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Highly efficient and visible-light-driven BiOCl for photocatalytic degradation of carbamazepine

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ABSTRACT

Visible-light-driven BiOCl microspheres were directly synthesized via a facile one-pot ethylene glycol mediated solvothermal method. The crystallinity, surface, optical and electronic properties of BiOCl samples were highly depended on the precursor concentration. Benefiting from the exposed (110) facet and oxygen vacancy, BiOCl-10 (synthesized from 0.02 mol of $Bi(NO_3)_3 \cdot 5H_2O$) displayed a maximum CBZ degradation efficiency of 70% after 180 min under visible light illumination. The reaction kinetics rate constant (k) of CBZ degradation in BiOCl-10 (0.0935 min^{-1}) was 52 times higher than ordinary BiOCl-1 (0.0018 min^{-1}). The improved photocatalytic activities of BiOCl-10 were attributed to the combination of enhanced CBZ adsorption, increased visible light absorption and efficient separation of photogenerated e^{-}-h^{+} pairs. Radicals and holes trapping experiments showed that $\bullet O_2^-$ and h^+ were predominant active species in the photocatalytic process. Most importantly, BiOCl-10 was also efficient in natural water without any additive. Our findings indicate that the BiOCl-10 photocatalysis can be used as an efficient and cost-effective technology for removal of recalcitrant pharmaceutical contaminants.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), as emerging pollutants, have now been of growing concerns. Among the PPCPs, carbamazepine (CBZ) is the typical representative, which is widely used as an antiepileptic and mood stabilising pharmaceutical. The world-wide consumption of CBZ is assessed to be 1014 t per year. Because of its low biodegradability and persistent nature, the removal efficiencies of CBZ in wastewater treatment plants are below 10% [1]. This makes most of CBZ discharged into aquatic environments and causes adverse effects on the water quality, ecosystem and human health [2].

Heterogeneous photocatalysis is one of the most promising techniques for environmental remediation [3]. Currently, TiO_2 is usually used for CBZ degradation. For example, TiO_2 (P25) was demonstrated to be more excellent in decomposing CBZ than both Hombikat UV100 [4] and 10-$MWCNT_{ox}$-TiO_2 composite [5]. However, low quantum yield and poor light harvesting ability confine the practical application of TiO_2 (P25). Accordingly, researchers have endeavored to develop novel photocatalysts. For example, Kaviyarasu and co-workers et al. have done a lot of meaningful work in the development of Co_3O_4 spinel nanoparticles [6] and NiO nano-sticks [7], as well as binary metal oxide nanocomposites (eg., CeO_2/Y_2O_3 [8,9], NiO/MgO [10]), which are effective for the degradation of bacteria and dye (RhB, MB, MO, and Rose Bengal dye). Besides, bismuth based photocatalysts including BiOX (X = Cl, Br and I) [11], Bi_2WO_6 [12] and $BiPO_4$ [13] were found to show excellent photocatalytic activity. Of these, BiOCl has drawn considerable attention due to its specific structure of $[Bi_2O_2]^{2+}$ interleaved with double Cl ions, where the photogenerated e^{-}-h^{+} pairs can be efficiently separated.

Very recently, our group has successfully synthesized hierarchical BiOCl microspheres via an ultrasound assisted solvothermal method. Furthermore, the superior photocatalytic activity of BiOCl for CBZ degradation was first demonstrated, in which the reaction rate constant value (k) was over 9.48 times higher than that of TiO_2 (P25). Ultrasonic irradiation minimized the aggregation of particles [14] and promoted the formation of loose hierarchical structure, which is beneficial for the light absorption. However, the wide band gap (3.08 eV for BiOCl) conspicuously hinders its photocatalytic applications under visible light irradiation [15,16].

Therefore, it is indispensable to develop highly efficient visible-light-driven photocatalysts. To date, many strategies have been done to improve the visible-light-driven activity of BiOCl. In which,

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the formation of heterojunction photocatalysts is expected to show excellent photoabsorption [17]. And constructing heterojunction by compositing BiOCl with other semiconductors has been proved to be an effective strategy to improve its visible-light photoactivity, such as BiOI/BiOCl [18], $BiVO_4$/BiOCl [19] and BiOCl/C_3N_4 [20]. In addition, decorating noble metals including Au and Ag has also proven to significantly increase the visible-light-harvesting ability [21]. But the high cost and the scarcity of noble metals hinders their applications on a large scale. On the other hand, these approaches mentioned above do not change and/or promote the intrinsic properties of BiOCl, such as optical property and charge transfer ability.

Recent studies have shown that the photocatalytic properties depend strongly on the superficial microstructures of materials [22]. And the optical properties of photocatalysts can be manipulated via surface microstructure control engineering, such as morphologies [23], surface electronic states, exposed crystal facets [24], defects [25,26], and surface complex [27]. For example, $V_{Bi}''V_O^{\cdot\cdot}V_{Bi}''$ vacancy was associated with the significantly promoted solar driven photocatalytic activity of ultrathin BiOCl nanosheets [24].

Template directed approach is one of the most important methodologies developed for fabricating inorganic nanostructures [28–31]. By using suitable templates (micelles, spent tea leaf, trimethyl ammonium bromide, and metal nanoparticles), various functional inorganic nanostructures displayed potent property-applications, such as water oxidation [32], heavy metal adsorption [33], dyes degradation [34], However, the surface microstructure control was a challenge in the preparation procedure of photocatalysts. The current strategy was often involved with extra additive (e.g. PVP [24]) or cumbersome post-treatment (e.g. hydrogen-treatment [25]). Therefore, it is essential to develop a simple method to adjust the surface microstructure for rational design and synthesis of visible-light-driven photocatalysts with high activity.

Herein, in this study, the structure and properties of BiOCl photocatalysts were tuned easily by adjusting the precursor concentration in a solvothermal route. The photocatalytic activities of the as-obtained photocatalysts are examined through the degradation of CBZ under visible light irradiation ($\lambda > 420$ nm). To understand the effects of precursor concentration on the structure and properties of BiOCl, the obtained materials were characterized by X-ray diffractometry (XRD), fourier transform infrared spectrometer (FTIR), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV–vis diffuse reflectance spectroscopy (DRS), nitrogen adsorption–desorption, X-ray photoelectron spectroscopy (XPS), photoluminescence emission (PL) and electrochemical measurements (photocurrent responses, PC and electrochemical impedance spectroscopy, EIS). Furthermore, the photocatalytic mechanism was systematically investigated by active species trapping experiment. Finally, the applicability of BiOCl-10 in actual wastewater was explored.

This study was aimed at increasing the visible-light-response of BiOCl for efficient degradation of carbamazepine. The correlation between catalyst characterization and activity was also analyzed. However, the effectiveness of the photocatalyst should be explored in a wide group of PPCPs (diclofenac sodium, sulfamethoxazole, hormones and so on) in nonspiked urban wastewater, which is a limitation in the present study.

2. Experimental

2.1. Materials and reagents

Bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$, A.R.) was provided by Sinopharm Chemical Reagent Co., Ltd. (SCRC, Shanghai, China). Potassium chloride (KCl, A.R.) was obtained from Dalian Meilun Biological Technology Co., Ltd (Dalian, China). Ethylene glycol (EG, A.R.) was provided by Tianjin Feng Chuan Chemical Reagents Co., Ltd (Tianjin, China). CBZ (>98%) was purchased from Aladdin (Beijing, China). All reagents were analytical grade and used directly as received. Deionized water was used throughout the experiments.

2.2. Preparation of BiOCl photocatalysts

BiOCl samples were synthesized using a facile one-step solvothermal approach, as previously reported with some modifications [35]. Typically, equivalent mole $Bi(NO_3)_3\cdot 5H_2O$ (0.002 mol) and KCl (0.002 mol) were dissolved in ethylene glycol (68 mL) with stirring to obtain a homogeneous solution. Then, the mixture was transferred to a 100 mL Teflon-lined autoclave and maintained at 160 °C for 12 h. After cooling down to room temperature, the product was centrifuged and washed three times by using ethanol and distilled water. Finally, the as-prepared samples were dried in an air oven at 50 °C (denoted as BiOCl-1).

BiOCl-5, BiOCl-10, and BiOCl-15 were prepared by the same procedure, except that both the concentrations of precursor $Bi(NO_3)_3$ and KCl were increased by 5, 10, and 15 times compared with BiOCl-1: BiOCl-5 was obtained at $Bi(NO_3)_3\cdot 5H_2O$ (0.01 mol) and KCl (0.01 mol), BiOCl-10 was obtained at $Bi(NO_3)_3\cdot 5H_2O$ (0.02 mol) and KCl (0.02 mol), and BiOCl-15 was prepared at $Bi(NO_3)_3\cdot 5H_2O$ (0.03 mol) and KCl (0.03 mol).

2.3. Characterization

The phase and composition of the samples were characterized using XRD (D8 ADVANCE) at 40 kV and 40 mA. FTIR measurements were carried out using a spectrometric analyzer with KBr pellets (Nicolet 6700). The morphologies were screened using SEM (America FEI, Quanta 200) and TEM (JEM-2100, Japan). Chemical compositions and element states of the derived products were examined using XPS analysis (ESCALab250Xi, Al Ka). The shift of the binding energy was calibrated by using the adventitious carbon signal (C1s peak) at 284.8 eV as an internal standard. A micromeritics ASAP 2020 (Norcross, GA) was applied to determine the specific surface area and pore volume of the samples. The optical properties of the samples were measured using a UV–vis spectrophotometer (UV–vis, Puxi TU-1901) equipped with an integrating sphere. The PL spectra of the as-prepared samples were measured by using an Edinburgh FLs980 fluorescence spectrophotometer to observe the combination rate of e^--h^+ pairs, and the EIS Nyquist plot and PC were determined using a CHI660E electrochemical workstation.

2.4. Photocatalytic activity

The CBZ solution of 2.5 mg/L was prepared as an objective pollutant to evaluate the activity of the photocatalysts. The liquid-phase photo-degradation of CBZ was carried out in a 100 mL beaker under visible light irradiation by a 350-W xenon lamp with a 420 nm cutoff filter. The photo-degradation reactor was placed 20 cm away from the lamp. In a typical experiment, 0.04 g of BiOCl photocatalyst was added to 50 mL of CBZ aqueous solution. Before irradiation, the suspension was magnetically stirred in the dark for 1 h to achieve equilibrium of adsorption-desorption. Then, the beaker was exposed to the irradiation. At certain interval, 3 mL of suspension was taken and centrifuged. The resulted supernatant solution was determined using a UV–vis spectrophotometer. The photocatalytic efficiency of the as-prepared BiOCl sample was calculated by the following formula: