ASTFE American Society of Thermal and Fluids Engineers

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

TFEC-2020-33117

Nanofluid Boiling and Sintering for Dye-Sensitized and Perovskite Solar Cell Application

Robert Svidron[1], Bryan Olefsky[1], Blen Teferi[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

TiO_2 nanoparticles are often used in the production of Dye-Sensitized and Perovskite solar cells due to their unique properties. These nanoparticles come in differing phases and morphologies. The purpose of this research is to apply nanofluid boiling method to deposit TiO_2 nanoparticles on FTO substrate and then investigate the effects of ramping rate and maximum temperature on characteristics of deposited nanoparticles on FTO substrate. It was observed that thickness of deposited nanoparticles depends on boiling time and concentration of nanofluid. The thickness of deposited nanoparticles changed linearly with nanofluid concentration and boiling period. Furthermore, the effects of different sintering strategies were investigated. The results indicated that the characteristics of a sintered sample is dependent on sintering strategies. As ramping rate decreased, the deposited nanoparticles fused and become more organized. Similar, effects were observed as maximum temperature increased from 150 ℃ to 550 ℃.

KEY WORDS: Sintering, TiO_2 nanoparticles, Deposition, Porosity, Ramping Rate

1. INTRODUCTION

Renewable energy is becoming one of the most sought-after methods of energy production of the modern age. The need for reliable, cleaner forms of energy is due, not only to the increase in energy production needs as the world population grows, but also as a result of the increasing information on how our fossil fuel energy consumption affects earth's climate. Of the many clean energy options available, solar energy is one of the most desirable. This is partially because of the wide variety of applications it can service. Sunlight is an abundant resource and has the ability to provide people all over the world with a clean and renewable energy source. Technological advances in the solar energy field have yielded substantial improvements in the collection and storage of renewable energy [1].

One of the most promising new developments in this field is the perovskite and dye-sensitized solar cells (DSSC). One of the reasons they are becoming so popular is the high conversion efficiency that they provide which places them in an elite category of very high performing clean energy solutions. TiO_2 is used as an electron transport material in the production due to its wide bandgap, and chemical and mechanical stability [1]. The two phases of interest of TiO_2 are the rutile phase and the anatase phase. These two phases of TiO_2 have unique crystalline properties that make them suitable for differing applications [2]. Overall, the rutile phase is commonly seen as the more favorable phase,

*Corresponding Author: svafaei@fsmail.bradley.edu

although there is still some debate about this in the scientific community. Rutile is often favored due to its ability to scatter light more effectively and lower cost for synthesis.

The photocatalytic activity of TiO_2 is not only limited to its phase, but also dependent on several other characteristics of TiO_2 that influence its suitability for energy applications such as its nanoparticular shapes. The shapes of the nanostructures are very important when considering the nanoparticles for use in solar cell applications. TiO_2 nanostructures take on shapes such as spheres, nanotubes, branched rods, and sheets. The form of the nanostructure is very important when considering the nanoparticles for use in solar cell applications. The shape of the nanostructure has a great deal to do with the photocatalytic properties of the material. TiO_2 particles that exhibit nanostructures with large surface areas are of particular interest as this will increase the light scattering properties of the material [3]. Furthermore, a larger surface area means that there is more space for dye absorption which is directly related to the efficiency of the DSSC. Achieving the synthesis of favorable nanostructures is paramount to the continued effort to push the power conversion efficiency of both perovskite solar cells and DSSCs forward [3,4].

In order to push the line of science forward and achieve maximum power conversion efficiency, a number of factors need to be considered. Characteristics such as interfacing quality, improved light scattering effects, higher overall surface area, and faster electron transport are of the utmost importance [5]. These factors are being studied extensively in laboratory settings where TiO_2 particles are being synthesized. Through various synthesis methods, scientists are controlling the factors that are known the affect each of the important qualities of an efficient TiO_2 nanoparticle. Because TiO_2 nanoparticles are largely believed to be the limiting factor for maximum power conversion efficiency, laboratory research in this area is extremely important for the green energy industry.

There are a variety of methodologies for the synthesis of TiO_2 nanoparticles, but there are three major methods that yield consistent results. These methods are the hydrothermal, solvothermal, and sol-gel methods. Hydrothermal methods use high pressure and temperature to control crystal growth in water. The growth morphology of the crystal structures can be regulated with this methodology. There are small variations that can be done in this process such as altering the reaction temperature or pressure in order to achieve differing results. Most hydrothermal methods are performed in the temperature range between 150 ℃ [6] and 220 ℃ [7]. Solvothermal methods are similar to hydrothermal methods, in the fact that they also use high temperatures and pressures. The solvent does not have to be water and the temperature is raised above the boiling point of the solvent at high pressures. Some solvothermal methods utilize an autoclave for thermal treatment as well. In comparison, sol-gel methods are more involved than either the hydrothermal or solvothermal methodologies previously mentioned. Sol-gel is a wet chemical method that includes hydrolysis, aging, drying, and densification in order to achieve crystallization [8]. An example of this method being used involved mixing titanium tetrachloride with ethanol and deionized water (DI) water. This mixing was done over the course of 24 hours. A portion of the resulting mixture was transferred to an autoclave where the pH was altered. Ammonium fluoride was added to the mixture in the autoclave and stirred while increasing the temperature inside the autoclave. This was done over the course of 24 hours upon which the mixture was allowed to cool, then filtered and annealing before the final product was obtained [9].

The standard methods used to analyse the morphology of TiO_2 nanoparticles is through XRD, TEM and SEM technologies, allowing the observation of important characteristics such as the phase of the TiO_2 nanoparticles (rutile or anatase), the shape of the nanostructure, and the overall surface area. In

the final step, the nanoparticles were used to test solar cell efficiency. In order to continue increasing the efficiency of solar cells, more research is needed in the area of TiO_2 nanoparticles and the process that integrates these nanoparticles into the devices.

2. EXPERIMENTAL METHODOLOGY

2.1 Boiling Device

In this research, nanofluid boiling method was used to deposit nanoparticles on fluorine-doped tin oxide (FTO) coated glass. A boiling device was designed and built for use in the deposition of rutile TiO_2 particles. This device served two main purposes. First, the device held a piece of FTO conductive glass in place so that deposition could occur during the boiling process. Second, the boiling device allowed for the nanofluid used in this experiment to be placed directly on top of the glass during boiling so that nanoparticles could deposit onto the conductive surface of the glass. The boiling device consists of three parts: the base, the insert, and the top piece. The configuration of these pieces is shown in Figure 1 below.

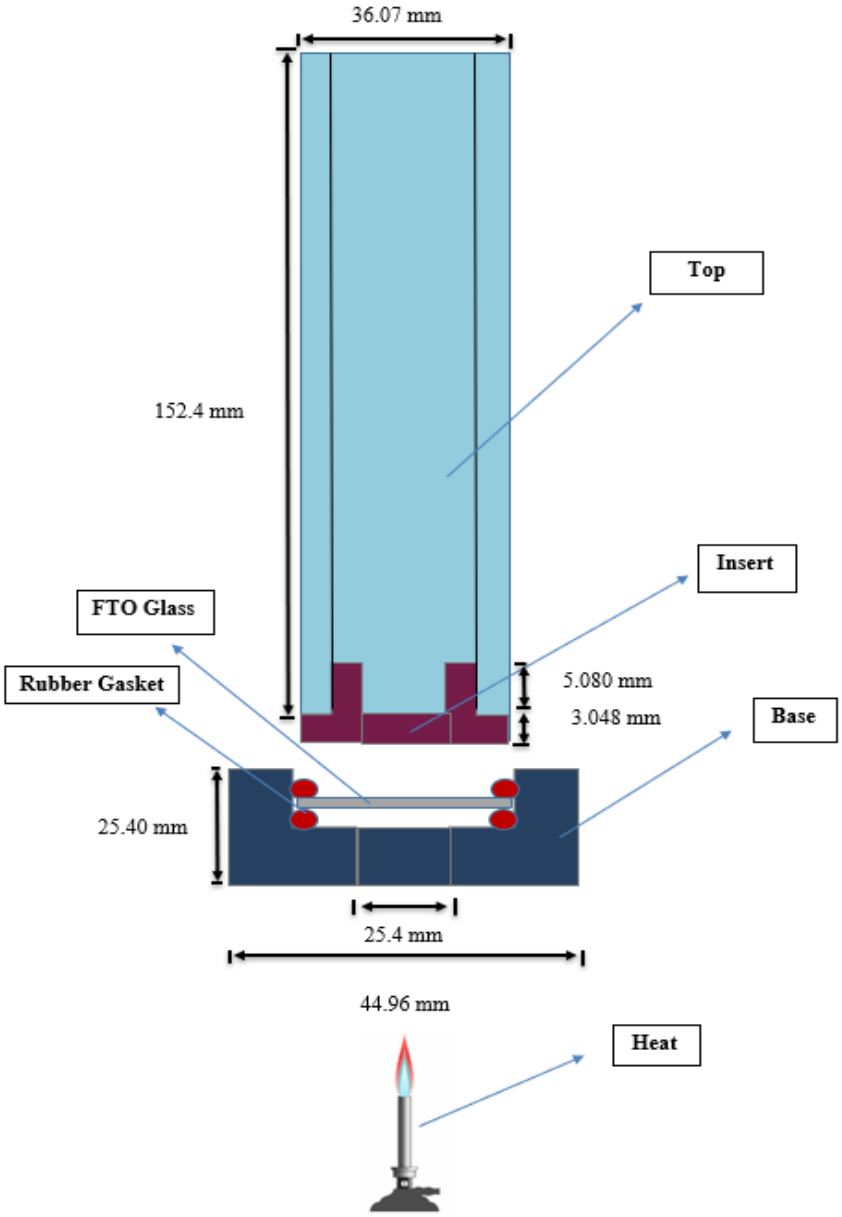

Fig. 1 Boiling Device Schematic with Dimensions

The FTO glass was inserted in between two rubber gaskets which protected the glass piece that rested in the base of the device. The insert was used to ensure the FTO glass had a smooth, flat contact with the top of the device. This minimized the stresses that the glass experienced during thermal expansion. Previous versions of the device experienced problems with glass breakage during the boiling process. The insert piece was created to mitigate this problem.

2.2 Preparation of the Nanofluid

The nanofluid solution used for deposition was prepared by mixing (5-minute mixing with a magnetic stirrer) nanofluid with ethanol to obtain a specific mass. The proper concentration of the nanofluid was determined through a series of trial runs. For this study, the following nanofluid concentrations were prepared: 0.0002%, 0.0004%, 0.0006%, and 0.0008%.

2.3 Deposition

A piece of FTO glass was washed with DI water and acetone and placed into the boiling device between two rubber gaskets. A multimeter was used to ensure that the conductive side of the FTO glass was facing up. The device was first filled with ethanol to check for leaking. If no leaking occurred, the ethanol was discarded and the prepared nanofluid was transferred to the boiling device. The boiling device was then placed onto a stand which suspended it 50 mm above a Bunsen burner set to a very low flame. This set up is shown in Figure 2 below.

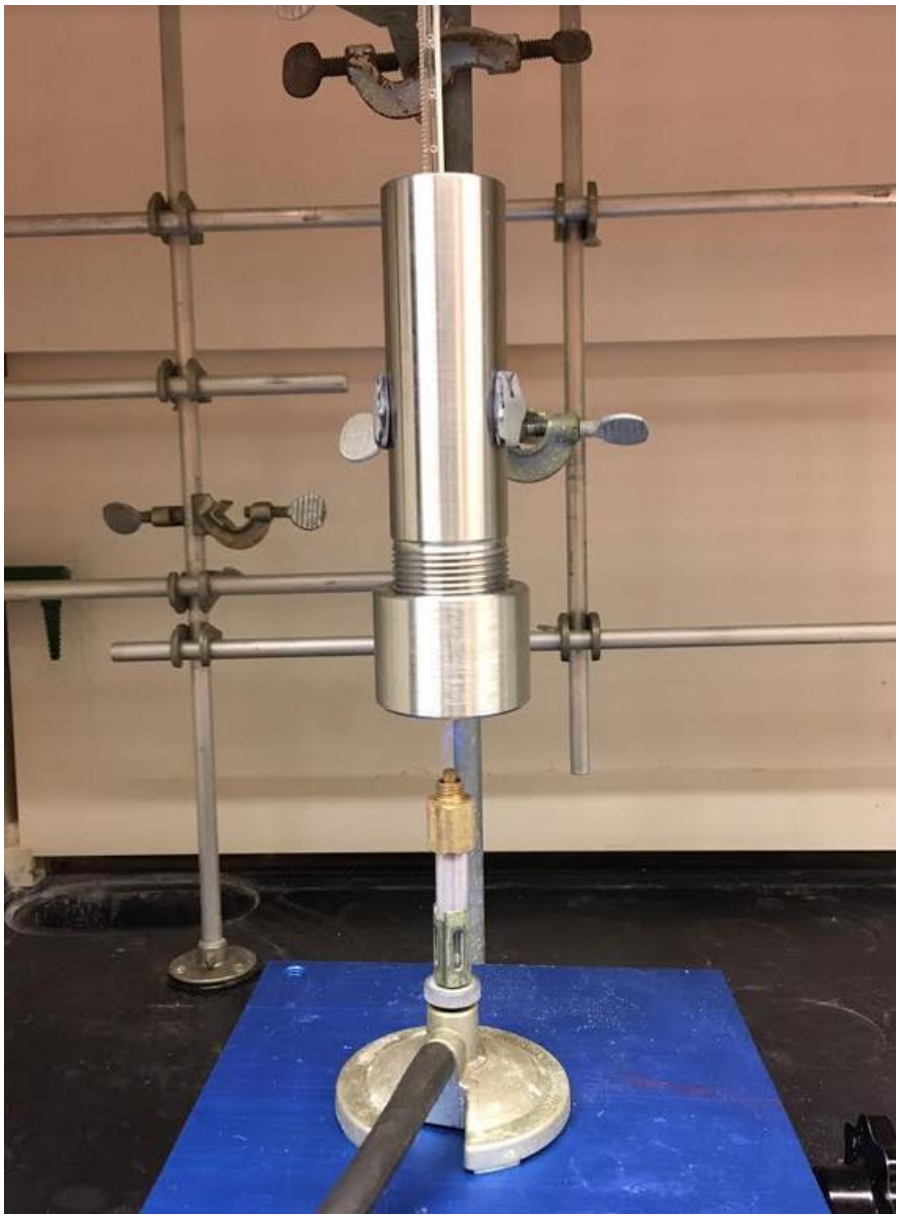

Fig.2 Boiling device setup for deposition

The temperature was monitored until boiling occurred. Once boiling began, a timer was set for a predetermined amount of time. Times varied depending on the trial. Once the time expired, the device was removed from the flame and the FTO glass was removed from the device. A scanning electron microscope (SEM) was used to analyse the results. In particular, the thickness of the deposition was measured as a function of concentration of the nanofluid and as a function of boiling time. Figure 3 below shows an image captured using the SEM. The thickness of the deposit is shown as well as the scale used.

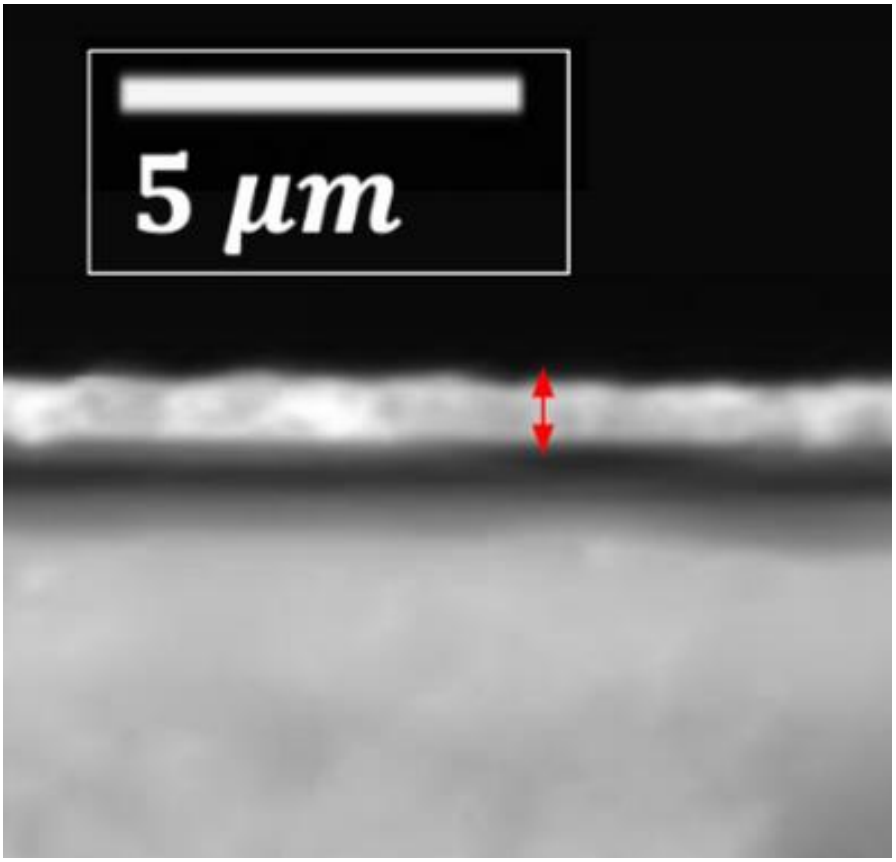

Fig.3 SEM photo showing the deposition layer on the FTO glass.

2.4 Sintering Strategies

A KDF 007-Plus Burn Out Furnace, pictured in Figure 4 below, was used for sintering the samples created during deposition. Three factors were explored in the sintering process. The effects of changing ramping rate, maximum temperature, and hold time were varied independently while holding each of the other factors constant. A SEM was used to analyze the results of each sintering strategy.

Fig.4 KDF 007-Plus Burn Out Furnace used for sintering.

The samples used for sintering were created using a 0.0006% nanofluid concentration boiled for 10 minutes each in the boiling device pictured in Figure 1. Each of the samples was placed in the oven individually so that no contamination between samples could occur. The first run varied ramping rate while holding the maximum temperature constant at 550 ℃ and the hold time at 30 minutes. The ramping rates used were 1 ℃ per minute, 2 ℃ per minute, 5 ℃ per minutes, 10 ℃ per minute, and 20 ℃ per minute. The second run varied maximum temperature while holding the ramping rate constant at 1 ℃ per minute and the hold time at 30 minutes. The variation in maximum temperature was as follows: 550 ℃, 450 ℃, 350 ℃, and 150 ℃. The results of these trials were evaluated using an SEM.

3. RESULTS AND DISCUSSION

3.1 Relationship between Concentration and Deposit Thickness

The results of the deposition trials where concentration was varied with constant time were analyzed using an SEM. Figure 5 shows the results of these trials.

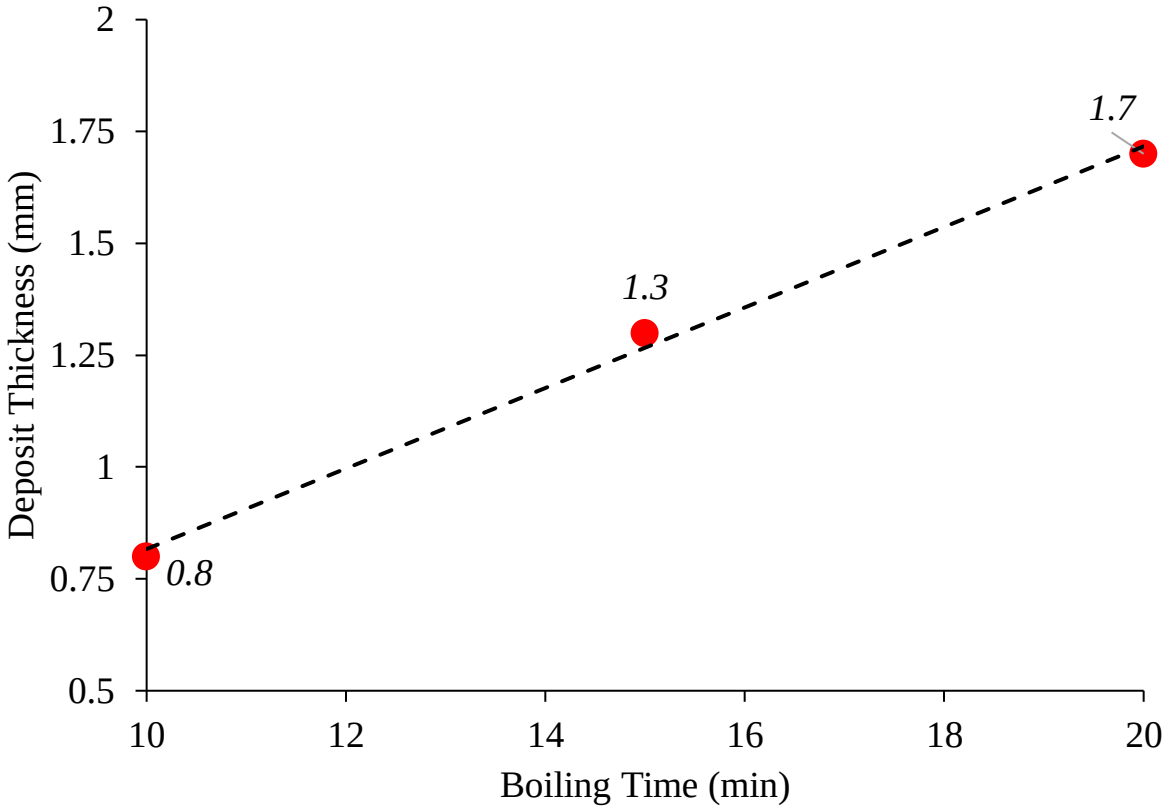

Fig.5 The relationship between deposit thickness and nanofluid concentration

The concentration and deposit thickness show a strong linear relationship as evidenced by the 0.9938 coefficient of determination. As the concentration of the nanofluid increased, so did the thickness of the deposit.

3.2 Relationship between Time and Deposit Thickness

The results of the deposition trials where boiling time was varied with constant concentration are shown in Figure 6 below.

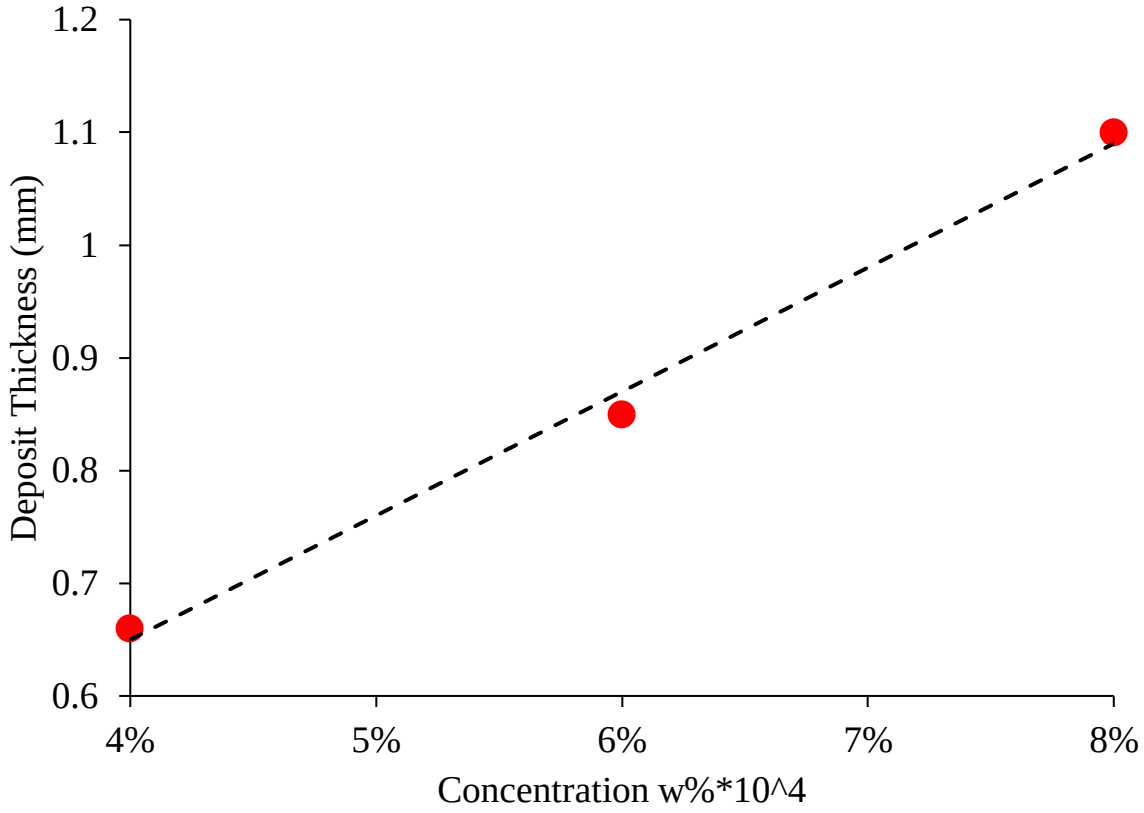

Fig.6 Deposit thickness plotted as a function of boiling time

Once again, the relationship is shown to be a strong linear relationship, with a 0.9959 coefficient of determination. As the boiling time increased, so did the thickness of the deposit.

3.3 Sintering Analysis

The effects of varying ramping rate and maximum temperature are still not well documented in the relevant literature. The goal of this analysis is to better understand how varying each of these parameters affects the overall quality of the deposited samples. These parameters were varied one at a time while holding all of the others constant. The results of the SEM analysis of the sintering samples show that changing the sintering strategy has a noticeable effect on the quality of the sample. The analysis found that slower ramping rates yield the best porosity. This can be seen in the images displayed in Figure 7 below.

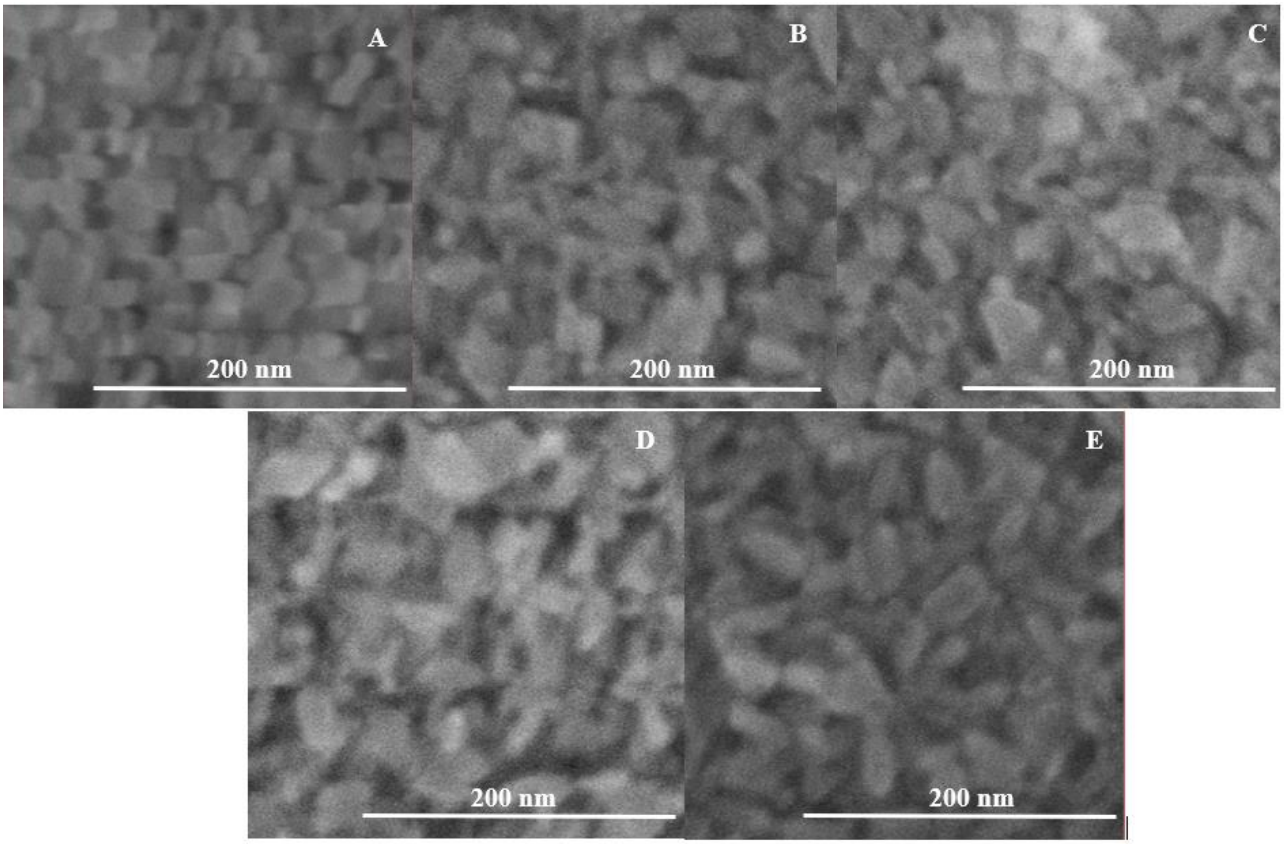

Fig.7 SEM images of sintering samples where ramping rate was varied. Ramping rates for A through E were 1 ℃/minute, 5 ℃/minute, 10 ℃/minute, 20 ℃/minute, and no sintering respectively.

The uniformity of the TiO_2 nanoparticle film shown in image A is better than that of images B through E. This is believed to be because a slower ramping rate yields more time for crystal growth to occur. The samples that experienced faster ramping rates such as sample D display lots of conglomeration and fusion of the nanoparticles. It is believed that as the ramping rate is decreased, the fused particles break down into smaller, more organized sections.

In Figure 8 below, the maximum temperature was varied while the ramping rate and hold time were kept constant. The samples in images A through D were subjected to maximum temperatures of 550 ℃, 450 ℃, 350 ℃ and 150 ℃ respectively, while image E is included as the datum where no sintering was performed on the sample. The quality of the uniformity of the films goes up as the maximum temperature increases. Image A has a smooth, porous texture, while images C and D have noticeably large clumps of material with less visibly evident porosity. The samples that are most conducive to solar cell applications are those that were sintered at 550 ℃ and 450 ℃, as they exhibit permeable layers of TiO_2 nanoparticles. The effects that higher maximum temperature had on the samples are similar to those observed at slower ramping rates. The particles appear much more organized and less conglomerated at higher sintering temperatures.

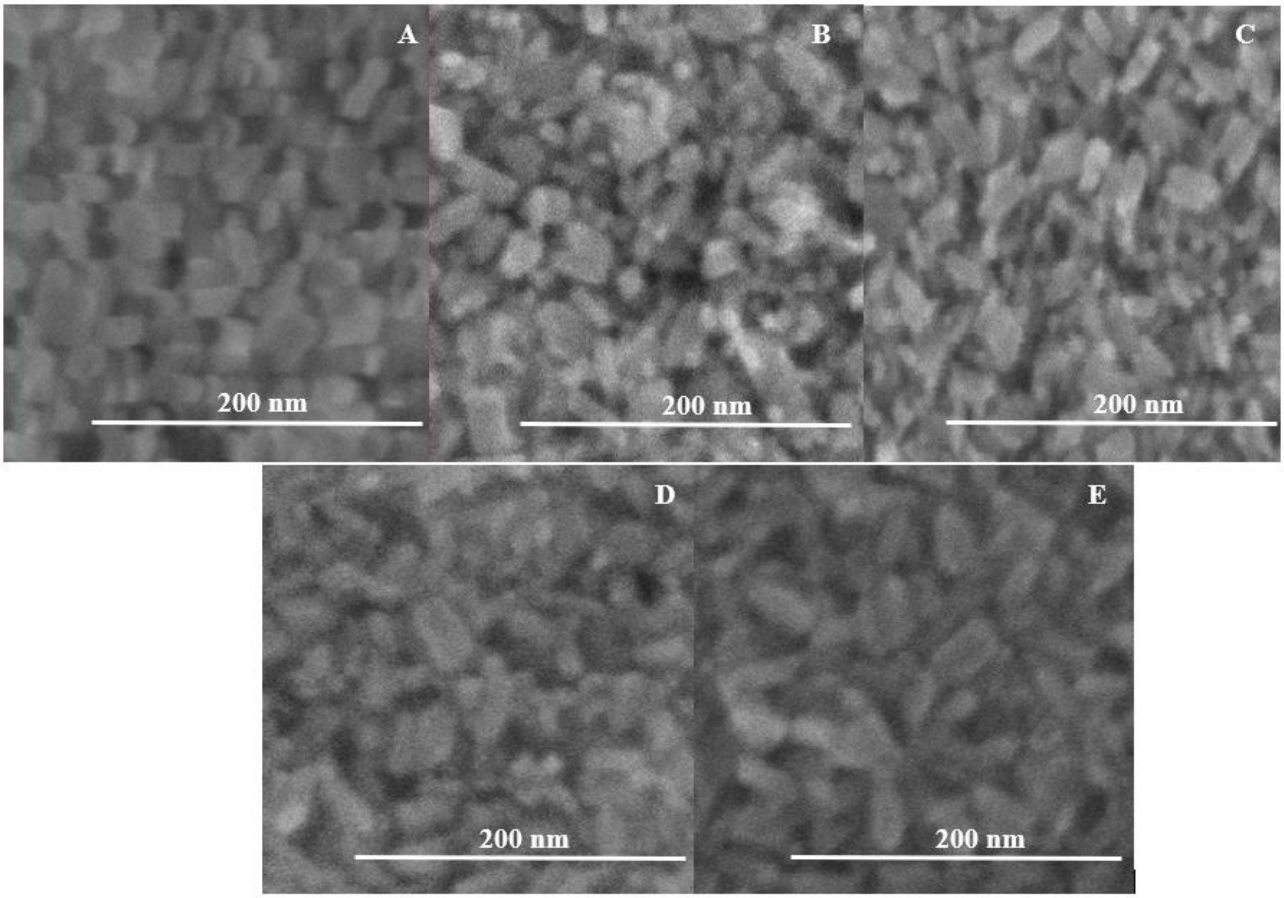

Fig.8 SEM images of sintering samples where maximum temperature were varied. Maximum temperature for samples A through E were 550 ℃, 450 ℃, 350 ℃, 150 ℃, and no sintering respectively.

4. CONCLUSIONS

Deposition and sintering strategies for TiO_2 nanoparticles were investigated in this research. It was observed that there is a linear relationship between the overall thickness of the TiO_2 deposition and the boiling time and concentration of the nanofluid. This shows that in order to increase the quality of a deposited sample, longer boiling periods or higher concentrations of nanofluid should be considered. In the analysis of the various sintering strategies used, sample data collected from an SEM was used to determine the quality of the samples. The uniformity of the TiO_2 nanoparticle films was improved with decreasing ramping rate and increasing maximum temperature. Research in these areas is on-going for the team with the goal of continuing to increase the efficiency of solar cells in the future.

REFERENCES

[1] Ramakrishnan, V.M., Natarajan, M., Santhanam, A., Asokan V., Velauthapillai, D., "Size Controlled Synthesis of TiO2 Nanoparticles by Modified Solvothermal Method towards Effective Photo Catalytic and Photovoltaic Applications." *Materials Research Bulletin*, vol. 97, 2018, pp. 351–360., (2017).

[2] Chen, H., Su, C., Chen, J., Yang, T., Hsu, N., Li, W., "Preparation and Characterization of Pure Rutile TiO2Nanoparticles for Photocatalytic Study and Thin Films for Dye-Sensitized Solar Cells." *Journal of Nanomaterials*, vol. 2011, pp. 1–8, (2011).

[3] Zhang, J., Zhou, P., Liu J., Yu, J., "New Understanding of the Difference of Photocatalytic Activity among Anatase, Rutile and Brookite TiO2." *Phys. Chem. Chem. Phys*., vol. 16, no. 38, pp. 20382–20386, (2014).

[4] Jena, A.-K., Kulkarni. A, Miyasaka, T., "Halide Perovskite Photovoltaics: Background, Status, and Future Prospects", *Chem. Rev.*, 119(5), pp. 3036-3103, (2019).

[5] Ahn, Y.A., Cheon, H.K., Kim, W.D., Kang, Y.J., Kim, J.M., Lee, D.W., Cho, C.Y., Hwang, Y.H., Park, H., Kang, J., Kim, S.H., "Aero-Sol–Gel Synthesis and Photovoltaic Properties of Mesoporous TiO2 Nanoparticles." *Chemical Engineering Journal*, vol. 188, pp. 216–221, (2012).

[6] Sofyan, N., Ridhova, A., Yuwono, A.H., Udhiarto, A., Fergus, J.W., "Synthesis of TiO2 Nanoparticles at Low Hydrothermal Temperature and Its Performance for DSSC Sensitized Using Natural Dye Extracted from Melastoma Malabathricum L. Seeds." *International Journal of Energy Research*, vol. 43, no. 11, pp. 5959–5968, (2019).

[7] Chen, H., Su, C., Chen, J., Yang, T., Hsu, N., Li, W., "Preparation and Characterization of Pure Rutile TiO2Nanoparticles for Photocatalytic Study and Thin Films for Dye-Sensitized Solar Cells." *Journal of Nanomaterials*, vol. 2011, pp. 1–8., (2011).

[8] Nunes, D., Pimentel, A., Santos, L., Barquinha, P., Pereira, L., Fortunato, E., Martins, R., "Synthesis, Design, and Morphology of Metal Oxide Nanostructures." *Metal Oxide Nanostructures*, pp. 21–57., (2019)

[9] He, J., Du, Y., Bai, Y., An, J., Cai, X., Chen, Y., Wang, W., Yang, X., Feng, Q., "Facile Formation of Anatase/Rutile TiO2 Nanocomposites with Enhanced Photocatalytic Activity." *Molecules*, vol. 24, no. 16, p. 2996., (2019)