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Enhancement of photocatalytic performance of TiO_2 produced by an alcohothermal approach through inclusion of water

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ABSTRACT

High crystallinity of TiO_2 nanoparticles (NPs) with exposed {0 0 1} facets was prepared by an alcohothermal method without the addition of any specific organic reagents, in which titanium isopropoxide was used as the titania precursor, water and ethanol (0.6/90–5/90, v/v) as the reaction medium. The X-ray powder diffraction (XRD) and transmission electron microscope (TEM) measurements showed that water played an important role in conducting the size, shape, crystallinity and microstructure of TiO_2 NPs. The photoluminescence spectroscopy and photocurrent measurements indicated that enhanced crystallinity could hinder effectively the recombination and promote significantly the separation of electron–hole pairs in TiO_2 NPs. These will contribute to the enhancement of photocatalytic performance. Methyl orange photodegradation under UV light confirmed that high crystallinity of TiO_2 NPs did exhibit a high photocatalytic activity due to the effective separation of photoinduced charges and exposure of highly reactive {0 0 1} facets.

1. Introduction

Metal oxides such as TiO_2 and ZnO have been widely used in many fields including photochromic devices, sensors, solar cells, and especially used as photocatalysts to decompose organic contaminants and split water [1–6]. A number of researches have shown that several factors can influence its photocatalytic activity. These factors include crystal structure, crystallinity, morphology, particle size distribution and specific surface area [7–12], in which the crystallinity of TiO_2 plays an important role in the excited carrier (electron or hole) transport, and hence affects its photocatalytic activity.

During the past decades, many strategies have been used to develop TiO_2 materials, including sol–gel, micelle/reverse micelle, sonochemical synthesis, hydro-/solvothermal method [13–17]. Among them, a hydrothermal technique (i.e., high-temperature, high-pressure) has been proved to be a promising route for constructing TiO_2 with small grain sizes, high specific surface areas, and high crystallinity [18]. Instead of aqueous system, alcohol was chosen for the synthesis of TiO_2. This solvothermal technique offers some advantages over hydrothermal technique. For instance, solvothermal technique avoids contaminations from ion species dissolved in water, improving the quality of product. It also makes it possible to probe the role of water in the preparation of TiO_2 in same phase.

Endeavors have been focused on the influence of water on the size, shape and crystallinity of TiO_2 produced by solvothermal method. For example, Zheng et al. [14] reported that including a trace amount of water in benzyl alcohol and oleylamine medium and eliminating the use of carboxylic acid type capping agents were the two keys to integrate the structural diversity of TiO_2 from aqueous systems into large-quantity synthesis in nonaqueous systems. Do et al. [16] claimed 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 TiO_2 nanocrystals. Li et al. [19] detailed how to control the size, shape and dispersibility of TiO_2 through fine adjustment of the reaction parameters. Similarly, Liu et al. [18] found that primary particle sizes of TiO_2 could be tuned by adjusting various reaction parameters including the amount of water under mild solvothermal conditions. As afore-mentioned,

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however, most works about the influence of water on the size, shape and crystallinity of TiO_2 [14,16,19] were carried out by using organic agents such as oleylamine, oleic acid, linoleic acid, triethylamine and cyclohexane. Only few work [18] investigated the role of water in the synthesis of TiO_2 in alcohol medium without such organic agents by alcohothermal method. Therefore, it is necessary to investigate the influence of water on the size, shape, crystallinity, microstructure, and especially the photocatalytic activity of TiO_2 produced by alcohothermal method in alcohol medium.

In our previous work [20], we found that a trace amount of water in the ethanol dispersion of graphene oxide could promote the growth and enhance the crystallinity of TiO_2. Excitedly, it could lead to the formation of TiO_2–graphene composites with exposed {0 0 1} facets by a one-pot solvothermal approach. Inspired by our previous work [20], we think it is possible that the artificial addition of water to ethanol could also enhance the crystallinity of TiO_2 and result in the formation of TiO_2 with exposed {0 0 1} facets by alcohothermal method at the same time. Interestingly, we synthesized TiO_2 with exposed {0 0 1} facets by alcohothermal approach without any organic agents introduced as earlier publication, only by using titanium isopropoxide (TIP) as the titania precursor, ethanol and a certain amount of water as the reaction medium. Furthermore, the presence of water could tailor the crystallinity, and the shape that tends to exhibit equiaxed geometry bounded by crystallographic facets. Importantly, the synthesized TiO_2 samples presented high photocatalytic activity under UV light, probably due to effective separation of photoinduced charges based on the enhanced crystallinity and exposure of high reactive {0 0 1} facets.

2. Experimental

2.1. Materials

Titanium isopropoxide (TIP, 97%) was purchased from Sigma–Aldrich. Absolute ethanol was 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 MV cm).

2.2. Synthesis of TiO_2

TiO_2 nanoparticles (NPs) were synthesized using absolute ethanol and TIP as the starting materials, according to our previous work [20]. In a typical experiment, the desired amount of water was mixed with absolute ethanol and then determinate TIP was added into this mixture drop by drop under strongly stirring. The volume ratio of TIP/water/absolute ethanol is 3:X:90. After sonication for 1 h, the crystallization of TiO_2 was achieved through one-step alcohothermal reaction at 180 °C for 24 h. The resulting TiO_2-X NPs (X means the volume (mL) of water used) 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). Specific surface area was investigated by nitrogen adsorption/desorption analysis using a nitrogen surface area analyzer (ASAP 2020, USA). 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.

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 TiO_2-0 and TiO_2-4 films electrodes (1 cm × 1 cm) 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 (λ = 254 nm) on and off were measured at 0.0 V.

2.5. Photocatalytic activity measurement

Photocatalytic performance of TiO_2 NPs was studied by degradation of methyl orange (MO). 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 NPs to reach adsorption equilibrium. Subsequently, the mixture was exposed to UV irradiation by two germicidal lamp (λ = 254 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. Photocatalytic performance

The photocatalytic activities of TiO_2 samples were measured by the photodegradation of MO as model reaction under UV light irradiation, and the results are shown in Fig. 1a. The normalized temporal concentration changes C/C_0 (C_0 and C are the concentrations of dye in solution at time 0 and t, respectively) of MO during the photodegradation were proportional to the normalized maximum absorbance A/A_0 and derived from the changes in the dye's absorption profile (464.2 nm) at a given time interval. The TiO_2-0 showed low photocatalytic activity for degradation of MO. All of the TiO_2-X (X = 0.6–5) samples exhibited a considerable increase in the photodegradation of MO in comparison to the catalyst of TiO_2-0, indicating that inclusion of water during the alcohothermal reaction was helpful for enhancing photocatalytic activity of TiO_2.

To further understand the reaction kinetics of the MO degradation, we applied the pseudo-first order model as expressed by equation $\ln(C_0/C) = kt$, which is generally used for photocatalytic degradation process if the initial concentration of pollutant is low [21]: where C_0 and C are the concentrations of dye in solution at time 0 and t, respectively, and k is the pseudo-first-order rate constant. Fig. 1b depicted the photocatalytic reaction kinetics of MO degradation based on the data plotted in Fig. 1a. A better correlation to the pseudo-first-order reaction kinetics ($R > 0.9855$) was observed from these results. The reaction constant k followed the order TiO_2-4 > TiO_2-3 > TiO_2-5 > TiO_2-1.2 > TiO_2-0.6 > TiO_2, from 0.0134 min^{-1} to 0.0012 min^{-1}, as demonstrated in Fig. 1b. Namely, the TiO_2-4 suggested the best photocatalytic performance toward the degradation of MO. The MO degradation activity of TiO_2-4 was increased to 11.2 times than that of TiO_2-0. Clearly,