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Controllable Synthesis of TiO_2 Submicrospheres with Smooth or Rough Surface

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Titanium dioxide (TiO_2) submicrospheres (SMs) have been successfully synthesized via a solvothermal method by hydrolysis of tetrabutyl titanate in ethanol solution with the cetyltrimethylammonium bromide (CTAB) presented. The SMs are composed of closely packed rod or tetragonal nanoparticles (NPs), and the inner structure of SMs depends on whether the hexamethylenetetramine (HMTA) was introduced in the reaction or not. The surface and inner morphologies, structure, and optical properties of the SMs were investigated.

Though enormous progress has been made in fabricating transition metal oxide nanocrystals with controllable morphologies, it is still a key goal in modern materials chemistry and has attracted substantial interests in recent years.[1] As an important wide-band gap semiconductor ($E_g = 3.2\,\text{eV}$), TiO_2 has attracted intensive attention because of outstanding physicochemical properties and broad applications in photocatalysts, water splitting, and gas sensors.[2] Generally, different applications require different morphologies, crystallinity, and size of TiO_2 nanomaterials.

Recently, controlling the microscopic morphology of TiO_2 nanomaterials is feasible and further tailoring the corresponding properties as a function of the nanomaterials is widely studied. Up to now, various TiO_2 nanostructures such as hollow spheres, nanotubes, and porous structures have been synthesized.[3] Among these, several synthetic routes including chemical and physical methods for generating various TiO_2 nanomaterials have been developed.[4] As a competitive alternative, solvothermal methods have been extensively used to generate novel materials with unusual properties due to avoiding the presence of water for water-sensitive reactions. It has been employed to synthesize various TiO_2 nanomaterials with controlled shape.[5] For instance, Nam and Han investigated the preparation of TiO_2 by solvothermal reaction of titanium tetraisopropoxide in different alcohol solvents. The results show that the physical properties of the products, such as crystal size, shape, and structure, are strongly influenced by the types of solvents used during the reaction.[6] Herein, we present a controllable synthesis route for preparing TiO_2 SMs with different surface morphologies by a mild solvothermal method. As shown in Figure 1, the internal structure and external morphology of TiO_2 SMs are significantly influenced by a weak organic alkali, HMTA.[11] This strategy offers an effective approach for preparation of TiO_2 SMs or other metal oxide nanomaterials to meet different applications.

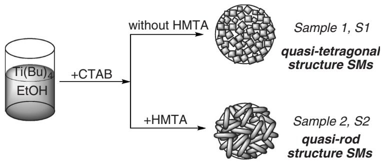

Figure 1. Schematic diagram for the formation of TiO_2 SMs.

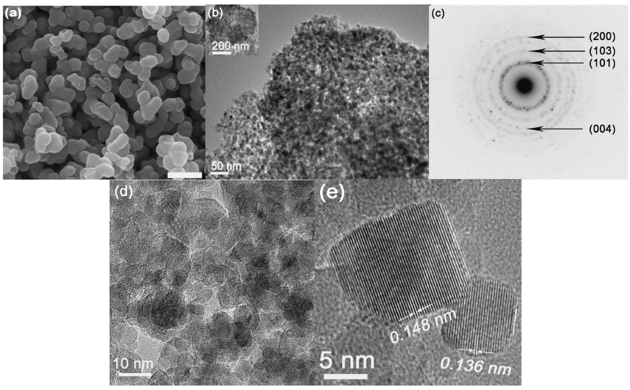

Figure 2. FESEM (a, scale bar is 1 μm) and TEM images (b, the insert at low magnification), SAED patterns (c), and HRTEM images at different magnification (d, e) of S1 SMs.

Figure 2a shows field emission scanning electron microscopy (FESEM) image of S1 SMs. Uniform spheral crystals of nanometer-size are almost the exclusive products in our synthesis. Transmission electron microscopy (TEM) (Figure 2b) clearly shows that those SMs are spherical with a diameter of ca. 400 nm and a composition of closely packed small NPs. The selected area electron diffraction (SAED) pattern in Figure 2c reveals the polycrystalline features of the samples, these patterns agree well with the structure of anatase. The corresponding high-resolution TEM (HRTEM) image (Figure 2d) clearly shows that many quasi-tetragonal TiO_2 nanocrystals with an edge length from 10 and 20 nm were packaged in the SMs. Moreover, these NPs have obvious preferential lattice orientation and display good crystallinity; inspection of the particles at high magnification indicates that each particle is a well-ordered single crystal, as shown in Figure 2e. Measuring the distance between two adjacent lattice fringes gives values of 0.148 and 0.136 nm, which correspond to the lattice spacing of (204) and (116) planes of anatase TiO_2, respectively. The results further confirmed that the SMs consist of small quasi-tetragonal TiO_2 NPs with different preferential orientations, and it presents polycrystalline features on the whole.

The morphology of S2 was investigated by electron microscopy observations when the HMTA was added to the reaction. The FESEM image (Figure 3a) illustrated that the

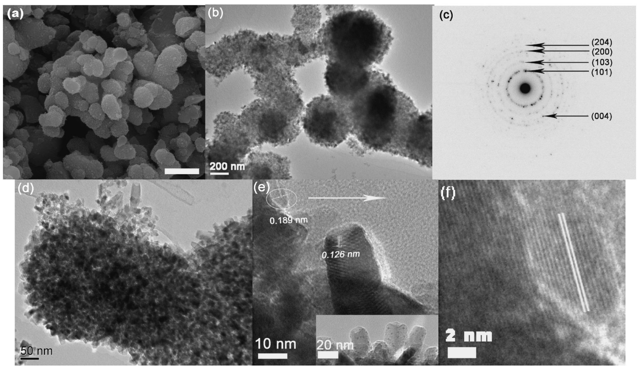

Figure 3. FESEM (a, scale bar is 1 µm) and TEM images (the insert at low magnification) (b), SAED patterns (c), and HRTEM images at different magnification (d–f) of S2 SMs.

surface of S2 is rougher than that of S1 SMs. Figure 3b shows a low-magnification TEM image of S2 SMs, it can be seen that the size is about 250 to 400 nm. The SAED pattern (Figure 3c) reveals the polycrystalline features of the samples, and their patterns agree well with the structure planes of anatase. Figures 3d and 3e show the HRTEM image of the edge on the TiO_2 SMs, it is clearly seen that 20 nm in diameter and 50 nm in length rod-like NPs were packed in the SMs. The HRTEM image, which was recorded from the edge of the TiO_2 SMs, exhibits good crystallinity. Measuring the distance between two adjacent lattice fringes (Figure 3e) gives values of 0.189 and 0.126 nm, which corresponds to the lattice spacing of (200) and (215) planes of anatase TiO_2, respectively. It is seen that the lattice planes of the depicted particles are almost perfectly aligned (Figure 3f). This further confirms the SMs with rough surface, and it consists of small rod-like TiO_2 NPs with different preferential orientations.

The use of HMTA is reported widely in the growth of acicular ZnO nanorods.[7] The HMTA hydrolyzes to form ammonia and formaldehyde above 70 °C. Meanwhile, OH^- concentration increases because of the hydrolysis of HMTA. Some possible Ti-coordination complexes will form in reaction solution, act as nuclei, and finally produce quasi-rod structure; further detailed studies on the formation mechanism of the SMs are currently in progress.

The structure of SMs is confirmed by powder X-ray diffraction (XRD), as shown in Figure 4a; the reflection peaks coinciding with the (101), (004), (200), (211), (204), and (215) planes have been assigned to pure anatase phase TiO_2 (JCPDS PDF 21-1272). Moreover, the XRD patterns measured from the S1 and S2 clearly show the differences in the peak width and intensity. Additionally, the Debye–Scherrer formula $D_{hkl} = k\lambda/\beta\cos\theta$ was used to estimate an average crystallite size of samples from the XRD patterns.[8] It is obvious that the diameter of S2 is larger than that of S1 sample because of the compared results of FWHM. Furthermore, calculations using strongest peaks (101) give grains sizes of 8.7 and 23.4 nm, respectively, which are comparable to the HRTEM results and reveal that many small NPs were closely packed in the SMs. The redispersed dried TiO_2 samples were further characterized by UV–vis absorption spectra to compare their optical properties (Figure 4b). No obvious differences between the S1 and S2 can be observed, and the spectra show a strong adsorption in the UV region, the results are in agreement with other reports.[9] It is noteworthy that the different inner morphology in the TiO_2 SMs will cause the different adsorption intensity (the same concentration). Some light would be reflected when UV light illuminated onto SMs with a smooth shell, and the rough shell can absorb more light because the UV–vis light can have multiple-reflections among the quasi-rods, as schematically outlined in the insert of Figure 4b.[10]

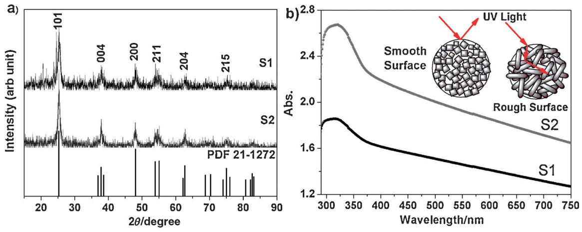

Figure 4. Typical XRD patterns and UV–vis absorbance spectra of S1 and S2 SMs.

In summary, TiO_2 SMs with smooth and rough surface were prepared successfully by a mild solvothermal method. The inner structure and external morphology can be mediated by HMTA. The method makes possible the production of various SMs with different inner structure and surface morphology for meeting different applications.

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References and Notes

1 a) W. Wu, Q. G. He, C. Z. Jiang, *Nanoscale Res. Lett.* **2008**, *3*, 397. b) W. Wu, X. H. Xiao, T. C. Peng, C. Z. Jiang, *Chem. Asian J.* **2010**, *5*, 315.

2 a) C. X. Wang, L. W. Yin, L. Y. Zhang, L. Kang, X. F. Wang, R. Gao, *J. Phys. Chem. C* **2009**, *113*, 4008. b) E. S. Kwak, W. Lee, N.-G. Park, J. Kim, H. Lee, *Adv. Funct. Mater.* **2009**, *19*, 1093.

3 a) T. H. Eun, S.-H. Kim, W.-J. Jeong, S.-J. Jeon, S.-H. Kim, S.-M. Yang, *Chem. Mater.* **2009**, *21*, 201. b) T. Berger, J. M. Delgado, T. Lana-Villarreal, A. Rodes, R. Gomez, *Langmuir* **2008**, *24*, 14035.

4 X. Chen, S. S. Mao, *Chem. Rev.* **2007**, *107*, 2891.

5 Z. B. Wu, Z. L. Gu, W. R. Zhao, H. Q. Wang, *Chin. Sci. Bull.* **2007**, *52*, 3061.

6 W. S. Nam, G. Y. Han, *Korean J. Chem. Eng.* **2003**, *20*, 1149.

7 a) K. Govender, D. S. Boyle, P. B. Kenway, P. O'Brien, *J. Mater. Chem.* **2004**, *14*, 2575. b) Q. C. Li, V. Kumar, Y. Li, H. T. Zhang, T. J. Marks, R. P. H. Chang, *Chem. Mater.* **2005**, *17*, 1001.

8 In which D_{hkl} is the particle size parallel to the (hkl) plane, k is a geometrical constant with a typical value of 0.89 for a spherical particles, λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) in radians, and θ is the position of the diffraction peak.

9 a) A. M. More, T. P. Gujar, J. L. Gunjakar, C. D. Lokhande, O.-S. Joo, *Appl. Surf. Sci.* **2008**, *255*, 2682. b) J. T. Park, J. H. Koh, J. K. Koh, J. H. Kim, *Appl. Surf. Sci.* **2009**, *255*, 3739.

10 X. W. Zhang, J. H. Pan, A. J. Du, S. P. Xu, D. D. Sun, *J. Photochem. Photobiol., A* **2009**, *204*, 154.

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