

Research Letters

One-pot solvothermal preparation of S-doped BiOBr microspheres for efficient visible-light induced photocatalysis

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(Received 8 June 2013; accepted 4 September 2013)

Abstract

The S-doped BiOBr composite microspheres were successfully prepared through one-pot solvothermal method. The as-prepared samples exhibit higher photocatalytic activity for the degradation of Rhodamine B and phenol under visible light irradiation, attributed to the improvement of the photo-absorption property and the narrow band gap due to the dopants of S element. The higher efficiency for photodegradation of organic pollutant endows this material with a bright perspective in purification of waste water under visible-light irradiation.

Owing to industrialization and urbanization, the environmental pollution caused by hazardous wastes and toxic air contaminants has become an overwhelming problem. In order to address this issue, various technologies have been developed, including incineration,^[1] adsorption,^[2] and electrical discharge.^[3] Among these methods, photocatalysis has received considerable attention due to its high oxidizing capacity, photostability, and nontoxicity.^[4–9] Since the discovery of water electrolysis, titanium dioxide (TiO₂) has been widely used as a photocatalyst for degradation of organic contaminants.^[10–13] However, it requires high energy ultraviolet (UV) light to activate due to its large band gap, resulting in low-efficiency in utilization of visible light irradiation.^[14–16] As a result, many efforts have been devoted to explore the visible-light-induced photocatalysts.

Bismuth oxyhalides compounds have recently attracted intensive interest in solar energy conversion due to their high photocatalytic activity and stability under UV and visible light irradiation,^[17–19] Among bismuth oxyhalides, BiOBr which crystallizes possess the tetragonal matlockite structure, a layered structure composed of $[Bi_2O_2]^{2+}$ layers interleaved with double Br layers.^[20,21] It has received remarkable attention owing to its stability, suitable band gap, and relatively superior photocatalytic ability.^[22,23] So far, a variety of BiOBr nano- and micro-structures, including nanoplates, nanobelts, and microspheres prepared by numerous methods, have been used as photocatalysts to degrade organic contaminants.^[24,25] However, the photodegradation ability of BiOBr still cannot meet the demand of practical applications. To date, continuous attempts have been conducted to improve the photocatalytic activity of BiOBr.^[26–31] It is indispensable

to boost the photocatalytic efficiency by modifications.^[32–34] The photocatalytic properties of these compounds can be improved by incorporation of a highly reactive component, such as cation, anion, and metal oxides.^[21,35] For example, the Fe-doped BiOBr,^[9] Ti-doped BiOBr,^[27] and Mn-doped BiOBr^[36] exhibited outstanding activities under visible light irradiation. It was also shown that the optical response of TiO₂ could be shifted from UV to visible region by doping with nonmetal atoms.^[37–39] Ohno et al.^[39] has predicted that doping with S would be most effective in nonmetal doped TiO₂. When S atoms were incorporated into TiO₂, S⁶⁺ and S⁴⁺ states could replace Ti⁴⁺, and S²⁺ could replace O atoms.^[38–40] It is believed that doping with S also may improve the photocatalytic ability of BiOBr.

Here, a novel visible light-activated S-doped BiOBr has been prepared by a facile and a rapid solvothermal method. The physicochemical properties of the as-prepared samples have been characterized in detail. Time-dependent evolutions of crystal structure and morphology were investigated systematically by x-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and Energy Dispersive x-ray Spectroscopy (EDS) in order to elucidate the possible growth mechanism of the S-doped BiOBr and the possible formation process of the S-doped BiOBr microspheres was proposed. Moreover, the photocatalytic ability of S-doped BiOBr was evaluated by the degradation of Rhodamine B (RhB) and phenol. The results reveal that the as-prepared novel S-doped BiOBr microspheres exhibit outstanding activities under visible light irradiation, far exceeding that of pure BiOBr.

Figure 1 displays the related XRD patterns of the S-doped BiOBr samples after solvothermal treatment. The XRD pattern



Figure 1. XRD patterns of the BiOBr and S-doped BiOBr samples.

for pure BiOBr is also added in for comparison. It is clearly seen that all the diffraction peaks of pure BiOBr sample can be well matched with the tetragonal phase of BiOBr (JCPDS no. 73-2061). The XRD pattern for the S-doped BiOBr exhibits some detectable dopant related peaks besides the typical tetragonal structure of BiOBr crystal and the asymmetry of the (110) peak of the two samples due to the low content and high dispersity of dopants of the S element (Fig. S1).

The structure and morphology of the as-prepared samples were characterized by FE-SEM and transmission electron microscopy (TEM) measurements. As shown in Fig. 2(a), the S-doped BiOBr samples consist of flower-like microspheres with uniform size of 1.5-3 µm in diameter. The microsphere assembled by many nanosheets with a size of less than 200 nm in diameter can be observed in its higher magnification FE-SEM image [Fig. 2(b)]. Compared with S-doped BiOBr microspheres, the flower-like BiOBr microspheres with a diameter of $1-2 \mu m$ are assembled by the nanosheets with a diameter of 300-400 nm [Fig. S2(a)]. They are larger than the nanosheets of S-doped BiOBr. However, by increasing the component of thiourea in the reaction, only nanosheets can be observed [Fig. S2(c)]. The S component inserted to the crystal of BiOBr instead of Bi by increasing the doping amount of S may change the growth and arrangement of the crystal. The structure of the as-prepared S-doped BiOBr samples was further investigated by high-resolution TEM (HR-TEM), as shown in Figs. 2(c) and 2(d). The lattice spaces of 0.28 and 0.33 nm are corresponding to the planes of (012) and (011) of BiOBr, respectively.^[38,39] In addition, the TEM and selected area electron diffraction pattern reveals that the sample has a poly-crystalline nature [inset in Fig. 2(d)].

Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves were conducted to further investigate the porous structure of the as-prepared samples. The as-prepared samples exhibit the Type IV isotherms characteristic of mesoporosity (Fig. S3). The



Figure 2. FE-SEM images (a and b) of the as-prepared S-doped BiOBr samples. TEM (c) and HR-TEM images (d) of the as-prepared S-doped BiOBr samples.

Brunauer-Emmett-Teller specific surface areas and pore volumes of the as-prepared samples are summarized in Table S1. The specific surface area of S-doped BiOBr (30.2 m^2/g) is lower than that of BiOBr (33.9 m^2/g). However, the S-doped BiOBr (30.8 mL/g) has the higher pore volume compared with that of BiOBr (21.1 mL/g). The higher pore volume is believed to have a positive role in the enhancement of photocatalytic activity for photocatalyst.^[41,42] The absorption edge and band-gap energies of the as-prepared samples were determined by UV-vis diffuse reflectance spectra (Figs S4 and S5). It can be founded that the S-doped BiOBr exhibit the strongest absorption under the visible light region and the absorption edge of the as-prepared BiOBr samples have red-shift from 440 nm to nearly 570 nm after being doped with S. Moreover, the band gap energy of the S-doped BiOBr is estimated to be 2.21 eV by fitting to a plot of Kubelka-Munk function versus energy (hv), which is much lower than that of BiOBr of 2.94 eV. The stronger absorption and the smaller band gap contributed to the enhancement of photocatalytic activity of the as-prepared samples.^[27-29]

The time-dependent tests were conducted to understand the formation process for the S-doped BiOBr microspheres under solvothermal conditions. The as-prepared samples were investigated by XRD, FE-SEM, and EDS. As shown in Fig. 3, the XRD patterns reveal that BiOBr could be formed quickly, and the diffraction peaks of the as-prepared sample can be indexed to the tetragonal phase of BiOBr with reaction time at 0.5 h. When the reaction time prolonged to 1 h, all the diffraction peaks of the BiOBr and a new weak peak at 2θ = 28.7° can be observed. By prolonging the reaction time, the intensity of diffraction peak at 2θ =28.7° become stronger with the reaction time at 12 and 48 h. These results indicate that the crystallization of BiOBr has been effected by S doping under the longer reaction time.



Figure 3. XRD patterns of the as-prepared S-doped BiOBr samples at different reaction stages.

For investigation, the form process of S-doped BiOBr microspheres, the morphologies of the samples are explored at different reaction stages (Fig. S6). BiOBr aggregates are firstly formed by mixture of the reagents before solvothermal treatment. By prolonging the reaction time, BiOBr microspheres with sizes of 1-2 µm can be formed with the assistance of surfactant. Further increasing the reaction time, the S-doped BiOBr microspheres with sizes of 1.5-3 µm can be formed. With the assistance of EDS analysis, the samples are composed of the elements Bi, O, and Br at a reaction of 1 h (Fig. S7). After the reaction of 48 h, the relative content of Bi element increased significantly due to the S overlapping. The proportion between Bi and O elements is improved while decreasing in Bi and Br due to S doping. Based on the results available, a possible mechanism for forming S-doped BiOBr flower-like microspheres can be deduced as shown in Scheme S1.

RhB ($C_0 = 10 \text{ mg/L}$) was used as a probe molecule to investigate the photocatalytic performance of the S-doped BiOBr microspheres. As shown in Fig. 4(a), the adsorption–desorption



Figure 4. The photocatalytic degradation ability over BiOBr and S-doped BiOBr samples under visible light irradiation (a) and cycling runs for RhB photodegradation over S-doped BiOBr samples (b).



equilibrium for the as-prepared samples can be reached after stirring for 1 h under dark condition. The adsorption ability for the S-doped BiOBr sample is almost 24%, slightly larger than that of BiOBr (20%) and P25 (17%). The photodegradation rates for the S-doped BiOBr and BiOBr photocatalysts are listed in Table S1. As observed, the photocatalytic processes of the as-prepared samples follow pseudo-first-order reaction. Neither photolysis (without photocatalyst) nor catalysis (without light) shows the catalytic ability on RhB degradation, suggesting that photocatalytic activity is induced by photocatalysis. For comparison, the RhB molecules can be completely degraded by S-doped BiOBr photocatalysts within 1 h under irradiation of visible light. However, only about 45% is degraded over BiOBr after irradiation for 1 h. The relatively higher photocatalytic activity of S-doped BiOBr photocatalysts may result from the doping with S, which is beneficial to narrow the band gap and transfer photogenerated electrons, thereby improving the photocatalytic activity.^[38–40] The degradation of RhB is negligible using P25 as a photocatalyst because it cannot be excited under visible light for its large band gap. In addition, the recycling experiments were performed to evaluate the durability of the S-doped BiOBr photocatalysts. As shown in Fig. 4(b), RhB molecules can be completely degraded after 7 runs (1 h for each run), indicating the good durability of the S-doped BiOBr photocatalysts. The photo-catalytic degradation property of colorless phenol in a liquid-solid system (5%, v/v) over the S-doped BiOBr was also investigated under similar conditions. The concentration change of methanol in the photo-catalytic degradation system was evaluated by the gas chromatography, as shown in Fig. S8. Sixty-nine percentage of the phenol can be degraded by S-doped BiOBr photocatalysts within 2 h.

For investigation of the plausible reaction mechanism for the superior photocatalytic activity of the S-doped BiOBr and detecting the active species during photocatalytic reactivity, hydroxyl radicals (•OH), the superoxide radical $(O_2^{\bullet-})$, and holes (h⁺) were investigated by adding 1.0 mM isopropyl alcohol (IPA, a quencher of •OH), p-benzoquinone (BQ, a quencher of $O_2^{\bullet-}$), and triethanolamine (TEOA, a quencher of h^+), respectively (Fig. 5).^[26,33,43] The results of trapping experiments are similar to the photocatalytic activity test above. It can be seen that the photocatalytic decoloration of RhB is declined slightly by the addition of 1 mM IPA. However, by addition of 1 mM BO or 1 mM TEOA into the reaction system, the decolorization rate of RhB is decelerated significantly. Therefore, it can be concluded that $O_2^{\bullet-}$ and h^+ are the main active species for decolorization of RhB solution under visible light irradiation, rather than •OH. On the basis of our experimental results and the reported literatures,^[33,44] the possible photocatalytic mechanism of the S-doped BiOBr photocatalysts is depicted in Scheme 1. Under the visible light irradiation, the photogenerated holes and electrons are in their valance band and conductance band, respectively. The S doping not only narrows the band



Figure 5. Trapping experiment of active species during the photocatalytic degradation of RhB reaction.

gap but also shifts up the conduction band (CB) edge. The doping with S introduced a valence band of impurities which can narrow the band gap of BiOBr.^[45] The CB of pure BiOBr is around 0.2 eV that cannot make the O₂ form O₂⁻⁻ which has the standard redox potentials of -0.046 eV.^[45,46] Hence, the CB of BiOBr has shifted to negative than -0.046 eV to reach the standard redox potentials of O₂/O₂⁻⁻ by doping with S. The photogenerated holes and O₂⁻⁻ have a strong oxidation potential and serve as active sites responsible for RhB photodegradation.



Scheme 1. Schematic illustration of the photocatalytic mechanism of RhB degradation over S-doped BiOBr photocatalyst.

Conclusion

In summary, the S-doped BiOBr has been successfully prepared by solvothermal method. The formation mechanism of the resultant samples was proposed based on the XRD, FE-SEM, and EDS analysis. The results reveal that the S-doped BiOBr microspheres are self-assembled by formed BiOBr microsphere firstly, and then S doped into BiOBr microsphere. Compared with pure BiOBr, the resultant S-doped BiOBr exhibits higher photocatalytic activity and excellent durability for degradation of RhB under visible light irradiation, attributing to the doped S can reduce the bandgap of BiOBr.

Supplementary materials

For supplementary material for this article, please visit http:// dx.doi.org/10.1557/mrc.2013.34

Acknowledgments

This work was financially supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry (1001603-C), the "521 Talents Training Plan" in ZSTU, and the National Natural Science Foundation of China (51133006) and Public Technological Research Project of Zhejiang Province (2012C21098). X. L. thanks the Innovative Program for Graduate Students of Zhejiang Sci-Tech University through Grant YCX12013 and 2013YSPY14.

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