Construction of hierarchical square biscuit-shape BiOBr photocatalyst with enhanced visible-light-response photocatalytic activities

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Abstract
Herein, we first explore an efficient solvothermal method to fabricate hierarchical square biscuit-like BiOBr architecture (SBBA), and further utilize it as a visible-light-responsive photocatalyst. The photocatalytic performance of the resultant SBBA is comprehensively evaluated by photocatalytic degradation of methyl orange solution as a model wastewater under the visible light irradiation. The SBBA photocatalyst with a band gap of ~2.56 eV exhibits remarkable photocatalytic activities in terms of degradation efficiency and reproducibility. More importantly, a plausible electron transfer and involved degradation mechanism are put forward. The excellent photocatalytic activities consolidate it as a promising photocatalyst in practical wastewater treatment.

1. Introduction

Over the past decades, the heterogeneous semiconductor photocatalysts have sparked worldwide interests for decomposing organic contaminants in wastewater [1, 2]. Especially in recent years, bismuth oxybromide (BiOBr) has received increasing attentions due to their high visible light responsivity and striking photocatalytic capability [2–4]. As is well established, the size, shape and morphology of semiconductors all play important roles in their photocatalytic activities [5–8]. Thus, various BiOBr photocatalysts with distinct microstructures, including nanoparticles, nanosheets (NSs) and microspheres, etc, have been extensively explored [9–11]. Particularly, the micrometer-size BiOBr architectures constructed with nanoscaled building blocks would be more favorable for the photocatalytic applications, in view of their remarkable advantages, such as efficient inhibition of particle aggregation, higher light-harvesting capacity, and much easier solid/liquid separation [8, 12]. For instance, Huo et al synthesized the NSs-assembled BiOBr microspheres, which demonstrated an even better photoactivities under visible light, when compared to the BiOBr bulk plates [12]. Additionally, Li and co-workers prepared hollow microspheres for efficient degradation of the rhodamine B [13]. However, it is still great challenge to explore simple and large-scale synthetic strategies for advanced higher-level BiOBr photocatalysts.

In this work, the hierarchical square biscuit-like BiOBr architecture (SBBA) was first prepared via a facile yet scalable solvothermal method. The photocatalytic activities of the as-prepared SBBA were evaluated in detail by using the methyl orange (MO) as a model pollutant under the visible light irradiation. Appealingly, the obtained SBBA demonstrates the removal rate (~100%) of the MO over the SBBA just after the 60-min visible light irradiation, and exceptional recyclability. More importantly, the involved photocatalytic degradation mechanism of the MO over the SBBA was also tentatively put forward here.
2. Experimental

2.1. Synthesis of the SBBA
All the chemicals were of analytical grade, and used as received without further purification. Typically, 1 mmol of Bi(NO₃)₃ · 5H₂O was dissolved well into 20 ml of acetic acid to obtain the solution A. And 1.2 mmol of cetyltrimethyl ammonium bromide was dissolved well into 20 ml of glycerol to form the solution B. And then, the solution A was added dropwise into the solution B. After stirred vigorously for 30 min, the mixture was further transferred into a Teflon-lined stainless steel autoclave (50 ml in volume). After maintained at 180 °C for 24 h, the gray SBBA precipitate was finally collected by centrifugation, washed with deionized water and absolute ethanol in order, and further dried at 60 °C for 5 h before further characterizations.

2.2. Materials characterization
The crystalline phase, morphologies and chemical states were characterized by x-ray diffraction (XRD, Max 18 XRD, Japan), field emission scanning electron microscopy (FESEM, LEO 1530VP), transmission electron microscopy (TEM), high-resolution TEM (HRTEM, JEOL-2010) and x-ray photoelectron spectroscopy (XPS, PHI5000 x-ray photoelectron spectrometer). PL spectrum was recorded on an Edinburgh FLS 980 instrument with the excitation wavelength 360 nm. UV–vis absorption diffuse-reflectance spectrum was recorded on a Hitachi U-3010 spectrophotometer by using BaSO₄ as the reference.

2.3. Evaluation of photocatalytic performance
Photocatalytic activity experiments were conducted by using a 500 W Xe arc lamp with a 400 nm cutoff filter to simulate the visible light. Typically, 0.2 g of the photocatalyst was dispersed in 100 ml of the MO aqueous solution (1 × 10⁻⁵ M) in a quartz reactor. Prior to the illumination, the suspension solution was continuously stirred in dark for 40 min to reach the sorption equilibrium. Subsequently, the solution was further exposed to visible light irradiation. At given intervals, 3 ml of the MO solution was taken out, and then centrifugated to remove the photocatalyst. The concentration was monitored by colorimetry with a double-beam spectrophotometer (Shimadzu UV-3600, Japan).

3. Results and discussion

3.1. Structural and physicochemical analysis of the SBBA
Figure 1(a) shows typical wide angle XRD pattern of the as-prepared SBBA product. Obviously, all these distinctive reflections can be indexed well as the tetragonal BiOBr with a space group of P4/nmm (129) (JCPDS card no. 09-0393). Of especial note, no any characteristic signals for other impurities can be detected, indicating the successful fabrication of the phase-pure BiOBr.

XPS measurement is further conducted to examine specific elemental makeup and oxidation states of the as-obtained SBBA, and corresponding XPS profiles are depicted in figures 1(b)–(d). The XPS survey scanning spectrum (figure S1 is available online at stacks.iop.org/MRX/7/035906/mmedia) confirms the co-existence of the elemental Br, Bi and O in the SBBA. The characteristic peaks centered at binding energies (BEs) of 159.2 and 164.9 eV are attributed to the Bi 4f½/2 and Bi 4f½/2 of the Bi 4f (figure 1(b)), respectively. Figure 1(c) illustrates the Br 3d spectra at BEs of 68.6 and 69.6 eV, which are related to the Br 3d½/2 and Br 3d½/2, respectively. As for the O 1s spectra (figure 1(d)), the fitted peak at 530.5 eV is typical of oxygen species in the crystal lattice, and the well-resolved one at 531.8 eV corresponds to the surface oxygen-containing groups (such as, O₂⁻, H₂O, etc), and the oxygen vacancies (Vo), which favors for reducing the recombination of electron-hole pairs, hence improving the comprehensive photocatalytic activities of the SBBA.[3, 14]

The low-magnification FESEM images (figures 2(a), (b)) reveal that the resultant SBBA photocatalyst is composed of many uniform square biscuit-like architectures with an edge length of ∼4 μm and a thickness of ∼1.5 μm. Closer examinations (figures 2(c)–(f)) visually confirm the unique hierarchical architecture, where many nanocubes of ∼200 nm in size are located on the surface of the NSs-assembled square biscuit-like architecture. Further TEM observations (figures 2(g), (h)) evidence the layered feature of the cubes themselves. Apparently, the well-defined lattice fringes of ∼0.25 and ∼0.32 nm (figure 2(i)) correspond to the (101) and (110) crystalline planes of the polycrystalline SBBA, respectively.

Figure 3(a) displays the UV–vis diffuse-reflectance spectrum of the resulted SBBA product. Obviously, the SBBA photocatalyst exhibits pronounced photo-absorption property in the UV region, and more strikingly, the absorption even can expand to the visible light region. The non-steep shape and strong absorption in the visible light region especially from approximately 500 to 800 nm evidently indicate the enhanced visible light absorption capability of the SBBA. It may originate from the impurity levels of the SBBA, such as Vo, adventitious carbon, etc rather than just the intrinsic band gap transition between the valence band (VB) and...
conduction band (CB) [15], which can be fully evidenced by its gray color (the inset in figure 3(a)). The remarkable photo absorption here would promisingly guarantee the exceptional photocatalytic activities of the SBBA under visible light irradiation. Besides, as examined from figure 3(a), the wavelength of the absorption
edge is $\sim 484$ nm, from which the band gap can be calculated as $\sim 2.56$ eV, benefitting for the efficient degradation of the pollutant MO under visible light irradiation.

### 3.2. Photocatalytic evaluation

Photocatalytic activities of the SBBA are elaborately evaluated by the photocatalytic degradation of the MO under the visible light irradiation ($\lambda > 400$ nm). For comparison, the direct photolysis without any catalysts and the dark adsorption with the SBBA as well as photocatalytic degradation with the P25 are also comprehensively evaluated. As shown in figure 3(b), the direct photolysis of the MO under visible light irradiation is negligible, implying the relative stability of the MO to the visible light. Prior to the illumination, the 40-min internal is applied to observe an adsorption–desorption equilibrium between the MO and photocatalysts in the dark. Compared with the commercial P25, the SBBA presents an especially poor adsorption capacity towards the MO. However, assisted by the visible light irradiation, the SBBA photocatalyst exhibits much higher photocatalytic activities than the P25, as observed in figure 3(b). More impressively, merely after the 60-min visible light irradiation, the removal rate of the MO over the SBBA is nearly 100%, much higher than the P25 ($\sim 25.2\%$). The higher photocatalytic performance of the SBBA was consisted with its poor PL activity (figure S2). Apart from the adsorption removal, there is a slight degradation of the MO over the P25 in the given reaction period of 60 min owing to the photosensitization effect on the P25 surface. The improved photocatalytic activities of the SBBA should be ascribed to its stronger light absorption property and suitable band gap for efficient utilization of the visible light. Besides this, in the photocatalytic degradation process, the unique microstructures of the SBBA also can guarantee its more surface activation sites for organic molecules and reactive radicals [4, 16–19].

A plausible electron transfer and photocatalytic degradation mechanism for the MO over the SBBA is tentatively proposed, as schematically illustrated in figure 3(c). Notably, the SBBA photocatalyst can absorb visible light due to its narrow band gap and strong light absorption ability in the visible light region. Under the visible light irradiation, the photoelectrons become free, and then the photo-generated electrons can jump from the VB mainly consisting of Br$_{4p}$ and O$_{2p}$ orbitals to the CB derived from Bi$_{6p}$ orbitals, while the holes stay in the VB (equation (1)). Owing to the intramolecular $\pi-\pi^*$ transition in the MO, the photosensitization effect also exists (equation (2)), and the resulting photoelectrons are immediately injected into the CB of the SBBA. Simultaneously, the collected electrons in the CB can be once again captured by the V$_{0}$ in the SBBA photocatalyst, thus leading to the efficient electron-hole separation, which renders more time to degrade the MO. Subsequently, the captured electrons can reduce O$_2$, and transfer O$_2$ to highly active $\cdot$O$_2$ radicals (equation (3)), which can be further confirmed by the trapping experiments of scavengers (figure S3). It is due to the higher redox potential of Bi$^{V}$/Bi$^{III}$ (1.59 V versus NHE) than the MO (1.48 V versus NHE) that the direct
oxidation degradation of the MO by holes is energetically possible [20]. Therefore, the dye MO can be photocatalytically degraded by $O_2^-$ radicals and holes through a series of reactions (equation (4)).

$$\begin{align*}
\text{BiOBr} + h\nu(E_g) &\rightarrow h\nu^+ + e^-_\text{CB} \quad (1) \\
\text{MO} + h\nu &\rightarrow \text{MO}^+ + e^- \quad (2) \\
e^- + O_2 &\rightarrow O_2^- \quad (3) \\
O_2^- + h^+ + \text{MO} &\rightarrow \text{CO}_2, \text{H}_2\text{O}, \text{mineral products} \quad (4)
\end{align*}$$

The stability of photocatalysts is another key factor for their practical application. The circulating runs in photocatalytic degradation of the MO over the SBBA were examined, as shown figure 3(d). After each degradation cycle, the SBBA was separated by centrifugation. Strikingly, the photocatalytic activity of the SBBA still remains ~97% after six re-cycles under the same photocatalytic conditions, highlighting that the photocatalytic activity of the SBBA is highly reproducible.

4. Conclusions

In conclusion, we first prepared hierarchical square biscuit-like BiOBr architecture for photocatalytic degradation of the organic MO via a solvothermal method. The resulted SBBA photocatalyst exhibited superior photocatalytic activities for efficient degradation of the MO under visible light irradiation with a plausible electron transfer and photocatalytic mechanism. More significantly, the methodology here holds enormous promise in versatile fabrication of other Bi-based architectures as visible-light-responsive photocatalysts.

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