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# The effect of sonication power on the sonochemical synthesis of titania nanoparticles

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**Titanium dioxide ($TiO_2$) nanoparticles were synthesized by a sonochemical method. $C_{12}H_{28}O_4Ti$ (Tetraisopropyl titanate), ethanol ($C_2H_5OH$), sodium hydroxide (NaOH) and deionized water were used as the initial materials. The output power of the ultrasonic device plays the most important role in the size and morphology of the final products. Sonochemical processes at different sonication power were carried out at synthesis temperature (50 °C) for 1.5 h and then the materials were washed and dried at room temperature for 48 h. To determine the particle size and also evaluate the morphological properties, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used. TG/DTA analysis was used to for determine the temperature and time of crystallization. From TEM observations the size of titanium dioxide nanoparticles is estimated to be significantly smaller than ~12 to ~30 nm.**

**Key words: Sonochemical, Cavitation, Sonication power, Nanoparticles, Titanium dioxide.**

## Introduction

Nowadays nano-semiconductors have become one of the most attractive aspects of materials research. Among these nano materials, titanium dioxide has become the most interesting material due to its physical and chemical properties.

The control of morphology, particle size, particle size distribution, phase composition and porosity of $TiO_2$ nanoparticles are vital factors in determining the properties of the final material. $TiO_2$ has three polymorphic phases namely anatase, rutile and brookite. Among these three crystalline phases, the anatase phase exhibits the highest photocatalytic activity.Rutile- $TiO_2$ is known as a white pigment because of its high scattering effect which leads to protection from the ultraviolet light [1, 2].

$TiO_2$ is one of the most extensively studied oxides because of its remarkable optical and electrical properties [3]. $TiO_2$ has extensive applications in photocatalysts [4], gas sensors [5], self cleaning surfaces [6], water and air purification components [7] and pigments [8]. Moreover, the rutile structure a has high dielectric constant, electrical resistivity [9] and refractive index which makes it a relevant choice for dye-sensitized solar cells(DSCs) [10] and capacitors [11] as well.

In recent years, nano $TiO_2$ has been synthesized via different methods such as thermal hydrolysis [12], chemical bath deposition (CBD) [13], sol-gel [14-17], hydrothermal processes [18-20], microemulsion processes [21-24] and pulsed laser evaporation [25] etc. Among the different methods of synthesis which have been used by several researchers, the direct chemical method has some advantages including easy operation, being fast, low cost and high efficient. In addition to $TiO_2$, this method has been also successfully applied for the synthesis of several other types of nanostructured materials such as ZnO [26].

Recently, sonochemical methods, a chemical reaction of the starting materials in the presence of applied high frequency ultrasonic waves, has been employed for several purposes and the effect of ultrasound on chemical reactions is not well understood, however it is mostly believed that a sonication acoustic cavitation phenomenon generates cavities in the liquid solution of the reactants. The cavitation processes consist of the creation, growth and implosive collapse of gas vacuoles in the solution. According to the "hot-spot" theory, extreme temperatures (> 5000 K) and high pressures (> 1000 atm) occur within the bubbles during cavitational collapse [27-30]. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals, $H^+$ and $OH^-$ when $H_2O$ is sonicated for example. The liberated radicals therefore, may lead to various chemical and physical effects in reaction pathways and mechanisms. Moreover, the other benefit in using ultrasonic waves in reactions is believed to be providing highly-intensive mixing especially in viscous media. This would lead to an acceleration effect in chemical dynamics and rates of the reactions. Therefore, by this circumstance,

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different properties of the final products such as particle size, shape and its purity would be controlled by as sonication output power, temperature, the solvent, the chemical species and their concentrations in the reaction mixture.

Using ultrasonic wave to synthesis as an external source of energy, affects the final properties of products. As mentioned before, this energy even can change the chemical route of synthesized particles. Due to the mentioned phenomena and by considering the reduction in size by increasing sonication power, the whole optical properties of synthesized nano particles could change. This can cause severel differences in the nature of the materials obtained. In semiconductors, the reduction in size can influence the wavelength of optical absorption edge and consequently the band gap energy [31]. Thus besides the differences in morphology and particles size of synthesized particle, the band gap energy which acts as a main character of semiconductors in all aspects, should be investigated carefully [32].

In the present paper, $TiO_2$ nanoparticles were synthesized via a sonochemical method. Temperature and sonication power were investigated in current issue as variables. TEM and XRD investigations were used to studying morphological and structural characteristics of nanomaterials.

## Experimental

### Materials and equipment

An amount of tetraisopropyl titanate ($C_{12}H_{28}O_4Ti$, Merck), sodium hydroxide (NaOH, Merck), ethanol ($C_2H_5OH$, Merck, 99.99%) and deionized water were used to synthesize the pure nanosized $TiO_2$ particles.

A high-intensity ultrasonic probe (Misonix S3000, Ti horn, 20 kHz, 100 W/cm$^2$, USA) and a flat-bottomed Pyrex glass vessel (total volume of 150 ml) were used for the ultrasound irradiation.

### Synthesis of nano $TiO_2$ via sonochemical method

NaOH was dissolved in deionized water and the solution (1 M, 50 ml) was added drop-wise to an aqueous $C_{12}H_{28}O_4Ti$ solution that was dissolved in ethanol (0.25 M, 50 ml) within about 30 minutes at a synthesis temperature of 50 °C. During this process, the solution was irradiated with an ultrasonic horn at different sonication powers. The solution was irradiated with ultrasonic irradiation for the different initial sonication powers listed in Table 1. The initial power (W) given by the operation and the ultrasound intensity (W/cm$^2$) was determined by sonicator. The sonochemical reaction was continued for 60 minutes and different $TiO_2$ samples were prepared by this procedure under different conditions.

**Table 1.** The samples synthesized at different sonication power at 50 °C

| V | IV | III | II | I | Sample |
|---|---|---|---|---|---|
| 1 | 3 | 5 | 7 | 9 | Initial sonication power (W) |
| 9 | 15 | 24 | 33 | 48 | Ultrasound intensity (W/cm$^2$) |

During the sonochemical reaction, it was observed that the color of the slurry changed gradually from colorless (before the reaction) into white-lactic. These changes of colors in the solution occurred as $TiO_2$ nanoparticles were prepared.

Finally, precipitated particles were collected, filtered and washed carefully with methanol and double distilled water to remove by-products. All the prepared samples were dried in air at room temperature for 48 h.

### Characterization

The $TiO_2$ nanoparticles were characterized by different techniques. The evaluation of crystal structure and determination of crystallite size were by X-ray diffraction (XRD) patterns (SIEMENS, D5000) with Cu-K$_\alpha$ radiation source. An acceleration voltage of 30 kV with a 25 mA current flux and an angular speed of 2°/minute were used to record the patterns in the 2θ range of 20°-70°. Thermogravimetry differential thermal analysis (TG-DTA) was simultaneously used in air at a heating rate of 10 K·minute$^{-1}$ (STA 1640).

The morphology of the prepared samples was analyzed using a transmission electron microscope (ZEISS, Germany). TEM samples were prepared by dispersing a few drops of $TiO_2$ on carbon films supported by copper grids.

## Results and Discussion

### X-Ray Diffraction analysis

Fig. 1 shows the XRD patterns of $TiO_2$ nanoparticles prepared via a sonochemical method. Fig. 1(a) shows the XRD pattern of $TiO_2$ nanoparticles prepared via a sonochemical method at 50 °C. Fig. 1(b) and Fig. 1(c) show the XRD patterns of $TiO_2$ for samples (I, V) that were calcined at 500 °C for 1 h. It is seen that anatase (JCPDS.

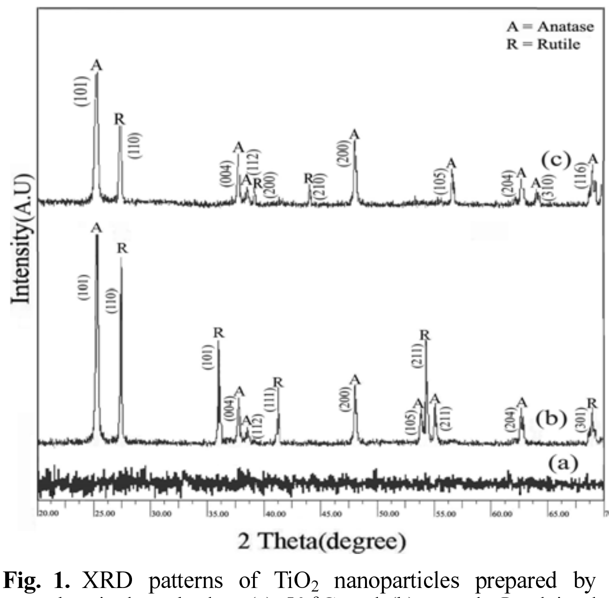


**Fig. 1.** XRD patterns of $TiO_2$ nanoparticles prepared by a sonochemical method at (a) 50 °C and (b) sample I calcined at 500 ° for 1 h (c) sample V calcined at 500 °C for 1 h.

Pattern 21-1272) and rutile (JCPDS. Pattern 21-1276) phases exist in the diffractograms.

In the X-ray diffractogram of all the samples, the characteristic peaks of anatase and rutile at ($2\theta = 25.2^o$, $37.8^o$, $38.5^o$, $48^o$, $53.8^o$, $55.0^o$, $62.6^o$, $64.1^o$, $68.8^o$) and ($2\theta = 27.4^o$, $36.0^o$, $39.2^o$, $41.2^o$, $44.1^o$, $54.3^o$, $69^o$) were observed, respectively. Also, the present method has been shown to be advantageous as it has been able to retain the anatase and rutile phases of $TiO_2$ even at 500 °C, while there are reports that the anatase can be converted to the rutile phase at temperatures higher than 450 °C [12].

The peak broadening of an XRD reflection can be used to estimate the crystallite size based on Scherrer's equation as follows [33]:

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

where $D$ is the crystallite size (nm), $k$ is a shape-sensitive coefficient (0.9, assuming spherical spheres), $\lambda$ the wavelength of the X-ray beam ($\lambda = 0.15406$ nm for Cu-$K_\alpha$ radiation), $\beta$ the full width at half maximum (FWHM) for the diffraction peak under consideration, and $\theta$ the diffraction angle.

The average crystallite sizes of the rutile and anatase phases determined from Scherrer's equation are about 8 nm.

## TG-DTA analysis

The XRD results showed that the initial product had amorphous characteristics. Thermogravimetric and differential thermal analysis (TG/DTA) was used to determine the temperature and time of crystallization of $TiO_2$ nanoparticles. Fig. 2. Shows TG-DTA curves of $TiO_2$ nanoparticles obtained from the suspension sonicated for 1.5 h at 50 °C.

According to Fig. 2, the samples were heat treated at 500 °C for 1.5 hour to obtain the crystalline titanium dioxide nanoparticles. A main exothermic peak at around 500 °C is detected in the TG-DTA curve. The exothermic peak at around 500 °C shows the crystallization temperature of the amorphous particles and the formation of $TiO_2$ phase occurs in this process. The TG-DTA curve shows that the weight loss is about 15%. The weight loss remains constant while the DTA curve decreases with an increase in the temperature because this weight loss depends on the intrinsic value of the material and is realized in a special temperature range and is independent of an increase in the temperature.

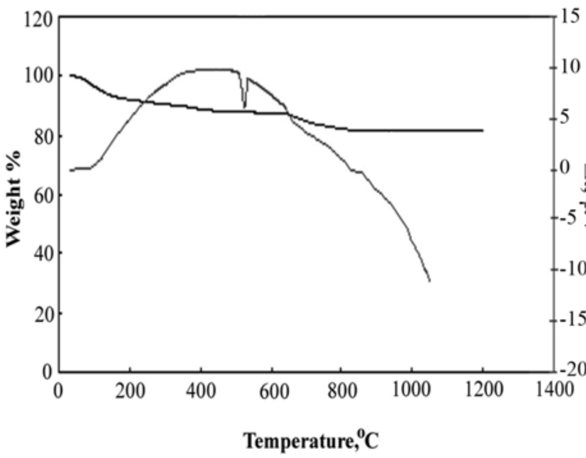


**Fig. 2.** TG-DTA curves of the nanopowders synthesized by ultrasound irradiation for 1.5 h at 50 °C.

## TEM analysis

Fig. 3. shows TEM images of $TiO_2$ nanoparticles prepared with different intensities of ultrasound waves. The particle sizes of $TiO_2$ from the TEM images are listed in Table 2. The average size of $TiO_2$ nanoparticles was increased from 12 to 30 nm when the intensity of the ultrasound waves was decreased from 48 W/cm$^2$ to 9 W/cm$^2$ in this process (Fig. 4).

A study of the morphology of nanoparticles in this sonochemical process showed that with different ultrasound intensity, the morphology of $TiO_2$ nanoparticles is nearly spherical and semi spherical with a smooth geometry. From TEM images of these nanoparticles, it can be clearly seen that the nanoparticles have some aggregation. Also, the images proved that the $TiO_2$ nanoparticles were agglomerated in some places.

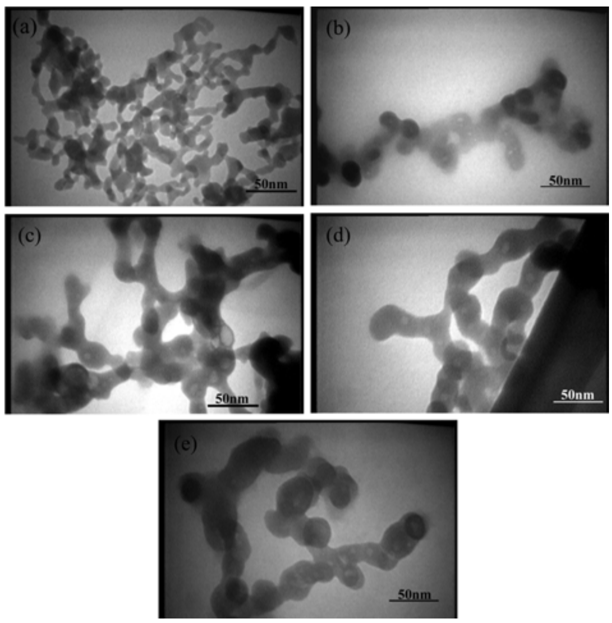


**Fig. 3.** Transmission electron microscopy (TEM) images of $TiO_2$ nanoparticles calcined at 500 °C and synthesized at (a) 48 W/cm$^2$ (b) 33 W/cm$^2$ (c) 24 W/cm$^2$ (d) 15 W/cm$^2$ (e) 9 W/cm$^2$.

**Table 2.** Particle sizes of synthesized samples from TEM images

| Sample | Particles Size(nm) |
|---|---|
| I | 12 |
| II | 18 |
| III | 23 |
| IV | 28 |
| V | 30 |

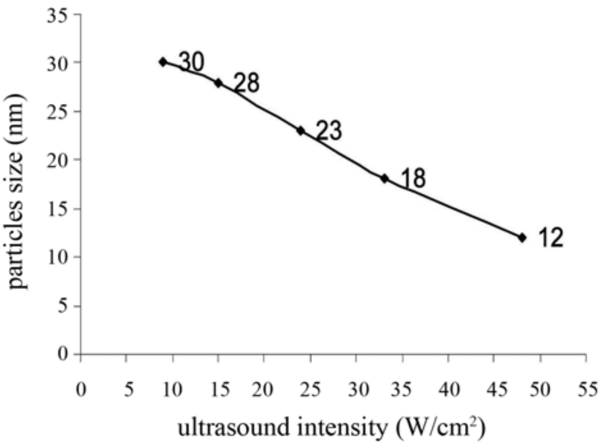


**Fig. 4.** Variation of particles size vs. the ultrasound intensity.

**Effect of ultrasound intensity (sonication output power)**

The results obtained in this section show that the ultrasound intensity plays very important roles in the morphological and dimensional properties of titanium dioxide nanoparticles. Also, in this process, the ultrasound intensity plays two different roles. 1) the dispersion of $TiO_2$ nanoparticles and 2) the production of $TiO_2$ nanoparticles with broken chemical bonds.

In the case of ultrasound intensity, increasing the ultrasound intensity increases the cavitations phenomenon so the collapsed cavity in the solution creates a shockwave and hence the particles size is decreased. Also, the shockwaves on the surface are known to create a localized erosion which is responsible for many sonochemical effects on heterogeneous reactions [34]. Moreover, the shockwaves created by homogeneous cavitations can create high velocity inter-particle collisions [34-36].

The final results indicate that the sonochemical method can be easily controlled and is expected to be applicable for fabrication of other nanosized particles.

## Conclusions

In this paper, $TiO_2$ nanopowders were synthsized via a sonochemical method successfully. The processing conditions have important effects on the morphology, particle size and the formation of a stable phase. Also, increasing the ultrasound intensity decreases the particle size of the $TiO_2$. With an increase in the calcination temperature about 450 $^oC$, the anatase phase can be converted to the rutile phase.

According to the results, the median size of the particles is about 12-30 nm and the average size of the crystallite for two stable phases (anatase and rutile) in this process is about 8 nm. The morphology of particles is spherical and semi spherical.

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