

Fabrication and photocatalytical properties of flower-like TiO₂ nanostructures

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Abstract: Three-dimensional (3D) flower-like anatase TiO₂ nanostructures and flower-like titanate nanostructures were successfully synthesized via hydrothermal synthesis followed by post-treatment from titanium powder. The flower-like anatase TiO₂ nanostructures were characterized in detail with scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-vis spectrum and nitrogen adsorption-desorption measurement, respectively. It is found that the flower-like TiO₂ nanostructures have a high specific surface area and a large light-harvesting efficiency. The photocatalytical activity of the flower-like anatase TiO₂ nanostructures was determined by degradation of methylene blue in aqueous solution, and was compared with commercial P25 titania. It is revealed that the photocatalytical activity of the flower-like anatase TiO₂ nanostructures is enhanced a lot. The apparent rate constant of the flower-like anatase TiO₂ nanostructures is almost 2 times that of P25 titania.

Key words: Ti powder; hydrothermal synthesis; flower-like; TiO₂; photocatalysis

1 Introduction

Titanium dioxide (TiO₂) is one of the most important transition metal oxides which has been widely used in catalysis, photovoltaic cells, self-cleaning devices, sensors, Li-ion battery materials, optical emission, water-splitting, paints, paper, cosmetics, and so on[1–4]. It is found that the application of TiO₂-based devices is strongly dependent on its own crystalline structure, morphology and phase dimension[3–7]. Therefore, the controlled synthesis of TiO₂ nanostructures with different shapes and sizes has been developed in recent years. So far, most synthetic efforts have been directed toward monodisperse nanoparticles, nanotubes, nanowires, and nanoribbons. The synthesis of 0-dimensional (0D) and one-dimensional (1D) nanostructures has been widely investigated and well developed. However, reports on the synthesis of complex three-dimensional (3D) titania nanostructures remain uncommon. On the other hand, recent research on the synthesis of 3D nanomaterials shows that this kind of nanostructure may have potentially to explore their novel

properties[8–11]. For example, flower-like TiO₂ nanostructures, which were synthesized by a hydrothermal method using TiCl₄ as raw material, exhibited enhanced light adsorption and photocatalysis[10]. Brookite TiO₂ nanoflowers, which were synthesized by a hydrothermal method from TiOSO₄, had larger permittivity than anatase TiO₂ products[11]. However, flower-like TiO₂ nanostructures, which are fabricated from Ti powders through a hydrothermal method, to the best of our knowledge, have never been reported.

In this work, we report a facile hydrothermal synthesis of flower-like anatase TiO₂ nanostructures and flower-like titanate nanostructures, which are composed of nanoribbons, from titanium powder. The prepared flower-like anatase TiO₂ nanostructures have a high specific surface and a large light-harvesting efficiency and. And they exhibited high photocatalytical activity for degradation of methylene blue (MB).

2 Experimental

Flower-like anatase TiO₂ nanostructures were

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fabricated through a hydrothermal reaction between NaOH solution and the mixture of Ti powders, H_2O_2 and HNO_3 , followed by heat treatment. In a typical procedure, 0.1 g Ti powders ($\sim 80 \mu\text{m}$, 99.9% purity, Beijing Chemical Factory) were dissolved in 150 mL 9 mol/L $\text{H}_2\text{O}_2 + 0.1 \text{ mol/L HNO}_3$ aqueous solution at $80 \text{ }^\circ\text{C}$ for 2 h. After the solution was cooled to the room temperature naturally, 5 mL such solution was mixed with 15 mL concentrated NaOH solution (40%, mass fraction, Tianjin Fengchuang Chemical Factory, China). Then, the mixed solution was placed in a Teflon-lined autoclave and was kept at $150 \text{ }^\circ\text{C}$ for 3 h. After that, the products were collected by centrifugation and thoroughly washed with high purity water (18 M Ω) and 0.1 mol/L HNO_3 aqueous solution, until pH was 7.0. Finally, the white product was annealed at $450 \text{ }^\circ\text{C}$ for 2 h in air.

The phase identification of the samples was conducted with powder X-ray diffractometer (XRD, Bruker D8 Advance, Cu K_α radiation $\lambda = 1.54056 \text{ \AA}$). The morphologies and composition of the samples were observed on field-emission scanning electron microscope (FE-SEM, Hitachi S-4800 with energy disperse spectroscopy (EDS) capabilities). The UV-vis absorption spectra of the samples were observed with Varian Cary 5000 equipped with an integrating sphere. The Brunauer-Emmett-Teller (BET) surface area measurements were carried out by N_2 adsorption at 77 K using an ASAP2020 instrument.

Photocatalytic activity of the flower-like anatase TiO_2 nanostructures was evaluated in terms of the decolorization MB dye under ultraviolet (UV) irradiation. flower-like anatase TiO_2 sample of 10 mg was dispersed into 100 mL 10 mg/L MB solution and stirred in the dark for 2 h to reach a complete adsorption-desorption equilibrium. Then the solution was irradiated with $\sim 0.5 \text{ mW/cm}^2$ UV light (with a wavelength peak at 365 nm) under continuous stirring. With a given irradiation time interval, some specimens (5 mL) were taken from the dispersion and were centrifuged (4 000 r/min). The clear upper solution was subjected to an UV-Vis spectrophotometer (Shanghai Spectrum Instruments Co., Ltd., WFJ721E). The concentration of MB was determined from the absorbance at the wavelength of 665 nm. For comparison, P-25 was used as the benchmark to evaluate the photocatalytic activity of the flower-like TiO_2 nanostructures. P-25 is a mixture of anatase ($\sim 79\%$) and rutile ($\sim 21\%$) TiO_2 and it is currently considered to be one of the best commercial TiO_2 photocatalysts.

3 Results and discussion

Typical FE-SEM images of flower-like titanate nanostructures and flower-like TiO_2 nanostructures are

shown in Fig.1. As shown in Fig.1(a), the titanate product contains numerous flower-like nanostructures. These flowers are composed of nanoribbons. Fig.1(b) shows the SEM image of the flower-like TiO_2 nanostructures. It reveals that moderate high-temperature annealing dehydration process does not destroy the 3D hierarchical structural motif of the flower-like TiO_2 nanostructures. The TiO_2 nanostructures maintain the flower-like morphology. Energy dispersive spectrometer (EDS) analysis (inset of Fig.1(b)) shows that flower-like titania nanostructures are chemically composed of Ti, O elements (C element was originated from conductive carbon tapes and Si element was originated from Si substrate). This demonstrates that complete ionic exchange between Na^+ and H^+ is achieved.

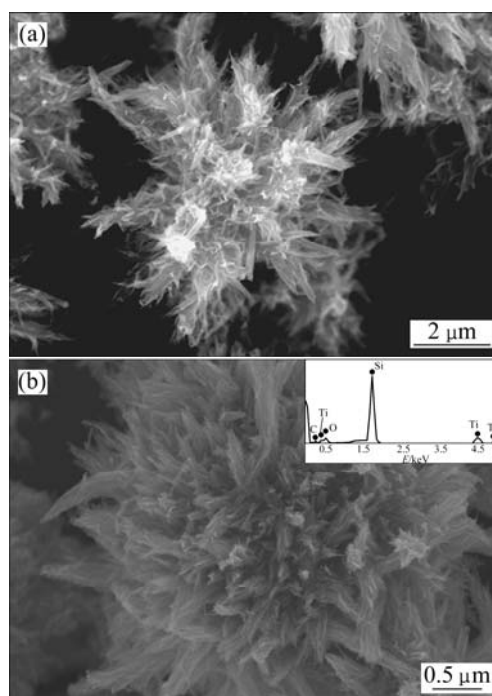


Fig.1 FE-SEM images of flower-like titanate nanostructures (a) and anatase flower-like TiO_2 nanostructures (b) (inset: EDS spectrum of flower-like TiO_2 nanostructures)

The corresponding XRD patterns recorded from flower-like titanate nanostructures and flower-like TiO_2 nanostructures are shown in Fig.2. The crystal of the products before annealing treatment is not very fine. According to the previous studies, the observed 2θ values for the XRD at 9.1° , 24.5° , 48.3° , and 62.5° can be attributed to (020), (110), (200), and (002) faces of $\text{H}_2\text{Ti}_3\text{O}_7$, respectively[12–13]. This XRD result suggests that the flower-like nanostructures is a kind of layered titanate. After being annealed at $450 \text{ }^\circ\text{C}$ in air for 2 h, all the relatively sharp peaks could be indexed as anatase TiO_2 , which are in good agreement with the reported values of Joint Committee on Powder Diffraction

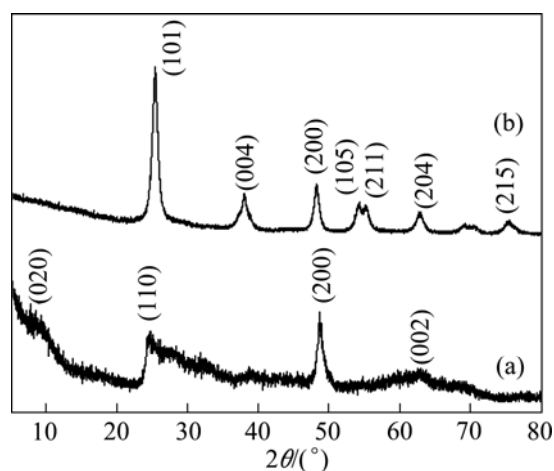


Fig.2 XRD patterns of flower-like titanate nanostructures (a) and flower-like anatase TiO₂ nanostructures (b)

Standards (JCPDS) card No. 21-1272. There are no characteristic peaks of impurities, such as sodium titanium oxide, conforming that Na⁺ is removed completely.

The surface area and the porosity of the flower-like anatase TiO₂ nanostructures were measured by nitrogen adsorption-desorption. According to the Brunauer–Emmett–Teller (BET) method, the specific surface area of the flower-like TiO₂ nanostructures is 134.7 m²/g, which is higher than that of Degussa P25, ~50 m²/g. And the pore volume of the flower-like TiO₂ nanostructures is 0.21 cm³/g. Fig.3 shows the pore size distribution plot, which was obtained by using the Barrett-Joyner-Halenda (BJH) method (dV/dD is pore volume of sample). It can be seen that the flower-like TiO₂ nanostructure has a narrow pore-size distribution with an average pore diameter of ca. 42.1 nm. This high porous structures with high specific surface area is beneficial to light-harvesting and mass transport[14–19].

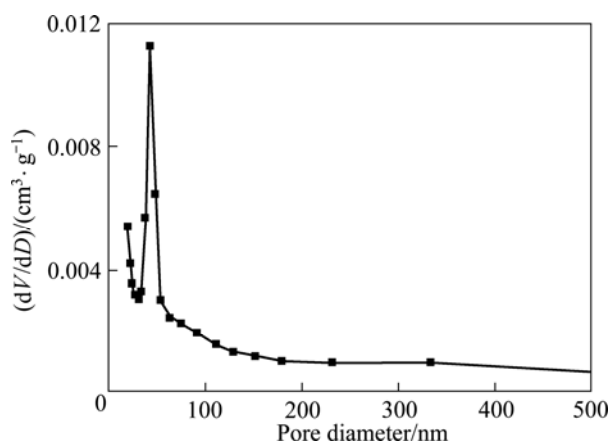


Fig.3 Pore size distribution of flower-like anatase TiO₂ nanostructures

The UV-visible absorption spectra of the flower-like anatase TiO₂ nanostructures and commercially-available P25 titania are shown in Fig.4. It can be seen from Fig.4 that the absorption of the flower-like TiO₂ nanostructures is stronger than that of P25. This may be due to the porous structure of the flower-like TiO₂ nanostructures, which is believed to favor the harvesting of light due to multiple scattering of light within the porous framework[14–16]. Therefore, the light-harvesting efficiency of flower-like TiO₂ nanostructures would be larger than that of P25.

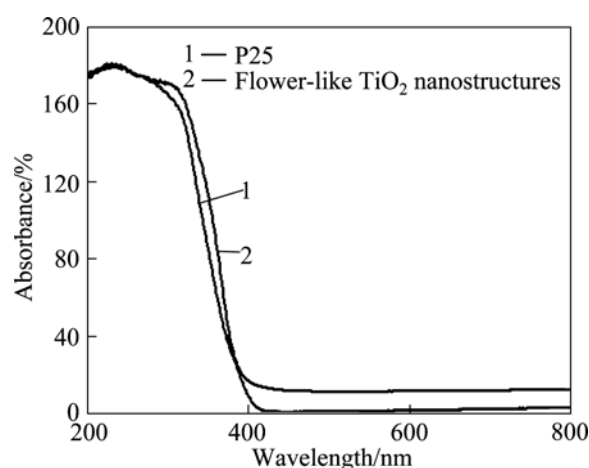


Fig.4 UV-visible absorption spectra of P25 and flower-like anatase TiO₂ nanostructures

The photocatalytic activity of the flower-like TiO₂ nanostructures was further studied. Fig.5(a) presents the variation of MB concentration by recording the UV-vis spectra at interval of 10 min during the photochemical degradation of MB on the flower-like anatase TiO₂ nanostructures and P-25 TiO₂ under UV irradiation. The linear relationship of $\ln \rho_0/\rho$ vs time (Fig.5(b)) shows that the photocatalytic degradation of MB follows the pseudo-first-order kinetics:

$$\ln \frac{\rho_0}{\rho} = kt \quad (1)$$

where ρ_0/ρ is the normalized MB concentration; t is the reaction time; and k is the apparent reaction rate in terms of min⁻¹. The apparent photochemical degradation rate constant for the flower-like anatase TiO₂ nanostructures is $2.25 \times 10^{-2} \text{ min}^{-1}$, which is almost 2 times that for the P-25, $1.21 \times 10^{-2} \text{ min}^{-1}$, further confirming that the flower-like anatase TiO₂ nanostructures exhibit high photocatalytic efficiency. The enhanced photocatalytic activity of the flower-like anatase TiO₂ nanostructures can be attributed to their high surface area and large light-harvesting efficiency. Usually, a large surface area can offer more active adsorption sites and photocatalytic reaction centers[17–19]. Moreover, the

porous structure is believed to favor the light-harvesting and mass transport[14–16]. All of these enhance the rate of photocatalytic reaction.

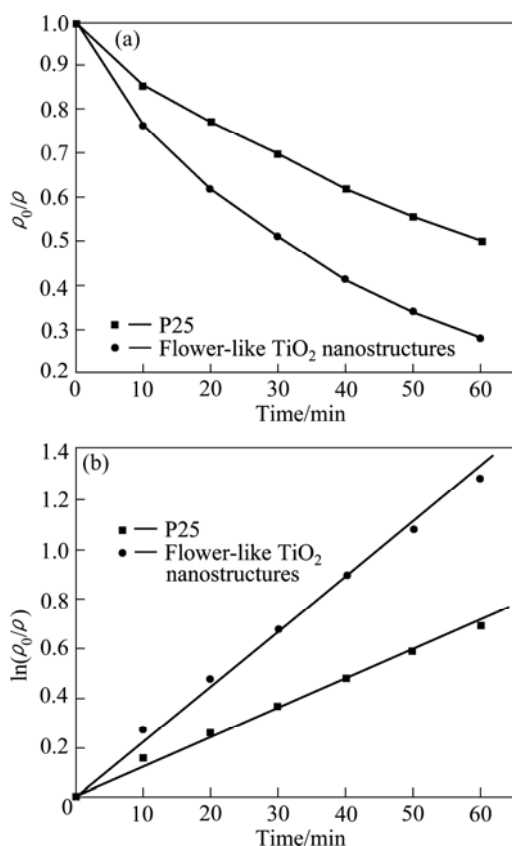


Fig.5 Variation of MB concentration by photochemical reaction with P-25 TiO₂ and flower-like anatase TiO₂ nanostructures under UV irradiation (a) and pseudo-first-order kinetic rate for photochemical degradation of MB (b)

4 Conclusions

1) A simple, inexpensive, and mild synthetic process is reported to synthesize flower-like anatase TiO₂ nanostructures from Ti powder.

2) The synthesized flower-like TiO₂ nanostructures have a high BET surface area of 134.7 m²/g.

3) The flower-like TiO₂ nanostructures exhibit a large light-harvesting efficiency.

4) The photocatalytic efficiency of the flower-like TiO₂ nanostructures is almost 2 times that of P25 titania.

5) Owing to their large specific surface area and high photocatalytic activity, the flower-like TiO₂ nanostructures can be further applied in the areas of separation technology, solar cells, sensors, Li-ion electrode materials and so on.

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