



Low-temperature hydrothermal synthesis of BiPO₄ for Rhodamine B removal

Nguyen Duc Van*, Doan Tuan Anh

Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi 100000, Vietnam

*Email: vannd@ims.vast.ac.vn

ARTICLE INFO

Received: 15/12/2021

Accepted: 20/3/2022

Published: 30/3/2022

Keywords:

BiPO₄, Photocatalysis,
 Rhodamine B, Hydrothermal
 method.

ABSTRACT

The synthesis and Rhodamine B removal efficiency of monazite monoclinic BiPO₄ by hydrothermal route using Bi(NO₃)₃·5H₂O, K₂HPO₄·3H₂O and HNO₃ as starting materials were presented in this work. The obtained samples were characterized by X-ray powder diffraction, high-resolution transmission field-emission scanning electron microscopy and diffuse reflectance UV-Vis spectrometry. The results showed that, by selecting suitable reaction parameters, the pure monazite monoclinic phase of BiPO₄ was received readily at hydrothermal temperature as low as 130 °C, considerably lower than that reported previously. The obtained monazite monoclinic phase of BiPO₄ powders exhibited a high removal efficiency of 96% for 150 min under 365nm - UV irradiation. The mechanism of the Rhodamine B photodegradation reaction over the synthesized monazite monoclinic BiPO₄ was also proposed.

Introduction

Novel bismuth-containing complex oxide-based photocatalysts have been drawn much attention in recent decades with numerous promising applications such as environmental remediation, water splitting, etc. [1-4]. Among them, bismuth(III) orthophosphate, BiPO₄, was known as a low-cost, chemical stable and highly photoactive alternative to traditional titanium dioxide [5-8]. However, most of current works concentrated on the monazite monoclinic polymorphic type (nMBIP, space group: P2₁/n) of BiPO₄ due to the fact that its photocatalytic activity is ten times higher than that of other polymorphisms, namely, monoclinic (mMBIP, space group: P2₁/m) and hexagonal (HBIP, space group: P3₁21) [9]. For the synthesis of this nMBIP photocatalyst, the hydrothermal method was the most frequently used in comparison to others like sol-gel [10], electrospinning [10], solvothermal [11]. However, it

was surveyed in literature that, in order to obtain the pure nMBIP powders, the hydrothermal temperature of over or equal to 140 °C was usually required to avoid the phase competition with mMBIP and HMIP polymorphisms [12-13]. Particularly, for the case of published HNO₃-assisted hydrothermal synthesis procedures without using any other additives, the pure nMBIP powders were only provided when the reaction temperature reached to 180 °C [14].

This work presented the low-temperature hydrothermal synthesis of monazite monoclinic BiPO₄ powders using Bi(NO₃)₃·5H₂O, K₂HPO₄·3H₂O and HNO₃ as starting materials. The photodegradation of Rhodamine B (RhB) under 365nm-ultraviolet irradiation over synthesized samples was also evaluated.

Experimental

Chemicals and Methods

All chemicals required for the synthesis of nMBIP powders, namely, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and HNO_3 were purchased from Sigma-Aldrich without further purification.

The characterizations of synthesized samples were carried out by using X-ray diffraction (XRD) (Bruker AXS D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), field-emission scanning electron microscopy (FESEM) (Hitachi S-4800 microscope), and diffuse reflectance UV-Vis spectrometry (DR-UV-Vis, Jasco V670 spectrometer).

Synthesis of nMBIP powders

Firstly, 0.97 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 ml of 4M HNO_3 solution during stirring. The obtaining solution was added dropwise into another beaker containing 0.456 g $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ dissolved in 40 ml of distilled water under vigorous stirring for 30 min. This mixture was transferred into a 120-ml Teflon-line stainless steel autoclave, filled up to 80% of its volume with distilled water. The hydrothermal reactions were conducted at certain temperatures ranged from 110 to 150 °C for 24 h under autogenous pressure. The resulted white solid was then collected, washed with distilled water three times before being dried at 50 °C for 12 h.

Evaluation of photocatalytic activity

0.1 g of the nMBIP sample synthesized at 130 °C for 24 h was dispersed in 100 ml of an aqueous solution of rhodamine B 5.10^{-6} M during stirring. Prior to UV irradiation with a 70W UV lamp ($\lambda = 365 \text{ nm}$; light intensity: $1.0 \text{ mW}\cdot\text{cm}^{-2}$), this solution was stirred for 60 min in the dark to obtain an adsorption-desorption equilibrium. During the photodegradation reaction, at each time interval of 30 minutes, 5 mL of testing solution was withdrawn, and centrifuged to remove the all suspended photocatalytic powders for the RhB concentration determination on a Shimadzu UV-1800 spectrophotometer. For the sake of comparison, the RhB photocatalytic test was also carried out for the blank sample (without any catalysts) with the same procedure described above.

Results and discussion

XRD patterns of the as-synthesized BiPO_4 samples synthesized hydrothermally at different temperatures for 24 h were shown in Figure 1. For the sample synthesized at 110 °C, beside the diffraction peaks that are belonging to nMBIP phase, there is another unknown peak. As temperature reached 130 °C, not only high intensity diffraction peaks at 2-theta angle of 19.02, 21.33, 27.15, 29.08, 31.19, 34.48° corresponding to the (0 1 1), (-1 1 1), (2 0 0), (1 2 0), (0 1 2), (-2 0 2) lattice planes, respectively, but also all observable peaks are well indexed to the crystalline phase of nMBIP (PDF standard card No. 15-0767). Thus, when the hydrothermal reaction was carried out at or over 130 °C, the crystalline phase of nMBIP was received purely. In comparison to reported works, this temperature value was remarkably lower while the reaction is also clearly shorter [14-15]. Thus, it is clearly that by selecting the suitable precursors, the nMBIP phase were stabilized to form while other BiPO_4 polymorphic phases were not detected.

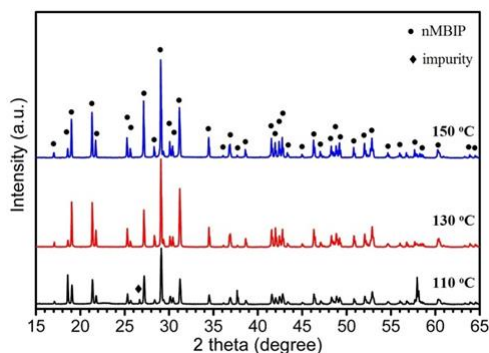


Figure 1: XRD diagrams of BiPO_4 samples synthesized hydrothermally at: a) 110; b) 130 and c) 150 °C for 24 h

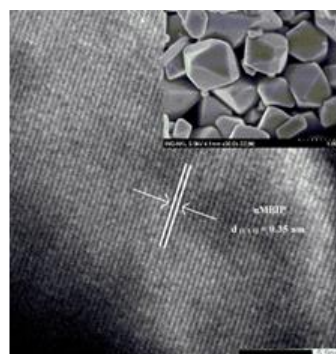


Figure 2: HRTEM and SEM (inset) images of nMBIP sample synthesized at 130 °C for 24 h

As shown in Figure 2 (inset), in the SEM image of nMBIP sample synthesized at 130 °C for 24 h, vertex-truncated octahedrons with an average size of 1.0 μm were found to be dominated. Furthermore, in the HRTEM image, lattice fringes with d -spacing value of

0.35 nm corresponding to (1 1 1) lattice plane of nMBIP phase, indicating that, microscopically, the as- sample synthesized at optimized conditions contained the monazite monoclinic polymorphic type (nMBIP, space group: P21/n) only.

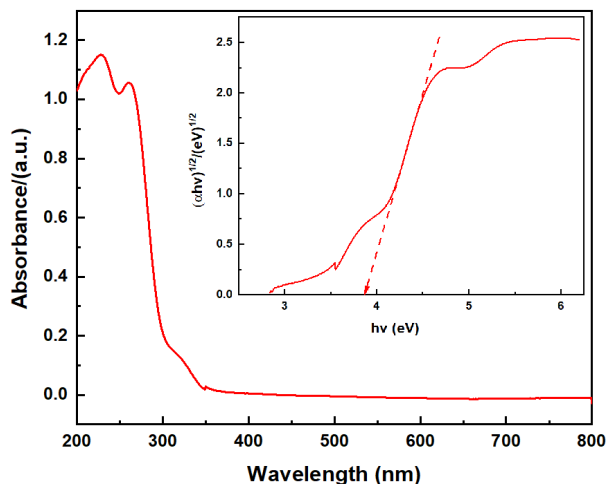


Figure 3: DR-UV-Vis spectrum and Tauc's plot of nMBIP sample synthesized at 130 °C for 24 h.

As shown in Figure 3, from the recorded DR-UV-Vis spectrum and the derived Tauc's plot, the band band energy value of 3.87 eV was calculated for the pure nMBIP sample. This value fell in the common range found for monazite monoclinic BiPO₄ compound [14, 15].

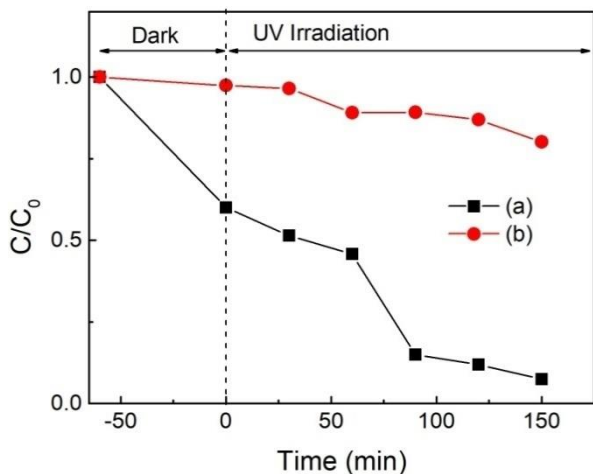
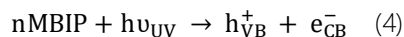


Figure 4: Photodegradation of Rhodamine B under UV irradiation over a) nMBIP and b) blank samples

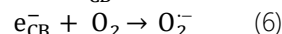
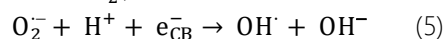
From Figure 4, the RhB removal efficiency of nMBIP for 150 min under 365nm-UV irradiation is 96.5 % while that of the blank sample valued at only 23 %. So, in comparison to the blank sample BiPO₄ sample, the nMBIP sample exhibited not only a higher photodegradation but also a higher adsorption efficiency.

Similar to Refs. [16, 17], the mechanism of the RhB photodegradation reaction in aqueous medium containing nMBIP as a photocatalyst can be proposed as follows:

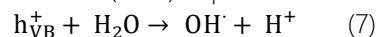
a) Photogenerating of photoexcited electrons (e_{CB}^-) in the conduction band (CB) and photoexcited holes (h_{VB}^+) in the valence band (VB) of UV-irradiated nMBIP.



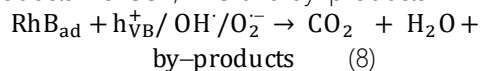
b) The oxidation of dissolved oxygen in aqueous medium by photoexcited electrons to radical species like $O_2^{\cdot-}, OH^{\cdot}$.



c) The reaction between photoexcited holes with electron donors (H₂O) to provide OH^{\cdot} free radicals



d) The oxidation of surface-adsorbed Rhodamine B (RhB_{ad}) by photoexcited holes and free radicals such as like $O_2^{\cdot-}, OH^{\cdot}$, etc. to form photodegraded products like CO₂, H₂O and by-products



Finally, the recyclability testing results of RhB over the monazite monoclinic BiPO₄ sample synthesized by hydrothermal route were tabulated in Table 1 for three recycling photocatalytic runs under 365nm-UV illumination. One can realize that the RhB removal efficiency decreased slightly to 92.5 and 90.2 % for the second and the third cycles, respectively. This slight decrease in RhB removal efficiency revealed that the synthesized nMBIP sample is reusable.

Table 1: Photodegradation recyclability test of rhodamine B over nMBIP sample synthesized at 130 °C for 24 h under UV irradiation

Number of cycles	1 st	2 nd	3 rd
RhB removal efficiency (%)	96.5	92.5	90.2

Conclusion

By selecting the suitable precursors for a facile synthesis procedure, the pure monazite monoclinic phase of BiPO₄ was received readily at hydrothermal temperature as low as 130 °C while other comparative BiPO₄ polymorphic phases were suppressed completely. The obtained monazite monoclinic phase of BiPO₄ powders exhibited a high Rhodamine B

removal efficiency of 96% for 150 min under 365nm-UV irradiation.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2019.301.

References

1. A. D. Paola, E. García-López, G. Marci, L. Palmisano, *J. Hazard. Mater.* 211-212 (2012) 3-29. <https://doi.org/10.1016/j.jhazmat.2011.11.050>
2. H. K. Timmaji, Bismuth – based oxide semiconductors: mild and practical applications, Ph. D dissertation, The Univeristy of Texas at Arlington, 2011.
3. C. M. Suarez, M. Hernandez, N. Russo, *Appl. Catal. A-General* 504 (2015) 158-170. <https://doi.org/10.1016/j.apcata.2014.11.044>
4. G. K. Tripathi, R. Kurchania, *Opt. Quant. Electron.* 49 (2017) 203-219. <https://doi.org/10.1007/s11082-017-1042-3>
5. G. Li, Y. Ding, Y. Zhang, Z. Lu, H. Sun, R. Chen, *J. Colloid Interface Sci.*, 363 (2011) 497-503. <https://doi.org/10.1016/j.jcis.2011.07.090>
6. L. She, G. Tan, H. Ren, J. Huang, C. Xu, A. Xia, *RSC Adv.*, 5 (2015) 36642-36651. <https://doi.org/10.1039/C5RA02629F>
7. X. Tian, T. Xu, Y. Wang, S. Meng, *RSC Adv.*, 7, (2017) 36705-36713. <https://doi.org/10.1039/C7RA06560D>
8. C. Pan, Y. Zhu, *Environ. Sci. Technol.*, 44 (2010) 5570-5574. <https://doi.org/10.1021/es101223n>
9. C. Pan, D. Li, X. Ma, Y. Chen, Y. Zhu, *Catal. Sci. Technol.*, 1 (2011) 1399-1405. <https://doi.org/10.1039/C1CY00261A>
10. G. Liu, S. Liu, Q. Lu, H. Sun, Z. Xiu, *Ind. Eng. Chem. Res.*, 53 (2014) 13023-13029. <https://doi.org/10.1021/ie4044357>
11. F. Xue, H. Li, Y. Zhu, S. Xiong, X. Zhang, T. Wang, X. Liang, Y. Qian, *J. Solid State Chem.*, 182 (2009) 1396-1400. <https://doi.org/10.1016/j.jssc.2009.02.031>
12. J. Wang, J. Li, H. Li, S. Duan, S. Meng, X. Fu, S. Chen, *Chem. Eng. J.*, 330 (2017) 433-441. <https://doi.org/10.1016/j.cej.2017.07.121>
13. Nguyen Duc Van, *Ceram. Int.*, 45 (2019) 1447-1449. <https://doi.org/10.1016/j.ceramint.2018.09.264>
14. Y. Zhang, R. Selvaraj, M. Sillanpää, Y. Kim, C.-W. Tai, *Chem. Eng. J.*, 245 (2014) 117-123. <https://doi.org/10.1016/j.cej.2014.02.028>
15. L. Li, J. Xu, C. Guo, Y. Zhang, *Front. Environ. Sci. Eng.*, 7 (2013) 382-387. <https://doi.org/10.1007/s11783-013-0504-5>
16. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, *Appl. Catal. B-Environ.*, 31 (2001) 145-157. [https://doi.org/10.1016/S0926-3373\(00\)00276-9](https://doi.org/10.1016/S0926-3373(00)00276-9)
17. Nguyen Duc Van, *Ceram. Int.*, 44 (2018) 19945-19949. <https://doi.org/10.1016/j.ceramint.2018.07.260>