Preparation of Mesoporous $\text{Bi}_4(\text{GeO}_4)_3$ Microspheres from $\text{Na}_4\text{Ge}_9\text{O}_{20}$ Template Microspheres for Photodegradation of Reactive Brilliant Red X-3B

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Abstract Mesoporous materials have attracted increasing attention due to their wide application. In this paper, the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres were firstly prepared by solvothermal method. Then, the as-prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres were dispersed into $\text{Bi}(\text{NO}_3)_3$ solution, and the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres with mesoporous structure were formed due to the solid-state reaction between bismuth nitrate and $\text{Na}_4\text{Ge}_9\text{O}_{20}$. The morphology, structure and optical properties were characterized by SEM, EDS, XRD, FITR, BET and UV–Vis diffuse reflectance analysis. The as-prepared products exhibited excellent photocatalytic performance for degradation of reactive brilliant red X-3B under the UV light irradiation. A possible photocatalytic mechanism was discussed as well.

KEY WORDS: Mesoporous; Microspheres; Photocatalysis

1 Introduction

Mesoporous materials have attracted increasing attention due to their wide application in the fields of separation, photocatalysis, sensors, battery materials, pharmaceutical carriers, solar cells and magnetic materials [1–7]. Over the past decades, many mesoporous metallic oxides, such as TiO_2 , Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, had been synthesized, and they

also exhibited excellent properties in their application area [8–10]. But the studies on mesoporous multimetallic oxide were still less. Compared with metallic oxides, multimetallic oxides had a distinctive space structure, which brought up their outstanding photoelectric performances. Therefore, the mesoporous multimetallic oxides had been attracting more and more attention. As a result of unremitting efforts of researchers, a series of mesoporous multimetallic oxides such as $\text{Bi}_{20}\text{TiO}_{32}$, MgTa_2O_6 and Bi_2WO_6 had been synthesized via evaporation-induced self-assembly (EISA) route or hydrothermal method [11–13]. Nevertheless, there was still a challenge on preparation of mesoporous multimetallic oxides due to the high-temperature requirement for EISA route or uncontrollability of products' micromorphology for hydrothermal method [4–16].

Fortunately, the hydrothermal method was a promising method for synthesis of mesoporous multimetallic oxides. Many mesoporous multimetallic oxides, such as BaTiO_3 , Bi_2WO_6 and BiPO_4 , were successfully synthesized via hydrothermal method [17–22]. Ye et al. [23] reported the synthesis of mesoporous Zn_2GeO_4 nanoparticles through a facile hydrothermal method, and the specific surface of the

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mesoporous Zn_2GeO_4 was reached up to $90.5 \text{ m}^2/\text{g}$. In the past decades, $\text{Bi}_4(\text{GeO}_4)_3$ nanoparticles have been widely studied owing to their outstanding electro-optic, luminescence, radiation energy absorption properties [16–26]. But the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres with mesoporous structure for photocatalysis have not been reported yet.

Herein, we reported a two-step route for preparation of mesoporous $\text{Bi}_4(\text{GeO}_4)_3$ microspheres. Firstly, $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres were prepared by hydrothermal method. Then, the as-prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres were dispersed into $\text{Bi}(\text{NO}_3)_3$ solution, and the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres with mesoporous structure were formed due to the solid-state reaction between bismuth nitrate and $\text{Na}_4\text{Ge}_9\text{O}_{20}$. The morphology, structure, optical properties and photocatalytic property for degradation of RBRX-3B were discussed in this paper.

2 Experimental

2.1 Chemical Reagents

The germanium oxide (GeO_2 , AR), sodium hydroxide (NaOH , AR), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AR), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR), nitric acid (66–68 wt% HNO_3 solution) and other reagents were all purchased from Sinopharm Chemical Reagent Company, and all chemicals were used without further purification.

2.2 Synthesis of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ Microspheres

$\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres were synthesized by solvothermal method. In a typical procedure, 0.08 g of NaOH was dissolved in 30 mL ethanol. Then, 0.47 g of GeO_2 was added into the above NaOH solution with vigorous magnetic stirring for an hour. After that, the white suspending liquid was transferred to a 50-mL Teflon-lined stainless steel autoclave and kept 160°C for 24 h and then cooled to room temperature (RT). At the end of reaction, the pH value of the reaction system was controlled to nearly 7. The white precipitation was collected and washed by ethanol for three times and then dried at 60°C for 6 h.

2.3 Synthesis of Mesoporous $\text{Bi}_4(\text{GeO}_4)_3$ Microspheres

The mesoporous $\text{Bi}_4(\text{GeO}_4)_3$ was synthesized using prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres as templates to react with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Typically, 0.178 g of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ powders was dispersed in 20 mL ethanol, and 0.97 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL of 0.05 mol/L HNO_3 solution. Next, the $\text{Bi}(\text{NO}_3)_3$ solution was added into the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ suspensions dropwise with stirring. The mixed

solution was stirred magnetically for 8 h at 60°C . Cooled to RT naturally, the mixed solution was centrifuged with a speed of 5000 r/min. Finally, the obtained light yellow powders were dried at 80°C for 4 h.

2.4 Characterizations

The crystal structures of the as-prepared samples were analyzed with a Bruker AXS D8 Advance X-ray diffractometer (XRD, $\text{CuK}\alpha$) with a scan rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range of 10° – 80° . The Fourier transform infrared (FT-IR) spectroscopy analysis was carried out by Nicolet 5700. The morphology and microstructure of products were investigated by Hitachi S4800 field-emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 10 kV. The Brunauer–Emmett–Teller (BET) specific surface area of the products was determined by a high-speed automated area and pore size analyzer (3H-2000PS1, China).

2.5 Measurement of Photocatalytic Activity

The photocatalytic activities of the samples are evaluated by the photodegradation of RBRX-3B in aqueous solution under UV light irradiation with a 300-W lamp to provide UV light ($\lambda \leq 400 \text{ nm}$). Before irradiation, 20 mg as-prepared catalysts were added into 50 mL RBRX-3B solution under magnetic stirring for 1 h to ensure the adsorption–desorption equilibrium. Then, the solution was stirred and exposed to the UV light irradiation. An amount of aliquots were taken away and separated as-prepared catalysts using centrifugation at different designated time. The upper layer was appropriately diluted, and the RBRX-3B concentration (C) was measured by JASCO V-570 UV–Vis–NIR spectrophotometer (Japan). The degradation rate (R) could be expressed as $R = 100\% \times (C_0 - C_t)/C_0$, where C_0 is the original concentration of RBRX-3B, and C_t is the concentration of RBRX-3B at time t .

3 Results and Discussion

The mesoporous $\text{Bi}_4(\text{GeO}_4)_3$ microspheres are prepared through two-step reaction processes, as schematic shown in Fig. 1. The $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres are firstly prepared via solvothermal method. Then, the as-prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ microspheres are dispersed into $\text{Bi}(\text{NO}_3)_3$ solution, and the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres with mesoporous structure are formed maybe due to the possibility of solid-state reaction between bismuth nitrate and $\text{Na}_4\text{Ge}_9\text{O}_{20}$.

The morphology and microstructure of the as-prepared products are investigated by SEM. As-prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ have a good dispersity with the diameter of about 250 nm,

Fig. 1 Schematic diagram of the two-step reaction process for $\text{Bi}_4(\text{GeO}_4)_3$ preparation

and the morphology of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ is sphere, indicating the sphere templates have successfully formed, which is shown in Fig. 2a. Figure 2b shows the EDS pattern of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ sample from which the Na, Ge and O were detected. The XRD pattern of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ is shown in Fig. 3a, and all the peaks can be indexed to the phase $\text{Na}_4\text{Ge}_9\text{O}_{20}$ (JCPDS card no. 73-1587). As shown in Fig. 3b, the strong absorption peaks observed at 483 , 765 and 1449 cm^{-1} are, respectively, corresponding to the stretching vibrations of Ge–O, Na–O bonds and carbonate and bicarbonate ions, and the absorption peaks at 1650 cm^{-1} result from water molecules adsorbed on the surface of the $\text{Na}_4\text{Ge}_9\text{O}_{20}$ sample [27–30].

As shown in Fig. 4a, the as-prepared $\text{Bi}_4(\text{GeO}_4)_3$ microspheres exhibit a good dispersity and the diameter of $\text{Bi}_4(\text{GeO}_4)_3$ microspheres of about $1\text{--}3\text{ }\mu\text{m}$ (Fig. 4b). A large number of pores can be observed on the surface of $\text{Bi}_4(\text{GeO}_4)_3$ microspheres, as shown in Fig. 4c. The porous structure of $\text{Bi}_4(\text{GeO}_4)_3$ microspheres will be further confirmed by Brunauer–Emmett–Teller (BET). The EDS patterns verify the existence of Bi, Ge and O in $\text{Bi}_4(\text{GeO}_4)_3$ (see Fig. 4d), and the ratio of atoms approximates to chemical formula of $\text{Bi}_4(\text{GeO}_4)_3$, if as-prepared Bi–GeO microsphere material is synthesized from $\text{Na}_4\text{Ge}_9\text{O}_{20}$ ($\text{Na}_{12}\text{Ge}_{27}\text{O}_{60}$) by ions substitution of Bi^{3+} for Na^+ . And the ideal composition of products will be become $\text{Bi}_4\text{Ge}_{27}\text{O}_{60}$ by considering charge neutrality. However, the synthesized substance is $\text{Bi}_4(\text{GeO}_4)_3$ that is confirmed by EDS analysis. This indicates that $\text{Bi}_4(\text{GeO}_4)_3$ is not formed

purely as the result of ion exchange. There is the possibility of solid-state reaction between bismuth nitrate and $\text{Na}_4\text{Ge}_9\text{O}_{20}$.

The crystal structure of as-prepared samples is characterized by X-ray diffraction firstly. As shown in Fig. 5a, the diffraction peaks of as-prepared samples can be well indexed to cubic phase $\text{Bi}_4(\text{GeO}_4)_3$ (JCPDS card no. 89-1419, $a = b = c = 10.513\text{ }\text{\AA}$). The $\text{Bi}_4(\text{GeO}_4)_3$ is known as a colorless compound, but the as-prepared product is light yellow color, and peak intensities at (220), (400) and (422) are much stronger than the intensity from the $\text{Bi}_4(\text{GeO}_4)_3$. Thus, the sample may contain other impurities, such as Bi_2O_3 , $\text{Bi}_{12}\text{GeO}_{20}$ and Bi_2GeO_5 . Figure 5b exhibits the FT-IR spectrum of $\text{Bi}_4(\text{GeO}_4)_3$ sample. The absorption peaks observed at 430 , 474 and 574 , 609 , 705 , 781 , 816 cm^{-1} are attributed to vibration modes of the Ge–O and Bi–O bonds, respectively [27, 31]. The absorption peaks at 1035 , 1361 and 1460 cm^{-1} are assigned to the stretching vibrations of carbonate and bicarbonate ions derived from carbon dioxide [28, 29].

Nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves are conducted to investigate the porous structure of the as-prepared samples. As shown in Fig. 6a, the as-prepared samples exhibit the Type IV isotherms with a hysteresis at the relative pressure of 0.5, indicating the characteristic of mesoporosity. The specific surface area and average pore diameter of $\text{Bi}_4(\text{GeO}_4)_3$ microspheres are measured to be $43.56\text{ m}^2/\text{g}$ and 3.79 nm , respectively. The absorption edge and band-gap energies of the as-prepared samples were determined

Fig. 2 SEM image **a** and the EDS result **b** of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ sample

Fig. 3 XRD pattern **a** and FT-IR spectrum **b** of as-prepared $\text{Na}_4\text{Ge}_9\text{O}_{20}$ sample

Fig. 4 SEM images of $\text{Bi}_4(\text{GeO}_4)_3$ sample with different magnifications **a–c** and EDS result of $\text{Bi}_4(\text{GeO}_4)_3$ sample **d**

Fig. 5 XRD pattern **a** and FT-IR spectrum **b** of $\text{Bi}_4(\text{GeO}_4)_3$

Fig. 6 Nitrogen desorption isotherm and pore size distribution **a** and UV-Vis diffuse reflectance spectra of $\text{Bi}_4(\text{GeO}_4)_3$ **b**

by UV-Vis diffuse reflectance analysis, as shown in Fig. 6b. It can be found that the $\text{Bi}_4(\text{GeO}_4)_3$ exhibits strong absorption under the UV light region. The band-gap energy of the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres is estimated to be 3.1 eV by fitting the plot of Kubelka-Munk function versus energy ($h\nu$). The larger specific surface and lower band-gap energy are contributed to the enhancement of photocatalytic activity of the as-prepared samples [32, 33].

The photocatalytic performance of the as-prepared products is investigated to degrade RBRX-3B under the UV light irradiation. As is shown in Fig. 7a, the photocatalysts are dispersed in RBRX-3B solution and resultant solutions are placed in dark for the adsorption-desorption equilibrium. Under UV light irradiation, the $\text{Bi}_4(\text{GeO}_4)_3$ exhibits a high-efficiency photocatalytic activity, and more than 99% of RBRX-3B could be degraded within 8 min. In contrast, the degraded performance of TiO_2 is not good, and only about 42.6% of RBRX-3B can be removed within the same reaction time. To illustrate the superiority of our support, the recycle experiment on the catalytic degradation of RBRX-3B is carried out. The efficiency of catalytic reaction is still maintained without significant decline even after the five cycles, indicating the excellent durability of the resultant product, as shown in Fig. 7b.

In order to investigate the possible reaction mechanism for degradation of RBRX-3B over $\text{Bi}_4(\text{GeO}_4)_3$ photocatalyst, the hydroxyl radicals ($\cdot\text{OH}$), superoxide radical ($\cdot\text{O}_2^-$) and holes (h^+) which are active species during photocatalytic reaction are detected. 1.0 mmol/L isopropyl alcohol (IPA) (a quencher of $\cdot\text{OH}$), p-benzoquinone (BQ) (a quencher of $\cdot\text{O}_2^-$) and triethanolamine (TEOA) (a quencher of h^+) were, respectively, added into solution to investigate the active species. The method was similar to the former photocatalytic activity test, and the results are shown in Fig. 8a. It can be found that the photocatalytic degradation of RBRX-3B decreased obviously with the addition of TEOA, BQ and IPA. Therefore, it can be concluded that the h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are the main active species of the $\text{Bi}_4(\text{GeO}_4)_3$ products in aqueous solution under UV light irradiation.

A possible photocatalytic mechanism of the $\text{Bi}_4(\text{GeO}_4)_3$ photocatalysts is illustrated in Fig. 8b. The photogenerated e^- can transit to conduction band (CB) with the UV light irradiation. On the surface of $\text{Bi}_4(\text{GeO}_4)_3$, part of photogenerated e^- are trapped by the oxygen to form $\cdot\text{O}_2^-$. The RBRX-3B can be degraded to nontoxic terminal product over $\cdot\text{O}_2^-$. Besides, the h^+ on the valence band also has a strong oxidation potential and can serve as active species to cause the oxidation of

Fig. 7 Photocatalytic degradation of RBR-3B **a** and cycling runs for the photocatalytic degradation of RBRX-3B **b**

Fig. 8 Trapping experiment results of active species during the photocatalytic reaction **a** and schematic illustration of the $\text{Bi}_4(\text{GeO}_4)_3$ photocatalytic mechanism of RBRX-3B degradation **b**

H_2O to form $\cdot\text{OH}$. Both h^+ and $\cdot\text{OH}$ can lead to the photodegradation of RBRX-3B.

4 Conclusions

In summary, the $\text{Bi}_4(\text{GeO}_4)_3$ microspheres were prepared by a two-step route. The as-prepared $\text{Bi}_4(\text{GeO}_4)_3$ microspheres exhibited a good dispersity with diameter of about 1–3 μm . The specific surface area and average pore diameter of $\text{Bi}_4(\text{GeO}_4)_3$ microspheres were measured to be 43.56 m^2/g and 3.79 nm, respectively. The $\text{Bi}_4(\text{GeO}_4)_3$ microspheres exhibited strong absorption under the UV light region. The photocatalytic performance of the as-prepared products was investigated by degradation of RBRX-3B under the UV light irradiation and exhibited higher photocatalytic degradation efficiency than that of pure TiO_2 . A possible photocatalytic mechanism of the $\text{Bi}_4(\text{GeO}_4)_3$ photocatalysts was discussed, and the h^+ , $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were the main active species of the $\text{Bi}_4(\text{GeO}_4)_3$ products in aqueous solution under UV light irradiation.

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References

- [1] A. Stein, *Adv. Mater.* **15**, 763 (2003)
- [2] G. Xi, J. Ye, *Chem. Eur. J.* **16**, 8719 (2010)
- [3] F. Chen, M. Liu, *Chem. Commun.* **18**, 1829 (1999)
- [4] F. Chen, Z. Shi, M. Liu, *Chem. Commun.* **21**, 2095 (2000)
- [5] M. Vallet, F. Balas, D. Arcos, *Angew. Chem. Int. Ed.* **46**, 7548 (2007)
- [6] R. Zhou, Q. Zhang, E. Uchaker, J. Lan, M. Yin, G. Cao, *J. Mater. Chem. A* **2**, 2517 (2014)
- [7] M. Hu, J. Jiang, Y. Zeng, *Chem. Commun.* **46**, 1133 (2010)
- [8] X. Zhang, V. Thavasi, S. Mhaisalkar, S. Ramakrishna, *Nanoscale* **4**, 1707 (2012)
- [9] F. Jiao, J. Jumas, M. Womes, A. Chadwick, A. Harrison, P. Bruce, *J. Am. Chem. Soc.* **128**, 12905 (2006)
- [10] Y. Si, X. Tang, J. Ge, S. Yang, M. El-Newehy, S. Salem, A.L. Dey, J. Yu, B. Ding, *Nanoscale* **6**, 2102 (2014)
- [11] L. Kong, H. Chen, W. Hua, S. Zhang, J. Chen, *Chem. Commun.* **18**, 4977 (2008)
- [12] J. Kondo, M. Uchida, K. Nakajima, L. Daling, M. Hara, K. Domen, *Chem. Mater.* **16**, 4304 (2004)
- [13] B. Tang, G. Jiang, Z. Wei, X. Li, X. Wang, T. Jiang, W. Chen, J. Wan, *Acta Metall. Sin. (Engl. Lett.)* **27**, 124 (2014)
- [14] X. Fan, J. Gao, Y. Wang, Z. Li, Z. Zou, *J. Mater. Chem.* **20**, 2865 (2010)
- [15] N. Zhang, S. Ouyang, P. Li, Y. Zhang, G. Xi, T. Kako, J. Ye, *Chem. Commun.* **47**, 2041 (2011)
- [16] G. Jiang, X. Wang, Z. Wei, X. Li, X. Xi, R. Hu, B. Tang, R. Wang, S. Wang, T. Wang, W. Chen, *J. Mater. Chem. A* **1**, 2406 (2013)
- [17] Z. Hou, P. Ferreira, P. Vilarinho, *Chem. Mater.* **21**, 3536 (2009)
- [18] P. Chen, L. Zhu, S. Fang, C. Wang, G. Shan, *Environ. Sci. Technol.* **46**, 2345 (2012)
- [19] G. Liu, S. Liu, Q. Lu, H. Sun, Z. Xiu, *Ind. Eng. Chem. Res.* **53**, 13023 (2014)
- [20] S. Sun, W. Wang, J. Xu, L. Wang, Z. Zhang, *Appl. Catal. B* **106**, 559 (2011)
- [21] X. Zhang, J. Huang, K. Ding, Y. Hou, X. Wang, X. Fu, *Environ. Sci. Technol.* **43**, 5947 (2009)
- [22] X. Fan, Y. Wang, X. Chen, L. Gao, W. Luo, Y. Yuan, Z. Li, T. Yu, J. Zhu, Z. Zou, *Chem. Mater.* **22**, 1276 (2010)
- [23] N. Zhang, S. Ouyang, T. Kako, J. Ye, *Chem. Commun.* **48**, 1269 (2012)
- [24] K. Lee, *Appl. Opt.* **30**, 4453 (1990)
- [25] K. Ok, E. Chi, P. Halasyamani, *Chem. Soc. Rev.* **35**, 710 (2006)
- [26] M. Lalic, S. Souza, *Opt. Mater.* **30**, 1189 (2008)
- [27] J. Liu, G. Zhang, *Cryst. Eng. Commun.* **15**, 382 (2013)
- [28] J. Evans, T. Whateley, *Trans. Faraday Soc.* **63**, 2769 (1967)
- [29] H. Tsuneoka, K. Teramura, T. Shishido, T. Tanaka, *J. Phys. Chem. C* **114**, 8892 (2010)
- [30] A. Miller, H. Charles, *Anal. Chem.* **24**, 1253 (1952)
- [31] L. Pei, Y. Yang, L. Yang, C. Fan, C. Yuan, Q. Zhang, *Solid State Commun.* **151**, 1036 (2011)
- [32] G. Jiang, B. Tang, X. Li, Z. Wei, X. Wang, W. Chen, J. Wan, L. Shen, *Powder Technol.* **251**, 37 (2014)
- [33] S. Vadivel, P. Keerthi, M. Vanitha, A. Muthukrishnaraj, N. Balasubramanian, *Mater. Lett.* **128**, 287 (2014)