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Titanium Nanoparticles Synthesized Via Hydrothermal Reaction

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Executive Summary

The overall goal of this project was to determine how operating conditions (time and temperature) affect the size of titanium nanoparticles/nanotubes synthesized by hydrothermal growth. Altogether, 5 different trials were completed varying the hydrothermal growth time and temperature as follows: 120°C for 24 hours, 120°C for 48 hours, 150°C for 24 hours, 180°C for 24 hours, and 180°C for 48 hours. After completing all of these experiments, various tests were conducted to determine how time and temperature affected the final product. By using x ray diffraction (XRD), the crystallography of the nanoparticles/nanotubes was determined. The XRD data showed that all of the samples prepared had the same crystal structure with the exception of the samples run at 180°C. The 180°C samples showed that there was possibly some residual sodium ions in the sample that did not get removed in the ion exchange step. To verify if this was the case, and to check to see that nanotubes were made, scanning electron microscope (SEM) images were taken and energy dispersive spectroscopy (EDS) was conducted. These images showed that nanotubes were formed at all of the temperatures (120°C, 150°C, and 180°C) with the samples at 180°C having significantly longer tubes than the 120°C and 150°C samples. The EDS also confirmed that all of the samples were composed of titanium and oxygen atoms.

Various conclusions can be drawn from the work done during this project. First and foremost, the hydrothermal synthesis route for producing titanium nanotubes is a valid approach. This was shown though SEM analysis as well as XRD. In addition to confirming that nanotubes were formed, SEM analysis also showed that temperature has a far greater effect on tube length and diameter than time does. This effect was apparent by the large size increase from 120°C to 180°C samples compared to the 24 versus 48 hour samples.

There have been various positive impacts from the completion of this project. By working with various testing methods such as SEM, XRD, and EDS the fundamentals behind each of those tests are now better understood. After collaborating with a variety of different people, communication skills have also been improved. By keeping a lab notebook and maintaining written communication between the multiple people involved in the project, written communication skills have been greatly improved as well. All of the various lab work completed through the duration of the project has also increased various analytical and procedural skills.

Moving forward, various work could continue to be completed in regards to this project. Higher temperatures should be investigated to determine if there is a maximum temperature at which the nanorods begin to decrease in size. Optimization of the hydrothermal procedure would also be a good idea to decrease the amount of time it takes to synthesize the nanorods. By generating more samples, a correlation between DLS data and tube length and diameter could also be drawn which would allow a much faster determination of tube dimensions. Tube length and diameter could also be determined using TEM. Finally, hydrothermal synthesis of different types of nanorods could also be investigated.

Introduction

The main focus of this project was to determine how reaction conditions affect the particle size of titanium nanotubes/nanoparticles. These particles were prepared using a hydrothermal approach which starts with a basic water solution reaction at moderate temperature followed by an acidic ion exchange reaction. Using this hydrothermal method, five experiments were completed. The hydrothermal temperature and time were the variables of interest and they varied from 120°C to 180°C and from 24 hours to 48 hours. Once all the samples were synthesized they were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD). Using these techniques, the length, diameter, and crystalline structure were measured.

Much discussion has gone into how the titanium nanoparticles are actually formed during the hydrothermal synthesis.[6,3] Some believe that the most critical step in the synthesis is the post treatment with an acid in order to remove the Na^+ ions and exchange them with H^+ ions.[6] These studies showed that if the post hydrothermal treatment is not carried out, the titanate is not converted to anatase TiO_2 (nanotubes/nanoparticles). Although it is believed that the post treatment plays a huge role in the formation of nanoparticles/nanotubes, the environment during hydrothermal treatment is also very important. The solution must be very basic as it was found that the nanomaterials/nanotubes were not formed if an NaOH solution of <5M is used during the hydrothermal process.[3]

Many efforts have been made to characterize titanium nanotubes synthesized by a hydrothermal reaction [4,5] Of those, XRD and SEM are the most common. XRD is used to

characterize the crystallographic structure of the nanoparticles/nanotubes and SEM is used to determine the morphology of the particles.[4]

Due to their tube like properties, titanium nanoparticles have many different applications. One interesting application is for water treatment. When used to coat a ceramic semiconductor, they were found to degrade the organic material present in the water thus effectively purifying the water.[4] Overall, the most widely used application of titanium nanotubes is for anti-wear/anti corrosion coatings. It was shown that in a Ni/TiO2 based coating, as the amount of TiO2 increased, the anti-wear and anti-friction properties increased.[1] Due to these properties, these materials would make suitable coatings for machine parts or other applications where it is imperative to have low friction and high corrosion resistance.

Background

The reaction of titanium powder into titania nanoparticles/nanotubes involves a series of reaction steps.[4] The first step in the process combines the titanium dioxide powder with a mixture of sodium hydroxide and water. The basic mixture allows the sodium hydroxide ions to attack the titanium dioxide molecules and cleave one of the Ti-O bonds when exposed to temperatures above 100°C in a sealed vessel (autoclave). After all of the titanium dioxide is converted to TiO^+ ions, the acid wash begins. This acid wash serves as an ion exchange step in which the acidic environment allows for the exchange of the sodium ion. Following the ion exchange step, the solution is subsequently washed with water and dried in a freeze vacuum cycle to neutralize the acidic solution and dry the powder.

Previous work has been conducted on hydroxyapatite (HA) nanorods in order to determine the effects of hydrothermal temperature and time on the length, diameter, and morphology of the final product.[2] It was shown that when working with the HA nanorods, increasing time and increasing temperature led to an increase in tube length and diameter. Specifically they were able to determine that temperature had a much greater effect on the size of the final material compared to time. They also showed that in the case of HA nanorods, the diameter increases much more substantially than the length.

Experimental

The hydrothermal reaction was carried out as shown in Table 1 in Appendix A. The various experiments focused on manipulating steps 8 and 9. Five experiments were run with steps 8 and 9 varying as follows: 120°C for 24 hours, 120°C for 48 hours, 150°C for 24 hours, 180°C for 24 hours, and 180°C for 48 hours. All other aspects of the procedure remained constant in order to remove any possible variation and allowed the time and temperature aspect of the hydrothermal reaction to be isolated and studied. All of the experiments proceeded as expected with no issues in the processing steps.

Methods

The final titanium nanoparticles were characterized using SEM, XRD, and EDS. SEM was used to determine the morphology of the nanoparticles/nanotubes and XRD was used to determine the crystal structure of the nanoparticles/nanotubes. EDS was used to determine the chemical composition of the samples to ensure the correct material was made.

The XRD data was generated using a powdered form of the samples. The powder was generated by using a spatula to crush each one of the samples. XRD works by subjecting a small sample of material to a beam of x-rays. These x-rays are diffracted at a certain angle depending on the crystal structure of the sample. This diffraction angle is ultimately used to characterize the sample.

SEM data was generated for all of the samples as well. They were all placed on a piece of carbon tape and thoroughly dispersed over the paper using a spatula. The EDS data was generated using these same samples. SEM works by subjecting the sample to a beam of electrons. These electrons interact with the sample and create a signal that is interpreted by an analyzer that ultimately creates an image. EDS also uses a focused electron beam but, instead of interpreting the signal from the electron beam, the analyzer interprets the x-ray beam emitted by the sample when exposed to a beam of electrons and determines the chemical composition of the sample.

Data and Results

After running all of the trials, the final products were successfully characterized using XRD, SEM, and EDS. There was immediately a visible difference in all the samples. The samples produced at 120°C were a very fine powder after the vacuum drying step where the samples produced at 150°C and 180°C were found to be much less powdery and contained multiple clumps of material. As far as time is concerned, there was not an observable visual difference between the 24 hour samples and the 48 hour samples for each of the temperatures.

Initially, to determine if all the samples had the same crystalline form, XRD was carried out. Figure 1 shows the XRD for the 120°C 48 hour sample and is a typical XRD pattern for titanium nanoparticles which are identified for having peaks at 2θ=25° and 48°.[4] (Note that the 120°C 24 hour and the 150°C 24 hour sample had very similar XRD patterns to that of Figure 1.) These peaks are specifically used to identify the anatase phase of titanium nanoparticles and help determine if a good product was made. Figure 2 is the XRD pattern obtained for the 180°C 48 hour sample and is very similar to the 180°C 24 hour sample. It is apparent that there are some differences between Figure 1 and Figure 2, specifically the large peak at 11° in Figure 2.

To compare the shape and size of the particles for each sample, SEM analysis was conducted. Magnification up to 25KX was obtained and is shown in Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7. The 180°C and 150°C samples showed clear tube-like structures where the 120°C samples resembled more crystal or sheet-like properties. The SEM images also showed that the 180°C nanorods were much larger in size (both length and diameter) than the 150°C and 120°C samples with the 180°C 24 hour sample having an average diameter of 200nm

and the 150°C 24 hour sample having an average diameter of 50nm (determined using Image J software).

To verify that no foreign material was present in the samples, energy dispersive spectroscopy (EDS) was also conducted and is shown in Figure 8, Figure 9, Figure 10, Figure 11, and Figure 12. This analysis showed that all the samples contained the titanium and oxygen as expected, however, the relative amounts of titanium and oxygen in the 120°C samples were different than those of the 150°C and 180°C samples. The 120°C samples had a lower molar ratio of oxygen to titanium compared to the 150°C and 180°C samples which had roughly a 4:1 molar ratio of oxygen to titanium.

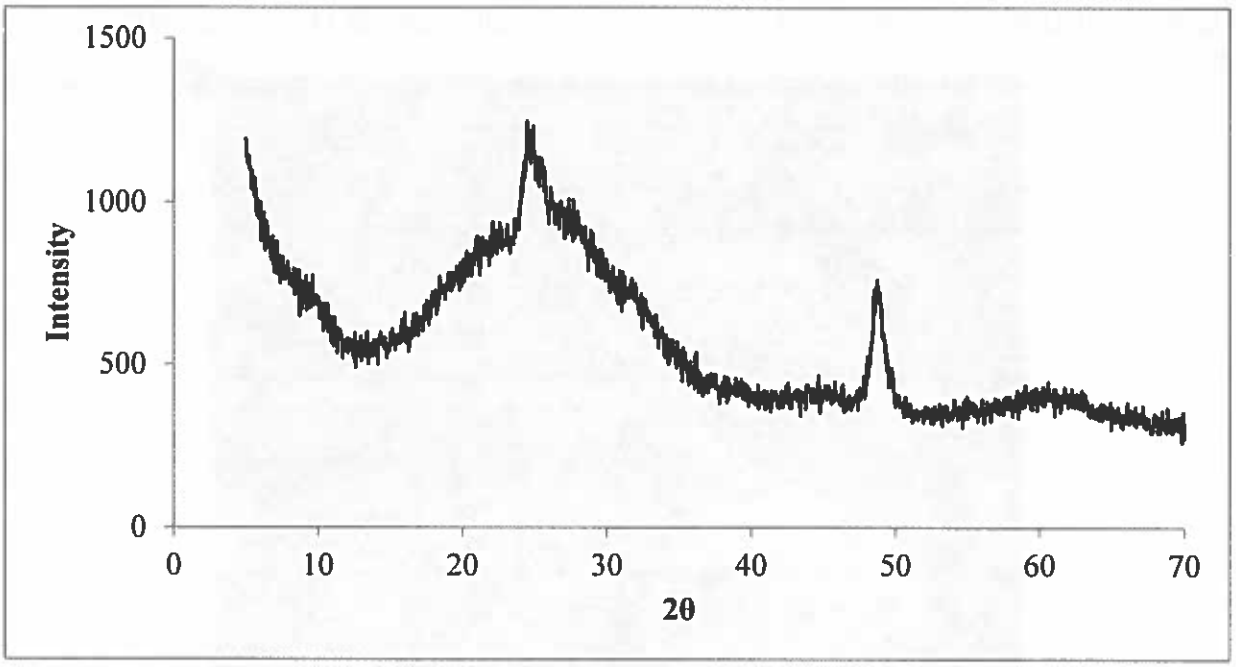

Figure 1. XRD pattern for the 120°C, 48 hour sample. Peaks at 25° and 48° are shown.

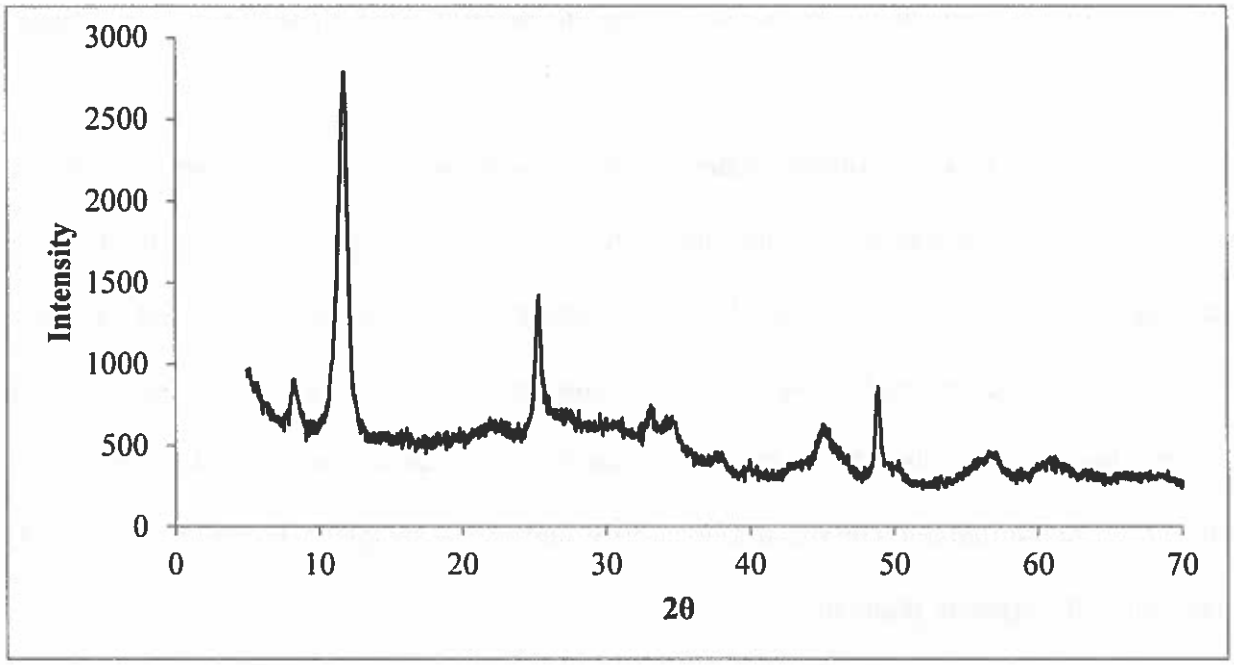

Figure 2. XRD pattern for the 180°C, 48 hour sample. Major peaks at 11°, 25°, and 48° are shown.

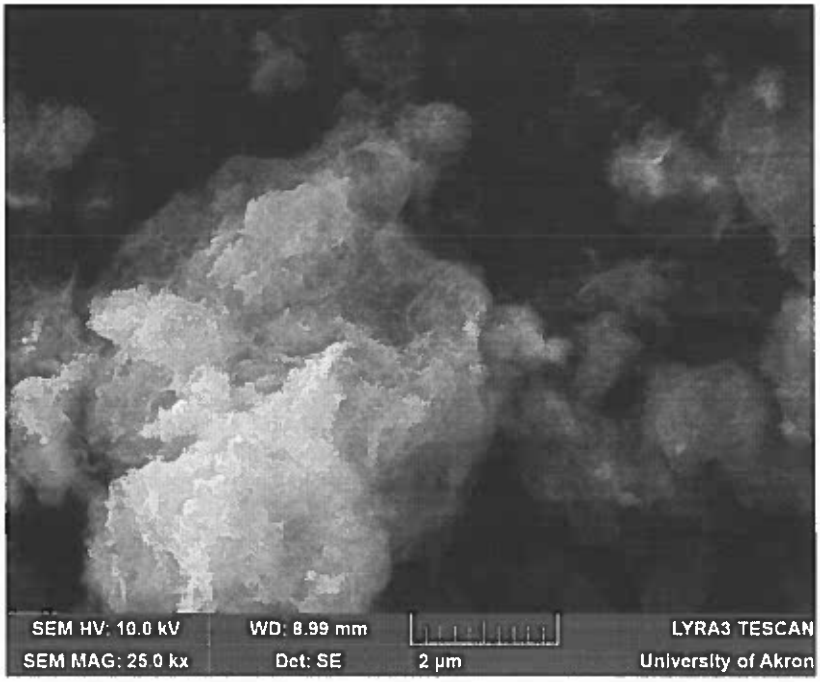

Figure 3. SEM image of the 120°C 24hr sample magnified to 25KX.

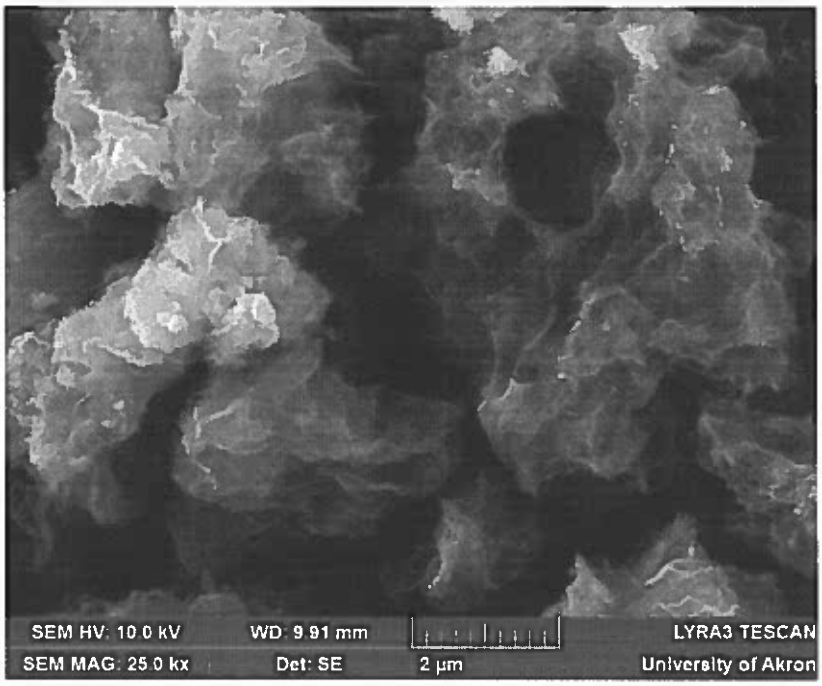

Figure 4. SEM image of the 120°C 48hr sample magnified to 25KX.

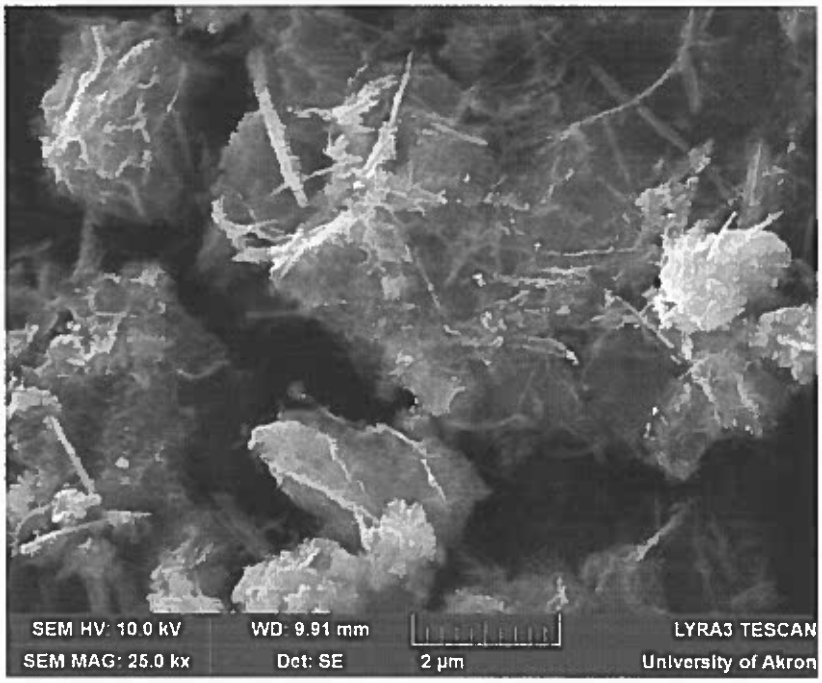

Figure 5. SEM image of the 150°C 24hr sample magnified to 25KX.

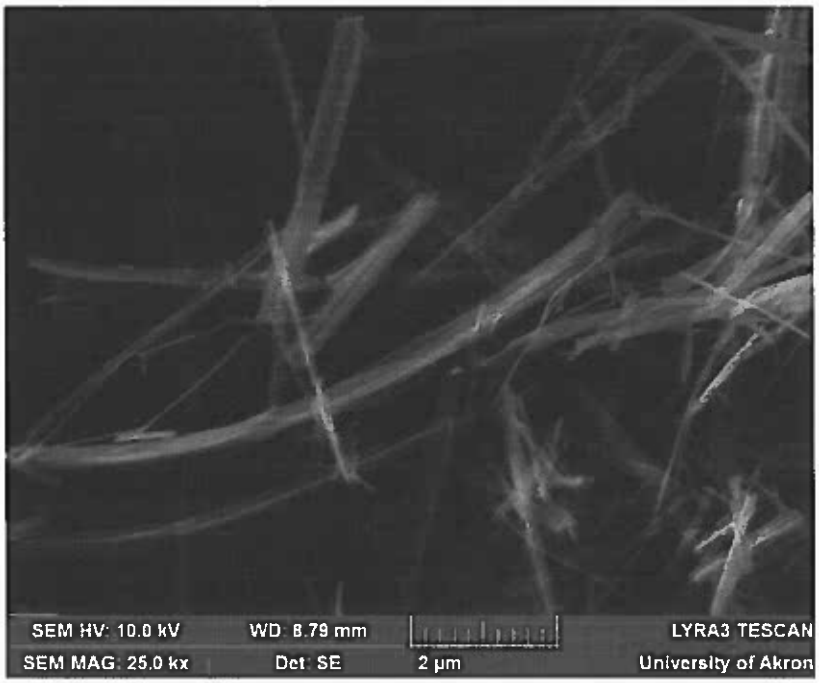

Figure 6. SEM image of the 180°C 24hr sample magnified to 25KX.

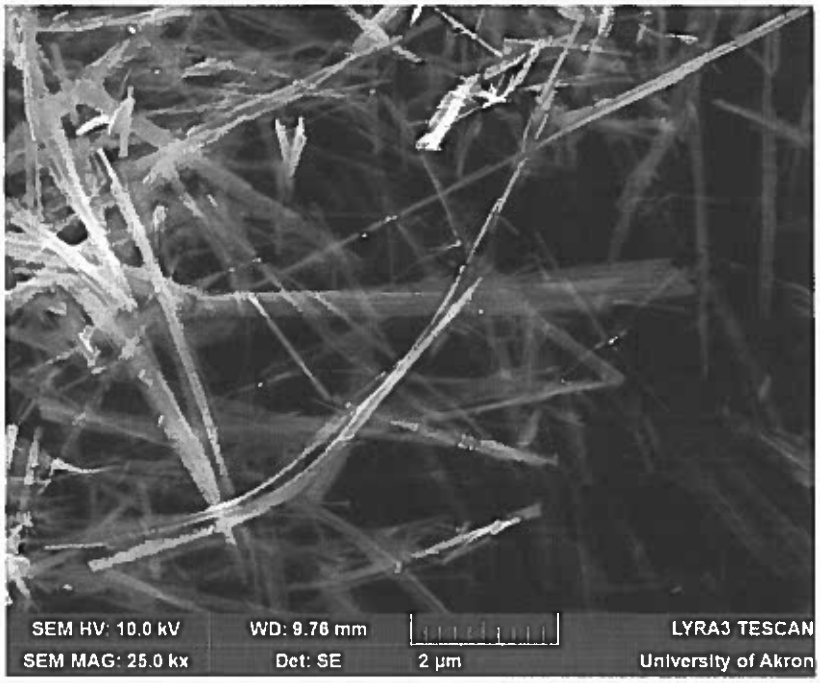

Figure 7. SEM image of the 180°C 48hr sample magnified to 25KX.

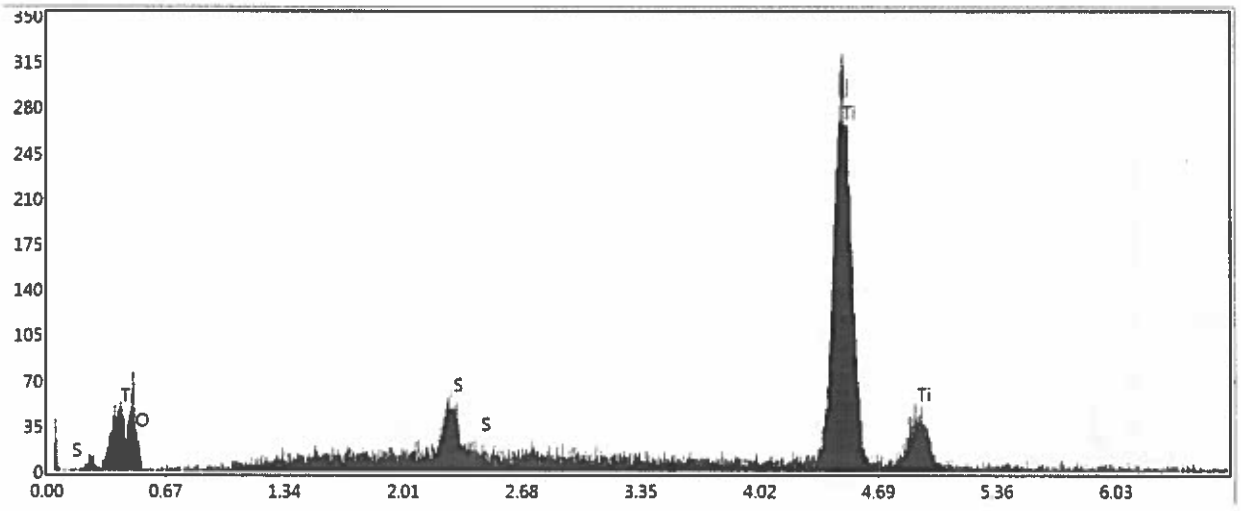

Figure 8. EDS analysis conducted on the 120°C 24hr sample. It showed 84wt% titanium and 11wt% oxygen (2.5:1 molar ratio of Ti to O)

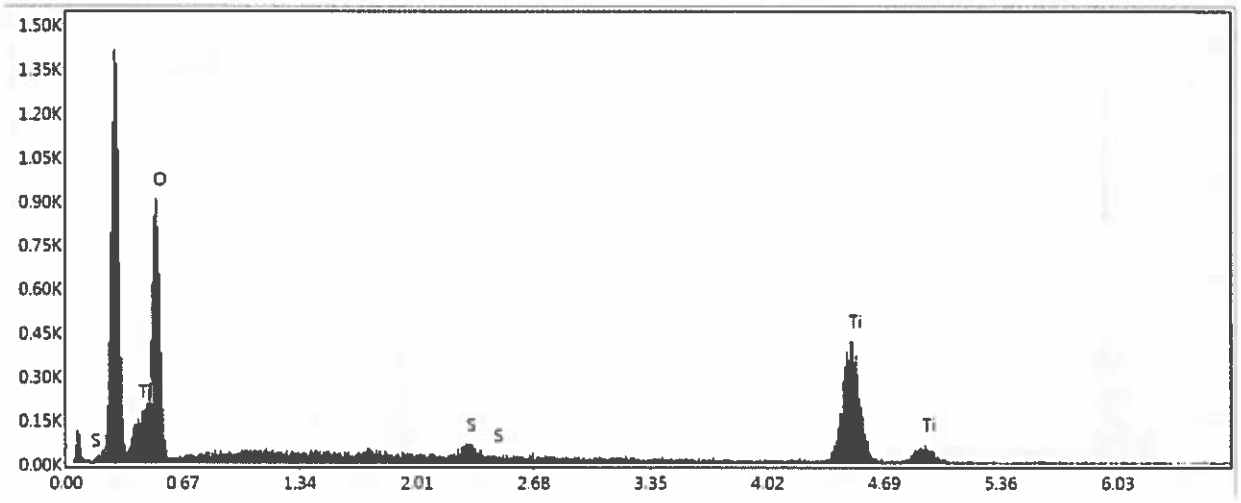

Figure 9. EDS analysis conducted on the 120°C 48hr sample. It showed 44wt% titanium, 55wt% oxygen (1:3.7 molar ratio of Ti to O)

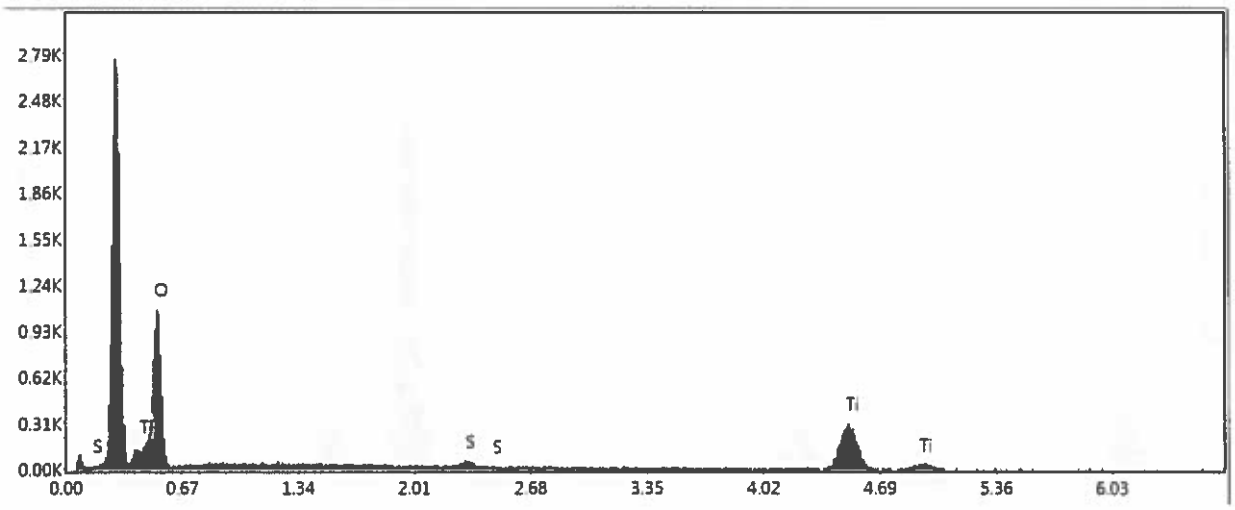

Figure 10. EDS analysis conducted on the 150°C 24hr sample. It showed 62wt% oxygen and 37wt% titanium (1:5 molar ratio of Ti to O)

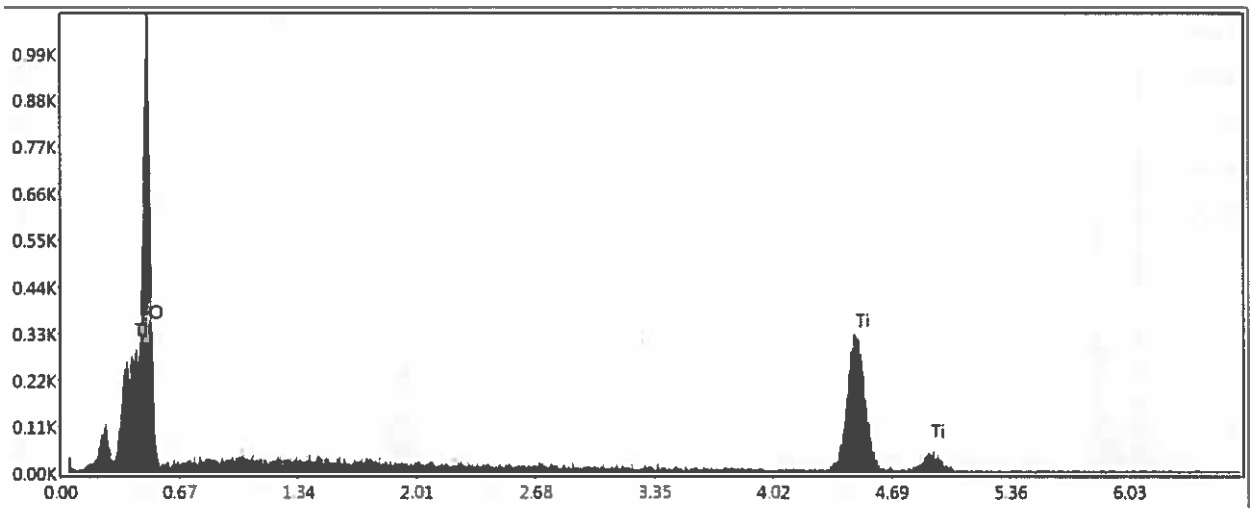

Figure 11. EDS analysis conducted on the 180°C 24hr sample. It showed 55wt% oxygen and 45wt% titanium (1:3.6 molar ratio of Ti to O)

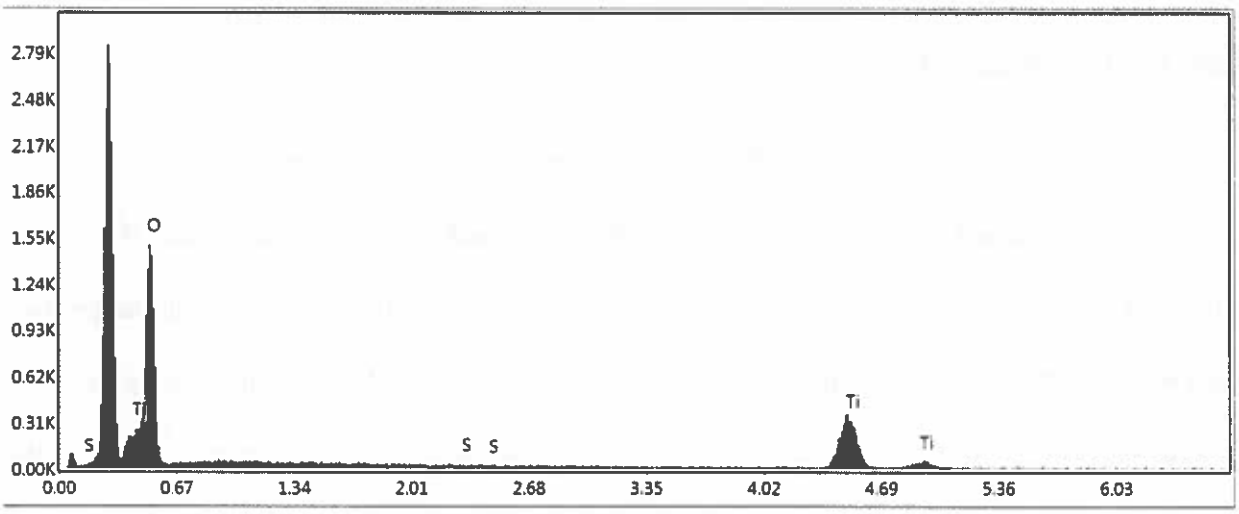

Figure 12. EDS analysis conducted on the 180°C 48hr sample. It showed 66wt% oxygen and 34wt% titanium (1:5.8 molar ratio of Ti to O)

Discussion/Analysis

The work completed on hydrothermally synthesized titanium nanotubes/nanoparticles has led to many conclusions. Immediately following the synthesis of the materials, the visual differences pointed to a possible difference in particle size with 180°C samples being larger than the 150°C or 120°C samples. The visual similarities between the 24 and 48 hour samples could also demonstrate that the mixtures fully reacted after only 24 hours. To test this hypothesis, the SEM images were used and showed that large conglomerates of particles were formed at 120°C and 150°C, but not 180°C. This observation could be caused by the smaller particles in the 120°C and 150°C samples having higher cohesive forces between each other which would make it more difficult to fully separate them. The size difference between the 180°C particles and the 120°C and 150°C particles also leads to the conclusion that the growth rate is more rapid at 180°C compared to 150°C or 120°C. The growth rate at 180°C is roughly 4 times higher than the growth rate at 150°C (determined using the average diameters and the 24hour hold time). The little difference observed between the 120°C 24 hour and 120°C 48 hour as well as the 180°C 24 hour and 180°C 48 hour sample could indicate that the reactions have reached completion at the 24 hour mark which would prevent any further formation to occur to the 48 hour samples. Although temperature was clearly shown to have a major effect on the tube size, reaction time is also very important in reaching a complete reaction/tube formation.

The XRD and EDS testing also helped characterize the samples. Initially, it was thought that the 180°C samples were not properly washed in the ion exchange step. This was apparent because of the peak at 11° in the 180°C which indicates that residual Na^+ ions could still present in the sample or that nanoribbons were formed.[5] To determine if residual Na^+ ions are in the

sample, EDS was conducted and revealed that no sodium ions were present in either of the 180°C samples which meant that the ion exchange step was sufficient. Even though this was a positive result, the EDS analysis led to another discovery about the 120°C 24 hour sample. Since a TiO_2 molecule has two oxygen atoms for every titanium atom, there should be at least a 2:1 molar ratio of oxygen to titanium. With this in mind, there could be an issue with the 120°C 24 hour sample as far as the nanorods are concerned as there is higher molar ratio of titanium to oxygen (2.5:1). To ultimately verify if this is an issue, further magnification (using TEM) of the 120°C sample is required to see if nanotubes have been formed. It was shown that samples synthesized at 120°C show tube lengths of around 100nm.[3] If this is the case, it would be very difficult to see the tube-like structure when magnified to only 25KX. If the TEM images show that nanotubes were not formed, then 120°C is not a sufficient temperature to promote the growth of nanorods. The 180°C and 150°C samples also showed interesting EDS results. Those samples contained much more oxygen than is expected for the 2:1 ratio. This result could be caused by the formation of nanoribbons or other forms of the titanium nanoparticles other than the anatase phase (TiO_2) that have chemical formulas such as $Ti_3O_7nH_2O$ that have a higher molar ratio of oxygen to titanium.[5]

Conclusions

The work completed for this project successfully confirms that titanium nanorods increase in size as hydrothermal time and temperature are increased. Originally Jin et al showed that as hydrothermal time and temperature increases, the particle size of the HA nanorods increases.[2] Very similar results were obtained with the titanium nanorods synthesized for this project with both the length and diameter of the particles increasing in size with elevated

temperatures and times as verified though SEM analysis. The hydrothermal method for producing titanium nanorods also proved to be a valid synthesis approach. This synthesis method will allow for future work to be conducted on various corrosion resistant coatings as well as future work on hydrothermally grown nanomaterials. In the future, more experiments could be conducted in order to determine the temperature at which the maximum sizes of titanium nanorods are formed. Other types of nanorods could also be studied through the hydrothermal synthesis method in the future. Another possible route this project could take in the future is one of process optimization where the process as a whole is studied to determine how cycle time could be decreased.

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Appendix A

Table 1. Standard operating procedure for the hydrothermal reaction.

Step	*Procedure*
1	Obtain all raw materials: • Titanium oxide (P25) • Sodium hydroxide • DI water
2	Obtain Teflon-lined autoclave
3	Measure out the following amounts of each material and add them to the Teflon lined autoclave in the respective order: 1. 1g Titanium oxide 2. 10g sodium hydroxide 3. 20g Di water (place Teflon lined autoclave on scale and add water) CAUTION: Be sure to wear nitrile gloves and safety glasses while handling all material.
4	Place mixing bar inside the Teflon lined autoclave
5	Mix for 3 hours with lid on the Teflon lined autoclave • Ensure mixing is occurring before placing the lid on
6	Remove from mixing plate and use magnet to remove stir bar
7	Place Teflon lined autoclave inside metal autoclave and tighten the lid • Ensure that the metal bar is used to completely tighten the lid
8	Place autoclave inside oven and start timer
9	After the reaction is complete remove the autoclave from the oven CAUTION: Be sure to wear thermal protective gloves when removing sample from oven.
10	Let the sample stand for 5 hours before removing the lid to allow it to cool
11	Remove material from the teflon lined autoclabve and place it in a 300mL beaker • Use a spatula to aid in removing the material • Rinse the Teflon lined autoclave with water and add it to the beaker
12	Add 300mL of water to the beaker and place a stir bar in the beaker

13	Mix contents of beaker for 10min
14	Prepare 0.1M sulfuric acid solution: 1. Obtain a 5L flask 2. Add 4L of DI water to flask 3. Add 40g of sulfuric acid 4. Secure lid on bottle and shake mixture thoroughly CAUTION: Be sure to wear nitrile gloves and safety glasses while handling all material.
15	Take beaker off stir plate and allow to phase separate
16	Remove the upper aqueous layer by pouring off the top layer • Be sure not to lose any of the solid material
17	Place remaining slurry in a 600mL beaker
18	Add 400mL 0.1M sulfuric acid to the 600mL beaker mix CAUTION: Be sure to wear nitrile gloves and safety glasses while handling all material.
19	Check the pH of the mixture using litmus paper • If the pH is 1 or less continue to next step • If the pH is higher than one, remove the upper aqueous layer once again (be sure not to lose any of the solid material) and repeat the previous step
20	Mix solution for 5hrs then remove upper aqueous layer
21	Repeat the previous step 3 times (for a total of 20hours of mixing)
22	Stop mixing and remove upper acidic layer from sample
23	Add remaining mixture to a vacuum filtration unit while using 2 filter papers • It is advantageous to use a vacuum pump if one is available
24	Wash the material with water until the pH becomes neutral • Be sure to periodically check the pH of the material by using litmus paper at the bottom of the Buchner funnel
25	Remove the remaining paste from the vacuum filtration setup using a spatula. Place the material in a 20mL sample vile
26	Place paraffin over the vile and poke holes (about 6-7) near the opening of the vile
27	Place sample in -80°C freezer for 5hrs

28	Remove sample from freezer and place in a freeze dry cycle for 24hrs CAUTION: Be sure to wear insulated gloves when removing sample from freezer.
29	Remove sample from freeze dry cycle and place in plastic sample bag CAUTION: Be sure to wear nitrile gloves and safety glasses while handling all material. Handle powder material in a hood to ensure no dust particles are inhaled.

Appendix B

DLS data was generated for some of the samples and is shown in Table 2. This data was used to determine what pH of solution would produce the smallest diameter. These results showed that a neutral pH resulted in the smallest particle diameter, however, the samples run at a pH of two showed unreasonably high particle size. The DLS data ultimately led to the determination of the best pH to disperse the titanium nanorods/nanoparticles in. Seeing as the neutral to slightly basic pH led to the lowest particle diameter, these solutions would be the best candidates for fully dispersing the particles. The higher diameters observed at the low pH values as well as the high pH values is a result of particles conglomerating which is not good for proper dispersion.

Table 2. DLS data for the samples.

Sample	*120°C 24hr pH2*	*120°C 48hr pH2*	*120°C 24hr pH4*	*120°C 48hr pH4*	*120°C 24hr pH6*	*120°C 24hr pH10*	*150°C 24hr pH2*	*180°C 24hr pH2*	*180°C 24hr pH6*	*180°C 24hr pH10*
Pass 1 (nm)	884.67	21,224.97	1,225.87	10,224.39	763.81	463.16	12,599.93	11,423.98	852.85	3,333.30
Pass 2 (nm)	746.41	789.91	1,161.62	15,599.70	734.64	579.98	21,803.32	13,429.78	614.65	1,077.55
Pass 3 (nm)	793.76	852.47	963.63	27,267.61	683.32	491.10	18,010.43	23,698.54	709.63	5,145.89
Mean (nm)	808.28	7,622.45	1,117.04	17,697.23	727.25	511.42	17,471.22	16,184.10	725.71	3,185.58
std error	40.56	6,801.28	78.92	5,030.49	23.53	35.22	2,670.44	3,801.58	69.23	1,176.75
std dev	70.26	11,780.17	136.69	8,713.07	40.75	61.00	4,625.33	6,584.52	119.91	2,038.19