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Low temperature preparation of flower-like BiOCl film and its photocatalytic activity

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The BiOCl thin film with flower-like sphere structure was prepared at a low temperature by the alcoholysis-coating method using $BiCl_3$ as precursor. The obtained thin film was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), electronic energy spectrum (EDS) and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS). And the results showed that the obtained BiOCl film without calcination was composed of flower-like sphere structure with tetragonal phase and had a good absorption for ultraviolet. The photocatalytic activity of BiOCl thin film was also evaluated by the degradation of methyl orange in water under UV light irradiation. The degradation experimental results confirmed that the film prepared at low temperature possessed a high photocatalytic activity and could achieve 97% degradation to 10 mg/L methyl orange solution after 150 min UV light irradiation. The stability of the obtained BiOCl thin film was also good and its photocatalytic activity still remained an above 94% removal of methyl orange after being used four times. In addition, a possible formation mechanism of BiOCl thin film was also inferred and the results suggested that the ethylene glycol solvent may contribute to the forming flower-like sphere structure.

flower-like BiOCl film, low-temperature preparation, photocatalytic activity

1 Introduction

Photocatalytic technology is a kind of advanced oxidation technology, which can utterly oxidate organics in water into CO_2, H_2O or other small molecular materials though the ·OH generated during the reaction. Therefore it is an environment-friendly technology. In order to solve the problems existing in photocatalytic technology, such as the low utilization of light, the recombination of photogenerated electron-hole pairs and practical application problems, some of the researchers focus on the modification of original photocatalysts (such as TiO_2) and further mechanism study [1, 2], while other researchers focus on developing new photocatalysts [3, 4]. BiOCl, as a kind of semiconductor photocatalytic material, is attracting more and more attention in recent years, because of its excellent photocatalytic activity. And BiOCl with layer structure belongs to indirect band gap semiconductor, which can promote the separation of electrons and holes effectively to obtain good photocatalytic activity [5]. BiOCl has a band gap of 3.2–3.5 eV [6–9] and has a better photocatalytic activity than TiO_2 (P25, Degussa) to methyl orange under the UV irradiation [7]. It was reported that BiOCl could decompose RhB under visible light irradiation efficiently due to dye sensitization [10]. Chang [11, 12] prepared BiOX (X = Cl, Br, I) powder photocatalysts using $NaBiO_3$ and HX aqueous solutions as raw materials, and the results of photocatalytic degradation demonstrated that the prepared photocatalysts expressed high photocatalytic activity to PCP-Na under Xenon lamp irradiation. Our group also found that the semiconductor materials of bismuth oxyhalide compounds had good photocatalytic activity, and

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prepared BiOCl and BiOCl/BiOBr by simple hydrolysis method using $BiCl_3$ and $BiBr_3$ as raw materials [13, 14]. Our study showed that this hydrolysis method was environment-friendly and energy-saving, and had promising application. Zhu [15] synthesized 3D hierarchitectures (HAs) of BiOCl by a template-free solvothermal method using $BiCl_3 \cdot 5H_2O$ as raw material and glycol as solvent, which has good photocatalytic activity to RhB under the UV light irradiation. Chen [16] used $Bi(NO_3)_3 \cdot 5H_2O$ and CTAC as the Bi source and Cl source respectively, containing teflon lining stainless steel reaction kettle as the reactor, and prepared BiOCl in the solvothermal method, which has photocatalytic activity to both methyl orange and RhB degradation under the UV light irradiation. Certainly, some researchers also prepared the BiOCl thin film by physical vapor deposition and chemical oxidation method [17].

At present, many reports have described the preparations and properties of BiOCl photocatalyst and their applications. They mainly focus on the powder BiOCl, while the preparation and photocatalytic activity of BiOCl thin film are barely reported at home and abroad. Although powder photocatalyst has larger surface and higher reaction rate than film photocatalyst and it is easy to prepare, the powder is poorly dispersed in solution, and difficult to separate and recycle, especially the tiny particles with micro-nano structure. Therefore, the immobilized BiOCl catalyst, which is convenient to solve the problem of solid-liquid separation and cyclic utilization, may deal with the organic pollutants in water, but also is convenient to extend to resolve organic pollutants in air. Generally, the preparation methods of film photocatalysts mainly include anodic oxidation method [18], sputtering method [19] and coating method [20, 21]. In this work, the BiOCl thin film is prepared in the alcoholysis-coating method, which is simple and easy to operate and does not need high temperature heat treatment. The prepared BiOCl thin film is well crystallized with flower-like sphere structure. At the same time, the BiOCl thin film photocatalysts possess the relatively large specific surface area after immobilization and excellent photocatalytic activity under UV light irradiation.

2 Experimental

2.1 Materials and measurements

Chloride bismuth ($BiCl_3$, AR) was purchased from Shanghai Hengxin Chemical Reagent Co., other reagents were purchased from Tianjin Medical Company, and all the reagents were used without further purification.

The dry process of BiOCl film was conducted using a drying oven (101-1A, Tianjin Thai Frost Instrument Co., LTD) and the calcination process was conducted in a muffle furnace (TDW, Yuyao Oriental Electrical Instrument Factory). In photocatalytic activity test process, a UV lamp (250 W, main wavelength at 365 nm, Tianjin Boruite Lighting Electric Co., Ltd.) was used as the side light source. The VARIAN CARY 50 Probe type UV-vis spectrophotometer was used to detect the concentration of methyl orange. The phase and composition of the samples were characterized by X-ray diffraction (XRD) using a D/Max-2500 diffractometer at a voltage of 40 kV and a current of 100 mA with Cu-Ka radiation, employing a scanning rate of 8 °/min in the 2θ ranging from 5° to 70°. The morphologies and microstructures (SEM) and electronic energy spectrum (EDS) of as-prepared samples were examined by Nanosem430 field emission scanning electron microscopy. The UV-vis diffuse reflective spectrum (DRS) of the sample was tested by a Varian Cary type 300 UV-vis spectrophotometer.

2.2 The pretreatment of Ti substrate

Ti sheets (80 mm × 10 mm × 2 mm) were burnished using abrasive paper firstly, then placed into 10% (quality ratio) oxalic acid solution and boiled at 90 °C for 3 h. Subsequently, Ti sheets were put into 10% HCl solution for 1 h. The treated Ti sheets were cleaned using distilled water, and then placed into acetone to prevent oxidation by air.

2.3 Preparation of the BiOCl film

In a typical experimental procedure, 0.100 g of $BiCl_3$ was added to 5 mL ethylene glycol at room temperature firstly. Then the solution was heated at 60 °C with stirring to produce transparent liquid. After another 10 min stirring at 60 °C, concentrated aqueous ammonia was dropped into the solution to adjust pH value to 9, and this pH value was maintained at 60 °C for 1 h, a white emulsion was obtained. Then the white emulsion was coated on Ti substarte, and the coated film was dried at 80 °C. After repeating the above coating and drying operation several times, the BiOCl film coated on Ti surface was obtained, and the film was dried at 80 °C for 3 h in order to remove the ethylene glycol completely. If necessary the sample was calcined in the muffle furnace at 200 °C or 400 °C for 3 h, and then cooled to room temperature naturally. The sample was dipped into distilled water for 2 h, and then the white BiOCl thin film photocatalyst was obtained finally.

2.4 Photocatalytic activity experiment

The photocatalytic activity of the samples was evaluated by the gradation of a methyl orange (MO) dye solution. Ti sheet coated with BiOCl film was hung in a cylindrical quartz glass reactor, in which 50 mL 10 mg/L MO solution was poured. Then it was irradiated by a 250 W ultraviolet lamp with a main emission wavelength of 365 nm. During the reaction, MO solution was aerated by air thought a min-type pump to keep the solution in flowing state. At given intervals of illumination, the samples of the reaction solution were taken out and analyzed using a UV-vis spec-

trometer (VARIAN CARY 50Probe). The degradation efficiency (D) of MO was calculated by the following formula:

$$D = \left(1 - \frac{c_t}{c_0}\right) \times 100\%$$

in which c_0 was the initial concentration of MO, c_t was the concentration of MO after reaction t minutes.

3 Results and discussion

3.1 XRD analysis

Figure 1 showed the XRD patterns of the Ti substrate and samples calcined at different temperature. All the detectable peaks in this pattern could be assigned to the tetragonal BiOCl (JCPDS 06-0249), except the peaks of Ti substrate at 35.2°, 38.3°, 40.2° and 53.0° (marked in the figure). This was probably related to the breakdown of BiOCl thin film by X-ray. No other crystalline impurities were detected, which demonstrated that the products were very high-purity and single-phase. Compared with the sample prepared without calcination, the diffraction peaks of samples calcined at 200 °C and 400 °C turned narrow, the reason of which might be that the crystallinity of BiOCl was changed better after high temperature calcination.

3.2 SEM and EDS analysis

The morphology of the samples was detected by SEM. The images of BiOCl thin films without calcination, calcined at 200 °C and 400 °C are shown in Figure 2(a), (b) and (c), respectively. It can be seen that the BiOCl thin film without calcination presents a morphology of flower-like sphere assembled of nanosheets, and the diameter of the sphere ranges from 1 to 2 μm. With the rise of calcination temperature, the flower-like sphere was destroyed firstly, and then film sample was sintered. The EDS spectral graph of sample (a) is shown in Figure 2(d). This result was agreement with that reported in the literature [22]. The spectrum showed that the sample was composed of Bi, O and Cl elements. The quantitative analysis displayed that the ratio of each element in the quality was Bi:O:Cl = 79.15:7.03:13.82, which was close to the stoichiometric ratio of BiOCl (80.23:6.14:13.62).

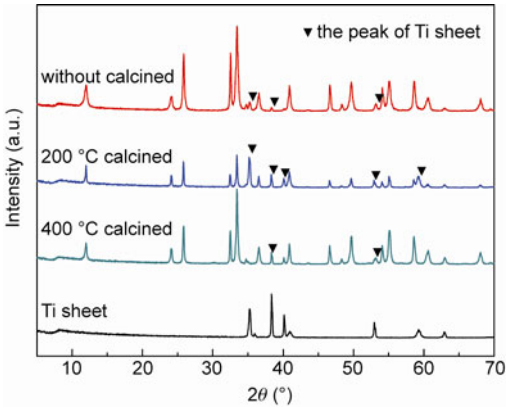

Figure 1 XRD patterns of samples and Ti substrate.

3.3 UV-vis DRS absorption spectrum

In order to investigate the optical absorption property of as-prepared sample, the UV-vis diffuse spectrum of the BiOCl thin film sample without calcination was tested, and the result was shown in Figure 3. It showed that the optical absorption scope of BiOCl thin film was in the UV area of $\lambda < 400$ nm. As BiOCl is an indirect band gap semi-conductor, its band gap energy (E_g) can be estimated by plotting $(Ahv)^2$ versus photo energy hv as shown in the inset in Figure 3. By extrapolating the E_g value of the sample BiOCl was about 3.38 eV, which is near 3.40 eV reported in the literature [23], so the obtained BiOCl thin film is a broad band gap semiconductor and can response to ultraviolet light. The wider distance between conduction and valence band indicates that the light induced electron-hole pairs should have stronger reduction-oxidation ability. Hence, the sample should have ideal photocatalytic activity under the ultraviolet irradiation.

3.4 Photocatalytic activity of BiOCl film

3.4.1 Photocatalytic activity of BiOCl films calcined at different temperatures

To investigate the influence of calcining temperatures on the photocatalytic performance of BiOCl thin film, the photocatalytic activities of samples calcined at different temperatures of 80 °C, 200 °C and 400 °C were evaluated and the results were shown in Figure 4. It can be seen that the calcination process can not improve the photocatalytic activity of the film, especially, the photocatalytic activity of the film decreased obviously after calcined at 400 °C. Combined with the analysis of the SEM images, the possible reason could be that the film was sintered under the 400 °C calcination, its flower-like sphere structure was damaged, the specific surface area of this photocatalyst decreased and the contacting area of the photocatalyst with solution also decreased. As a result, the utilization rate of light was reduced, and the photocatalytic activity was turned poor subsequently when BiOCl thin film calcined at 400 °C was used. Contrary the specific surface area of sample without calcination is the largest in three samples, so its photocatalytic activity is the best. Hence the BiOCl thin film without calcination was chosen as photocatalyst in the following study.

3.4.2 Study of degradation process

The MO degradation process was studied using BiOCl film without calcination as photocatalyst and the result was shown in Figure 5. Figure 5(a) showed the UV-vis absorbance characteristics of MO at different time during the photocatalytic degradation process. It could be seen that the maxi-

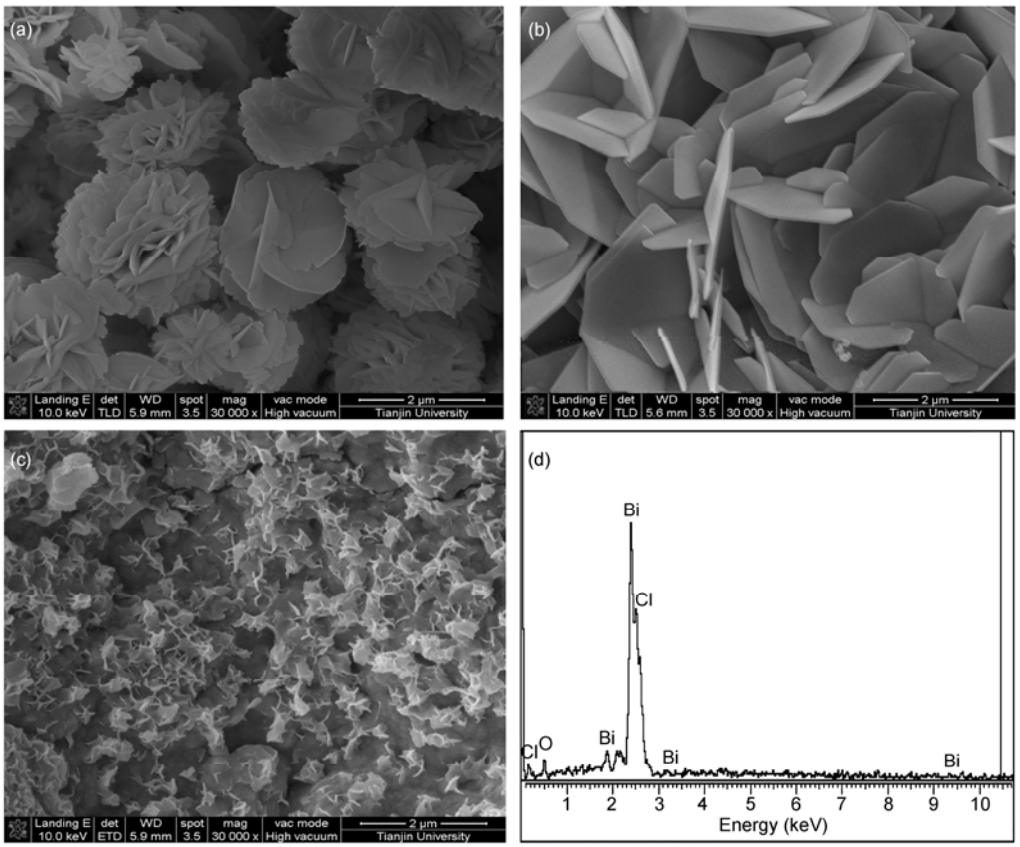

Figure 2 SEM images of samples and EDS spectrum, (a) without calcination; (b) calcined at 200 °C; (c) calcined at 400 °C; (d) EDS spectrum of the sample (a).

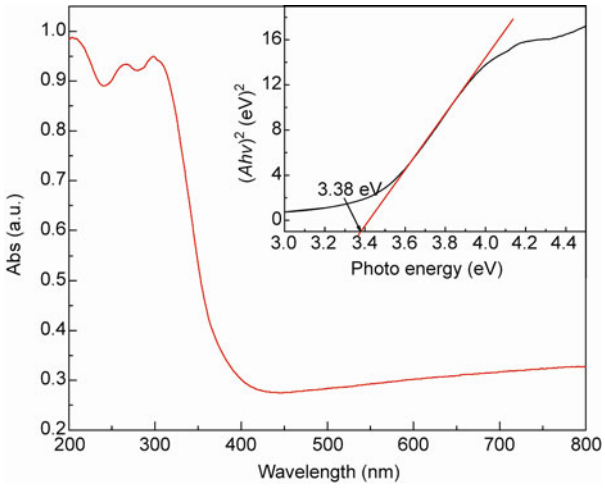

Figure 3 The UV-vis DRS spectrum of BiOCl film without calcinations.

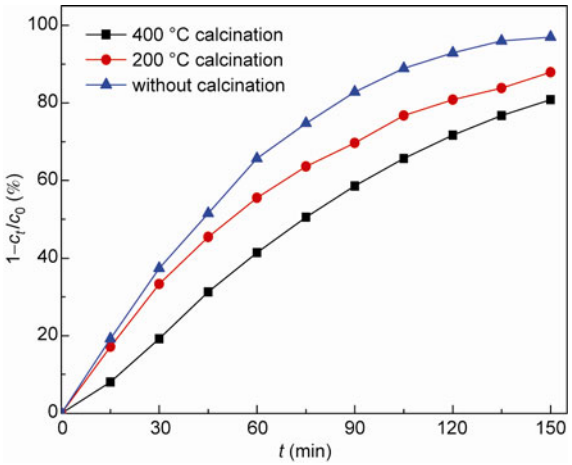

Figure 4 Photocatalytic activity of BiOCl films calcined at different temperatures.

mum absorbance peak of MO was at 463 nm. This peak value decreased steadily with the increasing irradiation time and the orange color of the solution also turned light gradually, suggesting that the MO was degraded efficiently under UV irradiation. When the reaction time reached 150 min, the absorption peak of MO turned very low, indicating that almost all the MO in the solution had been decomposed. In order to clarify the role of light, catalyst and light combined with catalyst in photocatalytic degradation of MO, we designed three experimental processes of photolysis (without catalyst), adsorption (without light) and photocatalysis (light and catalyst), and the results were shown in Figure 5(b). It could be seen that the BiOCl film had a very weak adsorption to MO under dark condition, which can be almost

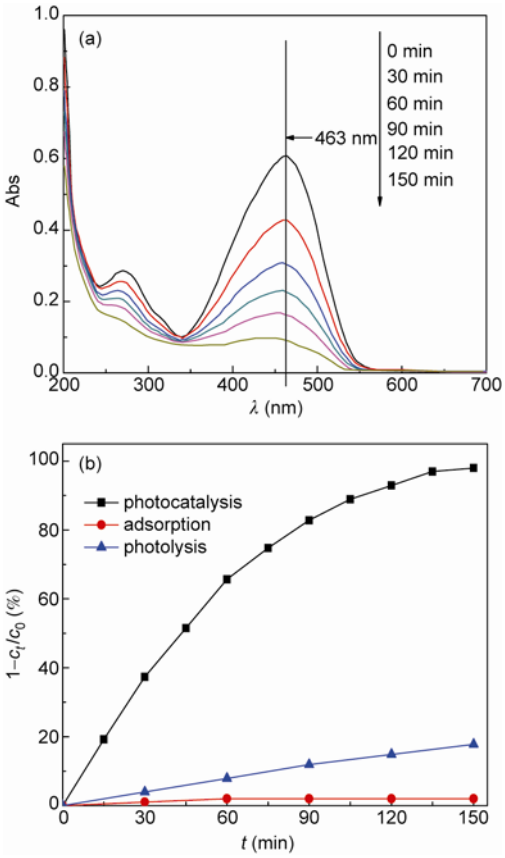

Figure 5 Study of MO degradation process. (a) UV-vis absorbance scanning curve of MO; (b) the processes of photolysis, adsorption and photocatalysis.

negligible; in the absent of BiOCl film catalyst MO could be degraded about 17% after 2.5 h UV irradiation; while the degradation rate of MO can reach 97% after reaction 2.5 h under the cooperation of light and BiOCl film. So the degradation of MO can be mainly owned to the photocatalysis, in addition, the BiOCl film had better photocatalytic activity than the TiO_2 film reported in literature [21].

3.4.3 Cyclic utilization

Compared with powder catalyst the biggest advantage of the immobilized thin film catalyst is to avoid the complicated solid-liquid separation process, thus the film catalyst can be reused directly. In order to check the recyclability of BiOCl film for the photocatalytic degradation of MO, the BiOCl thin film photocatalyst was reused for three times, the corresponding degradation results for MO solution were shown in Figure 6. After each 150 min reaction, the BiOCl thin film was only cleaned using distilled water, and then dried in air for the next use. From Figure 6 it can be seen that the catalytic activity of BiOCl thin film deceased a little after three times recycle, but the degradation rate of methyl orange still remained higher than 94%. Hence, the BiOCl film photocatalyst has a good stability and can be reused several times without special treatment. Therefore it can be inferred that this novel BiOCl thin film photocatalyst prepared in this method not only could decompose methyl orange efficiently under UV irradiation, but also showed a higher photocatalytic activity in cyclic utilization, and had potential application in the treatment of dyes wastewater.

3.5 A possible fabrication mechanism of the formation of flower-like BiOCl thin film

The flower-like sphere structure of BiOCl thin film prepared in alcoholysis-coating method in this paper was similar with the microsphere structure of BiOCl powder prepared in solvothermal method [15], in which the formation of BiOCl microspheres followed a glycol-assisted growth process [23]. We think the fabrication mechanism of the

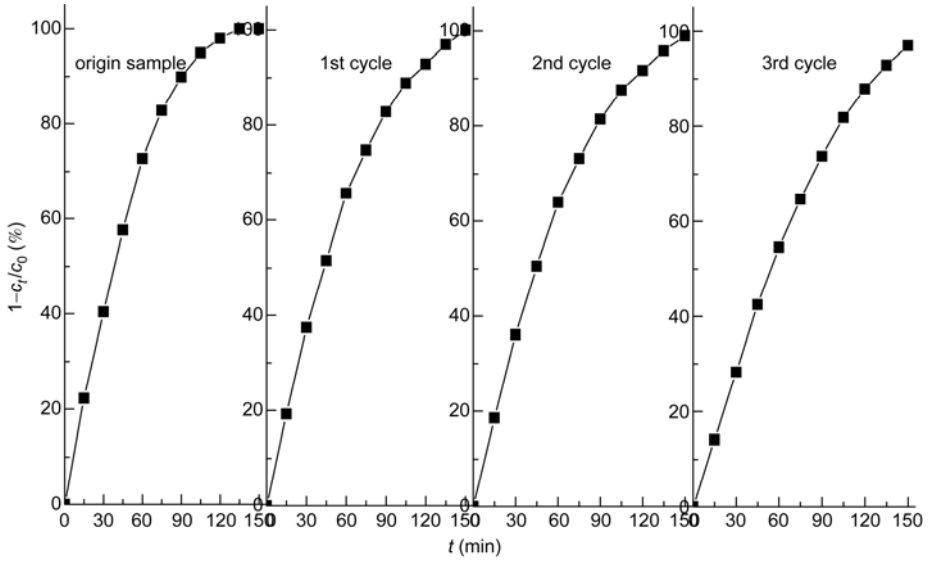

Figure 6 The cyclic utilization of BiOCl film without calcinations.

flower-like sphere structure of BiOCl thin film also can be explained by the glycol-assisted growth process. When $BiCl_3$ was added to ethylene glycol, since ethylene glycol had weak acidity and was easy to absorb moisture, and $BiCl_3$ was also easy to absorb moisture from the air, the following chemical reaction might happen [23]:

$$x\mathrm{Bi}^{3+} + z\mathrm{H_2O} + y\mathrm{EG} \rightarrow \mathrm{Bi}_x(\mathrm{EG})_y(\mathrm{OH})_z + z\mathrm{H}^+ \quad (1)$$

Since Bi^{3+} has big radius, strong polarization and deformation capacity, it can overcome the space resistance and form complexes with high ligancy [24]. An associating reaction of the metal alkoxide formed in reaction (1) proceeded in the following heating process. In the association reaction, empty metal atomic orbital could accept lone electron pair from oxygen in alkoxy to form bridge bond [25], and then the Bi–O–Bi structure in 3D space was formed. Because ethylene glycol has the ability of interlinking action [23], the Bi–O–Bi structure can draw other Bi^{3+} from solution gradually to form larger Bi–O–Bi assembly structure. In order to achieve the high ligancy of Bi, these Bi–O–Bi structures might be radial. When aqueous ammonia was added to the system, the metal alcohol salt with Bi–O–Bi assembly structure began to hydrolyze, the OH^- would replace ethylene glycol to form BiOCl [23] as shown in reaction (2):

$$\mathrm{Bi}_a(\mathrm{EG})_b(\mathrm{OH})_c + c\mathrm{OH}^- + a\mathrm{Cl}^- \rightarrow a\mathrm{BiOCl} + b\mathrm{EG} + c\mathrm{H_2O} \quad (2)$$

Finally, flower-like BiOCl was formed. In order to understand the formation mechanisms of flower-like BiOCl, we investigated the influences of ethylene glycol in the growth processes. We replaced ethylene glycol by ethanol and prepared BiOCl film under the same conditions. The SEM images of two films were compared in Figure 7. The figure showed that the film prepared using ethylene glycol as solvent had flower-like sphere microstructure, while the film prepared using ethanol as solvent did not have. Therefore, ethylene glycol played an important role in the formation of the flower-like sphere microstructure of BiOCl film. This was probably because ethanol as a kind of monohydric alcohol did not have the ability of interlinking action [23] as ethylene glycol. The flower-like sphere structure has unique space structure and big specific surface area, which is beneficial to the contact of the catalyst and organic matter and can improve the optical utilization rate.

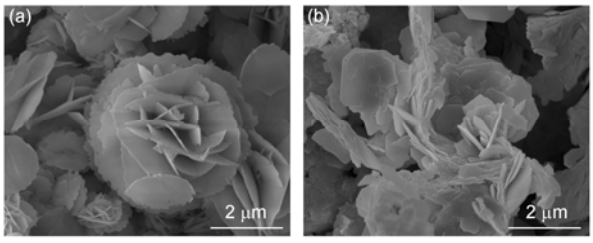

Figure 7 SEM of BiOCl films prepared using different solvents: (a) ethylene glycol; (b) ethanol.

4 Conclusion

The BiOCl thin film photocatalyst was prepared in alcoholysis-coating method using $BiCl_3$ as raw materials and ethylene glycol as solvent. The crystalling phase, composition, morphology and optical absorption properties of as-prepared BiOCl film were characterized, and the results showed that the obtained BiOCl thin film was composed of flower-like sphere structure with tetragonal phase and had a good absorption for ultraviolet. This special flower-like sphere structure can increase the specific surface area of the BiOCl film photocatalyst, which makes the film have high photocatalytic degradation activity to methyl orange and good stability under UV irradiation. This BiOCl thin film prepared by alcoholysis-coating method used in this paper does not need high temperature calcination and special reactor, and the preparation process is simple, energy-saving and environmentally friendly. Therefore it has potential application in the treatment of dyes wastewater.

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