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An Alkoxide Free Sol-Gel Synthesis of Nanosized TiO_2

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ABSTRACT

Nanosized TiO_2 with anatase structure has been prepared by a non-alkoxide sol-gel route from an aqueous solution of titanyl sulfate. This paper investigated the influence of stirrer speed on anatase precipitation carried out in batch mode. Stirrer speed was varied between 400 and 1000 rpm. The intensity of stirring determined the final particle size of anatase aggregates in suspension. Changes to primary agglomerate and crystal population due to varying stirrer speed were reported. In our study, the smallest aggregates (mean size of 6-8 nm) were obtained at a stirrer speed of 1000 rpm. It was also found that the anatase to rutile phase transformation began at 800°C of calcination. A calcination treatment, from 400 to 1000°C, was applied. The degree of crystallinity and purity of the synthesized materials were reported. The crystalline anatase particles had an average particle size of 10-20 nm between the calcination temperature 400-600°C. The powders were characterized by powder X-ray diffraction (XRD), the morphology and grain size of the titania particles were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD patterns indicated that the samples were crystalline titania which had very broad and small peaks of anatase phase. The TEM observations showed the vast majority of particles were quasispherical; the average size distribution of particle was about 20 nm. The TEM results supported the conclusions derived from the XRD data. Finally, the amorphous hydrous and crystalline titania particles were characterized by thermogravimetric (TGA) and differential thermal analysis (DTA).

Key words: sol-gel, nanosized, anatase, titania, titanyl sulfate, non-alkoxide

INTRODUCTION

The production of particles with a specific size and morphology is of primary importance for the development of new materials. Mesoscale spheres of ceramic nanomaterials are of particular interest for fundamental research in order to interpret physical properties or surface interactions quantitatively as a function of the morphology and size of the spheres. Recently, the importance of tailored particles has been recognized in a number of applications such as ceramics (Wei *et al*., 1999; Assmann *et al*., 2004; Sivakumar *et al*., 2004), solar cells, photonic crystals, pigments (Lee and Chen, 2001; Allen *et al*., 2002; Assmann *et al*., 2004) and catalysts (Yamazaki *et al*., 2001; Yasir *et al*., 2001; Sathyamoorthy *et al.,* 2001; Sivakumar *et al.* 2002; Ma *et al*., 2002; Kandavelu *et al*., 2004; Baiju *et al*., 2005). Among the many metal oxides and their inorganic-organic hybrid materials used for the above applications, one of the most important and

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complex in this regard is titanium dioxide (titania). To date, research activities into the photochemical properties of titania relate to a number of areas. Titania exists in three crystal structures (anatase, rutile and brookite) and each behaves differently. Even the same form if prepared by different methods can also show different properties due to different surface area, porosity, and functional groups at the surface. Two morphologies of titania, anatase and rutile, exhibit 6 : 3 coordination whereas the anatase forms a distorted octahedral structure the rutile forms slender primatic crystal that is often twinned. Differences in the photoactivities of these two modifications of titania depends markedly upon the history of the synthetic methods. Thus, different approaches to their synthesis have been developed (Wang and Ying, 1999) : (i) inert gas condensation, (ii) flame synthesis by $TiCl_4$ oxidation, (iii) oxidation-hydrothermal synthesis of metallic Ti, and (iv) hydrolysis precipitation of titanium alkoxides of chlorides. Of particular interest is synthetic method (iv), the wet-chemical synthesis, or the sol-gel approach. The hydrolytic sol-gel method allows compositional and microstructural tailoring through controlling the precursor chemistry and processing conditions. Sol-gel processing provides for excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. It involves the formation of a metal-oxo-polymer network from molecular precursors such as metal oxides of metal salts. Sivakumar *et al.* (2002; 2004) have reported that the sol-gel method becomes one of the successful and simple techniques for preparing nanosized titania. Most of earlier attempts used titanium alkoxides as precursors in the sol-gel route. As precursors of monodispersed oxide powders, however, inorganic compounds may be more economical than alkoxides and a few attempts were reported in this direction (Sivakumar *et al.*, 2002). Recently, Wei *et al.* (1999) prepared nanodispersed spherical TiO_2 powder, of average particle size 80 nm, by forced hydrolysis of $Ti(SO_4)_2$ aqueous solution containing sulfuric acid under boiling reflux condition. Sivakumar *et al.* (2002) synthesized nanocrystalline anatase with high surface area by homogeneous precipitation of aqueous titanyl sulfate solution at room temperature. In this study, the processing parameters in an alkoxide free sol-gel synthesis of anatase titania nanoparticles were investigated. Factors affecting the sol-gel process include the reactivity of inorganic titanium salt, pH of the reaction medium, calcination temperature, the influence of varying stirrer speeds on the formation of anatase particles, and the nature of hydrolytic solvent and peptisation reagent. By varying these processing parameters, materials with different microstructure and surface chemistry can be obtained.

MATERIALS AND METHODS

Synthesis

Titanyl sulfate (98% $Ti(SO_4)_2$), obtained from Sigma-Aldrich Laborchemikalien Co., was dissolved in 500 ml of deionized water (0.2 M) and subjected to precipitation by the slow addition of ammonium hydroxide solution (10% NH_4OH) under constant stirring (400 rpm) by a mechanical stirrer at room temperature (30°C). The hydrolysis was controlled with the addition of NH_4OH, until the reaction mixture attained a pH between 7 and 8. White precipitate of hydrous oxide was produced instantly, and the mixture was stirred at the constant rate for at least 1 hour. The precipitate obtained was separated from the mother liquor by vacuum filtration with 0.2 μm micropore filter (diameter = 47 mm) and washed repeatedly with deionized water until the precipitate became free from sulfate ion (confirmed by $BaCl_2$ test). The precipitate was converted into a stable sol by dispersing it into 1000 ml of boiling (100°C) distilled water, followed by peptisation with addition of 10% HNO_3. The stable sol of pH 1.8 – 2.2 was aged 12 hours at room temperature. The sol to gel conversion was achieved by raising the pH to 6, by dropwise addition of 10% NH_4OH solution. The gel was again kept at 40°C for 24 hours and then dried at 90°C in an oven over a period of 24 hours. The amorphous precipitate was then subjected to either calcination or hydrothermal treatment. The dried gel was calcined at various temperatures i.e. 400, 600, 800, and 1000°C in separate batches for 2 hours with a heating rate of 10 – 15°C min^{-1}. The influence of varying stirrer speeds on the crystallinity of titania particles was studied by precipitating 0.2 M $Ti(SO_4)_2$ with 10 % NH_4OH under various stirrer speeds from 400 to 1000 rpm for 1 hour at room temperature.

Methods of characterization

Thermal analysis and the water content of the gel was determined thermogravimetrically using a Perkin Elmer – thermonalyzer TGA7 (O_2 atmosphere, heating rate 10°C min^{-1}) combining thermogravimetry (TG) and differential scanning calorimeter DSC7. The gel and the calcined powders were characterized by powder X-ray diffraction (XRD) using a diffractometer of Rigaku (Model Miniflex) with graphite monochromated Cu K_α radiation at a scanning rate of 4.0 deg.min^{-1} in 2θ range 5.0 – 80.0°. To determine the average crystallite size, peak broadening analysis was applied to anatase (101) diffractions using Scherrer's equation (Bai *et al.*, 1999; Wang and Ying, 1999; Sivakumar *et al.*, 2002). The morphology and grain size of the titania particles were examined by a Joel JSm-5800 scanning electron microscope (SEM) and a Joel JEM-2010 transmission electron microscope (TEM) operating at 200 kV. Drops of a powder suspension were added to carbon-coated copper girds in TEM sample preparation.

RESULTS AND DISCUSSION

The precipitates from sol-gel processing of titania were amorphous in nature. A significant weight loss was noted in the TGA curves (Figure 1a) for the dried titania gels at 90-95°C undergoing a total weight loss of 7.36% with two decomposition steps between the analysed temperature of 30-800°C. The weight loss below 150° was due to the removal of loosely bound water in the gel network. The decomposition step between 230 and 300°C (55.67%wt. loss) was due to the decomposition of nitrate ions as well as the dehydroxylation of the gel. The DTA pattern (Figure 1b) was complementary to the TGA observations. The very small exothermic peak centered around 390°C represented the decomposition of nitrate species along with dehydroxylation of titanium species, which was supported by the corresponding weight loss in the TGA curve. A calcination treatment (from 400 to 1000°C) was applied : these temperatures were also necessary to eliminate water and other inorganic species from the hydrous gel (Figure 2).

The change in titania gel particle size with constant stirring time (1 hour) at different stirrer speeds was investigated. SEM images of gel particle sizes are illustrated in Figure 3 and the TEM micrograph of the sample prepared under the same experimental conditions except stirrer speed at 1000 rpm is described in Figure 4. This was clear evidence that stirrer speed had a significant influence over the final aggregate size. At 400 rpm, aggregates appeared to be larger, and gradually reduced in size with higher stirrer speed. If we compare SEM images for 400, 600 and 800 rpm, we notice that the reduction in size is followed by an increase in the number of aggregates. Sathyamoorthy *et al.* (2001) have reported that the kinetics of precipitation remains unchanged for varying stirrer speeds. Therefore, the difference in size and number of aggregates at different stirrer speeds must maintain equal mass in all cases. Figure 4 illustrated the maximum reduction in mean particle size of aggregates for stirrer speed of 1000 rpm from TEM microphotograph. In the case of anatase, similar observations were deduced from experimental results of Sathyamoorthy *et al.* (2001). They described the attractive force as

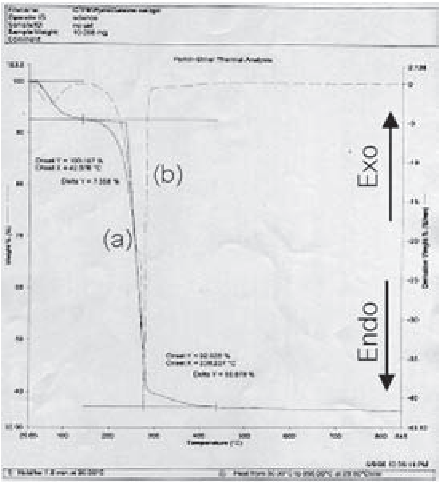


Figure 1 Thermogravimetric (a) and differential thermal (b) analysis curves of amorphous titania gel (0.2 M TiO_2, with stirrer speed 1000 rpm).

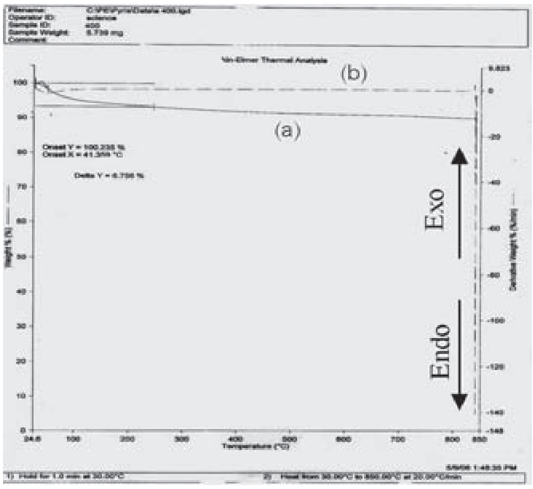
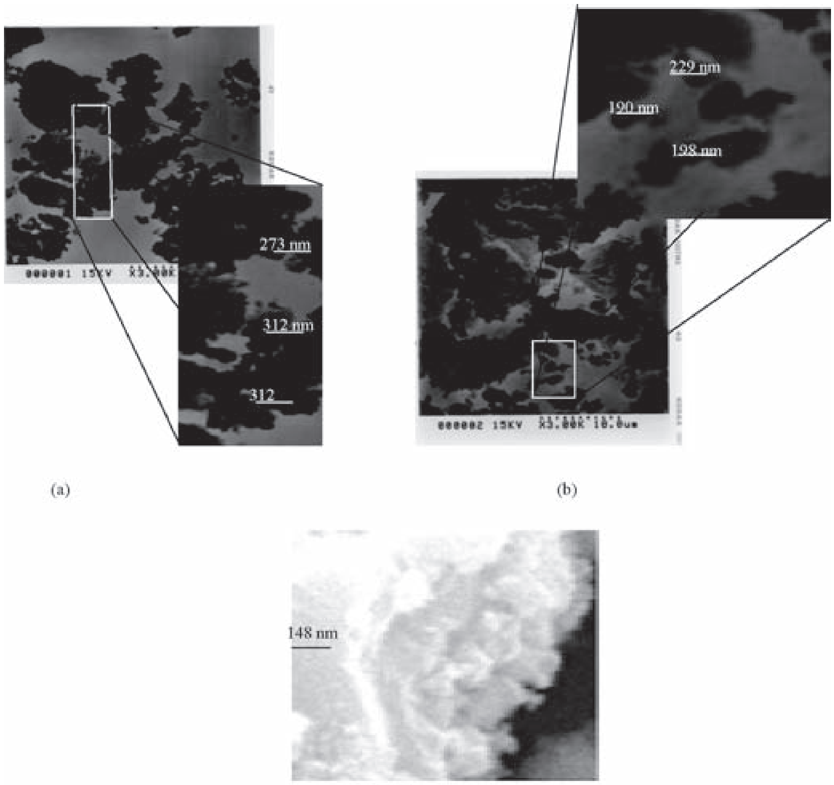


Figure 2 Thermogravimetric (a) and differential thermal (b) analysis curves of 400°C calcined titania gel (0.2 M TiO_2, with stirrer speed 1000 rpm).



(a)

(b)

(c)

Figure 3 Scanning electron micrographs of amorphous titania gel (0.2 M TiO_2) in the form of aggregates recovered at the end of 1 hour; precipitation for different stirrer speeds : (a) 400 rpm (b) 600 rpm and (c) 800 rpm.

mainly physical since the breakage of these aggregates to primary agglomerates is possible via changes to the surface chemistry alone. So, it is possible that beyond a certain stirrer speed, shear forces acting on the aggregates have the maximum effect, and the aggregates simply break into their minimum size.

Figure 5 showed the TEM micrographs of the gel and the calcined powders at various temperatures. It was evident that in the great majority of particles, the largest size was not over 50 nm and the average size was about 20 nm. Calcination at higher temperatures increased the mineralization accompanied by an increase in the crystallite size (Table 1). Further calcination of the powder at 600°C for 2 hours showed the marginal increase in the crystallite size to 20 nm with only

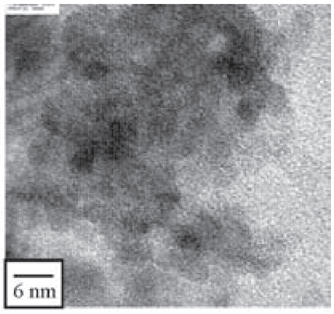


Figure 4 TEM microphotograph of amorphous titania gel (0.2 M TiO_2) in the form of aggregates recovered at the end of 1 hour precipitation for a stirrer speed of 1000 rpm.

Table 1 Crystallite size from TEM micrograph of titania from different calcination temperatures.

Temperature (°C)	Crystallite size (nm)
90	<9
400	10
600	20
800	40

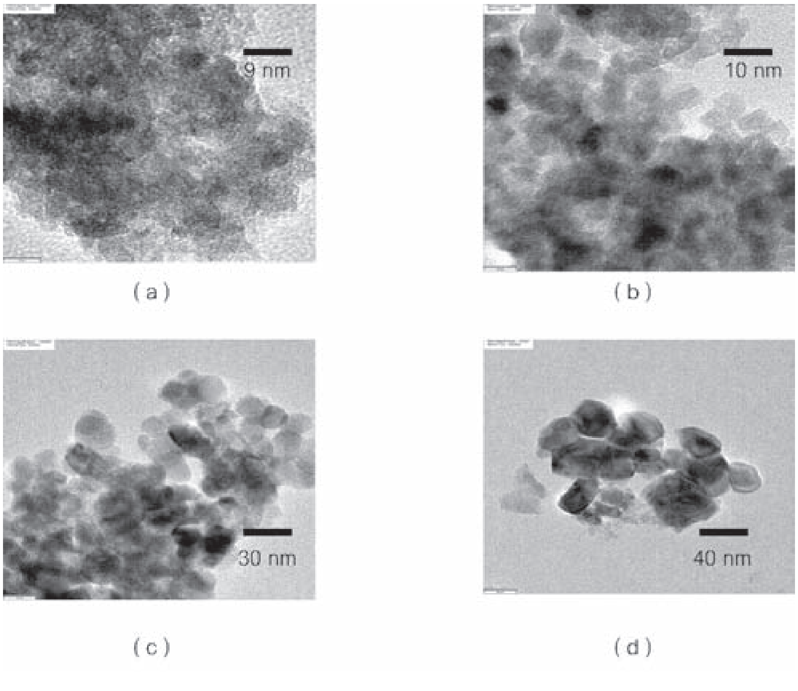


Figure 5 TEM microphotograph of titania particles (0. 2 M TiO_2, stirrer speed 1000 rpm for 1 hour precipitation) synthesized by (a) no calcination and calcination at (b) 400°C (c) 600°C and (d) 800°C.

anatase phase (XRD results).

X-ray diffraction patterns of the gel dried at 90°C and calcined at 400-1000°C showed well-defined diffraction peaks corresponding to the anatase phase (Figure 6). The amorphous gel began to crystallize upon heat treatment at 200°C, as indicated by the emergence of a very broad, low-intensity XRD peak associated with anatase (101) diffraction (Wang and Ying, 1999). Calcination at low temperature could not completely crystallize the material, giving a mixture of amorphous and nanocrystalline titania. To convert the sol-gel derived sample fully to crystalline TiO_2, a calcination treatment of 400 and 600°C were applied. Anatase was the metastable phase of titania, typically associated with high surface areas; it underwent a transformation to the rutile phase upon thermal treatment typically at 800-1200°C (Sivakumar *et al.*, 2002).

The crystallite sized (D) were calculated using Scherrer's eqution as :

$$D = \frac{k\lambda}{\beta \cos\theta}\left(\frac{360}{\pi}\right)$$

Where λ is the wavelength of the Cu $K_{\alpha 1}$ radiation, θ is the diffraction angle of the (*hkl*) reflection, k is a unit cell geometry dependent constant whose value is typically between 0.85 and 0.99 (for this study, k = 0.9) and β is the half-width at the half maximum of a step-scan profile of the (*hkl*) peak after correction for $K_{\alpha 1}$ - $K_{\alpha 2}$ separation and instrumental broadening. The calculated sizes are glown in Table 2.

Figure 6 (c) showed that the gel calcined at 800°C was a mixture of anatase and rutile phases, with a rutile fraction of 10.68%, having a crystallite size larger than the anatase phase. The rutile fraction in the sample was determined by measuring the XRD intensities of anatase (101) and rutile (110) from the equation :

$$W_R = \frac{1}{1 + 0.8\left(\frac{I_A}{I_R}\right)}$$

Where W_R is the weight fraction of the rutile present, I_A and I_R are the X-ray integrated intensities of anatase and rutile reflection, respectively (Sivakumar *et al.*, 2002). X-ray intensities of anatase (101) and rutile (110) are presented in Figure 7. Calcination at 1000°C resulted in pure rutile phase with a crystallite average size of 31 nm.

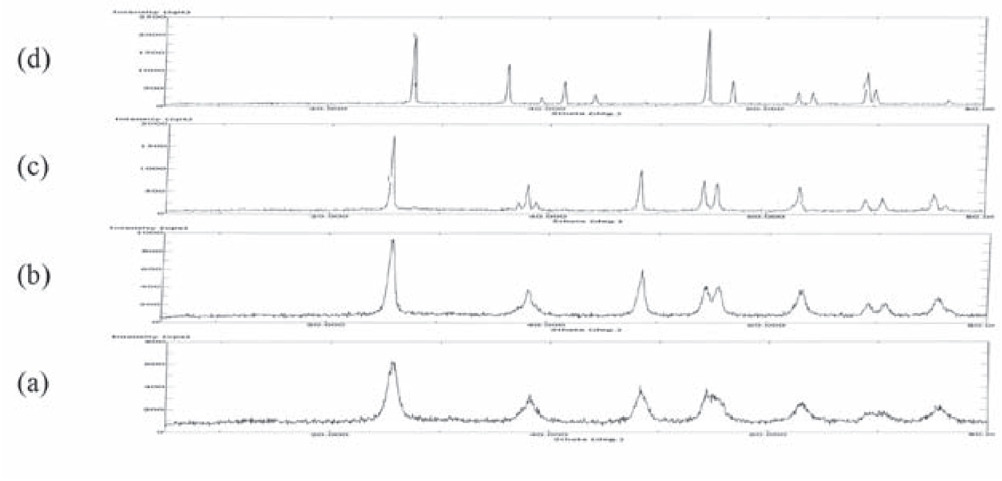


Figure 6 XRD patterns of nanocyrstalline anatase titania gel calcined at (a) 400°C (b) 600°C (c) 800°C and (d) 1000°C, The samples (0.2 M TiO_2 with stirrer speed 1000 rpm for 1 hour) were characterized after calcination for 2 hours.

CONCLUSION

In this study, we have reported a method for the synthesis of nanosized anatase by homogeneous precipitation of aqueous titanyl sulfate solution at room temperature. The observed enhancement in the properties such as anatase-rutile phase stability, crystallite size and morphology fraction prepared by the present method indicates the novelty of the synthesis procedure over the alkoxide-free sol-gel method. In particular, we have successfully synthesized the monodisperse titania particles with diameters of 10-32 nm in a reproducible way by using the sol-gel route. We have shown that both primary agglomerates and crystals of anatase are significantly affected by variation in stirrer speed. The smallest aggregates (6-8 nm) are formed when the highest stirrer speed is used (1000 rpm). Nanocrystalline anatase of crystallite size of 6-8 nm formed as low as 90°C, has been prepared by this method. The gel retains the pure anatase phase with a 14.2 nm crystallite size even after calcination at 600°C for 2 hours.

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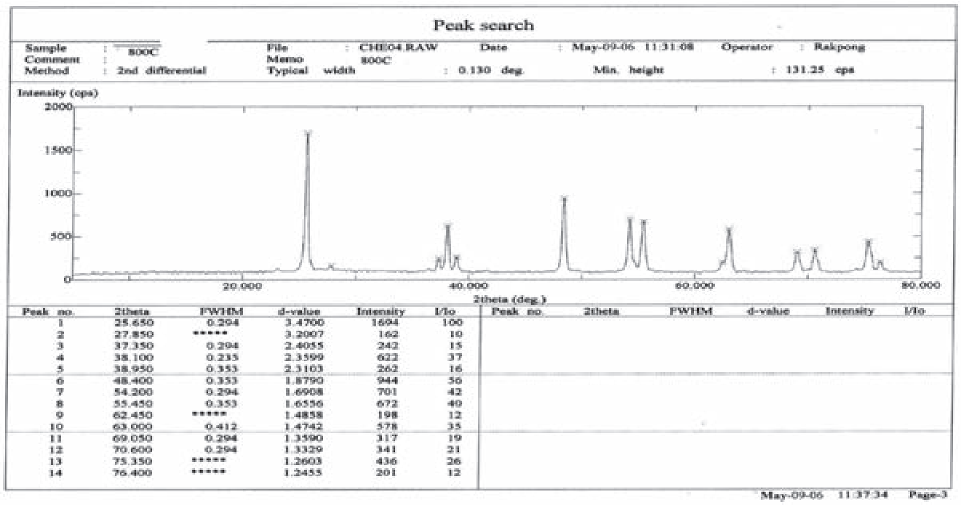
Table 2 Crystalline phase and crystallite size of titania from different calcination temperatures.

Temperature (°C)	Phase	Crystallite size, D (nm)		
		D_{101}	D_{200}	D
90	Anatase	6.8	6.9	6.8 – 6.9
400	Anatase	10.7	11.2	10.7 – 11.2
600	Anatase	13.6	14.8	13.6 – 14.8
800	Anatase + Rutile	26.4	28.3	26.4 – 28.3
1000	Rutile	29.6	32.1	29.6 – 32.1



Peak search

Sample : 800C
Comment :
Method : 2nd differential
File : CHE04.RAW
Memo 800C
Typical width : 0.130 deg.
Date : May-09-06 11:31:08
Min. height : 131.25 cps
Operator : Rakpong

Peak no.	2theta	FWHM	d-value	Intensity	I/Io
1	25.650	0.294	3.4700	1694	100
2	27.850	*****	3.2007	162	10
3	37.350	0.294	2.4055	242	15
4	38.100	0.235	2.3599	622	37
5	38.950	0.353	2.3103	262	16
6	48.400	0.353	1.8790	944	56
7	54.200	0.294	1.6908	701	42
8	55.450	0.353	1.6556	672	40
9	62.450	*****	1.4858	198	12
10	63.000	0.412	1.4742	578	35
11	69.050	0.294	1.3590	317	19
12	70.600	0.294	1.3329	341	21
13	75.350	*****	1.2603	436	26
14	76.400	*****	1.2455	201	12

Peak no.	2theta	FWHM	d-value	Intensity	I/Io

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Figure 7 XRD intensities of nanocrystalline titania sample calcined at 800°C (0.2 M TiO_2, stirrer speed 1000 rpm for 1 hour).

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