STRUCTURE CONTROL AND ITS INFLUENCE ON PHOTOACTIVITY AND PHASE TRANSFORMATION OF TiO$_2$ NANO-PARTICLES

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Abstract. Nanocrystalline titania (nominally TiO$_2$) has received great attention in recent years due to its unique dielectric, optical and catalytic properties. Photocatalysis is being exploited for the destruction of water and airborne organic pollutants. Properties influencing photocatalytic activity of titania particles include surface area, crystallinity, crystallite size and crystal structure. In this study, the properties of titania are systematized with respect to thermal history and processing parameters. Methods are described to manipulate polymorphic phase transformations and photoactivity of nanocrystalline TiO$_2$ powders synthesized by a sol-gel route. The characteristics of the materials were investigated using HRTEM, XRD Rietveld refinement, and UV-Vis spectrometry and correlations drawn between structure, crystallite size, chemical composition and photoactivity. The quantum size effect was observed in the size-controlled nanocrystalline TiO$_2$ particles.

1. INTRODUCTION

Titania is a promising material for photoelectro-chemical energy production and photocatalytic applications for the removal of various organic toxins from air and water [1,2]. The basic principle of semiconductor photocatalysis involves the migration of photon-generated electrons and holes to exposed surfaces where they can react with adsorbed reactants as redox sources, leading to the decomposition of pollutants. There are three common titania polymorphs – anatase, brookite and rutile. The anatase-type has been selectively used for photocatalytic applications due to its superior photocatalytic activities. However, the polymorphic transformations of titania are complex, depending on grain size, impurities, composition, and so on.

The preparation of ultrafine titania powders has been investigated using various methods, including vapor decomposition [3], hydrothermal treatment [4], and oxidation of titanium powder [5]. Sol-gel syntheses are widely used for fabricating transition metal oxides with nanoscale microstructures and provide excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. However, sol-gel-derived precipitates of titania precursors are amorphous in nature.

In a previous investigation [6,7], we successfully synthesized nano-crystalline titania at low temperature by manipulating key processing parameters that control precursor crystallization. In this paper, we extend this systematic study to provide further insights into methods to control both the phase and microstructure of nano-sized titania and to correlate these properties with photocatalytic activities.

2. EXPERIMENTAL

Tetrabutyl titanate Ti(O-Bu)$_4$ was used as the metal oxide precursor and anhydrous ethanol (EtOH) employed as solvent. The rate of hydrolysis was adjusted by introduction of hydrochloric acid (HCl). Details are reported elsewhere [6]. The drying of the wet-gel was conducted in two ways. Either the gel was vacuum dried at 60 °C, or the material was air-

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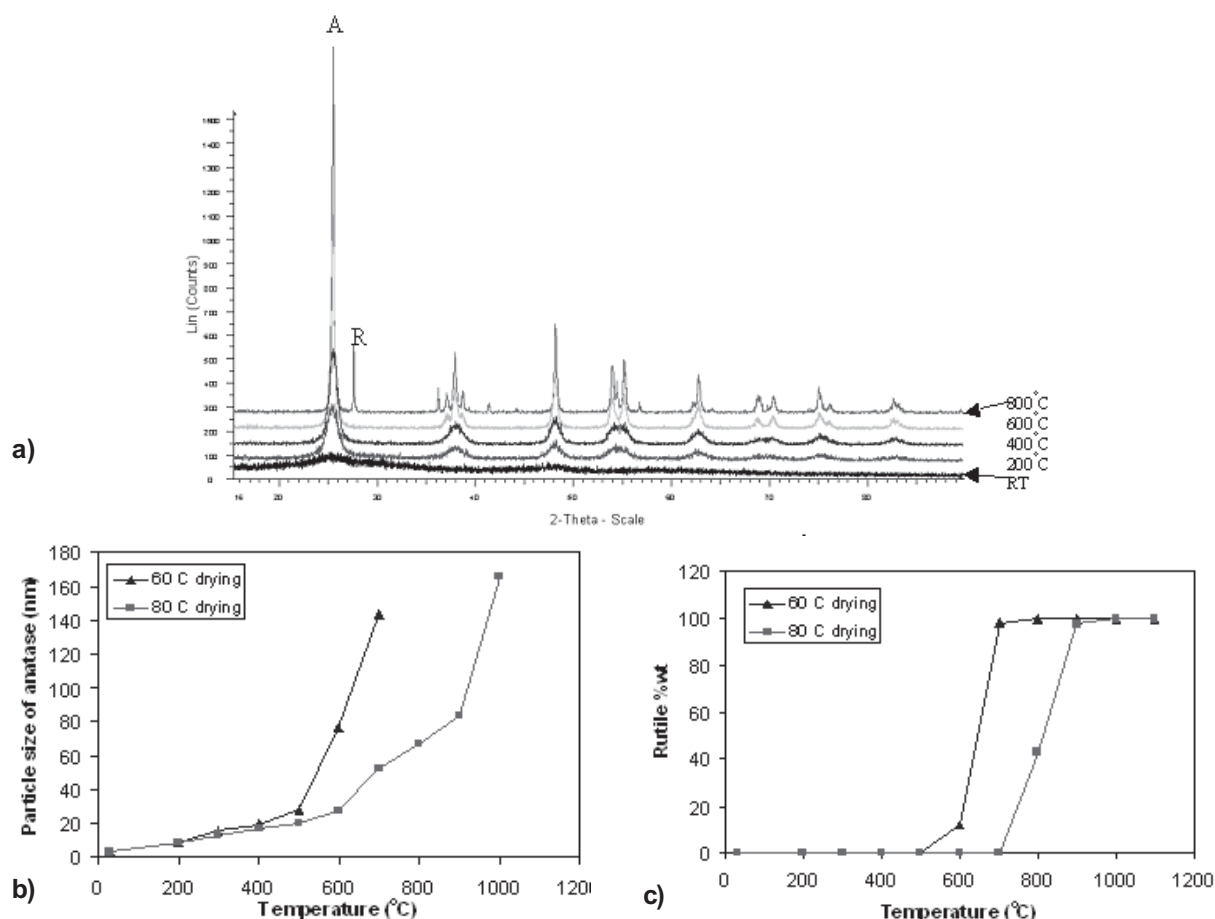Corresponding author: Ying Li, e-mail: yli@ntu.edu.sg

Fig. 1. XRD patterns and Rietveld analysis of gel dried at 80 °C followed by sintering at different temperatures for 2h.

dried using an evaporator followed by vacuum drying at 80 °C.

X-ray diffraction (XRD) patterns were recorded using a Siemens diffractometer (D5005) with CuKα radiation. Unit cell parameters, particle size and polymorph content were determined by the Rietveld method using a fundamental parameter algorithm [8]. Transmission electron microscope (TEM) specimens were suspended in distilled water, dispersed ultrasonically to separate individual particles, and one or two drops of the suspension deposited onto holey-carbon coated copper grids. High resolution electron microscope (HREM) and bright-field images were collected using a JEOL JEM-3010 TEM operated at 300 kV. Powder and solution samples were used for the absorption studies on a Jasco V-550 UV-Vis spectrophotometer. The quantum size effect was estimated directly from the diffuse reflectance spectra. Decomposition of methylene blue was selected as an indicator of photocatalytic activity.

3. RESULTS AND DISCUSSION

Titania powders derived from the gel dried at 80 °C, were sintered at temperatures up to 1000 °C to study their phase stability and microstructural evolution, as well as photocatalytic activity. These results were compared with those of titania powders prepared from vacuum dried gel at 60 °C.

3.1. Phase development

Fig. 1a shows the XRD patterns of titania powders from gel dried at 80 °C followed by sintering at different temperatures for 2h. Only one crystalline phase, anatase, exists below 800 °C. At lower temperatures, the Bragg reflections for anatase are broad with low intensities indicative of ultrafine particles. The starting transformation temperature of anatase to rutile (A→R) was 800 °C, which is 200 °C higher than that observed for titania gels dried at 60 °C. After rutile formed at 800 °C, its concentration in-

creased rapidly until at 1100 °C all anatase transformed into rutile.

Particle size changes of anatase, as determined by Rietveld analysis, are plotted in Fig. 1b. At lower temperature (< 300 °C), grain growth was slow, especially in the gel dried at 80 °C, where evolution was retarded significantly compared to the gel dried at 60 °C. For example, at 600 °C, anatase in the gel dried at 80 °C had a particle size of 28 nm, while in the gel dried at 60 °C it was 77 nm. This particle size difference may be explained as follows. Compared to the gel vacuum dried at 60 °C, the wet-gel evaporator-dried at 80 °C would be depleted in ethanol and other volatile organics, leaving water to be subsequently evaporated through the vacuum pump. This suggests the structure of the dry gel may be different, resulting in distinct nano-domains of titania, that could affect the nucleation and the surface structure of anatase particles. These factors could be responsible for the delayed crystal growth of anatase during heat treatment.

The phase transformation from anatase to rutile (A→R) as a function of temperature is depicted quantitatively in Fig. 1c. Formation of rutile was retarded by 200-300 °C in the gel dried at 80 °C compared with gels dried at 60 °C. Anatase was persistent until 800 °C in the former gel, while A→R transformation was essentially complete in the later gel at same temperature. Complete conversion of A→R was achieved at 1100 °C, which is 300 °C higher than that of gel dried at 60 °C. Particle size plays a critically important role in determining thermodynamic stability of titania polymorphs at ultrafine sizes. It has been reported that anatase smaller than a critical size (11 nm) is more stable than rutile and brookite at room temperature [9]. In this study, one reason for the delay of the A→R transformation in the gel dried at 80 °C during sintering is the slower crystal growth of anatase, leading to smaller grain sizes compared to the gel dried at 60 °C. But the critical size is much larger than 11 nm, and for example, anatase persisted to 700 °C with an average particle size of 52 nm. This difference in stability may be influenced by the surface/interface structure, where nucleation of the anatase to rutile transformation is initiated. Drying conditions may influence the surface/interface of the nano-particles, which in turn affect the nucleation of rutile.

3.2. Microstructure evolution

Powder samples subjected to different heat treatments were analyzed using TEM. The TEM micrographs suggest that the samples have negligible
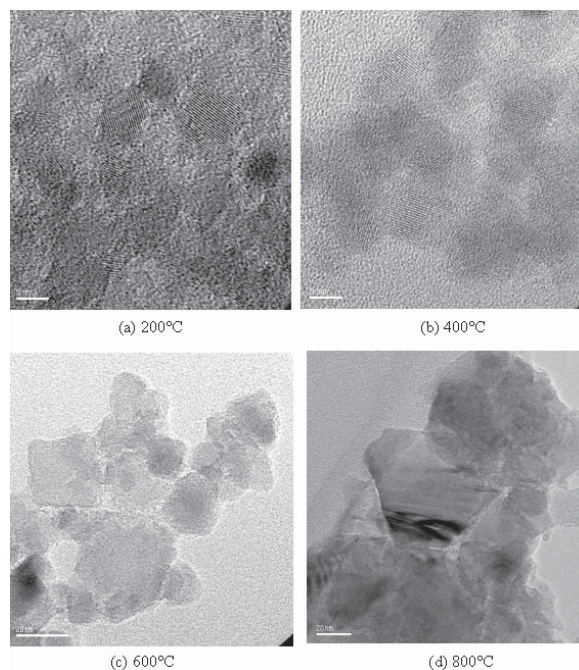

Fig. 2. HRTEM and TEM micrographs showing the morphological changes of gel dried at 80 °C during subsequent heat treatment.

agglomeration (Fig. 2). The average sizes determined by direct observation are consistent with those calculated from XRD Bragg reflection broadening. All samples have a narrow particle size distribution. HRTEM images (Figs. 2a and 2b) indicate that the titania samples were well crystallized even for grains as small as 8 nm. At lower temperatures titania particles are spherical. Coarsening at higher temperatures results in larger faceted crystals. TEM confirmed the principle difference between the two gel routes is crystal size, with powders from the gel dried at 80 °C having smaller dimensions. This difference became increasingly apparent at higher sintering temperatures.

3.3. Quantum size effect and photoactivity

The UV-Vis diffuse reflectance spectra for powdered samples prepared from gels dried at 80 °C showed a blue shift with decreasing particle size, as shown in Fig. 3a. This quantum size effect is prominent when average particle sizes are <10 nm, while the spectral edges for 500 and 700 °C heat treated powders approach the reflectance spectrum for bulk anatase materials. This result is consistent with other researchers [10]. Powders sintered at 300 °C for 2h
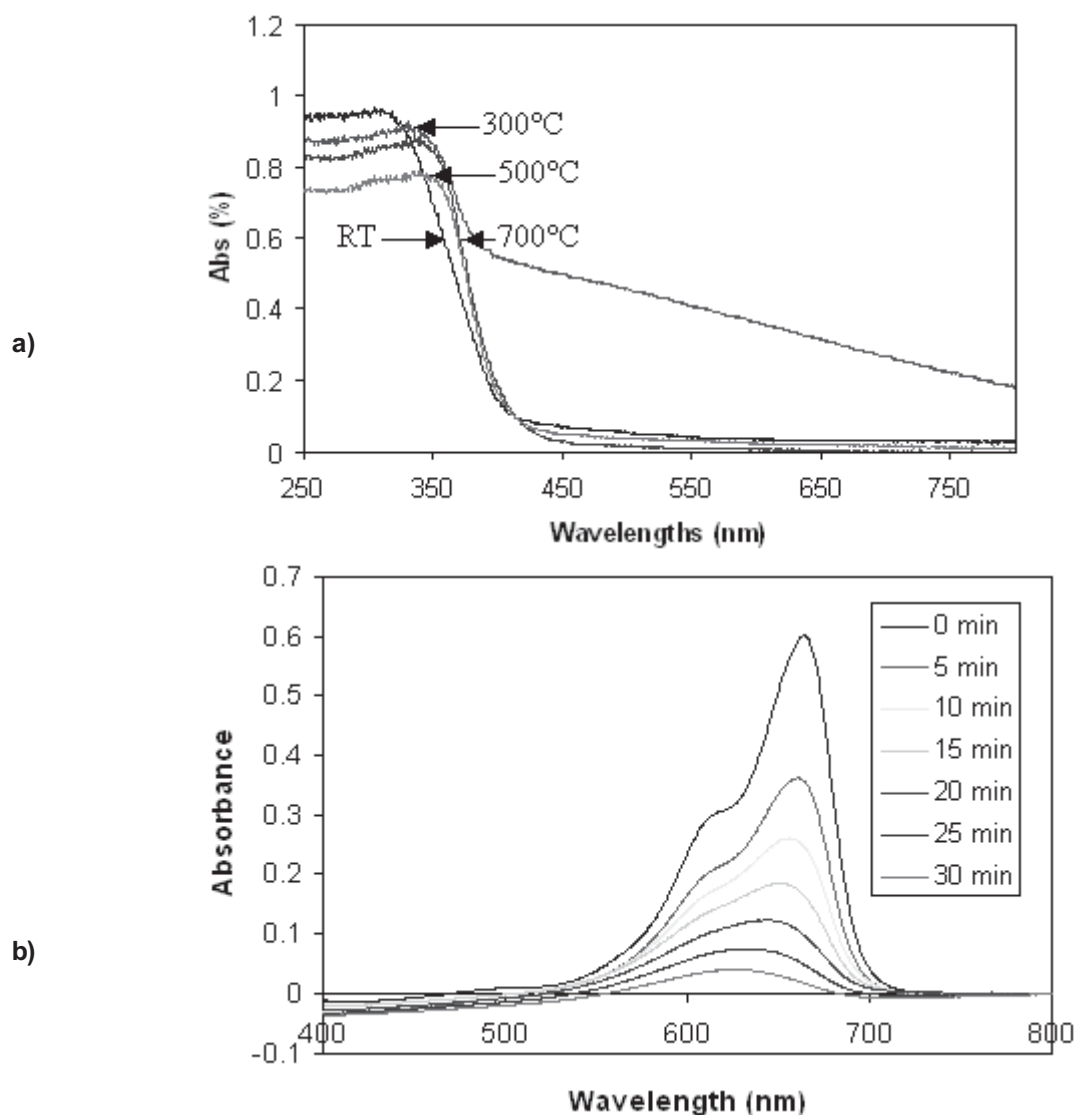
Fig. 3. UV-Vis spectrum of titania powders from gel dried at 80 °C showing the quantum size effect and photoactivity in the nano-titania.

showed absorbance in visible light region, which may arise from the surface state formed during organic decomposition [11].

Fig. 3b illustrates the photocatalytic activity of titania powders from gels dried at 80 °C as monitored by changes in the absorbance curve of methylene blue during UV irradiation of up to 30 min. Absorption of the indicator by the powders without UV irradiation was negligible. It was also found, but not shown, that the rate at which the intensity of the absorption peak (~ 650 nm) decreased was dependent on titania particle sizes.

Particle size is an important parameter for catalysis as it directly impacts the specific surface area of a catalyst. At smaller size, the number of active surface sites increase, as does the surface charge carrier transfer rate in photocatalysis. The volume charge carrier recombination can also be reduced by reduction in particle size. However, photocatalytic efficiency does not increase monotonically with decreasing particle size, because surface recombination of charge carriers becomes an important process in ultrafine semiconductor particles [12]. Besides, the surface state of the titania particle will also affect photocatalytic activity. In this study, it was found that titania powders with a particles size ~50 nm displayed the highest photocatalytic activity.

4. CONCLUSIONS

Anatase nano-titania particles with negligible agglomeration and narrow particle size distribution were synthesized at low temperatures through careful control of process parameters. It was found the drying regime of the wet-gel is an important parameter affecting particle size and phase stability. The particle growth in gels dried at 80 °C, with a two-step drying procedure (evaporator and vacuum pump), was retarded significantly. The starting and ending transformation temperature of anatase to rutile was delayed 200-300 °C compared to the gels dried by a single-stage at 60 °C through a vacuum pump. The quantum size effect was observed in the synthesized anatase powders, moreover, the photocatalytic activity of anatase nano-powders was dependant on both particle size and surface state.

ACKNOWLEDGEMENT

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