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Visible light response and superior dispersed S-doped TiO_2 nanoparticles synthesized via ionic liquid

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ABSTRACT

Visible light response and superior dispersed S^{6+}-doped TiO_2 nanoparticle catalysts (S-TiO_2) were prepared via ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate. The phenol was used for the evaluation of the S-TiO_2 photocatalytic activity. S-TiO_2 was characterized by XPS, UV–vis DRS, FE-SEM, TEM, XRD, TG/DSC, FTIR, and BET. The results showed that S-TiO_2 with appropriate S doping prepared via ionic liquid had smaller particle size, better dispersion, higher activity, and higher surface area (S_{BET}) than that prepared in water. Cationic S^{6+} incorporation into TiO_2 lattice substitutes for Ti^{4+} lattice site, generates Ti–O–S bonds in TiO_2, and leads to the formation of donor defect levels in band gap, so that the photocatalytic sensitization of TiO_2 has been extended to visible light region. The optimal content in S doping for the better photocatalytic performance can optimize electrical properties of the intrinsic *n*-type TiO_2 by adding the adequate amount of donor defect of S_{Ti}^{2+} for considering the lifetime of the photo-induced charge pairs.

1. Introduction

The rapid development of using TiO_2 photocatalytic oxidation technology in solving the pollution problems of water, air, and soil etc. has been fulfilled in recent years [1–8]. However, the material applications still have many drawbacks, which includes the limited utilization of solar energy at wavelength longer than 387 nm [9–12] and low quantum efficiency and catalytic activity [13,14]. To overcome the problems, researchers have been actively developing sun light responsive catalyst to expand its spectral response to the visible light range with wavelength longer than 387 nm, and to increase surface area (S_{BET}) of the catalyst to improve the quantum efficiency [15–17]. Transition metal ion doping, noble metal deposition, semiconductor compounding, dye sensitization, and catalyst reduction treatment to form TiO_x with $x < 2$ can significantly improve visible light catalytic activity of TiO_2, but the catalyst activity, stability, absorption efficiency, and the service life are still difficult to guarantee [11].

Recently studies showed that N, C, S, F, I, etc. doping can improve the visible light response of TiO_2 [17–22]. The current water-based preparation techniques include the precipitation-sol method, liquid phase hydrolysis, hydrothermal method, and spray pyrolysis to synthesize non-metallic doped TiO_2 catalyst for visible light catalysis [22–27]. However, TiO_2 catalysts prepared by the traditional chemical methods are still facing several limitations in activity. Although the reports about the N, C, S, F, and I doped TiO_2 catalysts synthesized with non-aqueous or less aqueous solvents are rarely seen in recent years, some scholars have used ionic liquid to synthesize nano-TiO_2 [28–33]. Ionic liquid is a solution entirely composed of anion and cation. As compared with the conventional chemical solvents, ionic liquids have many advantages such as low vapor pressure, high thermal stability, and chemical stability over a wide window of electrochemical potentials. Ionic liquid has been used for the organic [33] and catalyst syntheses [29,30]. The preparation approach of inorganic particles via ionic liquid is quite similar to that via ligands [34,35]. During reactions, ionic liquid not only plays the role of structure-directing agent, but also is able to control the product morphology and phase [21,33]. Although there were works on the TiO_2 prepared by ionic liquid, the S-doped TiO_2 by ionic liquid has few reports. In this study, we synthesized the S-doped TiO_2 nanoparticle catalyst via ionic liquid. Effects of ionic liquid and S-doping on microstructure and photocatalytic activity of TiO_2 were systematically studied.

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2. Experimental

2.1. Ionic liquid preparation [36]

The first step, at constant temperature of 25 °C in oil bath under magnetic stirring condition, 0.2 mol N-methyl imidazole and 0.24 mol *n*-butyl bromide were slowly added to a three-necked flask and stirred for 30 min, then the liquid was heated to 70 °C with a holding period of 1 h to obtain a white viscous liquid of bromide 1-Butyl-3-methylimidazo or [Bmim]Br, labeled as liquid M.

The second step, at room temperature and the stirring condition, 0.2 mol potassium hexafluorophosphate was added into the liquid M which was obtained by the first step, then 100 ml water was added and reacted for 2 h. After stirring and holding the solution still, it was divided into two layers, the upper layer was aqueous solution and the lower layer was colorless and transparent solution of 1-butyl-3-methylimidazolium hexafluorophosphate, labeled as [Bmim]PF_6. Using a separator funnel to separate [Bmim]PF_6 from water and after a repeated washing step, ionic liquid of [Bmim]PF_6 was obtained without the detectable Br^- by testing with 0.1 mol/L $AgNO_3$ reagent.

2.2. Catalyst preparation [37]

Under the stirring condition, 5 ml $TiCl_4$ was added into [Bmim] PF_6 to form the $TiCl_4$ solution with stirring for 30 min, then the solution was dropped into 5 ml H_2O with further stirring for 20 min. In order for the precipitation to occur, the solution was adjusted to pH = 7 by adding $NH_3 \cdot H_2O$ and stirring for 30 min. The obtained gel was washed with distilled water until no Cl^- was detected, then washed by ethanol twice. Then the washed precipitate together with a certain amount of thiourea (Th), based upon the molar ratios *n*(Ti)/*n*(Th) at 5/1, 5/2, and 5/3, were added into ethanol with stirring for 2 h. By using ethanol alone, the problem of the low solubility of thiourea in water was avoided. After the mixture solution was kept still for 10 h, the sediment solid was dried, ground, and calcined at 400–1000 °C for 2 h in air. For comparison, we also synthesized un-doped TiO_2 via ionic liquid, labeled as pure TiO_2, and S-doped TiO_2 in water with the molar ratios *n*(Ti)/*n*(Th) = 5/2, labeled as S-TiO_2/H (5/2).

2.3. Catalyst characterization

The surface composition, chemical state, and elemental content of the catalyst were investigated by XPS with Physical Electronics PHI5700 photoelectron spectrometer under the Al Kα ($h\nu$ = 1486.6 eV) radiation after the calibration with carbon C1*s* ($E\alpha$ = 284.6 eV). Energy threshold structure and light absorption properties of samples with $BaSO_4$ as a reference were analyzed by TU-1901 UV–vis spectrophotometer equipped with an integrating sphere. The crystal structure of samples was characterized by X-ray diffractometer (Rigaku, Japan) with the Cu Kα radiation. The average crystallite size was computed according to the Scherrer formula. TG/DSC analysis was performed on STA-449 thermal analyzer with a heating rate of 10 °C/min in air. Interphase development was studied on Nicolet-380 Fourier transform infrared spectrometer with sample embedded in a KBr pellet. The sample particle size and morphology were examined by JSM-7610F field-emission scanning electron microscopy and TECANAI-10 transmission electron microscope. N_2 adsorption-desorption experiments were performed on SSA4300 type porosity and specific surface area analyzer with the sample degassed at 200 °C for 2 h before the test. Specific surface area was calculated according to the BET equation. Pore size distribution was calculated according to the BJH formula.

2.4. Photocatalytic measurements

The photocatalytic reactions were performed in a home-made quartz jacketed reactor [38]. A 350W Xe with a 400 nm filter built in the quartz tube was used as the visible light source. The reaction temperature was maintained at 25 °C by flushing cooling water over the outer jacket of the reactor. The reactor was wrapped by aluminum foil in order to avoid additional interference. The photocatalytic degradation was tested in a 250 ml phenol solution of 50 mg/L with the catalyst concentration kept at 1.0 g/L. Before photocatalytic reaction, the reactant mixture was stirred in the dark for 30 min to obtain the adsorption-desorption equilibrium between phenol and catalyst before illumination. Air supply to the reactor was maintained at a flow rate of 80 ml/min in order to mix phenol with dissolved oxygen. 5 ml sample was taken every 20 min from the reactor, followed by centrifugation. Absorbance of the supernatant was measured with the TU-1901 UV–vis spectrophotometer at the light wavelength of 270 nm. The concentration of phenol was calculated with the Lambert-Beer law.

Photocatalytic activity under sun light was also performed. 0.1 g catalyst was added into 100 ml phenol solution of 50 mg/L in a petri dish of 15 cm in diameter. The reactant mixture was stirred for 30 min to obtain the adsorption-desorption equilibrium between phenol and catalyst. Then the petri dish sealed with plastic foil was exposed to sun light for testing from 10:00 AM till 4:30 PM in May at Fujian, China.

3. Results and discussion

3.1. Photocatalytic activity

Fig. 1 shows the visible light activities for the S-doped TiO_2 catalysts prepared via ionic liquid with (a) different *n*(Ti)/*n*(Th) ratios after calcination at 600 °C and (b) different firing temperatures at the *n*(Ti)/*n*(Th) ratio of 5/2. Catalytic activity of TiO_2 was significantly enhanced after the S substitution. It was the 600 °C-calcined S-TiO_2 (5/2) to show the highest activity for completely removing phenol in 80 min. However, phenol removals by pure TiO_2, P-25, and S-TiO_2/H (5/2) in 80 min only achieved 13.6%, 7.9%, and 75.2%, respectively. It looks like that the S doping in TiO_2 is the critical step to have the fast phenol degradation rate and the S doping in TiO_2 with an ionic liquid instead of aqueous method can further enhance the catalytic activity. For S-TiO_2 calcined at different temperatures, the phenol removal rate increased and reached to the maximum at 600 °C, then continuously dropped at higher temperatures. Fig. 2 shows the results of catalyst activities under sun light. It still manifests that S-TiO_2 prepared via ionic liquid has higher activity than that in water. S-TiO_2 almost completely removed phenol in the test period, but the phenol was removed 26.8% by pure TiO_2, 19.6% by P-25, and 82.4% by S-TiO_2/H (5/2).

3.2. XPS analysis

XPS survey spectrum of 600 °C-calcined S-TiO_2 (5/2) catalyst is shown in Fig. 3a. Ti, O, N, S, and C element peaks were observed in spectrum. The C1*s* peak originated from the adventitious carbon. The peak at 401.9 eV attributed to the adsorbed N_2, while no lattice N1*s* peak around 396 eV was observed [17,39]. The high resolution Ti2*p* XPS spectra of TiO_2 and S-TiO_2 are shown in Fig. 3b. The binding energy peaks of Ti2*p*3/2 and Ti2*p*1/2 were found at 458.7 eV and 464.5 eV for TiO_2, respectively, and at 458.4 eV and 464.2 eV for S-TiO_2. The spin-orbital doublet splitting (D) (Ti2*p*3/2-Ti2*p*1/2) of 5.8 eV suggests the 4+ state for Ti [40]. This small negative shift of binding energy of Ti2*p* for S-TiO_2 (0.3 eV) in

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