

A Novel and Facile Method to Synthesize Self-Assembled BiOCl Core-shell Microspheres Composed of Nanoplates

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The self-assembled BiOCl core-shell microspheres composed of nanoplates have been successfully prepared using solvothermal method using ethylene glycol and polyvinylpyrrolidone (PVP) as solvents. XRD, SEM, EDX, XPS and DRS characterizations have been performed to study the crystal structure, morphology, composition and optical property of the as-prepared BiOCl materials. The XRD results indicate that the obtained BiOCl materials are high-purity and single-phase. The SEM results show that the as-prepared BiOCl powders are core-shell microspheres with diameters about 1 μm , and the core and shell of these microspheres are composed of many longitudinal grown nanoplates. The EDX and XPS results reveal that the atomic ratio of Bi/O/Cl in the sample is approximately equal to 1:1:1. Moreover, the DRS spectra reveal that the band gap of the resulting sample is estimated to be about 2.92 eV. The results of photocatalytic activity show that the as-prepared BiOCl core-shell microspheres exhibit more excellent activity than P25 (Degussa, commercial TiO₂ powder manufactured by flame hydrolysis) under visible light irradiation.

Keywords: BiOCl, core-shell microspheres, solvothermal method, crystal structure, XPS.

1. INTRODUCTION

Bismuth oxychloride (BiOCl) has been attracted many attentions owing to its potential photocatalysis application [1, 2], besides being applied in ionic conduction, ferroelectric materials and pigments [3, 4]. Therefore, various synthesis methods have been developed successfully to prepare BiOCl samples, such as hydrolysis process [5], reverse micro-emulsion synthesis [6] and solvothermal process [7]. The obtained BiOCl samples present different morphologies including nano-scale particle, nanosheet and micro-scale morphology assembled with nanosheet. For instance, Deng Z.-T. et al. have firstly reported that two-dimensional (2D) single-crystalline bismuth oxyhalides (BiOX, X=Cl, Br) micro- and nanostructures, such as nanoplates, nanosheets, and microsheets, were synthesized in a large scale by a simple wetchemistry approach of hydrogen peroxide (H₂O₂) direct oxidation of bulk metal bismuth (Bi) particles in a mixed solution followed [8]. Ding L.-Y. et al. have reported uniform BiOCl hierarchical microspheres assembled by nanosheets with tunable thickness were synthesized via a simple solvothermal route using acetic acid and methanol as solvents [9]. Hao H.-Y. et al. obtained BiOCl microspheres and microflowers by a simple solvothermal method using bismuth nitrate and sodium chloride as solvent, respectively [10]. Wu Y.-P. et al. obtained BiOCl microrings composed of nanoplatelets via a simple hydrothermal method using an oleic acid contained solvent as a reaction medium [11]. However, to the best of our knowledge, there has not been a study on the preparation of BiOCl 3D microspheres with core-shell structure so far.

In this study, BiOCl core-shell microspheres were synthesized by solvothermal method using ethylene glycol and PVP as solvents. In addition, the phase structure, morphology and composition of the resulting BiOCl sample were investigated in detail.

2. EXPERIMENT

2.1. Preparations of BiOCl microspheres

BiOCl microspheres with core-shell structure were prepared via solvothermal method. 0.2 g Bi(NO₃)₃·5H₂O was added into mixture solution of ethylene glycol and polyvinylpyrrolidone (PVP). Then, the hydrochloric acid containing stoichiometric amounts of HCl with the Bi/Cl molar ratio of 1 was added into the above solution, and the resulting mixture was adjusted pH value to 3 with Na₂CO₃. After stirring for 30 min at room temperature, the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was allowed to be heated at 160 °C for 6 h and then cooled to room temperature. The resulting precipitates were filtered and washed with ethanol and deionized water thoroughly and dried at 100 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) measurement was employed on a XRD-6000 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) irradiated with a scanning rate of 2 min⁻¹. Scanning electron microscopy (SEM) measurement was conducted with a JSM-6700 LV electron microscope operating at 5.0 kV. X-ray photoelectron spectroscopy (XPS) data were recorded using a Perkin-Elmer PHI 5600

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electron spectrometer using achromatic Al K α radiation (1486.6 eV) with Ar sputtering to remove the surface layer of the sample. UV-vis diffuse reflectance spectra (DRS) were recorded at room temperature with the JASCO 570 spectrophotometer equipped with an integrated sphere.

2.3. Photocatalytic reaction

The photocatalytic property of BiOCl was evaluated by decomposing rhodamine B (RhB). The reaction suspensions were obtained by adding 10 mg BiOCl powders into 200 mL of 10 mg/L RhB aqueous solution at room temperature under vigorously stirring. The photocatalytic reaction was irradiated using a 250 W xenon lamp equipped with a 420 nm cutoff filter, which can thoroughly eliminate radiation below 420 nm and guarantee the entire catalysis process exposed to visible light. Supernatant of RhB was obtained and the concentration of RhB was determined by UV-vis spectroscopy at its characteristic wavelength of 553 nm.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the as-synthesized BiOCl sample. As shown in Fig. 1, it can be seen that BiOCl sample shows very strong reflection peaks at $2\theta = 12.11, 24.25, 25.97, 32.75, 33.62, 36.65, 41.12, 46.88, 49.91, 54.24, 55.24, 58.85, 60.88$ and 68.37° .

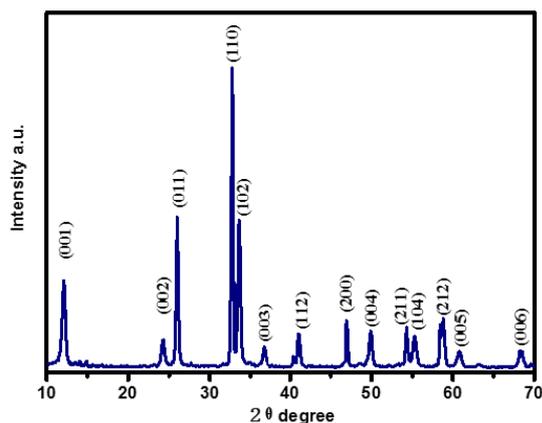


Fig. 1. Typical XRD pattern of the prepared BiOCl core-shell microspheres

These reflection peaks correspond to the BiOCl planes of (001), (002), (011), (110), (102), (003), (112), (200), (004), (221), (104), (212), (005) and (006), respectively, which can be readily indexed to the tetragonal phase of

BiOCl (JCPDS Card No. 85-0861).

No peaks of metal Bi or any other phases are detected, indicating that the product is very high-purity and single-phase sample. In addition, the intense and sharp diffraction peaks suggest that the as-synthesized products are well-crystallized.

Fig. 2 shows the SEM and EDX spectrum of the as-prepared BiOCl sample. As shown in Fig. 2 a, it is found that the fabricated BiOCl is microsphere with diameter about 1 μm . As shown in Fig. 2 b, it is found the obtained microspheres is core-shell structure and the core or shell of these microspheres are composed of longitudinal grown nanoplates, which is different from the reported papers [12–14]. The results from EDX spectrum (Fig. 2 c) show that the as-prepared microspheres contain Bi, O and Cl, and no contamination elements are detected.

The chemical composition of BiOCl microspheres is further investigated by XPS. The XPS spectrum in Fig. 3 a reveals that as-prepared sample is composed of elements of Bi, O and Cl, which is in agreement with the results of EDX. As shown in Fig. 3 b, it could be seen that Bi 4f peaks are found at 158.8 eV (Bi 4f 7/2) and 164.2 eV (Bi 4f 5/2), indicative of Bi³⁺ in the obtained BiOCl microspheres [15].

Fig. 3 c shows that the peak binding energy of 532.1 eV is assigned to O 1s, which is arisen from oxygen in BiOCl. Fig. 3 d shows the Cl 2p peak is associated with binding energy of 197.9 eV, which is characteristic of Cl in BiOCl materials [16]. These results show that the chemical states of element composed the sample are Bi³⁺, O²⁻ and Cl.

The optical properties of as-prepared BiOCl sample was studied using UV-vis diffuse reflectance spectra (DRS), as shown in Fig. 4 a. It is found that the BiOCl sample exhibits strong photo absorption in the UV region and relatively weak absorption in the visible light region. The UV-vis absorption edge of as-prepared BiOCl catalyst is at about 424.6 nm.

As an indirect transition semiconductor, the band edge of BiOCl sample is obtained according to the energy dependence relation of:

$$ah\nu = k(h\nu - E_g)^{1/2}, \quad (1)$$

where a , $h\nu$, k and E_g are the absorption coefficient, discrete photon energy, proportionality constant and band gap energy, respectively. The plot of the $(ah\nu)^{1/2}$ versus photo energy ($h\nu$) of BiOCl sample can be fitted into a line (as shown in Fig. 4 b). The band gap energy of the BiOCl sample is calculated to be about 2.92 eV, implying the BiOCl microspheres may have visible light photoactivity.

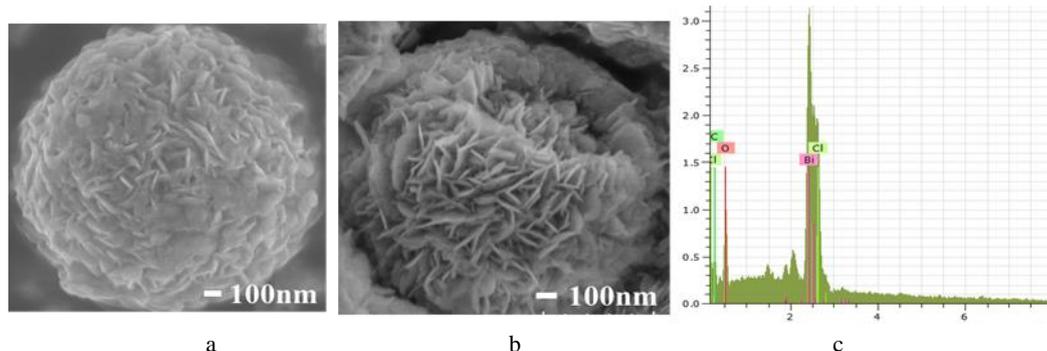


Fig. 2. a, b – SEM image; c – EDX spectrum of the BiOCl core-shell microspheres

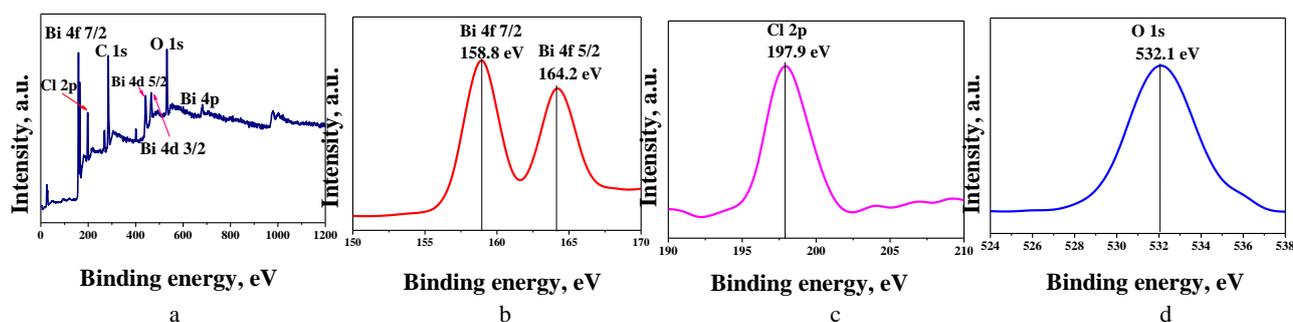


Fig. 3. XPS spectra of the BiOCl core-shell microspheres: a – survey spectrum; b – Bi 4f; c – O1s; d – Cl2p

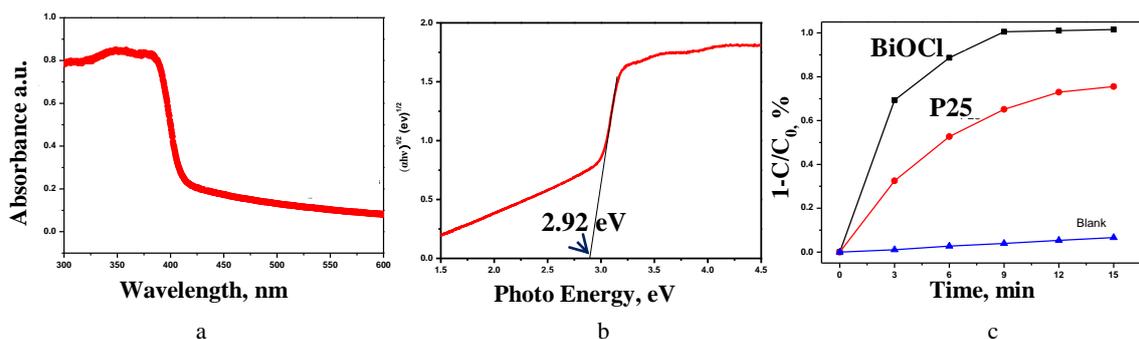


Fig. 4. a – DRS spectrum; b – the $(ah\nu)^{1/2}$ vs. $h\nu$ (b) of as-prepared BiOCl samples; c – photodegradation of RhB under visible light

Fig. 4 c shows the photocatalytic activities of the BiOCl core-shell microspheres and commercial TiO_2 (P25, Degussa) as a comparison. In the absence of catalysts, RhB could be degraded under simulated solar light irradiation, but the reaction was very slow and only 10 % of RhB was removed in 15 min irradiation. The removal efficiency was enhanced significantly in the presence of P25 or as-prepared BiOCl catalysts. There was 100 % degradation of RhB for as-prepared BiOCl nanoplates in only 10 min irradiation. However, only 68 % RhB molecules were decomposed using the P25 nanomaterials as photocatalyst, when the photodegradation reaction was proceeded past 15 min. Based on these results, it can be seen that the as-prepared BiOCl showed about two times RhB degradation than P25.

4. CONCLUSIONS

The BiOCl samples have been prepared using solvothermal method. They are phase-pure and hierarchical microspheres with core-shell structure. The chemical states of element composed the sample are Bi^{3+} , O^{2-} and Cl⁻. Moreover, the bandgap energy of the BiOCl product is about 2.92 eV, which shows an obvious absorption capability in the UV–vis region. The prepared BiOCl core-shell microspheres exhibited more excellent activity than P25 under visible light irradiation.

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