Ethylene diaminotetraacetic Acid Assisted Synthesis of Bismuth Oxide/Indium Oxide Microspheres with Good Photocatalytic Performance

Zeyang Xue, a, b Yajing Mao, a Chunhu Yu, a, Mingchang Wang, c Chuangang Fan, a, † Lizhai Pei a, b, ‡

a School of Materials Science and Engineering, Anhui University of Technology, Ma’anshan, Anhui 243002, P. R. China
b Key Laboratory of Metallurgical Emission Reduction & Resources Recycling, Ministry of Education, Anhui University of Technology, Ma’anshan, Anhui 243002, P. R. China
c College of Chemistry and Chemical Engineering, Hainan Normal Technology, Haikou, Hainan 571158, P. R. China
† Corresponding author: cgfan1967@163.com
‡ Corresponding author: lzpei1977@163.com

Received: 6 February, 2021; Accepted: 23 March, 2021; Published: 3 April, 2021

Bismuth oxide/indium oxide microspheres have been synthesized by a facile ethylenediaminotetraacetic acid (EDTA)-assisted hydrothermal process using sodium bismuthate and indium nitrate as raw materials. The obtained products were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and solid ultraviolet-visible diffusion reflectance spectroscopy. XRD and SEM observations show that the obtained microspheres consist of tetragonal Bi2O3 and cubic In2O3 phases with a smooth surface and diameters between 150 nm and 1 μm. EDTA, hydrothermal temperature, and reaction time play essential roles in the formation of the bismuth oxide/indium oxide microspheres. The tetragonal Bi2O3 and cubic In2O3 phases are formed with increasing the hydrothermal temperature and the reaction time. Photocatalytic performance of the bismuth oxide/indium oxide microspheres was evaluated by photocatalytic degradation of rhodamine B in an aqueous solution with solar light irradiation. A rhodamine B degradation ratio depends on the solar light irradiation time and the microspheres dosage. Rhodamine B with 10 mg L⁻¹ can be entirely removed by more than 10 mg of the bismuth oxide/indium oxide microspheres in the 10 mL aqueous solution under solar light irradiation for 6 h.

Keywords Bismuth oxide/indium oxide microspheres; Ethylenediaminotetraacetic acid; Rhodamine B; Solar light; Photocatalysis

I. INTRODUCTION

Water pollution by different pollutants including toxic solvents, dyes, soils, and paints has been a serious social issue owing to rapid development of modern industrialization and urbanization. Rhodamine B is an important water soluble xanthene dye which has been widely applied in the fields of textile, paint, paper, plastics, and printing industries [1]. However, wastewater with rhodamine B dye can cause series of diseases including skin and visceral treat, hemorrhage, nausea, and even cancer [2, 3]. Rhodamine B is stable and difficult to be degraded under natural environment. Therefore, it is essential to remove rhodamine B in the wastewater for environmental protection and human health.

Some methods have been developed to remove rhodamine B in wastewater, such as an electrosorption method, an adsorption method using carbon derived from Gmelina aborea leaves (GALAC), and a photocatalytic removal route [4–6]. Photocatalytic removal technology takes advantages of a simple wastewater treatment process, low cost, and high efficiency, exhibiting great application potential for the removal of organic pollutants [7, 8]. Bismuth oxide belongs to a kind of efficient photocatalyst and attracts great research interest for the degradation of organic pollutants because of a low-cost preparation, a suitable band energy, and good absorbability of visible light [9, 10]. However, the photocatalytic performance of bismuth oxide for the degradation
of organic pollutants is still low under visible light irradiation which can mainly be ascribed to the limited solar light absorption and the high charge carrier recombination ratio [11, 12]. Combination structured materials by combining semiconductors with various band gaps are considered as an effective method to design high-efficiency photocatalysts based on bismuth oxide, such as carbon-bridged Bi$_2$O$_3$/TiO$_2$ nanotube arrays, Bi$_2$O$_3$-ZnO nanoparticles and CdS/BiOCl/Bi$_2$O$_3$ double composite to enhance the photocatalytic performance [13–16]. The combination with two kinds of semiconductors can adjust migration paths of photogenerated electrons and holes at the interface of the combination and can expand the visible light absorption range promoting the utilization efficiency of the solar light [17]. Indium oxide has also attracted great interest for the photocatalytic removal of organic pollutants owing to its good physicochemical stability and wide visible light absorption performance [18, 19]. Combining bismuth oxide and indium oxide to form bismuth oxide/indium oxide is expected to improve the photocatalytic performance.

In our previous research [20], sheet-shaped bismuth oxide/indium oxide heterojunctions were synthesized by simple hydrothermal route using sodium bismuthate and indium nitrate as raw materials without any surfactants. The obtained sheet-shaped bismuth oxide/indium oxide heterojunctions showed good photocatalytic performance toward rhodamine B under ambient conditions with the irradiation of natural solar light. In a typical photocatalytic reaction process, 10 mg of powder were added to the reaction cell and stirred for 20 min to separate the microspheres from the reaction solution. The entire mixture solution was covered by the natural solar light and stirred magnetically during the solar light irradiation. An aliquot was taken at the given time interval and centrifuged to separate the microspheres from the reaction solution. The photocatalytic degradation ratio (PDR) was calculated using the following formula:

\[
PDR = \left(1 - \frac{C_t}{C_0}\right) \times 100,
\]

where $C_0$ and $C_t$ are the absorbance intensity of the initial rhodamine B that reaches adsorption equilibrium and rhodamine B treated by the bismuth oxide/indium oxide microspheres at the given time interval, respectively.

III. RESULTS AND DISCUSSION

The XRD pattern of the synthesized sample obtained from 180°C for 24 h adding 5 wt% EDTA is shown in Figure 1. The positions of the diffraction peaks were consistent with those of the tetragonal Bi$_2$O$_3$ standard peaks (JCPDS card, No. 65-1209) and cubic In$_2$O$_3$ standard peaks (JCPDS card, No. 06-0416). In addition, no characteristic peaks of other phases are observed, indicating that the synthesized
sample is composed of tetragonal Bi₂O₃ and cubic In₂O₃ phases.

Morphology and size of the synthesized sample obtained from 180 °C for 24 h adding 5 wt% EDTA were analyzed through SEM observation (Figure 2). It is shown from Figure 2(a) that the bismuth oxide/indium oxide sample has regular and smooth spherical shape. The bismuth oxide/indium oxide microspheres have diameters between 150 nm and 1 μm [Figure 2(b)]. In addition, the microspheres stack on each other without aggregation, indicating that the obtained bismuth oxide/indium oxide microspheres have good dispersion. The morphology and the size of the bismuth oxide/indium oxide microspheres are similar to those of the microspheres reported by other groups [24, 25].

EDTA belongs to a kind of effective coordination compound for synthesizing functional materials with special morphologies, such as SnO₂-deposited ZnS nanorods [26] and MoS₂ nanospheres [27]. To analyze the role of EDTA on the formation of the bismuth oxide/indium oxide microspheres, the morphology and structure features of the bismuth oxide/indium oxide products obtained from various amounts of EDTA are shown in Figures 3 and 4. When no EDTA was added, hydrothermal temperature and reaction time were kept at 180°C for 24 h, the products are mainly composed of sub-microscale cubes with the width of 150–600 nm [Figure 3(a, b)]. No spherical morphology is obtained. The sub-microscale cubes morphology is entirely different from the bismuth oxide/indium oxide microspheres, confirming the role of EDTA on the formation of the spherical morphology. Adding the EDTA amount to 1 wt%, it is observed that the morphology of the products changes to sphere-like structures with diameters between 100 nm and 1 μm besides irregular particles [Figure 3(c, d)]. Increasing the EDTA concentration to 3 wt%, the products are mainly composed of spherical structures with diameters between 100 and 600 nm [Figure 3(e, f)]. The phases of the bismuth oxide/indium oxide products were identified by X-ray diffraction (XRD).

Figure 1: XRD pattern of the indium oxide/bismuth oxide microspheres synthesized from 180°C for 24 h using 5 wt% EDTA.

Figure 2: SEM images with different magnifications of the indium oxide/bismuth oxide microspheres synthesized from 180°C for 24 h using 5 wt% EDTA.

Figure 3: SEM images of the samples synthesized from 180°C for 24 h using EDTA with different concentrations; (a, b) without EDTA, (c, d) 1 wt%, and (e, f) 3 wt%.
oxide/indium oxide products obtained from different EDTA concentrations are same (Figure 4). No other phases are formed besides the tetragonal Bi₂O₃ and cubic In₂O₃ phases, showing that EDTA has no role in the phase formation of the bismuth oxide/indium oxide microspheres.

Hydrothermal temperature and reaction time have also important roles in the formation of microscale and nanoscale structures, as has been confirmed in our preceding research [28, 29]. Keeping the EDTA concentration of 5 wt%, the morphology and phase evolution of the bismuth oxide/indium oxide products with changing the hydrothermal temperature and reaction time have also been analyzed. SEM images and XRD patterns of the samples synthesized from 24 h at various hydrothermal temperatures are shown in Figure 5 and 6, respectively. It is seen that the products consist of irregular particles with the average size of 200 nm when the hydrothermal temperature was kept at 80°C [Figure 5(a, b)]. Increasing the hydrothermal temperature to 120°C, some spherical particles with diameters between 100 nm and 1 μm are formed besides irregular particles [Figure 5(c, d)]. The XRD patterns of the bismuth oxide/indium oxide products synthesized from 24 h at 80 and 120°C, respectively, are same (Figure 6), showing that both are composed of tetragonal Bi₂O₃ and cubic In₂O₃ phases.

Figure 7 shows SEM images of the samples synthesized from different reaction time at 180°C using 5 wt% EDTA. At the initial reaction stage, when the reaction time is 0.5 h at 180°C, the products are composed of irregular particles with the average size of 100 nm and no spherical structures are formed [Figure 7(a, b)]. Increasing the reaction time to
12 h, the products are mainly comprised of spherical structures with diameters between 100 and 600 nm besides a small amount of irregular particles [Figure 7(c, d)]. Different from the above-mentioned results of the structural analysis, the products are composed of an amorphous state when the reaction time was kept for 0.5 h at 180°C [Figure 8(a)]. With increasing the hydrothermal reaction time to 12 h, the amorphous state was transferred into tetragonal Bi2O3 and cubic In2O3 phases [Figure 8(b)]. The temperature and reaction time-dependent results on the formation of the bismuth oxide/indium oxide microspheres show that the hydrothermal temperature and the reaction time play important roles in the formation of microsphere morphology. The tetragonal Bi2O3 and cubic In2O3 phases are formed with the increase of the reaction time.

Based on the above-mentioned experimental results with different hydrothermal growth conditions, it is obvious that the addition of the EDTA has an essential role in the formation of the bismuth oxide/indium oxide microspheres. Sodium bismuthate and indium nitrate serve as Bi and In sources, respectively, and bismuth oxide/indium oxide nuclei are formed at the initial hydrothermal reaction stage as is confirmed from the hydrothermal temperature and reaction time-dependent results. EDTA acts as a soft template inducing the formation of the bismuth oxide/indium oxide spherical structure [30, 31]. Increasing the hydrothermal temperature and the reaction time, the bismuth oxide/indium oxide microspheres are finally formed, and EDTA was removed by centrifugation and washing processes.

Solid UV-DSR spectrum was measured to analyze the band gap of the bismuth oxide/indium oxide microspheres. Figure 9 shows a Tauc plot of the indium oxide/bismuth oxide microspheres synthesized from 180°C for 24 h using 5 wt% EDTA. The inset in the upper-left part is the solid UV-DRS spectrum of the indium oxide/bismuth oxide microspheres.

![Figure 8](image1.png)  
**Figure 8:** XRD patterns of the samples synthesized from different time at 180°C using 5 wt% EDTA; (a) 0.5 h and (b) 12 h.

![Figure 9](image2.png)  
**Figure 9:** Tauc plot of the indium oxide/bismuth oxide microspheres synthesized from 180°C for 24 h using 5 wt% EDTA. The inset in the upper-left part is the solid UV-DRS spectrum of the indium oxide/bismuth oxide microspheres.

Figure 10 shows the UV-vis absorption spectra of rhodamine B under solar light irradiation for different times using the bismuth oxide/indium oxide microspheres. (b) Degradation ratio of rhodamine B. The bismuth oxide/indium oxide microspheres were 10 mg and the rhodamine B concentration was 10 mg L⁻¹.

![Figure 10](image3.png)  
**Figure 10:** (a) UV-vis absorption spectra of rhodamine B under solar light irradiation for different times using the bismuth oxide/indium oxide microspheres. (b) Degradation ratio of rhodamine B. The bismuth oxide/indium oxide microspheres were 10 mg and the rhodamine B concentration was 10 mg L⁻¹.
The obtained bismuth oxide/indium oxide microspheres possess a narrow band gap and can absorb the visible light. Therefore, the photocatalytic performance of the obtained bismuth oxide/indium oxide microspheres was studied using cationic dye rhodamine B as a model pollutant under solar light irradiation. Figure 10(a) shows the UV-vis absorption spectra of rhodamine B with the irradiation of the solar light for different time using the bismuth oxide/indium oxide microspheres. The corresponding degradation ratio under solar light irradiation for different time is shown in Figure 10(b). To study the photo-degradability, the photocatalytic experiments were carried out under two experimental conditions: (1) the rhodamine B solution in the absence of bismuth oxide/indium oxide microspheres under solar light irradiation and (2) the rhodamine B solution in the presence of bismuth oxide/indium oxide microspheres without solar light irradiation. It is seen that the rhodamine B can only be photocatalytically degraded under solar light irradiation using the bismuth oxide/indium oxide microspheres. Increasing the solar light irradiation time, the maximum absorption peak of rhodamine B decreases obviously [Figure 10(a)]. It is observed that rhodamine B can be entirely degraded in the presence of the bismuth oxide/indium oxide microspheres and solar light irradiation after 6 h of the photocatalytic reaction time [Figure 10(b)]. Compared with the photocatalytic degradation efficiency using sheet-shaped bismuth oxide/indium oxide heterojunctions in our previous research [20], the bismuth oxide/indium oxide microspheres show a better photocatalytic performance for rhodamine B degradation under solar light irradiation.

To investigate the role of the bismuth oxide/indium oxide microspheres dosage, the dosage of the bismuth oxide/indium oxide microspheres was changed from 2.5 to 20 mg in the 10-mL rhodamine B solution. The rhodamine B concentration and the solar light irradiation time were kept at 10 mg L\(^{-1}\) and 6 h, respectively, in the whole experiments. The UV-vis absorption spectra of rhodamine B and the degradation ratio using different dosages of the microspheres are shown in Figure 11. The degradation ratio of rhodamine B increases from 41.9 to 66.5% when the microspheres dosage is changed from 0.25 to 0.5 mg mL\(^{-1}\). Further increasing the microspheres dosage to more than 1.0 mg mL\(^{-1}\), rhodamine B can be entirely photocatalytically degraded. The results may be caused by the increase in the number of the active sites on the bismuth oxide/indium oxide microspheres with increasing the microspheres dosage. The generation of ‘OH radicals, which are necessary for the photocatalytic degradation of rhodamine B, is enhanced [8]. Photo-generated electron-hole pairs are generated continuously with the bismuth oxide/indium oxide microspheres absorbing the solar light energy which is more than the band gap of the microspheres [32]. The photo-generated holes in the bismuth oxide/indium oxide microspheres react with water molecules, generating the ‘OH radicals. The ‘OH radical is a kind of strong oxidant, and organic pollutant molecules are decomposed into...
biodegradable small molecules [33]. The possible reaction process can be expressed as the following equations:

\[
\begin{align*}
\text{bismuth oxide/indium oxide} + h\nu & \rightarrow h^+ + e^- \quad (1) \\
O_2 + e^- & \rightarrow \cdot O_2^- \quad (2) \\
H_2O + h^+ & \rightarrow OH + H^+ \quad (3) \\
OH^- + h^+ & \rightarrow OH \quad (4) \\
\text{rhodamine B} + \cdot OH/\cdot O_2^-/h^+ & \rightarrow \text{CO}_2 + H_2O \quad (5)
\end{align*}
\]

The photocatalytic cyclic experiments of the bismuth oxide/indium oxide microspheres for rhodamine B degradation were conducted to show the photocatalytic stability of the obtained microspheres. The dosage of the microspheres is 10 mg in the 10-mL rhodamine B solution (the concentration of 10 mg L\(^{-1}\)). The photocatalytic degradation ratio still reaches 95.3% after five cyclic experiments (Figure 12). The result shows that the bismuth oxide/indium oxide microspheres have good photocatalytic stability for rhodamine B degradation. Table 1 shows the comparison of the photocatalytic performance of rhodamine B using different photocatalysts. Compared with the photocatalysts for the rhodamine B degradation reported by other groups [8, 20, 33, 34], the bismuth oxide/indium oxide microspheres show better photocatalytic activity toward rhodamine B.

**IV. CONCLUSION**

In summary, bismuth oxide/indium oxide microspheres have been synthesized by a facile EDTA-assisted hydrothermal process using sodium bismuthate and indium nitrate as the raw materials. The as-prepared bismuth oxide/indium oxide microspheres synthesized from 180°C for 24 h using 5 wt% EDTA consist of tetragonal Bi\(_2\)O\(_3\) and cubic In\(_2\)O\(_3\) phases with a smooth surface and diameters between 150 nm and 1 μm. Morphology, the size, and the structure of the bismuth oxide/indium oxide products can be tailored by varying the amount of EDTA, hydrothermal temperature and reaction time. By increasing the EDTA concentration, the hydrothermal temperature, and the reaction time, the bismuth oxide/indium oxide microspheres with tetragonal Bi\(_2\)O\(_3\) and cubic In\(_2\)O\(_3\) phases are finally formed. The band gap of the bismuth oxide/indium oxide microspheres is 2.95 eV which can absorb the visible light. Rhodamine B with the concentration of 10 mg L\(^{-1}\) can be entirely removed by more than 10 mg bismuth oxide/indium oxide microspheres in 10 mL aqueous solution under solar light irradiation for 6 h. The bismuth oxide/indium oxide microspheres exhibit great application potential for the removal of organic pollutants.

**Acknowledgments**

This work was supported by the Natural Science Foundation of Anhui Province of P. R. China (2008085ME172) and Student Innovation and Entrepreneurship Training Program of P. R. China (202010360025).

**Table 1**: Comparison of the photocatalytic performance of rhodamine B using different photocatalysts.

| Photocatalyst                                      | Light source | Degradation time (min) | Degradation ratio (%) | Refs.    |
|---------------------------------------------------|--------------|------------------------|-----------------------|----------|
| Ni-Cu@multi-wall carbon nanotubes                 | UV light     | 50                     | 98                    | [8]      |
| Sheet-shaped bismuth oxide/indium oxide hetero-junctions | UV light     | 360                    | 100                   | [20]     |
| CaCu\(_3\)TiO\(_{12}\) embedded polyethersulfone hollow fiber membrane | UV light     | 40                     | 74.66                 | [33]     |
| TiO\(_2\) nanotubes coated on polyurethane        | UV light     | 320                    | 28                    | [34]     |
| Bismuth oxide/indium oxide microspheres          | Solar light  | 360                    | 100                   | This work                             |
[17] M. A. Gondal, M. A. Dastageer, L. E. Oloore, and U. Baig, J Photochem. Photobiol. A 343, 40 (2017).
[18] G. Zhang, J. Sun, D. Chen, N. Li, Q. Xu, H. Li, J. He, and J. Lu, J. Hazard. Mater. 398, 122889 (2020).
[19] N. Guo, H. Liu, Y. Fu, and J. Hu, Optik 201, 163537 (2020).
[20] H. J. Chen, Z. Wang, Z. Y. Xue, C. H. Yu, L. Z. Pei, and C. G. Fan, Cryst. Res. Technol. 55, 2000093 (2020).
[21] J.-C. Sin, C.-A. Lim, S.-M. Lam, H. Zeng, H. Lin, H. Li, and A. R. Mohamed, J. Phys. Chem. Solids 140, 109382 (2020).
[22] R. Gao, D. Qian, and W. Li, Trans. Nonferr. Metal. Soc. China 20, 432 (2010).
[23] B. A. Kouadio, F. Mei, T. Li, and L. Pang, J. Taibah Univ. Sci. 11, 1306 (2017).
[24] H. Deng, X. L. Li, Q. Peng, X. Wang, J. P. Chen, and Y. D. Li, Angew. Chem. Int. Ed. 44, 2782 (2005).
[25] Y. Liu, C. Mi, L. Su, and X. Zhang, Electrochim. Acta 53, 2507 (2008).
[26] J. Lee, Y. Kim, J. K. Kim, S. Kim, D.-H. Min, and D.-J. Jang, Appl. Catal. B 205, 433 (2017).
[27] Y. Zhang, W. Zeng, and Y. Li, Appl. Surf. Sci. 455, 276 (2018).
[28] Y. Zhang, F. Lin, T. Wei, F. Qiu, Y. Ma, and L. Pei, Int. J. Mater. Res. 109, 1035 (2018).
[29] L. Z. Pei, F. F. Lin, F. L. Qiu, W. L. Wang, Y. Zhang, and C. G. Fan, Mater. Res. Express 4, 075047 (2017).
[30] Y. Qi, J. Shen, Q. Jiang, B. Jin, J. Chen, and X. Zhang, Adv. Powder Technol. 26, 1041 (2015).
[31] W. Zhu, G. Zhang, J. Li, Q. Zhang, X. Piao, and S. Zhu, CrystEngComm 12, 1795 (2010).
[32] X. Qu, M. Liu, Z. Gao, H. Zhai, W. Ren, L. Shi, and F. Du, Appl. Surf. Sci. 506, 144688 (2020).
[33] T. A. Otitoju, D. Jiang, Y. Ouyang, M. A. M. Elamin, and S. Li, J. Ind. Eng. Chem. 83, 145 (2020).
[34] P. Liu, H. Liu, G. Liu, K. Yao, and W. Lv, Appl. Surf. Sci. 258, 9593 (2012).

All articles published on e-J. Surf. Sci. Nanotechnol. are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0). You are free to copy and redistribute articles in any medium or format and also free to remix, transform, and build upon articles for any purpose (including a commercial use) as long as you give appropriate credit to the original source and provide a link to the Creative Commons (CC) license. If you modify the material, you must indicate changes in a proper way.

Published by The Japan Society of Vacuum and Surface Science