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Photocatalytic activity of nitrogen doped rutile TiO_2 nanoparticles under visible light irradiation

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Abstract

This work provides the design and synthesis of nitrogen doped rutile TiO_2 nanoparticles working as efficient photocatalysts under visible light irradiation. Nitrogen doped rutile TiO_2 nanoparticles are synthesized through the surface nitridation of rutile nanoparticles, which have been prepared in advance. The experimental results show that the nitrogen element is easily doped into the lattice of TiO_2 nanoparticles and its doping amount increases with the decrease of nanocrystallite size. The photocatalytic activity of the nanoparticles under visible light irradiation is correlated not only with the amount of doped nitrogen element but also with the morphology and crystallinity of nanoparticles.

Keywords: A. Nanostructures; B. Chemical synthesis; C. X-ray diffraction; D. Catalytic properties

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1. Introduction

Owing to their potential applications in the photocatalytic degradation of organic pollutants and the conversion of solar energy to chemical energy, TiO_2-based photocatalysts with high photocatalytic activity under visible light have recently attracted extensive attention [1–4]. However, efforts were seldom devoted to the effect of size and shape of the visible-light photocatalyst on its photocatalytic activity, and the major reasons may be the following two points: (i) more notice is taken of the proper position of conduction band minimum and valence band maximum than the crystallite size for a kind of novel visible-light photocatalyst; and (ii) the ‘‘blue shift’’ of the absorbance edge derived from the decreased size of nanoparticles conflicts with the ‘‘red shift’’ required by visible-light photocatalysts. Nevertheless, due to the outstanding virtues of nanoparticles, such as the high specific area and fast charge carrier transfer on the surface of the nanoparticles, doping nanostructured TiO_2 with nonmetal dopants may be considered as an important strategy to enhance its visible light driven photocatalytic activity [5]. In the present paper, the visible-light photocatalytic activity of nitrogen doped TiO_2 nanorods rather than spherical nanoparticles has been investigated.

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2. Experimental

2.1. Preparation

In a typical synthesis, 15.0 mL of 3.0 M $TiCl_4$ solution was mixed with 30.0 mL of tetrabutyl titanate in an ice-water bath to gain the sol with stirring, and then 60.0 mL of oleic acid was added dropwise to the sol. After 5 min stirring, the mixture was transferred to a stainless steel autoclave lined with Teflon of 100 mL capacity and tightly closed, and then held at 180 and 220 °C for 24 h, respectively. The precipitates after the solvothermal treatment were washed well with ethanol for several times, collected from the solution by filtration, and dried at 60 °C in a vacuum oven overnight. The derived samples were designed as Sample A prepared at 180 °C and Sample B prepared at 220 °C, respectively. Then, a desired amount of the synthesized nanoparticles (Samples A and B) were charged into a tube furnace and heat-treated in an ammonia flow (1.0 L min^{-1}) at 500 °C for 3 h. The Samples A and B after nitridation treatment were designed as Samples C and D, respectively.

2.2. Characterization

The phase and crystallinity of the products were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 0.15418$ nm) at 40 kV and 100 mA on a Rigaku D/max 2550 V diffractometer. The morphology of products was observed by a transmission electron microscopy (TEM) on a JEOL-200CX electron microscope and a JSM-6700F field emission scanning electron microscope (FE-SEM). The specific surface areas were determined by the BET method, using a Micromeritics ASAP 2010 surface area analyzer. Prior to the measurement, the samples were degassed at 150 °C for 12 h in vacuum. The diffuse reflectance UV–vis spectra were acquired with a Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere attachment. The charge state of doped TiO_2 at the surface was investigated by X-ray photoelectron spectroscopy (XPS) using an Mg X-ray source (MgKα-300 W, Microlab MKII, VG Co., UK).

2.3. Photocatalytic reaction

Photocatalytic experiments were carried out in a Pyrex photoreactor containing a required amount of photocatalyst and methylene blue aqueous solution. A 300 W medium-pressure mercury lamp with 400 nm cut-off filters was used as a visible-light source, and cut-off filters were removed for the UV-light determination. Oxygen was bubbled into the solution throughout the photocatalytic experiment. 0.16 g of photocatalyst was suspended in a 400 mL 20 mg/L of methylene blue aqueous solution and kept in the dark for about 15 min so that the methylene blue finished absorption on the surface of the photocatalyst. The concentration of methylene blue after the adsorption experiment was taken as its initial concentration for calculation (c_0). It should be noted that methylene blue did not adsorb much on the surfaces of photocatalysts in the present experiments. The concentration of methylene blue in the solution was determined by monitoring the absorbance at 650 nm using Shimadzu UV-3101PC spectrophotometer.

3. Results and discussion

Surface nitridation treatment does not destroy the structure of the aggregates. Fig. 1(a) and (b) show the FE-SEM images of the samples before nitridation treatment, and Fig. 1(c) and (d) reveal the TEM pictures of the samples after nitridation treatment. It can be seen that the morphologies of the aggregates before nitridation treatment are similar with those after nitridation treatment. Fig. 1(c) reveals that the morphologies of Sample C are spherical aggregates with the diameter ranging from 0.7 to 1.0 μm. The inset of Fig. 1(c) depicts an individual spherical aggregate made up of nanorods, and the diameters of a single nanorod are 12–17 nm. The particles of Sample D are flocky aggregates other than nanorod aggregates (Fig. 1(d)). These kinds of aggregates of nanoparticles are easily recoverable in solution photocatalytic reactions [6]. As can been seen from the XRD patterns (Fig. 2), both of the two different aggregates are of rutile phase and nitrogen doping at 500 °C for 3 h does not change the crystal phase of the TiO_2 nanoparticles, only resulting in the growing up of the nanocrystallites. The wider peaks of sample B indicate its reduced crystallite size. The stronger ligand effect of oleic acid molecules adsorbed on the surface of TiO_2 nanocrystallites at higher temperature strongly hinders their growth and development, which results in the aggregates of tiny nanocrystallites