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Effects of pH on the Synthesis of TiO_2 Brookite Nanocrystals

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Abstract

Water is essential for the sustenance of all living organisms. There are many methods of water purification, and the most promising seems to be the use of nanotechnology. It has been found that titanium dioxide (TiO_2) nanoparticles (NPs) have photocatalytic properties which can be used for the degradation of organic pollutants in water. The light absorption of TiO_2 NPs can vary with the morphology of the nanoparticles. TiO_2 NPs have three different crystal forms: anatase, rutile and brookite. Past research showed that brookite-phase TiO_2 NPs absorb low UV-light frequencies, have a higher surface area and have a higher reduction potential compared to the other morphologies of the nanoparticles. These properties make brookite phase TiO_2 a better photocatalyst. This study consisted of the synthesis of brookite TiO_2 NPs by hydrothermal synthesis at different pH. Precursor samples were set to have a pH between 7.00 and 12.96 with the objective to determine the effects that pH has on size and shape of the brookite TiO_2 NPs. The samples were then characterized using the Scanning Electron Microscope FEI Quanta 450 (SEM) and the X-Ray Diffractometer MiniFlex II (XRD). It was observed that TiO_2 anatase was formed up to 10.27 pH and TiO_2 brookite was formed between pH 11.91 and 12.96. Based on the imaging obtained up to date, the size of both anatase and brookite seemed to increase as the pH increases; however, further in-depth studies should be performed.

1. Introduction

Solving environmental issues has become a great importance to society. Scientists have put a lot of effort to perfect water purification methods by using nanotechnology. These efforts have led to the experimentation with titanium dioxide (TiO_2) nanoparticles (NPs) as a photocatalyst. NPs are particles measured between 1 nm and 100 nm. The size of a material's particles can have an effect on its properties. The smaller the material's size in a given volume, the larger the surface area will be (Image 1).[1]

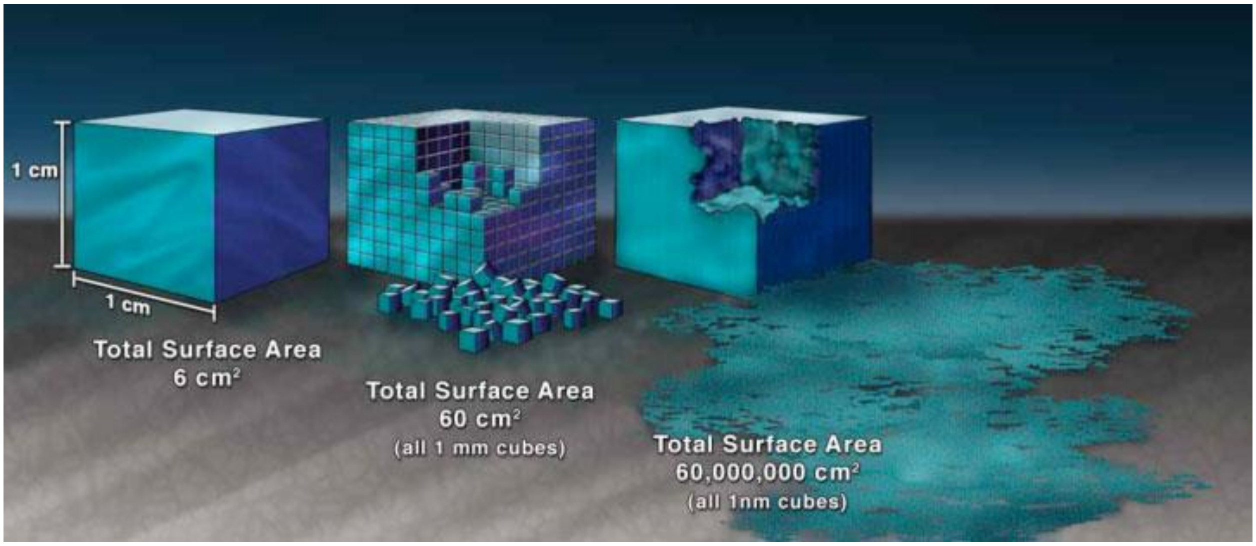


Image 1 Decrease of particles' sizes increase the surface area [1]

A large surface area allows materials to react with a higher amount of surrounding material. It has been found that a particle of TiO_2 has a wide band gap, high redox potential, low cost, chemical stability, and nontoxicity which makes a particle of TiO_2 an effective photocatalyst for organic pollution degradation. [2-7] But, at the same time, the compound has some limitations. Its wide band gap limits the UV absorption causing the compound to only utilize 3% to 5% of the solar energy absorbed for its activation .[8,9] The low percentage of utilized light is due to the small fraction accounted for UV light in solar energy compared to that of the visible light.[9] TiO_2 also photogenerates and recombines its electron-hole pairs during photocatalysis. Photocatalysis allows TiO_2 to react with light and oxidize or reduce materials forming different product which include hydrogen and hydrocarbons.[10] According with Nakata at el, the recombination of electron-hole pairs diffuse in the TiO_2 surface allowing to react with absorbed water molecules resulting in the formation of hydroxyl radicals. [10] Both the hydroxyl radicals and the photogenerated holes then oxidize near organic compounds on the TiO_2 surface. The electrons in the conduction band will react with the oxygen in the air and reducing the molecular oxygen into superoxide radical ($O_2^{\bullet -}$) (Image 2).

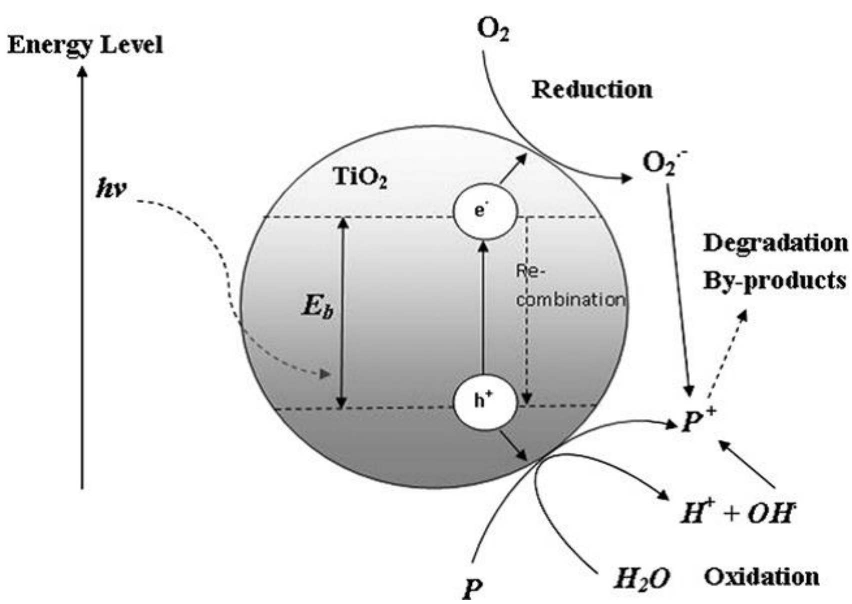


Image 2 Photocatalytic Process on the Surface of TiO_2 [11]

However, this photocatalytic process for degradation must have electron scavengers. The absence of these electron scavengers will cause the excited electrons in the conduction band recombine with the valence band holes in nanoseconds.[9]

Light absorption can vary depending on the morphology of TiO_2 nanoparticles, thus affecting the photocatalytic activity. TiO_2 NPs can be found in three different crystal forms, anatase, rutile, and brookite. Both anatase and rutile have tetragonal shape based on the crystal system. Brookite has an orthorhombic shape based on the crystal system (Image 3). [13]

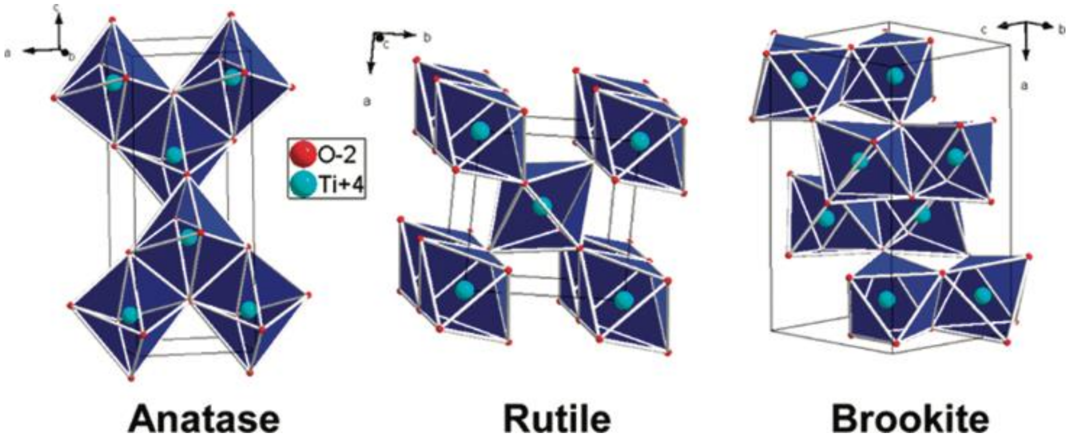


Image 3 Crystal forms of TiO_2: Anatase, Rutile, Brookite [13]

According to Liu et al.[14] the morphology of TiO_2 NPs can make the mass transportation, light harvesting, movement of charge acceleration and the separation of photogenerated electron-hole pair easier. It has been found that the precursor's conditions in which TiO_2 is synthesized can affect the product. Things such as the materials, the temperature, and the pH can promote the formation of different TiO_2 crystals and its sizes.[6,15-19] Kaplan et al. have shown that synthesizing TiO_2 particles in acidic conditions (pH 2.94) promotes the formation of anatase with a surface area of 132 m^2/g whereas synthesizing TiO_2 particles in alkali conditions promotes the formation of brookite with a smaller surface area of 25 m^2/g.[7] Previous research on the effects of pH on TiO_2 anatase have shown that as the pH increases the specific surface area increases.[20] Hu et al. have reported that slightly changing the pH in the synthesis of brookite from 12.5 to 12 affects how the NPs assemble with no mention of morphology change of the NPs themselves.[13] The shape of the crystals and their structure can be determined by using an x-ray powder diffractor (XRD), a scanning electron microscope (SEM), and/or transmission electron microscope (TEM). TiO_2 crystals can be synthesized using hydrothermal method. This method is a similar process to that of natural crystal formation. It also is simple, cheap, and flexible to conditions changes (pH, temperature, or reagent concentration). [21]

Past researchers at the University of North Carolina-Asheville (UNCA) have tried to replicate the experiment of Hu at el[13] by forming TiO_2 brookite NPs with a flower-like shape[15]. This research focuses on the synthesis of brookite TiO_2 NPs by hydrothermal synthesis with precursors with different pH and their analysis using XRD and SEM. Further research will focus on how the pH between 7 and 13 affects the morphology and crystalline structure of the brookite TiO_2 crystal NPs and their analysis using XRD and SEM.

2. Methodology

2.1 Preparation of brookite TiO_2 NPs

Brookite TiO_2 NPs were synthesized by hydrothermal synthesis.[4] 50 mL of 0.21 M NaOH solution was added to a solution of 0.31M $TiOSO_4 \bullet H_2O$ H_2SO_4 (deionized water was used as solvent) to form a titanate gel. The gel was stirred until it turned clear. 1M NaOH solution was added to the gel to raise the pH to the pH desired. The all pH measurements were done using a pH meter. The gel was then purified by alternating centrifugation and sonication. The sample was centrifuged 3 times for 5 minutes at 4000 rpm and sonicated 3 times for 2 minutes. The gel was then placed in a 50mL inner Teflon liner reactor chamber filled up to 80% (40mL). The pH was measured to verify the pH desired. If the pH was lower than the desired, 1M NaOH solution was used to raise the pH. The inner Teflon liner reactor chamber was placed in an autoclave and put into a furnace at a temperature of 220ºC for 48 hours. After the 48 hours, the sample was let to cool down and purified once more by alternating centrifugation and sonication. The sample was centrifuged 3 times for 5 minutes at 4000 rpm and sonicated 2 times for 2 minutes. The sample was left to dry overnight in the centrifuge tube wrapped in aluminum foil, with the lid off and in cabinet to prevent any interaction between the light and the samples. Once dried, the lid was put on.

2.1.1 preparation of brookite TiO_2 NPs with different pH before and after first purification

Following the methodology in 2.1, five samples were prepared. Their pH before first purification were set to 7, 8, 10, 11, and 12. After the purification and before putting the samples in the furnace, all samples' pH were set to 12.5.

2.1.2 preparation of brookite TiO_2 NPs with same pH before and after first purification

The methodology in 2.1 was used to prepare 14 samples. The pH of the samples before and after the first purification were set between 7.00 and 12.96.

2.2 Sample Characterization

The samples were analyzed using XRD. The scan was set to continuous with a step size width of 0.12 in the range of 15º – 80º with 15 steps. Each analysis took about 11 minutes. After the formation of brookite TiO_2 was confirmed by the XRD analysis, SEM was used to take images of the samples. For the imaging of samples following 2.1.1 methodology, the SEM was set to spot size 3.0 and high voltage 5.00 kV. For the samples following the 2.1.2 methodology, the SEM was set to spot size 3.0 and high voltage 2.00 kV.

3. Data

3.1 Collected Data From Purchased Crystalline Tio_2 Powder Structures: Anatase, Rutile And Brookite

Purchased TiO_2 anatase, rutile and brookite were analyzed using XRD for reference (Figure 1). The peak values were obtained from Kaplan et al and Paolo et al.[7,22] The peaks of interest ar 111 and 121 for brookite, 110 for rutile and 101 for anatase at angles between 15̊ and 35̊. These peaks show the crystalline phases of the samples. SEM was used to take an image of only TiO_2 brookite (purchased) since it is the crystalline structure of interest (Picture 1).

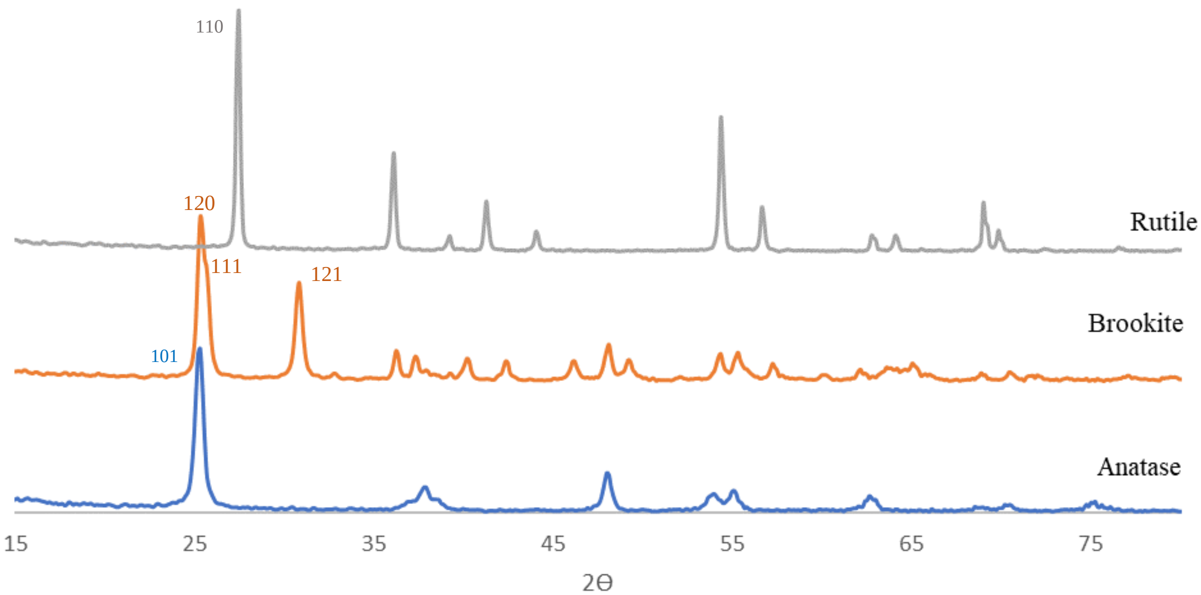
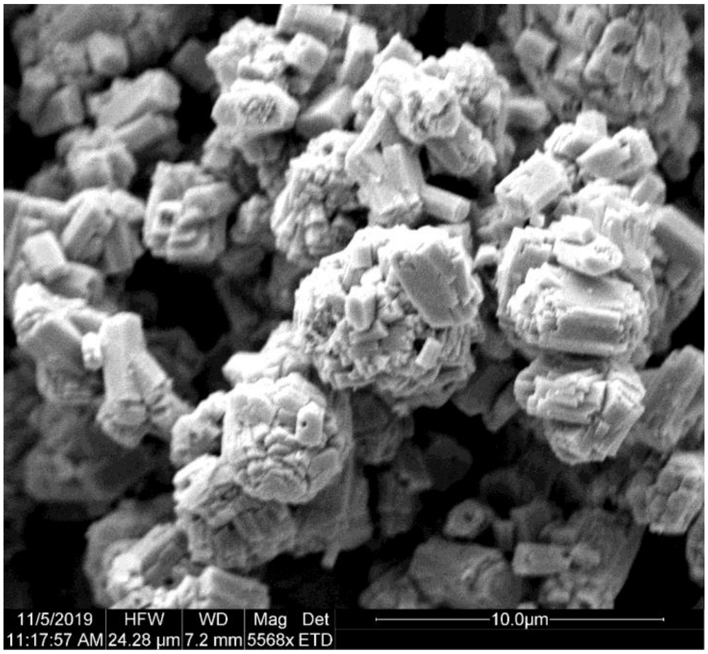


Figure 1. XRD pattern of purchased TiO_2 anatase, rutile and brookite



Picture 1. SEM of purchased TiO_2 brookite

3.2 Obtained Data From Experiment

The pH conditions of a samples have an important effect on the size and morphology of brookite TiO_2 product prepared by hydrothermal method. [6-7, 13, 15-18]

3.2.1 synthesized brookite TiO_2 NPs following 2.1.1 methodology

Figure 2 shows the XRD pattern of a TiO_2 the samples prepared under the same conditions mentioned in 2.1.1. When the samples' pH before purification were set to 7, 8, 10, 11 and 12, three diffraction peaks of interest can be observed. By comparing these peaks with the peaks 120, 111 and 121 of brookite in Figure 1, the brookite crystalline structure of TiO_2 was confirmed.

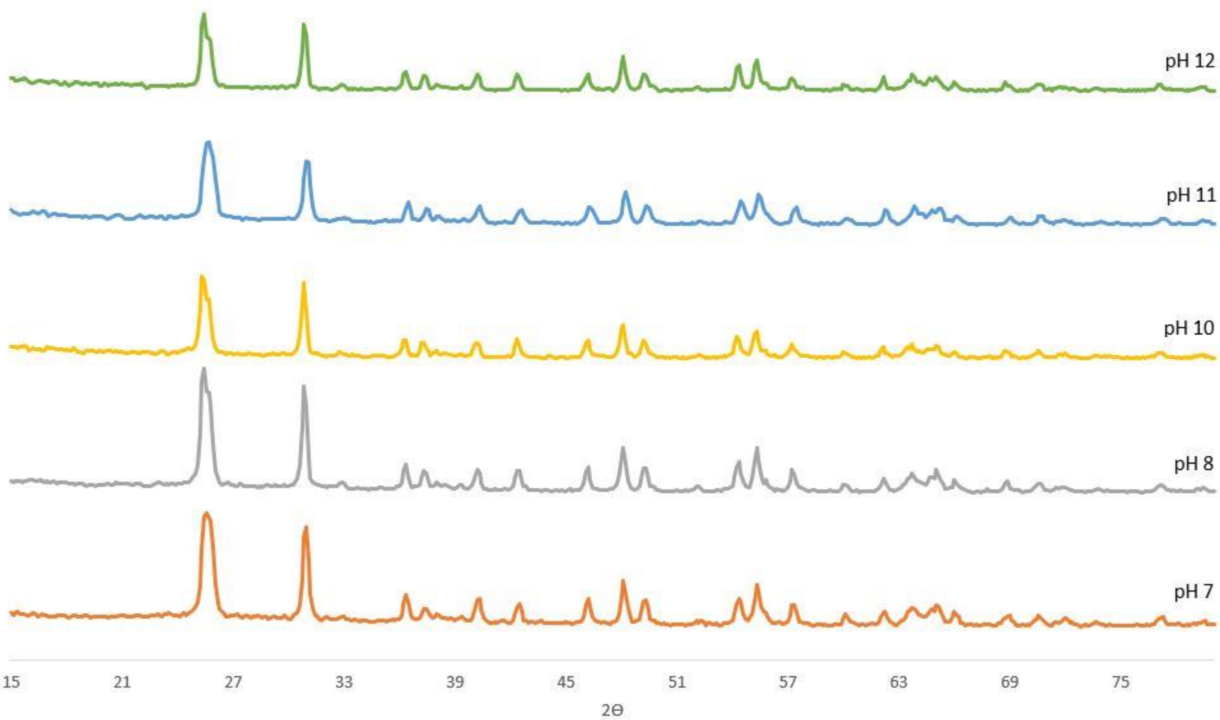
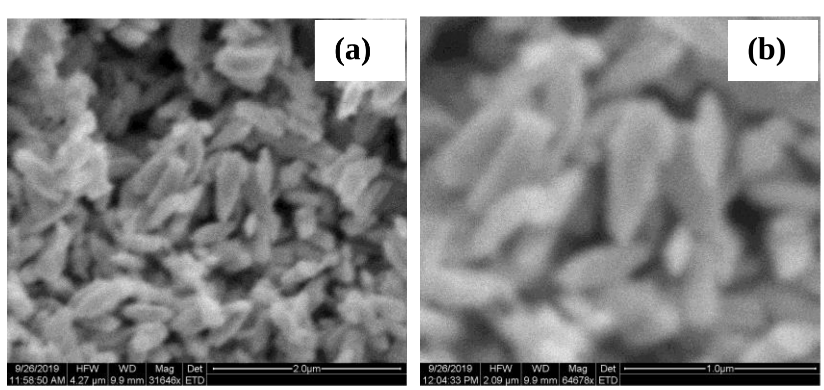
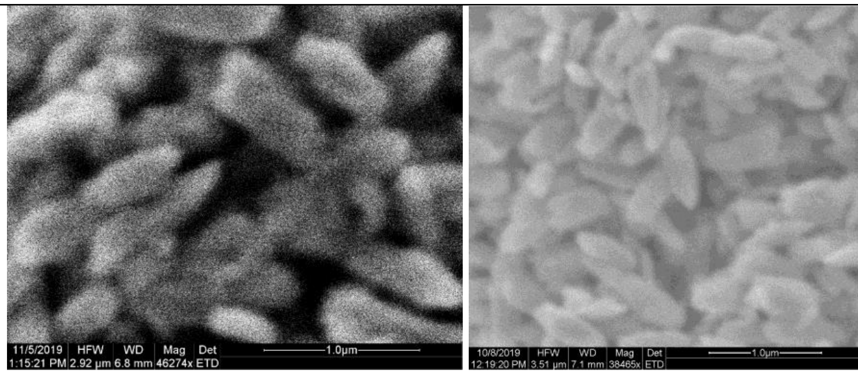


Figure 2. XRD pattern samples obtained at different pH before first purification

Picture 1 show images a-d of the morphology of brookite TiO_2 at pH 7 (a), 8 (b), 10 (c) and 12 (d). All images show agglomerates of nano-size particles. The particles in the samples had a width between 150 nm and 300 nm. The particles obtained are not considered nanoparticles since they do not measure between 1nm to 100nm. Compared to Picture 1, the particles obtained were not as agglomerated, were smaller and single particle size could be measured.



(c) **(d)**



Picture 1. SEM images of TiO_2 NPs at different pH before and after first purification

3.2.2 synthesized brookite TiO_2 NPs following 2.1.2 methodology

Figure 3 shows the XRD pattern of TiO_2 when the samples prepared under the same pH conditions mentioned in 2.1.2. When the samples' pH before purification were set from 7.00 to 8.93, a single peak (101) between 15̊ and 35̊ were present confirming the anatase crystalline structure. When the samples were set with a pH from 11.91 to 12.96, three peaks (120, 111 and121) were present confirming the brookite crystalline structure.

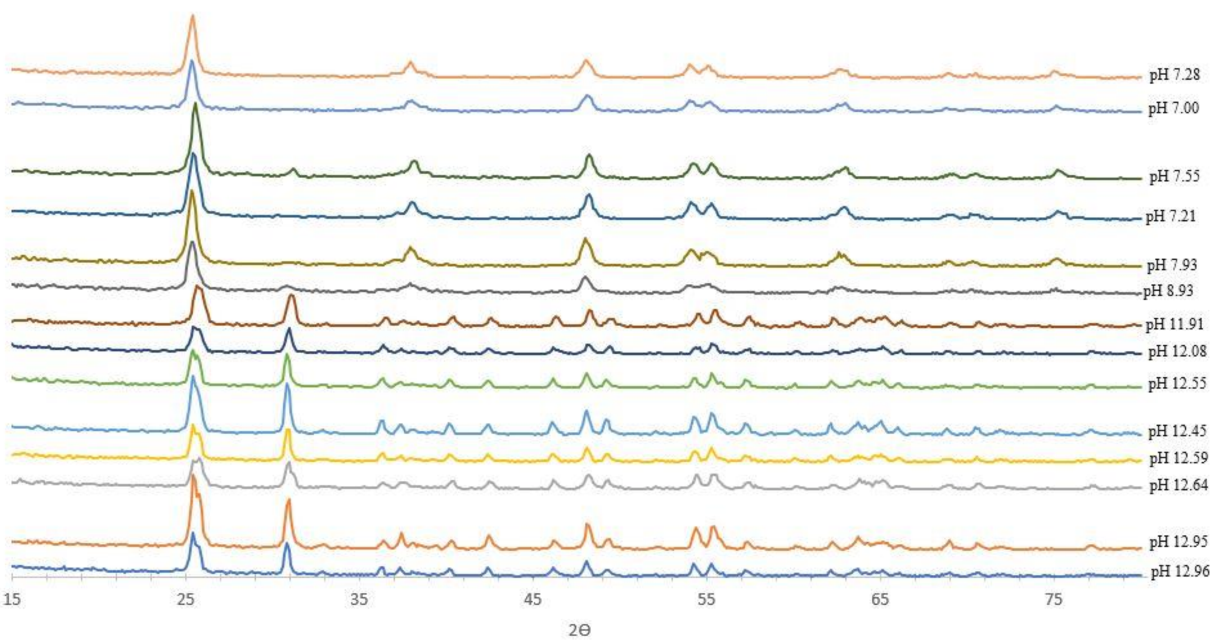


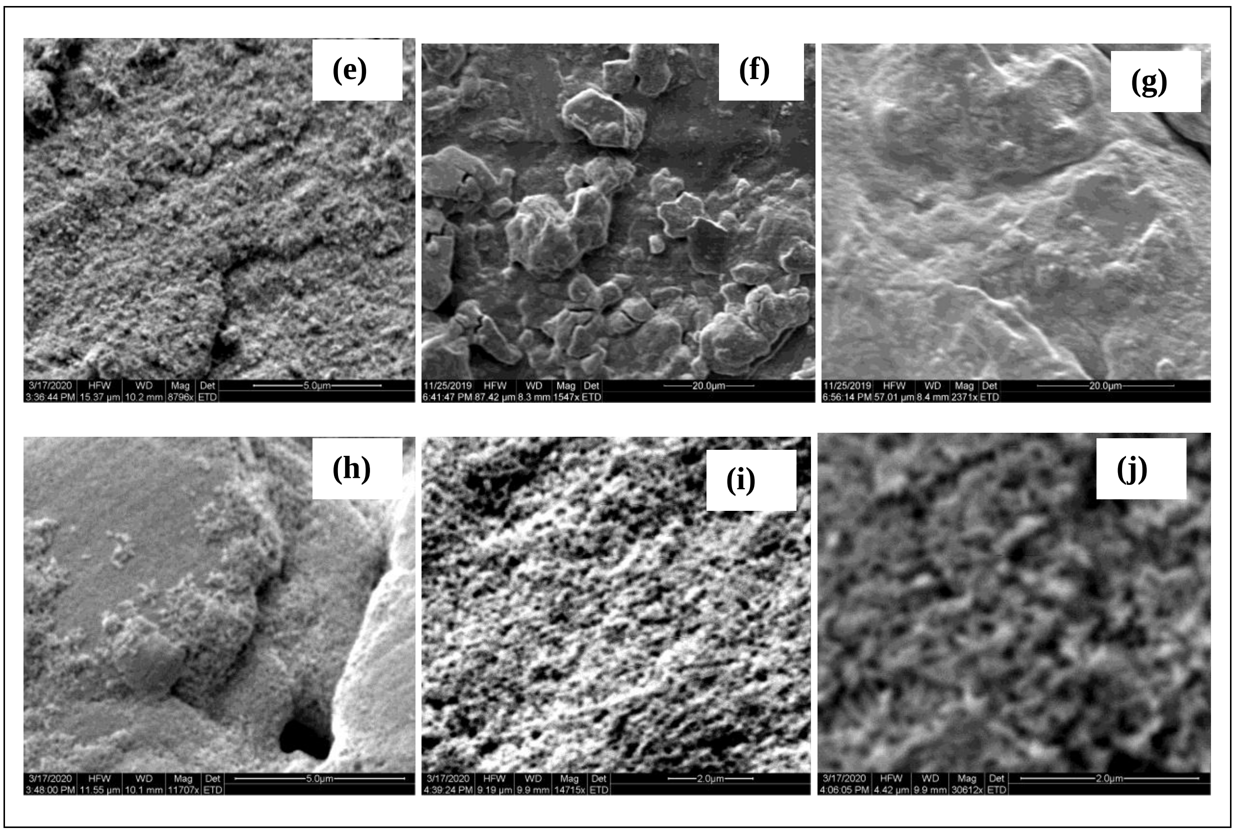
Figure 3. XRD patterns of samples with same pH condition before and after first purification

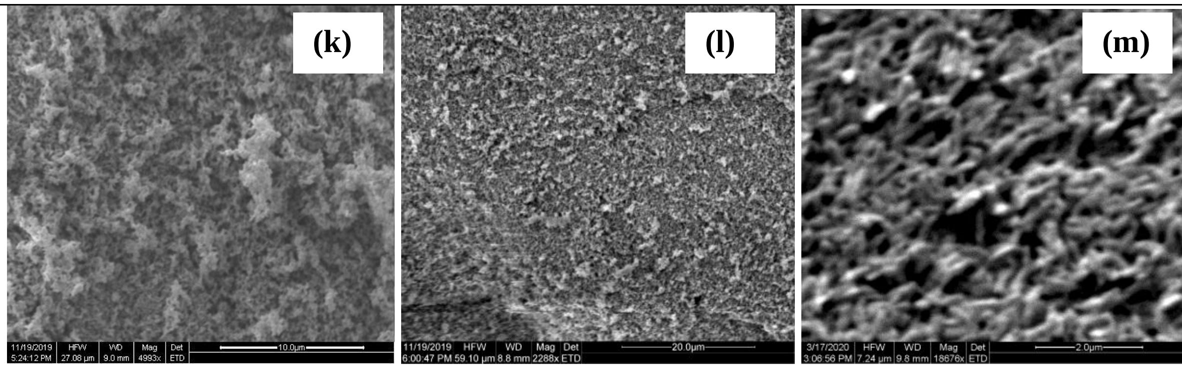
The synthesis of TiO_2 brookite was successful at pH from 11.91 to 12.96. The pH of the samples slightly decreased after the first purification and NaOH was used to increase the pH. The samples at pH 7.00 to 8.93 were determined to be TiO_2 anatase. The pH of the samples increased after the first purification and no NaOH was added. The change of pH of these samples are caused by the oxolation and deoxolation in TiO_2. Table 1 shows the change of pH of the samples after first centrifugation and their crystalline structure.

Table 1. Change of pH of the samples after centrifugation and their crystalline structure.

Initial pH	pH after centrifugation	TiO_2 Crystalline Structure
7.00	8.47	Anatase
7.21	9.40	Anatase
7.28	8.19	Anatase
7.55	10.27	Anatase
7.93	8.79	Anatase
8.93	9.82	Anatase
11.91	11.73	Brookite
12.08	11.73	Brookite
12.45	Unknown	Brookite
12.55	Unknown	Brookite
12.59	11.83	Brookite
12.64	11.86	Brookite
12.95	12.00	Brookite
12.96	12.03	Brookite

Picture 2 show the SEM images of the samples with pH 7.00 (e), 7.21 (f), 7.55 (g), 7.93 (h), 8.93 (i), 11.91 (j), 12.45 (k), 12.55 (l) and 12.95 (m). It can be observed that images e-i that are 000000000000000000000000000000TiO_2 anatase show larger particles compared to those of TiO_2 brookite in images j-m.





Picture 2. SEM images of TiO_2 NPs formed at different pH

4. Conclusion

Two methodologies were carried throughout the research. In the first methodology (2.1.1), the TiO_2 NPs were prepared with different pH before and after purifications. The results show that the synthesis of TiO_2 brookite particles was successful, however the particles' sizes obtained cannot be considered nanoparticles since they do not follow the nanoparticle parameters. It was determined that setting a different pH before first purification and same pH after purification (2.1.1) does not have an effect on the TiO_2 particles.

The second methodology (2.1.2), the TiO_2 NPs were prepared with same pH before and after first purification. The synthesis of TiO_2 brookite particles was successful when the pH before and after purification were set at 11.91 to 12.96. The samples set at pH 7.00 to 8.93 however were determined to be TiO_2 anatase particles. It was determined that pH did have an effect on size and morphology in the TiO_2 particles synthesis. The crystalline structure of TiO_2 NPs changes from anatase to brookite when the pH is close to 11.91 and above. Based on the imaging obtained up to date (Figures 7 to 15), the size of both anatase and brookite seemed to increase as the pH increases; however, further in-depth studies should be performed.

5. Acknowledgement

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