic ions containing materials with perceptive toxicity definitely hampered their further applications. Moreover, their usual large thickness or dimension may block sunlight absorption and prolong the holes transport distances. Thereby, the exploration of novel p-type metal-free cocatalysts with ultrathin structures may be an alternative strategy for enhancing the PEC performances of photoanodes.

Here, we demonstrate the rational fabrication of vertically aligned Bi_2MoO_6 nanosheet arrays with specifically {010} facets exposed, which were completely filled with valence-band oxygen atoms, on Fluorine-doped Tin Oxide (FTO) substrate by a simple hydrothermal reaction (Scheme 1). The Bi_2MoO_6 nanosheet arrays could yield a photocurrent density of 220 μA/cm2, which are more than two orders of magnitude higher than that of conventional Bi_2MoO_6 particles. Through tailoring the precursor concentration, it is easy to obtain a range of nanosheet film with different packing densities. Furthermore, the EIS and Mott-schottky plots clearly reveal that the facilitated electrons transfer and charge separation in the array structure. It is obviously that the Bi_2MoO_6 nanosheet array highly exposed with {010} facets could provide large surface area, uniform electrons transport pathways and exposed oxygen atoms, which remarkably facilitated the charge separation, resulting in the enhanced photoelectric performance. Moreover, unlike the previous metal electrocatalysts, the metal-free ultrathin g-C_3N_4 nanosheets were coated on the surface of Bi_2MoO_6 nanosheet array as oxygen evolution co-catalyst, resulting in higher photoelectrochemical activity compared to the pure Bi_2MoO_6 films.

2. Experimental section

2.1. Synthesis of Bi_2MoO_6 nanosheet arrary

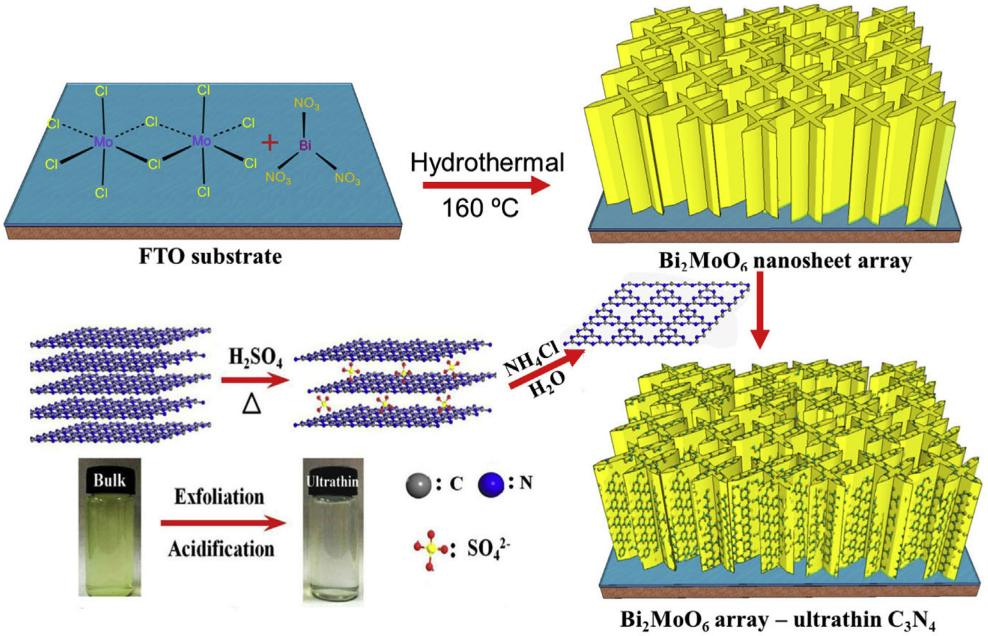
All chemical reagents were analytical grade and used as-received. As typically, $Bi(NO_3)_3 \cdot 5H_2O$ and $MoCl_5$ with atomic ratios of 2:1 were dissolved separately in 4 ml ethylene glycol as metal precursor solutions, 0.85 g polyethylene glycol 600 (PEG-600) was dissolved in 25 ml ethylene glycol to serve as the structure directing agent solution. Then the metal precursor solution, 8 ml structure directing agent solution and 30 ml ethanol were mixed together under magnetic stirring. Finally, the resultant suspension was transferred into a 100 ml autoclave. In order to obtain Bi_2MoO_6 nanaosheet array, the autoclave needs to be kept at 160 °C for 24 h by a hydrothermal reaction.

The prepared samples was cleaned with ethanol and dried in an oven at 70 °C. Finally, they were annealed in air at 500 for 2.5 h, and then a yellow-green film was obtained on the Fluorine doped tin oxide (FTO) (1.5 × 4 cm^2) substrate.

The prepared samples was cleaned with ethanol and dried in an oven at 70 °C. Finally, they were annealed in air at 500 °C for 2.5 h, and then a yellow-green film was obtained on the FTO substrate. Herein, the concentration of Bi^{3+} were controlled at 37.5 mM, 75 mM, 150 mM and 300 mM, respectively, and the correspond product were named as BM1, BM2, BM3 and BM4. For comparison, Bi_2MoO_6 particles were prepared by a traditional solid-state reaction described in Ref. [33].

2.2. Modified Bi_2MoO_6 nanosheet array with g-C_3N_4

The g-C_3N_4 nanosheet was obtained by acidify process described in Ref. [34], and the corresponding TEM image is shown in Fig. S2C. To prepare the modified array, 10 ml ethylene glycol was poured



Scheme 1. Schematic illustration of the synthetic process of vertically aligned Bi_2MoO_6 nanosheet array and exfoliation g-C_3N_4 and ultrathin g-C_3N_4 modified Bi_2MoO_6 photoanode.