{0 1 0}-FACET EXPOSED $BiSbO_4$ MICROSPHERES: LOW-TEMPERATURE SYNTHESIS AND METHYL ORANGE PHOTODEGRADATION ACTIVITY

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Nguyen Duc Van*[1], Doan Tuan Anh[1], Ta Thi Thao[2]
1. Institute of Materials Science, Vietnam Academy of Science and Technolog,
18 Hoang Quoc Viet, Caugiay, Hanoi 100000, Vietnam.
2. Faculty of Chemistry, VNU University of Science
19 Le Thanh Tong, 100000, Vietnam.
Email: vannd@ims.vast.ac.vn

TÓM TẮT

TỔNG HỢP VÀ NGHIÊN CỨU HOẠT TÍNH QUANG XÚC TÁC PHÂN HỦY METYL DA CAM CÁC VI CẦU $BiSbO_4$ CÓ ĐỊNH HƯỚNG MẶT NGOÀI {0 1 0}

Các mẫu vật liệu $BiSbO_4$ đơn pha được chế tạo bằng qui trình thủy nhiệt ở nhiệt độ thấp từ các tiền chất: $Bi(NO_3)_3$, HNO_3, Sb_2O_3 và ethylenediaminetetraacetic acid (EDTA). Các kết quả đo đặc trưng bằng các phương pháp nhiễu xạ tia X, kính hiển vi điện tử quét và kính hiển vi điện tử truyền qua phân giải cao chỉ ra rằng các mẫu đã chế tạo có chứa các vi cầu $BiSbO_4$ có chứa các hạt nano dạng hạt gạo có định hướng mặt ngoài {0 1 0}. Hiện tượng tăng đáng kể hiệu suất quang xúc tác phân hủy metyl da cam của mẫu chế tạo bằng phương phá thủy nhiệt so với mẫu chế tạo bằng phương pháp phản ứng pha rắn được giả thiết là do có phần đóng góp của các mặt ngoài {0 1 0} của các hạt nano $BiSbO_4$ dạng hạt gạo.
***Từ khóa**: $BiSbO_4$,vi cầu, định hướng mặt ngoài {0 1 0}, hoạt tính quang xúc tác.*

1. INTRODUCTION

The recent intensive studies on finding out alternatives to titanium dioxide in the field of photocatalysis led to a variety of novel photocatalysts including both UV and visible light (Vis) photoactive materials [1-5]. Similar to TiO_2, for these photocatalysts, crystal facet engineering has been applied as a novel efficient solution to enhance their photocatalytic activity and received much attention currently [6-9]. It is indicated in literature that for the case of photocatalytic samples enclosed by certain exposed facets, the surface energy of textured grains of these samples is higher than that of random oriented ones. As a result, these faceted grains enable to accelerate photocatalytic process stronger due to the adsorption-desorption rates of available species existing on the surface become faster [10]. It should be mentioned that, in order to engineering the shapes of photocatalysts to possess desirable exposed facets, the presence of structure-directing agents was often necessary due to the fact that the facets with high reactivity tend to diminish rapidly to minimize surface free energy during the crystal growth [11]. Considering the case of Bi-based ternary oxides, a novel promising photocatalyst for many applications such as environmental remediations, water splitting, CO_2 and energy conversion, the research approach of crystal facet engineering was employed for several UV- and Vis-photoactive compounds. For the case of bismuth(III) orthovanadate, $BiVO_4$, not only low- and high-index facet exposed but also coexposed

photocatalysts were already designed to boost the photogenerated charge separation, and as a result, to increase the photocatalytic activity under visible-light irradiation [12-14]. For BiOX (X = Cl, Br, I), another Bi-based Vis-photoactive compound, many results on tailoring its exposed crystal facets were found in literature [15-18]. Bismuth(III) orthophosphate, $BiPO_4$, a UV-photocatalyst with different low-index exposed facets and enhanced photocatalytic activity were also studied experimentally and theoretically [19, 20]. To the best of our knowledge, however, the crystal facet engineering in both senses of with and without structure-directing agents has not been reported yet to enhance the photocatalytic activity of $BiSbO_4$, a potential UV-photoactive compound [21-24].

We report herein the hydrothermal synthesis of $BiSbO_4$ microspheres with {0 1 0}-exposed facets. The photocatalytic activity of the synthesized samples was also tested via methyl orange photodegradation reaction under UV irradiation.

2. EXPERIMENTAL

To synthesize $BiSbO_4$, $Bi(NO_3)_3{\cdot}5H_2O$ (Aldrich), Sb_2O_3 (Aldrich), HNO_3 (BDH), EDTA were used without further purification. In detail, 0.146 g Sb_2O_3 (0.5 mmol) and 0.292 g EDTA (1 mmol) were added into a beaker containing 0.485 g (1 mmol) of $Bi(NO_3)_3{\cdot}5H_2O$ dissolved in a certain amount of 4M HNO_3 during magnetic stirring. The resulting mixture was subsequently transferred into a 100-mL Teflon-lined stainless steel autoclave, of which 75% of the volumetric capacity was filled by deionized water. The auctoclave was then heated at 160 ^oC for 24h under autogenous pressure. After the hydrothermal reaction finished and was cooled down to room temperature naturally, the as-prepared light yellow solids were filtered, washed with distilled water until the neutral pH was reached, and dried at 60 ^oC for 12 hours. For the sake of comparison, the bulk $BiSbO_4$ sample with random orientation was also prepared by using the traditional solid-state reaction as described elsewhere [25].

The structural, microstrutural and optical properties of synthesized samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer, CuK_α radiation (λ = 1.5406 Å)), high resolution transmission electron microscopy (HR-TEM, Jeol 2100), field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and diffuse-reflectance UV-Vis spectrometry (DR-UV-Vis, Jasco V670).

The photodegradation of methyl orange in aqueous solution over the synthesized samples (0.1 g) was carried out under UV irradiation with a 70W UV lamp (λ = 365 nm; light intensity: 1.0 $mW.cm^{-2}$). Prior to starting the photocatalytic reaction, this solution was stirred for 60 min in the dark before being irradiated to gain an adsorption-desorption equilibrium between the photocatalyst's surface. 5 mL of irradiated solution was withdrawn at each interval of 30 minutes during the photodegradation process. This aliquot was then centrifuged to remove all available suspended photocatalyst for methyl orange concentration evaluation by using a Shimazdu-1800 spectrometer.

3. RESULTS AND DISCUSSION

XRD patterns of the samples synthesized by EDTA-assisted hydrothermal and solid-state reactions were presented in Figure 1. It is clearly that for both these samples, diffraction peaks in XRD diagrams at 2-theta values of 27.29; 30.77; 33.37; 36.76 and 50.60^o can be indexed to (1 1 -2); (1 1 2); (2 0 0); (0 2 0) and (2 2 0) lattice planes of the monoclinic $BiSbO_4$ phase (PDF card: 01-086-0126), respectively. Interestingly, the $(I_{(0\ 2\ 0)})/ I_{(1\ 1\ 2)})$ intensity ratio of (1 1 2) and (0 2 0) peaks of the hydrothermal synthesized sample was 0.44, pronouncedly higher than that (0.19) of the standard pattern of monoclinic $BiSbO_4$ and of the bulk sample also. Thus, it can be suggested that by using $Bi(NO_3)_3$, HNO_3, Sb_2O_3 as hydrothermal precursors with the presence of EDTA as a structure-directing agent, crystal

growth is preferably oriented along *b*-axis crystallographic direction.

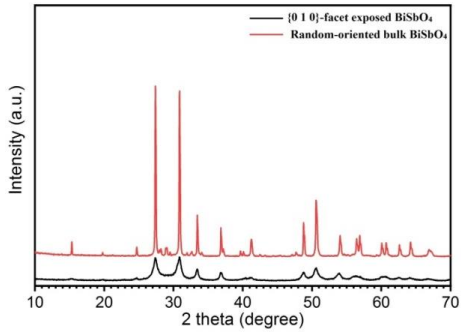
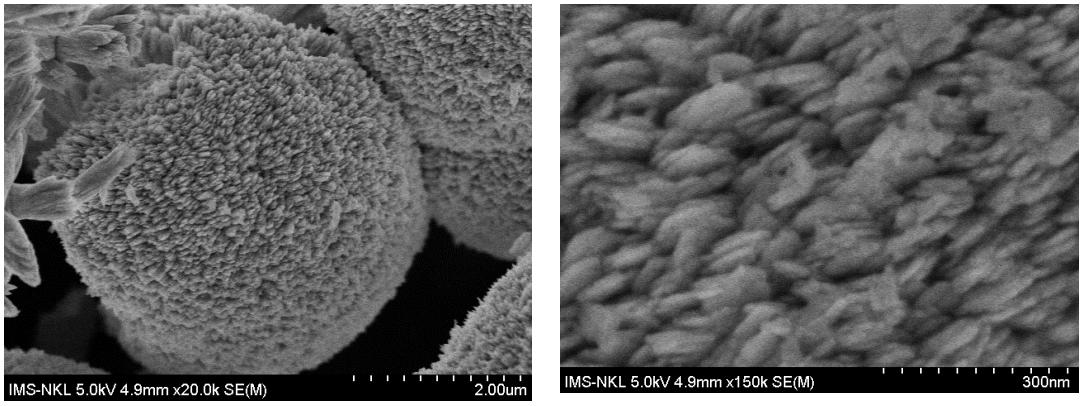


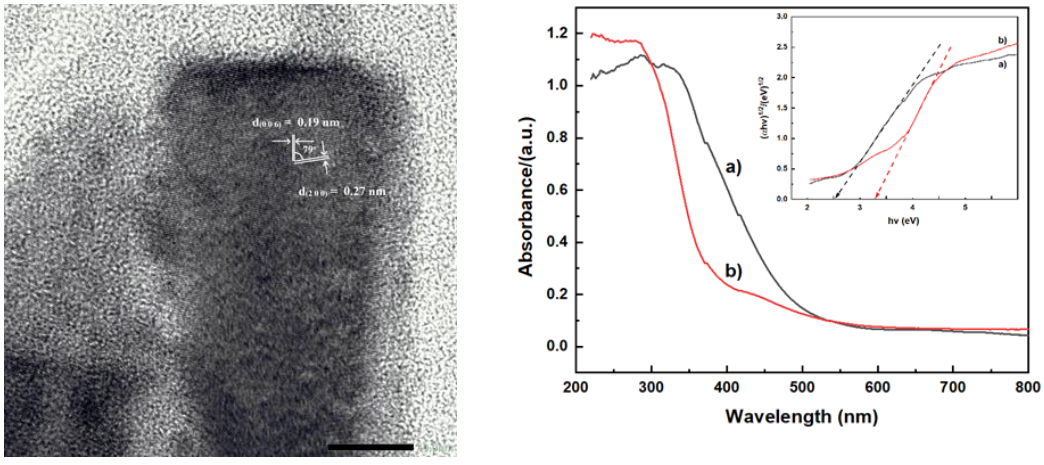
Figure 1. XRD patterns of the {0 1 0}-facet exposed and the random-oriented bulk $BiSbO_4$ samples

From the FE-SEM image shown in Fig. 2, microspheres with average diameters of 4μm were found to dominate in the EDTA-assisted hydrothermal synthesized sample. Moreover, each of these microspheres was comprised of nanoseeds with an average length of 60 nm and width of 15 nm (Fig. 2, inset). In the HRTEM image of a typical nanoseed, two observed lattice fringes with the spacing of 0.27 and 0.19 nm and the interfacial angle of 79.0° were corresponding to (2 0 0) and (0 0 6) planes of $BiSbO_4$, respectively (Fig. 3A). Based on calculation from these data, the nanoseed was concluded to be enclosed by {0 1 0} facets. Thus, HRTEM analysis confirmed the orientation grain growth along [0 1 0] crystallographic direction for the studied sample.



a) b)

Figure 2. SEM images of the {0 1 0}-facet exposed $BiSbO_4$ sample with magnification of a) 20,000 and b) 150,000



A) B)

Figure 3. A) HRTEM image of the {0 1 0}-facet exposed $BiSbO_4$ sample; B) DRUV-Vis spectra and Tauc's plot of a) the random-oriented bulk $BiSbO_4$ and b) the {0 1 0}-facet exposed samples

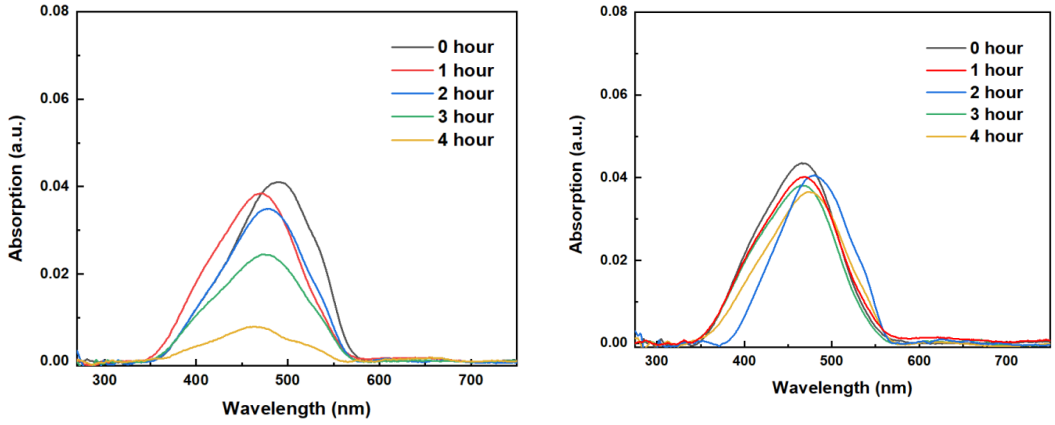
The DRUV-Vis spectra and derived Tauc's plots of the {0 1 0}-facet exposed and the random-oriented bulk $BiSbO_4$ samples were demonstrated in Fig. 3B. The band gap energy of the {0 1 0}-facet exposed $BiSbO_4$ sample was determined to be 3.30 eV while that of the random oriented $BiSbO_4$ sample valued at 2.55 eV. The significant difference in band gap energy of these two samples can be explained by the existence of oxygen vacancies in the bulk sample, similar to the published work [25]. The photodegradation of methyl orange over the {0 1 0}-facet exposed $BiSbO_4$ sample and the bulk counterpart under UV irradiation was presented in Figs. 4 and 5. After 4 hours of irradiation, the photodegradation efficiency of the faceted $BiSbO_4$ microspheres was as high as 80 %, considerably superior to that of the bulk sample (16 %). The existence of {0 1 0}-exposed facets was proposed to be the main factor leading to the increase in dye photodegradation efficiency of the {0 1 0}-facet exposed $BiSbO_4$ microspheres. The mechanism of MO photodegradation reaction can be described by the following steps, similar to that reported in literature [14, 26, 27].

1) Under UV irradiation, $BiSbO_4$ absorbed suitable irradiated photons to produce free electrons (Eq. (1)), which are then captured by dissolved oxygen (O_2) in aqueous medium to produce free radicals like $O_2^{\cdot-}$ and $OH^{\cdot}$ (Eqs. 2 and 3).

$$h\upsilon + BiSbO_4 \rightarrow BiSbO_4(h^+) + e^-_{CB} \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\cdot-} \quad (2)$$

$$e^- + O_2 + 2H^+ \rightarrow OH^{\cdot} \quad (3)$$



a) b)

Figure 4. UV absorption spectra of the time dependent photodegradation of MO using: a) the {0 1 0}-facet exposed and b) the random-oriented bulk $BiSbO_4$ as a photocatalyst

2) The methyl orange molecules, which were adsorbed on the surface of $BiSbO_4$ microspheres (MO_{ad}), are oxidized by photogenerated holes and other free radicals such as $O_2^{\cdot-}, OH^{\cdot}$ to form photodegraded products like CO_2, H_2O and other by-products.

$$MO_{ad} + h^+ / OH^{\cdot} / O_2^{\cdot-} \rightarrow CO_2 + H_2O + \text{by-products} \quad (4)$$

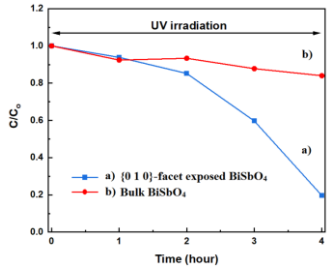


Figure 5. Methyl orange photodegradation under UV irradiation of: a) the {0 1 0}-facet exposed and b) the random-oriented bulk $BiSbO_4$ samples.

4. CONCLUSION

The $BiSbO_4$ microspheres with {0 1 0}-exposed facets were synthesized by hydrothermal method at 160ºC for 24 hrs from $Bi(NO_3)_3$, HNO_3, Sb_2O_3 and EDTA. The photodegradation efficiency of the faceted $BiSbO_4$ microspheres was as high as 80 %, considerably superior to that of the bulk sample (16 %). The significant increase in methyl orange photodegradation efficiency of the {0 1 0}-facet exposed $BiSbO_4$ sample in comparison to the bulk one was probably due to the existence of {0 1 0}-exposed facets.

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