



Improved photocatalytic activity of TiO₂ produced by an alcohothermal approach through in-situ decomposition of NH₄HCO₃

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ABSTRACT

High crystallinity of TiO₂ was prepared by a modified alcohothermal method, in which titanium isopropoxide was used as the titania precursor, absolute ethanol as the reaction medium, and NH₄HCO₃ as the raw materials for release of water, ammonia and carbon dioxides via in-situ decomposition. The X-ray powder diffraction (XRD) and transmission electron microscope (TEM) measurements showed that water and ammonia from the in-situ decomposition of NH₄HCO₃ played an important role in conducting the size, shape, crystallinity and microstructure of TiO₂. The photoluminescence spectroscopy and photocurrent measurements indicated that enhanced crystallinity could hinder the recombination and promote the separation of electron-hole pairs in TiO₂, which contribute to the improvement of photocatalytic activity. Methyl orange photodegradation under UV light confirmed that high crystallinity of TiO₂ did present a high photocatalytic activity due to the effective separation of photoinduced charges.

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1. Introduction

Environmental pollution is a serious problem that can cause illness and even death to human beings [1]. Heterogeneous photocatalysis appears to be one of the most efficient and economic techniques for the remediation of a contaminated environment [2–6]. Among various photocatalysts, TiO₂ is regarded to be the ideal one and has been extensively investigated by taking advantage of its excellent redox power, excellent photostability, ecofriendliness, and low cost [7–9]. How to improve the photocatalytic activity of TiO₂ has been an interesting research topic. Previous studies have reported that the photocatalytic activity of TiO₂ is greatly influenced by several physicochemical parameters, such as crystal structure, crystallinity, morphology, particle size distribution and specific surface area [10,11], in which the crystallinity of TiO₂ plays an important role in the excited carrier (electron or hole) transport, and hence affects its photocatalytic activity. Much effort has been devoted to increase the crystallinity

of sol-gel synthesized TiO₂ via a high temperature thermal treatment, generally calculation at above 500 °C [12]. However, such high temperature calculation would lead to the aggregation of particles, the decrease of specific surface area and the loss of surface functional groups [13,14].

Alternatively, solvothermal technique has been proved to be a promising route for constructing TiO₂ with small grain sizes, high specific surface areas, and high crystallinity [15]. Furthermore, the inclusion of water during solvothermal process could promote the growth of particle size, improve the crystallinity and form high-energy {001} facet [16–20], and thus enhance its photocatalytic activity. For instance, Wu et al. reported that TiO₂ produced by nonaqueous method through inclusion of a trace amount of water in benzyl alcohol and oleylamine medium exhibited conspicuous activity in the photocatalytic degradation of organic contaminants due to the large percentage of exposed high-energy facets [19]. Do et al. [20] found that the presence of an appropriate amount of water vapor along with the desired molar ratio of oleic acid/oleylamine played a crucial role in controlling size and shape of TiO₂ nanocrystals. In addition, studies of Liu et al. [15] and our group [17] certified the significant role of water in the synthesis of TiO₂ by alcohothermal method, which could tune the particle size, crystallinity, explosion high-energy facets and ultimately affect the photocatalytic activity of TiO₂. However, most reported works

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about the influence of water on the physicochemical performance of TiO_2 [17,19,21] were carried out with the introduction of special organic agents such as oleylamine, oleic acid, linoleic acid, triethylamine and cyclohexane. Additionally, addition water to the raw materials during solvothermal process has some drawbacks. First of all, it is difficult to control the vigorous reaction between titania precursors and water since most of titania precursors are easy to hydrolyze. On the other hand, the addition of water into alcohol medium could lead to homogeneous nucleation occurrence preferentially rather than heterogeneous nucleation, whereas heterogeneous nucleation is the key step for the preparation of TiO_2 -based composites. Therefore, it is desirable to investigate the influence of in situ water on the physicochemical and photocatalyst performance of TiO_2 . It is well known that NH_4HCO_3 will decompose into water, ammonia and carbon dioxide with the increase of temperature. Moreover, the decomposition products of NH_4HCO_3 have two key influences on the growth of TiO_2 particles. On one hand, the in-situ released water can accelerate the hydrolytic process to form TiO_2 with large particle sizes and high crystallinity. On the other hand, fresh formed ammonia renders TiO_2 with rhombus morphology [22].

Herein, TiO_2 was prepared by a modified alcohothermal method, using alcohol as the reaction medium, titanium isopropoxide as the precursor of TiO_2 , and NH_4HCO_3 as the raw materials for release of water, ammonia and carbon dioxides via in-situ decomposition. As a control, TiO_2 was also synthesized by alcohothermal method in a similar manner without the addition of NH_4HCO_3 . As expected, TiO_2 prepared by the former method exhibited much larger particle sizes and higher crystallinity than TiO_2 synthesized by the latter method, implying the important role of the decomposition products of NH_4HCO_3 in conducting the size, shape and crystallinity of TiO_2 . Importantly, the synthesized TiO_2 by the modified alcohothermal method presented high photocatalytic activity under UV light irradiation, probably due to effective separation of photoinduced charges based on the enhanced crystallinity.

2. Experimental

2.1. Materials

Titanium isopropoxide (TIP, 97%) was purchased from Sigma-Aldrich. Absolute ethanol and NH_4HCO_3 were obtained from Xilong Chemical Co., Ltd, China. The chemicals were used as received and all aqueous solutions were prepared with deionized water (resistivity = $18.2 \text{ M}\Omega \text{ cm}$).

2.2. Synthesis of TiO_2

TiO_2 were synthesized according to our previous work with some modification, using absolute ethanol, titanium isopropoxide (TIP, 97%, Sigma-Aldrich) and NH_4HCO_3 as the starting materials [17]. In a typical experiment, the desired amount of NH_4HCO_3 was mixed with absolute ethanol and then determinate TIP was added into this mixture drop by drop under strongly stirring. After sonication for 1 h, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed tightly, and then heated at 180°C for 24 h. After cooled to room temperature naturally, the resulting $\text{TiO}_2\text{-N}_x$ (x means the weight of NH_4HCO_3) were collected by centrifugation, rinsed by ethanol and dried under vacuum.

2.3. Characterization of samples

The X-ray powder diffraction (XRD) patterns were obtained on a Rigaku X-ray diffractometer to determine the crystallite identity of TiO_2 samples. The microscopic structures and particle sizes of TiO_2 samples were investigated with a JEM 2100 transmission

electron microscope (TEM). BET specific surface area was carried out using Quantachrome ASIQM000-200-6 automated gas sorption analyzer. Room temperature photoluminescence (PL) spectroscopy measurement at 325 nm excitations was performed using F-4600. UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). BaSO_4 was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The X-ray photoelectron spectroscopy (XPS) measurement was made on a KRATOS Analytical AXISHSi spectrometer with a monochromatized Al $K\alpha$ X-ray source (1486.6 eV photons). The binding energy scale was calibrated by Au $4f_{7/2}$ peak at 83.9 eV as well as Cu $2p_{3/2}$ peak at 76.5 and 932.5 eV.

2.4. Photoelectrochemical measurement

Photocurrent measurement was performed in a three-electrode quartz cells with 0.1 M Na_2SO_4 electrolyte solution. Platinum wire was used as counter and saturated calomel electrode (SCE) used as reference electrodes, respectively, and $\text{TiO}_2\text{-0}$ and $\text{TiO}_2\text{-N}_3$ films electrodes ($1 \times 1 \text{ cm}^2$) on FTO served as the working electrode. The photoelectrochemical experiment results were recorded with an electrochemical system (CHI-760C Instruments). Potentials were given with reference to the SCE. The photoresponses of the photocatalysts as UV light ($\lambda = 254 \text{ nm}$) on and off were measured at 0.0 V.

2.5. Photocatalytic activity measurement

Photocatalytic performance of TiO_2 was studied by degradation of methyl orange (MO) under UV light irradiation. In a typical process, 30 mg photocatalyst was added to 150 mL MO (15 mg/L) solution. Adsorption was then conducted in the dark for 30 min under magnetical agitation in order to make TiO_2 to reach adsorption equilibrium. Subsequently, the mixture was exposed to UV irradiation by two germicidal lamp ($\lambda = 254 \text{ nm}$, 8 W) at room temperature. Aeration was performed by an air pump to ensure a constant supply of oxygen and promoted complete mixing of solution and photocatalysts during photoreaction. The sample was collected by centrifugation at given time intervals and MO concentration was measured by UV-vis spectroscopy at 464.2 nm.

3. Results and discussion

3.1. Phase structures and morphology

XRD was conducted to characterize the influence of the in-situ water on the particle size and crystalline of TiO_2 , and the results were displayed in Fig. 1. It is clear that the peaks of $\text{TiO}_2\text{-0}$ sample at 2θ values of 25.3° , 37.8° , 48.0° , 53.9° , 55.1° , 62.7° , 68.8° , 70.3° and 75.0° can be indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) facets, the typical reflections of anatase phase structure of TiO_2 [10]. After introduction of different amount of NH_4HCO_3 during the alcohothermal process, only anatase phase of TiO_2 is detected, demonstrating that the in-situ water decomposed from NH_4HCO_3 does not change the phase of TiO_2 . However, it is worth noting that with the addition of NH_4HCO_3 , the intensity of TiO_2 characteristic peaks increases obviously and their shapes become sharper, which means the higher crystallinity and larger particle size of TiO_2 . Similar phenomenon was also observed in our previous work [17,18]. The reason is that a trace amount of water from the in situ decomposition of NH_4HCO_3 promotes the growth of crystallites and enhances the crystallinity of TiO_2 .

To evaluate the role of water and ammonia from the in-situ decomposition of NH_4HCO_3 in the growth of TiO_2 particles, TEM was carried out to characterize the microstructure and morphology

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