

## Fabrication and Characterization of Nanostructurally Flowerlike Aggregates of TiO<sub>2</sub> via a Surfactant-free Solution Route: Effect of Various Reaction Media

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Flowerlike submicrometer-scaled aggregates assembled with nanorod structures have been successfully fabricated via a simple surfactant-free solution process. The fabricated nanostructures exhibit high photocatalytic activity in the photodegradation of aqueous Methylene Blue solution.

The design and synthesis of nanostructures have attracted much interest in the past decades because of their potentially significant application.<sup>1,2</sup> Owing to its outstanding properties, nanostructured titanium dioxide (TiO<sub>2</sub>) has comprehensive applications in photocatalyst,<sup>3</sup> catalyst,<sup>4</sup> solar energy cell,<sup>5</sup> and gas sensor.<sup>6</sup> These applications are strongly dependent on the particle size, crystalline phase, morphology, crystallinity, and surface property. Many groups have carried out important works for the controlled synthesis of nanostructured TiO<sub>2</sub>.<sup>7–11</sup> Sol-gel synthesis of nanocrystalline TiO<sub>2</sub> has been extensively investigated with titanium alkoxides or halides as a precursor.<sup>7,8</sup> It is worth noting that the posttreatment following sol-gel process has a significant influence on the morphology of the gained TiO<sub>2</sub>. Wu et al. prepared uniform and unaggregated nanocrystals of pure anatase or rutile TiO<sub>2</sub> using a sol process followed by hydrothermal treatment.<sup>9</sup> Miao et al. developed a heating-sol-gel-template process for the growth of rutile or anatase TiO<sub>2</sub> nanorods consisting of corresponding nanoparticles by selecting a suitable heat-treatment program.<sup>10</sup> Recently, the effect of solvents on the crystalline phase and morphology has been considered as an important factor to the preparation of nanostructured TiO<sub>2</sub>,<sup>11</sup> and, therefore, the essentially different reaction media might be used to control the size, morphology and surface property of the derived TiO<sub>2</sub>. In this paper, our strategy is based upon the selection of various water-immiscible solvents that favor to form a two-phase interface where flowerlike nanostructures of TiO<sub>2</sub> are fabricated. The motif of our method is a simple and surfactant-free solution route with tetrabutyl titanate and TiCl<sub>4</sub> as mixed titanium sources followed by solvothermal treatment. In addition, the fabricated submicrometer-scaled flowerlike assemblies of nanorods exhibit high photocatalytic activity in the photodegradation of aqueous Methylene Blue solution.

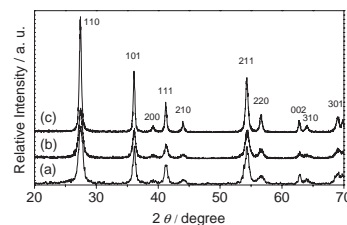
In our method, tetrabutyl titanate (Ti(OBu)<sub>4</sub>) and titanium tetrachloride (98% TiCl<sub>4</sub>) were used as the main starting materials without any further purification. A certain amount of titanium tetrachloride was dissolved into distilled water in an ice-water bath to obtain 3 M TiCl<sub>4</sub> as the stock solution. In a typical experimental procedure, in the fume cupboard, a proper amount of tetrabutyl titanate was added to benzene, oleic acid and water, respectively. Then a desired amount of 3 M TiCl<sub>4</sub> was added to the mixture to adjust the pH value to 1.5. The mixture was transferred to a stainless steel autoclave lined with Teflon,

80% filled, tightly closed, and then held at 140 °C for 22 h. The precipitates after the solvothermal treatment were washed well with ethanol for several times, collected from the solution by filtration, and dried at 60 °C in a vacuum oven overnight.

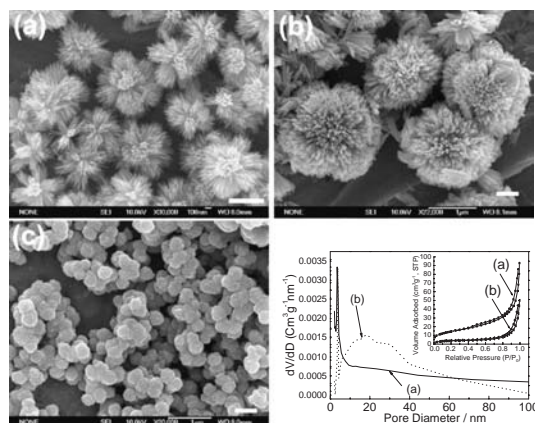
The phase and crystallinity of the products were characterized by powder X-ray diffraction (XRD) using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 100 mA on a Rigaku D/max 2550V diffractometer. The morphology of products was observed on a JSM-6700F field emission scanning electron microscope (FE-SEM). The average pore diameters were determined by the BJH method, using a surface area analyzer (Micromeritics ASAP 2010).

Figure 1 shows the XRD patterns of the products derived from the three different reaction media, respectively. It can be seen that all the products can be exclusively indexed as rutile phase of TiO<sub>2</sub> (S. G.: *P4<sub>2</sub>/mnm*;  $a = b = 4.593$  Å,  $c = 2.959$  Å; JCPDS No. 21-1276). No characteristic peaks were observed for other phases such as anatase or brookite.

Figure 2 shows the FE-SEM images of the products obtained with the three different additional reaction media: benzene, oleic acid, and water, respectively. It should be noted that there exists a tiny amount of water which come from 3 M TiCl<sub>4</sub> in the first two reaction media and the presence of water plays an important role in the crystallization of TiO<sub>2</sub>.<sup>12</sup> For the reaction media of benzene and oleic acid, similar morphologies of nanoflowers assembled with nanorods are gained although the different water-immiscible solvents are used. For benzene, the sizes of the nanoflowers are about 1  $\mu$ m, and the diameters of the nanorods are 7–10 nm (based on TEM determination, not shown here). However, there are also obvious distinctions between the two products. The nanoflowers, which grow up in benzene have more discrete petal-like structures than those in oleic acid, and at the same time the nanoflowers synthesized in oleic acid seem to be quasi-spherical assemblies and their nanorods have a low aspect ratio. This distinction also reflects in the BJH pore distribution of the two products (Figure 2). The product derived from oleic acid has the bimodal pore distribution, and the set of pores with wider dis-



**Figure 1.** XRD patterns of the products derived from (a) benzene, (b) oleic acid, and (c) water. All the products are exclusively indexed as rutile phase.

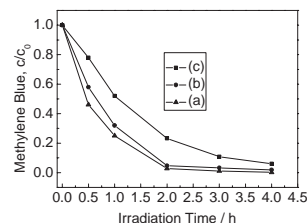


**Figure 2.** FE-SEM images of the products derived from (a) benzene, (b) oleic acid, and (c) water with the pH value of the systems kept the same; Scale bar indicates 500 nm.  $N_2$  adsorption-desorption isothermal (inset) and corresponding BJH pore-size distribution curve of the products derived from (a) benzene and (b) oleic acid. The pore-size distribution was determined from the desorption branch of the isothermal.

tribution indicates the gaps between the nanorods, showing the less gaps between nanorods. The differences of the product derived from oleic acid in the morphology from that derived from benzene might result from the adsorption of oleic acid on the tips of the nanorods.<sup>13</sup> However, the effect of water media on the morphology of the products is obvious. The product derived from water has the morphology of spherical agglomeration with needlelike surfaces, as it was reported previously.<sup>14</sup> No apparent nanorods can be distinguished from the aggregation.

Obviously, the nature of the three reaction media used here plays a crucial role in the formation of the final morphology of the products. For the flowerlike assembly, the water-immiscible reaction media are utilized to process the solvothermal treatment. It is the water-immiscible reaction media that supply the benzene/water interface for the nanoparticles to grow up to the desired morphology during the solvothermal process. Generally, the existence of the water-immiscible reaction media may isolate the primary particulates and inhibit the epitaxial growth of  $TiO_2$ , resulting in the preferential growth of rutile nanorods because of the presence of adsorbed water on the tips of the nanorods. When the reaction media is replaced by oleic acid, which is known to interact with  $TiO_2$  particulates, the aggregation among the nanorods does not occur, either. However, the adsorption of oleic acid on the surface of  $TiO_2$  makes the nanorods have a low aspect ratio. Different from the above two cases, when considerable amount of water is used as a hydrothermal process, the aggregation among the nanorods makes the final morphology of the product become spherically agglomerated particles with rough surfaces. Therefore, the amount of water in the reaction media is crucial to the control over the morphology of the final particles.

The photocatalytic activity of the three products was tested in the degradation of aqueous Methylene Blue solution. The suspensions were irradiated with a 300 W medium-pressure mercury lamp. The concentration of photocatalyst was 0.4 g/L. Oxygen was bubbled into reaction suspensions at a flow rate of 100 mL/min throughout the experiments. Samples were taken out at regular time intervals, and the concentration of Methylene



**Figure 3.** Photocatalytic activity of the products derived from (a) benzene, (b) oleic acid, and (c) water for MB photodegradation. The MB concentration was determined by monitoring the absorbance at 650 nm.

Blue in the aqueous solution was monitored using the Shimadzu UV-3101PC spectrophotometer. It can be seen that the products with the morphology of discrete nanorod assembly has higher photocatalytic activity than the spherically agglomerated particles (Figure 3). Additionally, this kind of nanostructurally submicrometer-scaled aggregates has the advantages of easily dispersing and recovering in solution in the photocatalytic application over the free-standing nanorods.

In summary, a simple method has been presented for the fabrication of flowerlike submicrometer-scaled aggregates assembled with nanorod structures. The addition of water-immiscible reaction media plays an important role in the formation of these kinds of nanostructures. The fabricated nanostructures exhibit high photocatalytic activity and this kind of nanostructures is expected to exhibit other distinguished performances in the applied fields of  $TiO_2$  materials.

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