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Preparation, characterization and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for electronic structures

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ABSTRACT

Fe-doped TiO_2 (Fe-TiO_2) nanorods were prepared by an impregnating-calcination method using the hydrothermally prepared titanate nanotubes as precursors and $Fe(NO_3)_3$ as dopant. The as-prepared samples were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction, X-ray photoelectron spectroscopy, N_2 adsorption–desorption isotherms and UV–vis spectroscopy. The photocatalytic activity was evaluated by the photocatalytic oxidation of acetone in air under visible-light irradiation. The results show that Fe-doping greatly enhance the visible-light photocatalytic activity of mesoporous TiO_2 nanorods, and when the atomic ratio of Fe/Ti (R_{Fe}) is in the range of 0.1–1.0%, the photocatalytic activity of the samples is higher than that of Degussa P25 and pure TiO_2 nanorods. At $R_{Fe} = 0.5\%$, the photocatalytic activity of Fe-TiO_2 nanorods exceeds that of Degussa P25 by a factor of more than two times. This is ascribed to the fact that the one-dimensional nanostructure can enhance the transfer and transport of charge carrier, the Fe-doping induces the shift of the absorption edge into the visible-light range with the narrowing of the band gap and reduces the recombination of photo-generated electrons and holes. Furthermore, the first-principle density functional theory (DFT) calculation further confirms the red shift of absorption edges and the narrowing of band gap of Fe-TiO_2 nanorods.

1. Introduction

In recent years, one-dimensional (1D) nanostructured materials have been extensively studied because of their distinctive geometries, novel physical and chemical properties and potential applications in nanoscale optical and electric devices [1–6]. Among the various oxide and non-oxide 1D nanostructured materials, titanate nanotubes have also received more and more attention due to their cheap fabrication, high specific surface area and pore volume and wide applications in photovoltaic cells, photocatalysis, catalytic supports and gas sensing since the innovative work was reported by Kasuga et al. [7–15]. Using a simple hydrothermal treatment of crystalline TiO_2 powders with NaOH aqueous solutions, high-quality titanate nanotubes with uniform diameters of around 10 nm were obtained and their specific surface area reached more than 400.0 m^2/g [13,14]. Unfortunately, the prepared titanate nanotubes, nanobelts and nanowires by the hydrothermal method show almost no photocatalytic activity for the photocatalytic oxidation of acetone in our experiment [16–19]. Considering their large specific surface area, high pore volume and unique morphology, the obtained nanotubes will offer new chance to design various 1D TiO_2-related photocatalytic materials by doping and calcinations [20–23].

To meet the increasingly stringent standards of environmental regulations, catalytic techniques are being applied in the fields of environmental protection. Photocatalysis is one technique that has great potential to control aqueous organic contaminates or air pollutants. It is believed to have several advantages over conventional oxidation processes, including (1) complete mineralization of the pollutants, (2) use of the near-UV or solar light, (3) no addition of other chemicals, and (4) operation at near room temperature [24–32]. Among various oxide semiconductor photocatalysts, titanium dioxide has been proved to be one of the best photocatalysts due to its biological and chemical inertness, strong oxidizing power, cost-effectiveness and long-term stability against photocorrosion and chemical corrosion for widespread environmental applications. However, due to its large band gap (3.2 eV), the currently used photocatalyst TiO_2 can only absorb a small fraction of solar energy, thus restricting its practical applications [33,34]. In view of the efficient utilization of solar energy, it is indispensable to develop a photocatalyst with high activities under visible-light irradiation [35,36]. Metal elements doping is one of the typical approaches to extend the spectral response of the titanium dioxide to visible-light region by providing defect states in the band gap [37–39]. Some metal elements such as Fe, Cr, Co, Mo and V have been employed to tune the electronic structure and

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enhanced the photocatalytic activity of the titanium dioxide [33,40]. Among these elements, Fe has attracted special attention. For example, Choi et al. [40] reported the highest chloroform degradation efficiency under UV irradiation for a sample containing 0.5 (at.%) Fe^{3+} and the substitution of Ti^{4+} ions in the titania lattice by Fe^{3+} ions was favored. Zhu et al. [41] recently used a sol–gel method to prepare Fe-TiO_2 and studied the effect of Fe^{3+} doping concentration on the photoactivity of yellow XRG dye. Cong et al. [42] studied the co-doping effect of N and Fe on TiO_2, which improved the activity under both visible and UV lights irradiation. It was commonly reported that the improvement of photocatalysts was attributed to the Fe^{3+} dopants which can help the separation of photo-generated electrons and holes, and also can absorb and utilize the visible light to photocatalyze the degradation of pollutants [43–45].

In this work, Fe-doped TiO_2 nanorods were prepared by a simple impregnating-calcination method using the hydrothermally prepared titanate nanotubes as precursors and $Fe(NO_3)_3$ as dopant. The photocatalytic activity of the samples was evaluated by the photocatalytic oxidation of acetone in air under visible-light irradiation. To the best of our knowledge, this is the first time to report the preparation and visible-light-driven photocatalytic activity of Fe-doped titania nanorods and first-principles study for their electronic structures.

2. Experimental details

2.1. Preparation of titanate nanotubes

Titanate nanotubes were prepared using a hydrothermal method similar to that described by Kasuga et al. [13,14]. TiO_2 used for the preparation of titanate nanotubes was Degussa P25 TiO_2 powders (P25) with crystalline structure of ca. 20% rutile and ca. 80% anatase and primary particle size of ca. 30 nm. In a typical synthesis, 1.5 g P25 was mixed with 140 ml of 10 M NaOH solution followed by hydrothermal treatment of the mixture at 150 °C in a 200 ml Teflon-lined autoclave for 48 h. After hydrothermal reaction, the precipitate was separated by filtration and washed with a 0.1 M HCl solution and distilled water until the pH value of the rinsing solution reached ca. 6.5, approaching the pH value of the distilled water. The washed samples were dried in a vacuum oven at 80 °C for 8 h.

2.2. Preparation of Fe-doped TiO_2 nanorods

Fe-doped TiO_2 (Fe-TiO_2) nanorods were prepared by an impregnating-calcination method using the as-prepared titanate nanotubes as precursors. The detailed experimental procedures are as follows: 0.2 g of titanate nanotube powders was mixed with 25 ml of ferric nitrate ($Fe(NO_3)_3$) aqueous solution. In order to eliminate the effect of pH, the pH values of all mixed solutions were adjusted to 5 with a dilute nitrate acid solution (0.1 M). The suspensions were stirred for 0.5 h and then placed at room temperature for 48 h. After that, the mixed solution was dried in an oven at 100 °C for 5 h to evaporate the water. The dried samples were ground and finally calcined at 500 °C in air for 1.5 h. The nominal atomic ratios of Fe to Ti, which hereafter was designated as R_{Fe}, were 0, 0.1, 0.25, 0.5 and 1.0 atomic% (at.%), and the obtained powders were labeled as R0, R0.1, R0.25, R0.5 and R1.0, respectively. The color of the calcined powder samples slightly changed and was from white to slight red with increasing R_{Fe}.

2.3. Characterization

The morphology observation was performed on a S-4800 field emission scanning electron microscope (SEM, Hitachi, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were conducted with a JEM-2100F electron microscope (JEOL, Japan), using a 200 kV accelerating voltage. X-ray diffraction (XRD) patterns, obtained on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation at a scan rate (2θ) of $0.05^\circ\ s^{-1}$, were used to determine the identity of any phase present and their crystallite size. The accelerating voltage and the applied current were 40 kV and 80 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB 210 XPS system with Mg Kα (1253.6 eV) source. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) of the samples were analyzed by nitrogen adsorption on an ASAP 2020 nitrogen adsorption apparatus (Micromeritics Instruments, USA). All the samples were degassed at 180 °C prior to nitrogen adsorption measurements. The BET surface area was determined by a multi-point BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The desorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method assuming cylindrical pore [46–48]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.994 was used to determine the pore volume and average pore size. UV–vis spectra were obtained on an UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in the UV–vis diffuse reflectance experiment.

2.4. Analysis of hydroxyl radicals (·OH)

The formation of hydroxyl radicals (·OH) on the surface of photo-illuminated TiO_2 was detected by the photoluminescence (PL) technique using terephthalic acid as a probe molecule, which readily reacts with ·OH to produce highly fluorescent product, 2-hydroxyterephthalic acid. The method relies on the PL signal at 425 nm of 2-hydroxyterephthalic acid. The PL intensity of 2-hydroxyterephtalic acid is proportional to the amount of ·OH produced on the surface of TiO_2 [49,50]. Experimental procedures were as follows; 0.1 g of TiO_2 powder sample was dispersed in a 20 ml of the 5×10^{-4} M terephthalic acid aqueous solution with a concentration of 2×10^{-3} M NaOH in a dish with a diameter of about 9.0 cm at ambient temperature. A 15 W daylight lamp (6 cm above the dishes) was used as a light source. The integrated visible-light intensity measured with a visible-light radiometer (Model: FZ-A, made in Photoelectric Instrument Factory of Beijing Normal University) was $2.9 \pm 0.1\ mW/cm^2$ with the wavelength range of 400–1000 nm. PL spectra of generated 2-hydroxyterephthalic acid were measured on a Hitachi F-7000 fluorescence spectrophotometer. After visible-light irradiation for every 15 min, the reaction solution was filtrated to measure the increase in the PL intensity at 425 nm of 2-hydroxyterephthalic acid excited by 315 nm light.

2.5. Measurement of photocatalytic activity

The visible-light photocatalytic activity experiments on the prepared samples and P25 for the photocatalytic oxidation of acetone in air were performed at ambient temperature using a 15 L rectangular photocatalytic reactor, as previously reported [51,52]. The photocatalysts were prepared by coating an aqueous suspension of the samples onto three dishes with diameters of 9.0 cm. The weight of catalysts used for each experiment was kept at ca. 0.3 g. The dishes containing catalysts were dried in an oven at 100 °C for about 2 h to evaporate the water and then cooled to room temperature before used. After sample-coated dishes were placed in the reactor, a small amount of acetone was injected into the reactor with a micro-syringe. The acetone vapor was allowed to reach adsorption equilibrium with catalysts in the reactor in the