



Preparation of porous TiO₂ powder with mesoporous structure by freeze-drying method



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ABSTRACT

In recent years, significant work has been dedicated to improve the photocatalytic efficiency of TiO₂ by increasing the specific surface area and broadening the light response range. In this paper, the TiO₂ gel was prepared by sol-gel method with P123 as the template and butyl titanate as the precursor. The TiO₂ powder was obtained by freeze-drying method. After being annealed in hydrogen atmosphere, the TiO₂ powder turned from white to black. SEM images and XRD patterns show that the TiO₂ gel presents porous structure after freeze-drying, and turns from amorphous phase to anatase phase after heat treatment in both air and H₂ atmospheres at 500 °C. N₂ adsorption-desorption isotherms show mesoporous structure for the porous TiO₂. XPS data show that Ti³⁺ exists on the surface of the black H₂ treated TiO₂ powder, which introduces the defect state into the TiO₂ band gap, narrowing the band gap to 2.03 eV. Compared with the sample treated in air atmosphere, the UV–vis absorption spectrum of the black TiO₂ extends to the whole visible range. Moreover, the black TiO₂ exhibits promoted photocatalytic activity under both UV and visible light.

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1. Introduction

Photocatalysis is a new technology developing rapidly in recent years to make use of solar energy for environmental purification and energy conversion. Among various photocatalysts, TiO₂ gained much attention in water treatment, air purification and solar cells because of its chemical stability, insolubility, light corrosion resistance, non-toxicity and low cost [1–8]. However, the photocatalytic efficiency of TiO₂ is low. One reason is that the micro structural defects and the low surface area of the catalyst result in low active sites for reaction, which inhibits the quantum efficiency. The other reason is the wide bandgap of TiO₂ ($E_g = 3.2$ eV for anatase TiO₂, and $E_g = 3.0$ eV for rutile TiO₂) makes intrinsic TiO₂ can work only under the UV light (about 5% of solar light), which limits the applications of TiO₂ in many aspects [9–15]. Therefore, increasing the surface area and expanding the photo response range are the main aspects to improve the photocatalytic efficiency of TiO₂.

Compared with the traditional ball-milling, vacuum-drying and heating-drying methods, the powder prepared by freeze-drying

has small size, regular shape, uniform distribution and less agglomeration. It is a promising method to prepare ultrafine powders [16]. At the same time, freeze-drying can inhibit the growth of ice crystals at low temperatures and prepare ceramic materials with directional holes, enabling TiO₂ nanopowders to have large specific surface area [17]. In addition, because the concentration of oxygen vacancies in the TiO₂ lattice is extremely sensitive to the oxygen partial pressure of the environment, annealing in different atmospheres is also an effective method to modify TiO₂ [18]. In vacuum or reducing atmospheres, the presence of Ti³⁺/oxygen vacancies can not only capture part of photo-induced electrons to reduce the recombination in charge transfer process [19], but also introduce the impurity states and reduce the band gap of TiO₂ to expand the light response range [20].

Because of its high specific surface area, developed pore structure, controlled pore size and easy modification, mesoporous TiO₂ can effectively enhance the photocatalytic and photoelectric conversion efficiency. In recent years, the modification of mesoporous TiO₂ has attracted enormous attention. Zhou prepared mesoporous TiO₂ with P123 as the template, and black ordered mesoporous TiO₂ (OMBT) was gained under hydrogen atmosphere. The OMBT had high specific surface area, and the light absorption extended from the UV region to the visible light region [21]. Pai mixed titanate

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isopropyl and polyester fiber prepared by condensation reaction and used freeze drying method to synthesized mesoporous TiO₂ nano powders. The sample has a BET specific surface area of 86 m² g⁻¹ [22]. However, the porosity and the pore size distribution were greatly influenced by the TiO₂ content on the polyester fiber and the viscosity.

In this study, TiO₂ gel was prepared by sol-gel method with P123 as the template and tetrabutyl titanate (TBOT) as the precursor. Then the porous TiO₂ powder with mesoporous structure was obtained by freeze-drying method. Finally, the TiO₂ powder was annealed in air and H₂ atmospheres at 500 °C, respectively. The band gap and the UV–vis absorption spectra of TiO₂ annealed in different atmospheres were studied.

2. Experimental

For the preparation of TiO₂ gel: 0.8379 g of P123 was dissolved in 4.2 mL anhydrous ethanol. The mixture of 3.8 mL butyl titanate and 1 mL glacial acetic acid (99.5 wt%) was added into the above anhydrous ethanol solution and fully stirred to obtain solution A. A certain amount of concentrated hydrochloric acid (38 wt%) was mixed with the solution containing 0.8 mL deionized water and 1.6 mL anhydrous ethanol to gain solution B (PH value = 1). Under intense agitation, solution B was added to solution A with a slow rate of 12 drops/min and stirred for 30 min. Finally the light yellow translucent wet gel was obtained and aged for 24 h at room temperature. The solution ratio (molar ratio) is that butyl titanate: P123: anhydrous ethanol: glacial acetic acid: deionized water = 1: 0.013: 14: 1.6: 4.

The TiO₂ gel was washed with deionized water and then centrifugally separated. The process was repeated for 3 times to remove the residual organic compounds. The obtained product was rapidly freeze-dried by liquid nitrogen (-196 °C, 5 min) and dried by vacuum drying for 48 h at a low temperature (-10 °C). Then the sample was heat-treated in air and hydrogen (10%H₂MACRO-BUTTON InsGlyph e90%Ar) atmospheres at 500 °C for 2 h to obtain air-TiO₂ and H₂-TiO₂, respectively.

As we mentioned before for the preparation of the sample for catalytic activity evaluation [23,24], 1.0 g as-prepared TiO₂ and 0.186 mL ethylene glycol solution were added into 10 mL ethanol, and magnetically stirred for 10 min and then ultrasonically cleaned for 5 min. After irradiation with UV light for 20 min, the sample was dried at 50 °C and finally collected. Photocatalytic activity was conducted under UV (30 W) or visible light (Xe: 300 W) irradiation to degrade methyl orange. The photocatalyst (0.1 g) was dispersed in 50 mL methyl orange solution (10 mg/L). The suspension was ultrasonically treated and stirred in the dark for 30 min before irradiation. During the degradation process, 5 mL of the reaction solution was taken out every 30 min.

The crystal structure of the synthesized TiO₂ powder was analyzed by X-ray diffraction (Shimadzu Limited, XRD-7000). The morphology of the TiO₂ powder was observed using a field emission scanning electron microscope (JEOL, JSM-6700F). The specific surface area of the TiO₂ powder was tested by BET N₂ adsorption-desorption method (BK122T-B). The chemical compositions of the sample were investigated by X-ray photoelectron spectroscopy (KRATOS, AXIS ultra DLD). UV–vis absorption spectra of the TiO₂ powder were acquired using a UV–visible spectrophotometer (PE, Lambda 950). Methyl orange adsorption spectra were obtained by using a UV–vis spectrophotometer (UV-5100) at 466 nm.

3. Results and discussion

3.1. Phase analysis and morphology observation

Fig. 1 shows the X-ray diffraction patterns of TiO₂ gel calcinated at different temperatures and atmospheres. Curve (a) shows no obvious characteristic peaks from the cold gel, indicating that the gel represents an amorphous structure after freeze-drying. Curve (b) shows weak peaks of anatase phase with heat-treatment at 300 °C, but the material remains mainly amorphous. Curves (c) and (d) show obvious diffraction peaks of anatase phase, suggesting that crystalline TiO₂ forms when treated in air and hydrogen atmospheres at 500 °C. The half width of the H₂-TiO₂ diffraction peaks is greater than that of air-TiO₂, indicating that the grain size of TiO₂ decreases after being annealed in H₂. Based on the XRD patterns, the average grain sizes of air-TiO₂ and H₂-TiO₂ are calculated to be 20 nm and 13 nm by the Scheele formula, respectively (Table S1, Supporting information).

Fig. 2 shows the SEM images of the TiO₂ gel before and after heat treatment in air. From Fig. 2(a), we can see the untreated gel exhibits a cluster of chrysanthemum and fishbone shapes after freeze-drying. From the enlarged image at the upper left corner, we can claim that the sample contains many needle-like pores perpendicular to the surface of the sample. The reason for this kind of morphology may be that after the TiO₂ gel is frozen, dendritic ice crystals form due to the solvent sublime and leave the same pore shape. As the gel has a certain viscosity and liquidity, tensile stress could be caused in the ice sublimation process, which makes the gel stretching as the chrysanthemum. As shown in Fig. 2(b), after the heat treatment at 500 °C in air, the fishbone shape disappears and porous morphology appears. The particle size is about 4–6 μm. From the enlarged image at the upper right corner, we can see that the pores of the sample distribute homogeneously, similar to the porous sponge. The reason may be that during the heat treatment, the organic impurities in the gel are removed and the growth of the TiO₂ crystal particles and the shrinkage of the gel channels occur simultaneously, leaving smaller and fewer channels compared with the sample after the freeze-drying process [25,26]. In order to see the sublimation trajectory of the ice crystals, we made a further analysis of the sectional view of the gel as shown in Fig. 2(c). As can be seen, the TiO₂ gel after freeze drying has a vertical directional channel with a diameter of about 10–15 μm. The reason for this

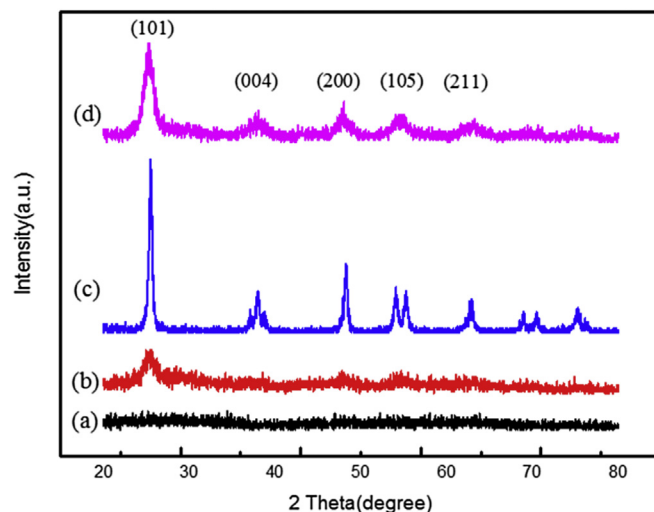


Fig. 1. X-ray diffraction patterns of TiO₂ gel calcinated at different temperatures and atmospheres (a) cold gel, (b) air-300 °C, (c) air-500 °C, (d) H₂-500 °C.

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