

# Effects of pH and Heating Time on the Synthesis of Titanium Dioxide Nanoparticles

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## Abstract

The application of nanotechnology in water treatment is of great importance as the need to purify water has become more evident due to factors like population growth, droughts, and inefficient purification methods. Titanium dioxide nanoparticles, (TiO<sub>2</sub> NPs), have grown in interest because of their photocatalytic abilities, and chemical stability. TiO<sub>2</sub> has three crystal structures: anatase, rutile, and brookite. Of the three polymorphs, studies show that brookite has greater surface energy, reacts under low levels of UV light, and decomposes organic matter more efficiently. This project analyzes the effect of pH, on the size and form of TiO<sub>2</sub> NPs. A hydrothermal synthesis was used to set the pH of the samples to 1,6,7,10.5 or 12.5. Sodium hydroxide, NaOH, and nitric acid, HNO<sub>3</sub>, were used to alter basicity and acidity. Four samples were made for each pH value and heated for 24,48,72 or 96 hours to evaluate the effects of heating time on crystal structure and size of TiO<sub>2</sub> nanoparticles. Particles were characterized using scanning electron microscopy, and powder x-ray diffraction. It was found that rutile mixed with anatase formed at a pH of 1.00. Anatase formed under acidic and neutral conditions, while brookite formed under basic conditions. The size of the particles did not increase with basicity or reaction time, but more agglomeration was observed. This method allowed for all crystal structures of TiO<sub>2</sub>, with an average size of 15.96 nm, to be synthesized by only altering the pH in the last step.

## 1. Introduction

Water is an essential component of all living organisms. However, factors like population growth, droughts, and inefficient purification methods have made the need for clean water more evident.<sup>1</sup> By providing new purification methods to replenish water, faster than it is exhausted, the issue of water shortage can better be addressed. One solution offered by scientists is the application of nanomaterials in water treatment.

Nanoparticles, NPs, are materials with a diameter between 1 and 100 nanometers. The size of the materials allows them to maintain a greater surface area to volume ratio, allowing for higher reactivity. Titanium dioxide, TiO<sub>2</sub>, is one of the most promising nanomaterials for water purification using photocatalysis. Photocatalysts are materials that provide energy in a reaction by absorbing energy from light; TiO<sub>2</sub> is activated by ultraviolet (UV) radiation. TiO<sub>2</sub> can be used as a photocatalyst in water treatment for water-splitting reactions and degradation of pollutants.<sup>2,3</sup> In addition to its photocatalytic abilities, TiO<sub>2</sub> is chemically stable, abundant, and nontoxic.<sup>4</sup> Current applications of TiO<sub>2</sub> NPs include solar cell fabrication, sunscreen, and self-cleaning glass.<sup>2</sup>

Modern water filtration methods utilize NPs of silver and TiO<sub>2</sub> for antimicrobials, disinfectants, and other decontaminant processes.<sup>1</sup> TiO<sub>2</sub>, unlike nano-silver, remains unchanged during the degradation of microorganisms and organic compounds, meaning it does not need to be replenished throughout the process. Additionally, the material is cost-efficient and relatively nontoxic making it ideal for this process.<sup>1</sup> Other research has used TiO<sub>2</sub> to remove pharmaceutical residues in water or other compounds such as organic dyes.<sup>5,6</sup> Additionally, TiO<sub>2</sub> NPs can be used to dope membranes for more efficient oil-water separation.<sup>7</sup> When NPs are used in water treatment, they must be

removed before redistribution. Current methods of removal utilize filtration and coagulation.<sup>8</sup> While nanotechnology is already being utilized in water filtration processes, it is unknown how varying crystal forms affect the process.

TiO<sub>2</sub> NPs exist in three known crystal polymorphs, or forms, anatase, rutile, and brookite. Anatase and rutile are tetragonal crystal structures, while brookite is orthorhombic (Figure 1).<sup>4</sup> Each polymorph exhibits different physical and chemical properties and therefore functionality. Among these properties are energy levels, enthalpy, reaction kinetics, and surface area.<sup>9</sup> Each form is synthesized uniquely with solution-phase preparation methods favoring the anatase structure.

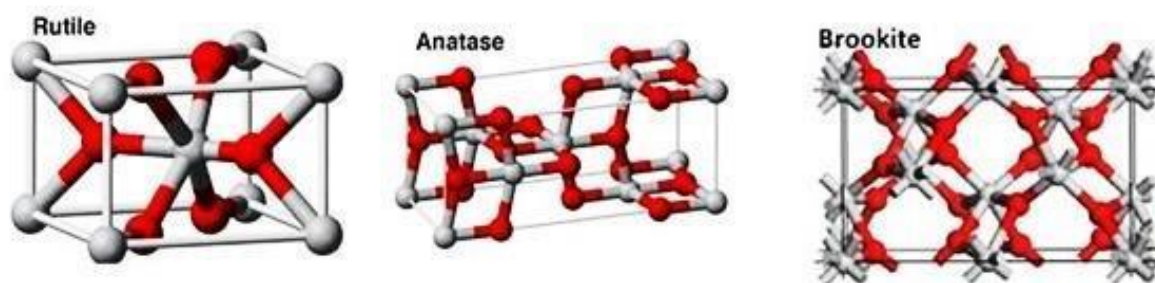


Figure 1. Titanium Dioxide Nanoparticle Polymorphs<sup>10</sup>

TiO<sub>2</sub> nanoparticles can be synthesized by techniques including, sol-gel, hydrothermal, precipitation, and solvothermal methods, with a preference for sol-gel methods. Using a sol-gel method, research shows that anatase nanocrystals are obtained at near-neutral pH values, with a pH of 6 and a pH of 8 both resulting in anatase. Using the same technique, a pH of 10 resulted in 98% by weight anatase and 2% by weight brookite.<sup>11</sup> Other studies found that anatase forms when the pH of the system is as acidic as 0.8 and as basic as 10.5; a pH of 10.5 resulted in a mixture of brookite and anatase. The research showed that an increase in the pH slightly increased the average crystalline size of anatase NPs. Additionally, it was found that neutral pH does not yield a crystalline structure but rather layered titanates.<sup>12</sup> Other studies have found that when using acid additives, pure anatase will form at pH values of 3, 6, and 10. Pure rutile was only formed at a pH of 6 with glycolic acid as the additive. Using the same additive pure brookite was formed at a pH of 10.<sup>4</sup> The results of previous research show that the polymorph formed is dependent on pH and more than one form may exist at the same pH, indicating the crystals may take on different forms as the reaction progresses. Anatase is the most studied structure, as it is easiest to synthesize.<sup>13</sup> The synthesis of brookite NPs is less studied, and therefore the functionality of these crystals is not well understood. Current research shows that brookite can be synthesized using hydrothermal treatment under basic conditions, with a pH of 12.5 being optimal.<sup>12</sup> By altering the pH to improve synthetic processes for TiO<sub>2</sub>, scientists can better understand the brookite properties and their potential applications.

One advantage of the brookite phase is that it has been shown to have larger surface energy than the anatase form.<sup>12</sup> Because of this difference some scientists hypothesize that brookite is more reactive than anatase and rutile in terms of unit-specific surface area.<sup>14</sup> However disagreements surround this hypothesis, meaning further research on the brookite phase is required. Another advantage of the brookite form is its ability to react despite low levels of UV light, giving it a photocatalytic advantage. Brookite has also been shown to oxidize, or decompose, organic matter and open aromatic rings more efficiently than rutile and anatase.<sup>15</sup>

Previous research at UNCA focused on the synthesis of brookite TiO<sub>2</sub> nanoflowers. This was done by varying temperature and time parameters in hydrothermal synthesis adapted from literature.<sup>12</sup> Additionally, alkali metal salt mineralizers were used to control surface structure and particle shape. This research was done at a pH of 12.5 and the optimum temperature for synthesis found was 220° C while the optimum reaction time was 24 hours.<sup>16</sup> To continue this work, other UNCA researchers have used hydrothermal synthesis with varying pH's between 7-12.6 to study effects on the brookite form. This research was done using hydrothermal synthesis, but the pH was varied at different synthetic points. One methodology maintained the same pH in between purification processes, the other varied pH between purification processes. Preliminary data showed that anatase formed at a pH of up to 10.27, while brookite formed at a pH of 11.91-12.96.<sup>17</sup> Based on imaging, the size and surface area of both anatase and brookite appeared to increase with basicity, however, further in-depth research needed to be done and is presented within.

This study aimed to understand the effects of pH and heating time on synthetic processes and on the shape and size of TiO<sub>2</sub> NPs, with a focus on the brookite crystal structure. This was done by using a hydrothermal synthesis and

varying pH with NaOH and HNO<sub>3</sub>. Additionally, each reaction was heated for 24, 48, 72, and 96 hours, to determine the effects of heating time on crystal form and size. The synthesized structures were characterized using SEM and XRD.

## 2. Experimental Methods

### 2.1 Synthesis

Synthesis of brookite TiO<sub>2</sub> NPs was done using a hydrothermal synthesis adapted from literature.<sup>12</sup> For each reaction, 50 mL of 0.21M NaOH was added to 25 mL of 0.31M TiOSO<sub>4</sub>•H<sub>2</sub>O H<sub>2</sub>SO<sub>4</sub>. Concentrated NaOH was used to raise the initial pH of the solution to 12.5. The solution was reacted for 30 minutes at ambient conditions allowing the white gel to fully precipitate. The mixture was split into two and centrifuged at 5000 rpm for 5 minutes. Each sample was decanted and suspended in 35 mL of deionized, DI, water. The suspension was then mixed by shaking and centrifugation, this was repeated 3 times. Water was added to each centrifuge tube to fill it up to 70% (35 mL) and 1M NaOH or 6M HNO<sub>3</sub> was used to alter the pH of the mixture to the final pH. The solutions were placed in a 50 mL Teflon-lined autoclave and heated in an air convection oven at 220° C for 24, or 48 hours. The procedure was repeated to have two other samples heated at 220°C for 72 and 96 hours. Upon heating, each colloid was centrifuged at 5000 rpm for 10 minutes, decanted, and suspended in 35 mL of DI water. The gel was then mixed by shaking and centrifuged; this process was performed at least 3 times or until the supernatant was clear. The samples were dried by heating in an oven, on a watch glass, at 100°C. After the sample was stored in a dark environment to prevent any reaction with light.

### 2.2 Characterization

The synthesized NPs were characterized using X-Ray Diffractometer MiniFlex II and Scanning Electron Microscope FEI Quanta 450. XRD was used to distinguish between crystal polymorphs by comparing them to purchased crystals and reported literature values.<sup>18-20</sup> The diffraction or XRD peaks are a result of differences in miller indices. Miller indices are three numbers (h, k, l) that indicate the orientation of a plane in the x, y, and z-direction in atoms of crystals. Different materials and crystal forms have unique miller indices and therefore unique XRD patterns. XRD can also provide information on average crystal size and percent composition if a mixture of crystal forms is present. Anatase (15-50 nm), rutile (30 nm), and brookite crystals (1-100 nm) were purchased from US Research Nanomaterials, Inc. XRD was done using a scan range of 15 ° to 69.9°. SEM was used to determine the shape of the crystals as well as to observe clustering, or agglomeration.

## 3. Results and Discussion

### 3.1 XRD Analysis

Polymorphs of TiO<sub>2</sub> were confirmed by comparing the XRD patterns of generated NPs to purchased crystals. Previous literature determined the miller indices and position of characteristic peaks in brookite based on Bragg's Law.<sup>18-20</sup> These positions and miller indices of these peaks are noted in Figure 2. The purchased and synthesized brookite crystals had the same peaks as those reported in the literature, as did anatase and rutile. Defying peaks of brookite include the doublet peak at 2θ of 25.77 degrees and the singlet peak at 2θ of 30.84 degrees. Characteristic peaks of rutile are the singlet peaks at 2θ of 27.33 degrees and 36.15 degrees. Anatase can be recognized by the singlet peak at 2θ of 25.59 degrees and the triplet peak at 2θ of 38.10 degrees.

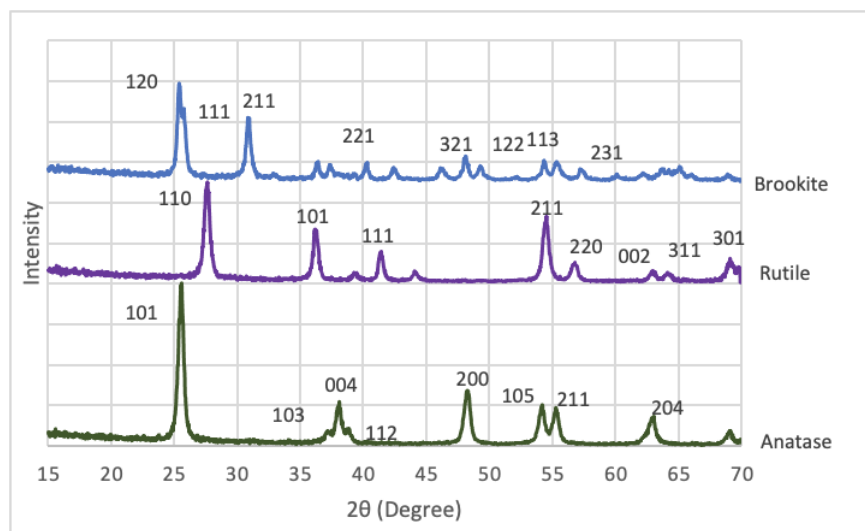


Figure 2. XRD Patterns of Purchased Anatase, Rutile, and Brookite

XRD patterns confirmed that samples with a final pH of 12.50 were brookite, as shown in Figure 3. XRD confirmed that the samples were purely brookite. The characteristic peaks of brookite including the doublet peak at  $2\theta$  of 25.77 degrees, and the singlet peak at  $2\theta$  of 30.84 degrees, aligned with that of synthesized samples. XRD also showed that increased heating time resulted in more narrow peaks, indicating a higher crystallinity.

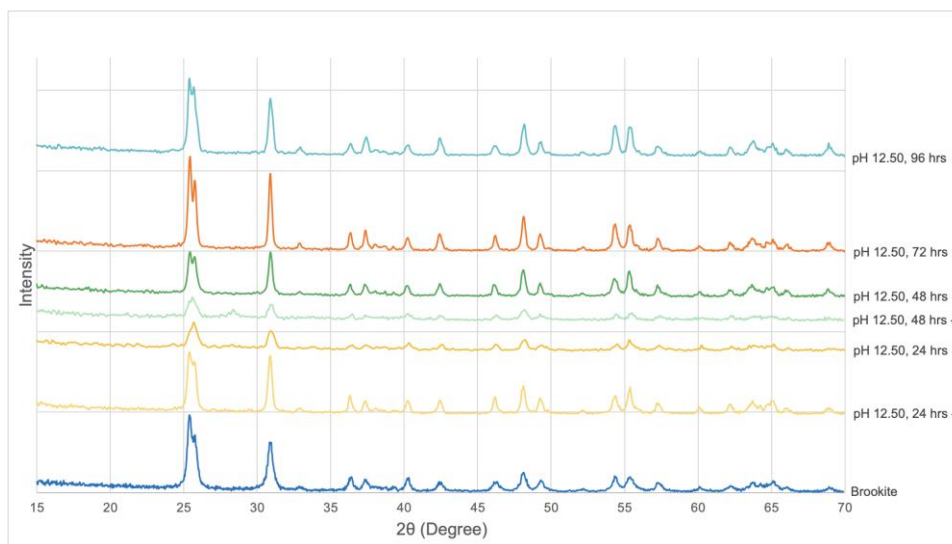


Figure 3. XRD Patterns of Purchased Brookite and Samples Synthesized at pH=12.50, second trial under the same conditions marked with a dash (-)

At pH 10.50, brookite was the primary product, as shown in Figure 4. This can be seen in that the peaks of each sample align to those of purchased brookite. An example is the brookite characteristic peak at  $2\theta$  of 25.77 degrees. However, not all samples were pure; this is most evident at a heating time of 72 hours. The triplet peak at  $2\theta$  of 38.10 degrees, correlating to anatase, can be seen in this sample. The concentration of anatase was low and not detected with XRD, indicating the samples were primarily brookite.

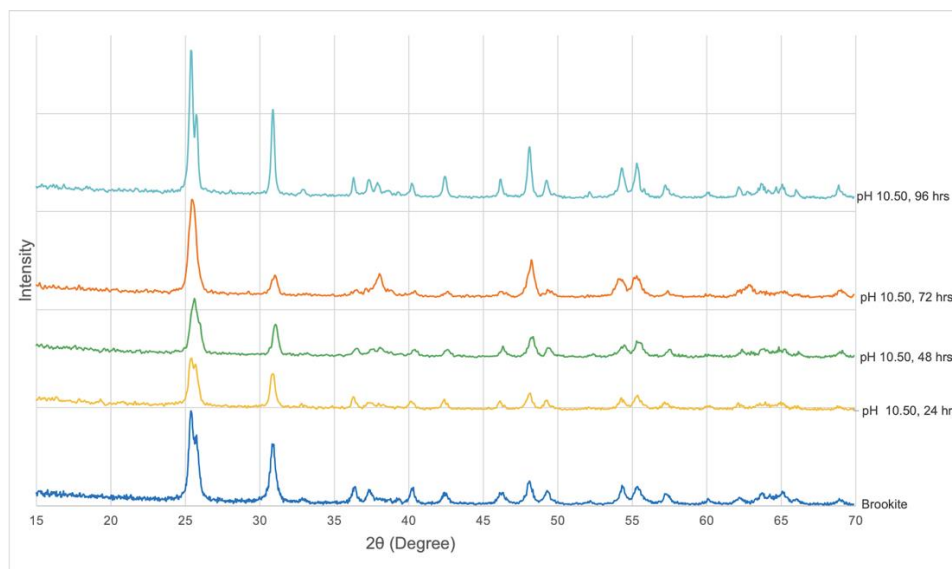


Figure 4. XRD Patterns of Purchased Brookite and Samples Synthesized at pH=10.50

Previous literature indicates that  $\text{TiO}_2$  nanoparticles will not form under neutral conditions, in the absence of NaOH or  $\text{HNO}_3$ .<sup>12</sup> In this experiment, the gel suspended in DI water, upon filtration, was found to have a basic pH. The pH was altered with  $\text{HNO}_3$  to bring it to neutral conditions. Given that the reaction was not done in the absence of  $\text{HNO}_3$  or NaOH, may explain why layered titanates were not obtained. Rather, at neutral conditions anatase was formed, as shown in Figure 5. At a heating time of 48 hours, a peak begins to emerge at a  $2\theta$  of 30.84 degrees; this peak aligns with that of brookite. The peak grew with increased heating time, indicating an even larger mixture of brookite at 72 hours. However, at 24 and 96 hours, pure anatase was obtained. Other samples, not included in this study, showed that primarily brookite formed at neutral conditions with 72 and 96 hour heating times. Additional work is needed to determine how these conditions affect the crystal structure of  $\text{TiO}_2$ .

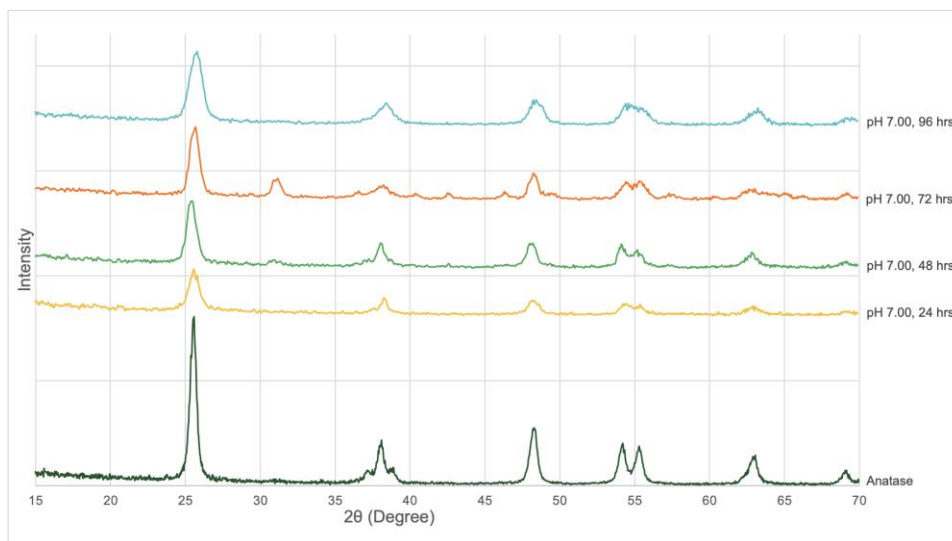


Figure 5. XRD Patterns of Purchased Anatase and Samples Synthesized at pH=7.00

At slightly acidic conditions, pH=6.00, anatase was obtained, regardless of heating time. This can be seen in Figure 6, where the peaks of purchased anatase align with the samples at all heating times.

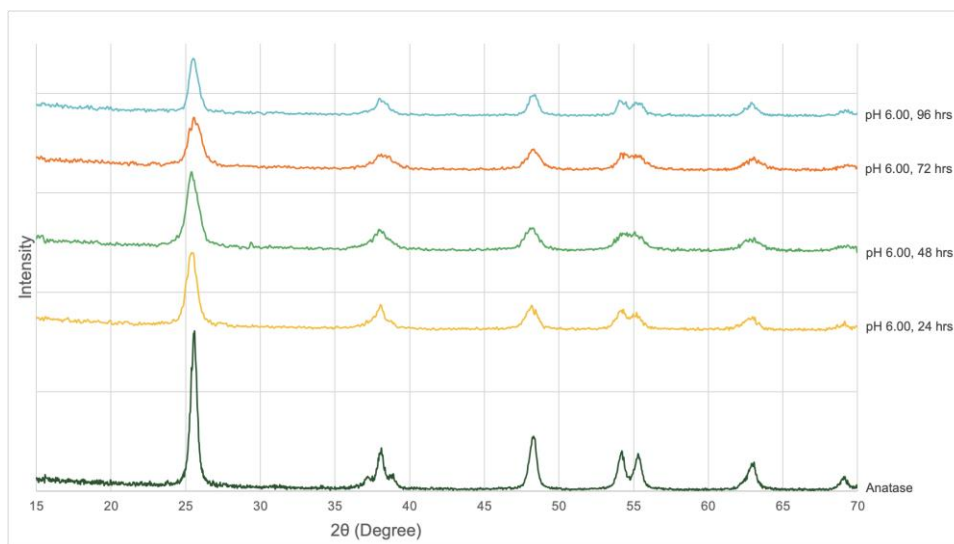


Figure 6. XRD Patterns of Purchased Anatase and Samples Synthesized at pH=6.00

At a pH of 1.00, a mixture of anatase and rutile was synthesized, as shown in Figure 7. The percent mixture of the samples did not significantly change with heating time, except for the sample at 96 hours which was 98.4% rutile. Samples below this heating time were 53.3%-85.5% rutile, with no pattern observed. Anatase can be identified by the peak at a  $2\theta$  of 25.59 degrees. When the sample was heated for 96 hours, the anatase peaks became smaller, while the rutile peaks grew in intensity. An exception to this trend was seen with the first trial at 48 hrs, where pure rutile was synthesized.



Figure 7. XRD Patterns of Purchased Anatase and Rutile, with Samples Synthesized at pH=1.00, second trial under the same condition marked with a dash (-)

As shown in Figure 8, very acidic pH values result in rutile and anatase. Acidic and neutral pH values result only in anatase, for a heating time of 24 hours. Basic pH values resulted in brookite. Samples heated at 24 hours, had wider peaks, indicating the particles were smallest at decreased heating time.

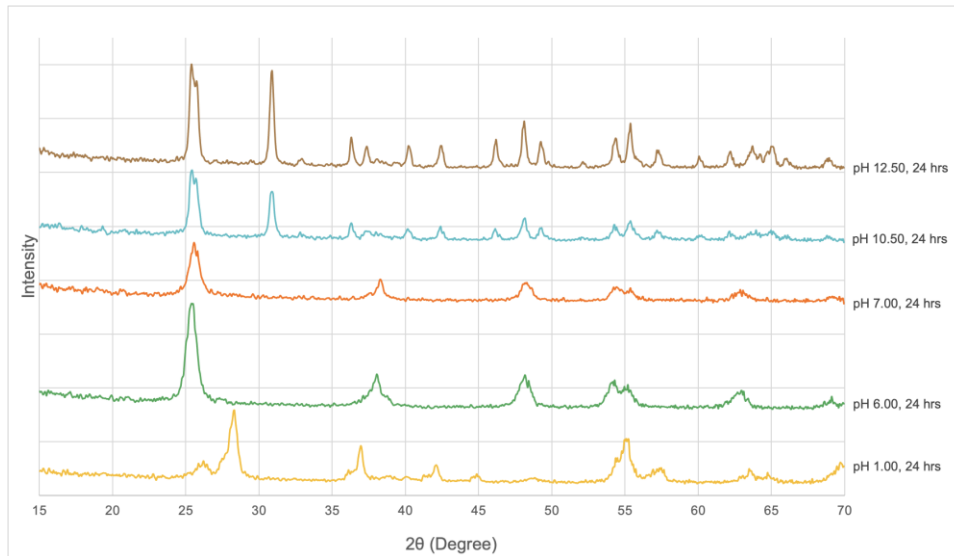


Figure 8. XRD Patterns of Samples Synthesized with 24 hour Heating Time

The samples with a heating time of 48 hours, followed the same trend as those heated at 24 hours. This can be seen in Figure 9.

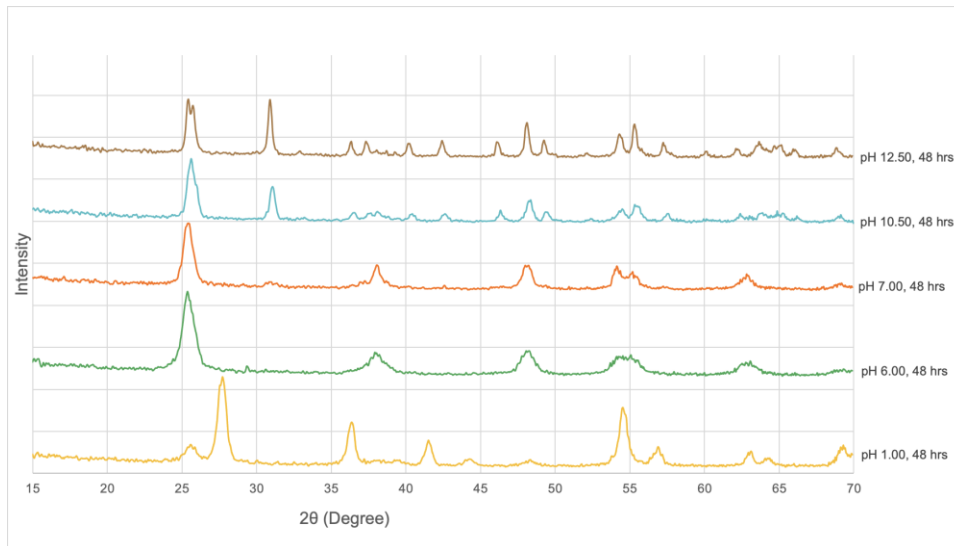


Figure 9. XRD Patterns of Samples Synthesized with 48 hour Heating Time

Samples with a heating time of 72 hours followed the same trend as those at 24 and 48 hours. However, as shown in Figure 10, increasing the heating time allowed for greater mixtures of crystal polymorphs. Samples with a higher pH value were shown to have narrower peaks, meaning the particles are larger. The samples heated for 72 hours also had higher intensities than those at 24 hours, indicating higher crystallinity.

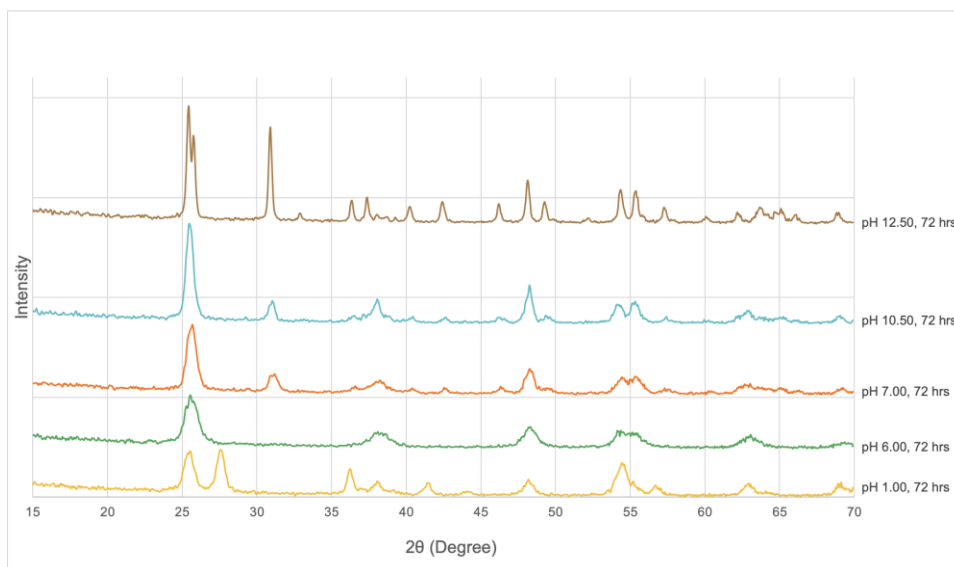


Figure 10. XRD Patterns of Samples Synthesized with 72 hour Heating Time

Samples with a heating time of 96 hours, followed the same trends as those at 72 hours. As shown when comparing Figure 8 and Figure 11, the longer the particles are heated the higher the crystallinity.

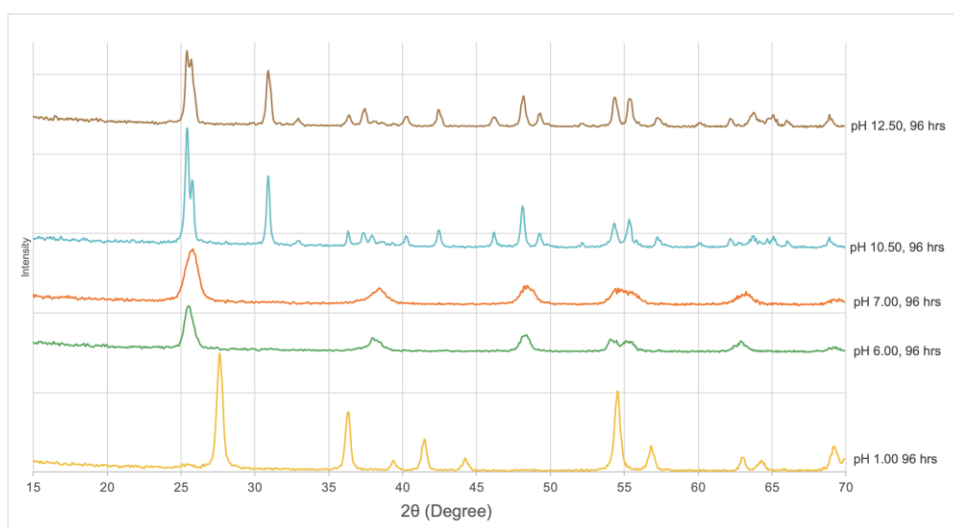


Figure 11. XRD Patterns of Samples Synthesized with 96 hour Heating Time

In addition to using XRD for determining crystal form, it was also used to determine the average size of synthesized NPs and the percent mixture of crystal phases within the samples. The percent mixture of samples with a pH of 1.00 and the average crystalline size of all particles are included in the SEM images of each sample in Figure 12. Samples synthesized at a pH of 1.00 were primarily rutile and anatase, both had an average crystal size of 12 nm. Samples with a pH greater than 1.00 were primarily pure, as shown by XRD, the percent mixture was not determined. At pH of 6.00, and 7.00 the average crystal sizes were 8.93 nm, and 10.91 nm respectively. At a pH of 10.50 and 12.50, the average sizes were 22.09 nm and 23.16 nm, respectively. A clear trend was not observed between the pH and average size, however, at higher pH values more agglomeration was observed. Samples synthesized with a heating time of 24 hours and 72 hours had average crystal sizes of 15.45 nm and 14.20 nm. At 72 hours and 96 hours, the samples were 17.08 nm and 17.10 nm. There is not a significant difference in size based on the heating time.

### 3.2 SEM Characterization

Secondary characterization of samples was done using SEM, which allowed for visualization of the shape and size of particle agglomeration. The figures do not show individual particles, but rather the agglomeration of many particles. Initially, it was believed that individual brookite particles were observed at high pH values, but the size of the particles, found using XRD, suggests otherwise. A summary of SEM imaging can be seen in Figure 12.

As the pH of the samples increased, so did the agglomeration. Individual particles were not distinguishable under any of the conditions, as the particles were too small. At acidic and neutral conditions, the particles seemed to agglomerate in the same manner, regardless of heating time. Further research needs to be done to understand if changes in acidity affect the agglomeration of the particles. At basic conditions, rod-like clusters were visualized. The clusters at a pH of 12.50, were larger than those at a pH of 10.50.

As the heating time of the samples increased, the agglomeration also increased. This trend is most evident at a pH of 12.50. Using SEM imaging, the size of particle clusters was estimated for samples synthesized at a pH of 12.5. The particle clusters with a heating time of 24, 48, 72, and 96 hours were approximately 1.5, 2, 6, and 6.8 $\mu$ m, respectively. The clusters more than quadrupled in size from 24 to 96 hours. The largest difference in agglomeration for brookite was observed when the heating time was adjusted from 48 hours to 72 hours. Additional heating beyond 72 hours did not have a drastic effect on the shape or size of the clusters, however, the particles heated for 96 hours were found to aggregate more uniformly. Of the polymorphs of TiO<sub>2</sub>, brookite was found to be most homogenous in shape.

	24 hours	48 hours	72 hours	96 hours
pH 1.00				
pH 6.00				
pH 7.00				

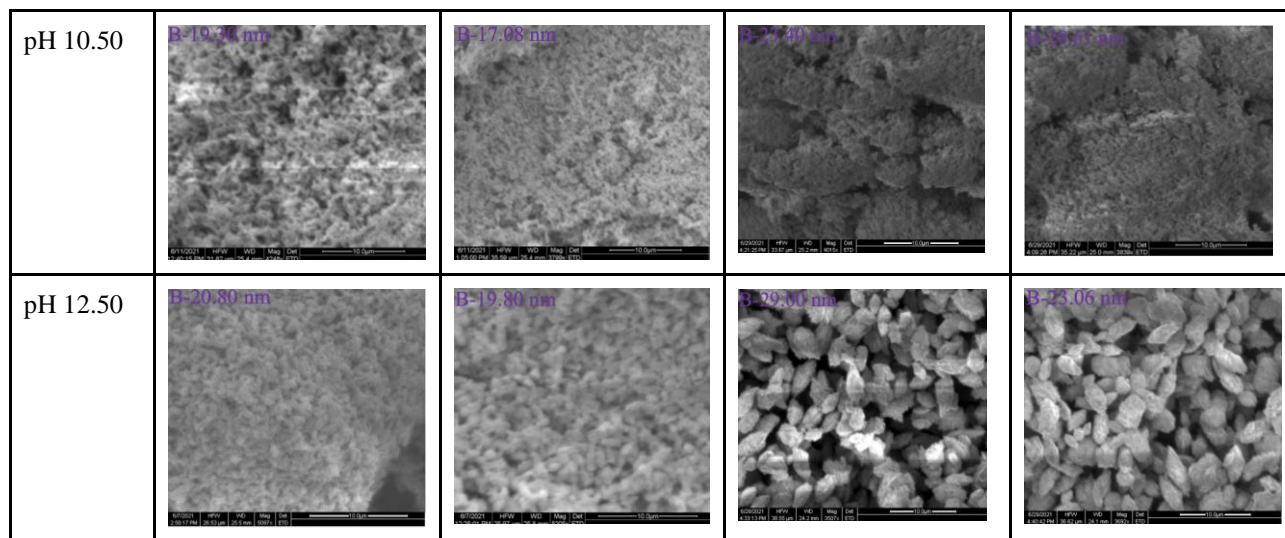


Figure 12. SEM imaging of all Synthesized Samples at Varying Conditions, all images were taken at 10  $\mu\text{m}$

As shown in Figure 13, samples synthesized at a pH of 12.50 with heating times of 72 and 96 hours, formed clusters much larger than those synthesized at low pH values. Individual clusters were visible as far back as 100  $\mu\text{m}$ . Particles with increased heating time and increased basicity were the largest, as supported by XRD, with the most agglomeration, as supported by SEM.

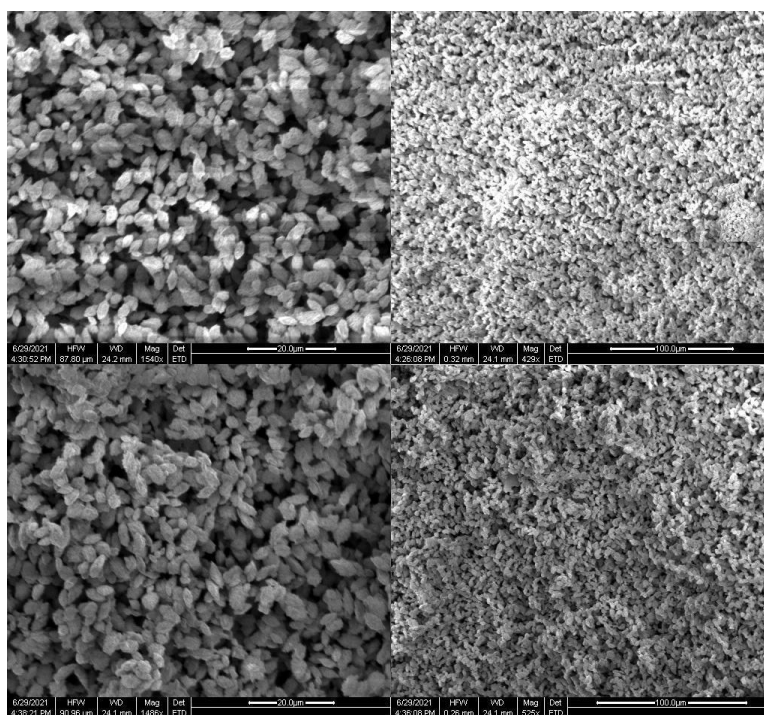


Figure 13. SEM Imaging of Samples Synthesized at pH of 12.50, top row heating time of 72 hours, bottom row heating time of 96 hours. Images on left taken at 20 $\mu\text{m}$ , images on right taken at 100  $\mu\text{m}$

## 4. Conclusion

A hydrothermal synthesis was used to successfully synthesize TiO<sub>2</sub> NPs in all three forms. Results showed that rutile and anatase formed at very acidic conditions. At slightly less acidic conditions and neutral conditions, only anatase was obtained. At basic pH values, brookite was formed. The size of the particles did not significantly change with basicity and increased heating time. However, at basic pH values, more agglomeration was observed with increased heating time. Further research is needed to determine if the same trends are observed under acidic conditions. The crystallinity of the samples also increased with increased heating time. While the polymorph did not change with increased heating time, the mixture content was affected by varying heating times. This was evident at a pH of 1.00 where the concentration of rutile may increase with longer heating times. Future work will utilize GC-MS to test the effectiveness of these NPs at breaking down volatile organic compounds for water purification.

## 5. Acknowledgments

The author would like to thank Dr. Oksana Love and the entire research team. The author would also like to acknowledge the UNCA Chemistry and Biochemistry Department. Additionally, the author would like to thank Furman University for allowing us to use their XRD.

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