A facile and efficient solvothermal fabrication of three-dimensionally hierarchical BiOBr microspheres with exceptional photocatalytic activity

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Three-dimensionally (3-D) hierarchical BiOBr microspheres have been successfully synthesized using a facile and efficient solvothermal method in the reaction system consisting of Bi(NO3)3•5H2O and KBr as well as ethylene glycol (EG). The characterized results showed that all BiOBr microspheres consisted of pure tetragonal BiOBr phase with good crystallinity. The photocatalytic property of 3-D BiOBr microspheres was investigated by the photodegradation of Rhodamine B (RhB) under visible light irradiation, the reaction results revealed that the as-prepared microspheres exhibited excellent visible-light-induced photocatalytic activity. Recycling test experiments indicated that the BiOBr microspheres had higher stability and recyclability.

1. Introduction

Recently, the investigations of visible-light-induced photocatalysts have attracted much attention owing to its promising application in solar energy transformation and environmental decontamination [1]. As is known to all, titanium dioxide (TiO2) is one of the most extensively researched photocatalyst for degradation of organic contaminants [2]. Unfortunately, less than 5% of the sunlight could be utilized by TiO2 particles due to its wide band gap (3.2 eV), which limited its further application in practice [3]. To date, large amounts of methods have been taken to improve the photocatalytic activity of photocatalysts, for instance, the modification of TiO2 [4,5] or exploring novel semiconductor materials with narrow band gap, which can be excited by the visible light [6].

As a group of V–VI–VII semiconductors [7], bismuth oxyhalides compounds (BiOX, X=Cl, Br and I) have drawn lots of interests due to their superior optical properties, the structural variability, excellent photocatalytic activity and stability [8,9]. In particular, the bismuth oxybromide (BiOBr) semiconductor, which was deemed as a promising visible-light-responsive photocatalyst with a simple p-type indirect band gap (Eg=2.9 eV) and tetragonal matlockite structure. The layered structure of BiOBr was thought to be accumulated by [Bi2O2]2+ slabs embedded in double slabs of Br−. In this unique structure, the related atoms and orbitals possess enough space to polarize. Subsequently, the formation of induced dipole could contribute to the effective separation of photon-generated electrons and holes [6]. As a result, the photocatalytic activity was enhanced enormously. Until now, various morphologies and structures of BiOBr micro/nanostructures have been obtained, such as nanoplates, nanoparticles, nanobelts and microspheres [10,11], etc. Thus, numerous synthetic methodologies were developed to fabricate these BiOBr micro/nanostructures including the polyvinylpyrrolidone-assisted solvothermal method [2], ionic liquid-assisted hydrothermal method [10], ultrasound-assisted anion exchange reaction and heating treatment method [12], hydrolysis method [13], precipitation-deposition method [14], etc. However, the approaches mentioned above also have some shortcomings, for example, using ionic liquid as source of bromine and solvent, or using toxic organic solvents and other co-catalyst, and the complicated preparation process by using ultrasonic or microwave equipments.

In this work, we developed a facile and efficient solvothermal method to fabricate the 3-D hierarchical BiOBr microspheres, and the adopted method could be operated conveniently and environmentally-benign. More importantly, the used raw materials (Bi(NO3)3•5H2O, KBr and EG) were nontoxic and inexpensive. Furthermore, the as-prepared photocatalysts exhibit hierarchically
porous microsphere morphology, which have strong optical adsorption ability and excellent photocatalytic activities for decomposing RhB under visible-light irradiation.

2. Experimental section

In a typical synthesis, a certain stoichiometric amounts of Bi (NO$_3$)$_3$·5H$_2$O were dissolved into 30 mL solution of EG with vigorously stirring, and then 0.001 mol KBr was added to the above mixture under continuously stirring for 0.5 h until a transparent solution was obtained. Finally, the miscible solution with different Bi/Br molar ratio was transferred into the 50 mL of Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 160 °C for 12 h, and then naturally cooled to room temperature. The resulting products were separated by centrifugation and washed with deionized water for three times and then dried at 60 °C for 4 h in an oven. Similarly, different molar ratios of Br to Bi (n(Br:Bi)=2:1, n(Br:Bi)=1:1 and n(Br:Bi)=1:2) were investigated, and the obtained 3-D hierarchical BiOBr microspheres were denoted as B-1, B-2 and B-3, respectively.

The crystal structure and phase compositions were identified by X-ray diffraction (XRD; Lab X XRD-6000). Scanning electron microscopy (SEM, FEI, Quanta250F) and transmission electron microscopy (TEM, JEOL, JEM-2100) were performed to observe the morphologies and nanostructures of all the 3-D hierarchical BiOBr microspheres samples. The component of as-prepared samples was also detected by energy dispersive X-ray spectrometry (EDX).

The photocatalytic activity of the 3-D hierarchical BiOBr microspheres has been investigated through the degradation of RhB solution (15 mg/L) under visible-light irradiation. A 300 W Xenon lamp (Nbet, HSX-F/UV300) was furnished as visible light source (λ ≥ 420 nm). Typically, 0.07 g of the photocatalyst was uniformly dispersed in a photocatalytic reactor containing 70 mL RhB solution. Subsequently, the suspension was magnetically stirred in the dark for 40 min in order to make the mixture reach the adsorption-desorption equilibrium. During the photoreaction, 3 mL of suspension was removed from the reactor at intervals of 5 min and then centrifuged for further analysis by a UV–vis spectrophotometer (UV1900PC). The procedure of recycling experiments of RhB decomposition on as-prepared BiOBr samples were same as mentioned above. The difference was that the visible light illuminating time was 30 min. After each recycling experiment, the separated catalyst was washed and dried at 60 °C for 30 min, which was then returned to the reaction system to carry out the photoreaction. The initial concentration of photocatalyst which dispersed in the fresh RhB solution was always kept in 1.0 g/L at each recycling experiment.

3. Results and discussion

The crystal structure and phase composition of the as-synthesized BiOBr microspheres were checked by XRD. As depicted in Fig. 1, it can be clearly seen that the diffraction peaks of B-1, B-2 and B-3 were quite similar and the corresponding planes could be indexed to the tetragonal phase of BiOBr with lattice constants of a=b=3.926 Å and c=8.103 Å (JCPDS no. 09-0393) [7,11,15,16]. In addition, the diffraction peaks of B-1 and B-2 observed in Fig. 1 are very sharp and intense, indicative of a higher crystalline degree for BiOBr microspheres. By contrast, the B-3 sample shows a relatively weak intensity of the diffraction peaks, suggesting that the higher Bi$^{3+}$ content in the reactive solution would lead to a faster reaction rate and thus induce a negative effect on the crystallization of the BiOBr microsphere. It’s worth noting that no other crystal phase could be detected in the XRD data, indicating that the pure BiOBr microspheres were obtained.

The morphology and microstructure of the 3-D hierarchical BiOBr microsphere samples with various Br/Bi molar ratios were investigated by SEM. Fig. 2A(a, c and e) shows that the as-prepared BiOBr samples possess almost the similar 3-D hierarchical microsphere morphology with a large diameter of approximately 2.5–3.5 μm. As can be seen from the high-magnification SEM images (Fig. 2A(b, d and f)), the entire 3-D hierarchical BiOBr microspheres were self-assembled by numerous nanosheets with a thickness from 20 nm to 30 nm. It should be noted that with the decreasing of Br/Bi molar ratio, the micro-spherical structure of BiOBr was becoming more and more smooth and uniform, which were in good agreement with the results of TEM images (Fig. 3(a, c and e)). Through careful observation, a number of opened hierarchically porous structures can be found on the surface of uniform microspheres, suggesting that the photocatalysts have large pore volume [17]. Importantly, the presence of hierarchical structures would supply more reaction active sites and benefit the separating efficiency of the photogenerated electron and hole, resulting in a considerable effect on the enhancement of the photoactivity of BiOBr [7]. Additionally, the chemical composition of as-prepared samples was also detected by EDX. Fig. 2B indicates that all of the 3-D hierarchical BiOBr microsphere samples contained elements of O, Br and Bi. The results of EDX analysis were consistent with that of XRD. By the way, the peaks of C and Si in the spectrum could be attributed to the presence of EG molecular and silicon substrate in the samples. Furthermore, the atomic ratios of Br/Bi were calculated to be approximately 0.94 for B-1, 0.89 for B-2 and 0.70 for B-3, respectively. This tendency of decline was reasonably agreed with the original different Br/Bi molar ratio.

As illustrated in Fig. 3, the lamellar structure could be observed from the rough edge of the TEM images of BiOBr samples, which further confirmed that the as-synthesized microspheres were composed of thin nanosheets. The selected area electron diffraction (SEAD) (inset of Fig. 3(a, c and e)) of the B-1, B-2 and B-3 also verified the good crystallinity of the BiOBr microspheres. Fig. 3(b, d and f) shows the HR-TEM images of BiOBr microspheres. The lattice fringes of the as-prepared samples could be observed obviously and the interplanar spacing value of 0.810 nm and 0.354 nm were well indexed to the (001) and (101) lattice plane of the tetragonal phase of BiOBr.

The photocatalytic activities of the as-prepared samples were evaluated by degradation of RhB under visible light irradiation. Meanwhile, commercial P25 TiO$_2$ and the blank control experiment (without photocatalyst) were also performed for comparison. As shown in Fig. 4A, the RhB molecule was very stable and
less than 2.9% RhB was removed in the absence of photocatalyst after 35 min visible light irradiation. In addition, it can be seen that the degradation efficiency of RhB could reach to 14.5% after the introduction of commercial P25 TiO₂, and the slight photodegradation can be ascribed to the photosensitization mechanism of RhB [4]. In contrast, the 3-D hierarchical BiOBr microspheres showed much better photocatalytic activity than that of P25 TiO₂ in the same reaction conditions. After 35 min visible light illumination, 91.1%, 95.9% and 88.6% of RhB have been decomposed by the as-synthesized samples B-1, B-2 and B-3, respectively. Among these 3-D hierarchical BiOBr microspheres, B-2 sample prepared with Bi/Br molar ratio of 1:1 exhibited the highest photocatalytic activity. Such a significant photocatalytic performance was mainly attributed to its larger pore volume, higher adsorption capacity and the efficient charge separation [10].

Recycling experiments of RhB decomposition over BiOBr microspheres were carried out under visible light irradiation. As can be seen in Fig. 4B, after five recycling photocatalytic reactions, both B-1 and B-3 samples partially lost their photocatalytic activity, and the degradation efficiency of B-1 sample dropped from the initial 89.1% to the last 50.0%. What’s worse, the degradation efficiency of B-3 sample was only 35.5%. However, the photocatalytic activity of B-2 sample was slightly decreased with increase of cycling times, and 71.6% of RhB dye could still be decomposed in the fifth cycling test. It should be noted that small amounts of catalyst mass loss would result in the gradual decrease of photocatalytic activity in the process of each recycling. Nevertheless, all of the samples could be easily separated from the mixture solution after a short time of physical sedimentation due to their large microspherical structure, suggesting that the 3-D hierarchical BiOBr microspheres...
with outstanding stability and recyclability have potential application in the clean-up of environment.

4. Conclusions

In summary, a facile and efficient solvothermal method was used to synthesize the 3-D hierarchical BiOBr microspheres. The as-prepared photocatalyst with Br/Bi molar ratio of 1:1 exhibited extremely excellent photocatalytic performance for degradation of RhB than other samples under visible light irradiation. Moreover, the microspheres possessed 3-D hierarchical structure and large particle size which in favor of its stability and recyclability.

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References