Composition and Structure Evolution of Bi$_2$O$_3$ Coatings as Efficient Photocatalysts

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Abstract: To overcome the recovery disadvantages of Bi$_2$O$_3$ photocatalyst in the form of powder, Bi$_2$O$_3$ photocatalyst coatings were developed via a ball milling, followed by the calcination method. The composition and structure evolution rules of the as-synthesized samples were analyzed based on XRD (X-ray powder diffraction) patterns and SEM (scanning electron microscope) observations. XPS (X-ray photoelectron spectroscopy) and UV-Vis (Ultraviolet-visible) spectra were also employed to characterize the samples. The results showed that monoclinic Bi$_2$O$_3$ coatings were obtained after sintering Bi coatings at 673 or 773 K for 2 h, while calcination at a higher temperature and for a longer time resulted in monoclinic and triclinic mixed-phase Bi$_2$O$_3$ coatings. Bi$_2$O$_3$ coatings with a radial growth structure assembled by nanosheets could be realized at a lower temperature lasting for a longer time, while sintering at a higher temperature with relatively short oxidation time led to tangential growth structure. Photodegradation of malachite green solution under simulated solar irradiation for 180 min showed that the largest degradation efficiency of 91.49% was achieved over the photocatalyst coatings calcined at 873 K for 5 h. Additionally, the degradation efficiency was maintained above 80% even after three cycles.

Keywords: Bi$_2$O$_3$; coatings; ball milling; photocatalyst

1. Introduction

Nowadays, environmental pollution and energy crisis cause extremely severe and destructive effects for human health and society development. Fortunately, photocatalysis technology appears as an efficient, economical, and environmental friendly technology, which can be applied in environmental remediation, as well as solar energy conversion, since it was discovered in 1972 [1–3]. To date, various types of semiconductor photocatalysts have been explored, especially the TiO$_2$-based photocatalysts which are always being ranked as the most researched ones [4–6]. However, their applications are retarded by low utilization efficiency for solar light absorption or a high recombination of charge carriers, thus making development of photocatalysts with visible light responsive ability indispensable. Recently, bismuth-based semiconductor photocatalysts have been demonstrated to exhibit superior photocatalytic activity under visible-light irradiation, and the interest in bismuth-based semiconductors is continuing to grow [7–12].

In order to push the applications of photocatalysts in practical industry fields, such as waste water treatment, the dispersity, recovery, and repeatability of the photocatalysts are of great significance. Yet, it is difficult to realize such an objective with photocatalysts in powder form, which impels the pursuit of a valid method to achieve improved recovery properties of photocatalysts. Among various
approaches, immobilizing photocatalyst particles onto some kind of supporter is effective at achieving such an objective. Hence, ZnO nanoparticles immobilized montmorillonite [13], Nano-TiO$_2$-loaded activated carbon fiber [14], TiO$_2$-montmorillonite composite [15], acid-treated vermiculite supported TiO$_2$ [16], TiO$_2$ supported silica nanolayers [17], TiO$_2$/HZSM-5 composite [18], and Ag–TiO$_2$ photocatalyst supported on glass fiber [19] were synthesized to improve the dispersity of photocatalyst particles and, consequently, photocatalytic performances.

With regard to bismuth-based loaded photocatalysts, there have been some reports as well. Wang et al. [20] synthesized Bi$_2$O$_3$/HZSM-5 composite photocatalysts via a facile ion-exchange method. The results showed that the Bi$_2$O$_3$/HZSM-5 composite photocatalyst acquires the highest photocatalytic activity for rhodamine B degradation at the optimal loading with 18 wt % Bi$_2$O$_3$ and proposed the synergistic effect between HZSM-5 and Bi$_2$O$_3$, namely, the special structure of HZSM-5 increased the number of the active sites to adsorb more dye molecules and photodegraded them on the Bi$_2$O$_3$ photocatalyst. Zhang et al. [21] immobilized the Bi$_2$WO$_6$/Bi$_2$O$_3$ composite onto the polyurethane sponge and obtained enhanced photocatalytic activity and reusability towards rhodamine B degradation. Jiao et al. [22] prepared the Mg/Al layered double hydroxide loaded Pd(II)-Bi$_2$O$_3$ via impregnation and calcination technique. The results displayed that the sample possessed high crystallinity, large specific surface area, and broad absorption in the visible region, which contributed to its excellent photocatalytic activity for methylene blue degradation.

To overcome the recycle problem thoroughly, Al$_2$O$_3$ balls with an average diameter of 1 mm were used as the substrate to prepare bismuth-based photocatalyst coatings. Metallic Bi powder was employed as the starting material to be coated on the surface of Al$_2$O$_3$ balls via a mechanical ball milling method, and Bi$_2$O$_3$ coatings were obtained by sintering the above Bi coatings. The composition and structure evolution rules of the as-synthesized samples were analyzed based on XRD (X-ray powder diffraction) patterns and SEM (scanning electron microscope) observations. The optical properties and the photo-degradation performances of the samples were also studied with the aim of providing a new type of bismuth-based semiconductor photocatalyst coating that is applicable to practical water cleaning or other contaminants disposal.

2. Experimental

2.1. Preparation of Bi$_2$O$_3$ Photocatalyst Coatings

Metallic Bi powder (purity of 99.5%) and Al$_2$O$_3$ balls (purity of 98.5%, average diameter of 1 mm) were used as the coating material and the substrate, respectively. The Bi coatings were prepared according to the following process: 20 g Bi powder and 30 g Al$_2$O$_3$ balls were poured into an Al$_2$O$_3$ bowl with a volume of 250 mL, which subjected to milling in a planetary ball mill at the rotation speed of 290 rpm for 10 h.

The series of Bi$_2$O$_3$ coatings were fabricated by calcining the above Bi coatings in an electric furnace at 673, 773, 873, and 973 K for different time (2, 5, and 10 h) and the corresponding samples were denoted as BC-673-2, BC-673-5, BC-673-10, BC-773-2, BC-773-5, BC-773-10, BC-873-2, BC-873-5, BC-873-10, BC-973-2, BC-973-5, and BC-973-10, respectively.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed on a Bruker D8 ADVANCE unit (Bruker, Billerica, MA, USA) using Cu Kα radiation to identify the crystalline phases of the coatings. The surface and cross-section morphologies of the coatings were observed by scanning electronic microscopy (SEM) on a Hitachi S-4800 microscope (Hitachi, Tokyo, Japan). The element valence state of Bi was analyzed with X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 250Xi energy spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The UV-Vis diffuse reflectance spectra of the coatings were recorded on a Lambda 750S UV/VIS/NIR spectrometer (PerkinElmer, Waltham, MA, USA).
Additionally, the absorbance of malachite green (MG) aqueous solution was tested with a 722 Vis spectrophotometer (Sunny Optical Technology (Group) Company Limited, Yuyao, China).

### 2.3. Photocatalytic Activity

The photocatalytic activities of the coatings were investigated by photodegradation of MG solution with concentration of 10 mg/L, which was performed in a CEL-LAB500 Photocatalytic Reactor from CEAULIGHT (Beijing, China). In detail, 0.1 g coatings were dispersed in 50 mL MG solution. Then, 500 W Xe lamp (light density was 75% ± 5% mW/cm²) was turned on to carry out the degradation experiment. During the reaction period, certain amount of MG solution was taken out, centrifuged to separate the photocatalyst, and the residual MG concentration was analyzed by the spectrophotometer at regular intervals.

### 3. Results and Discussion

#### 3.1. XRD Patterns

The XRD patterns of Bi and Bi₂O₃ coatings prepared at different oxidation temperature or time are displayed in Figure 1. The characteristic diffraction peaks of the as-prepared Bi coatings can be indexed to hexagonal Bi consistent with PDF card No. 44-1246. After thermal oxidation above 673 K, the Bi coatings all transformed to Bi₂O₃ coatings even though the oxidation was only maintained for 2 h. When the Bi coatings were oxidized at 673 and 773 K for 2 h, monoclinic Bi₂O₃ coatings were prepared. With the time extending to 5 and 10 h, the as-prepared Bi₂O₃ coatings not only consisted of monoclinic Bi₂O₃ phase (labeled by hollow square, PDF card No. 41-1449) but also triclinic Bi₂O₃ phase (labeled by circle, PDF card No. 50-1088). Nevertheless, for the coatings oxidized at 873 and 973 K, mixed-phase Bi₂O₃ were always obtained with the oxidation time ranging from 2 to 10 h. Additionally, the diffraction peaks from triclinic Bi₂O₃ became stronger with the temperature or time raising. Consequently, the coatings composition evolved from single phase to mixed phases with prolonged time at lower temperature or heightened temperature. Moreover, almost all the diffraction peaks of the samples shifted to smaller angel with the oxidation time prolonged, which may result from stress release that accumulated during the ball milling process.

![XRD Patterns](image)

**Figure 1.** XRD patterns of the as-prepared coatings: (a) BC-673-2, BC-673-5, BC-673-10, BC-773-2, BC-773-5, BC-773-10; (b) BC-873-2, BC-873-5, BC-873-10, BC-973-2, BC-973-5, BC-973-10.

#### 3.2. Microstructure Evolution of the Coatings

Figure 2a shows the surface and cross-section SEM images of initial Bi coatings. It could be found that continuous Bi coatings were formed by coalescence of the discrete islands on Al₂O₃ ball after mechanical ball milling at 290 rpm for 10 h. The surface of Bi coatings was relatively smooth
and the connection trace was obvious. From the cross-section image, one can see Bi coatings with average thickness of 30 μm were obtained. After the Bi coatings were thermally oxidized at different temperature for different time, a series of Bi₂O₃ coatings with harsh surface derived from distinctly different oxidation degree were synthesized. As a typical example, the micromorphologies of the BC-873-5 sample are displayed in Figure 2b.

![Figure 2](image_url)

Figure 2. The surface and cross-section morphologies of (a) Bi coatings and (b) BC-873-5.

To clarify the microstructure transformation of the Bi₂O₃ coatings with calcination temperature and time, the high-resolution SEM images of the coatings are revealed in Figure 3. When the Bi coatings were oxidized at 673 K for 2 h, Bi₂O₃ crystals grew into thin nanosheets along the radial direction of the ball and interwined with each other to form flower-like shapes at some surface areas. With the oxidation time prolonged to 5 h, large amounts of small nanosheets along the tangential direction of the ball were visibly displayed, and some nanosheets debris also existed along the radial direction. After the oxidation that lasted for 10h, the Bi coatings were oxidized adequately and formed large staggered nanosheets along the radial direction of the ball. Elevating the temperature to 773 K resulted in completely different growth direction of Bi₂O₃ crystals. Specifically, at the first oxidation stage, the Bi₂O₃ crystals appeared as irregular particles, which grew along the tangential direction of the ball. Then, nanosheets along the radial direction of the ball gradually occurred with the oxidation preserved for 5 h, and flower-like structure stacked by nanosheets were almost completely formed when the time prolonged to 10 h. The same structure evolution tendency was observed for Bi₂O₃ coatings sintered at 873 K, except that larger polygonal Bi₂O₃ crystals scattered fine nanoparticles on its surface were formed, and much fewer nanosheets along the radial direction of the ball were observed, even when the time increased to 5 and 10 h. For Bi₂O₃ coatings prepared at 973 K, much larger polygonal Bi₂O₃ crystals similarly scattered fine nanoparticles always emerged along the tangential direction of the ball in spite of the oxidation duration of 10 h. Hence, from the structure evolution rules of Bi₂O₃ coatings, it could be generally concluded that lower temperature apt to form radial growth structure with nanosheets was interlaced, and yet higher temperature apt to generate tangential growth structure consisted of irregular polygonal crystals and nanoparticles.
was elevated to 773, 873, and 973 K, the oxidation rates of Bi coatings were accelerated and the Bi coatings were relatively thicker, which hindered the Bi diffusion and thereby O2 diffusion increased, resulting from sufficient O2 around the coatings surface decreased and therefore Bi diffusion dominated, which led to overall radical growth of Bi2O3 crystals along the surface of Al2O3 ball. However, when temperature was elevated to 773, 873, and 973 K, the oxidation rates of Bi coatings were accelerated and the Bi2O3 coatings were relatively thicker, which hindered the Bi diffusion and thereby O2 diffusion dominated the oxidation, leading to tangential growth of Bi2O3 crystals. When time increased, O2 around the coatings’ surface decreased. Thus, the oxidation was dominated by Bi diffusion and radical growth of Bi2O3 crystals emerged. The growth tendency of Bi2O3 crystals on the surface of Al2O3 ball with calcination time is briefly illustrated in Figure 4. Specifically, the irregular crystals gradually grew larger along the tangential direction of the balls with the oxidation time extended and at appropriate time; Bi2O3 nanosheets along the radial of the balls appeared, which continued to increase and completely

Figure 3. The surface morphologies of Bi2O3 coatings: (a1) BC-673-2; (a2) BC-673-5; (a3) BC-673-10; (b1) BC-773-2; (b2) BC-773-5; (b3) BC-773-10; (c1) BC-873-2; (c2) BC-873-5; (c3) BC-873-10; (d1) BC-973-2; (d2) BC-973-5; (d3) BC-973-10.

3.3. Structure Evolution Mechanism

Based on the above SEM images analysis, the structure evolution mechanism was deduced as follows. When the Bi coatings were oxidized at 673 K, Bi and O2 diffusion first simultaneously occurred, resulting from sufficient O2 around the coatings surface and active Bi element; then, with time prolonged, O2 around the coatings surface decreased and therefore Bi diffusion dominated, which led to overall radical growth of Bi2O3 crystals along the surface of Al2O3 ball. However, when temperature was elevated to 773, 873, and 973 K, the oxidation rates of Bi coatings were accelerated and the Bi2O3 coatings were relatively thicker, which hindered the Bi diffusion and thereby O2 diffusion dominated the oxidation, leading to tangential growth of Bi2O3 crystals. When time increased, O2 around the coatings’ surface decreased. Thus, the oxidation was dominated by Bi diffusion and radical growth of Bi2O3 crystals emerged. The growth tendency of Bi2O3 crystals on the surface of Al2O3 ball with calcination time is briefly illustrated in Figure 4. Specifically, the irregular crystals gradually grew larger along the tangential direction of the balls with the oxidation time extended and at appropriate time; Bi2O3 nanosheets along the radial of the balls appeared, which continued to increase and completely
spread over the whole surface of the balls. Thus, Bi$_2$O$_3$ coatings with radial growth structure assembled by nanosheets could be easily realized at lower temperature lasting for longer time, while those with tangential growth structure could be simply achieved by controlling the temperature at higher level accompanied by relatively shorter oxidation time.

![Figure 4](image-url)  
**Figure 4.** The growth tendency of Bi$_2$O$_3$ crystals on the surface of Al$_2$O$_3$ ball with calcination time increasing.

3.4. XPS

The surface chemical composition and valence state of Bi element in BC-873-5 were investigated by XPS analysis, as illustrated in Figure 5. The binding energy was corrected by C 1s adventitious peak. Figure 5a shows the XPS survey spectra of BC-873-5, in which Bi and O elements can be clearly identified, confirming the formation of bismuth oxide. From the high resolution spectra of Bi element (Figure 5b), two strong peaks located at 158.98 and 164.28 eV are assigned to Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively, which is in agreement with the reported values, indicating Bi$^{3+}$ in the coating. The binding energy of Bi 4f peaks in BC-873-5 shifted to a larger value compared to BC-873-2 [23], implying the local environment and electron density surrounding Bi cation changed with the oxidation further proceeding. Figure 5c presents the high-resolution O 1s spectrum. The spectrum can be deconvoluted into two peaks. The peak at 529.7 eV is characteristic of O$^{2-}$ in Bi–O bonds, while that at 530.9 eV is characteristic of surface hydroxyl groups, which is very closed to the values reported in the literature [24,25].

![Figure 5](image-url)  
**Figure 5.** (a) XPS spectrum of BC-873-5; High-resolution XPS spectra of (b) Bi 4f and (c) O 1s in BC-873-5.
3.5. UV-Vis Diffuse Reflectance Spectra

UV-Vis diffuse reflectance spectra were measured to learn the optical properties of the as-prepared Bi$_2$O$_3$ coatings, shown in Figure 6. It can be noticed that when the calcination temperature was not higher than 773 K, the coatings sintered for 5 and 10 h showed apparently enhanced absorption abilities for visible light compared to those sintered for 2 h. However, there was no obvious difference among the absorption spectra of the BC-873 and BC-973 samples except BC-873-5, which displayed stronger absorption for visible light. According to the extrapolation principle, the absorption edges for BC-673 and BC-773 samples ranged from 526 to 536 nm, while those for BC-873 and BC-973 samples ranged from 532nm to 563nm, corresponding to band gaps of 2.20 to 2.41 eV according to the relationship between band gap ($E_g$) and absorption edge ($\lambda$) expressed as $E_g = 1240/\lambda$.

![Figure 6](image_url) UV-Vis diffuse reflectance spectra of the as-prepared coatings: (a) BC-673-2, BC-673-5, BC-673-10, BC-773-2, BC-773-5, BC-773-10; (b) BC-873-2, BC-873-5, BC-873-10, BC-973-2, BC-973-5, BC-973-10.

3.6. Photocatalytic Activities for Organic Dye

The photocatalytic activities of as-prepared coating samples were evaluated via photo-degradation of MG aqueous solution under simulated solar irradiation. The MG degradation efficiencies over the series of Bi$_2$O$_3$ photocatalyst coatings are displayed in Figure 7a. As shown, Bi$_2$O$_3$ photocatalyst coatings calcined at higher temperature (873 or 973 K) generally demonstrated higher activities for MG degradation comparable to that calcined at lower temperature (673 or 773 K). Additionally, the coatings calcined for 5 h possessed little better performances than those obtained at 2 or 10 h for all the series of samples. It is deduced that composition-like ratio of the two different Bi$_2$O$_3$ phases, microstructure, and particle size, and other related properties such as light absorption ability, comprehensively contributed to the activity difference among these coatings. Based on the XRD patterns, it can be inferred that mixed-phase Bi$_2$O$_3$ coatings degraded more dye than single-phase ones as triclinic Bi$_2$O$_3$ possessed better activity than monoclinic Bi$_2$O$_3$, as evidenced in the literature [26]. Besides, appropriate ratio of triclinic Bi$_2$O$_3$ and monoclinic Bi$_2$O$_3$ phases also played key role for the coating photocatalytic performances. The coatings with relatively higher ratio of triclinic Bi$_2$O$_3$ to monoclinic Bi$_2$O$_3$ demonstrated better performances, which was confirmed by higher activities of the BC-873 and BC-973 samples than BC-673 and BC-773 samples; yet, if the ratio of triclinic Bi$_2$O$_3$ to monoclinic Bi$_2$O$_3$ further increased, the coating photocatalytic activities basically showed a downward trend, exactly as the BC-973 samples contrast to BC-873 samples. In addition, in our case, Bi$_2$O$_3$ coatings with tangential growth structure and polygonal Bi$_2$O$_3$ crystals showed red shift of absorption edges, which led to much superior photocatalytic performances as well. Last, the highest activity was observed over BC-873-5 and approximately 91.49% of MG degradation efficiency was achieved after irradiating for 180min. The control experiments were also carried out and the results are shown in Figure 7b, from which one can see that when the substrate was used, approximately
29.93% of MG was degraded. Moreover, if no catalyst was added or no light used, the degradation efficiencies of MG decreased to 14.66% and 6.3%, respectively, which confirmed the key role of both photocatalyst and light. Besides, the reaction rate constants of the samples for MG degradation were obtained according to the method described in the literature [23] and were summarized in Table 1.

The reusability of the photocatalyst coating was also investigated by selecting BC-873-5 as the example. The repeated experimental results are shown in Figure 7c, from which it can be noticed that the photocatalytic activity of BC-873-5 reduced by a certain extent after three cycles, in spite of this, the degradation efficiency for MG was still maintained above 80%. These results evidently proved the validity of the coating as excellent and easily recycled photocatalysts for organic dye degradation.

![Figure 7](image-url)  
**Figure 7.** The degradation efficiencies of MG solution over the series of Bi₂O₃ photocatalyst coatings: (a) after irradiating for 180 min; (b) control experiment results; and (c) the reusability of BC-873-5.

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<th>Samples</th>
<th>Rate Constants (min⁻¹)</th>
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<tr>
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4. Conclusions

Bi$_2$O$_3$ photocatalyst coatings were developed via a ball milling followed by the thermal oxidation method. Oxidation under different temperatures and times resulted in quite different compositions and structures, which affected the related performances. The results showed that monoclinic Bi$_2$O$_3$ coatings were obtained at 673 or 773 K for 2 h, while oxidation at a higher temperature and a longer time resulted in mixed-phase Bi$_2$O$_3$ coatings. Moreover, Bi$_2$O$_3$ coatings with radial growth structure assembled by nanosheets could be easily realized at a lower temperature lasting for longer time, while those with a tangential growth structure could be simply achieved by controlling the temperature at a higher level accompanied by a relatively shorter oxidation time. Photo-degradation of malachite green solution under simulated solar irradiation demonstrated that the developed coatings possessed good photocatalytic activities and cycle performances. The easily recycled coatings provide a type of visible-light-driven photocatalyst suitable for practical water treatment application.

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Author Contributions: Lijun Cheng conducted the experiments and was the lead author. Liang Hao was the internal guider and Yun Lu was the external consultant.

Conflicts of Interest: The authors declare no conflict of interest.

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