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Synthesis and photocatalytic activity of sulfate modified Nd-doped TiO_2 under visible light irradiation

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Abstract: Nd-doped TiO_2 (NT) photocatalysts with different contents of Nd were synthesized by sol-gel method. Then sulfated Nd-doped TiO_2 (SNT) solid superacid photocatalysts were prepared by an incipient wetness impregnation technique. The photocatalytic activity of catalysts was evaluated by the photodegradation of methylene blue under visible light irradiation. Analytical results demonstrated that Nd doping inhibited the growth of TiO_2 crystallite and enhanced the thermal stability of anatase TiO_2. Meanwhile, sulfate ions modification increased the specific surface area of samples. In addition, the optical absorption edges of SNT photocatalysts shifted to longer wavelength compared with the undoped TiO_2. Such SNT with Nd dosage of 0.25 at.% exhibited the highest photocatalytic activity in the degradation of methylene blue upon irradiation with visible light.

Keywords: TiO_2; solid superacid; photocatalyst; visible light; methylene blue; rare earths

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Photocatalytic oxidation techniques have attracted much attention because of their potential application in water treatment and air purification[1,2]. Among various photocatalysts, TiO_2 has been regarded as one of the most promising photocatalysts owing to its strong oxidizing power, nontoxicity, low cost and stablility to light irradiation[3–5]. However, TiO_2 has wide band gap energy (3.2 eV), which limits its application in visible light range of solar spectrum. Moreover, the recombination of photogenerated electron-hole pairs leads to low photoquantum efficiency of TiO_2[6–8]. It is, therefore, necessary to modify the optical and electronic properties of TiO_2 to make it work under visible light.

Rare earth ions are known for their *f*-orbitals to form complexes with various Lewis bases and their oxides having characteristics of adsorption selectivity and thermal stability[9]. In recent years, many researchers have examined the effects of rare earth ions doping on photocatalytic properties of TiO_2[10–14]. Results indicate that the visible light photocatalytic activity of TiO_2 can be enhanced by doping rare earth ions[15–18]. However, the recombination of photogenerated electron-hole pairs of such photocatalysts is still higher thus leading to lower photoquantum efficiency. Recently, modified solid acid catalysts have gained much attention in isomerization reactions owing to their non-toxicity, high strength of acidity, and high activity at low temperatures[19–22]. This is mainly because of the thermal stability and acidity gained after sulfation process[23–25]. A few reports on sulfated TiO_2 solid superacid photocatalysts demonstrated that the sulfation could affect the crystalline structure and crystallinity, the surface chemistry and the pore structure, etc.[26], thus enhancing the photocatalytic activity of photocatalysts.

In the present work, we tried to combine the effects of both rare earth and sulfate ions to improve the visible light photocatalytic activity of TiO_2. A series of Nd-doped TiO_2 nanoparticles with different contents of Nd were prepared by sol-gel method. And then the solid superacid photocatalysts of sulfated Nd-doped TiO_2 were prepared by an incipient wetness impregnation technique. Finally, their photocatalytic activities were evaluated by using methylene blue aqueous solution as a model contaminant under visible light irradiation.

1 Experimental

1.1 Starting materials

All major chemicals were of AR grade and used without further purification. All solutions were prepared with deionized water. Tetrabutyl titanate and methylene blue were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. Neodymium nitrate was purchased from

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Guoyao Group Chemical Reagent Co., Ltd., China. Acetic acid and ammonium sulfate were obtained from Tianjin Damao Reagent Factory, China.

1.2 Synthesis of sulfated Nd-doped TiO_2 solid superacid photocatalyst

Undoped and Nd-doped TiO_2 photocatalysts with different contents of neodymium (Nd) were prepared by sol-gel method with the following procedure: Solution A, 10 mL tetrabutyl titanate was dissolved into 30 mL absolute ethanol with stirring for 30 min; solution B, a given amount of neodymium nitrate in the required stoichiometry (molar ratio of Nd/Ti=0, 0.125, 0.25, 0.5 and 1) was fully dissolved in 10 mL acetic acid. Then 10 ml distilled water and 30 mL absolute ethanol were added. Subsequently, solution B was added into solution A dropwise using a separatory funnel under vigorous stirring for 30 min. Afterward, the resulting colloidal suspension was stirred for 1 h and then aged for 2 h at room temperature. The gel was dried at 100 ºC under vacuum and then ground. Then Nd-doped TiO_2 with different Nd contents of 0.125 at.%, 0.25 at.%, 0.5 at.% and 1 at.% (simply "NT *x* at.%" for short) photocatalysts were obtained.

Sulfated Nd-doped TiO_2 solid superacid photocatalysts were prepared by incipient wetness impregnation technique using ammonium sulfate as a source of sulfate ions. The as-prepared Nd-doped TiO_2 photocatalysts were added into ammonium sulfate solution (0.5 mol/L) and stirred for 8 h. Then the sulfated samples were filtrated and dried in an air oven at 100 ºC and subsequently calcined at 300, 400, 500, 600 and 700 ºC for 2 h. Sulfated Nd-doped TiO_2 (simply "SNT" for short) solid superacid photocatalysts were then obtained. For comparison, sulfated TiO_2 (simply "ST" for short) sample was also prepared using undoped TiO_2.

1.3 Catalyst characterization

X-ray diffraction (XRD) spectra was recorded with an AD/MAX 2500 diffractometer using Cu Kα radiation. The measurements were carried out at 40 kV tube voltages and 200 mA current. The crystallite size of the samples was calculated using the Debye-Scherrer equation. The specific surface areas (BET) of the powder samples were determined by the amount of nitrogen adsorption at liquid nitrogen temperature (Quantachrome, USA). The morphology of samples was evaluated by field emission scanning electron microscopy (FESEM, JEOL-6340F) with an accelerating voltage of 15 kV. The chemical composition of the sample was determined using an energy dispersive X-ray spectrometer (EDS) attached to the SEM. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken over a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. FT-IR spectra of samples were recorded with a Perkin-Elmer (Spectrum One-B) FT-IR spectrometer in the range of 4000–400 cm^{-1}. All IR measurements were carried out at room temperature using KBr technique. UV-vis absorption spectra of the samples were obtained using an UV-vis spectrophotometer (Cary 100) with $BaSO_4$ as reference.

1.4 Evaluation of photocatalytic activity

The photocatalytic activity of the catalysts was evaluated by degradation of methylene blue (MB) under visible light irradiation. A 300 W Xe lamp (PLS-SXE300) was used as the light source and the visible wavelength was controlled through a 420 nm cut filter, which was hanged in a dark box and kept at about 15 cm on the top of photoreactor. A general photocatalytic procedure was carried out as follows: 0.1 g of catalyst was suspended in a fresh aqueous MB dye solution (C_0=0.01 g/L, 100 mL). The suspension was stirred in the dark for 30 min to ensure establishment of adsorption-desorption equilibrium of MB dye. The samples were collected at regular irradiation intervals, and the concentration changes of MB solution were measured using an UV-vis spectrometer at 665 nm (λ max). The photocatalytic activity of catalyst was evaluated by the degradation rate (*D*) of the samples. The equation of the degradation ratio is as follows:

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where *D* is the degradation ratio, A_0 is the initial absorbance of MB, and A_t is the absorbance of MB after "*t*" minutes.

2 Results and discussion

Fig. 1 shows the XRD patterns of the SNT photocatalysts calcined at 600 ºC with different Nd contents. All the identified peaks can be assigned to the tetragonal

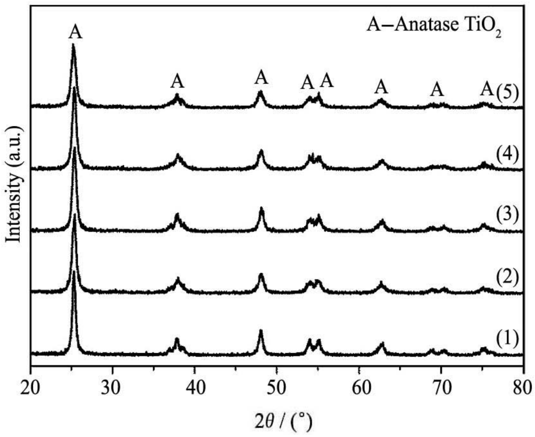

Fig. 1 XRD patterns of SNT photocatalysts with different Nd contents

(1) 0; (2) 0.125 at.%; (3) 0.25 at.%; (4) 0.5 at.%; (5) 1 at.%