In Situ Growth of the Bi$_2$S$_3$ Nanowire Array on the Bi$_2$MoO$_6$ Film for an Improved Photoelectrochemical Performance

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**Supporting Information**

**ABSTRACT:** A single-crystalline Bi$_2$S$_3$ nanowire array (Bi$_2$S$_3$NWA) is synthesized by an in situ hydrothermal reaction on the surface of a Bi$_2$MoO$_6$ film. As no additional source of Bi$^{3+}$ is provided during the process, the Bi$_2$MoO$_6$ layer acts as the Bi$^{3+}$ source for the synthesis of Bi$_2$S$_3$ nanowires. The fabricated Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA electrode exhibited an increased photoelectrochemical (PEC) sulfite oxidation activity, which is attributed mainly to the effective interface obtained by the in situ hydrothermal growth, compared to other Bi$_2$S$_3$ electrodes. The generated electron from the Bi$_2$S$_3$ conduction band rapidly transfers to that of Bi$_2$MoO$_6$, yielding an enhanced electron separation of Bi$_2$S$_3$. Furthermore, the single-crystalline Bi$_2$S$_3$ nanowire can provide a fast electron pathway to Bi$_2$MoO$_6$ through its single domain, which also contributes to the improved PEC activity.

**INTRODUCTION**

Utilization of sunlight has been considered a promising solution to overcome the exhaustion of fossil fuels.$^1$ The development of semiconductor photoelectrodes has attracted considerable attention for the efficient conversion of solar energy.$^{2−14}$ The examination of the semiconductors in photoelectrochemical (PEC) cells is a fast and simple method to characterize their electrochemical behaviors.$^3$ Although many semiconductors have been examined as photoelectrodes,$^{2−15}$ most of them have modest PEC efficiencies owing to the narrow visible light absorptions and unavoidable electron−hole recombinations. To decrease the bulk recombination, nanostructures, such as nanoparticles and nanorods, have been studied as photoelectrodes,$^{16}$ which can enhance the kinetic parameters of the PEC reactions because of the reduced hole diffusion length. The shape, size, and connection of the nanostructures can affect the charge transport properties and thus, play a critical role in the efficiency of PEC cells. However, these nanostructures exhibit several disadvantages, such as a reduced space charge region and high surface recombination.$^6$ Therefore, further studies are required to optimize the sizes and shapes of nanostructures for improved PEC performances.

Bismuth sulfide (Bi$_2$S$_3$) has attracted large interest as a sensitizer for photovoltaic and PEC cells owing to its narrow band gap of approximately 1.3 eV and large absorption coefficient.$^{19−25}$ However, the reported photocurrent is considerably lower than its theoretical maximum ($\sim$30 mA/cm$^2$). The recombination at the surface and in the bulk state of Bi$_2$S$_3$ leads to a lower PEC conversion efficiency. One-dimensional Bi$_2$S$_3$ structures such as nanorods and nanowires have been studied as photoelectrodes, which can provide the advantages of a reduced hole diffusion length and enhanced charge transport properties.$^{26−30}$ On the other hand, the Bi$_2$S$_3$ nanowires must be grown on a conductive substrate to enable efficient interactions for improved PEC properties. As most Bi$_2$S$_3$ nanowires are prepared as powdered samples, their deposition on substrates is another challenging process.$^{31}$ To decrease the interface resistance between the Bi$_2$S$_3$ nanowire and the conductive substrate, an in situ synthetic method is required. Thus, a simple synthesis on the substrate is required to reduce the fabrication complexity of the PEC devices. In this paper, we report a facile synthesis of a Bi$_2$S$_3$ nanowire array (Bi$_2$S$_3$NWA) on a Bi$_2$MoO$_6$ layer by an in situ hydrothermal method. The Bi$_2$S$_3$NWA was uniformly fabricated and well connected on the Bi$_2$MoO$_6$ layer. Structural characterizations were carried out by transmission electron microscopy (TEM), Raman spectroscopy, and X-ray diffraction (XRD). Compared to other Bi$_2$S$_3$ electrodes, the fabricated Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite exhibited an increased PEC sulfite oxidation activity, which is attributed mainly to the effective interface obtained by the in situ growth. This unique composite also has dual electrochemical functions, as a light absorber (Bi$_2$S$_3$NWA) and an electron acceptor (Bi$_2$MoO$_6$ layer). The generated electron from the Bi$_2$S$_3$ conduction band rapidly transfers to that of Bi$_2$MoO$_6$, yielding an enhanced charge separation of Bi$_2$S$_3$. In addition, the single-

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crystalline Bi$_2$S$_3$ nanowire can provide a fast electron pathway through its single domain, which also contributes to the increased PEC activity.

**RESULTS AND DISCUSSION**

**Fabrication of the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA Composite Electrode.** Bi$_2$S$_3$NWA was synthesized in situ on the surface of a Bi$_2$MoO$_6$ film (Scheme 1). The Bi$_2$MoO$_6$ film was fabricated by a drop-casting method of a precursor solution onto a fluorine-doped tin oxide (FTO) substrate and subsequent annealing at 500 °C for 3 h in air (Figure 1a). Bi$_2$S$_3$NWA was then directly grown on the Bi$_2$MoO$_6$ film by a hydrothermal reaction (Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA). Figure 1b shows a scanning electron microscopy (SEM) image of Bi$_2$S$_3$NWA fabricated on Bi$_2$MoO$_6$. The nanowires have an average width of 87 ± 14 nm and a length of 1.2 ± 0.2 μm (Figure S1).

Figure 1c,d shows XRD patterns of the Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite films, respectively. The diffraction peaks of Bi$_2$MoO$_6$ are indexed to the orthorhombic structure (Joint Committee on Powder Diffraction Standards (JCPDS) no. 21-0102), indicating its high crystallinity (Figure 1c). Figure 1d shows the XRD pattern of the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite. New peaks are detected in addition to the Bi$_2$MoO$_6$ peaks, which correspond to the Bi$_2$S$_3$ phase (orthorhombic, JCPDS no. 17-0320). Additional phases such as Bi$_2$O$_3$ and MoO$_3$ were not discovered in the XRD patterns (Figure 1d).

TEM and high-resolution TEM (HRTEM) analyses were carried out to identify the structural composition of the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite (Figures 2 and S2). The
HRTEM images of an edge of a single Bi$_2$S$_3$ nanowire show the lattice spacings of 0.25 and 0.20 nm corresponding to the (420) and (002) planes (Figure S2a,b). The fast Fourier transform patterns indicate the single-crystalline Bi$_2$S$_3$ nanowire, reflecting the fast crystalline growth toward the [001] direction (Figure S2b). Energy-dispersive X-ray spectrometry of the nanowires showed an average atomic ratio of 39:60 (Bi/S), indicative of the 2:3 atomic composition. A spatial elemental mapping was performed on a Bi$_2$S$_3$ nanowire to evaluate the distribution of each element (Figure 2c–f). The nanowire was composed of Bi and S in the ratio of 2:3 (Figure 2d,e), while the substrate was composed of Bi and Mo in the ratio of 2:1 (Figure S2). The elemental mapping confirmed that the Bi$_2$S$_3$ nanowires were directly grown on the Bi$_2$MoO$_6$ layer (Figure S2).

Figure 3 shows Raman spectra of the Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite films in the range of 50–900 cm$^{-1}$. The Raman peaks of the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite at 98, 188, 236, and 255 cm$^{-1}$ are in agreement with those of the orthorhombic Bi$_2$S$_3$ (red line in Figure 3). Bi$_2$MoO$_6$ peaks are not observed in the spectrum of Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA, indicating that the Bi$_2$S$_3$ layer is uniformly grown on the surface of the Bi$_2$MoO$_6$ layer. The surface states of both Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA films are further characterized by X-ray photoelectron spectroscopy (XPS) (Figure 4). The two high peaks at 164.1 and 158.8 eV are assigned to Bi 4f (Figure 4a,b). The S 2s peak at 224.8 eV (S$^{2−}$ in the metal sulfide) is detected only for the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA composite film, but not for the Bi$_2$MoO$_6$ film (Figure 4c,d). Therefore, the XRD, SEM, TEM, Raman spectroscopy, and XPS results verify the presence of Bi$_2$S$_3$NWA on the Bi$_2$MoO$_6$ surface.

Sulfide anions (S$^{2−}$) were produced by the decomposition of thiourea during the hydrothermal reaction. Small amounts of Bi$^{3+}$ and Mo$^{6+}$ ions were also generated by the dissolution of Bi$_2$MoO$_6$ during the reaction. The solubility of Bi$_2$S$_3$ in an aqueous solution is considerably lower than that of molybdenum sulfide, which have $K_{sp}$ values of 1.0 x 10$^{-97}$ and 2.2 x 10$^{-56}$, respectively. The Bi$^{3+}$ ions reacted more rapidly than the Mo$^{6+}$ ions with S$^{2−}$ ions forming the Bi$_2$S$_3$. As no additional source of Bi$^{3+}$ was provided during the process, the Bi$_2$MoO$_6$ layer acted as the Bi$^{3+}$ source for the growth of Bi$_2$S$_3$ nanowires. As the Bi$_2$S$_3$ has an extremely low solubility ($K_{sp}$ of 1.0 x 10$^{-97}$), the hydrothermal sulfidation of the Bi$_2$MoO$_6$ may spontaneously follow the etching and regrowth mechanisms proposed by Chen et al. The Bi$_2$S$_3$ nanowires grow rapidly along the direction vertical to the substrate in a large amount of S$^{2−}$. To obtain a reliable growth, the reaction solution with the Bi$_2$MoO$_6$ substrate was heated at a relatively low temperature (60 °C for 4 h) in the presence of a large amount of S$^{2−}$ (0.2 M of Na$_2$S). The surface of Bi$_2$MoO$_6$ was initially white, but after the reaction for 4 h, it turned to black brown, indicating the formation of Bi$_2$S$_3$ (Figure S3). The Bi$_2$S$_3$ layer grew larger and then reorganized forming amorphous Bi$_2$S$_3$ particles, but not nanowires. However, several Bi$_2$S$_3$ nanowires were grown on the surface of the Bi$_2$MoO$_6$ electrode at 100 °C for 4 h. Therefore, both large amounts of S$^{2−}$ and a high reaction temperature (above 100 °C) were needed to follow the etching process.

Figure 3. Raman spectra of Bi$_2$MoO$_6$ and Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA electrodes.

Figure 4. XPS spectra of (a) Bi 4f, (c) Mo 3d for Bi$_2$MoO$_6$, (b) Bi 4f, and (d) Mo 3d and S 2s for the Bi$_2$MoO$_6$/Bi$_2$S$_3$NWA electrode.
and regrowth mechanisms for the growth of Bi₂S₃ nanowires on the Bi₂MoO₆ surface. The unreacted Mo⁶⁺ ions were analyzed by inductively coupled plasma atomic emission spectroscopy. The Mo⁶⁺ ions remained in the solution throughout the reaction without the formation of a molybdenum sulfide film.

PEC Characterization of the Bi₂MoO₆/Bi₂S₃NW Composite Electrode. Various Bi₂MoO₆/Bi₂S₃ heterostructures were prepared by well-known synthesis methods to compare the PEC performances of the Bi₂MoO₆/Bi₂S₃NW electrodes (Scheme 2). The structures are denoted as Bi₂MoO₆/

Scheme 2. Schematic Image of the Preparation of Bi₂MoO₆/Bi₂S₃ Hetero-Structures

A sacrificial reagent, sodium sulfite (Na₂SO₃), was used to examine the PEC performance. Sulfite anions (SO₃²⁻) are an efficient hydroxyl radical (•OH) scavenger and react in most diffusion-controlled rates. Therefore, the SO₃²⁻ oxidation is a suitable model reaction for the measurement of the degree of bulk recombination of the semiconductor. It is considered to provide a surface transfer efficiency of almost 100% during the PEC measurement owing to the fast kinetics at the semiconductor–solution interface.

The PEC performances of the electrodes were investigated using linear sweep voltammetry (LSV) for sulfite oxidation (0.1 M Na₂S + 0.1 M Na₂SO₃). The LSV was carried out in the range of −0.9 to −0.1 V versus Ag/AgCl at a scan rate of 20 mV/s with a chopped UV–visible irradiation (Figures 5 and S6). All electrodes successfully generated anodic photocurrents, which confirmed their n-type characteristics. The photocurrent of the Bi₂MoO₆/Bi₂S₃NW electrode was 7.6 mA/cm² at −0.2 V (vs Ag/AgCl), while that of Bi₂MoO₆/Bi₂S₃(Drop), fabricated by drop-casting the Bi₂S₃ nanowires onto the Bi₂MoO₆ electrode, was 0.8 mA/cm² at the same potential (black bars in Figure 5b). The fabricated Bi₂MoO₆/Bi₂S₃NW electrode exhibited highly increased PEC activity compared to the Bi₂MoO₆/Bi₂S₃(Dip), which is attributed to the effective composite interface obtained by the in situ growth. The photocurrent of the Bi₂MoO₆/Bi₂S₃(Dip) and Bi₂S₃NW were 2.2, and 0.7 mA/cm², respectively, at the same condition (black bars in Figure 5b), which indicates the importance of single-crystalline Bi₂S₃ nanowires on the

Figure 5. (a) LSVs of the Bi₂MoO₆/Bi₂S₃NW composite under a UV–visible illumination (back side) in a solution of 0.1 M Na₂SO₃ and 0.1 M Na₂S recorded at a scan rate of 20 mV/s and a light intensity of 100 mW/cm². (b) Photocurrent densities of the electrodes having Bi₂MoO₆/Bi₂S₃ heterostructures under UV–visible (black) and visible (red) illuminations at an applied potential of −0.20 V vs Ag/AgCl. (c) Action spectrum and (d) current–time response curve of the Bi₂MoO₆/Bi₂S₃NW composite at an applied potential of −0.50 V vs Ag/AgCl.
Bi2MoO6 substrate. The photocurrent of the Bi2MoO6/Bi2S3NWA electrode was also several times higher than those of the Bi2MoO6/Bi2S3(Drop), Bi2MoO6/Bi2S3(Dip), and Bi2S3NW electrodes under the visible light irradiation (red bars in Figure 5b).

Figure 5c presents the action spectrum of the Bi2MoO6/Bi2S3NWA electrode, which shows the photocurrent depending on the wavelength, acquired with an interval of 10 nm. The portion of the visible light region (>425 nm) is about 85%, which matches well with Figure 5a. Furthermore, the band gap was determined using the wavelength of the onset photocurrent. The action spectrum indicates a band gap of 1.35 eV. It is well matched with the absorption spectrum (Figure S5). The Bi2MoO6/Bi2S3NW electrode exhibits an identical onset wavelength as that of Bi2S3 (about 1.3 eV),25 which indicates that Bi2S3NWA is the main absorber for the PEC reaction. The band gaps of the electrodes were also calculated by the Tauc equation.43 The direct band gaps of the heterostructures (Bi2MoO6/Bi2S3(Drop) and Bi2MoO6/Bi2S3NWA) are almost identical (Figure S5), and thus, the band gap difference is not the main factor for the PEC activity in the case of the Bi2MoO6/Bi2S3 heterostructures.

To evaluate the stability of Bi2MoO6/Bi2S3NWA, chronoamperometry was carried out under a UV−visible illumination (Figure 5d). The current transient upon the light irradiation was usually attributed to the dynamic balance of photogenerated electrons and their consumption at the semiconductor−solution interface.44,45 This is a characteristic indication of surface recombination even in the sacrificial reagent.46 Although the Bi2MoO6/Bi2S3NW electrode exhibited initial decreases in the photocurrent, the photocurrents stabilized at steady-state values for 2 h in the presence of the sacrificial reagent (Figure 5d).

In order to understand the mechanism of the increased PEC activity of the Bi2MoO6/Bi2S3NWA electrode, the flat-band potentials of Bi2MoO6 and Bi2S3 were measured. The Mott−Schottky (MS) plots were recorded using a Na2SO4 solution (Figure 6a,b).30 The MS plot indicated that the flat-band potential of Bi2S3 is approximately 0.15 V [vs normal hydrogen electrode (NHE)] with an n-type behavior. The flat band potential of Bi2MoO6 estimated using the MS plot was approximately 0.25 V (vs NHE). The conduction band edge ($E_{CB}$) is considered to be more negative than the flat band potentials by approximately 0.1 V.23,30 Therefore, the typical $E_{CB}$ and valence band edges ($E_{VB}$) of Bi2S3 are approximately 0.05 and 1.40 eV, respectively, (vs NHE), while those of Bi2MoO6 are approximately 0.15 and 2.95 eV (vs NHE), respectively, which are matched well with the literatures.30 Figure 6c shows possible photogenerated electron−hole pathways based on the MS plots: (1) electron transfer from the $E_{CB}$ of Bi2S3 to that of Bi2MoO6, (2) hole transfer from the $E_{VB}$ of Bi2MoO6 to that of Bi2S3, and (3) electron−hole recombination at the Bi2S3−Bi2MoO6 interface.

$E_{CB}$ and $E_{VB}$ of Bi2MoO6 are more positive than those of Bi2S3, favorable for the charge separation of Bi2S3. The origin of the increased PEC activity of the heterostructure compared to that of the bare Bi2S3 electrode is attributed to the enhanced charge separation of Bi2S3 on the Bi2MoO6 electrode (pathways 1 and 2 in Figure 6c) under the solar light irradiation. Furthermore, the Bi2MoO6/Bi2S3NWA electrode fabricated in situ has an effective interface with a lower resistance (reduced pathway 3 in Figure 6c) than that of the Bi2MoO6/Bi2S3(Dip) electrode. In addition, the Bi2S3 nanowires can provide fast electrical pathways to Bi2MoO6 through their single domains, compared to that of the Bi2MoO6/Bi2S3(Dip) electrode.
CONCLUSIONS

The Bi₂MoO₆/Bi₂S₃ NWA electrode was prepared by the in situ growth reaction. The Bi₂S₃ nanowires were homogeneously grown on the Bi₂MoO₆ layer. As no additional source of Bi³⁺ was provided during the process, the Bi₂MoO₆ layer acted as the substrate and the Bi³⁺ source for the synthesis of Bi₂S₃ nanowires. The spontaneous growth of Bi₂S₃ nanowires from the Bi₂MoO₆ by the etching and regrowth mechanisms provided a suitable interaction with the Bi₂MoO₆ substrate. The fabricated Bi₂MoO₆/Bi₂S₃ NWA electrode exhibited an increased PEC activity compared to other electrodes. The increase in activity was attributed mainly to three factors: (1) increased electron separation of Bi₂S₃ on the Bi₂MoO₆ layer as E_CB and E_VB of Bi₂MoO₆ were more positive than those of Bi₂S₃, encouraging charge separation of Bi₂S₃, (2) a suitable interface obtained by the in situ synthetic method, and (3) single-crystalline Bi₂S₃ nanowires which provided a fast electron pathway through the nanowire.

METHODS

Materials. An FTO-coated glass (TEC 15, WY-GMS) was used as the substrate for the thin-film electrode. Bi(NO₃)₃·5H₂O (99.999%, Sigma-Aldrich) and (NH₄)₆Mo₇O₂₄·4H₂O (99.98%, Sigma-Aldrich) were used as metal precursor salts. Thiourea (≥ 99%, Sigma-Aldrich), hydrochloric acid (36.5%, Junsei), ethylene glycol (≥99%, Sigma-Aldrich), isopropyl alcohol (99.5%, Junsei), sodium sulfate (≥ 98%, Sigma-Aldrich), sodium sulfate (99.0%, Daejung Chemicals), and sodium sulfide nonahydrate (96.0%, Junsei) were used as received. Deionized water was used as the solvent in all electrochemical experiments.

Fabrication of the Bi₂MoO₆ Film on FTO. FTO substrates were cleaned in deionized water and ethanol, and then sonicated in ethanol for at least 1 h. Drop-casting was carried out to fabricate the thin-film electrodes. A solution of 15 mM Bi₂MoO₆ precursor (an atomic ratio of Bi/Mo of 2:1) in ethylene glycol was prepared and then applied onto the FTO substrate (15 mM, 200 µL). The prepared film was annealed at 500 °C for 3 h (with a ramp time of 3 h) in air to form the Bi₂MoO₆ thin film.

Fabrication of Bi₂S₃ NWA on Bi₂MoO₆/FTO. Bi₂S₃ nanowires were directly grown on the surface of the Bi₂MoO₆ layer using an in situ hydrothermal reaction. The Bi₂MoO₆ layer on the FTO substrate was horizontally placed into a 50 mL Teflon-lined stainless-steel autoclave. A reaction solution was prepared by adding thiourea (7.9 mmol) into deionized water (30 mL). The reaction solution was transferred into an autoclave, and then heated in an electric oven at 140 °C for 4 h. The resulting Bi₂MoO₆/Bi₂S₃ NWA composite electrode was dried at 50 °C in air.

When the reaction solution was maintained at 140 °C for 48 h, Bi₂S₃ nanowires were grown directly on the surface of the FTO substrate. The nanowires fully covered the FTO substrate, and the majority were slightly tilted on the substrate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02111.

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Notes

The authors declare no competing financial interest.

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