Effect of HNO₃ on the Synthesis of TiO₂ Nanostructures by Hydrothermal Process

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Abstract

TiO₂ nanostructures of various phases and morphologies were synthesized by HNO₃ assisted hydrothermal process with respect to the acid molarity (1M, 3M, and 8M), temperature (110, 140, and 180 °C), and time (1, 3, and 6 h). The phases developed, crystal structure, and morphology of the nanostructures synthesized were investigated using X-Ray diffractometer, scanning electron microscope, and transmission electron microscope. The experimental results revealed that HNO₃ concentration, synthesis temperature, and duration have a profound effect on the phase formation, phase composition, and morphology of the resulting TiO₂ nanostructures.

1. Introduction

Titania (TiO₂) nanostructures have been intensively researched for numerous applications in many fields such as photocatalysis, photovoltaic cells, energy storage, and gas sensors [1-3]. There are three natural polymorphs of TiO₂ namely; anatase, brookite, and rutile. Anatase is mostly studied polymorph of TiO₂ because of its superior opto-electronic performance. Recently, phase pure rutile, brookite, and mixtures of the two and three of the polymorphs have been reported to exhibit comparable performance for photocatalysis and solar cells [4]. Indeed, for each application careful tailoring of specific properties such as phase composition, surface area, and morphology is requested. Accordingly, several TiO₂ nanostructures such as spheres, nanorods, and nanotubes have been synthesized using different techniques including sol-gel, electrochemical, sonochemical, and hydrothermal [5-7].

Hydrothermal process is a one-step environmentally friendly method to synthesize nanostructured materials. The starting material and synthesis conditions (time, temperature, pH, catalyzer type) affect the properties and performance of final product. The acid media used in the preparation significantly influence the crystal structure and photocatalytic activity of TiO₂ nanocrystals [8]. Low concentration of acids promotes the formation of anatase while high concentrations encourage the formation of rutile [1, 9]. Other than pH, acid type is also effective on the morphology and crystal structure of TiO₂. Specifically, use of CH₃COOH results in anatase formation, HCl favors the formation of rutile crystals, and HNO₃ yields anatase and rutile mixtures [9-11].

Crystal structure is mostly related to morphological feature of TiO₂. Rutile is the most stable phase of TiO₂. However, anatase becomes the most stable phase in nanoscale due to low surface energy of this polymorph. As particles grow, anatase to rutile transformation occurs [12]. Although there are many publications reporting acid assisted hydrothermal synthesis of TiO₂, the overall mechanism which is affected by many mechanisms is yet unclear.

The purpose of this investigation was to carry out a systematic study for the synthesis of TiO₂ nanostructures in various morphologies and crystal structures using HNO₃ assisted hydrothermal treatment. The effects of synthesis temperature and time, and acid molarity on the evolution of TiO₂ nanostructures were researched. Results revealed that the most important parameter for the development of a given TiO₂ phase is the molarity of the acid though synthesis time and temperature are effective on phase share and crystallinity.

2. Experimental Procedure

2.1. Powder Synthesis

The TiO₂ nanoparticles were synthesized through a procedure described previously [13]. Synthesis began by diluting concentrated HNO₃ (Aldrich 70%) with distilled water to obtain 1, 3, and 8M HNO₃ solution. Then, 10 mL of titanium tetra isopropoxide (TTIP, Aldrich 97%) was added dropwise into the freshly prepared HNO₃ solution during magnetic stirring at 300 rpm for 15 min. White precipitates formed immediately after TTIP addition in the solution consisting 1M and complete dissolution formed by 3
and 8M acid catalyst. The solution of 150 mL was transferred into the Teflon lined vessel of the high pressure hydrothermal reactor. The capacity of the vessel was 250 mL. Hydrothermal treatment was performed at temperatures of 110, 140, and 180 °C for 1, 3, and 6 h. Nanopowders synthesized were coded according to acid molarity, time and temperature as tabulated in Table 1. In the codes, the digit next to P represent acid molarity, the second digit represents the synthesis time in h, and the last digit is reserved for the second digit of synthesis temperature.

Table 1. Experimental and structural parameters of the nanoparticles synthesized.

<table>
<thead>
<tr>
<th>Code</th>
<th>Percentage of the phases (wt %)</th>
<th>Crystallite size of the phases (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>R</td>
</tr>
<tr>
<td>P111</td>
<td>89</td>
<td>8</td>
</tr>
<tr>
<td>P311</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>S811</td>
<td>56</td>
<td>44</td>
</tr>
<tr>
<td>P318</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>P338</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>P368</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>P318</td>
<td>-</td>
<td>&gt;99</td>
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<tr>
<td>P864</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>P868</td>
<td>59</td>
<td>41</td>
</tr>
</tbody>
</table>

A: Anatase, R: Rutile, B: Brookite, NC: Not calculated.

2.2. Characterization

The nanopowders synthesized were detected by an X-ray diffractometer (Rigaku, D/MAK/B). The phase composition, purity, and crystallinity of all the nanopowders were identified through the X-Ray diffraction (XRD) analysis conducted in the continuous scan mode at a rate of 0.03°/s. The phase content of the nanopowders was calculated by Rigaku 4.1 Software. The average crystallite size of each phase was calculated by using the Scherer equation with respect to FWHM. Anatase crystal size was determined from (101) plane at 2θ of 25.3°, (004) plane at 2θ of 37.6°, and (200) plane at 2θ of 48°. Crystal sizes for brookite and rutile were determined from (121) plane at 2θ of 30.8° and (110) plane at 2θ = 27.4°, respectively. The same amount (~ 0.2 g) of powder was used for every analysis. Lattice parameters of the nanopowders were calculated also from the XRD data.

Surface morphology, size, and shape of the nanopowders were examined using a FEI, Nova Nanosem field-emission scanning electron microscope (FESEM) at operating voltage of 18 kV. High resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) examinations were carried out with a JOEL TEM 2100 microscope at an operating voltage of 200 kV.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

XRD patterns of the selected nanopowders synthesized are given in Figure 1. The nanoparticles exhibited the characteristic peaks corresponding to anatase (PDF no. 12-1272), and/or brookite (PDF no. 29-1360), and/or rutile (PDF no. 21-1276) phases. No peaks belonging to other TiO$_2$ phases or contaminations were detected.

![Figure 1. XRD patterns of the nanopowders synthesized.](image)

The first three patterns shown in Figure 1 are related to the effect of acid molarity. X-Ray pattern of P111 shows that nanopowder consists of phase pure anatase. The HNO$_3$ assisted hydrothermal synthesis produced anatase-rutile mixtures due to the fact that Ti has higher affinity to NO$_3$ ions than to Cl ions. Higher affinity of Ti to NO$_3$ promoted anatase crystallization. The broadening of 101 peak of anatase indicates the small size of crystallites present in the nanopowder. The phase percentages and crystallite size of the nanopowders as calculated by the Scherrer equation were given also in Table 1. Increasing amount of NO$_3$ ions favors corner shared bonding between the complex ions. Thus, rutile phase evolves by increasing acid molarity while broadening decreases as indicated in the XRD pattern of P311. Further increase in acid molarity increases anatase percentage without a significant change of crystallite size as depicted in the pattern of P811.

The second three patterns in Figure 1 are related to the effect of time. Phase pure anatase is obvious in the XRD patterns of P318. When the synthesis duration increases to 3 h, crystallinity also increases in anatase phase. Rutile transformation is realized when catalyzer amount is increased. Further increase of synthesis duration favors the formation of a large amount of rutile with a small amount of anatase implying nearly entire transformation from anatase to rutile.
The last three patterns shown in Figure 1 are for the effect of temperature. An interesting result is the detection of phase pure rutile structure at the lowest temperature of 110 °C because of the high amount of acid catalyzer which promotes rutile formation. When the temperature increases to 140 °C, the structure turns into phase pure anatase. This result is attributed to the development of very fine crystals at this temperature. Further increase in temperature to 180 °C favors the growth of anatase and rutile phases together along with the broadening of 101 and 110 peaks.

3.2. Morphological Analysis

Figure 2 shows the representative FESEM images of selected powders. FESEM image of P338 shown in Figure 2 (a) indicates that nanostructures are prone to agglomeration. FESEM image of P111 shown in Figure 2 (b) illustrates that the agglomerated nanostructures in micrometer scale spheres are being etched by acid catalyzer. These etched structures form bundles as depicted in Figure 2 (c), FESEM image of P311. Etching of the catalyzer is probably a selective process which targets particular planes.

FESEM image of P368 is shown in Figure 2 (d). Rod arrays can be seen clearly. As indicated in Figure 1, the sample consists of largely rutile phase. Etching process of acid catalyzer resulting in rutile phase evolves in rod arrays. In order to do a detailed investigation, HRTEM analysis were done to the powders. Nanoparticle forms can be seen clearly in P368 as illustrated in Figure 3. A hard agglomeration is realized that after sonication for sample preparation, the nanoparticles were not separated. The lattice fringes measured is 0.33 nm belongs to rutile (110). The findings suggest that the growth direction is [001] that is perpendicular to the [010] direction. The SAED pattern shown in the inset in Figure 3 (a) suggests the existence of anatase (004) plane that verifies the growth of rutile phase on the surface of anatase crystals during the hydrothermal synthesis. The crystals grow in one direction to form ellipsoids. The bundle like structure obtained in P861 is indicated in Figure 3 (b). The findings prove that etching process occurs to diminish (001) planes of rutile which is the most energetic plane of rutile phase. This structure is considered to form with the nucleation and growth of the crystallites and selective etching of the rod arrays due to strong acid concentration.

Figure 3. HRTEM images of nanopowders (a) P368 and (b) P368. Inset in (a) shows SAED pattern of the powder.

Acid catalyzers lead the final morphology by NO₃ adsorption to the surfaces of nanostructures. Cl ions form rod structure [14]. NO₃ ions are known to attract Ti atoms as proven in this study. Various morphologies of particles form by the influence of NO₃ ions that promote anatase crystallization due to lower surface energy. In strong acid concentration, anatase grains agglomerates quickly because of the high energy of nanostructures. The (004) planes of anatase structure dominate the whole surface and increase the surface energy. The energetic planes increase the total energy of the system and rutile transformation starts to decrease the energy. As a result of this transformation a core-shell structure evolves. The core-shell structure is etched by HNO₃ selectively (see Figure 2 (b)) to release the rutile surface of (110) planes. As the morphology turns into oriented grains, the growth of the most energetic plane of rutile (001) is limited by the NO₃ ions in the solution. Thus, the oriented structure grows in the [001] direction forming 1D structure in this plane. Because of etching, pedals grow in [001] direction and a rod array structure forms as indicated in Figure 3 (b). Similar results have been reported by Lin et al. [16] for the synthesis of rutile TiO₂ by HCl assisted hydrothermal treatment.
4. Conclusions

Phase pure anatase and rutile nanostructures could be obtained using hydrothermal process catalyzed by 1 M and 8 M HNO₃. But phase pure brookite could not be synthesized considering the conditions studied. Binary and ternary phase mixtures could be synthesized including anatase-rutile and anatase-rutile-brookite phases. Low amount of acid catalyzer favors the formation of anatase. Increase of acid molarity increases rutile content. The highest acid molarity leads anatase formation reversely. As duration increases rutile content also increases. The lowest temperature results in rutile formation using highest amount of acid catalyst. Increasing temperature leads anatase formation and further increase of temperature results in anatase rutile mixture. The phase transformation occurs with thermodynamic rules. However, as dissolution of particles continue in the acidic environment it is easy to predict the final phase. Thus synthesis is controlled by both thermodynamics and kinetics.

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References