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Synthesis, characterization, and photocatalytic activity of $TiO_{2-x}N_x$ nanocatalyst

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Abstract

Nitrogen-doped titanium dioxide powders were prepared by wet method, that is, the hydrolysis of acidic tetra-butyl titanate using aqueous ammonia solution, followed by calcination at temperatures about 350 °C. The catalysts exhibited photocatalytic activity in the visible light region owing to N-doping. The light absorption onset of $TiO_{2-x}N_x$ was shifted to the visible region at 459 nm compared to 330 nm of pure TiO_2. An obvious decrease in the band gap was observed by the optical absorption spectroscopy, which resulted from N2p localized states above the valence band of $TiO_{2-x}N_x$ (compared to TiO_2). The $TiO_{2-x}N_x$ catalyst was characterized to be anatase with oxygen-deficient stoichiometry by X-ray diffraction (XRD), surface photovoltage spectroscopy (SPS) and X-ray photoelectron spectroscopy (XPS). The binding energy of N1s measured by XPS characterization was 396.6 eV (Ti─N bonds, β-N) and 400.9 eV (N─N bonds, γ-N_2), respectively. The photocatalytic activity of $TiO_{2-x}N_x$ under visible light was induced by the formation of β-N in the structure. Photocatalytic decomposition of benzoic acid solutions was carried out in the ultraviolet and visible (UV–vis) light region, and the $TiO_{2-x}N_x$ catalyst showed higher activity than pure TiO_2.

Keywords: Photocatalyst; Visible light; Wet method; N-doped TiO_2; Benzoic acid

1. Introduction

Semiconductor-based photocatalysis, as an effective means of alleviating very low concentrations of pollutants including airborne pathogenic microorganisms, viruses, and volatile organic contaminants, has attracted extensive interests [1–5], after the discovery of the photoinduced decomposition of water on TiO_2 reported by Fujishima and Honda [6]. It is well known that titanium dioxide was the most effective photocatalyst and was widely applied in the purification of air and water, solar system. However, most of these investigations were carried out under ultraviolet (UV) light, because TiO_2 photocatalyst showed relatively high activity and chemical stability under UV light ($\lambda \leq 387.5$ nm). Nevertheless, solar energy contains only about 5% UV light and the rest is visible light. In order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reaction, the development of photocatalysts showing high activity under visible light irradiation is needed. For this purpose, coupling with organic dye sensitizers or metal oxides [7–9], doping of TiO_2 with transition metals [10,11] and reduced forms of TiO_x photocatalysts [12] have been investigated. However, most of these catalysts do not show long-term stability or do not have sufficiently high photocatalytic activities for a wide range of applications. Asahi et al. [13] reported that N-doped TiO_2 showed photoabsorption at wavelengths longer than 400 nm. They have also reported that the N-doped TiO_2 has photocatalytic activity under visible light during the photodegradation of acetaldehyde and methylene blue. Then, some researchers prepared the N-doped TiO_2 and obtained many results [14–17]. At present, the N-doped TiO_2 films or powders are prepared by: (1) sputtering TiO_2 targets for several hours in an N_2/Ar gas mixture and then annealing in N_2 gas [13], (2) treating anatase TiO_2 powders in an NH_3/Ar atmosphere to produce photocatalysts [14,15], and (3) a hydrolytic process using a $TiCl_3$ or $Ti(SO_4)_2$ solution and an ammonia solution [16,17].

The previous researches have proved that photocatalytic activity is strongly related to the crystallinity, particle size and specific surface area of the photocatalyst [18–20]. Although

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three of the TiO_2 polymorphs, rutile, anatase and brookite occur in nature, usually, only anatase and rutile can be utilized as photocatalysts. The photocatalytic activity of brookite has been seldom investigated. Both anatase and rutile can be described in terms of distorted TiO_6 octahedra, that is, Ti^{4+} ions surrounded by six O^{2-} ions. The rutile structure has a slight orthorhombic distortion, while the anatase octahedron is more distorted. Moreover, anatase has greater Ti–Ti distances than rutile (3.79 and 3.04 Å versus 3.57 and 2.96 Å), but shorter Ti–O distances (1.934 and 1.980 Å versus 1.949 and 1.980 Å) [21]. The different structures result in different electronic band properties. The band gap of anatase is 3.2 eV [22], while that of rutile is slightly smaller at 3.0 eV [23]. So, anatase is usually considered to be more active than rutile crystalline form in photocatalytic research.

Under these circumstances, we demonstrated a simple hydrolysis method of nitrogen-doped TiO_2 ($TiO_{2-x}N_x$) using tetra-butyl titanate as titanium source. The new method avoided the laborious process compared to the traditional hydrolysis methods using inorganic titanium sources that need washing off residual SO_4^{2-} and Cl^- [16,17]. The experiment results indicated that the $TiO_{2-x}N_x$ prepared here has highly visible light-induced photocatalytic activity for degradation of benzoic acid solutions. Moreover, the phase composition, particle size, microstructure, specific surface area and photoelectrochemical properties of the $TiO_{2-x}N_x$ were determined by X-ray diffraction (XRD), Brauenner–Emmet–Teller (BET), surface photovoltage spectroscopy (SPS), electric-field-induced surface photovoltage spectroscopy (EFISPS) and X-ray photoelectron spectroscopy (XPS) analyses.

2. Experimental

2.1. Preparation of $TiO_{2-x}N_x$

Tetra-butyl titanate ($Ti(OBu)_4$) solution was used as a titanium stock. Ammonia aqueous solution ($NH_3{\cdot}H_2O$) (25%) was used as a nitrogen source. Under stirring, 0.5 mL nitric acid (HNO_3) was added drop wise into a solution mixed with 20 mL $Ti(OBu)_4$ and 100 mL ethanol at room temperature. Here, HNO_3 was used as a chemical additive to moderate the reaction rate, in order to control the reaction kinetics. Then, 40 mL $NH_3{\cdot}H_2O$ was added dropwise under stirring to carry out hydrolysis. After continuously stirring for 60 min, the precursor was dried in an oven at 80 °C. Finally, the precursor was calcined at 350 °C for 1 h to obtain the $TiO_{2-x}N_x$. The color of the sample powder was grey. The $Ti(OBu)_4$ and $NH_3{\cdot}H_2O$ were obtained from Shanghai Reagent Co., China. At the same time, the pure TiO_2 was prepared by sol–gel [24] in order to compare with $TiO_{2-x}N_x$.

2.2. Analytical method

The crystal phases of the sample were analyzed by X-ray diffraction with Cu Kα radiation (XRD: model D/max-rB, Rigaku Co., Tokyo, Japan). The particles were spread on a glass slide specimen holder and the scattered intensity was measured between 10 and 90 °C at a scanning rate of $2\theta = 5$ °C/min with 0.02 °C increments. Nitrogen adsorption and desorption isotherms were collected at −196 °C on a quantachrome autosorb-1 sorption analyzer. The specific surface area was calculated using the BET model. The SPS instrument was assembled at Heilongjiang University, and monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF-XQ500W, China) through a double prism monochromator (SBP300, China). A lock-in amplifer (SR830, USA), synchronized with a light chopper (SR540, USA), was employed to amplify the photovoltage signal. The powder sample was sandwiched between two ITO glass electrodes. The UV–vis absorption spectra of the samples were recoded on a spectrophotometer (UV-3100, Shimadzu Co., Kyoto, Japan). The absorption percentage (A) was obtained by measuring the transmittance (T) and reflectance (R) of the powders, where $A = 100 - (T + R)$. A 60 mm-integrating sphere was used for the measurement, since the scattering effect was taken into account for the powders absorption. X-ray photoelectron spectroscopy with Al Kα X-rays (XPS: model PHI5700 ESCA, Physical Electronics USA) was used to evaluate the amount and states of the nitrogen atoms in these powders. All binding energies (BE) were calibrated by the BE (284.6 eV) of C1s, which gave BE values within an accuracy of ±0.1 eV.

2.3. Photocatalytic oxidation of benzoic acid under simulated sunlight

The photocatalytic activity of the prepared catalyst was estimated by decomposition of 25 mg L^{-1} benzoic acid (BA) using 0.1 g L^{-1} of photocatalyst dosage. The photoreactor consisted of a cylindrical borosilicate glass reactor, a cooling water jacket and a light source from a 125 W Xe lamp (Institute of Electric Light Source, Beijing) located axially at the center of the vessel. The effective volume of the photoreactor was 1250 mL. The Xe lamp usually was used as simulated sunlight because the energy distribution of the Xe lamp was identical to sunlight [25]. The photocatalyst powder was added directly into the air-bubbling benzoic acid solutions followed by ultrasonic dispersion for 20 min before irradiation. The solutions were kept at 25 °C by cooling water. A special glass atmolyzer as air diffuser was fixed at the bottom of the reactor to uniformly disperse air into the solution. After irradiation, the solution was filtered through a 0.45 μm membrane filter. The concentration of benzoic acid was determined by total organic carbon (TOC) measurements using TOC-V_{CPN} (Shimadzu).

2.4. The comparison of activity between $TiO_{2-x}N_x$ and TiO_2 under different irradiation wavelength

The photocatalytic activity of $TiO_{2-x}N_x$ and TiO_2 catalysts was estimated by measuring the decomposition rate of benzoic acid (25 mg L^{-1}) within 2-h reaction time, in which contains 60 mg of photocatalyst and 60 mL of benzoic acid solution. Ultrasonic was first used to disperse the photocatalyst in solution and a magnetic stirrer was used to mix the solution during the reaction. A 125 W Xe lamp was used to photo-irradiate the suspension. Different irradiation wavelengths were obtained by