Synthesis, characterization and photocatalytic activity of BiOBr–AC composite photocatalyst

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Article info

Article history:
Received 12 March 2013
Received in revised form 16 September 2013
Accepted 25 October 2013
Available online 7 November 2013

Keywords:
A. Hybrid
B. Environmental degradation
D. Surface analysis

Abstract

A series of mesoporous BiOBr–activated carbon (AC) composite photocatalysts with different content of AC were synthesized by an in situ loading solvothermal method. The obtained samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area and UV/vis diffuse reflectance spectrum (DRS). Results showed that the composite samples exhibit higher BET values and stronger adsorption ability for organic pollutants. Moreover, the existence of AC influenced the size of BiOBr deposited on ACs. High photocatalytic activity was observed for the degradation of the heteropolyaromatic dye methylene blue (MB) under both UV and visible light irradiation. Additionally, the results indicated that there was an optimum AC amount of 80% for obtaining the highest photocatalytic activity.

1. Introduction

Photocatalysis has been a great potential technology in environment management and clean energy exploitation. It has attracted widespread concentration in the past several decades. TiO₂ has been widely employed for photocatalytic applications, and a lot of progresses have been achieved [1–5]. However, TiO₂ can only be activated by the ultraviolet light (λ < 380 nm), which is only about 4% of the solar spectrum [6,7]. Considering visible-light accounts for 43% of the solar spectrum, the development of efficient visible-light-driven photocatalysts is becoming attractive and much effort has been devoted into this area [8–10].

To date, many oxides containing bismuth (Bi) have been found that they have high photocatalytic activity under visible light irradiation, such as Bi₂WO₆, BiVO₄, Bi₂MoO₆ [11]. And in recent years, bismuth oxide haloids (BiOXs, X = Cl, Br, I) have become one of the focused materials in the field of photocatalysis [12,13]. BiOXs have a layered structure consisting of alternately arranged [Bi₂O₂]₂⁺ mono layer and dual X⁻ layers [14]. This layered structure favors the separation of photo-induced electron–hole pairs, therefore BiOXs usually show excellent photocatalytic activity. Many research achievements have been achieved in the field of BiOBr [15–26]. For example, Huo’s group synthesized hierarchical flower-like BiOBr microspheres assembled with nanosheets, which had high photocatalytic activity under visible-light irradiation [27]. Also, BiOBr nanosheets-assembled microspheres prepared by Zhang and coworkers exhibited both strong adsorption ability and excellent photocatalytic activities for MO, RhB and phenol [28]. These contents revealed that BiOBr would be a promising photocatalyst in the treatment of organic pollutants.

At the same time, activated carbon (AC) is well known as one efficient support, due to its stability, mechanical resistance, high surface area and optimum porosity [29]. AC was also an effective adsorbent for the removal of a variety of organic pollutants. Therefore, the property of photocatalyst will be improved after be composited with AC [30–32].

So in this paper, the purpose is to find a way to synthesize BiOBr–AC composite photocatalysts with better photocatalytic activity. Then, the effect of AC on the performance of the composite photocatalysts was investigated to find an optimal condition. Therefore, the BiOBr–ACs were prepared by an in situ loading solvothermal method. The physical properties and photocatalytic activity of the as-prepared composite photocatalysts with different weight percentages of AC were studied.

2. Experimental setup

2.1. Synthesis

All chemicals involved were analytical grade and used without further purification.

BiOBr–ACs was prepared by an in situ loading solvothermal method. In a typical experiment for obtaining BiOBr–AC with 5 wt% AC, 0.0610 g AC was added into 80 mL ethylene glycol (EG) and ultrasonic treated for 90 min. Then, 4 mmol Bi(NO₃)₃·5H₂O...
and 4 mmol KBr were added into the above suspension. The sus-
pension was stirred for 40 min at room temperature. Then, the sus-
pension was transferred into a 100 mL Teflon-lined autoclave, and
maintained at 160 °C for 20 h. The final products were collected
and washed thoroughly with anhydrous ethanol and deionized
water after cooling to room temperature naturally. Finally, the
samples were dried in air at 60 °C for 2 d. Other samples were pre-
pared by the same procedure just with addition of different AC
weight. For comparison, pure BiOBr powder was also prepared by
the same method just without the addition of AC.

2.2. Characterization

The X-ray diffraction (XRD) pattern of the samples were mea-
sured on a diffractometer using monochromatized Cu K-beta radi-
ation under 40 kV and 100 mA and scanning over the range of
15° ≤ 2θ ≤ 80°. The surface morphologies and microstructures of
the prepared samples were observed by scanning electron micro-
scope (SEM), using Hitachi S-4800 scanning electron microscope.
The optical absorption property of catalysts was characterized by a
UV–vis spectrometer (UV3600, SHIMADZU). Brunauer–Emmett–
Teller (BET) surface areas measurements were carried out by
N2 adsorption at 77 K using an ASAP2020 instrument.

2.3. Photocatalytic experiment

Photocatalytic activity of the samples was evaluated by degra-
dation of MB under the irradiation of ultraviolet (UV) and visible
light. CEL-HXF300 Visual Light Source and CEL-HXUV300 Ultra
Violet Light Source were used in the present experiments. In every
experiment, 0.01 g sample was added into 100 mL MB solution
(30 ppm). The suspension was ultrasonic treated for 2 min, and
then it was stirred for 30 min in dark before light irradiation. At
15 min intervals, about 2 mL suspension was sampled and centri-
fuged. Finally, the UV/vis adsorption spectra of the centrifugated
solutions were analyzed using a UV–vis spectrometer (UV3600,
SHIMADZU).

3. Results and discussion

3.1. Characterization of BiOBr–AC composites

3.1.1. X-ray diffraction (XRD)

The as-prepared BiOBr–ACs with different AC amounts were
firstly analyzed by XRD (Fig. 1). It showed that all the diffraction
peaks of composites are consistent with the pure BiOBr, demon-
strating the high purity and single-phase of the as-prepared sam-

3.1.2. Scanning electron micrograph (SEM)

The SEM images of the resulting products are presented in
Fig. 2. It can be seen that the pure BiOBr is hierarchical 3D flow-
er-like microspheres with diameters of about 1 μm. The micro-
sphere is composed of many radially grown nanoflakes with a
thickness of about 10 nm (Fig. 2a). As to the BiOBr–ACs, lots of hi-

3.1.3. UV/vis diffuse reflectance spectrum (DRS)

The DRS of the as-prepared samples were shown in Fig. 3, which
was used to investigate the optical properties of as prepared sam-

3.1.4. Brunauer–Emmett–Teller (BET) surface area

The nitrogen adsorption–desorption method is used to study
the Brunauer–Emmett–Teller (BET) specific surface area of the
as-prepared samples. The obtained data for all samples were
shown in Table 1. It can be seen that all BiOBr–AC composites had higher values than pure BiOBr, which was due to the existence
of AC. And the BET surface area increased gradually with the
increasing AC content from 0% to 40%. Fig. 4 showed the nitrogen
adsorption–desorption isotherm of the BiOBr–ACs, which corre-

3.2. Photocatalytic activities

In order to evaluate the photocatalytic activity of the obtained
samples, photodegradation experiments of MB dye were con-
ducted under UV and visible irradiation conditions and the results
were shown in Fig. 5. From the figure, the adsorption and photocat-
alytic ability of as-prepared samples enhanced gradually with the
increasing content of AC from 10% to 80%. The trend are in good
accordance both under visible and UV light irradiation conditions.
And it should be noted that the pure BiOBr had stronger adsorption
and photocatalytic ability than BiOBr–10%AC while weaker than
the others. The efficiency of BiOBr–ACs on the degradation of MB
reach up to 85.70% for visible irradiation and 98.12% for UV
irradiation when the content of AC is 80%, which is the optimum

Fig. 1. XRD patterns of pure BiOBr and BiOBr–AC composites.
content. The high efficiency suggested that BiOBr–AC may be a promising excellent photocatalyst in the field.

Photocatalytic property of catalyst is related to many factors, such as optical absorption intensity, adsorption ability, crystallinity, BET surface area and so on. It is multi-factors that attributed

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**Table 1**
The BET surface area of as-prepared samples.

<table>
<thead>
<tr>
<th>BiOBr–AC</th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{BET}$ (m$^2$ g$^{-1}$)</td>
<td>23.46</td>
<td>45.52</td>
<td>80.83</td>
<td>148.53</td>
<td>206.46</td>
<td>256.37</td>
</tr>
</tbody>
</table>

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**Fig. 2.** SEM images of the samples: (a) pure BiOBr, (b) BiOBr–5%AC, (c) BiOBr–10%AC, (d) BiOBr–20%AC, (e) BiOBr–30%AC, and (f) BiOBr–40%AC.

**Fig. 3.** UV/vis DRS of pure BiOBr and BiOBr–AC composites.

**Fig. 4.** Nitrogen adsorption–desorption isotherm of the samples.
to the final photocatalytic activity. Compared to the pure BiOBr, composite samples have lower crystallinity, but stronger adsorption ability of organic compounds and stronger optical absorption intensity in visible light region. The combined result is that the photocatalytic property of BiOBr–10%AC is lower while others are stronger than that of pure BiOBr. Herein, optical absorption intensity, adsorption ability and crystallinity were effective factors to determine the photocatalytic activity. The efficiency can be improved via compositing AC when AC content exceeds a certain range (10%), resulted in that the positive influence of AC on adsorption ability is larger than the negative influence on optical absorption intensity and crystallinity. However, BiOBr–90%AC has higher adsorption ability while lower photocatalytic activity than BiOBr–80%AC, which may due to the negative impact in the use of light made by the overload of AC.

4. Conclusions

In summary, a series of mesoporous BiOBr–ACs photocatalysts with flower-like structures were synthesized by an in situ loading solvothermal method. The XRD results showed that AC would affect the crystallization of the samples, but it had no influence on their crystal phase. Results suggest that AC had influence on the optical absorption ability and the crystal size. Samples had higher BET surface areas and exhibited stronger adsorption ability when AC content increased. And the as-prepared samples showed stronger photocatalytic activity when AC content increased from 10% to 80%. The efficiency of BiOBr–AC on the degradation of MB can reach up to 85.70% and 98.12% under visible irradiation and UV irradiation, respectively.

Acknowledgements

We are grateful for grants from the National Key Basic Research Program (“973” Project) of China (No. 2010CB429006), National Science Fund for Distinguished Young Scholars (No. 51225901), the National Natural Science Foundation of China (No. 51108158), Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07101-008), the Research Fund for the Doctoral Program of Higher Education of China (511199611), The outstanding youth fund of Jiangsu Province (BK2012037).

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[13] Chang X, Huang J, Cheng C, et al. BiOBr (X=Cl, Br, I) photocatalysts prepared with flower-like structures were synthesized by an in situ loading solvothermal method. The XRD results showed that AC would affect the crystallization of the samples, but it had no influence on their crystal phase. Results suggest that AC had influence on the optical absorption ability and the crystal size. Samples had higher BET surface areas and exhibited stronger adsorption ability when AC content increased. And the as-prepared samples showed stronger photocatalytic activity when AC content increased from 10% to 80%. The efficiency of BiOBr–AC on the degradation of MB can reach up to 85.70% and 98.12% under visible irradiation and UV irradiation, respectively.

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