Research Article

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Controllable morphology of Bi_2S_3 nanostructures formed *via* hydrothermal vulcanization of Bi_2O_3 thin-film layer and their photoelectrocatalytic performances

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Abstract: Bi_2S_3 nanostructures with various morphologies were synthesized through hydrothermal vulcanization at different sulfur precursor (thiourea) concentrations. A 100 nm thick sputter-deposited Bi_2O_3 thin-film layer on a fluorine-doped tin oxide glass substrate was used as a sacrificial template layer. The etching of the Bi_2O_3 sacrificial template layer and the regrowth of Bi_2S_3 crystallites during hydrothermal vulcanization produced the different Bi_2S_3 nanostructure morphologies. The lowest sulfur precursor concentration (0.01 M) induced the formation of Bi_2S_3 nanosheets, whereas the Bi_2S_3 nanoribbons and nanowires were formed with increased sulfur precursor concentrations of 0.03 and 0.1 M, respectively. These results indicate that sputter-deposited Bi_2O_3 thin-film layers can be effectively used to form low-dimensional Bi_2S_3 crystals with controllable morphologies. Among the various Bi_2S_3 samples, the Bi_2S_3 nanosheets exhibited superior photoactive ability. The higher active surface area, surface defect density, light absorption capacity, and photo-induced charge separation ability of Bi_2S_3 nanosheets explain their superior photoelectrocatalytic degradation ability of rhodamine B dyes.

Keywords: hydrothermal vulcanization, sulfide nanostructure, photoelectrocatalyst

1 Introduction

Bi_2S_3 is characterized by high photoconductivity, a small direct energy gap (1.3–1.7 eV), and a large visible light absorption coefficient; moreover, it is photostable in a semiconductor–electrolyte configuration. Due to these characteristics, low-dimensional Bi_2S_3 has become one of the most innovative materials used in research on applications of photocatalysts, photoresponsive devices, and photoelectrochemistry [1,2]. The photoactive performances of photosensitive materials are dependent on the materials' size, shape, composition, crystallinity, and structure [3,4]. Therefore, the synthesis route and process parameters are key to synthesizing low-dimensional Bi_2S_3 crystals with desirable properties. Several methods have been adopted to prepare Bi_2S_3 crystals, including hydrothermal and solvothermal processing, the sol-gel process, and vulcanization [5–8].

Semiconductor crystal synthesis in an aqueous solution is generally considered a promising approach because it is a simple, low-cost, and low-temperature process with easy process control. Moreover, thermodynamics and kinetic obstacles are major factors affecting the morphology and defect density of as-grown nanomaterials; therefore, simple process parameter control is especially crucial in synthesizing nanomaterials with a highly reproducible crystal quality. Among the various chemical solution methods for the synthesis of Bi_2S_3 crystals, the hydrothermal method is an excellent option based on the aforementioned criteria [9]. When used in photoresponsive devices, the as-grown nanomaterials tend to firmly align on the substrates. The traditional hydrothermal route for synthesizing most nanomaterial systems usually requires a homoseed or heteroseed layer or execution under specific harsh parameters to obtain the as-grown nanomaterials with specific crystal alignments and to firmly attach them to the required substrate for applications in devices [10,11]. A hydrothermal-assisted vulcanization

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method has also been adopted to synthesize sulfide or oxide–sulfide composite systems using a pregrown oxide sacrificial template layer on the substrate in the vulcanization process [12,13]. Therefore, the integration of hydrothermal and vulcanization processes to synthesize Bi_2S_3 crystals firmly aligned on the substrates is also a promising approach for device applications. Hydrothermal vulcanization has been used to synthesize Bi_2S_3 – BiVO_4 microspheres by forming Bi_2S_3 on hydrothermally prepared BiVO_4 crystals [14]. Moreover, single-crystal Bi_2S_3 nanorods and nanosheet-decorated Bi_2O_3 microtubes have been prepared using the same sacrificial template synthesis method [15]. However, the use of hydrothermal vulcanization with a sacrificial template in the synthesis of single-phase Bi_2S_3 crystals with a high growth density that are firmly aligned in a specific orientation on the substrate has not been systematically investigated so far. *In situ* growth of nanostructures that are firmly attached to a specific substrate facilitates their direct application in devices and eliminates the complicated procedures required for secondary processing and integration.

In addition, the relationship between the structural evolution and photoactive properties of single-phase Bi_2S_3 crystals synthesized through hydrothermal vulcanization with a suitable oxide sacrificial template has not been investigated. In this study, hydrothermal vulcanization was used to grow Bi_2S_3 crystals on a substrate using a sputter-deposited Bi_2O_3 thin-film sacrificial layer. Through the adjustment of the concentration of the sulfur source during hydrothermal vulcanization, different pure Bi_2S_3 nanostructures on the substrate were successfully synthesized. The microstructure-dependent photoactive properties were also measured to evaluate these nanostructures' suitability for use in photoactive nanodevices.

2 Experiments

2.1 Preparation of Bi_2S_3 crystals

First, a 100 nm thick Bi_2O_3 thin-film layer was grown on a fluorine-doped tin oxide (FTO) glass substrate by radio frequency sputtering. A metallic bismuth disc of 2 inches diameter was used as the target. The working pressure is 20 mtorr, sputtering power is fixed at 30 W, and the ratio of argon to oxygen (Ar/O_2) is fixed at 1:1 during the thin-film sputtering process. The substrate temperature was maintained at 425°C, and the sputtering duration was 50 min. Second, the as-prepared Bi_2O_3 thin-film layer underwent the hydrothermal vulcanization reaction to form Bi_2S_3 crystals. Thiourea (TU) powder was dissolved

in distilled water, and TU aqueous solutions with molar concentrations of 0.01, 0.03, and 0.1 M were prepared for different sulfur sources to vulcanize the Bi_2O_3 thin-film layer. Then, 12.5 mL of the TU aqueous solution with various concentrations was transferred into Teflon-lined stainless steel autoclaves and the Bi_2O_3 thin-film layer/FTO substrates are immersed in the solution for the hydrothermal reaction. The hydrothermal reaction was conducted at 180°C for 3 h. After the hydrothermal reaction, the autoclave was cooled to room temperature naturally. The final products were washed with deionized water several times and dried in air at 60°C. Notably, no other bismuth source was added in the reaction solution during the hydrothermal vulcanization process in addition to the bismuth source from the Bi_2O_3 thin-film sacrificial layer.

2.1.1 Materials analysis

The crystal structure of various Bi_2S_3 crystals was characterized by X-ray diffraction (XRD; Bruker D2 PHASER) with monochromatic Cu-K α radiation. The surface morphology of the samples was investigated through a field emission scanning electron microscope (SEM : JSM-7900F, JEOL). A high-resolution transmission electron microscope equipped with a 1024 × 1024 CCD camera (HRTEM; Philips Tecnai F20 G2) was operated at 200 kV to study the microstructures of the samples. X-ray photoelectron spectroscopy (XPS ULVAC-PHI, PHI 5000 VersaProbe) with Al K α X-rays was used to detect the element binding state of the samples. The absorption spectra of various samples were obtained using an UV-Vis spectrophotometer (Jasco V750). The photoelectrochemical (PEC) performance, electrochemical impedance (EIS), and PEC degradation were conducted with a potentiostat (SP150, BioLogic). The active area of the sample used as a working electrode in this study was 1.0 cm². Saturated Ag/AgCl (in saturated KCl) and platinum (Pt) wire were used as the reference electrode and counter electrode, respectively, in the electrochemical system. A 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte. A 100 W Xenon lamp was used as the light source during the photoexcitation experiments. In the PEC-degradation experiment, rhodamine B (RhB) solution (10^{-5} M) was used as the target degraded pollutant. The residual concentration of RhB solution after different PEC-degradation processes was analyzed with a UV-vis spectrophotometer. The degradation level of RhB solution PEC-degraded by the Bi_2S_3 photocatalysts was defined as C/C_0 , C_0 and C being the initial RhB concentration and RhB concentration at reaction time t , respectively.

3 Results and discussion

The morphologies of Bi_2O_3 thin-film templates used in the various vulcanization processes are presented in the SEM images. In Figure 1(a), distinct sheet-like crystals distributed on a large scale were observed on the Bi_2O_3 thin-film template vulcanized with the lowest sulfur precursor concentration (0.01 M). The interconnected nanosheets were uniformly distributed on the substrate, forming an orderly array with a highly open structure. These sheet-like structures had the thickness of approximately 31–54 nm and a diameter of approximately 1.6–2.8 μm . When the concentration of the sulfur precursor was increased to 0.03 M, no sheet-like crystals were observed; in contrast, ultrathin, ribbon-like nanostructures appeared as shown in Figure 1(b). The surfaces of the ribbon-like crystals were smooth, and their periphery was straight; moreover, the nanoribbons covered the substrate completely and uniformly. The average length of the synthesized nanoribbons was approximately 2.1–3 μm , and their width was approximately 400–500 nm. Figure 1(c) presents the morphology of the product formed using the highest concentration of the sulfur precursor (0.1 M). Uniform nanowires can be clearly distinguished in the SEM image, and the nanowires have a homogeneous size with

an average diameter of approximately 100 nm and average length of 1 μm . The SEM images reveal that after hydrothermal vulcanization processes with different sulfur concentrations, the Bi_2O_3 thin-film templates formed nanostructures with various morphologies. During the hydrothermal vulcanization reaction, the Bi_2O_3 thin-film template layer reacted with S^{2-} ions from the added TU to form Bi_2S_3 crystals. The Bi_2O_3 thin-film crystals acted as the sacrificial layer and acted as a Bi^{3+} source for the formation of the Bi_2S_3 crystals during the hydrothermal vulcanization through the reactions proposed in Wu *et al.*'s work [16]. Ion exchange, in which the surface oxygen ions of the Bi_2O_3 thin-film template were replaced by sulfur ions, occurred during the hydrothermal vulcanization. Furthermore, the Bi^{3+} ions reacted with S^{2-} ions to form the Bi_2S_3 crystallites. Bi_2S_3 is much less soluble than Bi_2O_3 ; therefore, Bi_2O_3 can spontaneously undergo a sulfidation reaction with S^{2-} and perform anion exchange even in a low-temperature hydrothermal vulcanization process [17]. In this study, the amount of Bi^{3+} ions in the hydrothermal vulcanization process was fixed because the Bi_2O_3 thin-film template amount in the various vulcanization processes was the same; however, the S^{2-} sources differed due to the different added amounts of TU. The addition of different S^{2-} precursor concentrations

Figure 1: SEM micrographs of Bi_2S_3 crystals formed with Bi_2O_3 thin-film templates from various vulcanization processes: (a) 0.01 M TU, (b) 0.03 M TU, and (c) 0.1 M TU. (d) Illustration of formation mechanisms of Bi_2S_3 crystals *via* Bi_2O_3 thin-film template treated with various vulcanization processes. The Bi_2S_3 crystallographic plane has been marked in red.

in the hydrothermal vulcanization might have dominated the etching rate of the Bi_2O_3 thin-film template and controlled the formation rate of the Bi_2S_3 crystallites at the time of the synthetic reaction. Therefore, various morphologies of the Bi_2S_3 products were formed on the Bi_2O_3 thin-film template after vulcanization with different sulfur precursor concentrations. The etching of the Bi_2O_3 thin-film sacrificial layer and formation of Bi_2S_3 crystallites of various morphologies during different vulcanization processes are shown in Figure 1(d). A similar vulcanization process using BiVO_4 to form Bi_2S_3 crystals has also been used to synthesize a BiVO_4 - Bi_2S_3 nanowire composite [18].

Figure 2(a)–(c) show the XRD patterns of Bi_2O_3 thin-film templates treated with various hydrothermal vulcanization processes. In addition to the Bragg reflections from the FTO substrate, all samples showed distinct Bragg reflections originating from the crystallographic planes of the orthorhombic Bi_2S_3 structure according to JCPDS No. 17-0320 [19]. Notably, no impurities, such as Bi_2O_3 and Bi, were detected, which indicates that a high-purity Bi_2S_3 phase was synthesized *via* the given vulcanization processes. Furthermore, the Bragg reflections are narrow and

sharp, indicating that the Bi_2S_3 products are of high crystallinity. All the Bi_2S_3 samples show the intense (130) and (310) Bragg reflections. This crystallographic feature of the as-synthesized Bi_2S_3 samples is in agreement with the XRD results of hydrothermally derived ribbon-like Bi_2S_3 crystals [20].

Figure 3(a) shows a low-magnification TEM micrograph of a Bi_2S_3 nanosheet. The nanosheet exhibits a slightly rugged peripheral morphology and grows into a rectangular shape. The width of the sheet is approximately $1.4\ \mu\text{m}$, and the length is approximately $1.6\ \mu\text{m}$. Moreover, many irregular rippling stripes appeared on the surface of the sheet. Here, the appearance of ripples might indicate the existence of surface defects on the surface of the as-synthesized Bi_2S_3 nanosheet. The formation of similar surface ripples of the materials associated with crystal defects has been proposed previously [21]. Figure 3(b) demonstrates a HRTEM micrograph taken from the local region (marked with yellow circle) of the nanosheet. Visible lattice fringes with distinct and ordered arrangement in the local region are observed in the HRTEM output, which reveals its crystalline nature. In addition,

Figure 2: XRD patterns of Bi_2S_3 crystals formed with Bi_2O_3 thin-film templates from various vulcanization processes: (a) 0.01 M TU, (b) 0.03 M TU, and (c) 0.1 M TU. The enlarged XRD plots with 2θ at around 25° are also shown for clarity.

Figure 3: (a) Low-magnification TEM image of the Bi_2S_3 nanosheet. (b) HRTEM image of the Bi_2S_3 nanosheet taken from the local region. (c) SAED pattern of the Bi_2S_3 nanosheet. (d) EDS spectra of the Bi_2S_3 nanosheet. (e) Low-magnification TEM image of the Bi_2S_3 nanoribbon. (f) HRTEM image of the Bi_2S_3 nanoribbon taken from the local region. (g) SAED pattern of the Bi_2S_3 nanoribbon. (h) EDS spectra of the Bi_2S_3 nanoribbon. (i) Low-magnification TEM image of the Bi_2S_3 nanowire. (j) HRTEM image of the Bi_2S_3 nanowire taken from the local region. (k) SAED pattern of the Bi_2S_3 nanowire. (l) EDS spectra of the Bi_2S_3 nanowire.

some messy lattice images exist in the local regions of the HRTEM output, supporting reasonably that crystal defects are present in the Bi_2S_3 nanosheets. The lattice spacing of approximately 0.35 nm in the HRTEM output was indexed as the interplanar spacing of (130) of the orthorhombic structured Bi_2S_3 . A corresponding selected area electron diffraction (SAED) pattern of a single nanosheet is shown in Figure 3(c). The sharp, bright, and ordered spots corroborate that the nanosheet was highly crystalline. The spots in the SAED pattern could readily be indexed to (130) and (211), the crystallographic planes were determined to correspond to the orthorhombic Bi_2S_3 phase. The phase purity and chemical composition of the product were confirmed by energy-dispersive X-ray spectroscopy analysis. Figure 3(d) displays Bi and S are the main constituent elements in the sample except for the observed signals of Cu and C that originated from the copper grid. The molar ratio of Bi to S is estimated to be approximately 2:3 (Bi: 38.6%, S: 61.4%),

which is close to the standard stoichiometric composition of the Bi_2S_3 phase. Figure 3(e) presents a low-magnification TEM micrograph of a Bi_2S_3 nanoribbon. Figure 3(e) confirms that the Bi_2S_3 ribbon structure has a width of approximately 410 nm, which is consistent with the result of SEM observations. The Bi_2S_3 ribbon exhibits a flat, side-wall morphology and grows into a rectangular shape. Notably, the top region of the ribbon consisted of three facets, and the angle between the adjacent facets is approximately 158.8° . Moreover, the grayscale contrast reveals that the side-wall regions of the ribbon structure are thinner than the core region. More evidence on its structure and crystallinity was obtained from the HRTEM output (Figure 3(f)). Visible lattice fringes with a neat arrangement are displayed in Figure 3(f). It can be observed that the ordered lattice spacing is approximately 0.37 nm, corresponding to the interplanar distance of Bi_2S_3 (101). The SAED pattern in Figure 3(g) organized with sharp and orderly arranged spots evidences to the orthorhombic

Bi_2S_3 phase of the ribbon structure; moreover, it indicates that the ribbon has single crystallinity. Furthermore, the compositional purity of the Bi_2S_3 ribbon structure is evident in Figure 3(h), and the molar ratio of Bi to S is estimated to be approximately 2:3 (Bi: 36.6%, S: 63.4%) herein. Figure 3(i) shows the low-magnification TEM micrograph of a Bi_2S_3 nanowire. It is observed that the length of these nanowires has a large distribution whereas their diameter has a relatively narrow distribution. The mean diameter of the Bi_2S_3 nanowire was measured to be approximately 70 nm. In contrast to the ribbon structure, a two-facet structure was observed in the top region of the nanowire, and the angle between these two crystal facets was approximately 136.5° . The highly crystalline nature of the nanowire is clear from Figure 3(j). The clear lattice spacing of 0.39 nm is attributed to the interplanar distance of Bi_2S_3 (220). A corresponding SAED pattern of a single nanowire was further examined and its unique, sharp diffraction pattern (Figure 3(k)) could readily be indexed to (002), and (220) on two of the spots, which confirms that the nanowire is a single crystal and might have a [001] growth direction. This is in agreement with previous finding for Bi_2S_3 nanorods synthesized *via* a hydrothermal method [22]. The composition of the Bi_2S_3 nanowire is shown in Figure 3(l). A stoichiometric composition of the Bi_2S_3 nanowire was used in this study.

Figure 4(a)–(c) presents the narrow scan XPS spectra of the Bi 4f and S 2p regions taken from different Bi_2S_3 samples. Figure 4(a)–(c) show two predominant peaks centered

at the range of 158.6–159.0 eV and 163.8–164.1 eV, and these two strong peaks can be assigned to the binding energies of Bi 4f_{7/2} and Bi 4f_{5/2}, respectively. The binding energy feature of the bismuth herein closely matched with the Bi^{3+} in Bi_2S_3 crystals [23]. Moreover, the nearly symmetric shape of the Bi 4f peaks without distinct distortions at their shoulders excludes the presence of metallic Bi and Bi_2O_3 , and therefore Bi^0 binding energies appeared at 162.4 and 157.1 eV and Bi^{3+} binding energies of Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, appeared at 161.5 and 166.0 eV [23]. The spin–orbit doublet of S 2p spectra overlaps with the bottom regions of the Bi 4f spectra. The asymmetric S 2p spectra consist of two asymmetric peaks corresponding to S 2p_{3/2} and S 2p_{1/2}. The more intense subpeak centered at 161.1 eV is ascribed to S 2p_{3/2}, and by contrast, the peak with a lower intensity located at approximately 161.9 eV is assigned as S 2p_{1/2} in Bi_2S_3 . The binding energies of the S 2p doublet signals herein prove that sulfur exists in the S^{2-} state in the products. This is in agreement with the sulfur binding states in Bi_2S_3 nanowires synthesized *via* hydrothermal vulcanization [24]. Notably, the Bi 4f binding energy of Bi_2S_3 nanosheets exhibited a higher value in comparison with that of the Bi_2S_3 nanoribbons and nanowires (Figure 4(d)). This might be associated with the occurrence of more surface bismuth defects in the Bi_2S_3 nanosheets that affects the Bi 4f binding energy shifted to a higher binding energy [25,26]. The surface defects of semiconductors might act as charge traps and can prevent electron–hole recombination, thereby helping to improve the photocatalytic activity of semiconductors [27].

Figure 4: Narrow scan XPS spectra of the Bi 4f and S 2p regions taken from different Bi_2S_3 products: (a) nanosheet, (b) nanoribbon, and (c) nanowire. (d) Comparison of Bi 4f core-level binding energy of all products. (e) The representative O 1s spectrum of Bi_2S_3 nanosheets. The red line is the fitted result.

Furthermore, the representative O 1s spectrum of Bi_2S_3 nanosheets is shown in Figure 4(e). It has been shown that O 1s spectrum of $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{O}_3$ composites has an asymmetric O 1s peak feature [28]. In that work, the binding energies of 531.0 and 529.6 eV could be attributed to the H–O bond of the oxygen-containing species adsorbed on the surface and the Bi–O bond in the Bi_2O_3 crystal lattice, respectively. In contrast, the O 1s peak of Bi_2S_3 nanosheets herein has a symmetric feature and it centered at approximately 531.4 eV (calibrated with a C signal). This binding energy matches the bonding energy associated with the surface-adsorbed oxygen-containing species.

Figure 5(a) shows the representative UV-Vis absorption spectra of various Bi_2S_3 samples. The Bi_2S_3 products herein showed a good, correspondingly wide absorption range in the visible light region. Similarly, the hydrothermally derived Bi_2S_3 nanorods confirm the narrow band gap nature of the Bi_2S_3 , and it could absorb the spectra of the visible light region and show excellent photocatalytic performance in previous reported work [29]. Notably, the nanosheet-like Bi_2S_3 crystals exhibit more intense light

absorption intensity in the visible light region among various samples, indicating that the free-standing surface topography and large diameter of the sheet crystal are beneficial for improving the light capture efficiency. In contrast, the ribbon-like Bi_2S_3 crystals possess lower absorption intensity in the visible light region. This may be due to the ribbon structures mostly lying flat on the substrate and in such a morphology cannot effectively harvest the reflectance lights, further losing the light harvesting ability. This phenomenon has been confirmed in the differences in the light harvesting ability of chemical vapor-deposited titanium sulfide sheets with a flat stacked structure and a three-dimensional clustered appearance. Comparatively, the sheet-like crystals that are flat on the substrate have a smaller light absorption capacity [30]. In addition, it is known that the optical absorption properties of semiconductors are closely related to their optical energy band gap. Figure 5(b)–(d) shows the band gap energy evaluation of various Bi_2S_3 samples according to the conversion of the Kubelka–Munk function [4]. Bi_2S_3 is supposed to exhibit a direct transition in the band gap

Figure 5: (a) Optical absorption spectra of all Bi_2S_3 products. Band gap evolution of various Bi_2S_3 products: (b) nanosheet, (c) nanoribbon, and (d) nanowire.

measurement. Therefore, its optical band gap is deduced from the following conversion equation by considering the direct transitions for Bi_2S_3 : $(F(R)h\nu)^2 = A(h\nu - E_g)$, where E_g is the optical band gap corresponding to allowed direct transitions, $F(R)$ is the Kubelka–Munk function, $h\nu$ is photon energy, and A is a constant, respectively. The band gap energies of Bi_2S_3 nanosheets, nanoribbons, and nanowires were 1.41, 1.47, and 1.46 eV, respectively. These band gap energies are close to the reported values of the pure Bi_2S_3 phase [31]. It is found that the Bi_2S_3 nanosheets have the smallest band gap value. The smaller band gap might make the Bi_2S_3 nanosheets more efficient in photoexcitation under irradiation, and this might be beneficial for photoexcitation applications.

The electrochemical active surface area (ECSA) of various Bi_2S_3 crystals is further studied herein. ECSA is closely related to the number of surface active sites, which is effectively evaluated by the double-layer capacitance (C_{dl}), and C_{dl} is directly proportional to ECSA [32]. The cyclic voltammetry (CV) curves with different scan rates

(20–100 mV/s) of various Bi_2S_3 samples in the region of non-Faradaic potentials (−0.15 to 0 V vs Ag/AgCl) are shown in Figure 6(a)–(c). It can be seen that the CV curves of all Bi_2S_3 samples are typical in a rectangular shape between the measured potential region between −0.15 and 0 V, revealing a behavior of electrical double-layered capacitance [33]. As displayed in Figure 6(d), the C_{dl} values of various samples from CV curves can be evaluated from the linear relationship plot of the current density (Δj , calculated by $j_{\text{anodic}} - j_{\text{cathodic}}$) versus the scan rate. The extracted slope value of Δj versus the scan rate curves allows a comparison of ECSA size among various samples according to the correlation between the double layer charging current and electrochemical double-layer capacitance, that is, $\Delta j = \nu C_{dl}$, in which ν is the scan rate [33]. In Figure 6(d), the C_{dl} values of Bi_2S_3 nanosheet, nanoribbon, and nanowire structures are approximately 7.8×10^{-4} , 6.8×10^{-5} , and 5.1×10^{-5} mF/cm², respectively. Comparatively, the Bi_2S_3 nanosheet structure has the largest C_{dl} value and it has the highest current density at the given

Figure 6: CV curves at various scan rates of different Bi_2S_3 products: (a) nanosheet, (b) nanoribbon, and (c) nanowire. (d) The fitted C_{dl} results of various Bi_2S_3 products.

measurement condition, demonstrating that it has the largest ECSA as well as massive catalytic active sites. A large number of catalytically active sites of the sample can maintain a highly efficient electrochemical reaction between the sample and the ions of the electrolyte, and can promote the sample's impact on photo-/electrocatalytic performance [34].

Figure 7(a) displays the transient photocurrent responses of various Bi_2S_3 photoelectrodes under chopped illumination at 1 V vs Ag/AgCl. All the photoelectrodes exhibited a prompt response to the light under the test conditions. The photocurrent density of each sample remained stable after several cycles. The photocurrent density of the Bi_2S_3 nanosheet-based (0.083 mA/cm^2) photoelectrode was higher than that of the nanowire-based photoelectrode (0.036 mA/cm^2) and that of the nanoribbon-based photoelectrode (0.026 mA/cm^2). As photocurrent density increased, the separation efficiency of the photoinduced charge carriers in the semiconductors also increased, indicating the higher photocatalytic performance of semiconductors [35,36]. The higher photoresponse performance of the Bi_2S_3 nanosheet-based photoelectrode in this study might be associated with several factors. First, a smaller band gap energy in a semiconductor allows the semiconductor to absorb more light, and more electron-hole pairs can therefore be generated, thus producing greater photocurrent density [37]. This corresponds to the previous optical absorption analysis result in which the Bi_2S_3 nanosheet structure exhibited the highest light absorption, highest light-harvesting ability, and smallest energy gap among various samples. Second, according to earlier ECSA measurements, the Bi_2S_3 nanosheet has the highest electrochemically active surface area. A high electrochemically active surface area can improve PEC performance [38]. Third, in the preceding microstructural analysis, the Bi_2S_3 nanosheet exhibited a wrinkled

surface appearance, and in the HRTEM, it exhibited greater disorder and more irregular lattice stripe arrangements than the other samples. These phenomena increase the possibility of defects in nanosheets. Crystal defects in a nanosheet make the recombination of the photogenerated electron-hole pairs more difficult; therefore, a higher photocurrent value might be obtained. Improved PEC performance has also been exhibited by In_2S_3 nanoplates with a high surface defect density [39]. Figure 7(b) presents the Nyquist plots of various Bi_2S_3 photoelectrodes; these plots are used to analyze the interface charge transfer characteristics of the prepared samples. A smaller Nyquist curve radius indicates a lower charge transfer resistance in the electrode-electrolyte interface, a higher reaction rate on the photoelectrode, and a higher separation efficiency of photogenerated electrons and holes in the semiconductor [40]. All the Nyquist plots of the Bi_2S_3 photoelectrodes exhibit typical semicircular arcs with different curve radii. Furthermore, the plot of the Bi_2S_3 nanosheet-based photoelectrode contains the smallest semicircular radius among those of various samples. Although the semicircular radius of the Bi_2S_3 nanoribbon-based photoelectrode's Nyquist plot is comparable to that of the nanowire-based photoelectrode, the plot of the nanoribbon-based photoelectrode has a slightly larger semicircular radius than that of the nanowire-based photoelectrode. The Nyquist plots indicate that the Bi_2S_3 nanosheet-based photoelectrode exhibits the smallest charge transfer resistance, the most effective photogenerated electron-hole pair separation, and the fastest interface charge transfer among the various Bi_2S_3 samples. Conversely, the Bi_2S_3 nanoribbon-based photoelectrode has the largest charge transfer resistance and the slowest interface charge transfer among the samples. This preliminary result is consistent with the transient

Figure 7: (a) Photocurrent density versus time curves of various Bi_2S_3 photoelectrodes under chopped illumination at 1 V. (b) Nyquist plots of various Bi_2S_3 photoelectrodes under irradiation. (c) The possible equivalent circuit used for R_{ct} evaluation of various Bi_2S_3 photoelectrodes.

photocurrent response results displayed in Figure 7(a). Figure 7(c) presents the possible equivalent circuits for a quantitative analysis of the interfacial charge transfer ability of the various Bi_2S_3 photoelectrodes. A Randles equivalent circuit model comprising a series-connected resistor (R_s) and a parallel circuit ($R_{ct} - C_{dl}$) in the electrochemical half-cell was employed [41]. In the illustration, R_s represents solution resistance, C_{dl} represents the double-layer capacitor, and R_{ct} represents the charge transfer resistance. According to the fitting results of Nyquist data, the R_{ct} values of the nanosheet-, nanoribbon-, and nanowire-based photoelectrodes were approximately 1,041, 1,979, and 1,768 Ω , respectively. According to these results, the Bi_2S_3 nanosheet-based photoelectrode exhibited the lowest charge transfer resistance among the various photoelectrodes.

The electronic properties of the various Bi_2S_3 photoelectrodes are presented in the Mott–Schottky (M–S) plots (Figure 8). All the Bi_2S_3 photoelectrodes exhibited a positive slope in the M–S curves, reflecting the n -type nature of Bi_2S_3 . The flat band potential (E_{fb}) of the various Bi_2S_3 samples can be obtained from the tangent to the focal point of the X axis at $1/C^2 = 0$ in Figure 8, according to the M–S equation [42]. The E_{fb} values of the various Bi_2S_3 samples were approximately -0.254 , -0.232 , and -0.239 eV relative to normal hydrogen electrode (NHE) for the Bi_2S_3 nanosheet-, nanoribbon-, and nanowire-based photoelectrodes, respectively. The negative shift of the E_{fb} of an n -type semiconductor is closely related to its active surface area. For example, the E_{fb} values of the hydrothermally derived Bi_2S_3 nanorods differed from those of the nanoflowers. The V_{fb} value of the Bi_2S_3 nanoflowers with a larger active surface area was more negative than that of the Bi_2S_3 nanorods [43]. Moreover, electrochemically deposited ZnO nanopillars and nanotubes also exhibited different E_{fb} ; the ZnO nanotubes with a larger surface area exhibited a significant

negative shift in E_{fb} with reference to that of the ZnO nanopillars in the M–S measurements [44]. These examples indicate that a larger surface area corresponds to the presence of more active sites on the surface of a semiconductor, which promotes the transfer of more carriers on the surface of the sample and on the electrolyte, causing a change in the Fermi level of the semiconductor. As indicated in Figure 8, the E_{fb} of the Bi_2S_3 nanosheet-based photoelectrode exhibited a large negative shift with reference to that of other samples; this finding is consistent with the results of the previous surface active site analysis and of those in other published works [43,44].

Figure 9(a)–(c) presents the absorbance spectra intensity variations of an RhB solution with the Bi_2S_3 nanosheet, nanoribbon, and nanowire photocatalysts, respectively, under the given PEC-degradation conditions. The decreased absorbance spectra intensity of the RhB solution with irradiation time indicated that all the Bi_2S_3 photocatalysts exhibited effective PEC-degradation of the RhB solution. Figure 9(d) summarizes the variation in C/C_0 concentrations with respect to irradiation time at an applied bias potential of 1.0 V. After 80 min of irradiation, the Bi_2S_3 nanosheets, nanoribbons, and nanowires degraded approximately 89.2, 66.3, and 72.6% of the RhB solution, respectively, indicating that the Bi_2S_3 nanosheets degrade RhB most effectively under the same PEC-degradation conditions. Figure 9(e) displays the coloration variation of the RhB solution PEC degraded by the Bi_2S_3 nanosheets under different irradiation durations. The pink RhB solution gradually became transparent during 80 min of PEC degradation, indicating that the Bi_2S_3 nanosheets effectively degraded the RhB over time. Figure 9(f) presents the kinetic linear simulation curves of the PEC degradation of the RhB solution by various Bi_2S_3 samples according to a pseudo first-order kinetic model [38]. The rate constant k was evaluated to be 0.0204 min^{-1} for the Bi_2S_3 nanosheets, 0.0135 min^{-1} for

Figure 8: M–S plots of various Bi_2S_3 products: (a) nanosheet, (b) nanoribbon, and (c) nanowire.

Figure 9: The irradiation–duration-dependent absorption intensity variation of the RhB solution with various Bi₂S₃ photocatalysts at 1 V: (a) nanosheet, (b) nanoribbon, and (c) nanowire. (d) C/C_0 versus irradiation duration plot with various Bi₂S₃ photocatalysts at 1 V. (e) Decoloration of RhB solution with Bi₂S₃ nanosheets after different PEC-degradation durations. (f) $\ln(C_0/C)$ versus irradiation duration plot with various Bi₂S₃ photocatalysts at 1 V.

the nanoribbons, and 0.0159 min^{-1} for the nanowires. The rate constant k of the Bi₂S₃ nanosheets was the highest, whereas that of the Bi₂S₃ nanoribbons was the smallest, indicating that the nanosheet-structured Bi₂S₃ exhibited superior PEC performance.

The possible PEC-degradation mechanism of the Bi₂S₃ toward RhB solution is illustrated in Figure 10. The E_g (i.e., energy gap) values of the Bi₂S₃ nanosheets, nanoribbons, and nanowires were 1.41, 1.47, and 1.46 eV, respectively. The conduction band (CB) edge energy of *n*-type semiconductors is often approximately 0.1 eV more negative than the semiconductor's flat band potential [17]. Therefore, the CB values of the Bi₂S₃ nanosheets, nanoribbons, and nanowires can be estimated as -0.354 , -0.332 , and -0.339 eV (vs NHE), respectively. Furthermore, the valence band (VB) potential of a semiconductor can be calculated according to the equation $E_{CB} = E_{VB} - E_g$. The possible band structure of the various Bi₂S₃ samples can be constructed according to the approximate values of CB, E_g , and VB. A possible band structure of the Bi₂S₃ nanosheets is illustrated in Figure 10, and the related band edges are similar to those illustrated in other published works [45,46]. When the Bi₂S₃ nanosheets are irradiated with light, the electrons on the VB are easily

excited to the CB due to Bi₂S₃'s small band gap and leave holes on the VB, according to reaction (1). However, also due to the small size of the band gap, excited electrons and holes tend to recombine quickly [47], and a high carrier recombination rate in photocatalysts is undesirable. In a PEC-degradation system, a bias potential is applied to the Bi₂S₃ photoelectrode and an internal electric field is generated. Under the action of the electric field, the photogenerated electrons are forced to transfer from the CB of the Bi₂S₃ to the Pt electrode. At the same time, photogenerated holes are left on the Bi₂S₃ electrode, which leads to the efficient separation of photoinduced electrons and holes. Bi₂S₃ semiconductor's high carrier recombination rate of the photogenerated electrons and holes can thereby be substantially decreased. The CB (-0.354 eV) of Bi₂S₃ nanosheets lies at a more negative potential than the one-electron reduction potential (-0.33 eV) of O₂. The electrons are excited to the CB and are transferred to the Pt electrode, where they can react with oxygen to generate superoxide radicals, as indicated by reaction (2) [48]. The generation of superoxide radicals in this system can also be obtained through the reaction of electrons with O₂ adsorbed on the surface of Bi₂S₃, as indicated in reaction (3) [49]. The generated

Figure 10: The possible PEC-degradation mechanism of RhB solution with Bi₂S₃ photocatalysts.

superoxide radicals in the PEC degradation system can effectively degrade RhB dye according to reaction (6). In contrast, holes left in the VB (1.056 eV) have a negative potential greater than 2.2 eV (for $\cdot\text{OH}/\text{OH}$) and 2.38 eV (for $\cdot\text{OH}/\text{H}_2\text{O}$) [35]. Therefore, the holes on the VB of Bi₂S₃ do not react with water and hydroxide ions to produce hydroxide radicals. Furthermore, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital energy potentials of RhB dye are -1.42 and 0.95 eV (vs NHE), respectively [50]. In the PEC-degradation process, when RhB molecules are adsorbed on the surfaces of Bi₂S₃ nanosheets due to surface defects, RhB molecules are elevated to an excited state (RhB*) by light (reaction (4)). As the CB of Bi₂S₃ is more positive than the potential energy of the RhB LUMO, the RhB* transfers electrons to the CB of the Bi₂S₃ and transforms into a cationic dye radical (RhB⁺) (reaction (5)), resulting in a further degradation of the RhB dye molecules (reaction (6)) [51].

The superior PEC degradation ability of Bi₂S₃ nanosheet photocatalysts among various Bi₂S₃ photocatalysts can be attributed to several factors, according to the preceding analyses. A photocatalyst's active surface area affects its

degradation ability by allowing for greater contact with electrolytes and dyes [52]. Furthermore, the superior light-trapping ability and smaller band gap of Bi₂S₃ nanosheets, as compared with those of the other Bi₂S₃ samples, also contribute to their efficient PEC degradation of RhB solutions [53]. The desirable photocatalytic properties of photocatalysts have also been associated with surface defects, which act as charge traps and can effectively prevent photo-induced electrons and holes from recombining [27]. As described by Xu *et al.*, the higher surface defect density in the hydrothermally synthesized BiOCl nanosheets promotes superior photocatalytic performance relative to that of the less-defective nanosheets [25]. Similarly, the abundant defect structure of the Bi₂S₃ nanosheets contributes to its higher PEC-degradation efficiency compared with those among the various other samples. These results indicate that a Bi₂O₃ thin-film layer used to form free-standing Bi₂S₃ crystals in a flaky structure through hydrothermal vulcanization can be effectively used to degrade organic pollutants.

4 Conclusion

Bi₂S₃ nanostructures with different morphologies, including nanosheets, nanoribbons, and nanowires, can be synthesized using hydrothermal vulcanization. These Bi₂S₃ nanostructures can be firmly grown on FTO glass substrates using a Bi₂O₃ sacrificial thin-film layer during the hydrothermal vulcanization process. The formation of Bi₂S₃ nanostructures

involves the etching of the Bi_2O_3 sacrificial thin-film layer and the regrowth of Bi_2S_3 crystallites. The Bi_2S_3 nanosheets exhibit photoactive performance superior to that of Bi_2S_3 crystals with other morphologies. This can be attributed to the fact that Bi_2S_3 nanosheets have a larger active surface area, higher surface defect density, higher light absorption capacity, and lower recombination rate of photo-generated charges. Finally, comparison of PEC degradation of RhB solutions indicates that the ability of Bi_2S_3 nanosheets to degrade RhB dyes is superior to that of other Bi_2S_3 products. This study therefore demonstrated a promising approach to *in situ* growth of Bi_2S_3 nanostructures firmly aligned on an FTO substrate to be used in various PEC applications.

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