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

Amir Hassanjani-Roshan a,b,* , Seyed Mohammad Kazemzadeh a,b, Mohammad Reza Vaezi a and Ali Shokuhfar c

aMaterials and Energy Research Center, P.O. Box 14155-4777, Karaj, Iran
bEngineering Department, Islamic Azad University, Karaj Branch, Tehran, Iran
cAdvanced Materials and Nanotechnology Research Center; Faculty of Mechanical Engineering, K.N. Toosi University of Technology, Tehran, Iran

Titanium dioxide (TiO₂) nanoparticles were synthesized by a sonochemical method. C₄H₉O₂Ti (Tetraisopropyl titanate), ethanol (C₂H₅OH), 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 TiO₂ nanoparticles are vital factors in determining the properties of the final material. TiO₂ has three polymorphic phases namely anatase, rutile and brookite. Among these three crystalline phases, the anatase phase exhibits the highest photocatalytic activity. Rutile- TiO₂ is known as a white pigment because of its high scattering effect which leads to protection from the ultraviolet light [1, 2].

TiO₂ is one of the most extensively studied oxides because of its remarkable optical and electrical properties [3]. TiO₂ 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 TiO₂ 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 TiO₂, 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 cavitation collapse [27-30]. Under such extreme conditions the solvent molecules undergo hemolytic bond breakage to generate radicals, H⁺ and OH⁻ when H₂O 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,
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 several 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, TiO₂ 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 (C₁₂H₂₆O₄Ti, Merck), sodium hydroxide (NaOH, Merck), ethanol (C₂H₅OH, Merck, 99.99%) and deionized water were used to synthesize the pure nanosized TiO₂ particles.

A high-intensity ultrasonic probe (Misonix S3000, Ti horn, 20 kHz, 100 W/cm², USA) and a flat-bottomed Pyrex glass vessel (total volume of 150 ml) were used for the ultrasound irradiation.

Synthesis of nano TiO₂ via sonochemical method

NaOH was dissolved in deionized water and the solution (1 M, 50 ml) was added drop-wise to an aqueous C₁₂H₂₆O₄Ti 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/cm²) was determined by sonicator. The sonochemical reaction was continued for 60 minutes and different TiO₂ samples were prepared by this procedure under different conditions.

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 TiO₂ 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 TiO₂ 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-Kα, 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 TiO₂ on carbon films supported by copper grids.

Results and Discussion

X-Ray Diffraction analysis

Fig. 1 shows the XRD patterns of TiO₂ nanoparticles prepared via a sonochemical method. Fig. 1(a) shows the XRD pattern of TiO₂ nanoparticles prepared via a sonochemical method at 50°C. Fig. 1(b) and Fig. 1(c) show the XRD patterns of TiO₂ for samples (I, V) that were calcined at 500°C for 1 h. It is seen that anatase (JCPDS.

<table>
<thead>
<tr>
<th>V</th>
<th>IV</th>
<th>III</th>
<th>II</th>
<th>I</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>Initial sonication power (W)</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>24</td>
<td>33</td>
<td>48</td>
<td>Ultrasound intensity (W/cm²)</td>
</tr>
</tbody>
</table>
The effect of sonication power on the sonochemical synthesis of titania nanoparticles

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 \((2\theta = 25.2^\circ, 37.8^\circ, 38.5^\circ, 48^\circ, 53.8^\circ, 55.0^\circ, 62.6^\circ, 64.1^\circ, 68.8^\circ)\) and \((2\theta = 27.4^\circ, 36.0^\circ, 39.2^\circ, 41.2^\circ, 44.1^\circ, 54.3^\circ, 69^\circ)\) 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\(^\circ\)C, while there are reports that the anatase can be converted to the rutile phase at temperatures higher than 450\(^\circ\)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]:

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]  

(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\(^\circ\)C.

According to Fig. 2, the samples were heat treated at 500\(^\circ\)C for 1.5 hour to obtain the crystalline titanium dioxide nanoparticles. A main exothermic peak at around 500\(^\circ\)C is detected in the TG-DTA curve. The exothermic peak at around 500\(^\circ\)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.

**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. 2. TG-DTA curves of the nanopowders synthesized by ultrasound irradiation for 1.5 h at 30 °C.](image)

![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\(^2\).](image)

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particles Size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>12</td>
</tr>
<tr>
<td>II</td>
<td>18</td>
</tr>
<tr>
<td>III</td>
<td>23</td>
</tr>
<tr>
<td>IV</td>
<td>28</td>
</tr>
<tr>
<td>V</td>
<td>30</td>
</tr>
</tbody>
</table>
different roles. 1) the dispersion of TiO$_2$ nanoparticles and dimensional properties of titanium dioxide nanoparticles. Also, in this process, the ultrasound intensity plays two very important roles in the morphological and semi spherical.

In this paper, TiO$_2$ nanopowders were synthesized 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°C, 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.

Conclusions

In this paper, TiO$_2$ nanopowders were synthesized 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°C, 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.

References