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Visible Light Photocatalytic Properties and Thermochromic Phenomena of Nanostructured BiOCl Microspheres

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Black nanostructured BiOCl microspheres were directly synthesized by a hydrothermal method. The black ball-like BiOCl microspheres and black flower-like BiOCl microspheres were obtained using different surfactant. The color of the BiOCl microspheres turned from black to white when being annealed at 400 °C in air for 3 h and could be recovered to black by exposure to ultraviolet light for a few hours. The photocatalytic activity of both the black and the white BiOCl microspheres was characterized by the photo-degradation of methyl orange dye under visible light irradiation. The black ball-like nanostructure BiOCl displayed the best photocatalytic activity, compared with the white BiOCl and the black flower-like BiOCl. It can degrade the methyl orange dye to 20% within 70 min under visible light irradiation. The high activity of the BiOCl ball-like sphere may own to its special morphology, strong absorption in visible light range and the existence of oxygen vacancies.

KEY WORDS: Photocatalysis; Black BiOCl; Microsphere; Thermochromic

1. Introduction

Semiconductor photocatalysts are widely used in hydrogen generation, solar energy utilization and environmental remediation[1,2]. Recently, the semiconductor material BiOCl with a layer structure is more active than TiO_2 for promising practical industrial application due to its efficient photocatalytic activities, high physical and chemical stability, low cost and non-toxicity[3,4]. Until now, two dimensional BiOCl lamellae[5], flower-like BiOCl[6], BiOCl nanofibers[7], and other morphologies of BiOCl including BiOCl micro/nanostructures have been synthesized by low-temperature sonochemical route ultrasonic treatment, low-temperature chemical vapor transport, electrospinning method, respectively. And our group[8,9] has synthesized the BiOCl nanoflakes and nanowires array by anodic aluminum oxide (AAO) template via sol−gel combined with the vacuum air extraction method. Nevertheless, BiOCl is a type of wide band gap (ranging from 3.02 to 3.5 eV[10,11]) semiconductor material which can only be excited by UV light (5% of the solar light) or solar light irradiation. Hence, many efforts have been made to develop functional BiOCl based visible light photocatalysts by incorporating metal ions or compositing with other semiconductors[12−16].

However, to further improve the photocatalytic activity of BiOCl and obtain the efficient photocatalysis applied to environmental protection, some researchers have proved that intrinsic semiconductor photocatalysts with oxygen vacancies can absorb visible light and exhibit excellent photocatalytic activity under visible light[17−20]. Chen et al.[17] observed that disorder-engineered black TiO_2 can more efficiently harvest the infrared photons for photocatalysis than what bulk anatase can do. And the presumable reason was that the localization of both photo-excited electrons and holes prevented fast recombination. Both our group[11] and Ye et al.[19] ever reported black BiOCl had the ability to absorb visible light irradiation which was obtained from white BiOCl by UV light irradiation. And the reason for color of change was the creation of oxygen vacancies. The oxygen vacancies only trapped electrons for its positive charge and reduced the recombination of electrons and holes, which increased the mobility of holes.

In the present work, two kinds of black BiOCl nanostructured microspheres were synthesized directly with acetylacetone (AAT) and diethylene glycol (DEG), respectively, by a hydrothermal method. We adopted different solvents to control the formation of the black BiOCl crystals in order to obtain effective photocatalytic activities. The photocatalytic activities of the BiOCl nanostructure were investigated. And photoluminescence (PL) analysis was applied to understand the oxygen vacancy function.

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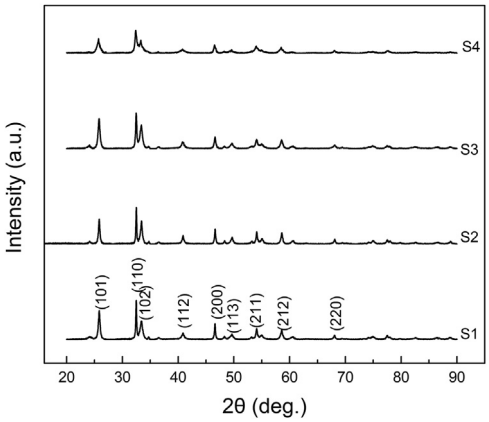

Fig. 1 XRD patterns of BiOCl (S1−S4).

2. Experimental

2 mmol $Bi(NO_3)_3$ $5H_2O$ was dissolved in 40 ml AAT or DEG, followed by adding 1 mmol $BiCl_3$. Subsequently, the solution was transferred into a teflon-lined stainless-steel autoclave, which was sealed and heated at 180 °C for 12 h, and then cooled down to room temperature. The precipitates were collected and washed by ethanol and deionized water repeatedly. Finally, the products were dried in vacuum at 80 °C for 10 h and denoted as S1 (the solvent is AAT) and S2 (the solvent is DEG), respectively. In addition, the samples S3 and S4 were obtained from the samples S1 and S2 which were annealed at 400 °C for 3 h in air, respectively.

The morphology of the as-synthesized BiOCl was characterized by scanning electron microscopy (SEM, Hitachi S-4800). The phase structure of BiOCl was carried out by X-ray diffraction (XRD) on a Bruker D8 diffractometer with Cu$K\alpha$ radiation. UV−Vis diffuse reflectance spectroscopy (DRS) was recorded on a UV−Vis spectrophotometer (HITACHI U-3010, Japan). The UV−Vis absorption spectra were also examined using the spectrophotometer U-4100. Photoluminescence (PL) spectra of the samples were obtained on laser confocal micro-Raman spectroscope (LabRAM Aramis) with 325 nm semiconductor laser as exciting sources at room temperature.

The photocatalytic activity of the as-prepared samples was investigated by the photo-degradation of methyl orange (MO) dye. The photo-degradation experiments were carried out under visible light irradiation whose source is a 300 W Xe lamp equipped with UV cut off filter to provide only visible light ($\lambda \geq 420$ nm). The distance between the Xenon lamp and the sample was about 30 cm. 20 mg of the as-prepared photocatalyst was suspended in 20 ml MO aqueous solution ($C_0 = 10$ mg/l) with constant stirring. Prior to irradiation, the suspensions were stirred in the dark for 2 h to ensure the adsorption−desorption equilibrium. The HITACHI U-4100 UV−Vis spectrometer was used to determine the concentration of MO solution during the photocatalytic degradation process. C_i is the photodegrade concentration. The percentage of degradation is reported as C_i/C_0.

3. Results and Discussion

3.1. Phase and morphology of the as-synthesized BiOCl microsphere

The phase structure and morphology of the as-synthesized products were characterized by XRD and SEM. Fig. 1 presents the XRD patterns of the BiOCl samples. Their diffraction peaks correspond to the (101), (110), (102), (112), (200), (113), (211), (212), and (220) planes, respectively, in which all the diffraction peaks can be perfectly indexed to the pure products of BiOCl with the tetragonal phase BiOCl (JCPDS card No. 06-0249). No other peaks arising from impurities can be found, indicating that pure BiOCl crystals have been successfully synthesized.

By visual observation, the BiOCl samples S1 and S2 display black. In order to shed more light on the nanostructure of these products, the SEM images of the samples are shown in Fig. 2. Fig. 2(a) is a large-scale overview with flower-like morphology of the sample S1. A magnified image of the sample S1 shown in Fig. 2(b) provides the detailed view of the structure. It can be found that the flower shape of the sample S1 consists of lots of thin flakes with thickness of 60 nm. As to the sample S2, the highly monodispersed rough ball-like spheres were obtained as shown in Fig. 2(c). The magnified SEM image for the sample S2 (Fig. 2(d)) reveals that the sphere is composed of thin plates. The nanoplates align radically and tightly to assemble into the uniform spheres, which is very different from the sample S1.

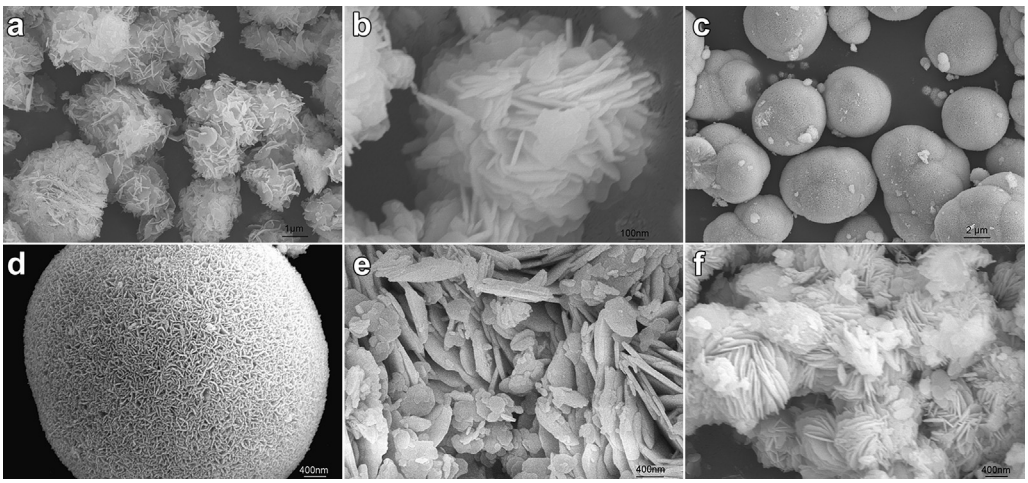

Fig. 2 SEM images of the BiOCl: (a, b) S1, (c, d) S2, (e) S3, (f) S4.