

## Synthesis of Single-Phase Anatase TiO<sub>2</sub> Nanoparticles by Hydrothermal Treatment

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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 hydrolyzed alkoxide was treated at various temperatures under different autogenic pressures. Two different reactors were employed as autoclaves for 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 using 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 could be seen in FE-SEM image of sample synthesized under temperature of 160 °C for 12 h using more nitric acid in the peptization step.

**Keywords:** Hydrothermal, TiO<sub>2</sub> Nanoparticles, Anatase, Peptization, Tetraisopropyl orthotitanate, Acetic acid, Autoclave.

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### 1. 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.

Among various crystalline phases of titania, 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 titania nanoparticles for these applications [6-8].

Functional properties of TiO<sub>2</sub> are influenced by many factors such as phase composition, particles size, surface area and preparation method [6].

In order to produce TiO<sub>2</sub> particles, several various preparation processes such as 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.

The purpose of this research is utilizing a facile hydrothermal route for synthesis of TiO<sub>2</sub> nanoparticles with uniform shape and means particle 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<sub>2</sub> nanostructures.

### 2. EXPERIMENTAL

All chemicals are of analytical grade and were used without further purification. 0.2 moles (58.6 g) of tetraisopropyl orthotitanate (Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> or Ti(O<sup>i</sup>Pr)<sub>4</sub>) was cooled in an ice-bath to decrease its condensation 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 the 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 the resultant mixed suspension down to room temperature, it was charged into an autoclave and heated at different conditions in terms of temperature, time and pressure.

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**Table 1** – Characteristics of samples synthesized under various experimental conditions

Sample	Pressure	Temperature (°C)	Filling Volume (%)	Residence Time (h)	Amount of Nitric Acid (mL)
H1	-	200	50	12	6
H2	-	160	50	12	6
H3	-	160	70	12	6
H4	-	200	70	12	6
H5	-	200	70	12	8
H6	-	200	70	6	6

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<sub>2</sub> in ethanol with trace amount of water produces. The resultant precipitates were dried at 50 °C for 24 h and were ground in a mortar to produce soft TiO<sub>2</sub> powder.

In the autoclave, 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, Philips Model PW3170) using Cu-K<sub>α</sub> 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 Scherrer equation [15]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where  $\lambda$  is the wavelength of the Cu-K<sub>α</sub> radiation (1.5406 Å),  $\theta$  the Bragg's diffraction angle,  $\beta$  the full width at half maximum intensity of the peak, and  $k$  a constant (~0.9).

Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi Model S-4160) was used to observe the microstructure, morphology and measuring the size of the TiO<sub>2</sub> nanoparticles by help of a image analyzer software.

### 3. RESULTS AND DISCUSSION

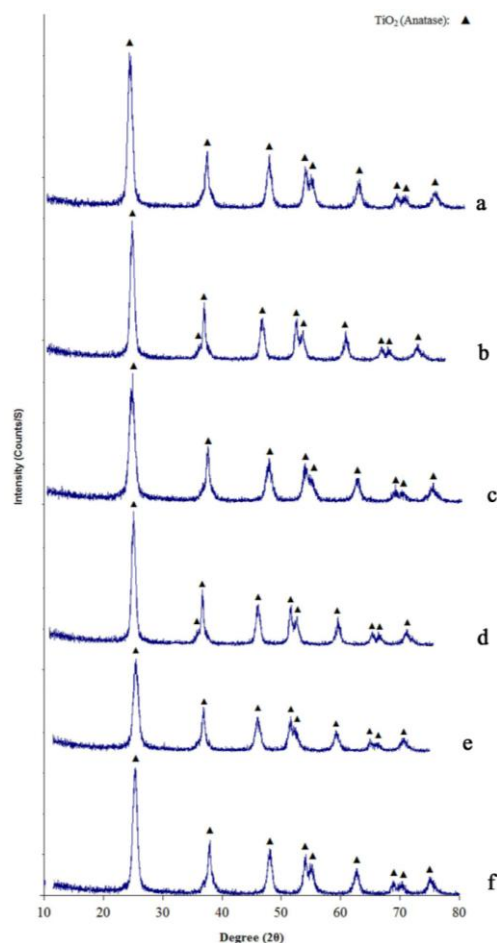
The use of acetic acid as modifier allows the control of both the degree of condensation and oligomerization and persuades the preferential crystallization of TiO<sub>2</sub> in the anatase phase. Without the control of the condensation reactions, an amorphous mass of agglomerated particles is immediately obtained after the addition of water [18].

Figure 1 displays the XRD patterns of the powder samples synthesized using the autoclave. It seems that all of the samples are only consist of anatase phase without any impurities.

The FE-SEM images of TiO<sub>2</sub> nanoparticles prepared at various working conditions by autoclave have been shown in the Figure 4.

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

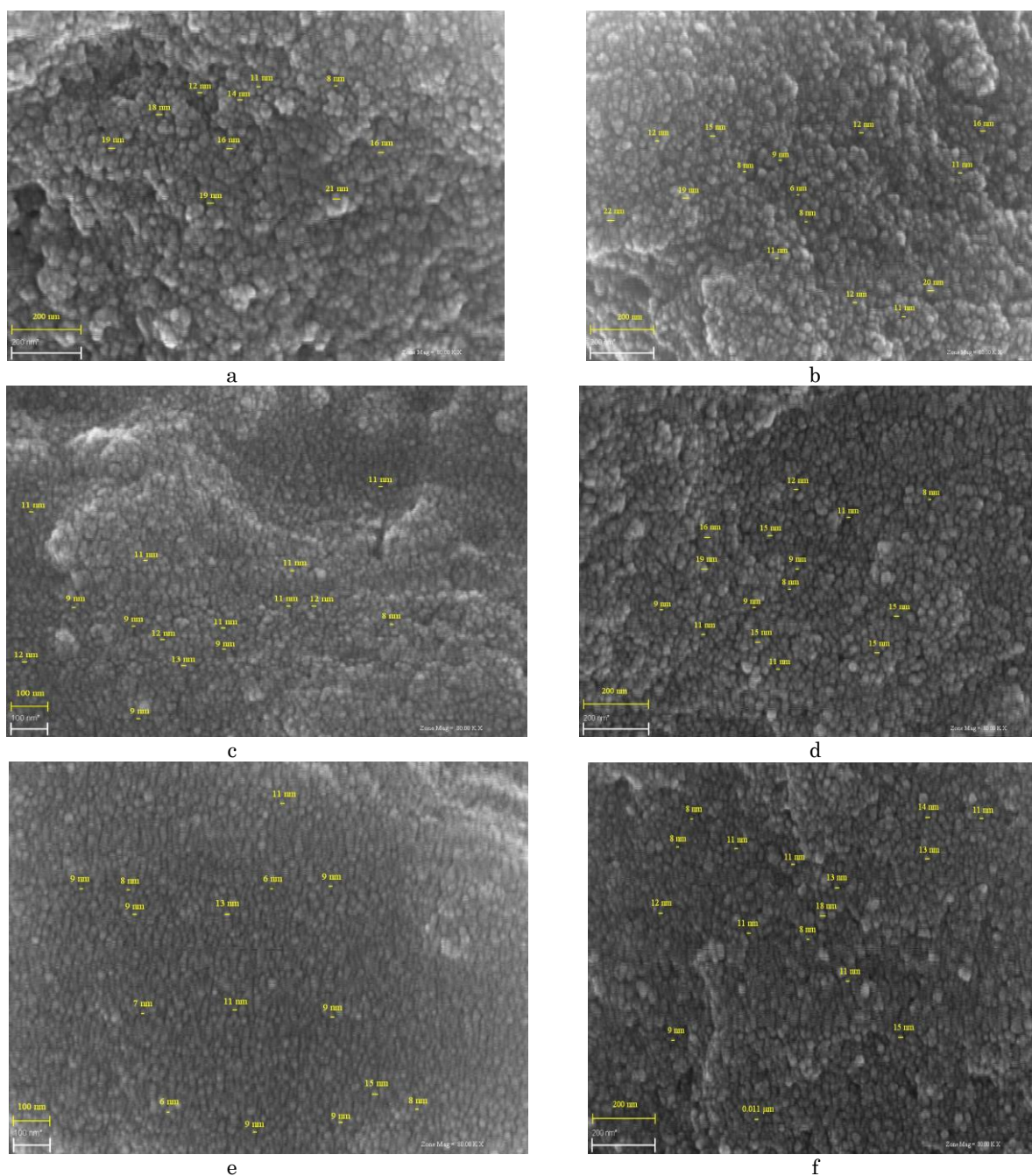
The experimental parameters such as solvent, degree of saturation, residence time, temperature and pressure may control the morphology and size of TiO<sub>2</sub> particles in the hydrothermal synthesis. Changes in any one of these parameters can lead to a modification in the morphology and size of final nanoparticles.



**Fig. 2** – XRD patterns of the (a) H1 , (b) H2 , (c) H3 , (d) H4 , (e) H5 , (f) H6 samples.

**Table 2** – Size characteristics of TiO<sub>2</sub> 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

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

#### 4. CONCLUSIONS

hydrothermal synthesis for production of titania nanoparticles have been performed by utilizing tetraisopropyl orthotitanate as the alkoxide and TiO<sub>2</sub> source, acetic acid as the modifier, water as the hydrolyzing agent and nitric acid as the peptizer.

XRD analysis was used to show that applied hydrothermal treatment can facily produce pure anatase TiO<sub>2</sub> and inhibits increases in the obtained crystallite

size. Crystallite sizes down to 7 nm could be estimated by XRD line broadening technique.

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<sub>2</sub> stable particles size in the range of used time.

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