On The Effect of Hydrothermal Temperature Treatment on the Phase Structure, Morphology and Optical Properties of TiO₂ Nanoparticles

Asmaa Dahy ¹, M. Dongol ², A. A. Ebnalwaled ¹,³*

¹ Electronics & Nano Devices Lab, Physics Department, Faculty of Science, South Valley University, Qena, 83523 Egypt.
² Nano & Thin Film Lab, Physics Department, Faculty of Science, South Valley University, Qena, 83523 Egypt.
³ Faculty of Nanotechnology for Postgraduate Studies, Cairo University, Sheikh Zayed Campus, 6th October City, Giza, 12588, Egypt
kh_ebnalwaled@yahoo.com

Abstract

In the current work, the morphology, structure, and optical properties of TiO₂ nanoparticles were studied to examine the effect of hydrothermal temperatures treatment on the nanoparticle’s properties. The prepared TiO₂ nanoparticles were analyzed by X-ray diffraction (XRD), high-resolution electron microscopy (HR-TEM), Fourier-transforming infrared spectroscopy (FTIR), and Ultraviolet-Visible (UV-Vis) spectrophotometers. Hydrothermal treatment leads to a crystalline transition from the anatase phase to the monoclinic phase in the commercial nanoparticles of TiO₂ and decreases the particle size. Results from the HR-TEM indicated that a nanosheet was observed in comparison to commercial TiO₂ nanoparticles after hydrothermal treatment. Analysis of UV-Vis revealed that the transmission and absorption of TiO₂ samples treated with different hydrothermal reaction temperatures were changed compared to the original sample. Taken together, hydrothermal temperature treatment signifies the morphology, structure, and optical properties of TiO₂.

Keywords: nanostructure, TiO₂, anatase, bronze, hydrothermal treatment.

Date of Submission: 20-08-2021  Date of Acceptance: 05-09-2021

I. Introduction

Titanium dioxide (TiO₂) nanomaterial is commonly regarded as a photocatalyst due to elevated levels of oxidation, nontoxicity, photoactivity, high chemical photostable levels and human and environmental safety [1-3]. A variety of applications, including solar cells, self-wash structure, water restoration, pollutant depletion, battery, and chemical sensors, are widely used in TiO₂ photocatalytic [4-6]. The photocatalytic behavior of TiO₂ nanostructures has been reported to be related to their particle size, specific surface area, morphology, and the synthesis process regulated by crystal structure [7, 8]. Therefore, TiO₂, as a photoelectrode material for solar cells, is commonly regarded as a photocatalyst due to elevated levels of oxidation and human and environmental safety [1-3]. A variety of applications, including solar cells, self-wash structure, water restoration, pollutant depletion, battery, and chemical sensors, are widely used in TiO₂ photocatalytic [4-6]. The photocatalytic behavior of TiO₂ nanostructures has been reported to be related to their particle size, specific surface area, morphology, and the synthesis process regulated by crystal structure [7, 8]. Therefore, TiO₂, as a photoelectrode material for solar cells of third generation, shows comparatively high efficiency [9]. Their functional capabilities have also not been studied directly, but they are thought to have a large potential as functional materials [10]. Consequently, it is essential to improve the method for selectively synthesizing superior properties of TiO₂ polymorphs.

Under ambient conditions, TiO₂ exists in eight polymorphs include rutile, anatase, and brookite which are in natural polymorphs. Other polymorphs include TiO₂ (B) (bruce), TiO₂ (H) (hollandite), and the other three polymorphs can only be produced synthetically in the laboratory [11, 12]. The TiO₂ polymorphic band gap energy varies from 3.0 to 3.4 eV, which directly influences the band structure of each of the phases [13]. Due to their stability and easy synthetization, anatase and rutile forms have the widest practical applications. However, there are only a limited number of methods for the single-phase synthesis of the other polymorphs forms, including brookite and TiO₂ (B) [11]. Certain methods for the synthesis of TiO₂ nanoparticles include the sol-gel process, hydrothermal synthesis, the metal-organic chemical vapor deposition (MOCVD), flame combustion, and electrochemical anodization [14] are used. There are numerous benefits for hydrothermal techniques because the process is simple, economical, and very low-temperature nanoparticles can be prepared [15]. The production of TiO₂ nanostructure is determined by the conditions of synthetization (pressure, reaction temperature, reaction time, the initial amount of TiO₂ and sodium hydroxide (NaOH) concentration, acid washing and calcination [8, 16]. By adjusting the synthesis conditions, the single phase and the morphological control of titania crystals can be obtained. Therefore, hydrothermal temperature is considered as an effective
parameter for controlling the growth process and properties of TiO₂ nanoparticles. So the aim of this study is to investigate the effect of hydrothermal temperature treatment on the phase structure, morphology and optical properties of TiO₂ nanoparticles, which will open the door for more application of TiO₂ nanoparticles.

II. Materials And Methods

2.1. Chemical reagents for the synthesis of TiO₂
Titanium dioxide extra pure (purity 98%) was purchased from Loba Chemie Pvt, India. Sodium Hydroxide Anhydrous NaOH extra pure grade (purity 98%) was purchased from Top Chem, Egypt. Both reagents were used as received without further purification. Hydrochloric acid (HCl) (ADWIC, El-Nasr Pharmaceutical Chemicals co., Egypt) at concentration of 30-34% was used for washing and furthermore with distilled water.

2.2. Synthesis of TiO₂ nanoparticles
Figure 1 shows a schematic diagram for the synthesis of TiO₂ nanoparticles.

First step (Mixing): 1.5 g of commercial TiO₂ (16.79 nm, S1) was mixed with 60 mL of 10M NaOH. The mixture further was stirred for 20 min in a beaker (dipped in acetone and alcohol, and then rinsed with distilled water). The mixture was then transferred to Teflon-lined autoclave (hydrothermal reactor). The autoclave was placed in a preheated electric oven at different temperatures (110 (S2), 150 (S2), or 170 °C (S3)) for 24 h under autogenously pressure and static conditions, and then air-cooled to room temperature.

Second step (Acid washing): The obtained products were collected and washed with dilute HCl (pH 1.6) for 24 h to remove most of NaOH.

Third step (Washing): The precipitate was further washed with distilled water until the pH of the supernatant was close to 7.

Fourth step (Calcination): The obtained powder was calcinated at 450 °C for 2 h.

![Figure 1. Hydrothermal method used to prepare TiO₂ nanoparticles at different reaction temperatures.](image)

2.3. Materials Characterization
After treatment of TiO₂ by hydrothermal method at different temperature, various techniques were used to evaluate their structure, morphology, and optical properties. In this study, we analyzed the TiO₂ samples using X-ray diffraction (XRD) pattern data at room temperature for powder samples of TiO₂ by a PANalytical X’Pert powder Cu-Kα radiation (λ=1.54056 Å). The morphologies of the samples (S₁, S₂, S₃, and S₄) were detected by high resolution transmission electron microscopy (HR-TEM) (JEOL, JEM-2100 – Japan). The Fourier-transform infrared spectroscopy (FT-IR) technique (Jasco Model 4100 – Japan) was used to characterize the bond structure of the TiO₂ nanoparticles. Furthermore, the optical properties were characterized by using UV-Vis Spectrophotometer (analytic Jena, spectord 200 plus, Germany).

III. Results and Discussion

3.1. Crystallinity and phase identification
The XRD patterns of the prepared TiO₂ powders under different hydrothermal temperatures and the commercial TiO₂ without any modifications are shown in figures (2 a & b). The XRD pattern results revealed the overall crystalline structure and phase purity of the TiO₂. Figure (2 a) shows most of the peaks in S₁ and S₂ could be recorded as anatase (A) TiO₂, which are essentially in approval with the reported values [File Card No: 01-089-4203] [17]. Nevertheless, the diffraction peaks of Rutile (R) can also be found in S₁, but only Rutile {R (110),(301)} can also be found in S₂ and approved with the reported values [File Card No: 00-002-0494] [18]. These results suggest that the peaks{R(101),(220)} vanish and all peaks in S₁ and S₂ are with a tetragonal structure.
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The bulk of the fields in figure (2 b) can be shown as TiO\(_2\) monoclinic (M) in S3 and S4 which basically are reversed by the values [File Card No:03-065-1156] [19]. Raising the temperature of the hydrothermal could increase the number of peaks in S3 and S4. In addition, increasing the temperature for hydrothermal TiO\(_2\) lead to a transition in the top location as some peaks moved marginally to an elevated angel, such as the top of plane M (301) and M (-302). Hydrothermal treatment causes a change in the structure of S1 as shown by XRD analysis. Increasing the hydrothermal temperature could decrease the sharpness and the amplitude of the peaks for S2, S3 and S4 indicating a low crystallinity of TiO\(_2\) nanoparticles compared with S1. The XRD spectrum reveals that the S3 and S4 are polycrystalline in nature having monoclinic structure. As shown from the XRD patterns, each peak has a finite width. The inter-planer spacing \(d\) for every peak was calculated according to the Bragg law:

\[ n\lambda = 2d \sin \theta \]  

where \(n\) is an integer determined by the order of diffraction (\(n=1\)); \(\lambda\) is the wavelength of x-rays, \((\lambda = 1.541838\,\text{Å})\); \(d\) is the spacing between the planes in the atomic lattice, and \(\theta\) is the angle between the incident ray and the scattering planes. The lattice parameters of anatase, monoclinic TiO\(_2\) were calculated using unit cell software. The method and implementation are described by Holland [20].

The formula for tetragonal system is:

\[ \frac{1}{d^2} = \left( \frac{h^2 + k^2}{a^2} \right) + \left( \frac{l^2}{c^2} \right) \]

\(a = b ≠ c, \alpha = \beta = \gamma = 90\)  

The formula for monoclinic system is:

\[ \frac{1}{d^2} = \frac{1}{(\sin^2 \beta)} \left( \frac{h^2}{a^2} + \left( \frac{k^2 \sin^2 \beta}{b^2} \right) + \left( \frac{\left( \frac{l^2}{c^2} \right) - \left( \frac{2h \cos \beta}{ac} \right)} \right) \right) \]

\(a ≠ b ≠ c, \alpha = \beta = \gamma = 90 ≠ \beta\)

The lattice parameters of TiO\(_2\) synthesized at different hydrothermal temperatures are shown in tables 1&2. Crystallite size (D) of the obtained TiO\(_2\) was calculated from the Debye–Scherrer’s formula as shown in table 3.

\[ D = \left( \frac{0.9 \lambda}{\beta \cos \theta} \right) \]  

Crystallite size is decreased by increasing the hydrothermal temperature (figure 3).
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Table 1. Lattice parameters of commercial TiO$_2$ and treated hydrothermal at 110$^\circ$ C.

<table>
<thead>
<tr>
<th>Calculated Lattice parameters (Å)</th>
<th>Lattice Parameters from standard card no 01-089-4203 Anatase</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ commercial</td>
<td>TiO$_2$ at 110$^\circ$ C</td>
</tr>
<tr>
<td>a = b</td>
<td>3.7757</td>
</tr>
<tr>
<td>c = a</td>
<td>9.48347</td>
</tr>
<tr>
<td></td>
<td>3.78548</td>
</tr>
<tr>
<td></td>
<td>9.49533</td>
</tr>
<tr>
<td></td>
<td>3.785</td>
</tr>
<tr>
<td></td>
<td>9.514</td>
</tr>
</tbody>
</table>

Table 2. Lattice parameters of TiO$_2$ treated hydrothermal at 150$^\circ$ C and 170$^\circ$ C.

<table>
<thead>
<tr>
<th>Calculated Lattice parameters (Å)</th>
<th>Lattice Parameters from standard card no 03-065-1156 Monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ at 150$^\circ$ C</td>
<td>TiO$_2$ at 170$^\circ$ C</td>
</tr>
<tr>
<td>a =</td>
<td>12.24163</td>
</tr>
<tr>
<td>b =</td>
<td>3.72763</td>
</tr>
<tr>
<td>c = a</td>
<td>6.51727</td>
</tr>
<tr>
<td>β=</td>
<td>107.70021</td>
</tr>
<tr>
<td>Vol cell</td>
<td>283.3189</td>
</tr>
<tr>
<td></td>
<td>12.11203</td>
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<td></td>
<td>3.76586</td>
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<td>6.5249</td>
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<td>107.05</td>
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<td></td>
<td>284.23</td>
</tr>
</tbody>
</table>

Table 3. TiO$_2$ particle size values at different synthesize conditions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Condition</th>
<th>Phase</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Commercial</td>
<td>Tetragonal</td>
<td>16.79</td>
</tr>
<tr>
<td>S2</td>
<td>Treated at 110°C</td>
<td>Tetragonal</td>
<td>11.61</td>
</tr>
<tr>
<td>S3</td>
<td>Treated at 150°C</td>
<td>Monoclinic</td>
<td>5.55</td>
</tr>
<tr>
<td>S4</td>
<td>Treated at 170°C</td>
<td>Monoclinic</td>
<td>3.95</td>
</tr>
</tbody>
</table>

Figure 3. TiO$_2$ particle size values at different preparation conditions.
3.2. FT-IR spectra for TiO$_2$

The FT-IR is obtained as transmission spectra of the KBr sample pellets to characterize the bond structure of the TiO$_2$ nanoparticles. Figure (4) shows the FT-IR of the TiO$_2$-NPs prepared by hydrothermal method at different reaction temperatures (S2, S3, and S4) and S1 in the range of 4000 to 400 cm$^{-1}$. Four absorption bands are observed in all samples, the first peak is appeared between 3700 to 3000 cm$^{-1}$ and it belongs to stretching hydroxyl (O-H), representing the water as moisture. The second peak is observed between 2400 and 2300 cm$^{-1}$, and this absorption band was likely related to the stretching vibrations bonds C=O and (O–H) respectively, existing between the adsorbed water molecules and indicating the higher amount of hydroxyl group. The third peak is observed between 1700 and 1600 cm$^{-1}$, and it belongs to stretching of titanium carboxylate. The fourth one in the spectrum between 800 and 450 cm$^{-1}$ is assigned to Ti-O stretching bands [22].

![FTIR spectra for TiO$_2$ nanoparticles](image)

Figure 4. FTIR analyses for TiO$_2$ nanoparticles (S1, S2, S3, and S4)

3.3. Morphology of TiO$_2$

The HR-TEM was employed to obtain direct information about the shape and the size of the TiO$_2$ nanoparticles. It is known that in HR-TEM technique, the interference between the transmitted and the scattered beams produce an interference image. As shown from figure (5), it has been found that the different reaction temperatures could influence the shape and the size of the original commercial TiO$_2$ nanoparticles. From figure 5 S1 sample appears in a spherical particle form. While, increasing the hydrothermal reaction temperatures from 110 °C to 170 °C causes a change in the TiO$_2$ nanoparticles from tube shape to the sheet form, as well as a decrease in their particle size. The average size of all samples in the range of 3-20 nm which approximately is in close agreement with the results obtained from the powder.
3.4. Optical properties of TiO$_2$

3.4.1. Optical properties

In general, the interaction between any materials and incident light leads to a maximum absorption at a particular wavelength. In the current work, the absorption spectrum is given by suspending nano-powders of TiO$_2$ in a distilled water at room temperature using UV-visible spectroscopy. Figure (6 a) illustrate the transmittance for all samples. From the figure, it is evident that different hydrothermal reaction temperatures of TiO$_2$ nanoparticles affected the transmission of the samples with compared to the original sample before hydrothermal effect. S2 has relatively a higher transmission along the visible wavelengths. Subsequently, S3 has transmission value less than the values of S4 and S1. Figure (6 b) shows the absorbance spectra of TiO$_2$ nanoparticles samples over a spectral ranging between 200 to 1100 nm. For TiO$_2$ nanoparticles, the absorption edge is observed to be shifted towards longer wavelengths with the increase of reaction temperature from 110 ºC to 150 ºC (figure 6 b). This means that the absorption band of TiO$_2$ nanoparticles is shortened to near UV's wavelengths and resulted in a narrow absorption band. The absorption edge of TiO$_2$ nanoparticles has precisely measured and found to be 255 nm at S2 and increased in S3 to reach a value of 275 nm. These are much lower values than that reported for TiO$_2$ in its bulk form which has a value of 374.9 nm. On the other hand, the absorption edge value of S1 and S4 are not changed with the increase of reaction temperature to 170 ºC and has a value around 297 nm. It is much lower value compared to that of the bulk TiO$_2$ (374.9 nm).
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The optical band gap with direct transition can be calculated from the following relationship [21].

\[ a h \nu = B(h \nu - E_g)^n \]  \hspace{1cm} (5)

where \( h \nu \) is a photon energy and \( B \) is a parameter which depends on the transition probability, \( \alpha \) is the absorption coefficient, \( E_g \) is the optical band gap and \( n \) is a number characterizing the transition process which may take values of 1/2 and 3/2 for direct allowed and forbidden transitions, respectively. The direct band gap energy \( (E_g) \) of the TiO\(_2\) samples is determined by fitting the absorbance data to the direct transition equation

\[ a h \nu = B(h \nu - E_g)^{\frac{3}{2}} \]  \hspace{1cm} (6)

Figure (7, a-d) shows the plotting of \((a h \nu)^2\) as a function of photon energy \( h \nu \). The values of the optical band gap \( E_g \) for the prepared TiO\(_2\) nanoparticles was calculated. Based on the optical measurements, the \( E_g \) values of TiO\(_2\) were found to be \((3.72, 3.62, 3.18 \text{ and } 3.06)\) eV for S1, S2, S3, and S4, respectively. This means that the energy band gap is decreased with the increase of the hydrothermal reaction time. Further, the decrease in the crystalline size has found to be accompanied by the decreasing in the energy band gap.
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IV. Conclusion:

In the present paper, TiO₂ nanoparticles were prepared under different hydrothermal temperature treatment (110 °C, 150 °C and 170 °C) and compared with the original commercial TiO₂ nanoparticles. We summarized our results that the hydrothermal temperature affects the crystalline phases of the TiO₂ nanoparticles. In addition, HR-TEM showed that the morphology of TiO₂ nanoparticles can be controlled by the treated temperature. UV-Vis analysis showed that different hydrothermal reaction temperatures of TiO₂ nanoparticles could affect the transmission and absorbance of the TiO₂ nanoparticles.

DOI: 10.9790/1676-1605010109  www.iosrjournals.org  8 | Page
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DOI: 10.9790/1676-1605010109 www.iosrjournals.org