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Effect of calcination temperature on the structural properties and photocatalytic activities of solvothermal synthesized TiO_2 hollow nanoparticles

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Abstract

TiO_2 hollow nanoparticles were prepared by the solvothermal method, calcined at different temperatures and characterized by XRD, BET, SEM, PL and FT-IR. The effects of morphology, size and calcination temperature on the photocatalytic activity of the prepared materials were discussed in detail. It was found that the calcination temperature altered the crystallinity, morphology, surface area, and the porous structure. The photocatalytic activity of the TiO_2 powders evaluated through photocatalytic degradation of gaseous acetone under UV-light irradiation, showed TiO_2 calcined at 250 °C to exhibit a higher photocatalytic activity than commercial powders (Degussa P25).

Keywords: TiO_2 hollow nanoparticles; Calcination temperature; Photocatalytic activity; Hydroxyl groups

1. Introduction

In recent decades, great efforts have been devoted to the removal of VOCs [1–5]. The photocatalytic oxidation process that uses a heterogeneous catalyst, which is one of the techniques that has been developed to treat pollutants, is regarded as a promising technology because it offers the possibility of completely decomposing toxic chemicals. Anatase titanium dioxide has recently proven to be a suitable semiconductor photocatalyst for widespread environmental applications because of its high chemical stability, inexpensiveness, and nontoxicity [6–10]. Considering that the special relationship between there morphology and properties, hollow spherical TiO_2 photocatalysts merit special attention due to the low density, high surface area, and increased light-harvesting capacity [11–13]. Recently, Lv et al. reported the fabrication of rugby-like anatase hollow nanoparticles by a template-free method [14], but unfortunately, the hollow nanoparticles prepared by this method show low ability to mineralize acetone in our study. Thermal treatment of TiO_2 provides a facile route to control the grain size, particle morphology, microstructures, phase composition and surface photoelectrochemical properties [15–17]. For TiO_2 photocatalyst, surface area and crystallinity are two crucial factors that affect the photocatalytic activity. Large surface area can bring about more reactant adsorption–desorption sites for the catalytic reaction, and provides more efficient transport channels for the reactant molecules. High crystallinity is essential to enhance the generation and migration of photo-generated electron/hole pairs in the bulk and surface of TiO_2. Therefore, a well crystallized TiO_2 nanostructure with large surface area is considered the preferred form. However, the achievement of perfect crystallized TiO_2 hollow structure usually conflict with the achievement of large surface area, because elevated calcination temperature applied to crystallize TiO_2 may cause the further growth or agglomeration of TiO_2 nanoparticles and finally reduce the specific surface area.

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In this work, we studied the balance between the specific surface area and crystallinity of TiO_2 hollow nanoparticles by varying the calcination temperature. The variation of the microstructure, crystalliny as well as the photocatalytic activity of the TiO_2 hollow nanoparticles calcined at different temperature has been studied comparatively.

2. Materials and methods

2.1. Synthesis

Tetrabutyl titanate (6.8 mL) was added to absolute alcohol (30 mL) to obtain solution A. NH_4HF_2 (0.57 g) was added to 60 ml water to obtain solution B. Then, solution A was dropwise added into solution B under magnetic stirring. After that, 40 mL of H_2O_2 (30 wt%) was added into the solution. The mixture was then transferred to a Teflon-lined autoclave (200 mL in volume) and solvotheromally treated at 150 °C for 10 h. The resultant precipitate was washed thoroughly with ethanol and deionized water, and then dried at 60 °C. At last, The as-prepared samples were finally calcined at different temperatures of 250, 350, 450, 550 and 650 °C for 1 h to remove organic surfactants and improve the crystallinity of the products. The products were denoted as T*X*, in which *X* is the calcination temperature.

2.2. Characterization

The X-ray diffraction (XRD) patterns obtained on an X'Pert PRO X-ray diffractometer using Cu Kα irradiation at a scan rate of $0.05^\circ\ 2\theta\ s^{-1}$ were used to determine the identity of any phase present and their crystallite size. The Brunauer–Emmett–Teller (BET) surface area and porous structure were evaluated on the basis of nitrogen adsorption isotherms measured on a Quantachrome Autosorb-1-C-MS. The BET surface area was determined by multipoint BET method using the adsorption data in the relative pressure (P/P_0) range 0.05–1.0. Desorption isotherm was used to determine the pore-size distribution via the Barret–Joyner–Halender (BJH) method. The morphology of prepared TiO_2 materials was observed by a scanning electron microscope (Sirion 200, FEI, Holand) at an acceleration voltage of 10 kV. Photoluminescence (PL) spectra of TiO_2 materials were obtained on a Jasco FP-6500 with exc=320 nm. FT-IR spectra were recorded on the Fourier transform infrared spectroscopy (Bruker EQVINOX 55) in the 400–4000 cm^{-1} wavenumber range. To prepare pellets, the samples were first ground to powder in an agate mortar and then mixed with KBr. A hydraulic press was used to press the resulting mixtures to discs of 10 mm in diameter at 5 MPa for 5 min.

2.3. Photocatalytic activity

Acetone is a common chemical that is used extensively in the industrial and domestic fields. Therefore, we chose it as the model contaminate chemical. The photocatalytic activity of the prepared materials during the photodegradation of gaseous acetone in the air under UV irradiation was measured in a 6.5 L stainless gas-phase batch reactor with a quartz window. The reactor was connected to a GC-9560 gas chromatograph, which was equipped with a methane converter, a Porapak R column and a PEG20M column via an automatically sampling ten-way valve (VALCO) with an air actuator and a flame ionization detector (FID). A thermocouple was placed in the TiO_2 material to measure its temperature. A heating device was used to maintain the reaction temperature of the photocatalytic system at approximately 353 K to ensure the complete evaporation of the acetone. An UV lamp (250 W) was used as the light source for the photocatalytic reaction. The catalysts (0.5 g) were prepared by coating a glass dish, which had a diameter of 13.0 cm, with an aqueous suspension of the prepared TiO_2 powder and setting it on the bottom of the reactor. The Hg lamp was turned on until the measured concentration of CO_2 remained unchanged, which was to ensure the removal of the adventitious organic compounds adsorbed on the TiO_2 catalyst and to establish the adsorption–desorption equilibrium of CO_2 on the TiO_2 catalyst. Subsequently, 2 μL acetone was injected into the reactor. Prior to photocatalytic oxidation, the acetone vapor diluted with air was pre-adsorbed on the catalyst before illumination. Next, the oxidation commenced when the UV lamp was turned on. The photocatalytic activity of the catalyst samples can be quantitatively evaluated by comparing the apparent reaction rate constants. The photocatalytic oxidation of acetone is a pseudo-first-order reaction and its kinetics may be expressed as follows: $\ln(C_0/C)=kt$ [18,19], where k is the apparent reaction rate constant, C_0 and C are the initial concentration and the reaction concentration of acetone, respectively. The concentration of the CO_2 produced was obtained by subtracting the initial concentration of CO_2 in the reactor from the final concentration. All of the contrast experiments were conducted under the same conditions.

3. Results and discussion

3.1. Phase structures and morphology

XRD was used to investigate the changes of the phase structure and the average crystallite size of the photocatalyst. Fig. 1 shows the effects of calcination temperature on phase

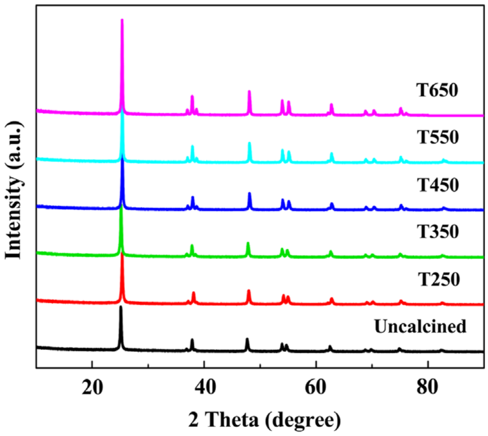

Fig. 1. XRD patterns of the prepared TiO_2 materials before and after calcination.