JOURNALOF

Ceramic Processing Research

# Synthesis of single-phase anatase TiO<sub>2</sub> nanoparticles by hydrothermal treatment with application potential for photoanode electrodes of dye sensitized solar cells

M. Montazeri-Pour, N. Riahi-Noori\* and A. Mehdikhani

Niroo Research Institute, Ceramic & Polymer Group, Tehran, Iran

Pure anatase powders of titanium dioxide with a homogeneous nanosized particles distribution were prepared by a facile hydrothermal route using solution of acetic acid and tetraisopropyl orthotitanate as the precursors with a molar ratio of 1 : 1. The modified and hydrolyzed alkoxide was treated at various temperatures under different autogenic pressures. Two different reactors were employed as autoclaves for the heating and generation of high pressures during the synthesis and crystallization of TiO<sub>2</sub> nanoparticles. The characteristics of TiO<sub>2</sub> powders obtained under various synthesis conditions were verified by using of X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The results indicated that particles size of the formed TiO<sub>2</sub> could be finely tuned by varying the experimental parameters of temperature, pressure and the amount of nitric acid in the peptization step. TiO<sub>2</sub> nanoparticles with good dispersion and mean size of about 9 nm, which was approximately consistent with size obtained from XRD line broadening technique, could be seen in FE-SEM image of sample synthesized under temperature of 160 °C for 12 hrs by using of more nitric acid in the peptization step.

Key words: Hydrothermal route, TiO2 nanoparticles, Anatase phase, Peptization.

## Introduction

Over the recent years, preparation of important metal oxide nanoparticles such as TiO<sub>2</sub>, ZnO and SnO<sub>2</sub> have attracted increasing attention from the scientific communities because of their extraordinary physical and chemical properties. Among them, Titanium dioxide (TiO<sub>2</sub>) is a wide band-gap semiconductor with energy of 3.0-3.2 eV and has great importance for utilizing solar energy and environmental purification. This material has been widely used for various applications such as semiconductors in dye-sensitized solar cells (DSSCs) [1, 2], photocatalysts [3], gas sensors [4], pigments [5] and so on because of its relative high efficiency and high stability.

 $TiO_2$  exists in three different crystalline phases. Rutile is thermodynamically the most stable of the  $TiO_2$  phases, whereas anatase and brookite are metastable and are readily transformed to rutile when heated [6]. Anatase  $TiO_2$ , having an energy band gap of 3.2 eV which is more than that of 3.06 eV for rutile, provides better electron transport rate, higher diffusion coefficient and more dye loading than rutile and brookite  $TiO_2$  phases [7, 8]. Therefore, among various crystalline phases of  $TiO_2$ , the anatase nanostructured phase is of great interest for application as the photoanode in DSSCs and consequently it is desirable to explore new approaches to synthesize high purity anatase  $TiO_2$  nanoparticles for these applications. Functional properties of  $TiO_2$  are influenced by many factors such as phase composition, particles size, surface area and preparation method [6].

In order to produce TiO2 particles, several various preparation processes such as the sol-gel process [9], solution combustion [10], microemulsion [11], chemical vapor deposition [12] and the hydrothermal process [13] have been reported. Hydrothermal synthesis has become one of the most promising nanoscale materials fabrication routes, where polymorphism, particles size, crystallinity and morphology of products could be very well controlled as required in comparison with any other techniques, because of highly controlled diffusion in the crystallization medium and phase transformation at relatively low temperature. Under hydrothermal conditions, the reaction solution develops an anomalous dielectric constant, density and ionic strength which cannot be achieved under ambient pressure and temperatures [14]. These conditions allow unusual reactions and decomposition of organic compounds to be carried out that facilitate the conversion of amorphous phase into nanocrystalline TiO<sub>2</sub> phase.

This work is aimed to utilize a facile hydrothermal route for synthesis of  $TiO_2$  nanoparticles with uniform shape and mean particles size of about 20 nm or less by using of two autoclave reactors. The synthetic approach described here can be extended to high volume synthesis of  $TiO_2$  nanostructures. Significant advantage of the applied approach is the prospect of production of appropriate transparent layers for DSSC

<sup>\*</sup>Corresponding author:

Tel:+982188079447

Fax: +982188364620 E-mail: nriahi@nri.ac.ir

Sample	Controllable parameter in the used autoclave reactor	Pressure	Temperature	Filling Volume Percent	Residence Time	Amount of Nitric Acid
H1	Pressure	24 atm	-	-	12 hrs	6 ml
H2	Temperature	_	200 °C	50%	12 hrs	6 ml
H3	Temperature	_	160 °C	50%	12 hrs	6 ml
H4	Temperature	_	160 °C	70%	12 hrs	6 ml
H5	Temperature	_	200 °C	70%	12 hrs	6 ml
H6	Temperature	_	200 °C	70%	12 hrs	8 ml
H7	Temperature	_	200 °C	70%	6 hrs	6 ml

 Table 1. Characteristics of samples synthesized under various experimental conditions.

photoanode, which may result in solar cells with more efficiency.

## Experimental

All chemicals are of analytical grade and were used without further purification. 0.2 moles (58.6 g) of tetra isopropyl orthotitanate  $(\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4 \text{ or Ti}(\text{O}^1\text{Pr})_4)$ was cooled in an ice-bath to decrease the condensation of it at an early stage of the process. Then 0.2 moles (12 g) of acetic acid (CH<sub>3</sub>COOH) was added all at once to it under magnetic stirring at room temperature.

The modified precursor was stirred for about 15 min and 290 ml water was quickly added to it with vigorous stirring (800 rpm). During the addition, a white precipitate was formed. One hour of stirring was used to achieve a complete hydrolysis reaction.

After adding a quantity of 6 ml or 8 ml of %65 nitric acid (according to the process conditions showed in Table 1), the mixture was heated from room temperature to 80 °C and peptized for 90 min in order to prevent the agglomeration of the particles present in the sol. After cooling of the resultant mixed suspension down to room temperature, it was charged into an autoclave and heated at different conditions in terms of temperature and time or pressure.

The detailed description about the preparation conditions of different samples is reported in Table 1. In order to evaluate the effect of amount of nitric acid in the peptization step on the final particles characteristics, a different amount of it was added to the H6 sample. After the autoclave was naturally cooled to room temperature, 2.4 ml of 65% nitric acid was added to the dispersion and it was treated with an ultrasonic instrument for 20 min. The suspension was centrifuged and washed with ethanol. This process was repeated for 3 times to remove unwanted nitric acid completely from the products. Finally, a white precipitate containing  $TiO_2$  in ethanol with trace amount of water produces. The resultant precipitates were dried at 50 °C for 24 hrs and were ground in a mortar to produce soft TiO<sub>2</sub> powder.

In the present study, two autoclave reactors were employed for heating of liquid suspension mixture under generated pressure during the hydrothermal synthesis of TiO<sub>2</sub>. In the first autoclave (with controllable pressure), the pressure was controlled by a gauge and an open glass beaker containing liquid mixture was placed in a desired position in the chamber of autoclave. Then the reactor was adjusted for generation of 24 atmosphere pressure automatically during the hydrothermal synthesis.

In the second autoclave (with controllable temperature), the temperature was controlled by one furnace and the Teflon-lined autoclave reactor was filled with liquid mixture up to 50% or 70% of the total volume, sealed into a steel vessel and maintained into the furnace without shaking or stirring during the heating. The furnace temperature was varied from 160 °C to 200 °C and the residence time was varied between 6-12 h under autogenic pressure developed inside the Teflon liners.

The crystal phase of TiO<sub>2</sub> powders was characterized via X-ray diffraction (XRD, PW3170, Philips) using Cu- $K_{\alpha}$  radiation in the range of 10° to 80° and accelerating voltage of 40 kV. The average crystallite size (D) of the samples was estimated from the line broadening of X-ray diffraction reflections using the classical Scherer equation [15]:

$$D = \frac{k\lambda}{\beta Cos\theta} \tag{1}$$

Where  $\lambda$  is the wavelength of the Cu- $K_{\alpha}$  radiation (1.5406 Ű),  $\theta$  the Bragg's diffraction angle,  $\beta$  the full width at half maximum intensity of the peak, and *k* a constant (~ 0.9).

A field emission scanning electron microscopy (FE-SEM, S-4160, Hitachi) was used to observe the microstructure, morphology and measuring the size of the  $TiO_2$  nanoparticles by help of a image analyzer software.

## **Results and Discussion**

Control of the hydrolysis process is a very important subject for synthesis of  $TiO_2$  in aqueous solution. Acidic conditions are required to prevent rapid hydrolysis of titanium compounds that this aspect is considered in the synthesis process employed in this work. In fact, The modification of  $Ti(O^iPr)_4$  with acetic acid reduces the availability of groups that hydrolyze



Fig. 1. XRD pattern of the H1 sample.

and condense easily through exchange of isopropoxy groups with acetate groups and the formation of a stable complex [16].

The crystalline phase of the synthesized H1 sample was analyzed by XRD, and its XRD pattern is shown in Fig. 1. The X-ray diffraction peaks are in good agreement with the standard spectrum of anatase TiO<sub>2</sub> (JCPDS, Card No: 73-1764) and it was found that all the dominant peaks observed at 20 values around 25.55, 38.09, 48.41, 54.22 and 55.40 in the XRD pattern are consistent with the (101), (004), (200), (105) and (211) planes reflections of anatase, respectively. Rutile and brookite phases were not detected.

It has been established that strong acids and high temperatures promote the protonation of Ti-O-Ti bridges and activate redissolution-precipitation reactions that ultimately lead to rutile. In contrast, in mild acidic media and low temperatures, the solid precipitates into small particles that have low solubility in the liquid. Therefore, Ostwald ripening is negligible and anatase as the precipitated phase preserved [17, 18].

The use of acetic acid as modifier allows the control of both the degree of condensation and oligomerization and persuades the preferential crystallization of  $TiO_2$  in the anatase phase. Without the control of the condensation reactions, an amorphous mass of agglomerated particles is immediately obtained after the addition of water [18].

Fig. 2 displays the XRD patterns of the powder samples synthesized by using of the second autoclave. It seems that all of the samples are only consist of anatase phase without any impurities. The microstructure of TiO<sub>2</sub> products was investigated by FE-SEM and typical image for H1 sample is shown in Fig. 3 The morphology of particles is near to a spherical shape. It seems interesting that many primary particles with size of 13 nm which is completely corresponding to the size estimated by line broadening technique of XRD peak could be detected in this image. However, the mean particles size was determined 20 nm for this image. The FE-SEM images of TiO<sub>2</sub> nanoparticles prepared at various working conditions by the second autoclave have been shown in the Fig. 4. Herein, the morphology

**Table 2.** Size characteristics of  $TiO_2$  nanoparticles for various samples.

-							
Samples	H1	H2	H3	H4	H5	H6	H7
Crystallite Size	13	11	10	8	10	7	9
Average Particles Size	20	15	13	11	12	9	12

of particles for all of the samples is near to a spherical shape similar to the H1 sample.

Table 2 summarizes the results of the  $TiO_2$  mean particles sizes deduced from FE-SEM images and crystallite sizes obtained from XRD patterns. The results show good agreement between  $TiO_2$  particle and crystallite size and trend of their fine variations within the experimental error.

The experimental parameters such as solvent, degree of saturation, residence time, temperature and pressure may control the morphology and size of  $TiO_2$  particles in the hydrothermal synthesis. Changes in any one of these parameters can lead to a modification in the morphology and size of final nanoparticles.

The coarsening process is based on the presence of a particles size distribution, where the stability of nanoparticles depends on their size. The Gibbs-Thomson equation relates the particle solubility,  $c_r$ , to the particle radius, r:

$$c_r = c_{\infty} exp\left(\frac{2\gamma V_m}{rRT}\right) \tag{2}$$

Where  $c_{\infty}$  is the solubility at a flat surface,  $\gamma$  is the surface energy at the solid-solution interface,  $V_{\rm m}$  is the molar volume, R is the gas constant and T is the temperature. With assuming that the growth rate is determined by diffusion of the solute from the smaller particles to the larger particles, the following rate law is obtained:

$$\overline{r}^{3} - \overline{r}_{0}^{3} = \frac{8\gamma D V_{m}^{2} c_{\infty}}{9RT} t$$
(3)

Where  $\overline{r}$  is the average particle radius at time t,  $\overline{r}_0$  is the average particles radius at time zero and D is the diffusion coefficient [19, 20].

Crystallization of the  $TiO_2$  nanoparticles probably occurs by a nucleation within the amorphous precursor solid, followed by Ostwald ripening. Taking into account the low solubility conditions and short residence times, we can conclude that growth of anatase particles is very limited.

The experimental data presented in Table 2 is verified and demonstrated in the following comparisons by proposing possible mechanisms. The results indicate that the average crystallite or particles size increases with temperature at a fixed residence time and pressure. Accordingly, the H2 sample crystallized during 12 hrs at 200 °C exhibit bigger size as compared to the H3 sample processed at 160 °C. The same trend is observed when we compare H4 and H5 samples. This observation



Fig. 2. XRD patterns of the samples: (a) H2 , (b) H3 , (c) H4 , (d) H5 , (e) H6 , (f) H7.



Fig. 3. FE-SEM Image of the as-obtained H1 sample.

Synthesis of single-phase anatase TiO<sub>2</sub> nanoparticles by hydrothermal treatment...



Fig. 4. FE-SEM Images of the samples: (a) H2, (b) H3, (c) H4, (d) H5, (e) H6, (f) H7.

can be explained based on the equation (3) where faster diffusion rates of atoms (with exponential dependence to the temperature) and higher solubility with increasing of temperature can promote the grain growth.

No significant change in the average crystallite size has been observed by decreasing of the residence time at a fixed temperature and pressure. The H7 sample crystallized during 6 hrs at 200 °C exhibit approximately the same size as compared to the H5 sample processed in 12 hrs. This phenomenon can be explained by considering the short residence times used in the experiments that could not affect the size of stable particles during these times.

The pressure of the system depends on the degree of

filling of the autoclave Teflon liner. For a typical hydrothermal synthesis experiment, the degree of filling is usually kept at 50-80% with a pressure of 200-3000 bar [21].

The filling volume percent of the mixture was adjusted from 50% to 70% of the Teflon liner volume to achieve the desired pressure in the second hydrothermal reactor, as explained in the experimental section. Therefore, when we compare the average crystallite or particles size of the two H2 and H5 samples and also H3 and H4 samples, it seems that by increasing of the filling degree of autoclave, the pressure was increased inside the Teflon liners and particles size is decreased. This effect was also probably responsible for formation of larger particles size in the H1 sample synthesized under lower pressure by using of the first autoclave.

Crystallization of  $TiO_2$  from the amorphous state is difficult to obtain at low temperatures. The peptization process is regarded as an efficient approach to help attaining the nanocrystalline phases at relatively lower calcination temperatures. The degree of aggregation of the clusters formed from primary particles is significantly reduced by peptizing the precipitates into colloidal sols [22, 23].

It was found that using of more amount of nitric acid lead to decrease of particles size in the H6 sample. The development of a strong electrostatic repulsive force among the  $TiO_2$  particles during peptization step and consequently formation of weakly agglomerated nanoparticles was probably responsible for this observation.

A high calcination temperature (above 450 °C) is usually required in many conventional synthesis techniques to form  $TiO_2$  particles with regular crystal structure and the removal of organic contents. However, the high temperature treatment can decline the surface area and loss of some surface hydroxyl or alkoxide groups on the surface of  $TiO_2$  which can promote agglomeration among the particles [14]. But applied hydrothermal process in this work at low temperature as well as appropriate peptization step could provide nanosized crystallized  $TiO_2$  with fully pure anatase crystalline form, fine particles size, more uniform distribution and high-dispersion.

There are good prospects that obtained nanoparticles because of having pure anatase phase structure and very fine size and consequently strong potential for amply absorption of sensitized dyes can be apt candidate for application in the transparent layers of photoanode electrodes of dye sensitized solar cells. Further studies on this subject and the dependence of photovoltaic efficiency to these powder particles characteristics are under way.

### Conclusions

The hydrothermal synthesis for production of  $\text{TiO}_2$ nanoparticles have been performed by utilizing tetraisopropyl orthotitanate as the alkoxide and  $\text{TiO}_2$ source, acetic acid as the modifier, water as the hydrolyzing agent and nitric acid as the peptizer. The XRD analysis indicated that the applied hydrothermal treatment can facilely produce pure anatase  $\text{TiO}_2$  and inhibits increases in the obtained crystallite size. Crystallite sizes down to 7 nm could be estimated by XRD line broadening technique. The FE-SEM results showed that mean particles size could be finely controlled in the range 9-20 nm by tuning of process parameters such as temperature, pressure and the amount of peptizer. The change of the residence time could not affect the final  $TiO_2$  stable particles size in the range of used time.

## References

- 1. B. O'Regan, M. Grätzel, Nature. 353 (1991) 737-739.
- 2. M. Grätzel, Nature. 414 (2001) 338-344.
- T.A. Kandiel, A. Feldhoff, L. Robben, R. Dillert, and D.W. Bahnemann, Chemistry of Materials. 22 (2010) 2050-2060.
- 4. Y.J. Choi, Z. Seeley, A. Bandyopadhyay, S. Bose, S.A. Akbar, Sensors and Actuators B. 124 (2007) 111-117.
- 5. A. Kalendova, D. Vesely and P. Kalenda, Pigment & Resin Technology. 39, 255-261.
- 6. X. Chen, S.S. Mao, Chemical Reviews. 107 (2007) 2891-2959.
- H. Cheng, J. Ma, Z. Zhao, L. Qi, Chemistry of Materials. 7 (1995) 663-671.
- N.-G. Park, J.V.D. Lagemaat, A. J. Frank, Journal of Physical Chemistry B. 104 (2000) 8989-8994.
- M. Hussain, R. Ceccarelli, D.L. Marchisio, D. Fino, N. Russo, F. Geobaldo, Chemical Engineering Journal. 157 (2010) 45-51.
- K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, Langmuir. 20 (2004) 2900-2907.
- F.A. Deorsola, D. Vallauri, Powder Technology. 190 (2009) 304-309.
- H. Lee, M.Y. Song, J. Jurng, Y.-K. Park, Powder Technology. 214 (2011) 64-68.
- A. Testino, I.R. Bellobono, V. Buscaglia, C. Canevali, M. D'Arienzo, S. Polizzi, R. Scotti, F. Morazzoni, Journal of the American Chemical Society. 129 (2007) 3564-3575.
- 14. K. Byrappa, M. Yoshimura, Handbook of hydrothermal technology, William Andrew Publishing, New York, 2001.
- 15. B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, Massachusetts, 1978.
- D.P. Birnie, N.J. Bendzko, Materials Chemistry and Physics. 59 (1999) 26-35.
- M. Andersson, L. Osterlund, S. Ljungstrom, A. Palmqvist, Journal of Physical Chemistry B. 106 (2002) 10674-10679.
- R. Parra, M.S. Goes, M.S. Castro, E. Longo, P.R. Bueno, J.A. Varela, Chemistry of Materials. 20 (2008) 143-150.
- G. Oskam, A. Nellore, R.L. Penn, P.C. Searson, Journal of Physical Chemistry B. 107 (2003) 1734-1738.
- D.V. Talapin, A.L. Rogach, M. Haase, H. Weller, Journal of Physical Chemistry B. 105 (2001) 12278-12285.
- J. Yu, "Synthesis of Zeolites", In: Introduction to Zeolite Science and Practice, Edited by J. Cejka, H.V. Bekkum, A. Corma and F. Schuth, Elsevier, 2007, pp. 39-104.
- 22. K.-N. P. Kumar, K. Keizer, A. J. Burggraaf, T. Okubo, H. Nagamoto, S. Morooka, Nature. 358 (1992) 48-51.
- 23. K.-N. P. Kumar, J. Kumar, K. Keizer, Journal of the American Ceramic Society. 77 (1994) 1396-1400.