BiOCl nanomaterials for photocatalytic degradations of nitrogenous organic compound

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Abstract—Different BiOCl hierarchical nanostructures with controllable morphologies were synthesized by a facile glycerol-mediated solvothermal method. Every products were subsequently and well crystallized characterized by a range of methods, such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD), high-resolution transmission microscopy (HRTEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED). The photocatalytic properties of the samples were further investigated through photocatalytic decomposition of Methyl Orange (MO) dye. The BiOCl hierarchical nanostructures was as a result of efficient photocatalytic activity under UV light irradiation, which can degrade MO in a few minutes.

1. Introduction
It is critical for people to treat wastewater including nitrogenous organic compound, photocatalysts have been get highly attentions as a potential approach to tackle these issues. Particularly bismuth oxychloride (BiOCl) as bismuth oxyhalides, which has great potentials to some excellent properties and applications in heterogeneous catalysis due to its unique structures and excellent properties[1]. Especially, microflowers BiOCl as a photocatalyst with the well abilities of water contaminate treatment under UV illumination was attribute to its excellent electrical and optical properties.

The degradation of nitrogenous organic remains insufficient. BiOCl has a typical layered structure, which consists of [Bi2O2] nanosheets is sandwiched by two slabs of negative Cl ions with an internal electrical field along the {001} direction. It is the unique structure that urges photoinduced charge carriers to easily facilitate separation and transfer leading to enhanced the photocatalytic performance. Up to now, a variety of methods to compose the BiOCl nanostructures with well-controlled morphologies including fibers, solid microspheres, nanoplates, nanoparticles, nanobelts, nanotubes, and microflowers of BiOCl. Among them, the 3D hierarchical structure of microflowers has been previously studied because of the larger surface areas, which also enhance their photocatalytic activities. Therefore, the 3D flowerlike BiOCl photocatalyst with predominant exposed {001} facets can be achieved promisingly in the field of environmental technologies.

In this study, 3D flowerlike and hierarchical BiOCl nanostructures with higher exposed {001} facets were synthesized by a economic and simple glycerol-mediated solvothermal method. Meanwhile, the degradation capabilities of prepared samples were assessed by decomposing Methyl Orange under UV light illumination. Furthermore, we intensively studied the relationship between the photocatalytic properties and the experimental parameters of the hierarchical BiOCl.
2. Experimental

2.1 Preparation of the BiOCl

All the chemical reagents used in our work included Bi (NO$_3$)$_5$·5H$_2$O, glycerol, AgNO$_3$, KCl, and Distilled water were analytically pure grade which could be used directly without further purification.

4 ml of KCl (0.12g) solution was added into the mixture of 0.776 g of Bi (NO$_3$)$_5$·5H$_2$O and 76 ml of glycerol. The above solution was stirring for 15 min in the room. Then transferred into 100 ml Teflon-lined autoclave and heated at 110ºC for 5 h. The obtained products was donated as T-1. Finally, the products were washed with pure water and ethanol three times using centrifugation in separately. It is need to dry at 65ºC before characterization. We prepared the other BiOCl powder by varying the experimental conditions, including the solvothermal temperature, time and the quantity of glycerol. All products are listed in the Table 1.

| Samples | Solvothermal time(h) | Solvothermal temperature(ºC) | Glycerol(ml) |
|---------|---------------------|-----------------------------|--------------|
| T-1     | 5                   | 100                         | 76           |
| T-2     | 7                   | 100                         | 76           |
| T-3     | 9                   | 100                         | 76           |
| T-4     | 10                  | 100                         | 76           |
| K-1     | 9                   | 100                         | 76           |
| K-2     | 9                   | 120                         | 76           |
| K-3     | 9                   | 140                         | 76           |
| G-1     | 9                   | 120                         | 19           |
| G-2     | 9                   | 120                         | 38           |
| G-3     | 9                   | 120                         | 93           |

2.2 Photocatalytic decomposition of Methyl Orange (MO)

A 0.025 g of prepared samples was added into 50 ml 10 mg/L MO solution in a tube. The above solution was kept stirring without light for 1 h in order to reach the equilibrium of adsorption-desorption before illuminating under UV light. The residual concentration was examined by a UV-vis spectrophotometer.

2.3 Characterization.

The crystalline of BiOCl were characterized through XRD patterns on Rigaku D/max 2550 using Cu Kα radiation (λ=0.15406 nm) within the scanning range 2θ=10°–90° in a step width of 0.02°. A transmission electron microscopy(TEM)morphologies and the field emission scanning electron microscopy (SEM) structures of the samples were investigated from an attached OXFORD-INCA on the electron microscope.

3. Results and discussion

The BiOCl products were synthesized by reacting Bi (NO$_3$)$_5$·5H$_2$O and KCl in glycerol solvent through a facile solvothermal method. In addition, the effects of experimental conditions including reaction temperature and reaction time, the amount of glycerol on the photocatalysis and morphology of samples have been deeply studied.

3.1 Effect of solvothermal reaction time

The effect of the solvothermal time on the catalysis and morphology of BiOCl was investigated by varying the reaction time and remaining the other conditions unchanged.
Fig. 1 XRD patterns of the BiOCl microflowers with different synthesized time for 5h (T-1), 7h (T-2), 9h (T-3), 10h (T-4)

The X-ray diffraction (XRD) pattern of the BiOCl products synthesized with different solvothermal time displayed in Fig. 1. From the Fig. 1., we can clearly see that the as prepared samples have the characteristic diffraction peaks which were well assigned to tetragonal structure of BiOCl (JCPDS card no.06-0249). It is observed that the diffraction of (001) peak located at 12° is relatively broad and weak in intensity, illustrating a slightly size along the {001} facets. Notably, the intensity ratio of the (110)/ (001) diffraction peaks is much higher comparing with the standard pattern, which could be ascribed to the construction of ultrathin building units along the {001} direction, implying a relatively large lateral size oriented along the {110} direction. Meantime, it is clearly that the diffraction peaks of T-1, T-2, T-3 and T-4 almost have not change even if alternating solvothermal time. Based on above consideration, the reaction time make no difference on the configuration of the BiOCl.

Fig. 2 SEM (a, b) of BiOCl miroflower (T-3); TEM image (c); HRTEM image (d) of BiOCl

The morphology and nanostructure of as-prepared BiOCl was characterized by SEM and TEM. A image (Fig. 2a) which showed the BiOCl has a structure of flowerlike with a diameter of 1-2μm. Moreover, hierarchical nanostructure are constitutive of dozens of 2D nanosheets with a lateral size about 500nm could be observed from the magnified SEM (Fig. 2b). The (TEM) (Fig. 2c) image further certifies the flower nanostructure is constructed by self-organized subunits[2]. From the HRTEM picture (Fig. 2d), the spacing lattice fringes were measured to be 0.273 nm should belonged to the {110} planes of the tetragonal structure BiOCl. In addition, the SAED (inset in Fig. 4d) exhibited a sharp spot pattern, showing the samples possess highly crystalline with characteristic {110}, {110}, and {002}.
facets in kept with the XRD results[3]. Based on the above discussion and the XRD results, the microflower BiOCl with high percentage of {001} facets exposure is synthesized successfully. The photocatalytic performance of the samples was evaluated by the degrading methyl orange under UV illumination. Prior to UV-light illumination, the MO solution over the catalyst were kept in the dark for 60min to reach the equilibrium state[4]. Temporal evolution of absorption spectra changes of MO solution decomposed by the BiOCl synthesized at 110ºC for 9h using 76ml glycerol is displayed in Fig.3a. The absorption degree of MO at 464nm was used to measured the photocatalytic process. It can be obviously seen that there is no shift of the character peak of MO, indicating that no other substance was produced. Additionally, the maximum absorption of MO solution sharply weaken within 2min, which imply that BiOCl (T-3) have a high photocatalytic activity.

Fig.3 Absorption profiles of MO with irradition time (a); degradation rate of MO in BiOCl through UV light illumination(b)

In order to evaluate the photocatalytic properties the effects of the samples (different solvothermal time)on the catalytic activity, the MO aqueous solution with the BiOCl catalyst was kept stirring in the dark to reach the equilibrium adsorption state before UV irradiation. The results presented in Fig.1 ,it was also worth noting that about 25, 37, 48, 30%. What’s more important, the MO was almost completely degraded after UV light irradiation for 6min. Furthermore, it can be seen that the T-2 obtained for reaction time of 9h manifests the better photocatalytic ability.

3.2 Effect of solvothermal reaction temperature
Based on the result of the effect of solvothermal time, we conducted experiment for 9h with 76ml glycerol changing the parameter of solvothermal reaction temperature.

Fig.4 XRD patterns of the BiOCl microflowers synthesized at 100ºC , 120ºC , 140ºC(T-3,K-2,K-3);degradation rate of MO over BiOCl(T-3, K-2, K-3) under UV light illumination
In the light of Fig.4a, it can be observed that BiOCl was not obtained when the solvothermal temperature is 90ºC. These results illustrate that reaction temperature of 100ºC is relative lower to the formation of BiOCl and the morphology of BiOCl is not affected by the temperature in an appropriated rang. From the Fig.4b, we can see that 30, 37 and 26% MO adsorption in the dark equilibration for T-3, K-2, K-3, respectively. It also can be seen that the as-prepared BiOCl can completely degrade MO within 8min. Furthermore, compared with the sample K-2, K-3, the T-3 obtaining at 100ºC exhibits higher photocatalytic activity for decomposing MO.

3.3 Effect of amount of glycerol

Fig.5 XRD patterns of the BiOCl microflowers synthesized with 19, 38, 76, 93ml (G-1, G-2, T-3, G-3); degradation rate of MO over BiOCl(G-1, T-3, G-2, G-3) under UV light illumination

On the basis of the above experimental results, the BiOCl were prepared with different volume of glycerol but with the constant of solvothermal temperature and time.

The XRD patterns of BiOCl samples synthesized at 100ºC for 9h with different moles of glycerol in Fig.5a. The photocatalysis of various BiOCl products (G-1, G-2, T-3 G-3) to degrade the MO was investigated under ultraviolet light irradiation is illustrated in Fig5b. It can further confirmed that G-1, G-2, T-3, and G-3 adsorbed about 16, 35, 27, 31% of MO solution, respectively. Most notably that the G-3 prepared with 76ml glycerol have a higher photocatalytic performance.

4. Conclusion

In summary, we have reported a facile synthesis of different BiOCl hierarchical nanostructures with controllable morphologies. The resultant BiOCl microflower with dominant {001} facets that is a vital factor for photocatalytic performances[5]. Therefore, the BiOCl exhibits a higher photodegradation activity, which can degrade nitrogenous organic compound completely within 6min under UV light irradiation. Furthermore, the morphology of BiOCl is not affected by he volume of glycerol, solvothermal time and temperature, but the solvothermal temperature must be in a reasonable scale. Finally, the products that obtained at 120ºC for 9h with 93ml glycerol preform the best photocatalytic ability.

References
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