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Fluorine mediated photocatalytic activity of $BiPO_4$

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ABSTRACT

The fluorine doped $BiPO_4$ (F-$BiPO_4$) photocatalyst was synthesized via an in situ fluorination method. The lattice oxygen of $BiPO_4$ was substituted by fluorine, resulting in the increased polarizability and thus an increased induced dipole moment of $BiPO_4$, which can increase the separation efficiency of electron-hole pairs. The photocatalytic activity of $BiPO_4$ was enhanced by about 30% when the molar ratio of F/Bi was 0.03. Not only the discoloration rate of methylene blue (MB) but also the mineralization rates of MB and phenol were accelerated by F-doping. The enhancement of photocatalytic activity by F-doping could be attributed to the stronger adsorption ability of the substrate, the larger amount of active facet and higher separation efficiency of electron-hole pairs resulted from the increased polarizability. Overdoping would decrease the photocatalytic activity due to the increased recombination rate of electron-hole pairs at high defect concentration.

1. Introduction

$BiPO_4$ is a newly discovered photocatalyst with more attractive UV light activity than TiO_2 (P25, Degussa) [1,2] and it has attracted increasing interest in the past few years [3–9]. It is not only efficient in decoloration of dye, but also superior in mineralization of the difficult degradable phenol. Synergy of $BiPO_4$ and adequate H_2O_2 can raise the removal efficiency of phenol greatly [10]. Therefore, $BiPO_4$ is a promising photocatalyst and has much potential in remediation of environment. However, similar to TiO_2, $BiPO_4$ is also a wide band gap (ca. 3.85 eV) photocatalyst and the quantum efficiency is not high enough to meet the requirement of industrial application. Thus, it still needs to improve the photo-performances of $BiPO_4$ photocatalyst. How to increase its quantum efficiency and extend its light absorption range?

Doping is one of the methods to modify the bulk and surface characteristics and thus the light absorption range as well as the photocatalytic activity [11]. Both metal and nonmetal doping, as well as co-doping [12] have been investigated, and there are many excellent reviews related to doping [13,14]. Although cationic metal doping can induce a red shift in the band gap transition and may enhance the photocatalytic activity under both UV and visible light, some cationic metal dopants may also serve as recombination centers for photogenerated charge carriers and result in reduced photocatalytic activity [14]. Anionic nonmetal doping such as C [15], N [16,17], P [18], S [19,20], F [21–25], I [26] seems to be more efficient and it is proved to have narrowed the band gap or improved the photocatalytic activity of different photocatalysts by inducing impurity states, which are supposed to be close to the valence band maximum. This can not only narrow the band gap, but also increase the separation efficiency of electron-hole pairs and thus the photocatalytic activity. Among the anionic nonmetal dopants, fluorine is investigated most extensively and has been demonstrated to improve the photocatalytic activity of TiO_2 [25,27,28] and non TiO_2-based photocatalysts [22,24,29–31]. Whether the photocatalytic activity can be improved and how much it can be improved by F-doping largely depend on the chemical nature of incorporated fluorine (such as adsorbed fluoride and lattice-doped fluorine) and the fluoride-mediated crystal modification and organization. Surface-fluorinated TiO_2 has been proved to be an effective surface modification method to improve its UV light photocatalytic activity [32], but it cannot induce strong visible light absorption [23]. Interestingly, Xing et al. [33] used a special structure of supported mesoporous catalyst to facilitate the surface fluorination of TiO_2, and it was found that the surface fluorination enhanced the UV light photocatalytic activity and together with the Ti^{3+} generation led to the excellent adsorption capacity and visible light photocatalytic activity of TiO_2. Lattice-doped fluorine can efficiently improve the photocatalytic activity [22,29] and sometimes can induce a red shift of the optical absorption edge of composite oxide photocatalyst [30]. For example, the fluorine interstitially doped $ZnWO_4$ can induce the distortion of WO_6 octahedron, resulting in an enhanced internal electric field and then an increased transfer rate of photogenerated electrons and holes to the catalyst surface, and thus an enhanced photocatalytic activity for degradation of Rhodamine B (RhB) and 4-chlorophenol (4-CP)

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[22,29]. Similar promotion in the photocatalytic activity over F-doped Bi_2WO_6 was also reported [24]. Is it possible to improve the photocatalytic activity of the excellent UV light responsive $BiPO_4$, and further induce its visible light photocatalytic activity by F-doping? This is an inviting question and deserves intensive investigation.

The present work intends to explore the preparation and performance enhancement of F-$BiPO_4$. The effects of fluorine on the crystal structure and photocatalytic activity of $BiPO_4$ have been investigated. Besides, detailed mechanism for the improved photocatalytic activity by F-doping has been discussed.

2. Experimental

2.1. Preparation and characterization of F-$BiPO_4$ photocatalysts

$BiPO_4$ and F-$BiPO_4$ were synthesized via a hydrothermal process. All chemicals used were analytic grade reagents. In a typical procedure, 8 mmol of $Bi(NO_3)_3·5H_2O$ and 160 mL distilled water were put into a beaker under magnetic stirring. Then 28.8 mmol $NaH_2PO_4·2H_2O$ and certain amount of NaF were added into the mixture and stirred for 1 h. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h. The products were washed three times with distilled water and dried at 120 °C for 8 h.

The products were characterized by X-ray diffraction (XRD) on Bruker D8-advance X-ray diffractometer at 40 kV and 40 mA for monochromatized Cu Kα1 ($\lambda = 1.5418$ Å) radiation. Morphologies of the prepared samples were further examined with transmission electron microscopy (TEM) by a Hitachi 7700 electron microscope operated at an accelerating voltage of 100 kV. UV–vis diffuse reflectance spectra (DRS) of the samples were measured by using Hitachi U-3010 UV–vis spectrophotometer. Raman spectra were recorded on a Horiba HR 800 spectrometer in the range of 100–1500 cm^{-1}. The excitation light was 514 nm. Chemical characterization of the sample surface was recorded with X-ray photoelectron spectroscopy (XPS ESCALAB 250Xi, Thermo Scientific). The charging effect was calibrated using the binding energy of C1s.

The photocurrent and Mott Schottky measurements were measured on an electrochemical system (CHI-660D, China). The as-prepared samples for the fabrication of photoanode were obtained by mixing 1 mL of ethanol and 10 mg of as-prepared photocatalyst homogeneously. Then the homogeneous mixture was spread on the indium tin oxide (ITO) conducting glass. After the films were dried under ambient conditions, they were sintered in air at 200 °C for 5 h. The photocurrent and Mott Schottky measurements were measured with a standard three-electrode cell with a working electrode (as-prepared photocatalyst films on ITO conducting glass), a platinum wire as counter electrode, and a standard calomel electrode (SCE) as reference electrode. 0.1 M Na_2SO_4 was used as the electrolyte solution. An 11 W ultraviolet germicidal lamp was used as the excitation light source.

2.2. Photocatalytic experiments

The photocatalytic activities were evaluated by the decomposition of MB under UV light ($\lambda = 254$ nm, 15 W) irradiation on an XPA photochemical reactor (Xujiang, Nanjing, China). A total of 25 mg of photocatalyst was dispersed in an aqueous solution of MB (50 mL, 0.02 mM). Before irradiation, the suspensions were first ultrasonicated for 10 min and then stirred for 30 min to ensure adsorption–desorption equilibrium between the catalysts and MB. At certain time intervals, 5 mL aliquots were sampled and centrifuged to remove the particles. The concentration of MB was analyzed by recording the absorbance at the characteristic band of 663 nm using a Hitachi U-3010 UV–vis spectrophotometer. The intermediates formed in the degradation process of MB were identified by HPLC (Lumtech) system. Venusil XBP-C_{18} (250 mm × 4.6 mm i.d., 5 μm) reversed phase column was used. The mobile phase consisted of two solutions namely A and B (60:40, v/v) with a flow rate of 1.0 mL min^{-1}. Solution A was made from 0.1 M ammonium acetate and acetic acid (pH 5.3), and solution B was acetonitrile. The UV detector was operated at 292 nm. Total organic carbon analyzer (Multi N/C 2100, Jena) was employed for mineralization degree analysis of MB and phenol solutions.

3. Results and discussion

3.1. Effect of F^- doping on the structure of $BiPO_4$

Fig. 1 showed the XRD patterns of $BiPO_4$ with different fluorine concentrations. The XRD profiles of the $BiPO_4$ and F-$BiPO_4$ samples could be indexed to the pure monoclinic phase (space group $P21/n$, JCPDS 15-0767. $a = 6.752$ Å, $b = 6.933$ Å, $c = 6.468$ Å). The peaks at 27.15°, 29.10°, and 31.22° could be assigned to (2 0 0), (1 2 0) and (0 1 2) crystal planes of monoclinic $BiPO_4$, respectively. Although the crystal phase was not changed by fluorine doping, the relative peak intensities of the (2 0 0), (1 2 0) and (0 1 2) planes were changed. The ratio of 200/120 firstly increased and then decreased

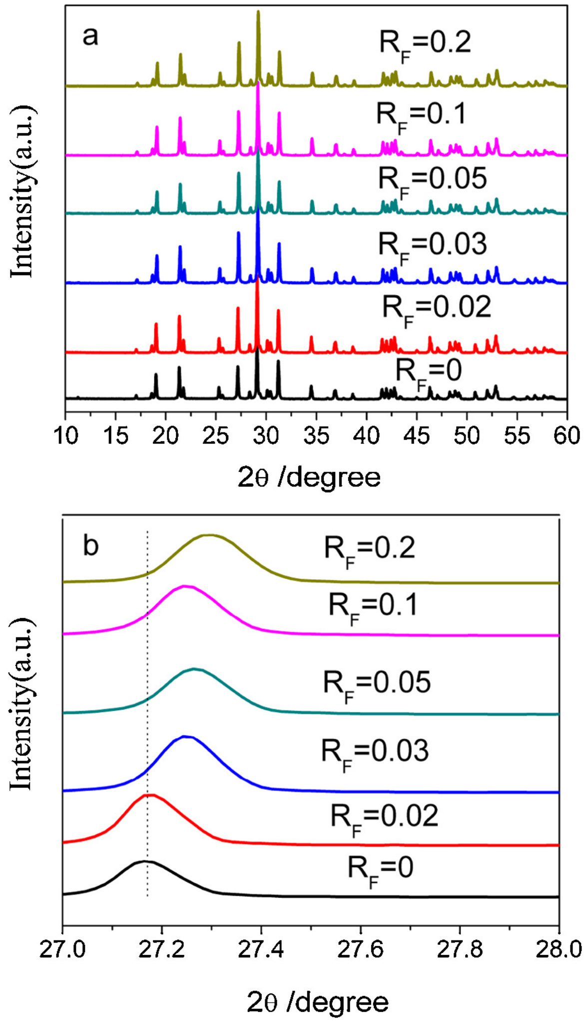

Fig. 1. (a) XRD patterns of $BiPO_4$ and F-$BiPO_4$; (b) diffraction peak positions of the (2 0 0) plane in the range of $2\theta = 27.0–28.0°$.