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Synthesis of octagonal microdisks assembled from anatase TiO_2 nanosheets with exposed {001} facets

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Abstract

Octagonal TiO_2 microdisks constructed orderly from anatase nanosheet building blocks (NSBBs) with exposed {001} facets were synthesized using a facile liquid phase precipitation method combined with subsequent heat treatment. The *in-situ* generated BF_4^- and F^- adsorbed onto {001} facets of NH_4TiOF_3 (as precursor of TiO_2) decreased the surface energy instead of extremely poisonous and corrosive HF. Polymer surfactant is likely to further stabilize the {001} facets and it may induce NH_4TiOF_3 nanocrystals as a linkage to align high-orderly by lateral expansion for the formation of NH_4TiOF_3 mesocrystals. Sintering temperature for the heat treatment of NH_4TiOF_3 microdisks has a considerable effect on TiO_2 microdisks for the extent of exposure of the {001} surface. Symmetrically growths on [100] and [110] directions parallel to the {001} surface are favored which lead to the well-defined octagonal flat-shape. TiO_2 microdisks show an excellent adsorption capacity in dark and enhanced reactive activity under irradiation of UV-light for the degradation of methylene blue, owing to the high-ordered organization of nanosheets and large exposure of high-energy facets.

Keywords: B. Electron microscopy; B. Surfaces; D. TiO_2; Photocatalysis

1. Introduction

Titanium dioxide (TiO_2), as one of the most advanced semiconductors, has drawn a great deal of scientific and technological attentions for its application in photocatalysis, solar cells, photonic crystals, and sensors in recent years [1–5]. Among these applications, photocatalysis has been studied most widely due to their potential in relieving the environmental contamination caused by chemical compounds and H_2 evolution by water splitting. Generally, the activity of photocatalysts dependents not only on the crystal phase and size but also on the surface states [6,7]. Both theoretical calculations and experimental results reveal that {001} facets of anatase exhibit higher photoactivity than {101} facets [8–10] in some cases. However, the surface free energies in anatase crystals are $\gamma\{110\}$ $(1.09\ J\ m^{-2}) > \gamma\{001\}$ $(0.90\ J\ m^{-2}) > \gamma\{100\}$ $(0.53\ J\ m^{-2}) > \gamma\{101\}$ $(0.44\ J\ m^{-2})$ [7,11]. The thermodynamically stable {101} facets make up more than 94% of the crystal surface (according to the Wulff construction) during the process of naturally crystallization [11]. In keeping with the energetics, it turns out to be an arduous challenge to synthesize TiO_2 with largely exposed {001} facets.

A significant breakthrough in the long-term desirable preparation of well-shaped crystals with exposed {001} facets was achieved by Yang and co-workers [10] in 2008. They proposed a theoretical prediction that the fluorine-terminated effect can reverse the relative stability of {101} and {001} facets and then successfully synthesized micro-sized anatase TiO_2 single crystal with 47% {001} surface by using HF as a capping agent and TiF_4 as precursor. With the same morphology controlling agent, Xie's group [12] obtained TiO_2 nanosheets with the highest percentage of the {001} surface up to 89% from tetrabutyl titanate as the Ti resource. During the following years, HF (or in the form of ammonium salt) remained to be the most common choice for fluorine-mediated formation of active-faceted titania nano, micro-sized [13–16]

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crystals (or hierarchical structures [17,18]). In order to minimize the employ of the extremely poisonous and corrosive HF, some researchers focused on developing less dangerous synthesis systems. For instance, the assistance of 2-propanol [13,19] or EDTA [20] could stabilize the F-adsorbed (001) facets and BF_4^- [21] might be an alternative fluorine provider. Nevertheless, far more efforts should be made for greener synthesis of TiO_2 materials with dominant {001} facets. Moreover, the above attempts were mostly carried through long-drawn hydrothermal treatment at relatively high temperatures (120–210 °C) or assisted by microwave heating. It requires expensive equipments and makes it more difficult for large-scale productions.

Besides, nanostructured architectures self-assembled from nanoscale building blocks have been as well a research focus for their potential in practical applications for aspects of environment and energy [22–25]. The superstructures, constructed from primary nanoparticles with high-energy surface, will be the new tendency in upcoming researches, as they are easy to separate and recover during repeated use [23]. It has been expected for high-order organization of nanosheets with the dominate {001} surface into micro-sized assemblies [26], so that the recovery problem of such surface-mediated photocatalysts could be solved after photocatalytic reaction.

Herein, we propose a mild and controllable liquid phase precipitation for fabricating NH_4TiOF_3 and subsequent heat treatment for topochemical transformation [16,27,28] from NH_4TiOF_3 to anatase TiO_2. High-order octagonal TiO_2 microdisks in crystallographic orientation can be obtained by self-assembly of anatase nanosheets with largely exposed {001} surface without the addition of HF/NH_4F. In this synthesis route, $(NH_4)_2TiF_6$ is used as Ti source for its controllable hydrolysis and containing for fluoride ions. Polyvinyl pyrrolidone (PVP) acts as both a capping agent to co-adsorb on the {001} surface together with *in-situ* generated BF_4^- and F^- and a linker to connect NH_4TiOF_3 nanocrystals. The obtained nanostructured TiO_2 microdisks perform an excellent adsorption capacity in dark and enhanced photoactivity under UV irradiation.

2. Experimental section

2.1. Preparation of NH_4TiOF_3

For a typical synthesis, the details would be as follows: 7 mL PVP aqueous solution (15 mg mL^{-1}) was added to 69 mL ethanol (≥ 99.7%), labeled as solution A, then ultrasonic treated for 15 min. A freshly prepared aqueous solution (12 mL) containing 0.002 M $(NH_4)_2TiF_6$ and 0.006 M H_3BO_3, labeled as solution B, was added to solution A. After ultrasonic treated for less than 1 min, the mixture was stored at 80 °C in a water bath for 2∼4 hours. The obtained particles were separated by centrifugation and washed twice with ethanol and thoroughly with DI water.

2.2. Preparation of TiO_2

Anatase TiO_2 was prepared by post-heat-treatment of NH_4TiOF_3 precursors. Typical heat process was carried through in a Muffle furnace at 500 °C for 2 h with a ramping rate of 5 °C min^{-1}. The converted productions were taken out for further characterization after nature cooling to room temperature in the Muffle furnace.

2.3. Characterization

X-ray diffraction studies of powder samples were investigated by X'pert X-ray diffractometer (XRD, X'pert PRO, Panalytical, Netherlands) with $CuK\alpha_1$ radiation (λ= 1.54056 Å) at 40 kV and 30 mA. The morphology of as-prepared and sintered particles was observed using scanning electron microscopy (FE-SEM, LEO1530). The micrographs and SAED patterns of samples were performed by transmission electron microscopy (HRTEM, JEM2100).

2.4. Photocatalytic activity measurement

Photocatalytic activity of TiO_2 powders was evaluated in terms of degradation of a methylene blue (MB) dye solution under UV-light irradiation. For the photodegradation measurements, two 8 W UV lamps were used as UV-light (λ=365 nm) source. 50 mg TiO_2 powders were dispersed in 50 mL MB aqueous solution (10 mg L^{-1}). The suspension (pH=3) was stirred in the dark for 1 h to reach adsorption equilibrium for MB and then irradiated with UV-light under widely stirring for 2 h. The concentration of the residual MB after every 30 minutes was determined from the absorption at the wavelength of 665 nm using a UV-visible spectrophotometer (UV-723PC).

3. Results and discussion

3.1. Deposition behavior of NH_4TiOF_3

3.1.1. Effect of ethanol

The fabrication of NH_4TiOF_3 is realized by a simple and mild liquid phase precipitation method with $(NH_4)_2TiF_6$ as the titanium source. H_3BO_3 is used as an F-scavenger to remove the generated F^- ions, pushing the hydrolysis reaction of Ti (IV) ions forward. The involved mechanisms can be explained by following equations:

$$[TiF_6]^{2-} + nH_2O \leftrightharpoons [TiF_{6-n}(OH)_n]^{2-} + nHF \quad (1)$$

$$[Ti(OH)_6]^{2-} + 2H^+ \leftrightharpoons TiO_2\downarrow + 4H_2O \quad (2)$$

$$H_3BO_3 + 4HF \leftrightharpoons H^+ + BF_4^- + 3H_2O \quad (3)$$

The gradually substitution of combined F^- ions in fluorotitanium complex ions by hydroxyl groups makes precipitation of solid phase go temperately. In our synthesis strategy, a pair of experiments with different composition of solvent was set to discuss the effect of ethanol on the hydrolysis. The solution systems in both experiments were as follows: a freshly