Synthesis of single-phase anatase nanocrystallites at near room temperatures

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Received (in Cambridge, UK) 15th December 2004, Accepted 22nd February 2005
First published as an Advance Article on the web 9th March 2005
DOI: 10.1039/b418821g

Single-phase aqueous solutions of nanocrystalline anatase titanium dioxide were produced under ambient pressure and at a temperature as low as 38 °C using the sol-gel process.

In recent years, nanocrystalline titanium dioxide has attracted increasing attention due to its fascinating properties and potential applications, *e.g.* photocatalysts,[1–3] photovoltaics,[4] gas sensors,[5] and electrochromic display devices.[6,7] Nanosized TiO_2 particles show high photocatalytic activities because they have a large surface area per unit mass and volume and hence facilitate the diffusion of excited electrons and holes towards the surface before their recombination.[8] Among the crystalline phases of TiO_2, anatase is reported to have the highest activity.[2] Several techniques such as sol-gel,[4] flame spray pyrolysis,[9] chemical vapor deposition,[10,11] pulsed laser deposition,[12] ion-assisted electron beam evaporation,[13] and atomic layer deposition[14,15] can be used to prepare crystalline titanium dioxide. Among these preparation techniques, the relatively simple sol-gel method is the most widely used. However, the disadvantage of all these techniques is that a high temperature process, usually around 450 °C, is required to produce anatase thin films. The formation of anatase titanium dioxide at low temperatures is important for the fabrication of transparent films on substrates with low heat resistance.

The preparation of anatase films by various low temperature methods such as boiling water of silica titania composites,[16] water vapor,[17] and microwave treatments[18] has been recently reported. Although anatase is the main product in hydrolytic sol-gel synthesis of nanocrystalline titania, brookite (a polymorph type of anatase) is also typically present in the final products. Brookite can be detected by the appearance of its (121) peak in powder X-ray diffraction (XRD) patterns at $2\theta = 30.8°$.[19] In some previous studies, the existence of significant brookite phase was overlooked.[20,21]

Recently, we have successfully grown anatase nanocrystallites from an ethanol-based colloidal sol using a simple hot water treatment at a temperature of 97 °C.[22] However, it is clear that formation of crystalline thin films of advanced materials such as semiconductors, ceramics, or their composites and/or hybrids at near room temperatures *via* wet chemical methods is of great importance, not only from the point of view of energy saving, as annealing post-treatment is avoided, but also for their application in low thermally resistant materials such as plastics, wood, papers, textiles, and biomaterials. Furthermore, to make the whole chemical approach environmentally friendly, the use of aqueous solutions instead of organic solvents is desired.

It has been reported that single-phase anatase can be synthesized by hydrolysis of titanium ethoxide in water at 70 °C.[23] However, Zhang *et al.* showed that careful inspection of Figures 8 and 10 in ref. 23 reveals that their synthesis product was a mixture of brookite and anatase, rather than pure anatase.[24] According to Zhang *et al.*, single-phase anatase could only be obtained by direct heat treatment at 375 °C of amorphous titania prepared at room temperature using the method described in ref. 23. Therefore, improved synthetic routes to produce single-phase nanocrystalline titania at low temperatures are still required.

Anatase nanoparticles with special morphologies were prepared by Chemseddine and Moritz by means of wet chemistry.[25] These nanocrystals were suspended in a solution with extremely dilute titanium concentration (1–12 µmol Ti per liter solution). However, an alternative method is needed to produce large enough quantities of anatase titania for most experimental studies.

More recently, Jung *et al.* have reported that anatase TiO_2 colloids could be prepared at a low temperature of 80 °C using nitric acid peptization of amorphous TiO_2 colloidal sol and freeze drying of the formed product. Nevertheless, brookite was a typical byproduct even after 168 h of peptization time.[26]

Following our recent observations that nucleation of brookite titania crystallites occurred at room temperature in a hydrolytic sol-gel synthesis using acetic acid as a catalyst,[27] we have decided to carry out a systematic study in order to investigate the effect of the acid and preparation temperature on the phase and size of colloidal titania crystallites in a modified preparation method. Thus, the TiO_2 sol was prepared by hydrolysis and condensation of titanium tetraisopropoxide (Aldrich, 97%) in acidic deionized water (0.7% nitric acid) containing ethanol (Riedel de-Haën, 99.8%), and acetic acid (Aldrich, 97%). The mixtures were heated at different temperatures, namely 23 (room temperature), 38, and 58 °C and vigorously stirred for 16 hours. The formed solutions were used to deposit thin films on glass and silicon substrates by spin coating at 1500 rpm for 50 seconds and on cellulosic fibers by dip coating, followed by pressing using a nip pressure of 2.75 kg/cm^2. The formed coating films were first air-dried for 1 hour and then oven dried at 38 °C for 12 hours. Solid titania powder could also be obtained from the corresponding sols by adding adequate amounts of 10% sodium carbonate until precipitation occurred. The formed suspensions were centrifuged twice at 2000 rpm for 3 minutes, followed by removal of the liquid phase. The precipitates were then washed twice with water, ethanol and finally with acetone before being dried in a preheated oven at 38 °C for 12 hours.

XRD (Bruker D8 Advance) examinations of the final products (Fig. 1) showed that CS23 is amorphous as demonstrated by a

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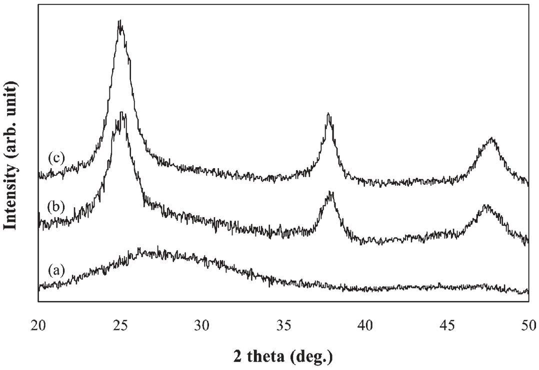

Fig. 1 XRD patterns of solid powder extracted from (a) CS23, (b) CS38, and (c) CS58.

broad peak centered at $2\theta = 26.8°$. On the other hand, anatase-associated peaks were observed in the spectra of CS38 and CS58. The amount of brookite can be quantified by XRD.[28] Careful investigation of the XRD spectra showed no traces of brookite in either CS38 or CS58. Half width analysis of the peak at around 25° was 2.2° for CS38 and 1.6° for CS58, suggesting that anatase crystallites with a smaller size are formed at lower preparation temperatures. Nevertheless, XRD of analogous colloidal solutions prepared without acetic acids showed no anatase-associated peaks. This highlights the role of acid peptization in the stabilization of crystalline TiO_2 at such low temperatures.[23,26]

Atom force microscopy (AFM, Seiko SPI 3800) of thin films deposited from CS38 (Fig. 2a) and CS58 (Fig. 2b) by spin coating on glass revealed a low porosity structure and a spherical morphology of the crystallites. The size of grains in the CS38 film was noticeably smaller (2–3 nm) than that of their counterparts of CS58 (4–5 nm). Aggregation of grains was clearly observed in CS38, suggesting that high tendency of clustering is a characteristic property of very small grains. These observations are consistent

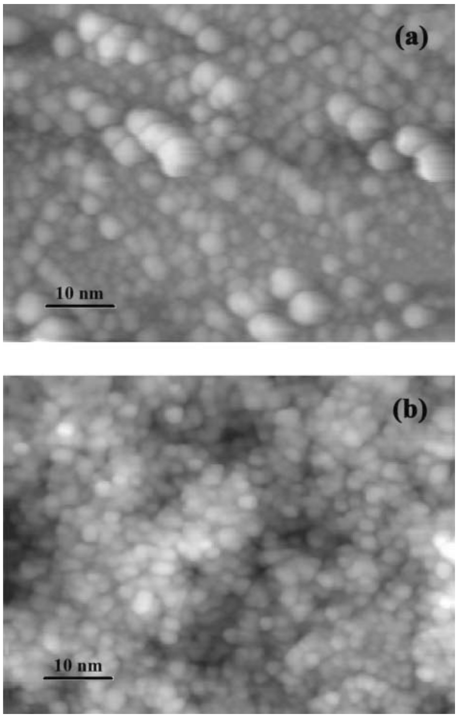

Fig. 2 Tapping AFM micrographs of thin films of (a) CS38 and (b) CS58 coated on glass.

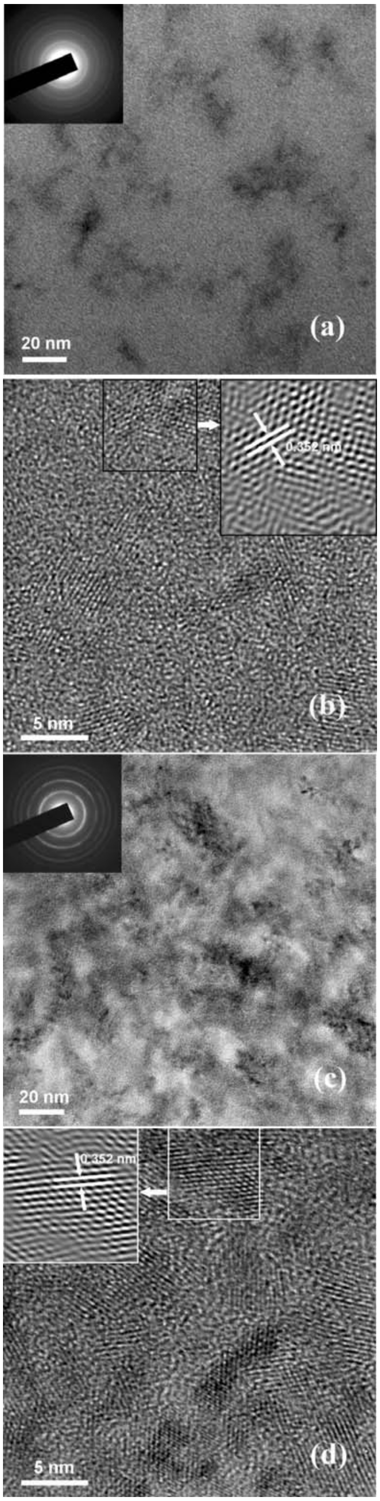

Fig. 3 Plan view TEM micrographs of (a) CS38 at low resolution; inset located on the top left corner is the corresponding selected area electron diffraction (SAED), (b) CS38 at high resolution, (c) CS58 at low resolution; inset located on the top left corner is the corresponding SAED and (d) CS58 at high resolution.

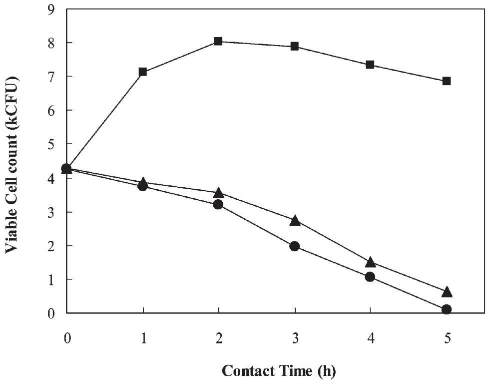

Fig. 4 Viable *SA* cell count as a function of time while in contact with different substrates: pristine cellulosic fibers (■), CS58-coated fibers (▲), and CS38-coated fibers (●). The cell count was determined by the surface-spread method.

with the calculated half width of the 101 peaks of CS38 and CS58 (Fig. 1), confirming that smaller crystallites were formed in CS38. Although such a difference in preparation temperature did not affect the phase of formed crystallites, it did have an effect on their size, suggesting that particle size can be tailored by temperature.

High resolution transmission electron microscopy (HRTEM, JEOL JSM-2010) of CS38 and CS58 (Fig. 3) confirmed earlier observations of phase and size of crystallites. Figs. 3a and 3c are bright field low resolution micrographs of CS38 and CS58, respectively. The insets, located on the top left corner of the images, show the corresponding selected area electron diffraction (SAED). Fig. 3b (CS38) and Fig. 3d (CS58) show lattice fringes with d-spacing of 0.352 nm and interplanar angle of 82.3°, which are characteristic values of the anatase phase. Sharper and more intense Debye–Scherrer rings were observed in Fig. 3c than those in Fig. 3a. This may be attributed to the difference in the size of crystallites as larger crystallites cause the formation of more intense electron diffraction spots. Extra effort was devoted to find any traces of the brookite phase; however nothing could be found, indicating that CS38 and CS58 were purely of the anatase phase.

When organic cellulose fibers, coated with CS38 and CS58, were placed in contact with an inoculum of *Staphylococcus aureus*, a gram-positive type of bacteria, under ambient cool white fluorescent light similar to normal office lighting, substrates coated with CS38 showed greater bactericidal photocatalytic activity than those coated with CS58 (Fig. 4). This may be attributed to a larger specific surface area of CS38 coatings as a result of their smaller crystallites. It is noteworthy to explain the increase of viable cell counts in pristine cellulosic fibers by the fact that cellulosic materials are good media for the growth of bacteria.[29]

As both optoelectronic properties and photocatalytic activity of titanium dioxide strongly depend on the phase and the size of crystallites, it can be here deduced that CS38 offers a promising approach to the ideal phase and size of crystallites that can be prepared using a low energy consumption approach. By avoiding the need for any post-deposition treatment, such colloidal solutions would be applicable to various low thermally resistant materials. This would open up new applications of these materials in fields such as biomembranes and tissues with low thermal resistance as well as in the biomimetic formation of highly integrated biomineral structures.

Financial support for this study was provided by a CERG project (PolyU5289/03E) and the Innovation and Technology fund (ITF) from the government of Hong Kong Special Administrative Region under grant No. K14. 56.ZPOD. We would like to thank Dr X. Po for her assistance with the AFM and Dr G. Pang for kindly supporting the TEM study.

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