Effect of Acid Catalyser on the Synthesis of Photocatalytically Active Titanium Dioxide Nanopowders

Ahmed Hafedh Mohammed Mohammed¹, Jongee Park¹, Abdullah Öztürk²

¹Atılım University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, 06836, Ankara, Turkey
²Middle East Technical University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, 06800, Ankara, Turkey

Abstract

Titanium dioxide (TiO₂) nanoparticles were synthesized via acid assisted sol-gel process using tetra-isopropoxide as a precursor to enhance photocatalytic activity. The effects of different acids namely; acetic acid, hydrochloric acid, and nitric acid on the formation and photocatalytic properties of TiO₂ nanoparticles were researched. All the nanoparticles synthesized at various conditions were characterized using XRD, SEM, and UV-Vis spectrophotometer. The results showed that only anatase phase of TiO₂ nanoparticles with different crystallite size and morphology were synthesized with respect to the kinds of acid and the procedure applied. The TiO₂ powder synthesized from HCl exhibited highest photocatalytic activity, and its methylene blue photodegradation efficiency was 76.2%, 95%, and 98.1% in 30, 60, and 90 min UV irradiation, respectively.

1. Introduction

Recently, different strategies like the ion exchange, membrane filtration, electrochemical methods, etc., have been employed to resolve the water pollution problems [1]. Many factors including the stable state of its chemical and optical properties, as well as many other advantages such as low cost, insolubility in water, high efficiency, and its harmless property, point out to use titania (TiO₂) as a photocatalyst in water treatment [2,3]. The production of a thin or thick film of TiO₂ is one of the important researches in the domain of the photocatalyst to optimize the coating of TiO₂ solution on the different substrates [4]. There are many techniques or methods used in the production of TiO₂ films. The sol-gel process is one of the best methods to prepare thin oxide coating since it has multiple advantages including easiness, low-cost, and better homogeneity in the products [5].

The objectives of this work are i) to investigate the effects of different acids and different pH on the formation, morphology, and structure of TiO₂ nanoparticles, ii) to determine the effects of the developed morphology on the photocatalytic activity (PA) of TiO₂ nanoparticles synthesized, iii) utilization of the TiO₂ nanoparticles synthesized in waste water treatment.

2. Experimental Procedure

2.1. Synthesis of TiO₂ Nanoparticles

TiO₂ nanoparticles were synthesized using tetra-isopropoxide (TTIP, Aldrich 97%) as a precursor. First, various amount of different acids: acetic acid (CH₃COOH, Merck 100%), nitric acid (HNO₃, Aldrich 70%), and hydrochloric acid (HCl, Aldrich 37%) were added to the beaker containing 0.9 mL distilled water and 23.5 mL ethanol absolute (C₂H₅OH, Merck 99%). Second, 2.35 mL of TTIP was added drop wise to the solution during magnetic stirring for 30 min at room temperature (~25 ºC). The acidity of the solution was adjusted to 4. The sol was kept at room temperature for 1 day to form a gel. Then, the gel was dried in an oven at 80 ºC for 24 h to remove all moisture and to get fine particles. The fine particles were obtained in the form of agglomerate that was crushed to obtain a powder. After that, the powders were calcined at 550 ºC for 1 h in air. The heating and cooling rates were 2 and 6 ºC/min, respectively for all powders. Dry gels synthesized by using CH₃COOH were calcined at temperatures of 450, 550, and 650 °C. The TiO₂ nanoparticles synthesized were coded as CH-4, HCl-4, and HN-4 for CH₃COOH, HNO₃, and HCl solutions, respectively.

A coating solution was prepared from the powder synthesized by using HCl as a catalyst to get a coating layer on the glass substrates by dip–coating technique. The glass substrate was cleaned by immersing it in the beaker containing ethanol for 2 h and then dried in an oven at 80 °C for 30 min. Second, the substrate was dip-coated by immersing it in the coating solution for a minute and then dried in an oven at 80 °C for 10 min. This operation was repeated one, three, and five times to increase the coated layer thickness. The three films prepared were calcined at 550 ºC for 1 h.
2.2. Characterization of TiO₂ Nanoparticles

The phase(s) present in the TiO₂ nanoparticles synthesized was identified using X-Ray Diffractometer (Rigaku, D/MAK/B, Tokyo, Japan). All powders were scanned continuously from 20 of 20º to 80º at a scanning rate of 2/min with 0.02º increments. The surface morphology and particle size of the powders were examined using scanning electron microscope (SEM, Nova Nanosem 430).

2.3. Photocatalytic Measurement

The photocatalytic activity of TiO₂ nanoparticles synthesized was evaluated through degradation of methylene blue (MB) solution under a 125 W UV lamp with a wavelength at 365 nm and continuous stirring using a magnetic stirrer. The distance between the source and the surface of Pyrex container (300 mL capacity) was 5 cm. The MB solution was prepared first by dissolving 20 mg of MB in distilled water to get a concentration of 20 mg/L and then adding TiO₂ nanoparticles to this solution under continuous stirring to get the TiO₂ /MB concentration of 100 mg/20 mL. Before illumination of the UV light, the suspension aqueous solution was stirred continuously in dark for 30 min to ensure adsorption/desorption equilibrium. A 3.5 mL of the suspension was withdrawn every 30 min under the UV light. Then, a separation of the powders was done by centrifuge, and was analyzed using the UV–Vis spectrophotometer (Shimadzu UV-1800) to determine the concentration of MB. The removal efficiency of the photocatalyst was calculated as follows:

\[
\text{Degradation} \% = \frac{(C_a - C)}{C_a} \times 100 \tag{2}
\]

Where \(C_a\) and \(C\) are the concentrations of MB at initial and different irradiation time, respectively [6].

2.4. Photocatalytic Reactor for Water Treatment

A monitoring system was designed to test the photocatalytic efficiency of the glass substrates coated with titanium dioxide. A 5000 mL glass basin with open nozzles above it and a nozzle below was designed to rotate the liquid using a pump (Shenchen, YZ1515x) with a speed of 150 rpm. The light used to irradiate the material to be stimulated was placed in the center of the glass basin. The design of a plastic circle containing a total of small openings in order to be placed cylindrical glass pillars that are covered with TiO₂ solution.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Analyses

XRD analysis of the as-synthesized powders by using different acids revealed that regardless of the kind of acid used, all of the as-synthesized powders were amorphous. Figure 1 shows the XRD patterns of the powders synthesized by using different acid and then calcined at 550 ºC. The peaks at the angles of 25.3, 37.8, 48, 54, 55, 62.8, 68.7, 70.3, and 75 º correspond to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes, respectively of the anatase phase of TiO₂. All the diffraction peaks agree with the anatase phase (JCPDS 21-1272). No peaks belonging to rutile and brookite phases were detected in the powders. Similar results were reported by Zhou et al. [7] who attributed the formation of only anatase phase to the strong chemical coordination of titanium.

![Figure 1. XRD patterns of the calcined nanoparticles synthesized by using different acids. A) CH-4, B) HCl-4, and C) HN-4.](image-url)
as the percent crystallinity of the powders. Phase composition and crystallite size are presented in Table 1.

**Table 1.** The crystallite size and phase composition of the powders synthesized by using different acids.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Kind of acid</th>
<th>Crystallite size (nm)</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH-4</td>
<td>CH₃COOH</td>
<td>23.82</td>
<td>Anatase</td>
</tr>
<tr>
<td>HCl-4</td>
<td>HCl</td>
<td>22.48</td>
<td>Anatase</td>
</tr>
<tr>
<td>HN-4</td>
<td>HNO₃</td>
<td>15.96</td>
<td>Anatase</td>
</tr>
</tbody>
</table>

The sol-gel formation made the rearrangement of arbitrary bonds in the precipitation process toward the defined structure of anatase. The presence of acid accelerated the formation of anatase [8]. Considering the structures of the titania polymorphs, it is obvious that linear chains can only form rutile-type nuclei, while skewed chains are restricted to forming anatase-type nuclei [9].

Figure 2 shows the XRD patterns of the powders synthesized by using CH₃COOH and then calcined at 450, 550, and 650 ºC in air for 1 h. Only anatase phase was detected in the XRD patterns for all of the powders calcined at different temperatures.

![Figure 2](image-url)

**Figure 2.** XRD patterns of the powders synthesized using CH₃COOH as a catalyst and then calcined at temperatures of D) 450 ºC, E) 550 ºC, and F) 650 ºC.

It was observed that as the calcination temperature increased, the intensity (accordingly the amount) of the anatase phase increased suggesting a better crystallinity. The increase in the anatase phase has reflected the increase in the crystallite size because high temperature increases the tendency of crystal growth; hence, to achieve complete crystallization [10].

### 3.2. SEM Analysis

The representative SEM images of the powders synthesized are shown in Figure 3. SEM examinations revealed that the morphology of all of the powders consisted of agglomerates of nanoparticles of various sizes. The average particle size as obtained by Image Processing analytical software was 11.8, 10.8, and 10.7 nm for the powders synthesized by using CH₃COOH, HCl, and HNO₃, respectively. The particle size as determined from SEM images is close to that calculated from XRD measurements. It is obvious that the smallest particle size belongs to the sample synthesized by using HNO₃. An irregular distribution of particles as either a single particle or a cluster of particles has been noticed. The images shown in Figure 3 revealed that the particles synthesized by using HCl as a catalyst are agglomerated as small clusters while the particles synthesized by using HNO₃ are highly agglomerated as chunks or blocks. It was clear that when CH₃COOH was used as a catalyst, particles agglomerated as a big chunk and the agglomerates were irregular in shape. The findings agree with those reported by Golobostanfard et al. [11] who prepared TiO₂ powder by the sol-gel process using TTIP as precursor followed by calcination at 450 ºC. They reported that the formation and morphology of TiO₂ could be affected by the type of acid.
3.3. Photocatalytic Activity

The blue color of MB solution was completely removed after 90 min of UV illumination for all of the powders synthesized by using CH$_3$COOH, HCl, and HNO$_3$. The degradation percentages were fairly close to each other although little differences that emerged after 30 and 60 min of illumination, where the photocatalysis efficiency for the prepared samples was HCl-4 > HN-4 > CH-4. The degradation was almost the same after 90 min of illumination as shown in Figure 4. It was inferred that there is a little effect on the activity of photocatalysis when the acid type is changed. However, in order for the material to have a good photocatalytic efficiency, it should have a high surface area and good crystallinity [12]. An increase in crystallinity lead to enhancement of photocatalytic activity but, at the same time reduces the surface area which eventually decreases photocatalytic activity due to increase in crystallite size [13].

3.4. TiO$_2$ Layer Coated on Glass Substrate

The glass pillars used in the monitoring system have been coated by using the TiO$_2$ nanoparticles having the highest PA. 30 of glass pillars was coated for 1 time, 3 times, and 5 times using 150, 450, and 750 mg of TiO$_2$ nanoparticles synthesized, respectively. Before starting the system to measure PA using a catalyst, the MB was examined without using the catalyst for 7 h to ensure that light used in the system does not affect the dye. After that, the examination was carried out on the coated pillars for 7 h. Percent MB degradation of the coated layers was noted at 1 h interval. The results showed that increasing the number of coating layers, hence increasing the amount of TiO$_2$, lead to increase in PA. The photocatalytic efficiency of TiO$_2$ could be affected by the crystalline structure and the surface morphology of films [14]. It is clear that the rate of photodegradation depends on the thickness of the substrate, the decay rate was found to increase with film thickness [15].

4. Conclusions

The kind of acid strongly influences the crystallinity, crystalite size, and morphology of TiO$_2$ nanoparticles. The crystallization of the anatase phase depended on the ions, where Ti has a higher affinity in the order to CH$_3$COO$^-$ ions > Cl$^-$ ions> NO$_3^-$ ions. Also, calcination temperature affects the crystallinity and the size of the crystals. TiO$_2$ nanoparticle synthesized using HCl has the highest photocatalytic activity. TiO$_2$ coated glass was successfully prepared with different cycles and found that the cycle influence on the photodegradation rate by increasing the coating layer of TiO$_2$.

Acknowledgments

The authors would like acknowledge the Scientific and Technological Council of Turkey (TUBITAK) for the partial financial support through project 216M391.

References