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A facile method to prepare mesoporous anatase TiO_2 materials in water at lower temperatures

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A B S T R A C T

Mesoporous anatase TiO_2 has been successfully prepared in water at lower temperatures than 90 °C. Firstly, amorphous TiO_2 gels were prepared by conventional sol–gel method at room temperature with tetrabutyl titanate as precursor, and then TiO_2 gels were directly put into water at temperatures of 50–90 °C for 0.5–10 h to form mesoporous anatase TiO_2. The as-prepared mesoporous TiO_2 was characterized by XRD, TEM, FTIR, Raman, UV–vis DRS, DSC–TGA, and XPS. The results showed that mesoporous anatase TiO_2 contained some organic residuals, the mean size of the TiO_2 nanocrystals was in the range of 3.5–5.4 nm, and their BET specific surface areas were in the range of 235–345 $m^2\,g^{-1}$. The photocatalytic activity of as-prepared TiO_2 was obviously higher than those of the commercial TiO_2 (P25) and TiO_2 calcined at 450 °C for 3 h under UV or visible light irradiation.

1. Introduction

Anatase crystalline TiO_2 has been widely used in many application fields, such as photocatalysts [1–6], electrochromic devices [7,8], photovoltaics [9,10], and luminescent devices [11,12], due to its unique properties of powerful oxidation ability, high photoactivity and quantum efficiency, good chemical stability, and nontoxicity. In general, anatase TiO_2 can be prepared by the sol–gel method with tetrabutyl titanate or titanium tetraisopropoxide as precursor, i.e., amorphous TiO_2 gels are firstly prepared by hydrolysis of the precursor in the presence of water and polycondensation at room temperature, and then are calcined at more than 400 °C to form anatase TiO_2 [13–15]. This preparation procedure not only needs high-temperature equipments and more energy consumption, but also easily leads anatase TiO_2 to decreasing its specific surface area due to microcrystal growth and collapse of the micropores and/or mesopores in TiO_2 during the calcination at more than 400 °C. The decrement in specific surface area of anatase TiO_2 is usually disadvantageous to its applications such as catalysis and photocatalysis. Therefore, it may be an important research field to look for a new method for preparation of anatase TiO_2 at lower temperatures.

So far, the most widely used method to prepare anatase TiO_2 at lower temperatures is the hydrothermal synthesis [16–19], in which the hydrothermal reactions of $Ti(OC_4H_9)_4$, $TiCl_4$ or other titanium compounds in solutions are conducted in Teflon-lined stainless-steel autoclaves at about 150 °C. The major drawbacks of this method lie in the low preparation efficiency of anatase TiO_2 and requirement of special preparation equipments under higher pressures, which restrict the anatase TiO_2 production in a large scale.

Recently, some groups reported several new methods for preparation of anatase TiO_2 under the conditions of conventional pressure and lower temperatures. Li et al. [20] reported a near room-temperature synthesis of high purity anatase TiO_2 nanocrystals from $TiCl_4$, and then the product needed to be baked at 87 °C for 3 days and subsequently washed several times a day for up to 60 days using a Beckman supercentrifuge to remove the main byproduct, organic species and Cl^- species on the sample surfaces. Cozzoli et al. [21] prepared oleic acid coated anatase TiO_2 by hydrolysis of titanium tetraisopropoxide with oleic acid as surfactant. The hydrolysis and crystallization of the product were carried out under mild reflux at 80–100 °C over 6–48 h. Hu et al. [22] prepared anatase TiO_2 by hydrolysis of titanium *n*-butoxide in abundant acidic aqueous solution and subsequent reflux at around 75 °C for 24 h. Hu et al. [23] prepared nanocrystalline anatase TiO_2 at 65 °C for 20 h via controlling the pH value (1.5). Liao et al. [24] synthesized amorphous TiO_2 powders by a rapid breakdown anodization process from Ti foil, and then obtained the crystallized TiO_2 via hot water treatment at 92 °C for 35 h. Li et al. [25] investigated the photocatalytic activity of anatase TiO_2 prepared with diethyl ether anhydrous as solvent at 100 °C. On the basis of their experiments, they drew a conclusion that anatase TiO_2 cannot be obtained by the same preparing route when absolute ethanol, a

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widely used solvent in the conventional sol–gel method, was used as solvent instead of diethyl ether anhydrous. Unfortunately, all the above-mentioned researches hardly discussed in detail the mesoporous structure of the as-prepared anatase TiO_2 materials and the affecting factors on their specific surface areas.

In general, TiO_2 gels contain a large of organic groups such as *n*-butyl when tetrabutyl titanate ($Ti(OC_4H_9)_4$) is used as titanium precursor due to incomplete hydrolysis of $Ti–O–CH_2–CH_2–CH_2–CH_3$. When these TiO_2 gels are put in hot water, the groups of $Ti–O–CH_2–CH_2–CH_2–CH_3$ in TiO_2 gels can further hydrolyze to form TiO_2 nanocrystals. In this reaction system, water is used as both reactant and dispersant agent. The existence of water possibly alleviates the collapse of micropores and/or mesopores which are produced during the heat-treatment of TiO_2 gels. Therefore, it is reasonable to infer that mesoporous TiO_2 with high specific surface area can be obtained by heat-treating TiO_2 gels in hot water.

In this work, a facile method was developed to prepare mesoporous anatase TiO_2 with high specific surface area in water at lower temperatures than 90 °C. Firstly, the TiO_2 gels were prepared by the conventional sol–gel method at room temperature. Secondly, the amorphous TiO_2 gels were directly put in water at temperatures of 50–90 °C for 0.5–10 h to form mesoporous anatase TiO_2. Thirdly, the TiO_2 samples were filtered, and extracted by absolute ethanol to remove the residual water, and then were dried in a vacuum oven at room temperature. The chemical composition, microstructure, and photocatalytic activity of the as-prepared TiO_2 were characterized and investigated.

2. Experimental

2.1. Preparation of anatase TiO_2

All the reagents in this work were purchased as A.R. grade and used without further purification. A typical procedure to obtain mesoporous anatase TiO_2 is described as follows. 30 mL of tetrabutyl titanate and 6 mL of acetic acid were respectively added into 39 mL of absolute ethanol under continuously stirring at room temperature, and the obtained solution was labeled as Solution A. 12 mL of deionized water, 18 mL of absolute ethanol, and 18 mL of acetic acid were mixed together under stirring to form Solution B. Then, Solution B was added drop by drop into Solution A under vigorous magnetic stirring at room temperature for 30 min. The obtained mixture was sealed and kept stirring for another 30 min. After aging at room temperature for 24 h, the resultant gel was directly put into water (the mass ratio of gel and water was 1:20) at temperatures of 50–90 °C for different time (0.5–10 h) to form mesoporous anatase TiO_2. Afterwards, the TiO_2 sample was filtered, and extracted by absolute ethanol for three times to remove the residual water, and then was dried in a vacuum oven at room temperature. The samples were labeled as TiO_2 (x °C, y h) or TiO_2 (x °C, y min), where x °C is the water temperature, and y h or y min is the heat-treatment time. The sample of TiO_2 (70 °C, 6 h) was calcined at 450 °C for 3 h, and the calcined sample was labeled as TiO_2 (450 °C, 3 h) for comparison.

2.2. Characterization

The patterns of small angle X-ray diffraction (SAXRD, 1–10°) and wide angle X-ray diffraction (WAXRD, 10–100°) were obtained by a Rigaku D/MAX-2500 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm), and the operating voltage and current were 40 kV and 150 mA respectively. The crystallite size of anatase TiO_2 was calculated from the line broadening by Scherrer's formula. The Brunauer–Emmett–Teller (BET) specific surface area and pore size measurements were performed by a Micromeritics TriStar II 3020 surface area and porosity system with nitrogen as an adsorptive gas. Transmission electron microscopy images were obtained by a JEOL JEM-2100F field-emission electron microscope

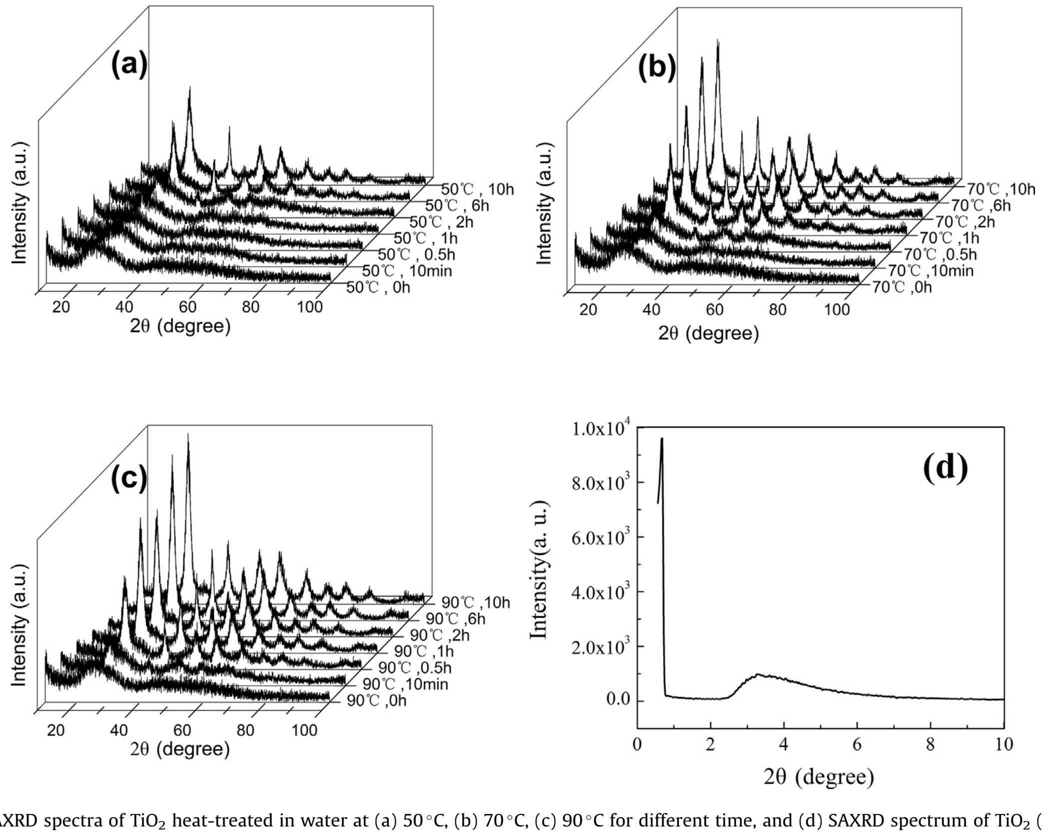

Fig. 1. WAXRD spectra of TiO_2 heat-treated in water at (a) 50 °C, (b) 70 °C, (c) 90 °C for different time, and (d) SAXRD spectrum of TiO_2 (70 °C, 6 h).