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Article

Microwave-assisted ionothermal synthesis of hierarchical microcube-like BiOBr with enhanced photocatalytic activity

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ABSTRACT

Bismuth oxybromide (BiOBr) with a hierarchical microcube morphology was successfully synthesized via microwave-assisted ionothermal self-assembly method. The as-obtained BiOBr was composed of regular multi-layered nanosheets, which were formed by selective adsorption of ionic liquids on the Br-terminated surface, followed by the formation of hydrogen bond-co- π - π stacking. The synthesized BiOBr exhibited high activity, excellent stability, and superior mineralization ability in the photocatalytic degradation of organic dyes under visible light owing to its enhanced light absorbance and narrow bandgap. Furthermore, photo-generated electrons were determined to be the main active species by comparison with different trapping agents used in the photocatalytic reactions.

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1. Introduction

Recently, microwave-assisted ionothermal synthesis has received considerable attention owing to its rapid volumetric heating, high reaction rate, short reaction time, enhanced product selectivity, environmental friendliness, and energy efficiency compared to conventional heating routes [1,2]. Meanwhile, ionic liquids (ILs) have been found to display high fluidity, low melting temperature, extended liquid-state temperature ranges, high ionic conductivity, ability to dissolve in various materials, and absent measurable vapor pressure [3,4]. In particular, ILs are good media for microwave absorption, leading to a high heating rate because of the presence of many

organic positive ions with a high polarizability [5]. To date, various functional materials have been synthesized by the microwave-assisted ionothermal method, including nanorods, nanowires, and hollow microspheres [6–13].

As is well known, photocatalysis is a powerful strategy for environmental cleaning via decomposition of organic pollutants or for H₂ production by water splitting [14,15]. Bismuth oxybromide (BiOBr) has received considerable attention due to its narrow energy bandgap for absorbing visible light, low photo-induced electron-hole recombination, nontoxicity, and strong oxidizing power [16–22]. Although various BiOBr photocatalysts have been synthesized by traditional solvothermal methods [23–27], the development of new, green, and efficient

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synthesis methods to achieve a novel structure is still required.

Herein, we reported for the first time the synthesis of hierarchical BiOBr microcubes by microwave-assisted ionothermal self-assembly method. This method required a short reaction time and could achieve the desired morphology and structure. Moreover, the as-prepared BiOBr exhibited high activity and excellent stability in photocatalytic degradation of organic dyes under visible light owing to its strong light harvesting ability and unique structure.

2. Experimental

2.1. Sample preparation

In brief, 1.68 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and the required amount of 1-hexadecyl-3-methylimidazolium-bromide (HB) were dissolved in 30 mL of ethylene glycol (EG) and magnetically stirred for 30 min to form a homogenous solution. The molar ratio of Bi to Br was controlled to be 0.4, 0.8, and 1.1 in three parallel experiments. The solution was then transferred into a 50 mL teflon-lined autoclave and heated to 160 °C by microwaves (2.45 GHz, 1000 W). After a desired reaction time, the mixture was cooled to room temperature. The product was separated by filtering, washed with ethanol, dried at 80 °C in air overnight. The final particles were then annealed at 400 °C for 4 h in air to promote crystallization. The as-synthesized BiOBr was denoted as BiOBr.

For comparison, BiOBr was also synthesized using 1-octyl-3-methylimidazolium-bromide (OB), 1-hexyl-3-methylimidazolium-bromide (hb), a mixture of KBr and 1-hexadecyl-3-methylimidazolium nitrate (HK), a mixture of KCl and HK, cetrionium bromide (CTAB), and a mixture of 1-methyl-imidazolium (MI) and KBr instead of HB, which were denoted as BiOBr (OB), BiOBr (hb), BiOBr (HK), BiOCl (HK), BiOBr (CTAB), and BiOBr (MI), respectively. Crushed BiOBr was synthesized by grinding 0.2 g of the BiOBr sample and ethanol for 120 min using a pestle and mortar.

2.2. Characterization

The crystal structure was investigated by X-ray diffraction (XRD, Rigaku D/Max-2000) and the fine structure was analyzed by Fourier transform infrared (FTIR) spectroscopy (NEXUS 470). The surface morphology was observed by transmission electronic microscopy (TEM, JEM-2010) and field emission scanning electron microscopy (FESEM, HITACHI S-4800); the compositional data of the samples were also recorded using energy dispersive X-ray spectroscopy (EDX). The thermal stability was investigated by a thermogravimetric analysis (TGA, DTG-60H). X-ray photoelectron spectroscopy (XPS, Versa Probe PHI 5000) was employed to determine the surface electronic states. All the binding energy values were calibrated using C 1s (284.8 eV) as reference. N_2 adsorption-desorption isotherms were measured on a TriStar II 3020 at -196 °C and the surface area was calculated by applying the Brunauer-Emmett-Teller (BET) model on the desorption branches. The optical properties were determined by ultraviolet-visible diffuse reflectance

spectra (UV-Vis DRS, Varian Cary 500). The surface photovoltage spectra (SPS) were measured on a self-designed system consisting of a 500 W xenon lamp (CHF XM500W, Stusstech) combined with a double-prism monochromator (Omini-500, Zolix) as the light source, a light chopper (~23 Hz, SR540, Stanford), and a lock-in amplifier (SR830-DSP, Stanford). The photovoltaic cell had a sandwich structure of ITO-sample-ITO.

2.3. Photocatalytic activity test

Photocatalytic degradation was carried out at 30 °C in a self-designed 250 mL reactor containing 0.025 g catalyst and 10.0 mg/L organic dye in a 100 mL aqueous solution. A 300 W Xe lamp was used as the light source, and light with a wavelength shorter than 420 nm was cut-off using a glass filter (JB-420 nm). During the reaction process, the mixture was sampled at specified time intervals for measuring the concentration of the unreacted dye using a UV-vis spectrophotometer (UV-7504PC) at the characteristic wavelength. The total organic carbon (TOC) was determined on a Vario TOC analyzer. The reproducibility of the results was checked by repeating the experiments at least three times and was found to be within acceptable limits ($\pm 6\%$).

3. Results and discussion

3.1. Structural characterization of microcube-like BiOBr

3.1.1. FESEM, TEM, XRD, and XPS results

The FESEM images of BiOBr (Fig. 1(a)–(c)) showed uniform microcubes of 4 μm assembled by nanosheets with thicknesses less than 50 nm. The TEM image (Fig. 1(d)) showed a solid

Fig. 1. FESEM (a–c), TEM (d), HRTEM images (e) (inset is the SAED image), and XRD patterns (f) of as-prepared BiOBr.

microcube. Meanwhile, the high-resolution TEM (HRTEM) image (Fig. 1(e)) demonstrated well-crystallized BiOBr mesocrystals corresponding to the (110) plane with a lattice spacing of 0.277 nm [27], which could be further confirmed by the selected area electron diffraction (SAED) patterns with scattered bright spots representing the (110) and (100) lattice planes, indicating tetragonal BiOBr mesocrystals (inset of Fig. 1(e)). Furthermore, the XRD result (Fig. 1(f)) demonstrated that the as-obtained BiOBr had a highly crystalline pure tetragonal phase (JCPDS No. 73-2061). In addition, the EDX spectrum (Fig. S1) determined the Bi/Br/O molar ratio to be 1.00:1.00:1.00 in BiOBr, corresponding to the pure stoichiometric ratio of BiOBr. The XPS results (Fig. S2) also confirmed the pure BiOBr phase with a Bi:O:Br molar ratio of 1.26:1.07:1.00 and Bi 4f, O 1s, and Br 3d binding energies of 164.7/159.4 [28], 530.2 [29], and 68.6 eV [30], respectively.

As shown in Fig. 2, only nanoparticles with a diameter of around 100 nm were obtained in the early stage. After microwave-assisted IL treatment for 1 min, these nanoparticles grew into separated nanosheets with a thickness of around 20 nm, which could be attributed to the selective adsorption of HB cations on different facets of BiOBr, leading to priority-orientated two-dimensional (2D) crystal growth. When the reaction time was increased to 30 min, these nanosheets assembled onto the original nanoparticles owing to the high surface energy and surface temperature resulting from the strong adsorption of the microwave, forming flower-like microspheres. Furthermore, at 40 min microcubes were assembled by the layer-by-layer mechanism due to the growth of the core nanoparticles into nanosheets. Moreover, with increasing quantity of HB, the as-prepared samples transitioned from microspherical BiOBr superstructures to flower-like structures and then microcube-like BiOBr with regular nanosheets (Fig. S3). Furthermore, the XRD patterns (Fig. 2(g)) suggested that the microwave-assisted IL method enabled the reaction to be completed within a very short time [31–36], possibly due to the

Fig. 3. Scheme of formation of hierarchical BiOBr microcubes under microwave-assisted ionothermal conditions.

strong microwave absorbance caused by the high ionic conductivity and polarizability of HB.

3.1.2. Formation of BiOBr

Fig. 3 briefly illustrates the formation of hierarchical BiOBr microcubes by microwave-assisted ionothermal self-assembly based on the above analysis. The $[\text{Bi}_2\text{O}_2]^{2+}$ could be formed via reaction (1) and (2) [29], followed by the formation of BiOBr nuclei by reaction (3) and (4).

The nanoparticles might stack through the selective adsorption of HB as the capping agent and mass diffusion. The superior advantage of the ILs could lead to hydrogen bond-co- π - π stacking in the liquid state [37]. The cations of the ILs could be

Fig. 2. FESEM images ((a)–(f)) and XRD patterns (g) of formation of BiOBr mesocrystals at different reaction times. (a) 0 min; (b) 1 min; (c) 5 min; (d) 20 min; (e) 30 min; and (f) 40 min. Scale bar: 1 μm .

easily adsorbed on the Br-terminated surface by electrostatic forces, and the hydrogen bond formed between the hydrogen atom at the C2 position of the imidazole ring and the bromine atom of Br^- [BiOBr] could act as an effective bridge to connect the Br-terminated plane of the produced metal-oxide nuclei and the cations of the ILs. Also, the IL cations would be aligned by additional π - π interactions among the imidazolium rings of HB to facilitate the proposed relocation of molecules based on HB's ability to self-assemble into stabilized ordered structures. The hydrogen bond-co- π - π stacking could decrease the polarity of the selective adsorption surface and thus restrain its microwave absorption ability, retarding the crystal growth of the 2D selective adsorption surface to form a 3D cubic architecture. The π - π stacking could result in strong cloud density and static repulsion in each nanosheet because the zeta potentials of BiOBr without calcination, BiOBr, and the mixture of BiOBr + EG + HB were -10.5 , -0.448 , and -0.345 mV respectively, which could adjust the intervals of the nanosheet and the thicknesses of the microcubes.

The TGA curve (Fig. S4) revealed a high organic content (ca. 12.7% by weight) in BiOBr without calcination. The DRS spectra in Fig. 4(a) revealed that BiOBr displayed a much higher light absorbance than crushed BiOBr (Fig. S5), which could be attributed to the multiple light reflections between the nanosheets in the microcubes. The bandgap obviously widened from 2.56 to 2.66 eV after crushing (inset of Fig. 4(a)). The SPS spectra (Fig. 4(b)) confirmed that BiOBr without calcination displayed several peaks due to the presence of various organic species. After calcination, only two photovoltaic peaks, corresponding to two discrete valence bands in BiOBr, were observed due to the presence of O 2p and Br 4p orbitals (inset of Fig. 4(b)) [38–40]. This could also account for the spectral responses in both UV and visible regions, which corresponded to an indirect bandgap of 2.56 eV in BiOBr (Fig. 4(a)) [41]. Moreover, the photovoltaic responses of mixed BiOBr, EG, and HB were weaker than those of BiOBr owing to the absence of the hydrogen bond-co- π - π stacking because BiOBr was covered by EG and HB, leading to limited light absorption. The FTIR spectra (Fig. S6) displayed significantly different structures for pure HB and BiOBr without calcination. We could observe an ab-

sorption band at 3077 cm^{-1} , corresponding to the stretching vibration of C-H in the imidazole ring. Meanwhile, the peaks at 1575, 1468, and 1174 cm^{-1} were attributed to the skeleton stretching vibration signal of the imidazole ring and became broader and weaker in the FTIR spectra of BiOBr [37]. These results indicated that there were strong interactions between the ILs and BiOBr, confirming the existence of the strong hydrogen bonds in C2(HB)-H-Br(BiOBr), which was similar to previous results [37,42]. Moreover, the peak at 1038 cm^{-1} , characteristic of the C-N stretching vibration ($\nu_{\text{C-N}}$) mode in the imidazole ring of BiOBr without calcination, became narrower and stronger than that observed in the spectra for HB and BiOBr + HB + EG. This could be ascribed to the stronger interaction between the aromatic rings and the BiOBr surface [37], as confirmed by the aforementioned SPS spectra. These results strongly supported that the hydrogen bond-co- π - π stacking was responsible for the formation of BiOBr microcubes.

Several additional experiments were conducted to confirm the above hypothesis. CTAB could not effectively achieve selective adsorption and hydrogen bond-co- π - π -stacking. When it was used instead of HB, only flower-like microspheres (Fig. S7(a) and (b)) of BiOBr were achieved due to the layer-by-layer structure [43]. When 1:1 mole ratio of OB or hb was used instead of HB, BiOBr formed well-organized stacked microcubes (Fig. S7(c) and (f)). Interestingly, the shorter the branched (carbon) chain on the N1 (IL), the weaker was the stereospecific blockade. When a mixture of HK and KBr replaced HB, BiOBr microcubes were obtained (Fig. S8(a) and (b)). Similarly, when a mixture of HK and KCl replaced HB, BiOCl microcubes were achieved (Fig. S8(c) and (d)). More interestingly, when a mixture of MI and KBr was used instead of HB, BiOBr microcubes was obtained even in the absence of an IL (Fig. S8(e) and (f)). These results further confirmed the key role of the hydrogen bond-co- π - π stacking in BiOBr formation.

3.2. Photocatalytic activity under visible light

As shown in Fig. S9, both BiOBr and crushed BiOBr displayed type IV adsorption-desorption isotherms with a distinct hysteresis loop characteristic of a mesoporous structure. The

Fig. 4. (a) UV-vis DRS of BiOBr and crushed BiOBr; inset: optical bandgap of BiOBr. (b) Normalized SPS spectra of BiOBr, BiOBr without calcination, and BiOBr + EG + HB; inset: bandgap structure of BiOBr.

Fig. 5. (a) Comparison of different morphologies of BiOBr at the normalized specific surface area in the photocatalytic degradation of RhB under visible light; (b) TOC analysis of BiOBr and crushed BiOBr; (c) Reproducibility of BiOBr; (d) Effect of different trapping agents to investigate the role of active radicals in BiOBr catalyst. Reaction conditions: 100 mL RhB aqueous solution 10.0 mg/L, 25.0 mg catalyst, 300 W Xe lamp ($\lambda > 420$ nm), and $T = 30$ °C.

BET surface area of BiOBr was determined to be 2.30 m²/g. After crushing, the BET surface area increased to 17.3 m²/g owing to the decreased particle size. From Fig. 5(a), we could see that no significant degradation in RhB occurred in the absence of a photocatalyst. Under visible light, RhB in the solution completely disappeared after 180 min of photocatalysis of BiOBr. Although crushed BiOBr exhibited a much higher specific surface area than BiOBr, its RhB degradation activity was far weaker (3.97%/m² versus 43.29%/m² or 68.68% versus 99.57%). Such phenomena were also observed during the photocatalytic degradation of MO (Fig. S10). This indicated that the multistage reflection of nanosheets in the BiOBr microcube photocatalyst could increase light absorption, narrow the bandgap, and generate more photoelectrons and holes, leading to enhanced photocatalytic activity. The conversion rate at 180 min was about 99.57% (~43.29%/m²), while the TOC removal (Fig. 5(b)) rate was only about 12.24%. These results indicated that only a small fraction of RhB was completely degraded and mineralized in CO₂. In addition, BiOBr showed superior photodegradation activity for RhB than flower-like BiOBr (BET surface area = 23.5 m²/g, [21]), indicating that the microcubic BiOBr mesocrystals facilitated charge transfer to improve the photocatalytic performance. Furthermore, BiOBr exhibited excellent stability, as shown in Fig. 5(c) with five recycles testing, which could be attributed to its highly crystalline nature that inhibited the decomposition of BiOBr. As is well known, because of the strong oxidizing ability of Bi³⁺ in Bi-based pho-

tocatalysts such as BiOX (X = Cl, Br, I), BiVO₄, Bi₂WO₆, Bi₂MoO₆, Bi₂O₃, Bi₂S₃, and bismuth titanate, they can be easily reduced to low valence states by photogenerated electrons. To confirm the stability of Bi³⁺ in BiOBr, XPS characterization tests were employed (Fig. S11). The XPS peak position showed no obvious changes, further indicating the excellent stability of our BiOBr photocatalyst.

To investigate the mechanism of the photodegradation of RhB, we used different trapping agents as scavengers, including ethylenediaminetetraacetic acid (EDTA), AgNO₃, tert-butyl alcohol (TBA), and benzoquinone (BQ), and explored the effects of photo-induced holes (h⁺), photogenerated electrons (e⁻), hydroxyl radicals (·OH), and superoxide anions (O₂^{·-}) on the photocatalytic reaction system. Fig. 5(d) shows the effect of various sacrificial agents on the photocatalytic activity. It was found that the addition of TBA weakly influenced the photocatalytic degradation of RhB, indicating that the active radical ·OH did not play a key role in RhB degradation. When adding BQ to capture O₂^{·-} as another active radical into the reaction system, the photocatalytic activity did not significantly change. Furthermore, the addition of EDTA considerably decreased the photocatalytic degradation of RhB compared to pristine BiOBr. In particular, adding AgNO₃ into the photocatalytic reaction system greatly reduced the degradation of RhB. It could be concluded that the main active species were the photogenerated electrons, which reacted with dissolved O₂ to produce O₂^{·-} and then oxidized pollutants.

4. Conclusions

In summary, novel BiOBr microcubes were prepared by microwave-assisted IL self-assembly through hydrogen bond-co- π - π stacking. The as-obtained BiOBr exhibited high activity in photocatalytic degradation of organic dyes under visible light owing to its narrow energy bandgap and strong light absorbance resulting from the multi-reflection of light within the microcubes. The main active species for the photo-degradation of pollutants were photogenerated electrons. Furthermore, organic dyes could be completely mineralized, showing good potential for practical application in dye-wastewater cleaning.

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Author contributions

Yingchun Miao and Zichao Lian performed the experiments; Yingchun Miao wrote this manuscript under the guidance of Prof. Hexing Li. All authors contributed to the general discussion and article revision.

Conflict of interest

The authors declare that they have no conflict of interest.

Supporting information

Supporting information is available in the online version of the paper.

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Graphical Abstract

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BiOBr with hierarchical morphologies and hydrogen bond-co- π - π stacking was successfully synthesized via microwave-assisted ionothermal self-assembly, and it exhibited high activity owing to the enhanced light absorbance and narrow bandgap.

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微波辅助离子热合成具有高光催化活性的 BiOBr 片层微米立方体

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摘要: 微波辅助离子热合成技术因其加热和反应速度快、反应时间短、产物选择性高、环保、节能等优点, 而广泛应用于纳米棒、纳米线和中空纳米微球等各种形貌功能材料的合成。BiOBr 光催化剂具有毒性低、光生空穴氧化能力强、光降解活性高等优点, 在光催化降解污染物方面研究非常广泛。虽然各种形貌的 BiOBr 光催化剂可以通过传统的溶剂热法合成, 但仍然需要开发绿色和高效节能的合成方法, 来设计新型结构和高光催化降解活性的 BiOBr 光催化剂。本文首次报道了由微波辅助离子热自组装的方法合成新型结构的 BiOBr 微米立方体。该 BiOBr 由规则的多层纳米片组成, 其通过在 Br-端表面上选择性吸附离子液体形成, 随后形成氢键的 π - π 堆叠。结果显示 BiOBr 是由厚度小于 50 nm 的纳米片组装成为 4 μ m 左右的纳米立方体。其中 Bi:Br:O 摩尔比为 1:1:1, 表明生成纯化学计量比的 BiOBr, 且具有高结晶度的纯四方相。我们通过添加不同的表面活性剂, 进一步确认氢键-co- π - π 叠层在 BiOBr 片层立方体形成中的重要性。

将 BiOBr 片层立方体研磨粉碎后其 BET 表面积为从 2.30 急剧增至 17.3 m²/g, 但其降解 RhB 活性却大幅度下降。由于纳米片层的层间反射和散射, 有效地提升了 BiOBr 的可见光吸收, 光学带隙由 2.66 窄化为 2.56 eV, 因而具有高的可见光光降解活性和优异的稳定性及矿化能力。光催化降解 180 min 后, 罗丹明 B 的转化率约为 99.57%, 而有机碳去除率高达 12.24%; 对于磨碎的 BiOBr 罗丹明 B 的转化率和有机碳去除率分别为 68.68% 和 8.62%。光催化反应前后的 BiOBr 中, Bi³⁺离子的 XPS 峰位置没有明显的变化, 进一步表明 BiOBr 光催化剂具有较高的稳定性。这种具有高活性、优异的稳定性以及高矿化能力的 BiOBr, 在实际应用光催化降解染料废水和清洁能源方面显示出很好的潜力。此外, 通过光催化反应过程中不同捕获剂的添加确定了光降解的主要活性物种。当加入硝酸银溶液的时候, 由于光生电子快速被 Ag⁺离子捕获, 光降解活性明显下降。活性物种的捕获实验表明, 光生电子为主要的活性物种。

关键词: 微波; BiOBr 片状立方体; 自组装; 光催化降解; 矿化能力

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