

# FACILE SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURE TITANIA PREPARED BY THERMAL HYDROLYSIS ROUTE

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## ABSTRACT

Titania (TiO<sub>2</sub>) is a highly promising photocatalytic material due to its unique electronic properties, robust physical and chemical stability, and significant potential for resolving a wide range of environmental issues. In this study, titania was successfully prepared using a facile one-step thermal hydrolysis of an aqueous TiOSO<sub>4</sub> solution. Based on XRD results and Debye-Scherrer calculations, the variation in ammonia concentration is directly in-line with the crystallite growth of the material from 8.39 nm at 5% ammonia to 14.11 nm at 25% ammonia. Our findings revealed that the synthesized material has higher thermal stability than other methods. The results indicate that the anatase to rutile transition occurs at temperatures above 700°C, while in other studies, the rutile phase usually occurs at 600°C. Based on the SEM results, the materials have a rough morphology, and irregular agglomerates with different sizes of titania were found. Further work is needed to control the morphology and size of the material for use as a highly efficient photocatalyst.

**Keywords:** Hydrolysis, Synthesis, Thermal, TiO<sub>2</sub>, TiOSO<sub>4</sub>, Titania.

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## INTRODUCTION

In the past few years, semiconductor photocatalysis has gained much attention due to its potential use in addressing environmental issues. Among the semiconductor materials, titania (TiO<sub>2</sub>) has been extensively explored because of its use in solar energy conversion, water purification, water splitting, CO<sub>2</sub> reduction, sensor devices, pigments, ammonia removal, phenol degradation, and antibacterial agents.<sup>1-10</sup> These wide ranges of applications are attributed to the unique properties of TiO<sub>2</sub>, for example, its strong chemical and physical stability, excellent optical and electronic characteristics, good photosensitivity, no toxicity, low cost, environmental friendliness, and absence of secondary pollutants.<sup>11,12</sup> Titania possesses three prevalent polymorphic forms, which are anatase, rutile, and brookite.<sup>13</sup> Each of these polymorphic forms of titania has different atomic arrangements and properties. Anatase has a tetragonal crystal structure with a space group of I41/amd.<sup>14</sup> It has a relatively high surface area, which makes it an excellent photocatalyst. Anatase has a lower density compared to rutile and brookite, and it absorbs a broader range of light wavelengths, including ultraviolet (UV) light. Due to its photocatalytic properties, anatase is widely used in various applications such as solar cells, self-cleaning surfaces, and environmental remediation. Rutile is the most stable phase and commonly occurring form of titania, while anatase and brookite are metastable phases that can be transformed into rutile at higher temperatures. It crystallizes in a tetragonal structure and belongs to the P42/mnm, consisting of corner-sharing TiO<sub>6</sub> octahedra.<sup>15</sup> Rutile is known for its excellent stability, high refractive index, and resistance to chemical and thermal degradation. Brookite is the least common polymorph of titania. It has an orthorhombic crystal structure with a space group of Pbcu and exhibits a unique combination of properties.<sup>16</sup> Brookite is often found in association with anatase and rutile forms. It is less commonly used in commercial applications compared to anatase and rutile but has been studied for its potential in energy conversion devices and photocatalysis. Further investigation indicates that pure anatase possesses an indirect bandgap configuration, in contrast to rutile and brookite, which possess a direct bandgap arrangement. This indirect configuration enables anatase to retain photo-excited electrons

and holes for a longer lifetime. Pure anatase also has the lightest effective mass compared to rutile and brookite. Therefore, the electrons and holes are able to move quickly from the bulk to the surface, leading to a reduced rate of recombination. As a result, it is not surprising that pure anatase has greater photocatalytic activity than brookite and rutile.<sup>17</sup> However, the mixture of anatase and rutile polymorph exhibits improved photocatalytic performance than pure anatase due to effective electron-hole separation of the materials.<sup>18</sup> Previous research has shown that different photocatalyst morphologies (0D, 1D, and 2D) can result in variable photocatalytic characteristics. A wide range of titania synthesis processes can accomplish this diversity. Different factors can determine titania's size, morphology, and composition, including the titanium precursor concentration, the length of treatment duration, the temperature, and the chemical species utilized.<sup>19-21</sup> Various synthesis methods, such as hydrolysis<sup>22</sup>, hydrothermal<sup>23</sup>, solvothermal<sup>24</sup>, sol-gel<sup>25</sup>, electrospinning<sup>26</sup>, and chemical vapor deposition<sup>27</sup>, have been reported to synthesize  $\text{TiO}_2$ . Among those methods, the hydrolysis method offers a simple, low-cost, and environmentally-friendly preparation of  $\text{TiO}_2$ . Many precursors have been commonly used for preparing  $\text{TiO}_2$ , including titanium(IV) isopropoxide,  $\text{TiCl}_4$ , and titanium(IV) butoxide. However, in the literature, it is rare to find the use of titanyl sulfate,  $\text{TiOSO}_4$ , as a precursor.  $\text{TiO}_2$  nanorods can be produced from ilmenite extraction through a series of oxidation processes with  $\text{Na}_2\text{S}$  and acid leaching with  $\text{H}_2\text{SO}_4$  to produce  $\text{TiOSO}_4$ , followed by a hydrolysis process using distilled water with the addition of  $\text{KCNS}$ .<sup>28</sup>  $\text{TiO}_2$  nanoparticles also can be prepared through microwave-assisted hydrothermal  $\text{TiOSO}_4$  and  $\text{NaOH}$  as a mineralizer solution.<sup>29</sup> To the author's knowledge, no research studies have been conducted on the synthesis of  $\text{TiO}_2$  through a straightforward thermal hydrolysis method of  $\text{TiOSO}_4$ . This study aimed to prepare nanostructured titania through a straightforward one-step thermal hydrolysis process of an aqueous  $\text{TiOSO}_4$  solution. Ammonia will be used to hydrolyze  $\text{TiOSO}_4$  because it is cheap and commercially available. This research offers a green, low-cost, simple, and efficient method through the thermal hydrolysis of  $\text{TiOSO}_4$ . The effect of varying concentrations of ammonia as a hydrolyzing agent will be investigated in this study. Furthermore, the titania's thermal stability will be studied and compared with other synthesis methods.

## EXPERIMENTAL

### Material and Methods

The  $\text{TiO}_2$  precursor, titanium(IV) oxysulfate ( $\text{TiOSO}_4$ ,  $\geq 29\%$  Ti based on  $\text{TiO}_2$ , Sigma-Aldrich), was utilized without requiring additional purification. Ammonia Solution 25% (Merck) was used as a solvent for the titanium oxysulfate. Deionized water was used in the experiments to wash the  $\text{TiO}_2$  precipitate.

### General Procedure

10 g of  $\text{TiOSO}_4$  was dissolved in distilled water at  $80^\circ\text{C}$  and stirred until homogeneous. Then the ammonia solvent was added slowly until the mixture turned white. The stirring was continued for 1 hour. The ammonia solvent percentage varied from 5, 10, 15, 20, and 25 wt.%. The white precipitate was dried for 24 hours at  $60^\circ\text{C}$  after being washed numerous times with distilled water. The as-prepared material was calcined at  $500^\circ\text{C}$  for 3 hours after drying to identify the crystal phase. To better understand the materials' thermal stability, the calcination temperature of the sample was altered from 500, 700, and  $1000^\circ\text{C}$ .

### Material Characterization

An X-ray diffractometer (JCM-7000) with a scanning rate of  $1^\circ$  per minute and a  $2\theta$  range of  $5^\circ$  to  $80^\circ$  was used to record XRD powder patterns. To determine the crystalline structure, phase transformation, and average crystallite size, the experiments utilized  $\text{Cu-K}\alpha$  radiation (with a wavelength of  $1.5418 \text{ \AA}$ ). Additionally, the optical properties of the materials were examined using a Shimadzu UV 1800 UV-visible spectrometer, covering a wavelength range of 200-800 nm. The bonding arrangement of titania synthesized by the hydrothermal method was examined using an ATR FTIR Cary 630 FTIR Spectrometer (Agilent) with a wavenumber range of  $4000\text{-}650 \text{ cm}^{-1}$ . A JEOL NeoScope JCM-7000 SEM running at 15 kV was used to take scanning electron microscopy (SEM) images of as-prepared titania.

## RESULTS AND DISCUSSION

In the present work, aqueous  $\text{TiOSO}_4$  was thermally hydrolyzed to produce  $\text{TiO}_2$ . Hydrolysis of aqueous  $\text{TiOSO}_4$  forms a white precipitate  $\text{TiO}(\text{OH})_2$ . Furthermore, the resulting  $\text{TiO}(\text{OH})_2$  precipitate was annealed

at 500°C to produce pure TiO<sub>2</sub>. Figure-1 shows that all prepared materials contain an anatase tetragonal crystal structure (JCPDS File No. 83-2243). The (101), (004), and (200) planes of anatase are ascribed to the diffraction peaks at  $2\theta = 25.3^\circ$ ,  $37.8^\circ$ , and  $47.0^\circ$ , respectively. Furthermore, XRD spectra revealed that no rutile phase was observed.

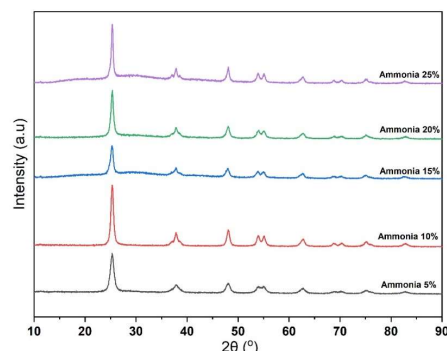


Fig.-1: XRD pattern of TiO<sub>2</sub> from Different Ammonia Concentrations

The Debye-Scherrer formula is applied for determining the size of crystallites (*D*) by analyzing the diffraction peak width located at  $25.4^\circ$ :

$$D = \frac{k \lambda}{\beta \cos \theta} \quad (1)$$

In this formula, *k* denotes the Scherrer shape factor (0.9),  $\lambda$  stands for the incident wavelength in angstroms (Å),  $\beta$  denotes the full-width half maximum (FWHM) in radians, and  $\theta$  represents the Bragg's diffraction angle at the maximum peak. Variations in ammonia concentration affect the crystallite size of TiO<sub>2</sub>. There is a tendency for the concentration of ammonia increases with the growth of TiO<sub>2</sub> crystal size. In this study, the average crystallite size along the plane (101) of TiO<sub>2</sub> was 8.39 nm, 9.00 nm, 11.26 nm, 12.32 nm, and 14.11 nm for ammonia concentrations of 5%, 10%, 15%, 20%, and 25% respectively. This finding was consistent with the previous investigation, which suggested that the ammonia concentration may be crucial for forming TiO<sub>2</sub> particles.<sup>30</sup> Ammonia serves as hydrolyzing agent and can interact with the TiO<sub>2</sub> surface, affecting the crystal growth kinetics and morphology. The interaction of ammonia with the TiO<sub>2</sub> surface can influence crystal growth in several ways. Ammonia molecules may participate in chemical reactions that contribute to the formation and growth of TiO<sub>2</sub> crystallites. Additionally, they can act as surface modifiers, affecting the surface energy and the attachment of precursor species, ultimately influencing the crystallite growth morphology and size. Higher ammonia concentrations provide a larger pool of ammonia molecules, increasing the likelihood of their interaction with the TiO<sub>2</sub> crystals. In addition, this research demonstrates that there is a linear relationship between the crystallite size and the pH value. The alkaline solution promotes the nucleation of TiO<sub>2</sub> particles; thus, the crystallite size increases in an alkaline condition.<sup>31</sup>

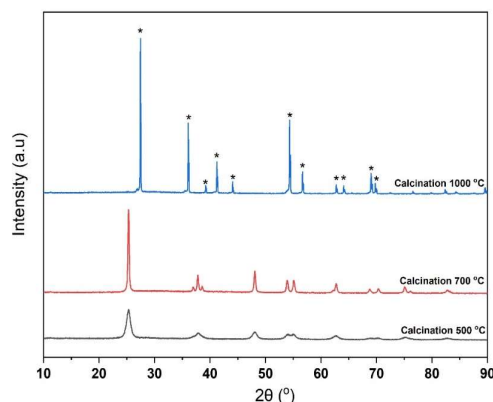


Fig.-2: XRD Pattern of TiO<sub>2</sub> in Different Calcination Temperature. (\*) Symbols Indicate the Appearance of Rutile Phase

In order to study the thermal stability and transformation of TiO<sub>2</sub> crystals prepared from a one-step thermal hydrolysis process, the sample obtained from 5% ammonia was annealed at temperatures of 500°C, 700°C, and 1000°C. The results of XRD spectra indicate that TiO<sub>2</sub> produced from this one-step thermal hydrolysis method has good thermal stability. It is proved that according to Fig.-2, the sample annealed at 700°C still contains a 100% anatase phase. Furthermore, after the sample was annealed at 1000°C, a 100% rutile TiO<sub>2</sub> phase was formed. This transformation will be further confirmed by the results of the electronic spectrum analysis using a UV-vis spectrophotometer. In this work, we assumed that the change from anatase to rutile happened at temperatures ranging from 750 to 900°C. In most cases, the transition temperature from anatase to rutile occurs between 500 and 600°C, with complete transformation to the rutile phase occurring at 600°C.<sup>32</sup> This work offers a facile method and obtains TiO<sub>2</sub> material with high thermal stability.

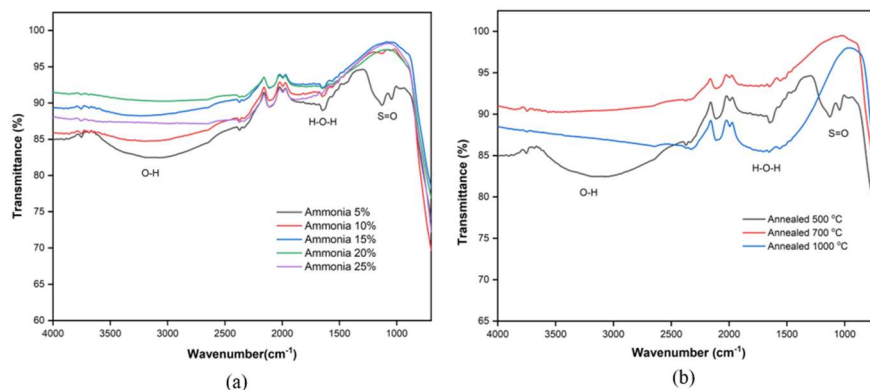


Fig.-3: ATR FTIR Spectra of Synthesized TiO<sub>2</sub> from Different (a) Ammonia Concentrations and (b) Annealing Temperature

The bonding arrangement present in materials was determined using ATR-FTIR spectroscopy (Fig.-3a and 3b). The O-Ti-O species are usually observed from the broad absorption band at 450 to 850 cm<sup>-1</sup>.<sup>33</sup> The H-O-H bending vibration of the physisorbed water on the material's surface was linked to the significant absorption band seen in all samples between 1600 and 1630 cm<sup>-1</sup>.<sup>34</sup> The vibrations of -OH groups on the surface of materials are linked to infrared spectra between 3600 cm<sup>-1</sup> and 3000 cm<sup>-1</sup>. The 5% ammonia variation material shows absorption bands at 1200 to 1050 cm<sup>-1</sup>, indicating stretching vibration of S=O bonds coordinated to the metal cation Ti<sup>4+</sup>.<sup>35</sup> In other words, the hydrolysis reaction using 5% ammonia was incomplete; thus, the sample still contained bidentate sulfate ions. Those peaks, as well as the vibration of hydroxyl groups, gradually disappeared after increasing the calcination temperature (Fig.-3b). All samples are measured for UV-visible radiation to determine the electronic characteristics of the prepared TiO<sub>2</sub> compounds. In order to achieve this objective, the Kubelka-Munk function, F(R), approximates the optical absorbance of the materials based on their reflectance (R).

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

From the Tauc plot, we can use the following equations to figure out the band gap energy of materials:

$$(F(R)hv)^{1/2} = A (hv-E_g) \quad (3)$$

Where E<sub>g</sub> denotes the band gap energy, A denotes a constant, h denotes the Planck constant, v denotes frequency, and 1/2 is the TiO<sub>2</sub> indirect nature transition.

As illustrated in Fig.-4, the linear portion of the plot of hv vs (F(R)hv)<sup>1/2</sup> is extrapolated to get the optical band gap energy calculation. These UV-Visible spectra can also be used to determine the transformation of anatase to rutile which shows different electronic characters. The calculation confirmed the XRD results that the rutile phase was formed at 1000°C with a bandgap value of 2.87 eV. Meanwhile, at 500°C and 700°C, the material was still in the anatase phase with bandgap values of 3.69 eV and 3.16 eV, respectively. The obtained anatase has a larger band gap than is usually found in the literature due to its morphology characteristic.<sup>36-38</sup> Figure-5 depicts a typical SEM micrograph of TiO<sub>2</sub> synthesized from 5% and 20% ammonia at 2500 magnification. Figure-5 is a representative image of the as-prepared material. The TiO<sub>2</sub>

material synthesized using the thermal hydrolysis method in this study has a rough morphology and varying size. This morphology may also affect the value of the TiO<sub>2</sub> anatase bandgap.

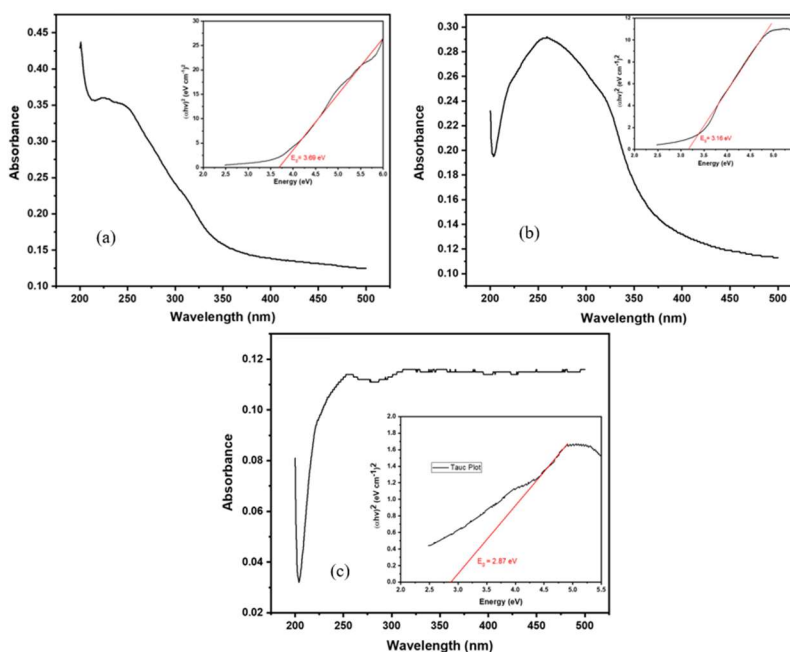


Fig.-4: TiO<sub>2</sub> Bandgap Estimation at (a) 500°C, (b) 700°C, and (c) 1000°C

The correlation between TiO<sub>2</sub> morphology and a higher bandgap than the common anatase can be attributed to the light scattering phenomenon. When the morphology of TiO<sub>2</sub> anatase exhibits a rough surface, it can promote a higher degree of light scattering and multiple light reflections within the material. This increased light scattering and path length can affect the absorption and emission of photons, contributing to an apparent increase in the effective bandgap energy. The SEM image is also in line with the calculation of the crystallite size of the material, where the addition of ammonia variations triggers the crystal growth of the material, resulting in a larger particle size. Further research is needed to control the material's morphology to obtain a material with better electronic properties.

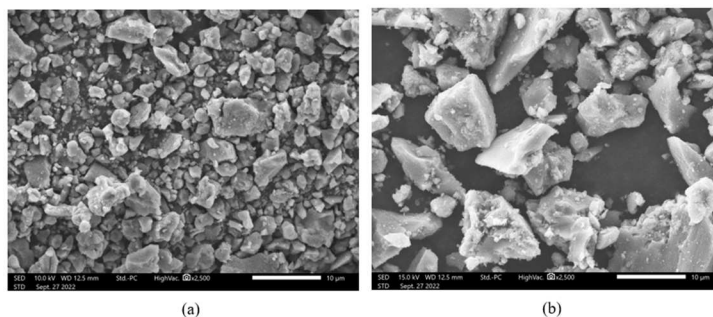


Fig.-5: SEM photographs of TiO<sub>2</sub> prepared from Different Ammonia Loading: (a) 5% and (b) 20%

## CONCLUSION

The present study successfully obtained nanostructure titania by one-step thermal hydrolysis of TiOSO<sub>4</sub> solution. The forming titania exhibits exceptional thermal stability owing to a greater degree of transformation from the anatase phase to the rutile phase at temperatures ranging from 750-900°C. The 100% rutile phase occurred at an annealing temperature of 1000°C. Furthermore, the electronic spectra confirmed this phase change from an anatase bandgap value of 3.69 eV to a rutile of 2.87 eV. The addition of ammonia as a solvent trigger the growth of material crystallites according to XRD and SEM results. The FTIR results showed that bidentate sulfate ions were still found in the material synthesized using 5% ammonia, thus requiring further annealing. This present investigation provides a facile method for



synthesizing TiO<sub>2</sub> particles; however, further research endeavors are warranted to control the shape and distribution of TiO<sub>2</sub> particles to fabricate a photocatalyst possessing optimal performance.

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### CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

### AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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