COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Shape control of anatase TiO_2 nanoparticles by amino acids in a gel–sol system†

Kiyoshi Kanie and Tadao Sugimoto*
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aobaku, Sendai 980-8577, Japan. E-mail: sugimoto@tagen.tohoku.ac.jp; Fax: +81-22-217-5153; Tel: +81-22-217-5153

Received (in Cambridge, UK) 19th March 2004, Accepted 18th May 2004
First published as an Advance Article on the web 17th June 2004

Ellipsoidal anatase TiO_2 nanoparticles of different aspect ratios were obtained by the gel–sol method in the presence of amino acids in which the resulting particles were basically single crystals, but highly rough surfaces or partly polycrystalline structures were observed with a high concentration of glutamic acid or aspartic acid.

The gel–sol method for the preparation of uniform particles in large quantities was first developed for the preparation of monodispersed pseudocubic hematite particles from ferric hydroxide gel.[1] Since the pseudocubic monodispersed hematite sol was transformed from the ferric hydroxide gel as a precursor solid, the procedure was denoted the "gel–sol method".[1,2] Thus, this method is based on a concept essentially reverse to the original sol–gel process, in which a sol as a dispersion of particles is precipitated first and then it turns into a continuous gel. The gel–sol method was found to have an advantage not only for the production of monodispersed particles in a simple process, but also for controlling their mean size and shape in a facile manner. For example, monodispersed ellipsoidal,[3] peanut-type,[3,4] and platelet-type[5] hematite particles of different sizes were fabricated in addition to the pseudocubes. With the progress of the gel–sol process many kinds of monodispersed particles have been produced by now.[2] In particular, we have proposed a new gel–sol procedure for the preparation of uniform anatase TiO_2 particles of different shapes such as ellipsoidal and cubes from a rigid $Ti(OH)_4$ gel with shape controllers.[6,7] This process consists of a first aging of 0.25 mol L^{-1} $Ti(TEOA)_2$ (TEOA: triethanolamine) complex with a given concentration of a shape controller for the formation of a rigid $Ti(OH)_4$ gel at 100 °C for 24 h and a second aging for nucleation and growth of anatase TiO_2 particles in the gel at 140 °C for 72 h. In this system, ammonia and primary amines as shape controllers were found to yield ellipsoidal particles by their specific adsorption to the crystal planes parallel to the *c*-axis of a TiO_2 particle, while sodium oleate and stearate produced cubic particles with sharp corners and edges. The objective of the present study is to report the effect of amino acids as a strong adsorptive to TiO_2[8] on the shape of anatase TiO_2 particles prepared in the gel–sol system in the presence of TEOA. The procedure was basically the same as in refs. 6 and 7 except that the concentration of $Ti(TEOA)_2$ complex was 0.10 mol L^{-1}. A schematic illustration of the gel–sol process is shown in Fig. 1. Further information on experimental details is provided as ESI.†

First, we examined the effect of the initial pH on the shape of the TiO_2 particles obtained in the absence or presence of glutamic acid (**GL**, 0.020 M). The particle shape turned into ellipsoidal above pH 10.5 even in the absence of **GL** owing to the specific adsorption of TEOA commonly included in all present systems. However, in the presence of **GL**, ellipsoids with a much higher aspect ratio were obtained at the same alkaline condition. In neutral and acidic media, we obtained cuboidal particles with rather round corners and edges in both systems with and without **GL**, because the adsorption of TEOA and **GL** to TiO_2 was negligible or extremely weak.[7,8] Fig. 2 shows TEM images of TiO_2 nanoparticles prepared at an initial pH of 10.5 in the absence (a) or presence of 0.020 M amino acids, including glycine (b), serine (c), lysine (d), aspartic acid (**AS**) (e), and **GL** (f). All of these particles were confirmed to be anatase TiO_2 particles by X-ray diffraction (XRD) analysis. Although the neutral amino acids such as glycine and serine and basic amino acid, lysine, slightly changed the shape of the particles from spindly to rod-like, their effect on the aspect ratio was rather small. On the other hand, acidic amino acids such as **AS** and **GL** were likely to yield spindly particles of a large aspect ratio. Since the amino groups of an amino acid seem to be responsible for its adsorption to TiO_2 particles, it is

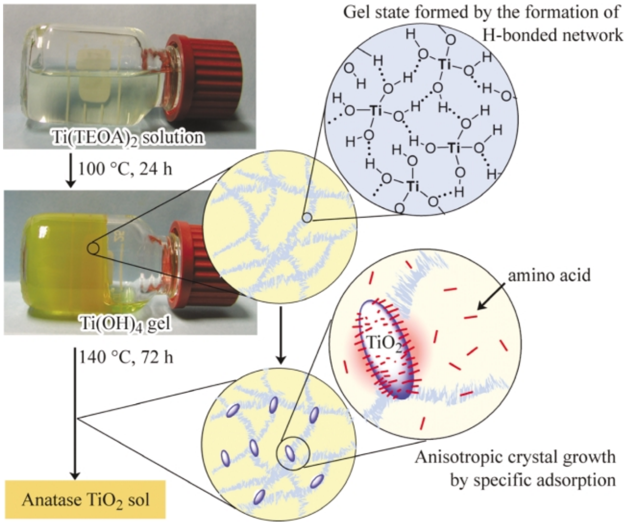

Fig. 1 Schematic illustration for the formation of anatase TiO_2 particles by the gel–sol method.

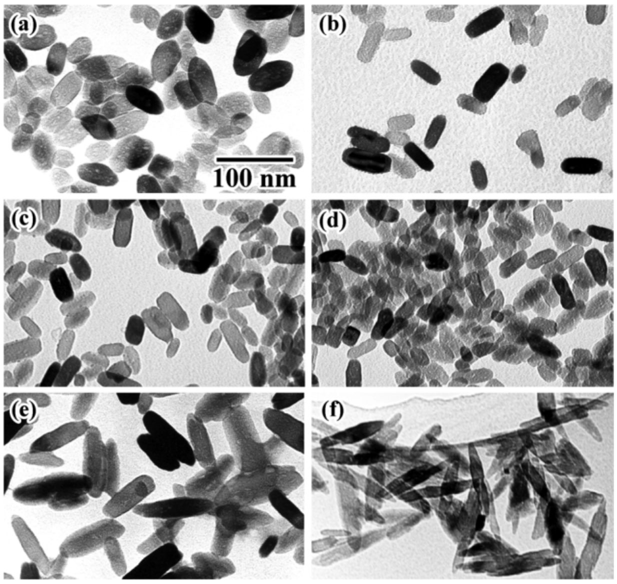

Fig. 2 TEM images of TiO_2 particles obtained by the gel–sol method without amino acid (a) and in the presence of 0.020 M glycine (b), serine (c), lysine (d), **AS** (e) and **GL** (f). The scale bar in (a) is common for all images.

---

† Electronic supplementary information (ESI) available: Experimental details and further TEM images. See http://www.rsc.org/suppdata/cc/b4/b404220d/

DOI: 10.1039/b404220d

reasonable that the adsorption increases with increasing pH and that the adsorption of lysine to amorphous TiO_2 particles is much stronger than **GL**, as found by Tentorio and Canova.[8] Nevertheless, the high aspect ratio of the anatase TiO_2 particles obtained with **AS** and **GL** in the present study may suggest a possibility of specific adsorption of these acidic amino acids to the crystal planes parallel to the *c*-axis of the tetragonal crystal system, rather stronger than the adsorption of the neutral and basic amino acids. For elucidation of this mechanism more detailed studies are needed.

Fig. 3 shows the effect of the concentrations of **AS** and **GL** on the shape of anatase TiO_2 particles. In this figure the ellipsoidal TiO_2 particles are clearly distinguished from the remaining amorphous $Ti(OH)_4$ gel network of undefined structure. TEM images of TiO_2 particles demonstrate that the phase transformation from $Ti(OH)_4$ gel to TiO_2 particles is retarded with increasing concentrations of these amino acids. However, if we prolong the aging times, the reaction can be completed. For example, while the reaction is finished within 1 day without **GL** at pH 10.5, it takes *ca.* 2 days with 0.010 M **GL** and *ca.* 6 days with 0.040 M **GL** for the completion of the reaction. If the concentrations of the amino acids is raised further, the reaction does not finish even after one week. In addition, the final particle volume was increased by extending the aging time, but the growth rate in the *c*-axis was hardly affected by an increase in the concentration of the amino acids. Similar trends were observed with ammonia[6] and primary amines.[7] It is obvious from these observations that the retarded phase transformation with the increase in the concentration of the amino acids is due to the inhibition of nucleation of TiO_2 by their adsorption to the embryos of the nuclei of TiO_2.[7] The increase in aspect ratio of the final product particles with increasing concentration of the amino acids must be due to the pronounced anisotropy by the promoted specific adsorption to the crystal planes parallel to the *c*-axis. Fig. 4 shows high-resolution TEM (HRTEM) images and the electron diffraction (ED) spots of the TiO_2 particles in Fig. 3(b), (c), Fig. 2(f), and Fig. 3(f), respectively. The crystal structure of the ellipsoidal TiO_2 particles was basically monocrystalline with the rotation axis in accord with the *c*-axis of the tetragonal system, as shown in Fig. 4. This is consistent with our finding for the ellipsoidal anatase TiO_2 particles controlled in shape with ammonia.[6] However, the surface structure was found to become rough and partly polycrystalline, when the concentration of amino acids was excessively high, as observed in Fig. 4(b), (c) and (d). This seems to be due to the formation of dents, valleys, or crevices as a result of the locally clustered adsorption of the amino acid molecules on the growing surfaces of the TiO_2 particles.

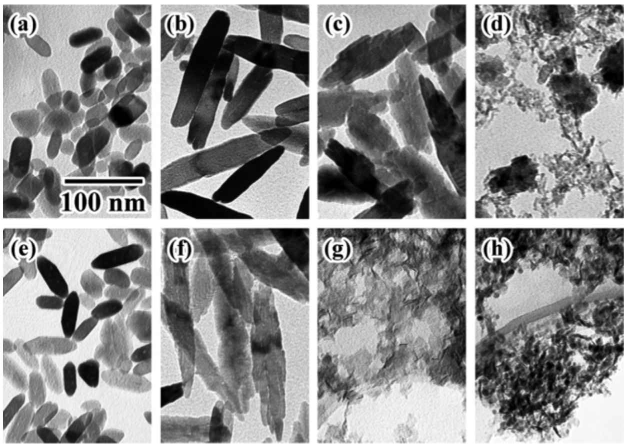

Fig. 3 TEM photographs of TiO_2 particles: (a) 0.010 M **AS**, 3 d; (b) 0.040 M **AS**, 3 d; (c) 0.060 M **AS**, 7 d; (d) 0.080 M **AS**, 7 d; (e) 0.010 M **GL**, 3 d; (f) 0.040 M **GL**, 6 d; (g) 0.060 M **GL**, 7 d; (h) 0.080 M **GL**, 7 d. The scale bar in (a) is common for all images.

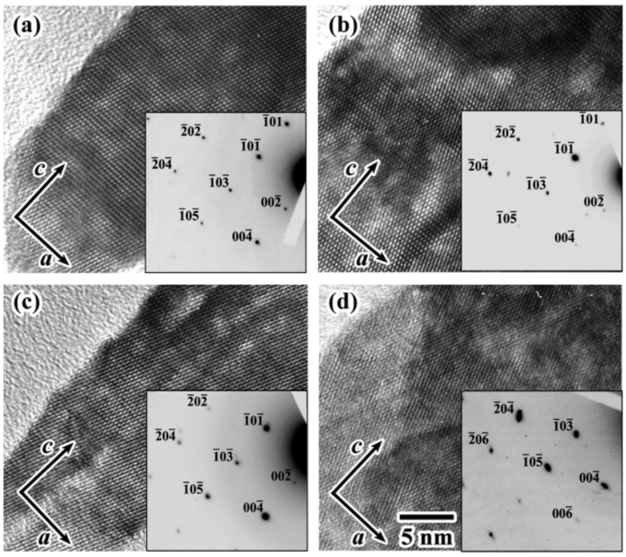

Fig. 4 HRTEM and ED images of TiO_2 particles: (a) 0.040 M **AS**, 3 d; (b) 0.060 M **AS**, 7 d; (c) 0.020 M **GL**, 3 d; (d) 0.040 M **GL**, 6 d. The scale bar in (d) is common for all images.

The shape control of TiO_2 particles progressively increases its importance as functional nanoparticles.[9] For example, shape control is equivalent to the control of the crystal facets, and is a decisive factor for functional semiconductors[10,11] and catalysts.[2] If the TiO_2 particles are used as a catalyst or a support for noble metal catalysts, then surface roughness is a desirable characteristic. Moreover, it has recently been found that a novel organic–inorganic hybrid liquid crystal with anisotropic TiO_2 nanoparticles could be fabricated only with ellipsoidal anatase TiO_2 particles of a high aspect ratio.[12] Therefore, it may be readily understood that the precise control of the morphology of functional nanoparticles is one of the most important techniques in modern nanotechnology.

References

1 T. Sugimoto and K. Sakata, *J. Colloid Interface Sci.*, 1992, **152**, 587; T. Sugimoto, K. Sakata and A. Muramatsu, *J. Colloid Interface Sci.*, 1993, **159**, 372.
2 T. Sugimoto, *Monodispersed Particles*, Elsevier, Amsterdam, 2001; T. Sugimoto, *Chem. Eng. Technol.*, 2003, **26**, 313.
3 T. Sugimoto, M. M. Khan and A. Muramatsu, *Colloid Surf. A*, 1993, **70**, 167.
4 T. Sugimoto, M. M. Khan, A. Muramatsu and H. Itoh, *Colloid Surf. A*, 1993, **79**, 233.
5 T. Sugimoto, S. Waki, H. Itoh and A. Muramatsu, *Colloid Surf. A*, 1996, **109**, 155.
6 T. Sugimoto, K. Okada and H. Itoh, *J. Colloid Interface Sci.*, 1997, **193**, 140; T. Sugimoto, K. Okada and H. Itoh, *J. Dispersion Sci. Technol.*, 1998, **19**, 143.
7 T. Sugimoto, X. Zhou and A. Muramatsu, *J. Colloid Interface Sci.*, 2002, **252**, 339; T. Sugimoto and X. Zhou, *J. Colloid Interface Sci.*, 2002, **252**, 347; T. Sugimoto, X. Zhou and A. Muramatsu, *J. Colloid Interface Sci.*, 2003, **259**, 43; T. Sugimoto, X. Zhou and A. Muramatsu, *J. Colloid Interface Sci.*, 2003, **259**, 53.
8 A. Tentorio and L. Canova, *Colloid Surf.*, 1989, **39**, 311.
9 S.-M. Lee, S.-N. Cho and J. Cheon, *Adv. Mater.*, 2003, **15**, 441; Y.-W. Jun, M. F. Casula, J.-H. Sim, S. Y. Kim, J. Cheon and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2003, **125**, 15981.
10 J. Hu, L.-S. Li, W. Yang, L. Manna, L.-W. Wang and A. P. Alivisatos, *Science*, 2001, **292**, 2060.
11 U. Diebold, *Surf. Sci.*, 2003, **48**, 53.
12 K. Kanie and T. Sugimoto, *J. Am. Chem. Soc.*, 2003, **125**, 10518.