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Research Article

An Experimental Study on the Shape Changes of TiO_2 Nanocrystals Synthesized by Microemulsion-Solvothermal Method

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Titanium dioxide (TiO_2) nanocrystals of different shape were successfully synthesized in a new microemulsion system through a solvothermal process. The TiO_2 nanocrystals were prepared from the reaction of tetrabutyl titanate (TBT), H_2O, and oleic acid (OA), which were used as solvent and surfactant at 300°C and 240°C in a stainless steel autoclave. The sphere, polygon, and rhombus-shaped nanocrystals have been prepared at 300°C and the dot- and- rod shaped nanocrystals have been synthesized at 240°C. The effect of the reaction time on the shape and size of TiO_2 nanocrystals in this method was studied in the present paper. The size distribution of TiO_2 nanocrystals prepared at 300°C for different hours is also studied. In addition, an attempt to describe the mechanism of shape change of TiO_2 nanocrystals was presented in this paper.

1. Introduction

Nanosized metal oxide particles have attracted great attention because of their unusual size-dependent optical and electronic properties over the last two decades. Among all the metal oxide, TiO_2, an important semiconductor, has been widely used in pigment, paints, additive, photovoltaic cell, gas sensors and photocatalysis. It is reported that nanoscale TiO_2 has peculiar properties which is not expected in bulk materials. TiO_2 is an anisotropic material with different phases, its properties are usually dependent on the size, shape, morphology, crystal structure, surface area and porosity [1]. It is essential to study the shape changes in the TiO_2 nano-crystalline growth process. There are a lot of reports focusing on the synthesis of various shapes of TiO_2 nanoparticles, such as sphere [2], rod [3], needle [4],wire [5], cube [6], bullet [7], diamond [7]. Several studies [3, 7] have synthesized two shapes in just one kind of chemical process, while few of them have studies the shape change process of the nano-crystalline in the chemical reactions.

Although numerous techniques were successfully used to synthesize nano-crystalline TiO_2, there were still several problems which were difficult to be solved. The TiO_2 nanomaterials prepared by the micelle method normally have amorphous structure, and calcination is usually necessary in order to induce high crystallinity, this process usually leads to the growth and agglomeration of TiO_2 nanoparticles [8]. Poor stability of the microemulsion systems, large size of TiO_2 nanocrystals and poor dispersion stability also exist under solvothermal conditions. In recently years, a series of new ways for nanoparicle synthesis have been designed. Microemulsion-hydrothermal/solvothermal method is a kind of way of them. This new method combines microemulsion techniques with a hydrothermal/solvothermal process, and it has been explored for the preparation of lots of nanocrystals such as $SrCO_3$ nanostructures [9], $Ca_{10}(PO_4)_6(OH)_2$ nanofibers [10], BaF_2 whiskers [11], wollastonite nanowires [12], cobalt nanorods [13], aluminium orthophosphate nanocrystals [14], PbS nanocrystals [15] and CdS nanorods [16].

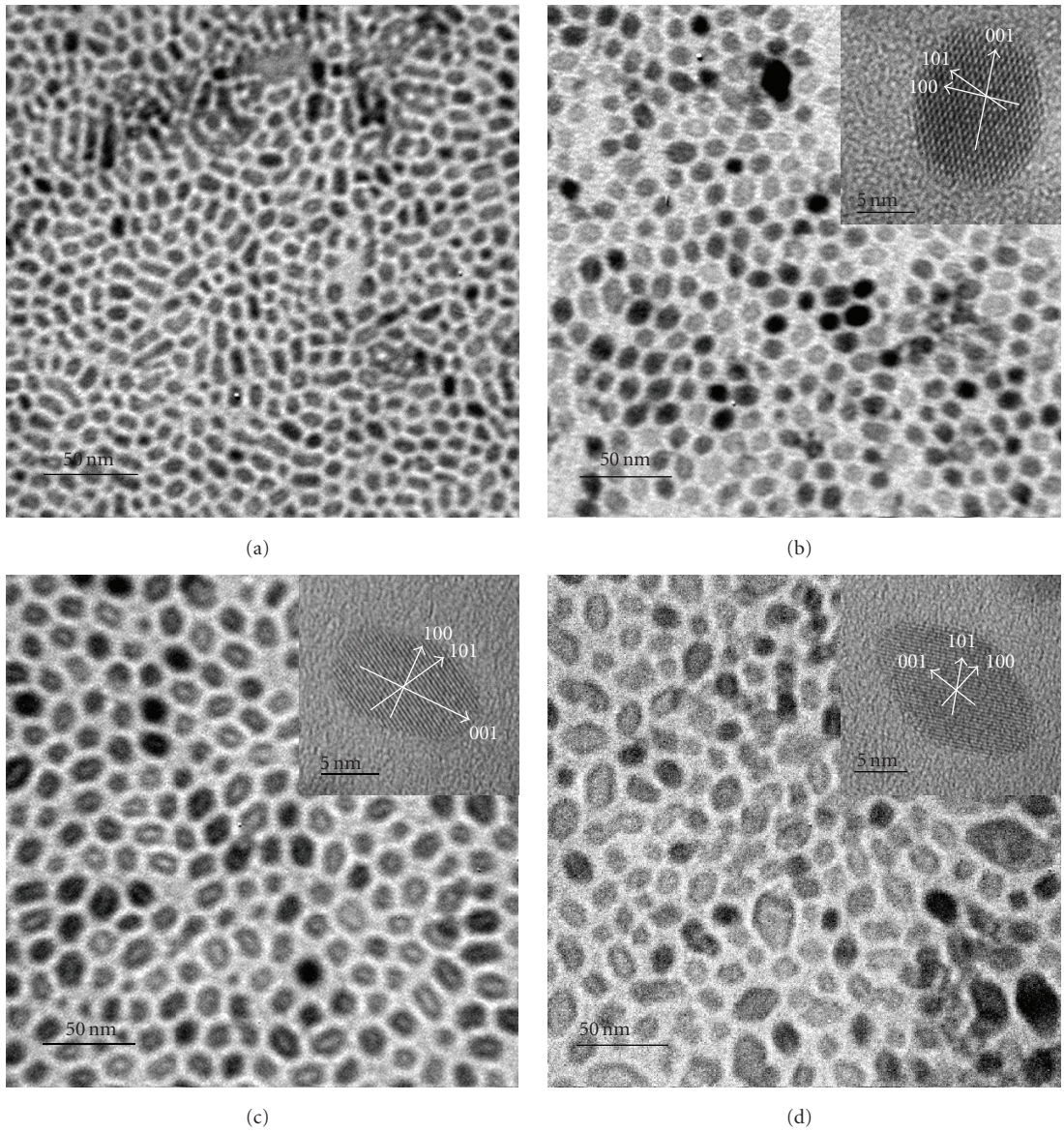

Figure 1: TEM images and HRTEM images of TiO_2 nanocrystals synthesized at 300°C for different times: (a) 0.5 hours; (b) 2 hours; (c) 4 hours; (d) 17 hours.

Here we introduced a new microemulsion-solvothermal method. A kind of new microemulsion system was prepared and a higher solvothermal temperature was chosen to obtain a better crystalline state. It was found that four kinds of shape of TiO_2 nanocrystals including sphere, polygon, rhombus and rod were successfully synthesized. The shape change process of TiO_2 nanocrystals were studied based on the experimental analysis.

2. Experimental

2.1. Synthesis. The TiO_2 nanocrystals were prepared by a microemulsion-solvothermal method. TBT and OA were of analytical grade and purchased from Shanghai Chemical Reagent Co. without further purification. The formation of monodisperse TiO_2 nanocrystals could be divided into two steps. Step 1: the synthesis of the microemulsion precursor. Step 2: the manufacture of TiO_2 nanocrystals in solvothermal process.

Step 1. 1.7 mL of TBT was dissolved in 18 ml of OA under vigorous stirring at room temperature. After an hour, 2.7 mL of deionized water was added into this solution dropwise. All the mixture solution was kept stirring for another 1 hour at room temperature in a separate flask to obtain a microemulsion precursor.

Step 2. The microemulsion precursor was put into a stainless steel autoclave. The autoclave was kept at 300°C for different reaction time (0.5 hours, 2 hours, 4 hours and 17 hours) in an electric oven. For comparison, the temperature at 240°C

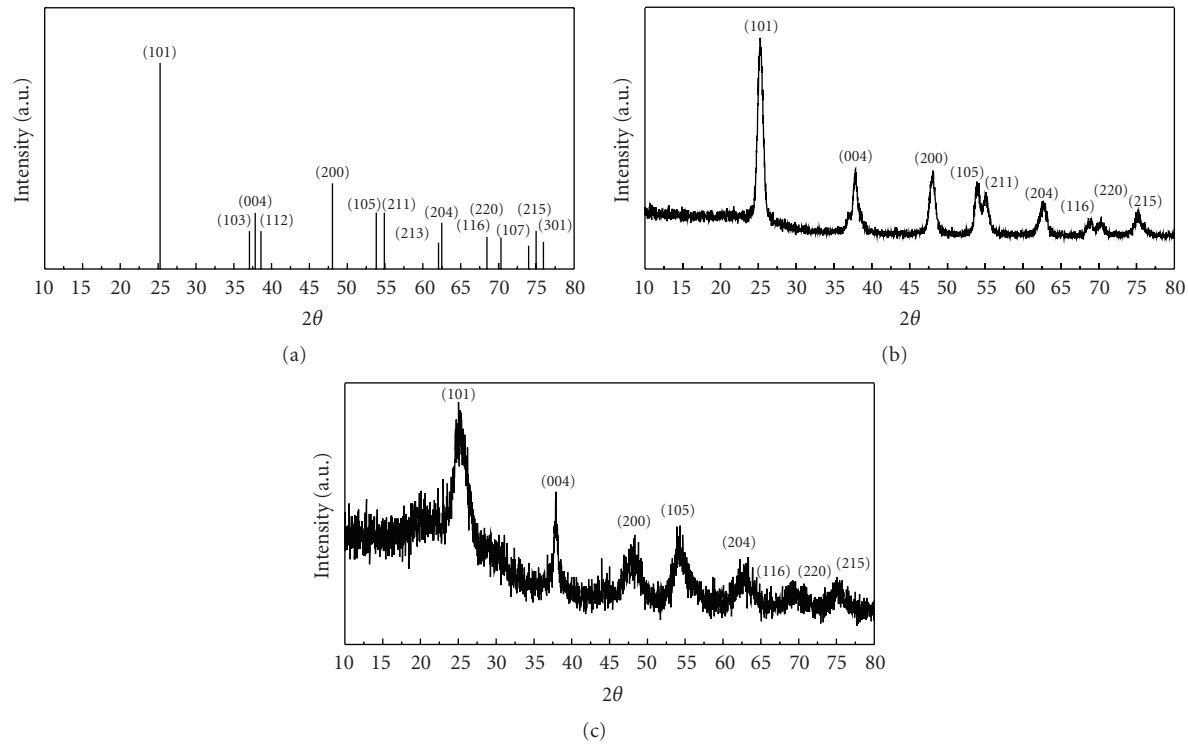

Figure 2: X-ray diffraction pattern of TiO_2 nanocrystals synthesized for 2 hours at 300°C and 240°C: (a) The standard spectrum of anatase titanium dioxide, (b) 300°C, (c) 240°C.

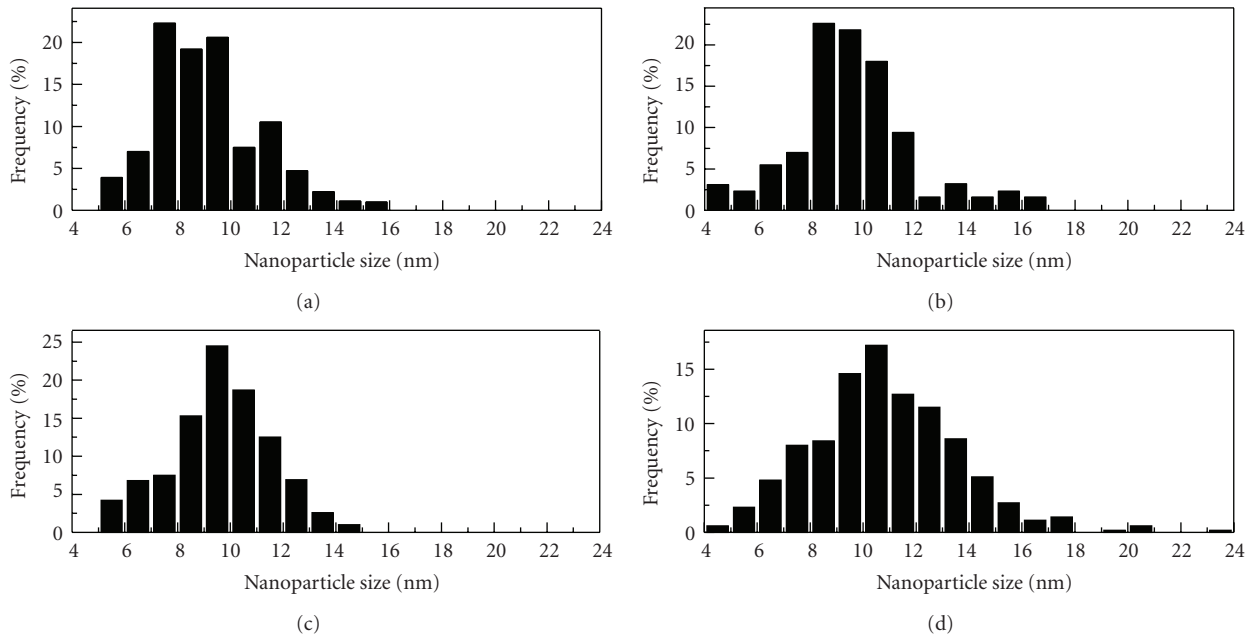

Figure 3: TiO_2 nanoparticle size distribution histogram (a) 300°C, 0.5 hours; (b) 300°C, 2 hours; (c) 300°C, 4 hours; (d) 300°C, 17 hours.

was also studied. After reaction, the TiO_2 nanocrystals were harvested by centrifugation and washed with ethanol once.

2.2. Characterization. Powder X-ray diffraction (XRD) data of the samples were collected on a philips PW1050 powder diffractometer with Cu Kα radiation source at 40 kV in the 2θ range of 10–80°. Transmission electron microscopy (TEM) measurement was carried out with a JEM-1230 microscope operating at 80 kV. High-resolution transmission electron microscopy (HRTEM) measurement was carried out with

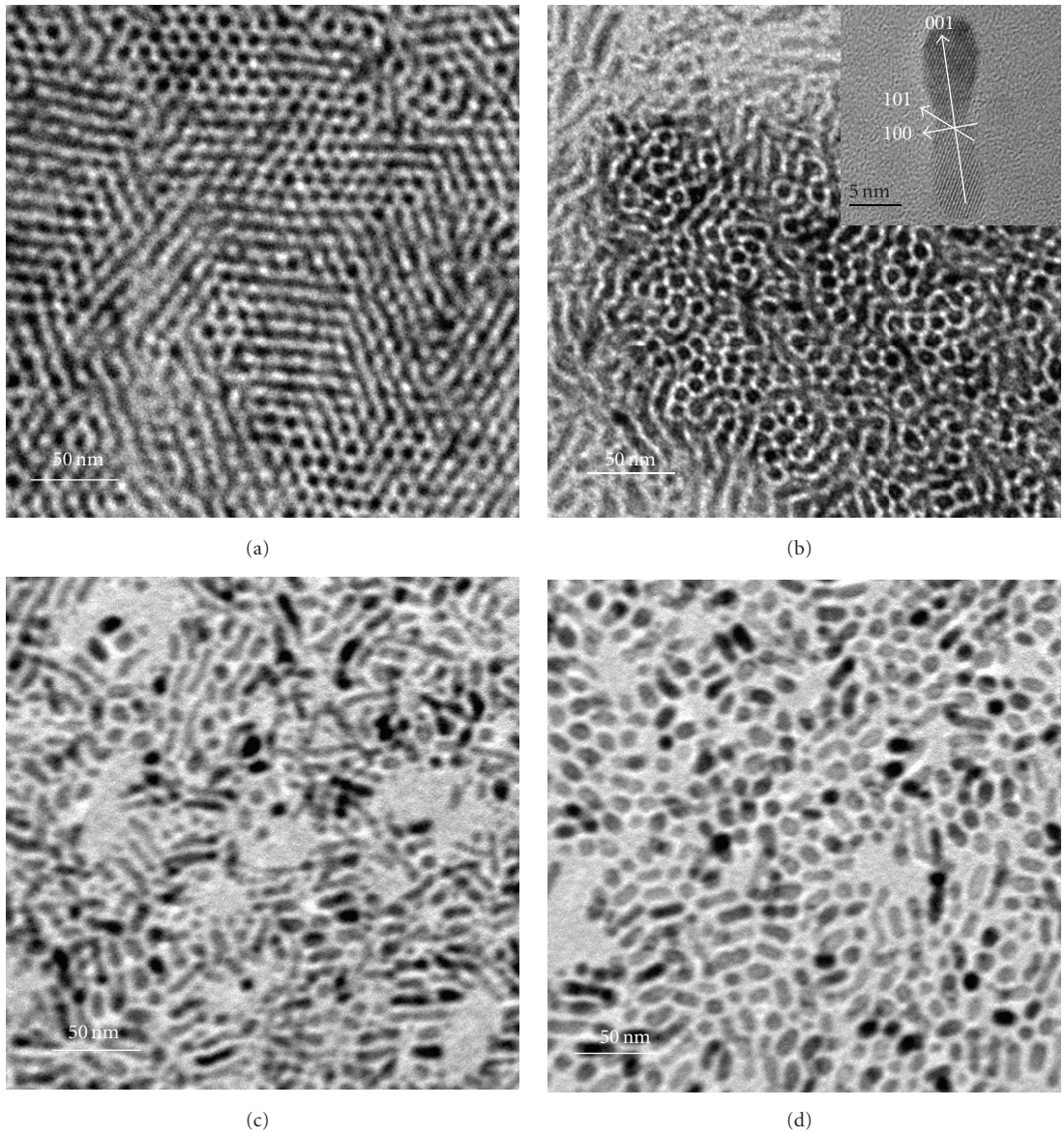

Figure 4: TEM images and HRTEM images of TiO_2 nanocrystals synthesized at 240°C for different time: (a) 0.5 hours; (b) 2 hours; (c) 4 hours; (d) 17 hours.

a JEM-200CX operating at 160 kV. The size distribution is obtained from TEM which contain thousands of nanocrystals using Scnimage, Photoshop and Origin software. For TEM and HRTEM specimen preparation, the products were redispersed in hexane and dried on the carbon-coated copper grid at room temperature before performance.

3. Result and Discussion

3.1. TiO_2 Nanocrystals Synthesis at 300°C. Figure 1 represents the TEM image of the TiO_2 nanocrystals prepared by microemulsion-solvothermal method for different time at 300°C. Several special shapes of TiO_2 nanocrystals including sphere, polygon and rhombus were obtained at this temperature. Figure 1(a) shows the TEM images of TiO_2 nanocrystals with sphere and smaller nanorods prepared at 300°C for 0.5 hours. Figure 1(b) shows the TEM and HRTEM images for nanocrystals with sphere shape prepared at 300°C for 2 hours. The TiO_2 nanocrystals are nearly close-packed and atomic lattice structure are clearly observed in HRTEM. Figures 1(c) and 1(d) shows the TEM and HRTEM images of TiO_2 nanocrystals with polygon and rhombus prepared at 300°C for 4 hours and 17 hours, respectively. Anisotropic crystal growth for TiO_2 nanocrystals could be observed from the HRTEM image of Figure 1(d). The growth rate in the (001) direction is much faster than those in other directions. Figure 2(b) shows the XRD pattern of this kind of TiO2 nanocrystals. Compared with the standard spectrum of anatase titanium dioxide shown in Figure 2(a), the main peaks corresponding to anatase TiO_2 including (101), (004),

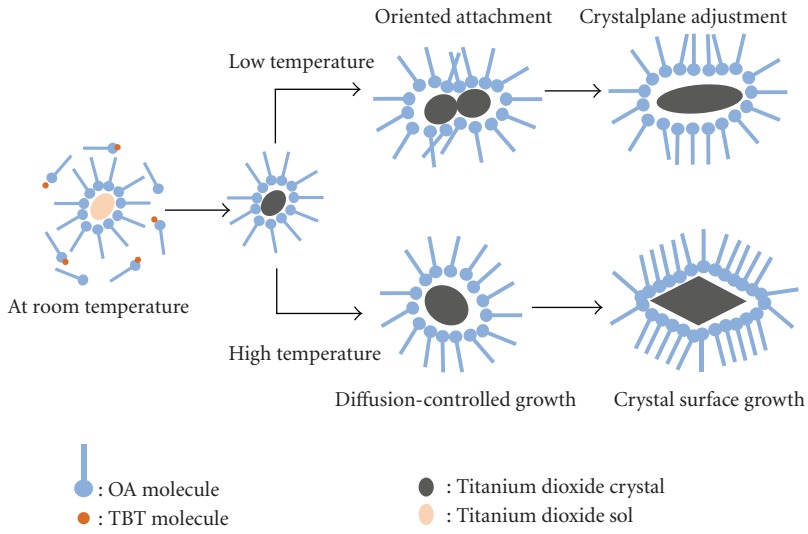

Figure 5: Schematic process on the nucleation and growth of the TiO_2 nanocrystals.

(200), (105), (211) and (204) are observed. The result is consistent with the XRD pattern of TiO_2 samples with 13 nm diameters reported by Niederberger [17]. In order to study the homogeneity of the nanocrystalline, we assume that these nanocrystals are spherical. The software can be used to calculate area of each nanocrysatals, and then the distribution of nanocrystals can be geted by the corresponding diameter. The size distribution of TiO_2 nanocrystals prepared at 300°C for different hours are also present in Figure 3. As the time increased, the average diameter of TiO_2 nanocrystals become larger and the particle size distribution become less uniform.

3.2. TiO_2 Nanocrystals Synthesis at 240°C. Figure 4 represents the TEM image of the TiO_2 nanocrystals by microemulsion-solvothermal method for different time at 240°C. Sphere and rod shapes of TiO_2 nanocrystals were obtained. Figure 4(a) shows a number of spherical nanocrystals prepared at 240°C for 0.5 hours. The spherical nanocrystals were combined together. A similar phenomenon could be seen more clearly in Figure 4(b) which shows TEM images of TiO_2 nanocrystals prepared at 240°C for 2 hours. Lots of nanorods rather than nanodots are also found in Figure 4(b) and a nanorod is chosen for HRTEM analysis. The nanorod is around 25 nm long and 6 nm wide and it can be seen as a combination of two smaller nanorods along (001) direction. Figures 4(c) and 4(d) shows the TEM images of TiO_2 nanorods at 240°C for 4 hours and 17 hours, respectively. More nanorods could be observed as the time increased, sphere nanocrystals disappeared for 17 hours. Figure 2(c) presents the XRD pattern of the TiO_2 nanorods at 240°C. The main peaks indicate the highly anatase1 crystalline structure of the TiO_2. Compared with Figure 2(b), the main peaks is quite broad, That represents the value of degree of crystallization synthesized at 240°C is much lower than that synthesized at 300°C.

3.3. The Shape Change Process of TiO_2 Nanocrystals. Figure 5 shows schematic process on the shape changes of the TiO_2 nanocrystals. It could be described as follows. In the presence of OA, reverse micelles are easily formed in nonaqueous media after a water drop. Moreover, TBT reacts with water in reverse micelles vigorously. As a result, spherical titanium dioxide sol micelles are formed at room temperature after water added. This process takes a long time along with the hydrolysis reaction. As the temperature is increased, the sol evolves will quickly transform into nanocrystalline, leading to the formation of small TiO_2 nanodots. When the reaction temperature is set at 300°C, due to the rapid nucleation of reactive intermediates, the TiO_2 nanodots will grow in a diffusion-control pattern, leading to the formation of spherical TiO_2 nanocrystals. With the extension of reaction time, the crystal surface energy will play a more important role for the shape of TiO_2 nanocrystals. Due to high surface energy of the {001} face [18], the spherical TiO_2 nanocrystals generated at the initial reaction stage grow along (001) direction. As a result, the spherical nanocrystals are easily transformed into polygon prismatic nanocrystals. As the nanocrystals grow along (001) direction, the specific surface area of TiO_2 nanocrystals along (001) direction is gradually lower, leading to two-dimensional growth of TiO_2 nanocrystals. Because the surface energy of the {100} face is higher than that of the {101} face, the shape of TiO_2 nanocrystals finally transform into rhombus with a further extension of time. When the reaction temperature is set at 240°C, the reaction rate of reactive intermediates decreases. As a result, the TiO_2 nanodots are easy to assemble together to form nano-rods by a kind of oriented attachment mechanism. The oriented attachment mechanism has been reported for a variety of metal oxide system [19, 20]. It is said that the oriented attachment between several sphere shaped nanocrystals makes the reduction of surface energy (it is ususlly observed in (001) direction because of high surface energy along (001) direction). Therefore

more stable rod shaped nanocrystals are formed at low temperature. These are our correlation analysis on the basis of experimental result, some detailed formation process of the TiO_2 nanocrystals still needs to be investigated further.

4. Conclusion

The anatase TiO_2 nanocrystals of different shapes have been successfully synthesized by microemulsion-solvothermal method using a new microemulsion system prepared by OA, TBT and H_2O. The sphere, polygon and rhombus shaped nanocrystals have been prepared at 300°C for 2 hours, 4 hours and 17 hours, respectively. and the dot and rod shaped nanocrystals has been synthesized at 240°C for 0.5 hours and 17 hours. The result indicates that the shape of TiO_2 nanocrystals could change from dot to sphere, polygon, rhombus at 300°C, and it could also change from dot to rod at 240°C with the increase of reaction time. This microemulsion-solvothermal method could provide another new way for the synthesis and control of other nanocrystals with some special morphology.

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References

[1] H. Jia, Z. Zheng, H. Zhao, L. Zhang, and Z. Zou, "Nonaqueous sol-gel synthesis and growth mechanism of single crystalline TiO_2 nanorods with high photocatalytic activity," *Materials Research Bulletin*, vol. 44, no. 6, pp. 1312–1316, 2009.

[2] 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.

[3] 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.

[4] 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.

[5] 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.

[6] 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.

[7] 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.

[8] X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications and applications," *Chemical Reviews*, vol. 107, no. 7, pp. 2891–2959, 2007.

[9] M. Cao, X. Wu, X. He, and C. Hu, "Microemulsion-mediated solvothermal synthesis of SrCO3 nanostructures," *Langmuir*, vol. 21, no. 13, pp. 6093–6096, 2005.

[10] M. Cao, Y. Wang, C. Guo, Y. Qi, and C. Hu, "Preparation of ultrahigh-aspect-ratio hydroxyapatite nanofibers in reverse micelles under hydrothermal conditions," *Langmuir*, vol. 20, no. 11, pp. 4784–4786, 2004.

[11] M. Cao, C. Hu, and E. Wang, "The first fluoride one-dimensional nanostructures: microemulsion-mediated hydrothermal synthesis of BaF2 whiskers," *Journal of the American Chemical Society*, vol. 125, no. 37, pp. 11196–11197, 2003.

[12] K. Lin, J. Chang, and J. Lu, "Synthesis of wollastonite nanowires via hydrothermal microemulsion methods," *Materials Letters*, vol. 60, no. 24, pp. 3007–3010, 2006.

[13] W. Liu, W. Zhong, X. Wu, N. Tang, and Y. Du, "Hydrothermal microemulsion synthesis of cobalt nanorods and self-assembly into square-shaped nanostructures," *Journal of Crystal Growth*, vol. 284, no. 3-4, pp. 446–452, 2005.

[14] M. Cao, X. He, X. Wu, and C. Hu, "Microemulsion-based solvothermal synthesis of aluminium orthophosphate nanocrystals," *Nanotechnology*, vol. 16, no. 10, pp. 2129–2133, 2005.

[15] J. Xiang, S.-H. Yu, B. Liu, Y. Xu, X. Gen, and L. Ren, "Shape controlled synthesis of PbS nanocrystals by a solvothermal-microemulsion approach," *Inorganic Chemistry Communications*, vol. 7, no. 4, pp. 572–575, 2004.

[16] P. Zhang and L. Gao, "Synthesis and characterization of CdS nanorods via hydrothermal microemulsion," *Langmuir*, vol. 19, no. 1, pp. 208–210, 2003.

[17] M. Niederberger, M. H. Bartl, and G. D. Stucky, "Benzyl alcohol and titanium tetrachloride—a versatile reaction system for the nonaqueous and low-temperature preparation of crystalline and luminescent titania nanoparticles," *Chemistry of Materials*, vol. 14, no. 10, pp. 4364–4370, 2002.

[18] M. Adachi, Y. Murata, J. Takao, J. Jiu, M. Sakamoto, and F. Wang, "Highly efficient dye-sensitized solar cells with a titania thin-film electrode composed of a network structure of single-crystal-like TiO_2 nanowires made by the oriented attachment mechanism," *Journal of the American Chemical Society*, vol. 126, no. 45, pp. 14943–14949, 2004.

[19] D.-F. Zhang, L.-D. Sun, J.-L. Yin, and C.-H. Yan, "Low-temperature fabrication of highly crystalline SnO_2 nanorods," *Advanced Materials*, vol. 15, no. 12, pp. 1022–1025, 2003.

[20] C. Pacholski, A. Kornowski, and H. Weller, "Self-assembly of ZnO: from nanodots to nanorods," *Angewandte Chemie. International Edition*, vol. 41, no. 7, pp. 1188–1191, 2002.