ASTFE
American Society
of Thermal and Fluids Engineers

5th Thermal and Fluids Engineering Conference (TFEC)
April 5–8, 2020
New Orleans, LA, USA

TFEC-2020-32013

SOLUTION-BASED MODIFICATION OF CHARACTERISTICS OF TIO2 NANOPARTICLES USING DIMETHYLFORMAMIDE

Lucas Splingaire[1], Udo Schnupf[2], Kazuhiro Manseki[3], Takashi Sugiura[3], Saeid Vafaei[1*]

[1]Mechanical Engineering Department, Bradley University, Peoria, IL, USA.
[2]Mund-Lagowski Department of Chemistry and Biochemistry, Bradley University, Peoria, IL, USA.
[3]Department of Chemistry and Biomolecular Science, Gifu University, Gifu, Japan.

ABSTRACT

In dye-sensitized solar cells, it has been observed that dyes have a higher affinity for anatase TiO2 nanoparticles in photoelectrodes. It has also been shown that having the TiO2 semiconductor layer in the solar cell allows for more favorable electron transport. Therefore, having a layer(s) of anatase TiO2 nanoparticles in a solar cell will increase the charge separation efficiency of the device. While a great amount of research has been done on the creation of TiO2 nanoparticles and their effect on the efficiency of dye-sensitized solar cells, not much is known of the effects of low-temperature synthesis of semiconductor TiO2 nanoparticles on these solar cells. In addition, most methods of producing anatase TiO2 nanoparticles require the use of a high-temperature oven for the purpose of a hydrothermal reaction. The purpose of this research is to discover a method of obtaining porous TiO2 semiconductor films comprised of anatase TiO2 nanocrystals using low-temperature synthesis of TiO2 without hydrothermal reactions of the TiO2 nanoparticles and to observe their characteristics. The TiO2 semiconductor nanoparticles were synthesized at 40 ^{o}C using $TiCl_4$ and dimethylformamide in an aqueous solution. A method of creating a reaction mixture to produce the semiconductor nanoparticles was slightly varied four times, and the results of each trial were investigated. This method involved the creation of the TiO2 nanoparticles through a low-temperature reaction and dry-freezing the nanoparticles to remove moisture and produce a powder that could be resuspended. Once the TiO2 nanoparticles were obtained using each method, their characteristics, including size and shape, were observed under a transmission electron microscope and X-ray diffraction.

KEY WORDS: Anatase, TiO2, nanoparticles, dye-sensitized solar cells, low temperature

1. INTRODUCTION

Due to the ever-increasing demand for clean and renewable energy, much research has been performed on solar cells. Specifically, dye-sensitized solar cells (DSSC) have received a great amount of attention. A dye-sensitized solar cell is a solar cell that collects the electrons released when light hits dye inside the cell. The dye is loaded onto a nanostructure of the DSSC forming a mesoporous layer [1]. To improve the efficiency of a DSSC, there are two important characteristics that must be optimized: the electron transport efficiency of the cell and the morphology of the nanostructure for dye loading. The larger the surface area of the nanostructure, the more dye that can be loaded onto it, thus improving its efficiency. A series of experiments have been performed to produce a nanostructure with an enlarged surface area for dye loading.

One of the most promising type of nanoparticles for this purpose is anatase titanium dioxide (TiO_2). Multiple methods for the synthesis of anatase TiO_2 nanoparticles have been reported in the literature [2-6]. One such method is the so-called hydrothermal process. This involves a reaction process where an aqueous

*Corresponding Author: svafaei@fsmail.bradley.edu

mixture is heated above 100 ^{o}C. A study by Chu et al. involved a solution consisting of titanium (Ti) and sodium hydroxide (NaOH) that was heated in an autoclave at 210 ^{o}C. The product was washed with hydrochloric acid (HCl), then heated again at 200 ^{o}C and washed with ethanol. The final product was allowed to dry overnight, producing powdered anatase TiO_2 nanoparticles [2]. The morphology of anatase TiO_2 nanoparticles can be determined in multiple ways of which the most common methods are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Upon testing the produced nanoparticles in a DSSC, Chu et al. observed an efficiency of 7.03% [2].

The sol-gel method represents another method of synthesizing anatase TiO_2 nanoparticles. This method involves the creation of a precursor solution for a gel network. An example of this method is a study by Lee et al. In their experiment they first prepared an aqueous stock solution of Ti^{4+} (0.5M) with a pH of 9.5 by mixing titanium (IV) isopropoxide (TIP) with triethanolamine (TEOA) with a 1:2 molar ratio respectively. The pH of the solution was adjusted to either 8.5 or 10.5 using perchloric acid ($HClO_4$) or sodium hydroxide (NaOH). Afterward, 0.4 M ethylenediamine (ED) solution was added as a shape controller. The solution was then placed in a stainless-steel autoclave at 100 ^{o}C for 24 hours and then an additional 72 hours at 140 ^{o}C . The first heating of the solution was performed to form a hydrolyzed gel network that would prevent extensive nucleation and serve as an anticoagulant that would fix the growing particles. The second round of heating was performed in order to promote the nucleation and growth of titania seeds. The resulting nanoparticles were separated from the gel via centrifugation and washed multiple times with NaOH, nitric acid (HNO_3), and finally with di-ionized water (DI) to remove residual organic compounds. The morphology of the synthesized nanoparticles and their crystalline structures were observed using a high-resolution TEM and XRD. Without using ED as a shape controller, Lee et al. observed the nanoparticles that were synthesized at pH of 8.5 to be spheres of radius 20 nm and at a pH of 10.5 to be rods of width 20 nm and length 100 nm. With ED added as a shape controller, the synthesized nanoparticles at a pH of 10.5 were found to be rods with width 20 nm and length 200 nm. The nanoparticles were then tested in a DSSC, and a light conversion efficiency of 5.3% was achieved [3].

Another example of hydrothermal synthesis is an experiment by Qiu et al. [4] where first hydrogen titanite was synthesized by mixing TiO_2 consisting of about 80% anatase particles of size 20-30 nm with NaOH to form an aqueous solution. This solution was then transferred to a Teflon-lined stainless-steel autoclave at 150 ^{o}C for 20 hours and then naturally cooled to room temperature. The resultant material was then stirred in HCl until a pH of 1-2 was reached. The product of this process was collected by filtration and washed with DI water several times [4]. Qiu et al. observed the morphology of the resultant nanoparticles via SEM to be nanospindles with diameters ranging from 6 to 45 nm and lengths ranging from 20 to 300 nm. These nanoparticles were then tested in a DSSC, and an energy conversion efficiency of 8.3% was achieved [4]. Yet another common method of synthesizing anatase TiO_2 nanoparticles is through a solvothermal reaction. A solvothermal reaction is like a hydrothermal reaction with the exception being that the precursor solution is non-aqueous. A study by Chen et al. [5] has shown that a mixture of TIP, hexadecylamine (HDA), absolute ethanol, potassium chloride (KCl), ammonia, and DI water was used to synthesize anatase TiO_2 nanoparticles. This was accomplished by mixing TIP with ethanol, KCl, and HAD, then using a Millipore filter to collect the TiO_2 beads that had formed after keeping the mixture static for 18 hours. These beads were washed with ethanol, then mixed with varying amounts of ammonia and heated at 160 ^{o}C for 16 hours in a stainless-steel Teflon-lined autoclave. The resulting powders were heated to 500 ^{o}C for 2 hours in air to remove any remaining organic compounds. After observing the morphology of the synthesized TiO_2 beads with a SEM and XRD, Chen et al. determined the surface area of the particles to be 108 m^2/g, and the pore size of each bead was measured to be between 14 and 22.6 nm. After being tested in a DSSC, the solar cell achieved an efficiency of 7.2% [5]. A recently reported example of a solvothermal synthesis of anatase TiO_2 nanoparticles was performed by Li et al. In this experiment, hierarchical TiO_2 microstructures (HM-TiO_2) were mixed with dimethylformamide (DMF), acetic acid (HAc) and tributyltin (TBT). This mixture was heated in a stainless-steel autoclave 200 ^{o}C for 12 hours, centrifuged and washed with ethanol 3 times, then dried overnight at 60 ^{o}C. Li et al. observed the morphology of the resultant nanoparticles using a SEM and XRD. The TiO_2 nanoparticles were determined to be spherical with a size of 1 nm and to have needle-like subunits pointing radially outward. They were also observed to have a high crystallinity with a grain size of 50.3 nm. The nanoparticles were then tested in a DSSC, and Li et al. observed a light conversion efficiency of 9.79% [6].

The purpose of this research was to develop a low-temperature method for synthesizing anatase TiO_2 nanoparticles that are also semiconductors. A commonality between each of the methods of previous studies found in the literature is the use of a high-temperature reaction, which can be both expensive and dangerous. In addition, none of these methods have produced anatase TiO_2 nanoparticles that are also semiconductors. Semiconductor TiO_2 nanoparticles will yield a much higher electron transport efficiency when placed in a DSSC. This is because they will allow the solar cell to collect electrons released by the dye more effectively by reducing the recombination of the electrons. In order to accomplish this, a low-temperature hydrothermal reaction was used to synthesize TiO_2 semiconductor nanoparticles, and a freeze-dry apparatus was used to remove moisture from the particles. The benefit of using a low-temperature reaction is that the process is not only much safer but also much less expensive. Instead of using a stainless-steel autoclave to heat the reaction and produce powdered nanoparticles, the powdered nanoparticles are produced by freezing the product of the reaction with liquid nitrogen and then removing moisture via a vacuum dry-freeze apparatus. In the following we will present the outcome of our study.

2. EXPERIMENTAL

2.1 Synthesis of TiO_2 semiconductor nanoparticles

The TiO_2 semiconductor nanoparticles were synthesized using four different synthesis pathways in which we varied the reaction mixture composition. We have varied NaOH amount (in methods 2-4) to change the reaction rate of Ti(IV) polycondensation reactions. The NaOH concentration has been systematically changed in order to understand crystal growth of TiO_2.

Method 1: The Ti(IV) solution was created through a mixture of NaOH (2.984 g) / DMF (160 mL) / $TiCl_4$ (90.49 g) / H_2O (680 mL) at 40 ^oC, shown in Figure 1 below.

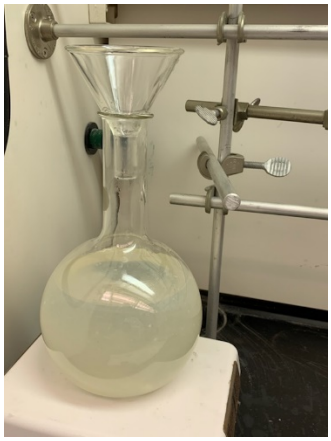


Figure 1: Ti(IV) solution is stirred in a 1 L volumetric flask.

First, 2.984 g NaOH was dissolved in 50 mL H_2O using a sonic bath. This solution was placed inside a 1 L volumetric flask. Next, 160 mL DMF was added to the solution and mixed using a magnetic stirrer. Then, 90.49 g $TiCl_4$ was mixed into the solution. Finally, 630 mL H_2O was added to the mixture. The reaction mixture was stirred at 40 ^oC for 4 days in a water bath, as shown in Figure 2 below.

Figure 2: The Ti(IV) solution is placed in a water bath at 40 ^{o}C for 4 days (left). The reaction results in the white, gelatinous TiO_2 being formed (right).

This resulted in a white, gelatinous TiO_2 substance being formed. In order to isolate the TiO_2 nanoparticles, all liquid needed to be removed. The gel was placed in a centrifugation container and centrifuged at 4000 rpm for 15 minutes. This resulted in the separation of the liquid from the TiO_2 gel, as shown in Figure 3.

Figure 3: The gel is centrifuged at 4000 rpm for 15 minutes (left). This results in most of the liquid being separated from the gel (right).

Most of liquid was discarded, and the gel was placed into three tubes and frozen with liquid nitrogen, as shown in Figure 4.

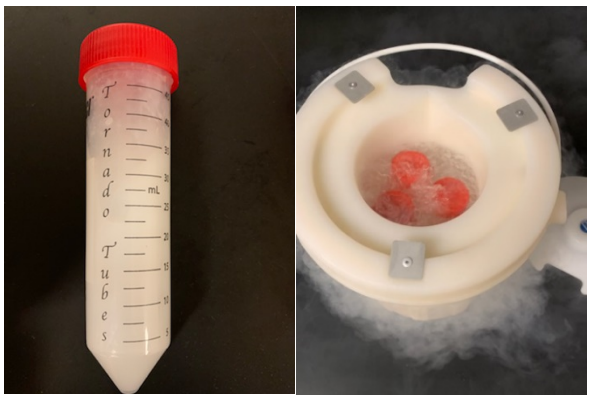


Figure 4: The TiO_2 gel is placed into tubes (left) and frozen in liquid nitrogen (right).

The caps of the tubes were removed, and the tubes were covered with a filter and placed in a jar (Figure 5 left), which was then placed in a vacuum freeze-dry apparatus at ~200 mTorr for 24 hours, as shown in the center of Figure 5. This process is used to remove any remaining moisture in the particles. This results in the TiO_2 becoming a white powder (Figure 5 on the right).

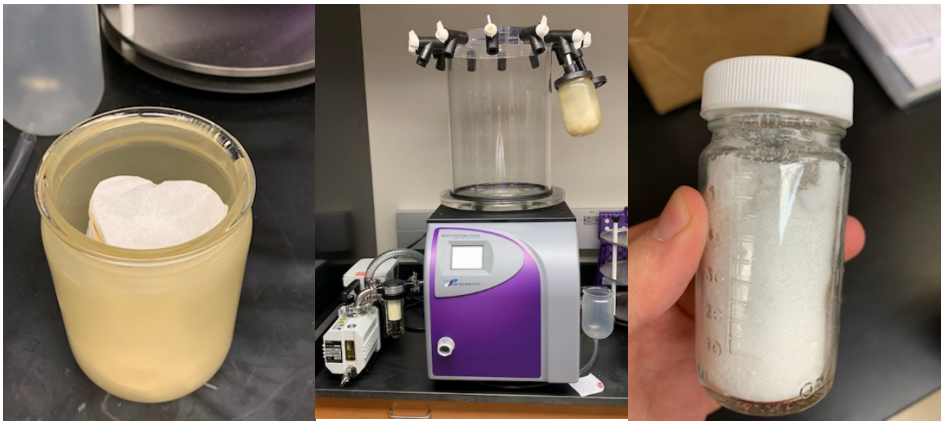


Figure 5: The frozen tubes were covered in a filter and placed into a jar (left), which is attached to a freeze-dry apparatus (center). After 24 hours at 200 mTorr, the TiO_2 nanocrystals have been obtained in powdered form (right).

Finally, in order to identify the characteristics of the TiO_2 semiconductor nanoparticles, they were observed under a transmission electron microscope.

Method 2: The same process described in Method 1 was followed with the exception being that double the amount of NaOH was used to create the Ti(IV) reaction mixture.

Method 3: The same process described in Method 1 was followed with the exception being that only half the amount of NaOH was used to create the Ti(IV) reaction mixture.

Method 4: The same process described in Method 1 was followed with the exception being that no NaOH was used to create the Ti(IV) reaction mixture.

2.2 Characterization of TiO_2 samples

The TiO_2 samples were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). These measurements were performed on Rigaku RINT Ultima/PC with monochromatic Cu Kα radiation and JEM-2100, respectively.

3. RESULTS AND DISCUSSION

In Method 2, after the 4 days of mixing and heating, the resultant mixture consisted of large chunks of white gel and a small amount of white liquid. The nanoparticles were observed to be Anatase from XRD pattern in Figure 6. The TEM measurement revealed that tiny nanoparticles with the dimensions of less than 5 nm were connected with each other (Figure 7). In Method 3, after the 4 days of mixing and heating, the resultant mixture consisted of small white chunks of gel and a white liquid. The nanoparticles that were prepared by reducing the NaOH amount resulted in the formation of low crystallization sample. The crystal phase could not be identified. TEM image showed that the TiO_2 samples had an aggregation of spherical nanoparticles with the size of ~ 5 nm (Figure 8).

Similar to the Method 3, the crystal phase could not be identified from XRD pattern for Methods 1 and 4 samples because of their low crystallinity. In method 1, the addition of the $TiCl_4$ produced a white gas and resulted in small solid particles being formed in the mixture. The resultant mixture after the 4 days of mixing and heating consisted of a white liquid and chunks of white gel. In Method 4 (non-NaOH), after the 4 days of mixing and heating, the resultant mixture consisted of very small white chunks of gel and a white liquid. These nanoparticles were observed to be aggregated structures as shown in the TEM images of Figure 9a and 9b.

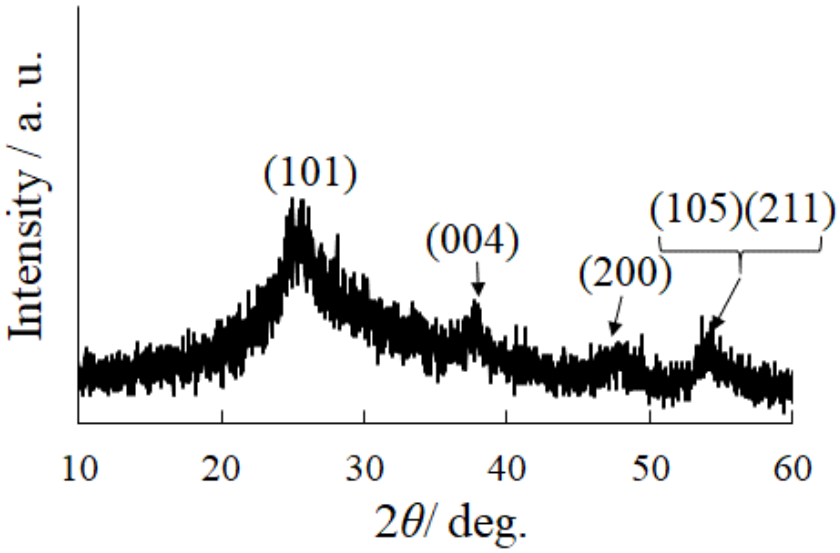


Figure 6: XRD pattern of Anatase TiO_2 particles prepared using Method 2. The sample was measured after freeze-drying process.

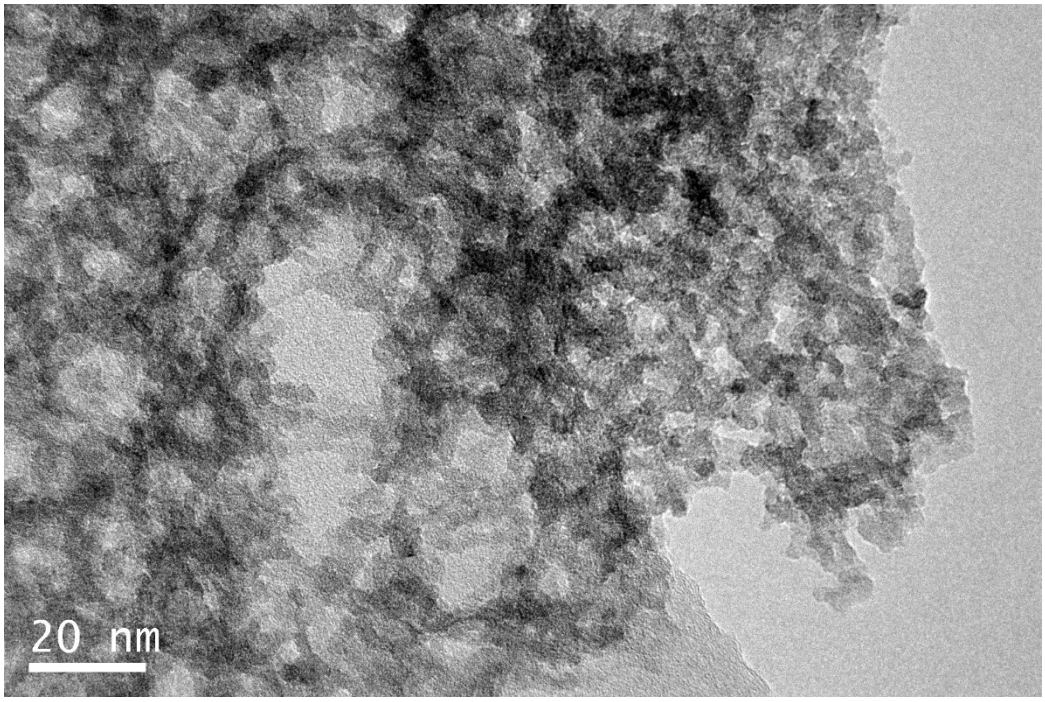


Figure 7: ATEM image of the TiO_2 particles after freeze-drying process prepared by Method 2.

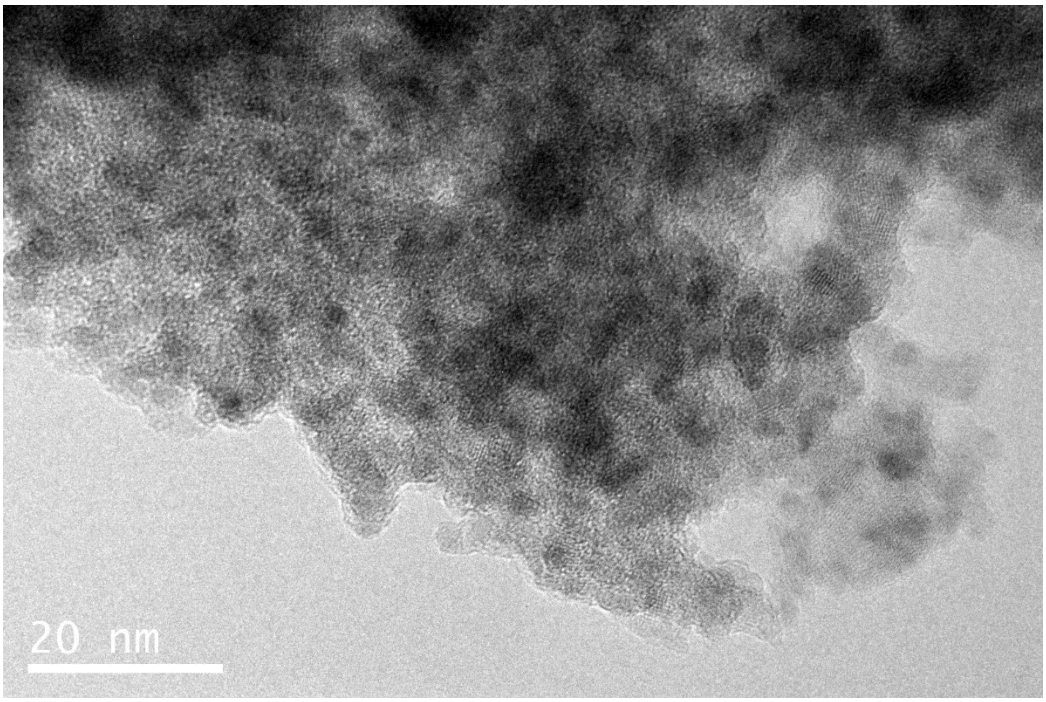
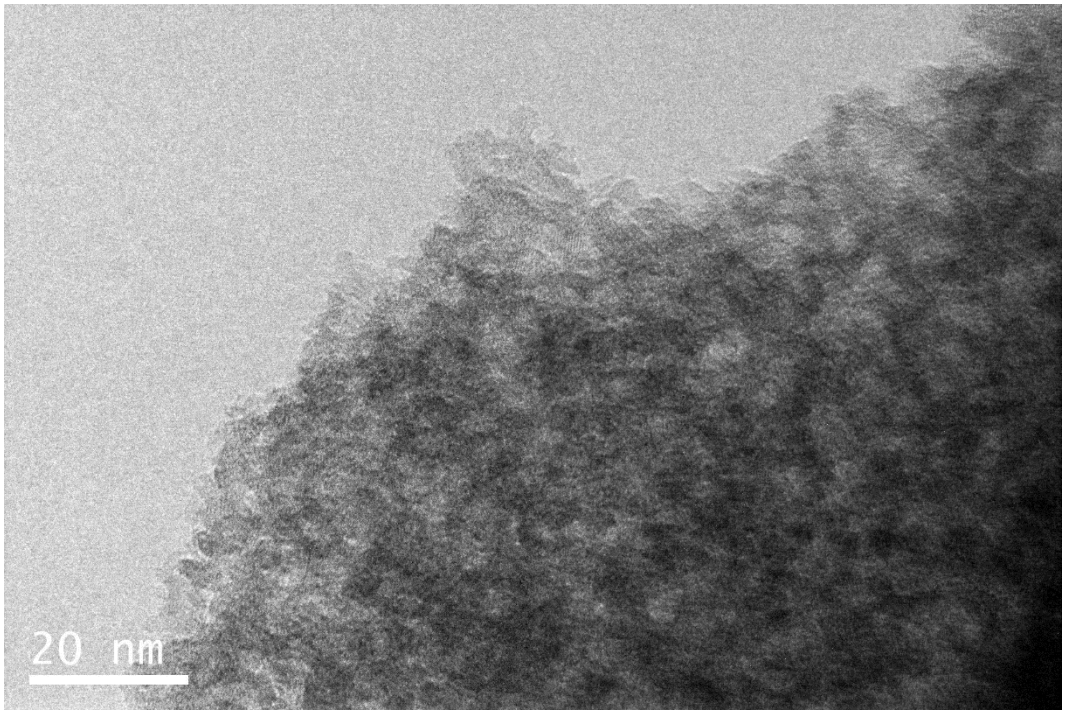


Figure 8: ATEM image of the TiO_2 particles after freeze-drying process prepared by Method 3.

(a)



(b)

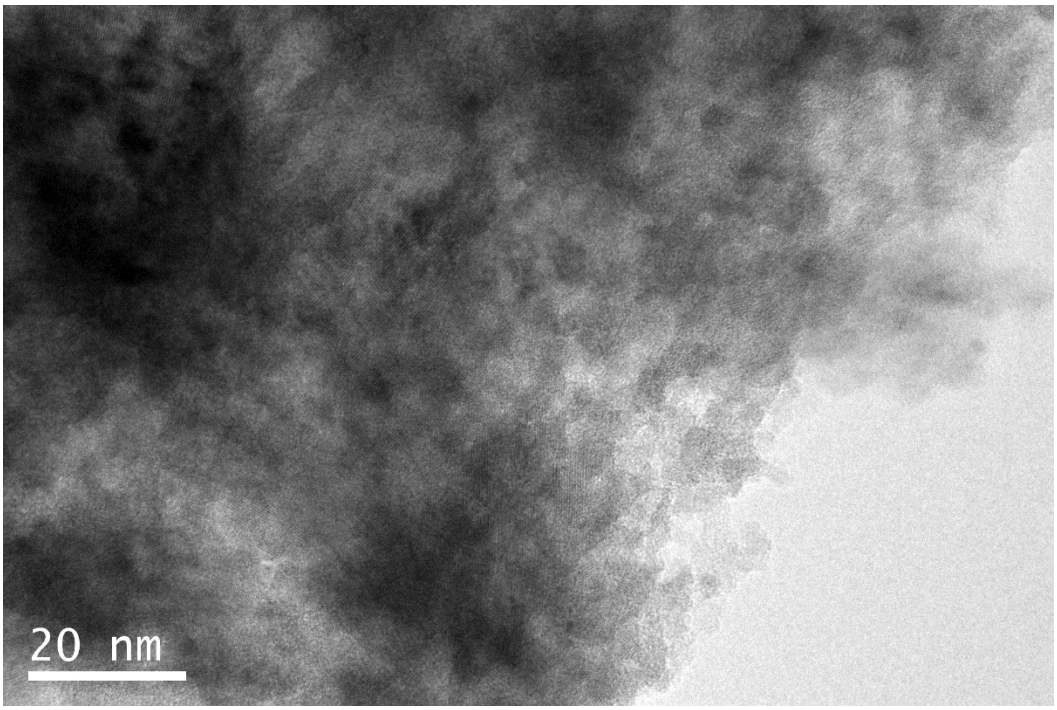


Figure 9: TEM images of the TiO_2 particles after freeze-drying process prepared by Method 1 (a) and Method 4 (b).

4. CONCLUSIONS

Our synthesis studies have shown that different morphologies of TiO_2 semiconductor nanoparticles can be synthesized using a low-temperature hydrothermal reaction consisting of titanium chloride ($TiCl_4$) as the titanium source in a solution of dimethylformamide (DMF) and a varied amount of sodium hydroxide (NaOH).

ACKNOWLEDGMENT

This work was supported by the Koshiyama Research Grant and JSPS KAKENHI Grant no. 15K05664 in Japan, Illinois Space Grant Consortium, USA., and Mund-Lagowski Department of Chemistry and Biochemistry at Bradley University.

REFERENCES

[1] Tański, T., Jarka, P., Szindler, M., Drygała, A., Matysiak, W., & Libera, M., "Study of dye sensitized solar cells photoelectrodes consisting of nanostructures", Applied Surface Science, 491, pp. 807–813, (2019).

[2] Chu, L., Qin, Z., Yang, J., & Li, X. A., "Anatase TiO2 Nanoparticles with Exposed {001} Facets for Efficient Dye-Sensitized Solar Cells", Scientific Reports, 5(1) (2015).

[3] Lee, S., Cho, I.-S., Lee, J. H., Kim, D. H., Kim, D. W., Kim, J. Y., Hong, K. S., "Two-Step Sol−Gel Method-Based TiO2 Nanoparticles with Uniform Morphology and Size for Efficient Photo-Energy Conversion Devices", Chemistry of Materials, 22(6), pp. 1958–1965, (2010).

[4] Qiu, Y., Chen, W., & Yang, S., Double-Layered Photoanodes from Variable-Size Anatase TiO2 Nanospindles: A Candidate for High-Efficiency Dye-Sensitized Solar Cells. Angewandte Chemie, 122(21), pp. 3757–3761, (2010).

[5] Chen, D., Huang, F., Cheng, Y.-B., & Caruso, R. A., "Mesoporous Anatase TiO2Beads with High Surface Areas and Controllable Pore Sizes: A Superior Candidate for High-Performance Dye-Sensitized Solar Cells", Advanced Materials, 21(21), pp. 2206–2210, (2009).

[6] Li, Z.-Q., Mo, L.-E., Chen, W.-C., Shi, X.-Q., Wang, N., Hu, L.-H., Dai, S.-Y., "Solvothermal Synthesis of Hierarchical TiO2 Microstructures with High Crystallinity and Superior Light Scattering for High-Performance Dye-Sensitized Solar Cells", ACS Applied Materials & Interfaces, 9(37), pp. 32026–32033, (2017).