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Research Article

Large-Scale Synthesis and Self-Assembly of Monodisperse Spherical TiO_2 Nanocrystals

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The spherical titanium dioxide nanocrystals were successfully synthesized in a new system through a solvothermal method. Prolonged reaction time can contribute to the improvement of the morphology and self-assembly behavior of TiO_2 nanocrystals. The central features of our approach are the use of rapid heating process and the use of both oleic acid and dodecylamine as two different capping surfactants to synthesize monodisperse TiO_2 nanocrystals.The morphologies and self-assembly behavior of TiO_2 nanocrystals are studied by transmission electron microscopy (TEM) analyses.

1. Introduction

The use of nanocrystals as "building blocks" for the self-assembly of new materials has attracted more and more attention these days because it provides a unique opportunity to bring together the inherent functionality and the collective properties of nanocrystals [1–4]. The morphology and interaction between the nanocrystals play an important role in the formation of self-assembled structures [5]. Nevertheless, the synthesis of monodisperse nanocrystals (size variation <5%) without a laborious size-sorting process only succeeds in some specific materials, which accounts for why rational planning of nanocrystals assemblies during synthesis is very difficult and most self-assembly processes are achieved with specific size and shape of nanocrystals [6]. Titanium dioxide (TiO_2) is one of the most essential semiconductors, playing an important role in many applications such as paints, pigment, additive, gas sensors, photovoltaic cell, and photocatalysis. There are many research groups who succeed in the synthesis of various shapes of TiO_2 nanoparticles, such as sphere [7], sheet [8], rod [9], wire [10], cube [11], needle [12], bullet, [13] and diamond [13].However, the self-assembly of anatase TiO_2 nanocrystals is not very successful. Our research group has obtained five different packing types (ribbon, smectic, domino, honeycomb, lamellar) of TiO_2 nanorod and until now still rare studies addressed the nanodot self-assembly of TiO_2 [14]. This is because the monodisperse TiO_2 nanodots are not easy to prepare. The morphology of nanocrystals can be tuned by varying reaction conditions. The surfactant has the ability to control the size and shape of the nanocrystals, especially for the synthesis of metal oxides. The selective bindings of different surfactant molecules to different facets of TiO_2 lead to the crystal growth along different directions [15]. In addition, it is much easier to prepare the monodisperse nanocrystals if we separate the nucleation and growth processes [16].

Here, we report the successful preparation of well-ordered arrays of TiO_2 nanocrystals whose predominant shape is sphere. The solvothermal method is an economical mass-production route for the synthesis of TiO_2 nanodots. Moreover, this provides an opportunity to rational planning of TiO_2 nanodots assemblies during synthesis. The central features of our approach are the use of rapid heating process and the use of both oleic acid and dodecylamine as two different capping surfactants to synthesize monodisperse TiO_2 nanodots. It was found that the morphology and self-assembly behavior of TiO_2 nanodots become perfect with increase of reaction time. The formation of well-ordered arrays of TiO_2 nanocrystals has also been discussed in this paper.

2. Experimental

The TiO_2 nanodots were prepared by a solvothermal method. Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$ or TBT), oleic acid ($C_{18}H_{34}O_2$ or OA), and dodecylamine ($C_{12}H_{27}N$ or DDA) were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd without further purification. In a typical synthesis, TBT (9 ml) was added dropwise to OA (72 ml) with magnetic stirring at room temperature for 1 h. DDA (18 ml) was then added and the resulting mixture was under stirring kept for 24 h. The solution would gradually tune form pale yellow to orange, indicative of the formation of titanium oleate complex. The high-pressure reactor (High-Pressure Laboratory Reactor BR-100: 100 ml, BERGHOF) was heated to 290°C before the obtained complex was transferred into it to ensure rapid heating. Then, the high-pressure reactor was kept at 300°C for 10 h. After the reaction had proceeded for 1 h, 3 h, 6 h and 10 h, the resulting solution containing the nanocrystals was extracted and then cooled to room temperature. The nanocrystals were finally dispersed into toluene, providing stable optically clear colloidal solution, and then placing a droplet of the colloidal solution onto a carbon-coated Cu grid to allow the solvent to evaporate under ambient condition.

The transmission electron microscopy (TEM) experiments were performed at 80 kV using a JEM-1230 TEM. The powder X-ray diffraction (XRD) data of the sample was collected on a philips PW1050 powder diffractometer with Cu Kα radiation source at 40 kV in the 2θ range of 20–80°.

3. Results and Discussion

Figure 1 shows TEM images of TiO_2 nanocrystals synthesized by solvothermal method for different time at 300°C. Average diameter of particles is (a) 5.6, (b) 7.0, (c) 8.0, and (d) 8.9 nm. As we have seen that the TiO_2 nanocrystals continue to grow with reaction times. However, the growth rate decreases due to decrease of titanium oleate complex concentration. The TEM images of Figures 1(a) and 1(b) contain a number of irregularly shaped nanocrystals and a part of the ordered regions. We only obtain a short-range arrangement of the TiO_2 nanocrystals rather than a long-range ordering which is mainly affected by the inhomogeneity of the nanocrystal shape and size. While, the TEM images of Figures 1(c) and 1(d) demonstrating the high size and shape uniformity of the nanocrystals make it possible to manipulate nanocrystals into a long-range ordered structure.

During the direct synthesis of monodisperse TiO_2 nanocrystals, we were able to ascertain that the use of rapid heating process and the use of both oleic acid and dodecylamine as two different capping surfactants can contribute to the preparation of the spherical TiO_2 nanocrystals. On one hand, the separation of nucleation and growth processes of the crystallization, which tend to take place at different temperatures, can help us to synthesize highly uniform nanocrystals [16]. The mixture was under stirring kept for 24 h because the nucleation was occurring at room temperature in the present system. After this, the reaction mixture was quickly heated to 300°C (Our monitoring data show that the temperature can rise to 213°C in five minutes) to ensure the growth of TiO_2 nanocrystals without additional nucleation. On the other hand, because the growth process is time-dependent, we could obtain different TiO_2 nanocrystals while the reaction mixture was aged at 300°C for different hours. The improvement of TiO_2 nanocrystals can be attributed to the thermodynamic driving force at higher temperature for a relatively long time. On the other hand, it is possible to get nanocrystals of different shapes by varying the surfactants. When only OA was used, it tends to adhere on almost all of the surfaces of TiO_2. The crystals grow mainly on high surface energy faces and favor the formation of nanorods. DDA have different functional groups with distinct binding strengths, which can be adsorbed on the different surfaces of TiO_2. It is therefore expected that the shape of TiO_2 nanocrystals can be prepared by modulating the OA/DDA volume ratio. When the TBT/OA/DDA volume ratio is 1 : 8 : 2, the spherical nanocrystals with uniform size are obtained. These results ascertain that the cooperative effect of a specific amount of OA and DDA can contribute to the formation of the spherical TiO_2 nanocrystals.

Figures 1(c) and 1(d) show a TEM of a monolayer TiO_2 nanocrystal, where most of the particles can be identified to have a spherical shape and a long-range ordered structure could be observed. The evaporation dynamics is one of the most parameters affecting the assembly behavior of nanocrystals, which is that the self-assembly of nanocrystals occuring during the solvent evaporation of a nanocrystal-containing solution. Slow solvent evaporation is considered essential to this process, in which the concentration of the nanocrystal-containing droplet increases gradually and the free volume available for each nanocrystal decreases as the solvent has evaporated [17]. A large cluster will be formed inside droplet to play a role as the nucleation site, and a long-range ordered structure will be formed after the new incoming nanocrystals find their preferred location on the growing cluster face. The nanocrystals inorder to get together to form a nucleation site are in need for sufficient time and the mobility provided by enough solvent. This explains why there will be no self-assembled pattern observed if the solvent evaporates very soon to dryness. In this experiment, despite using toluene that evaporated rapidly, the formation of the long-range ordered structure was still done. We believe that the self-assembly process may have occurred during the synthesis stage to some extent. This method may provide a reasonable plan to large-scale synthesis and self-assembly of monodisperse spherical TiO_2 nanocrystals.

The typical XRD patterns of powders synthesized by the solvothermal method are shown in Figure 2. The main peaks corresponding to standard anatase TiO_2 including (101), (004), (200), (105), (211), (204), (116), (220), and (215) are observed, which indicated that all samples are pure anatase phase without other TiO_2 polymorphs. It is apparent that no changes in crystal structure of the TiO_2 had occurred with the increase of reaction time. However, all the diffraction peaks of the samples become much sharper and stronger indicating improved degree of crystallinity. In addition, the intensity ratio of the (101) peak relative to the (200) peak is

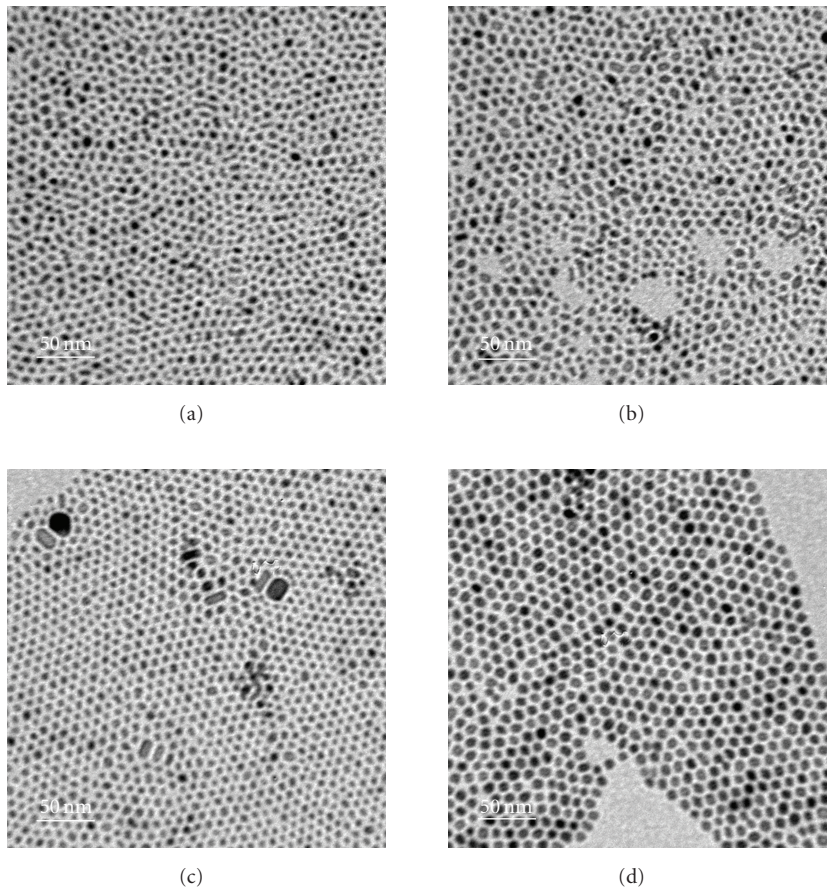

Figure 1: TEM images of TiO_2 nanocrystals grown at 300°C for different reaction times: (a) 1 h, (b) 3 h, (c) 6 h, and (d) 10 h. Average diameters of particles are (a) 5.6, (b) 7.0, (c) 8.0, and (d) 8.9 nm. All scale bars are 50 nm.

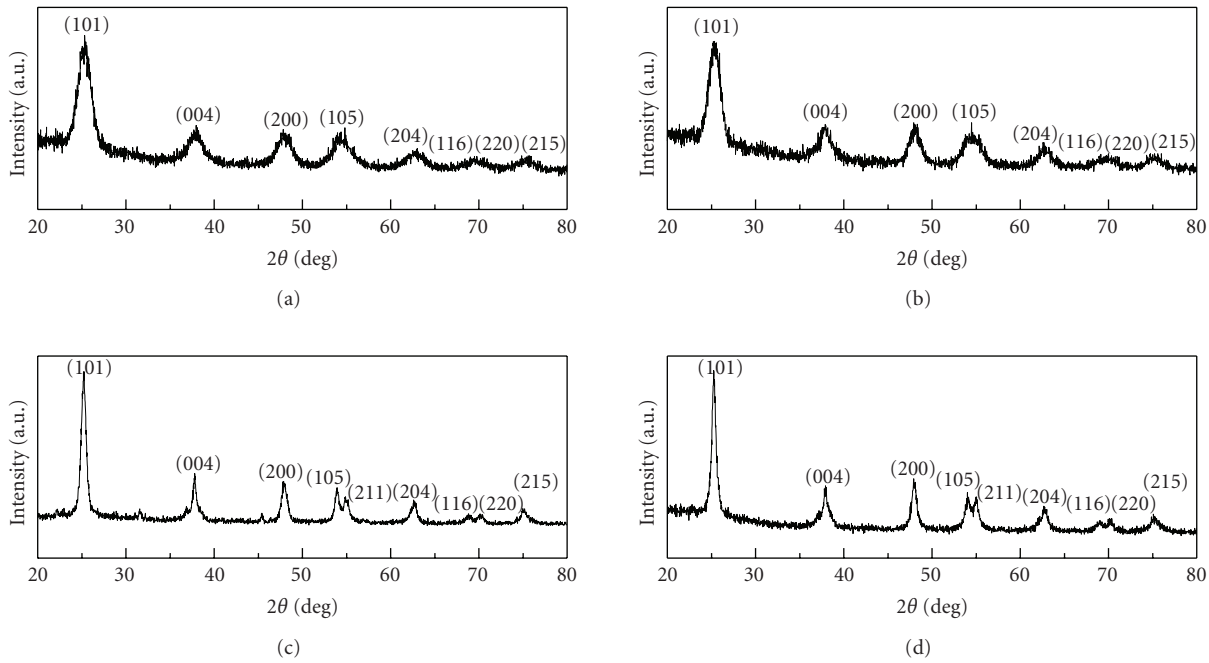

Figure 2: X-ray diffraction pattern of TiO_2 nanocrystals synthesised for different hours at 300°C: (a) 1 h, (b) 3 h, (c) 6 h, (d) 10 h.

2.75, which is almost consistent with the spherical or bulk TiO_2. Apart from TEM images of TiO_2 nanocrystals, this provides more evidence that the TiO_2 nanocrystals prepared by this new system are spherical in shape. All these XRD results can be ascribed to the inhibition of anisotropic growth of anatase TiO_2 nanocrystals.

4. Conclusion

In conclusion, we demonstrate the controlled growth of spherical titanium dioxide in a new system through a simple solvothermal method. The use of rapid heating process and the use of both oleic acid and dodecylamine as two different capping surfactants can contribute to the preparation of the monodisperse spherical TiO_2 nanocrystals. When the TBT/OA/DDA volume ratio is 1 : 8 : 2, the spherical nanocrystals with different diameters are obtained. With the improvement of the high degree of uniformity of TiO_2 nanocrystals, the self-assembled pattern could be observed. This novel approach could be extended to large-scale synthesis and self-assembly of some other metal oxides.

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References

[1] C. J. Kiely, J. Fink, M. Brust, D. Bethell, and D. J. Schiffrin, "Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters," *Nature*, vol. 396, no. 6710, pp. 444–446, 1998.

[2] Z. L. Wang, S. A. Harfenist, I. Vezmar et al., "Superlattices of self-assembled tetrahedral Ag nanocrystals," *Advanced Materials*, vol. 10, no. 10, pp. 808–812, 1998.

[3] D. V. Talapin, E. V. Shevchenko, C. B. Murray, A. Kornowski, S. Föraster, and H. Weller, "CdSe and CdSe/CdS nanorod solids," *Journal of the American Chemical Society*, vol. 126, no. 40, pp. 12984–12988, 2004.

[4] T. S. Sreeprasad, A. K. Samal, and T. Pradeep, "One-, two-, and three-dimensional superstructures of gold nanorods induced by dimercaptosuccinic acid," *Langmuir*, vol. 24, no. 9, pp. 4589–4599, 2008.

[5] E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, and C. B. Murray, "Structural diversity in binary nanoparticle superlattices," *Nature*, vol. 439, no. 7072, pp. 55–59, 2006.

[6] M. Niederberger and N. Pinna, *Metal Oxide Nanoparticles in Organic Solvents: Synthesis, Formation, Assembly and Application*, Springer, New York, NY, USA, 2009.

[7] J. Tang, F. Redl, Y. Zhu, T. Siegrist, L. E. Brus, and M. L. Steigerwald, "An organometallic synthesis of TiO_2 nanoparticles," *Nano Letters*, vol. 5, no. 3, pp. 543–548, 2005.

[8] H. G. Yang, G. Liu, S. Z. Qiao et al., "Solvothermal synthesis and photoreactivity of anatase TiO_2 nanosheets with dominant 001 facets," *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 4078–4083, 2009.

[9] Z. Zhang, X. Zhong, S. Liu, D. Li, and M. Han, "Aminolysis route to monodisperse titania nanorods with tunable aspect ratio," *Angewandte Chemie—International Edition*, vol. 44, no. 22, pp. 3466–3470, 2005.

[10] D. K. Yi, S. J. Yoo, and D.-Y. Kim, "Spin-on-based fabrication of titania nanowires using a sol-gel process," *Nano Letters*, vol. 2, no. 10, pp. 1101–1104, 2002.

[11] Y. Zhou, E.-Y. Ding, and W.-D. Li, "Synthesis of TiO_2 nanocubes induced by cellulose nanocrystal (CNC) at low temperature," *Materials Letters*, vol. 61, no. 28, pp. 5050–5052, 2007.

[12] C.-C. Weng, C.-P. Chen, C.-H. Ting, and K.-H. Wei, "Using a solution crystal growth method to grow arrays of aligned, individually distinct, single-crystalline TiO_2 nanoneedles within nanocavities," *Chemistry of Materials*, vol. 17, no. 13, pp. 3328–3330, 2005.

[13] Y.-W. Jun, M. F. Casula, J.-H. Sim, S. Y. Kim, J. Cheon, and A. P. Alivisatos, "Surfactant-assisted elimination of a high energy facet as a means of controlling the shapes of TiO_2 nanocrystals," *Journal of the American Chemical Society*, vol. 125, no. 51, pp. 15981–15985, 2003.

[14] B. Ye, G. Qian, X. Fan, and Z. Wang, "Self-assembled superlattices from colloidal TiO_2 nanorods," *Current Nanoscience*, vol. 6, no. 3, pp. 262–268, 2010.

[15] C.-T. Dinh, T.-D. Nguyen, F. Kleitz, and T.-O. Do, "Shape-controlled synthesis of highly crystalline titania nanocrystals," *ACS Nano*, vol. 3, no. 11, pp. 3737–3743, 2009.

[16] J. Park, K. An, Y. Hwang et al., "Ultra-large-scale syntheses of monodisperse nanocrystals," *Nature Materials*, vol. 3, no. 12, pp. 891–895, 2004.

[17] C. B. Murray, C. R. Kagan, and M. G. Bawendi, "Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies," *Annual Review of Materials Science*, vol. 30, pp. 545–610, 2000.