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Growth mechanism and photocatalytic activity of chrysanthemum-like anatase TiO_2 nanostructures

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Received 30 November 2015; received in revised form 3 January 2016; accepted 3 January 2016

Abstract

Chrysanthemum-like hierarchical anatase TiO_2 nanostructures self-assembled by nanorods have been successfully fabricated by a simple solvothermal route without using template materials or structure-directing additives. The products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Raman spectrometer system (Raman), UV–vis absorption spectroscopy (UV–vis) and N_2 adsorption–desorption measurement. The results indicate that synthesized chrysanthemum-like hierarchical anatase TiO_2 nanostructures have a spherical shape with an average diameter of 1.5 μm and they are composed of nanorods with a width of about 30 nm and a length of about 300 nm. The pore distribution of the sample exhibits two kinds of pores. Such mesoporous structure of the sample might be extremely useful in photocatalysis because they possess efficient transport pathways to the interior and supplies higher specific area for more pollutant molecules to be absorbed. In addition, the synthesized TiO_2 nanostructures show enhanced photocatalytic activity compared with commercial P25 for the degradation of RhB under UV light irradiation, which can be attributed to their special hierarchical structure and high light-harvesting capacity.

Keywords: A. Powders: chemical preparation; B. Spectroscopy; D. TiO_2; Photocatalytic activity

1. Introduction

Titanium dioxide (TiO_2), one of the most promising semiconductors, has been attracting much attention due to its wide range of applications, such as in photocatalysis [1], lithium ion batteries [2], and dye/quantum dot-sensitized solar cells [3]. Most of these excellent properties depend strongly on crystallinity, morphology and phase dimension of TiO_2 [4–6]. Now, there is an increasing interest in fabricating TiO_2 with novel morphologies and better crystallinity for desired applications. Among various morphological structures, TiO_2 nanomaterials with 3D hierarchical architectures have triggered considerable attention recently for their high surface-to-volume ratio and distinctive physicochemical properties [7–9]. To construct these structures, a number of methods have been developed and generally requires template and structure-directing agents [10–12]. However, these template materials and structure-directing agents need to be removed later, which can compromise the structural integrity and even cause secondary environmental pollution. In addition, additives involved in synthesis procedures also usually experience disadvantages of high cost and complex synthetic procedures [13,14]. Therefore, developing additives-free methods for preparation of 3D hierarchical TiO_2 nanostructures is more preferable due to their simplicity and adjustability.

In this paper, chrysanthemum-like hierarchical anatase TiO_2 nanostructures were successfully synthesized by a facile solvothermal method free from template and structure-directing agents. Growth mechanism and photocatalytic activity of chrysanthemum-like anatase TiO_2 nanostructures were investigated in detail by measuring XRD, SEM, TEM, UV–vis absorbance, Raman spectra, N_2 adsorption–desorption isotherms, pore size distribution, and degradation of Rhodamine B (RhB) under UV light irradiation.

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http://dx.doi.org/10.1016/j.ceramint.2016.01.011
0272-8842/

Please cite this article as: Z. Fan, et al., Growth mechanism and photocatalytic activity of chrysanthemum-like anatase TiO_2 nanostructures, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.011

2. Experimental

2.1. Material preparation

Tetrabutyl titanate (TBT) was of chemical reagent grade (CR), while absolute ethyl alcohol and glycerol were of analytical grade (AR). Reagents were used as received without further purification. In a typical case, 0.997 g tetrabutyl titanate (TBT) and 0.644 g glycerol were added in 15 mL absolute ethyl alcohol under magnetic stirring. The two solutions were mixed together, followed by stirring for 30 min. The clear solution was transferred into a 50 mL Teflon pot and sealed tightly in a stainless steel autoclave. The hydrothermal reaction was done at 170 °C for 1–24 h. After the autoclave was naturally cooled to room temperature, the products were washed with absolute ethanol. The white precipitates were collected and dried at 80 °C overnight, and then calcined in a Mufflefurnace at 500 °C for 2 h.

2.2. Characterization

The crystal phases of samples were analyzed by an X-ray diffractometer (XRD, XD-3) with CuKα radiation ($\lambda = 0.1506$ nm). The morphologies and sizes were characterized by a scanning electron microscope (SEM, S-4800) and a transmission electron microscope (TEM, JEM-2100). The UV–vis absorption spectroscopy was measured by an ultraviolet–visible–near infrared spectrophotometer (U-4100). The Raman spectrum was recorded by a Raman spectrometer system (inVia-Reflex) using a laser with 532 nm excitation at room temperature. Nitrogen adsorption and desorption isotherms were measured using an automatic specific surface area of microporous/mesoporous physical adsorption analyzer (ASAP 2020 V3.00H) at 77 K. Surface areas were determined by the BET method, and the mesopore size distribution was determined by the Barrett–Joyner–Halender (BJH) method. For the BJH analysis, the pore size distribution was obtained from the analysis of desorption branch of the isotherm.

2.3. Photocatalytic activity measurements

The photocatalytic activity of the as-prepared TiO_2 powders was evaluated by photodegradations of RhB under simulated UV lamp illumination at ambient temperature. The experimental details were as follows: 0.05 g sample was dispersed into a 20 ml RhB aqueous solution with a concentration of 1×10^{-5} mol/L in a 7.0 cm culture dish. A 15 W, 365 nm UV lamp placed 8 cm away from the culture dish was used as a light source to trigger the photocatalytic reaction. The aqueous solution of the RhB with the photocatalyst added was allowed to reach an adsorption–desorption equilibrium before UV lamp irradiation. As a comparison, experiments were also carried out to investigate the photocatalytic activity of commercial P25 powders.

3. Results and discussion

3.1. Structure analysis

The phase purity of the as-synthesized nanostructures was examined by XRD measurement. Fig. 1 shows the XRD pattern

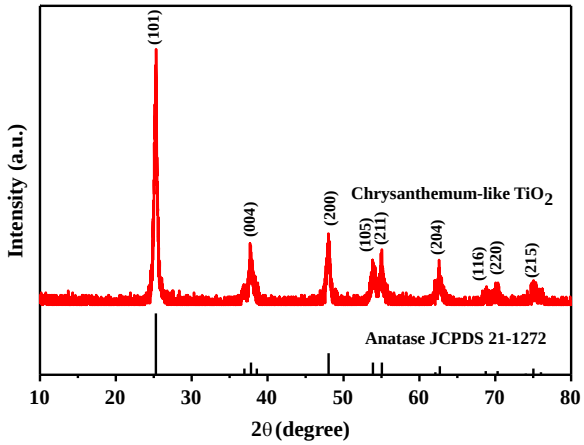

Fig. 1. XRD pattern of as-synthesized chrysanthemum-like hierarchical anatase TiO_2 nanostructures and the reference pattern of anatase TiO_2 (JCPDS 21-1272).

of chrysanthemum-like hierarchical anatase TiO_2 nanostructures. All the observed diffraction peaks can be perfectly indexed to anatase phase of TiO_2 (JCPDS 21-1272). No peaks of other impurity phases are observed in the powder pattern, indicating that pure TiO_2 is synthesized by the solvothermal method. The strong and sharp diffraction peaks indicate the good crystallinity of the as-synthesized product. Based on the XRD pattern, the average crystallite size calculated by Scherer formula [15] is about 18.7 nm.

3.2. Morphological observations and mechanism analysis

The morphology and structure of TiO_2 sample were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a and b shows the SEM images of TiO_2 sample, from which chrysanthemum-like hierarchical anatase TiO_2 structures of 1.5 μm in diameter can be clearly observed. It can be seen from Fig. 2b that the chrysanthemum-like hierarchical anatase TiO_2 nanostructures are composed by nanorods of about 30 nm in width and about 300 nm in length, which is further evidenced by TEM images (Fig. 2c and d). As shown in Fig. 2d, the TEM image reveals the porous structure of chrysanthemum-like hierarchical anatase TiO_2 nanostructures.

Fig. 3 shows the SEM images of the TiO_2 samples synthesized within different reaction times. To reveal the formation mechanism of chrysanthemum-like hierarchical anatase TiO_2 nanostructures, the detailed time-dependent morphology evolution process is investigated. It can be seen that TiO_2 solid spheres of about 700 nm in diameter were synthesized within 1 h, and contained some small protuberances on the surface. When the reaction time is 6 h, the small protuberances become larger on the surface of solid spheres. Within the reaction time of 12 h, the gradual dissolution of the solid spheres and small 1D nanorods form nonuniform chrysanthemum-like TiO_2. After reacting 24 h, no solid spheres remained, and the product is entirely composed of chrysanthemum-like hierarchical anatase TiO_2 nanostructures. Obviously, the morphology of TiO_2 nanostructure is sensitive to the reaction time, and suitable time is beneficial for the

Please cite this article as: Z. Fan, et al., Growth mechanism and photocatalytic activity of chrysanthemum-like anatase TiO_2 nanostructures, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.011