

Control synthesis and formation mechanism of sphere-like titanium dioxide

Sibo Xu, Jinxing Wang, Shifang Cheng, Bin Miao, Shahid Hussain, Wen Zeng

College of Materials Science and Engineering, Chongqing University, Chongqing 400044, People's Republic of China
E-mail: wjx@cqu.edu.cn

Published in Micro & Nano Letters; Received on 5th June 2014; Revised on 30th July 2014; Accepted on 27th November 2014

Using a simple hydrothermal method without surfactants and templates, different morphologies of titanium dioxide (TiO₂) have been synthesised such as nanocubes, nanosheets and microspheres. The effects of the addition of hydrofluoric acid (HF) and hydrogen peroxide (H₂O₂) in the preparation of TiO₂ were studied. It was found that more H₂O₂ may accelerate the formation of a spherical morphology and that HF has three roles: dissolving Ti powder, retarding the hydrolysis of titanium precursor and reducing surface energy. Reaction time has a significant effect on morphological transformation. The aggregation of microstructures is described, the effects of the addition of HF and H₂O₂ on the condition of aggregation have been studied. Photocatalysis measurements showed that sphere-like TiO₂ consisting of nanocubes exhibited the highest activity for degrading rhodamine B under UV light.

1. Introduction: Titanium dioxide (TiO₂), as one of the most important semiconductors, has been widely investigated for various applications in environmental protection [1], gas-sensors [2, 3], Li-ion battery materials [4] and so on. Particularly, among the TiO₂ crystalline phases, anatase has been proved to be the best in applications such as photocatalysts [5–10] and solar cells [11–13]. In addition, the unique physical and chemical properties of TiO₂ are affected not only by the intrinsic electronic structure, but also by their particle shape, size, organisation and surface properties [14, 15].

Abundant researches have focused on developing novel synthesis strategies to gain various structural forms of TiO₂ such as nanoparticles, nanotubes, nanorods and nano/microspheres. Recently, the synthesis of TiO₂ microspheres with diverse structures has attracted considerable attention, because of their excellent properties in applications [16–21]. So far, different structures of TiO₂ microspheres including hollow microspheres, modified microspheres and core-shell structured microspheres have been reported [22–24].

To obtain TiO₂ microspheres, the structure-directing reagent methods and template methods are the two widely used synthesis approaches. However, such methods usually involve using structure-directing reagents or templates, whose removal processes could be costly and troublesome. In this Letter, we describe a facile chemical process to synthesise TiO₂ micrometre spheres from titanium powder without using any surfactants or other templates. We find that H₂O₂ is necessary for the preparation of anatase TiO₂ crystals. Hydrogen peroxide (H₂O₂) will participate in the chemical reaction and have an effect on the morphology of TiO₂. To obtain regular TiO₂ crystals, H₂O₂ was used in our experiment. The effects of the addition of hydrofluoric acid (HF) and H₂O₂ on the prepared morphology TiO₂ were studied and an aggregation mechanism is proposed in this Letter.

2. Experimental

2.1. Synthesis: All chemical reagents were of analytical purity and used directly without further purification. TiO₂ was synthesised by a simple hydrothermal method in a Teflon-lined autoclave. In this study, three experimental programs were designed (namely S1, S2 and S3). Their detailed experimental parameters are shown in Table 1. For the preparation of S1, HF (40 wt% and 0.06 ml), 0.01 g of Ti powder (99.9% purity) and 27 ml of deionised water were mixed in a beaker and then the mixture was stirred vigorously for 10 min. After the addition of 0.5 ml of H₂O₂ (30 wt%) to the solution, a transparent yellow solution was observed. The mixture was transferred into a Teflon-lined autoclave and

maintained at 180°C for 12 h. After being naturally cooled down to room temperature, the white precipitates were collected by centrifugation and washed with deionised water and ethanol several times until the pH of the solution was neutral, and then dried at 80°C in air for 10 h. A similar procedure was followed for the preparation of S2 and S3.

2.2. Characterisations: The structure and morphology of the as-prepared samples were characterised by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). A Rigaku D/Max-1200X diffractometry with Cu K α radiation operated at 30 kV and 100 mA was employed for the

Table 1 Materials and synthetic conditions of different experimental programs

No.	Ti, g	HF, ml	H ₂ O ₂ , ml	Temperature, °C	Time, h
S1	0.01	0.06	0.5	180	12
S2	0.01	0.1	0.5	180	12
S3	0.01	0.1	0	180	12

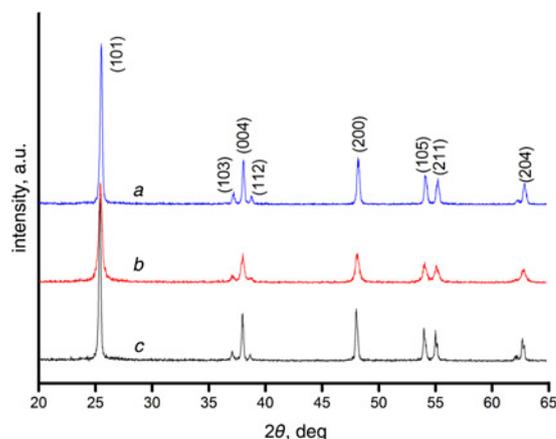


Figure 1 XRD patterns of the three precipitates at three programs
a S1 program (containing 0.1 ml HF and 0.5 ml H₂O₂ at 180°C for 12 h)
b S2 program (containing 0.06 ml HF and 0.5 ml at 180°C for 12 h)
c S3 program (containing 0.06 ml HF at 180°C for 12 h)

structure analysis. An Hitachi S-4300 scanning electron microscope (SEM) was employed for observations on the surface morphology.

2.3. Photocatalytic activity: The photocatalytic activities of different morphologies of the precursors were evaluated via degradation of methylene blue (MB) under UV light irradiation. A 300 W Hg lamp was used as the UV source. The lamp was placed beside the MB solution at a distance of 15 cm. In the typical reaction, 30 mg TiO₂ was added to 100 ml of 20 ppm MB dye solution. After that, the mixture was magnetically stirred in the dark for 1 h to establish an adsorption–desorption equilibrium and then the mixture was exposed to UV light (with a wavelength peak at 365 nm) with continuous stirring. The concentration of MB was determined from the absorbance at 665 nm. 4 ml of suspension was centrifuged to remove the catalysts

every 20 min. A transparent MB solution was analysed by UV–vis spectra with a Shimadzu UV-spectrophotometer 2100.

3. Structural characterisation

3.1. Crystal structure by XRD analysis: XRD patterns of the products prepared by the hydrothermal route are shown in Fig. 1. The patterns clearly demonstrate that the samples are tetragonal TiO₂ crystals, corresponding to the (101), (103), (004), (112), (200), (105) and (211) diffraction at 2θ of 25.303°, 36.948°, 37.792°, 38.565°, 48.035°, 53.884° and 55.059° (PDF No. 65-5714, $a = 3.785 \text{ \AA}$, $b = 3.785 \text{ \AA}$ and $c = 9.514 \text{ \AA}$). The strong and narrow peaks with no impurity indicate the good crystallinity and high purity of the as-prepared TiO₂ samples. This demonstrates that the precipitates obtained through the three synthesis approaches are all pure TiO₂ powder.

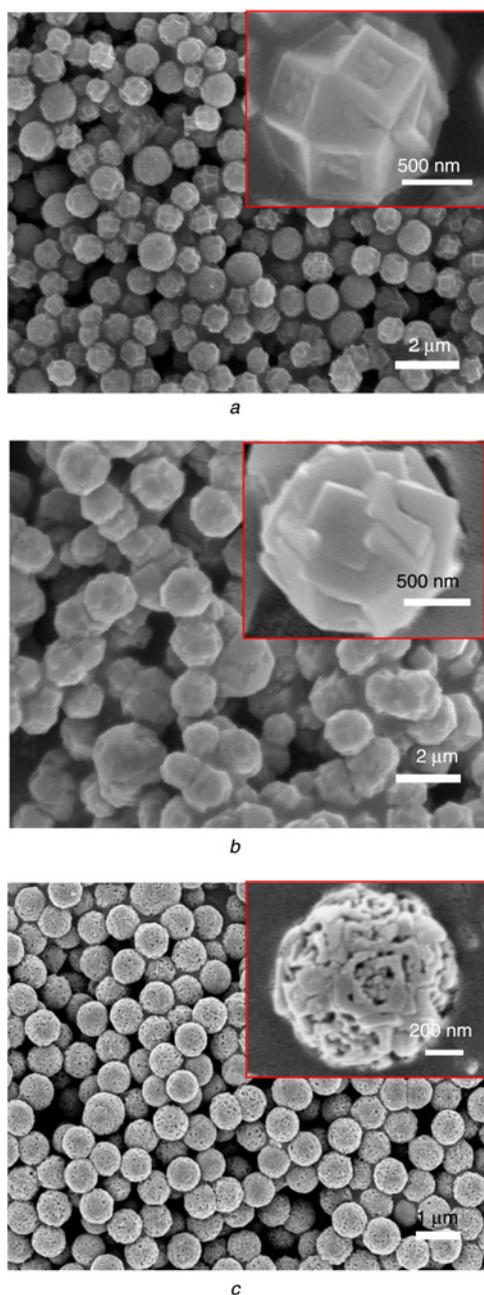


Figure 2 Three different morphologies of TiO₂ microspheres obtained
a S1 program (containing 0.06 ml HF and 0.5 ml H₂O₂ for 12 h)
b S2 program (containing 0.1 ml HF and 0.5 ml H₂O₂ for 12 h)
c S3 program (containing 0.1 ml HF for 12 h)

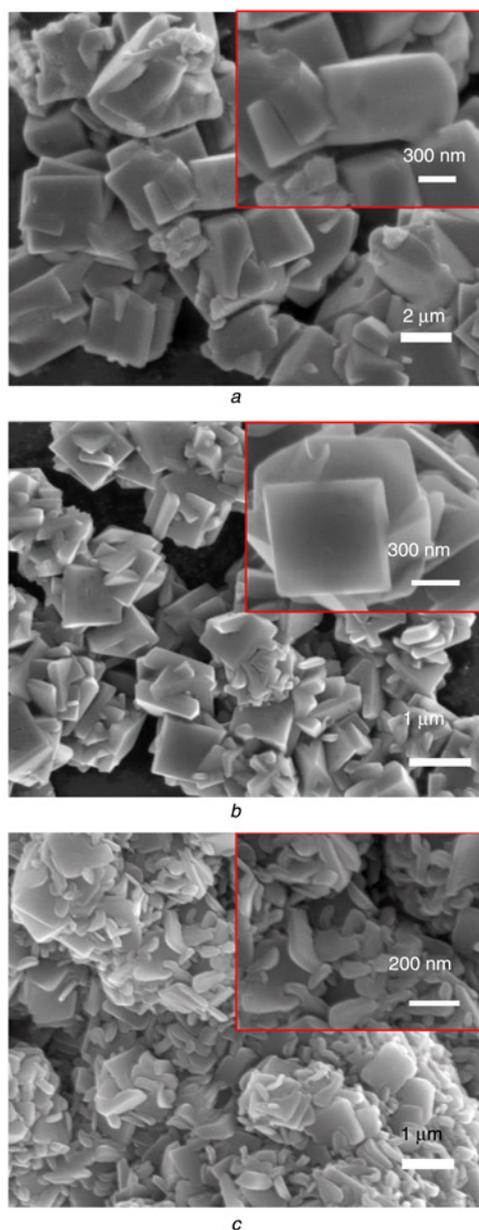


Figure 3 Three different morphologies of TiO₂ nanocrystals obtained
a S1 program for 6 h
b S2 program for 6 h
c S3 program for 6 h

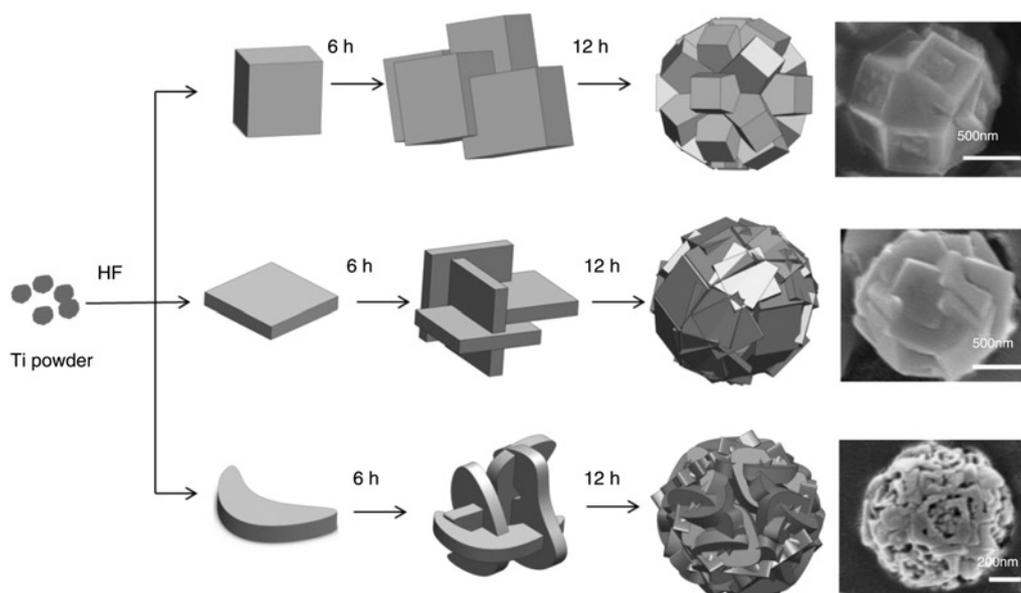


Figure 4 Schematic diagram for three different TiO_2 microstructures

3.2. Morphologies characterisation by SEM analysis: The morphologies of the prepared TiO_2 samples powders were further investigated by FE-SEM. It can be seen in Fig. 2a that there are a large quantity of hierarchical TiO_2 microspheres with diameters of about 0.6–1.2 μm . High-resolution SEM observations revealed that these microspheres are composed of many truncated tetragonal-pyramidal TiO_2 nanocrystals, and almost all of them show the same morphology. The lengths of these truncated tetragonal pyramids are about 200–300 nm and the widths of their top surfaces are about 300–500 nm (the inset of Fig. 2a). As shown in Fig. 2b, when 0.1 ml of HF and 0.5 ml of H_2O_2 solution are used, hierarchical TiO_2 microspheres with the sizes of about 0.8–1.6 μm are obtained. In a higher magnification SEM image (the inset of Fig. 2b), it can be clearly seen that the microspheres are assembled of nanosheets on the surface. The thickness and length of the nanosheets are estimated to be 100–200 nm and 400–500 nm, respectively. Typical FE-SEM of the as-synthesised product given in Fig. 2c reveals a spherical-shaped structure with diameters ranging from 0.5 to 1 μm . The FE-SEM image (top inset in Fig. 2c) of a typical microsphere reveals that the surface of these microspheres is covered by many irregular nanosheets with diameters ranging from 50 to 200 nm. Meanwhile, there are large amounts of caves on the surface.

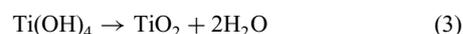
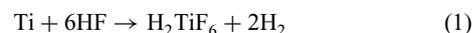
When the reaction time of all three samples is shorted to 6 h, with the other reactions unchanged, the obtained morphologies cannot be sphere-like. It can be seen from Fig. 3 that three different morphologies of TiO_2 nanostructures are synthesised. Fig. 3a clearly shows that many truncated tetragonal-pyramidal TiO_2 nanocrystals aggregate together with each other. Although similar situations also exist in Figs. 3b and c, regular and irregular nanosheets are generated in these two pictures, unlike Fig. 3a.

4. Results and discussion: It has been reported that hierarchically TiO_2 microspheres grow by the nucleation or collision of smaller particles adhering to each other [25, 26]. However, it is difficult to generate these morphologies according to their descriptions. Hence, it is necessary to give a clear explanation for the formation mechanism.

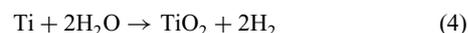
On the basis of the experimental results, we propose a formation mechanism of microspheres in three steps: (i) the TiO_2 nanocrystals formation stage; (ii) the immature spherical TiO_2 nanocrystals aggregates formation stage and (iii) the stage of further growth

into uniformly packed mature spherical TiO_2 aggregates. The schematic diagram of the growth mechanism of TiO_2 microspheres is shown as Fig. 4.

Under the hydrothermal condition, HF reacts with Ti powder at an early stage, leading to the formation of titanium fluoride complexes and the generation of H_2 gas. However, the hydrolysis of peroxotitanium acid under hydrothermal conditions is promoted to form anatase TiO_2 nanocrystals. The major reaction steps can be represented as follows [27]



During the crystal growth process, a single TiO_2 crystal is eroded by HF producing defects on the surface. It is likely that the immature spherical TiO_2 is formed through the aggregation of randomly oriented TiO_2 crystals and defect sites on the crystalline surfaces. Under hydrothermal conditions, these particles aggregate to form the transitional condition as shown in Fig. 3. As the reaction time is increased, the nanocrystals tend to form solid surfaces and the surface energy decreases. In the last stage, the multi-faceted TiO_2 spheres are formed as demonstrated in Fig. 2. Owing to the effect of HF, the combination of the three reactions (1)–(3) leads to (4)



Figs. 3a and b show that microspheres become thinner with the addition of HF when the dose of H_2O_2 is equal. The concentration of HF plays an important role in the formation of TiO_2 nanocrystals. It is known that fluoride ions can obviously reduce the surface energy of the (001) surface to a low level, because of the surface fluorination via dissociative adsorption of HF [8, 28, 29]. With reaction time increased, single crystalline grows along the [001] direction, which is the preferential growth direction for anatase crystallites under the influence of HF [30]. This leads to the formation of spherical-shaped TiO_2 possessing protrusive square-shaped surface structures as shown in Figs. 2a and b. Therefore, HF is believed to have triple roles here: to dissolve Ti powder, to retard

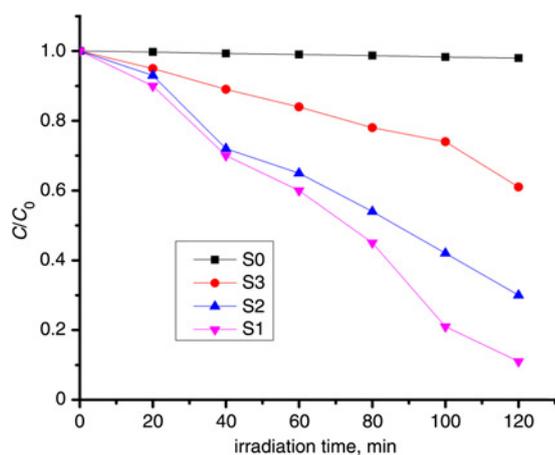


Figure 5 Photocatalytic activities of TiO₂ for RhB degradation: (black squares) S0 program (without photocatalyst), (pink inverted triangles) S1 program (containing 0.1 ml HF and 0.5 ml H₂O₂ at 180°C for 12 h), (blue triangles) S2 program (containing 0.06 ml HF and 0.5 ml H₂O₂ at 180°C for 12 h), (red circles) S3 program (containing 0.06 ml HF at 180°C for 12 h)

the hydrolysis of the titanium precursor and to reduce surface energy.

In the controlled experiment in which S3 was compared with S2, when no H₂O₂ is added, the irregular extensively aggregated TiO₂ product was obtained as shown in Fig. 3c. In the initial reaction stage, hydrolysis of H₂TiF₆ was very fast without a buffer or complexant solution such as H₂O₂, which resulted in the formation of hierarchical TiO₂ through the aggregation of randomly oriented TiO₂ crystals. Research has shown that Ti⁴⁺ can react with H₂O₂ to form a yellow titanium peroxide polymer, Ti₂O₅(OH)_x^{(x-2)-} (x = 1–6) [31]. This complex formation may further retard the hydrolysis rate of the titanium precursor. The relative slow hydrolysis rate could provide abundant time for the Ti–O–Ti chains packing better and growing well to form anatase single crystals. Meanwhile, more fluoride ions can be absorbed on the surface of the TiO₂ crystals so as to reduce the surface energy. More H₂O₂ may accelerate the hydrolysis of the titanium precursor and the formation of the spherical morphology. The aggregation of the TiO₂ product is because of the tendency to reduce the surface energy.

In all of the above, the slow hydrolysis and condensation rate are the key factors for the formation of multi-faceted TiO₂ microstructures.

The photocatalytic activities of the TiO₂ samples obtained at different reaction times were evaluated via measuring the photodegradation of RhB under UV light irradiation. The results are shown in Fig. 5. The order of photocatalytic activity of catalysts is as follows: S1 > S2 > S3. On the basis of experimental observation and results, we supposed that the surface morphologies made a great contribution to the photocatalytic activity. In our experiments, the specific surface areas of the three TiO₂ powders were investigated using nitrogen adsorption–desorption measurement. The specific surface area of S1 is 83.4 m²/g, which is higher than S2 (58.2 m²/g) and S3 (36.1 m²/g). Moreover, spheres like TiO₂ consisting of randomly packed nanocubes exhibited the highest activity. As is known, the photocatalytic activity is concerned with the morphology and specific surface area. In other words, the higher the specific surface area, the higher the photocatalytic activity.

5. Conclusion: Different morphologies of TiO₂ were successfully obtained using Ti powder and HF, including nanocubes, nanosheets and microspheres. The effects of additives HF and H₂O₂, and of reaction time on the formation of the microstructure have been discussed. The research showed that H₂O₂ could

promote the forming of anatase single crystals and the formation of a sphere-like morphology. The sphere-like TiO₂ consisting of randomly packed nanocubes exhibited the highest photocatalytic activity for degrading RhB under UV light irradiation. We found that these nanocrystals aggregated to form solid spheres with increase of the reaction time and an aggregation mechanism is proposed in this Letter.

6. Acknowledgments: This work was supported by the National Natural Science Foundation of China (no. 51302328) and supported in part by the Fundamental Research Funds for the Central Universities (no. CDJPY12130002).

7 References

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