

Growth Control of SnO₂ Nanoparticles Using a Low-Temperature Solution Process

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ABSTRACT

Perovskite solar cells, specifically using SnO₂ nanoparticles, have been extensively researched and are proving to be extremely promising in the field of renewable energy by increasing a solar cell's overall efficiency and lowering the cost of production. In this study, an experiment was performed to synthesize SnO₂ nanoparticles over 8 days. Day 1 was the synthesis which included the mixing of water, tin (II) chloride, methanol, sodium carbonate and dimethylformamide and then heated in a water bath at 28°C. Sampling of this solution started on day 4 of the experiment when sufficient particle growth was observed and stopped at day 8. Centrifuging, freezing, and freeze-drying were used for each sample to isolate the solid product. Transmission electron microscopy and X-ray powder diffraction was used to characterize the isolated nanoparticle. The results from the X-ray powder diffraction showed that each sample consisted of SnO₂ nanoparticles of different sizes. From the transmission electron microscopy on the samples showed that the overall size of the nanoparticles gradually increased during each additional synthesis day.

KEY WORDS: SnO₂, Nanoparticles, Freeze-Drying, Solar cells

1. INTRODUCTION

The ever increasing worldwide need for energy and environmental problems caused by fossil fuel use spawned an urging need for clean energy. This has led to a rapid hike in the development of renewable energy sources with solar power being one of the major candidates due to the sun being able to provide the ultimate solution to the challenge of sustainable energy supply. Generally, in a solar cell, electrons are released when the solar cell is hit by light; the electrons are then collected by the solar cell. There two common methods to generate solar power via solar cells and passive/active solar thermal systems. Focusing on the solar cells for electric power generation, there are different ways to harvest the solar energy of which the conventional solid-state solar panels are the most common. The cons of these silicon based solar panels are their production costs and their negative environmental impact. In recent years, different variations of solar cells have emerged promising low production costs and low environmental impact and of high efficiency such as perovskite solar cells (PSC) and dye-sensitized solar cells (DSSC). In these types of solar cells, one of the photo electrodes is composed of nano-crystalline material such as TiO₂ and/or SnO₂, forming the semiconductor layer for the photon-electron transfer process. The nano-crystalline material is placed on a transparent conducting glass in order to achieve a high specific surface area. This surface area is essential for the absorption of dye molecules or perovskite film which in turn plays a significant role in the amount of light that can be harvested by the solar cell [1]. Specifically, for the design of a DSSC a mesoporous layer is formed when the nanostructure of the DSSC is filled with dye [2], in which the dye acts as photon absorber and the nanostructure as electrons

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transmitter. The arrangement of the nanostructure and the electron transport efficiency are both components that are considered when improving the overall efficiency of the devices. The nanostructure arrangement and electron transport efficiency are key elements that require optimization to balance increased surface area for dye absorption with a decrease in transport efficiency. In PSC, the perovskite layer acts as a light absorber.

Recently, another metal oxide, tin(IV) oxide (SnO_2) has been explored as potential photo anodic material as an alternative to TiO_2 . SnO_2 has been well studied for example in connection with perovskite solar cells (PSCs) mostly due to its favorable attributes such as high electron mobility $\sim 100\text{--}200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) and wide bandgap of 3.6 eV compared to 3.2 eV for TiO_2 . The high mobility promotes faster transport of photo injected electrons and thereby reducing the recombination probability of photo induced electrons. In addition, SnO_2 forms a homo junction with the FTO substrate and thus resolves the high contact resistance issue as observed in heterojunctions formed with other oxides like TiO_2 . Despite the apparent advantages over TiO_2 there are some concerns using SnO_2 as electron transport layer and the main concern is that it suffers from degradation at higher temperature processes. Much research has been done to show that the efficiency of solar cells can be increased further using SnO_2 rather than TiO_2 .

Of particular importance is to understand the relationship between SnO_2 structures and PSC performance. Synthesis of SnO_2 is thus one of the crucial issues in the development of high efficiency PSC. There are many different synthesis methods described in the literature how to obtain nanoparticles of which three are commonly used: hydrothermal, solvothermal, and sol-gel methods. In the hydrothermal synthesis an autoclave is used to heat an aqueous reaction mixture at high pressures. In general, temperature, pressure, and reaction time are variables used to control the growth of the nanoparticles. Specifically, it allows the synthesis of exact size and shape distributions. The solvothermal method is analog to the hydrothermal method except that they are carried out in non-aqueous media. The disadvantage of these two methods is the high temperature and pressure, and the high cost of the autoclave to run at temperatures and pressures of up to 300°C and 10 bar, respectively [3,4]. The sol-gel method (chemical solution deposition) avoids the previously mentioned disadvantages and is a well-established synthetic approach for the preparation of metal oxides. In general, this process involves several steps: hydrolysis (metal precursor) and condensation, formation of 3D-gels, aging/growth, drying, densification, and crystallization. The sol-gel method can be carried out in aqueous and non-aqueous media. The disadvantages of the sol-gel method can be the cost of the raw-materials, such as metal-alkoxides precursors, and the annealing process to eliminate the organics from the oxide.

There have been a series of recent publication in the literature using SnO_2 in the production of PSCs. Yang et al. [5] investigated the efficiency using an EDTA-complexed SnO_2 (E- SnO_2) by mixing ethylenediaminetetraacetic acid (EDTA) with deionized water (DI) in the PSC. To characterize the E- SnO_2 , Yang et al. used X-ray photoelectron spectra (XPS) and atomic force microscopy (AFM). With XPS, the particles were studied after deposition on the quartz substrates. An AMF of the E- SnO_2 films showed that they had a root-mean-square roughness of 2.88 nm. For SnO_2 the electron mobility was found to be $9.92 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, $3.56 \times 10^{-5}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for EDTA, and $2.27 \times 10^{-3}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for E- SnO_2 . Overall they found that the tested PSCs had an efficiency of 16.4% - 21.6% depending on the construction of the PSC. Liu et al. [6] studied the effects of SnO_2 in perovskite solar cells (PSC) using a SnO_2 colloidal dispersion solution in water (68 %wt) instead of the organic metallic E- SnO_2 complex. Analysis of their PSC via XRD showed that their sample had large grains, good crystallinity, and reduced grain boundaries. Their PSC's efficiency ranged from 20 % to 21.3 % when compared to bare SnO_2 . A study done by Yi et al. [7] showed another example of SnO_2 being used in solar cells, with three PSCs prepared and compared: sol-gel SnO_2 (S- SnO_2), nano- SnO_2 (N- SnO_2), and bilayer SnO_2 (B- SnO_2) which included one layer of S- SnO_2 and one layer of N- SnO_2 . A gas quenching method was used on all their PSCs. The results from this experiment determined that the optimum S- SnO_2 PSC was 0.15 M with a thickness of 35 nm; the observed perovskite cell efficiency (PCE) was 12.97 % with a fill factor (FF) of 57.6 % and an average visible transmittance (AVT) of 83.47 %. The optimum N- SnO_2 PSC was 1 % w/v with a thickness of 15 nm that produced PCE of 14.05 % with an FF of 61.44 % and AVT of 84.57 %. In the end, the better option was the bilayer- SnO_2 PSC that was optimized at 0.15 M, 35 nm thickness S- SnO_2 and 1 % w/v, 15 nm thickness N- SnO_2 that increased PCE from 12.97 % to 16.84 % with a FF of 71.25 % and AVT of 83.51 %. In the B- SnO_2 PSC the nanoparticles filled the pin holes of the sol-gel layer and produced better crystallinity and less dislocation. It also produced higher electron mobility and a

lower electron trap density. Lastly, in the experiment performed by Xie et al. [8] consisted of using a precursor solution to developing a $\text{TiO}_2\text{-SnO}_2$ bilayer PSC. To analyze the SnO_2 nanoparticles, TEM and XRD were used. It was found that the nanoparticles size ranged from 3 to 5 nm with a lattice fringe interplane d spacing of 343 nm. The grain size stretched from 3 to 6 nm. The PCE of the SnO_2 PSC was found to be 15.29 %, while it was 12.07 % for TiO_2 and 17.19 % for $\text{TiO}_2\text{-SnO}_2$, meaning the $\text{TiO}_2\text{-SnO}_2$ PSC was the most efficient.

The motivation for this research was to develop a method of low temperature synthesis for SnO_2 and to determine the optimum reaction time (growth time) for the formation of SnO_2 nanoparticles for the use in PSCs. In addition, we used a freeze-dry method to remove the excess solvent from the solid nanoparticles. In the following sections the synthesis strategies used as well as the results of the study are presented.

2. EXPERIMENTAL

In the previously mentioned studies, SnO_2 was developed using EDTA by Yang et al. and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ by Yi et al. In this experiment, the SnO_2 particles were synthesized using ultra-pure water (UP-water), methanol, tin (II) chloride (SnCl_2), sodium carbonate (Na_2CO_3), and dimethyl formamide (DMF). First 300 mL UP-water and 300 mL methanol were mixed in a 1000 mL glass beaker then 6g of SnCl_2 were added and dissolved. Secondly, 6g of Na_2CO_3 were dissolved separately from the previous mixture in a beaker of UP-water (300 mL) using a sonic bath. DMF was then carefully added to the Na_2CO_3 solution under a hood. This solution was then slowly added to UP-water/methanol/ SnCl_2 mixture from the first step. The final solution (reaction mixture), shown in Figure 1, was left to stir, using a magnetic stirrer, for 3 days in a water bath set to 28°C before the first sample was taken.



Fig. 1: Final SnO_2 solution before placing in the water bath at 28°C Initial reaction resulted in a white milky solution.

Sampling was done by centrifuging (Figure 2) approximately 200 mL of the reaction mixture at 4000 rpm for 10 minutes, to remove the liquid from the solid. After sampling was completed each time, the flask was returned to the hot water bath at 28°C and continued to stir for another 24hrs for the next sampling.



Fig. 2: Samples were centrifuged for 10 minutes at 4000 rpm

The liquid was discarded, after which, the product was washed 2 times with a small amount of methanol. Finally, the remaining solid was picked up with 15-20 mL of UP-water and sonicated for ~5min for uniform dispersion of the solid. The solid/UP-water mixture was frozen with liquid nitrogen in a test tube for 10 minutes then placed in jar used in a vacuum freeze-drying apparatus.



Fig. 3: Frozen sample in freeze-dry apparatus

Sampling was done for 5 consecutive days starting on day 4 of the experiment. Each sample was studied with XRD and TEM in order to identify the characteristics of SnO_2 .

3. RESULTS AND DISCUSSION

The first sample was taken on day 4 of the experiment. As seen in Figure 4, the solution had developed a bright yellow tint compared to the previously white solution (see Figure 1).



Fig. 4: SnO₂ solution on day 4 of the experiment presented a bright yellow, cloudy appearance (left). After centrifuging, the sample had a lighter yellow, gel-like appearance (right).

The second sample was taken on day 5 of the experiment. Figure 5 shows the yellow color of the solution and the product produced after centrifuging. With this sample, there appeared to be more solid product after centrifuging than on day 4.



Fig. 5: SnO₂ solution on day 5 of experiment (left). More solid produced after centrifuging than previous day (right).

On Day 6 of the experiment another sample was taken from the solution with the color seen Figure 6. The product after centrifuging appeared to be a larger amount than the sample taken on day 5.

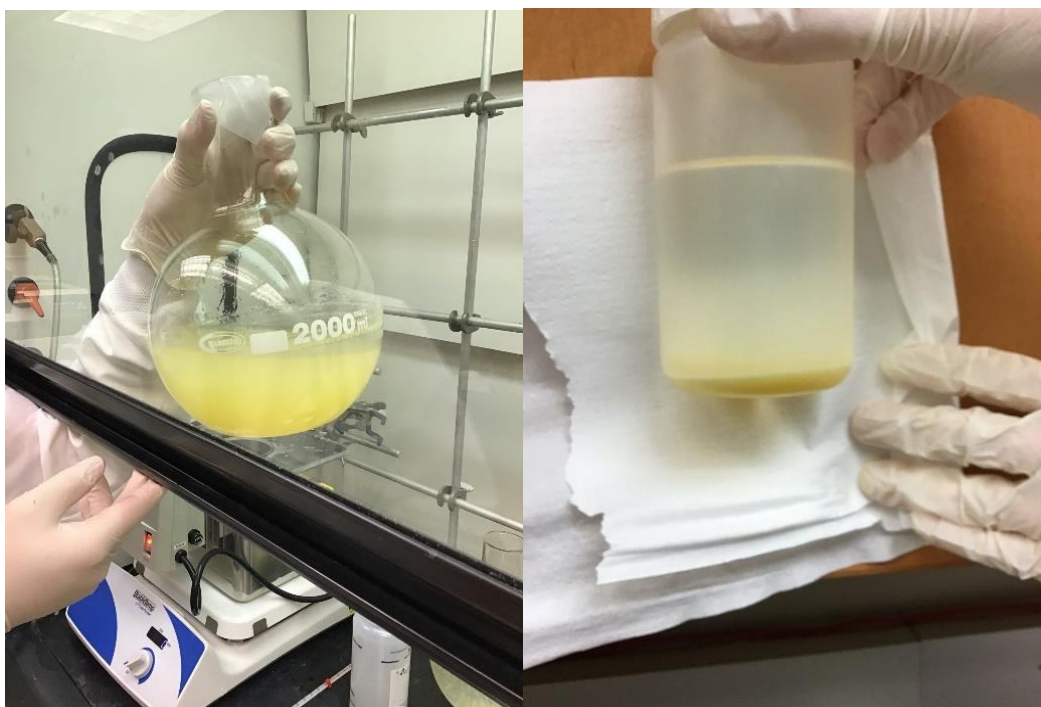


Fig. 6: SnO₂ solution on day 6 of experiment (left). More solid produced after centrifuging than previous day (right).

To identify the size of the SnO₂ particles on this day, TEM was performed on the dried sample. The results produced from this test can be seen in Figure 7.

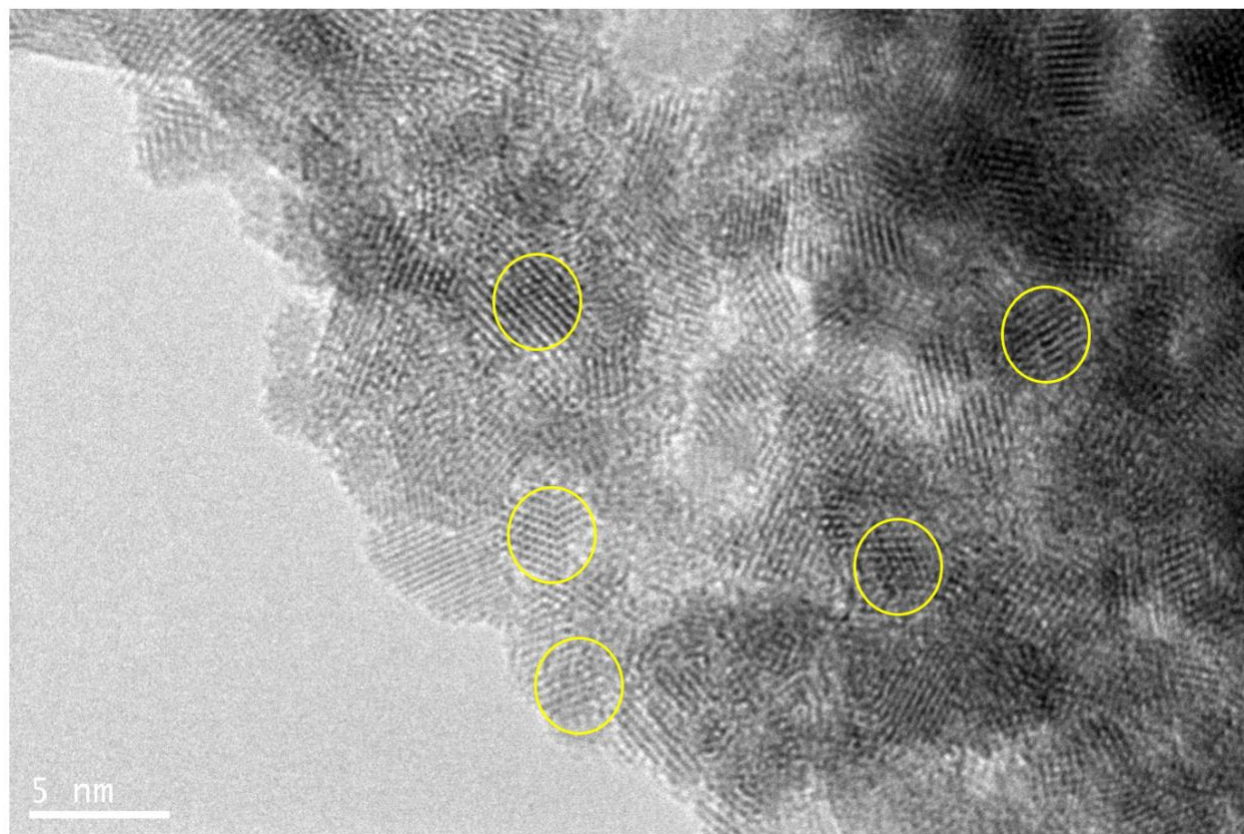


Fig. 7: TEM of day 6 sample. Yellow circles indicate fringe interplanes.

On Day 7 of the experiment another sample was taken from the even darker yellow solution, as seen in Figure 8.

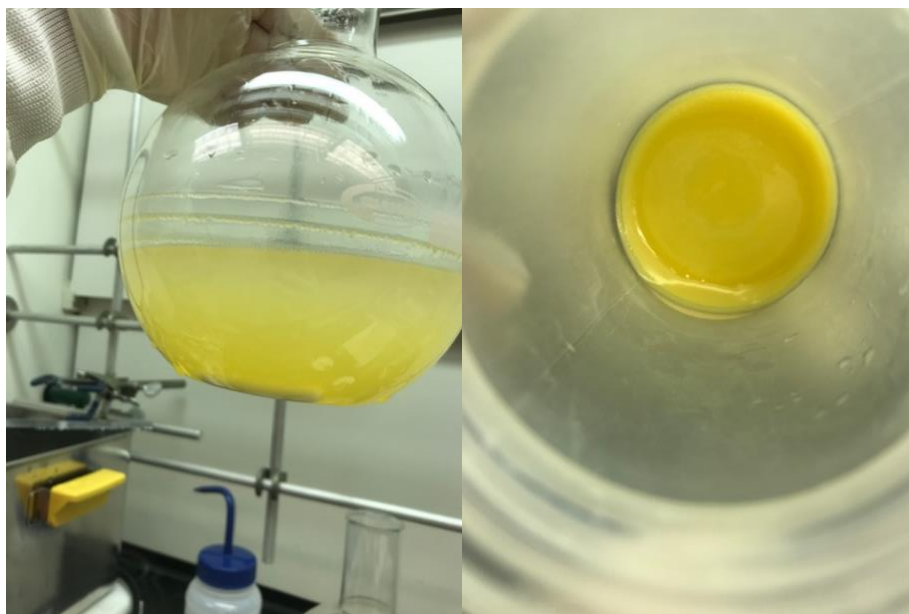


Fig. 8: SnO_2 solution on day 7 of the experiment (left). Sample produced more of a thicker, darker product after centrifuging than previous day (right).

For the final day of sampling, on day 8 of the experiment, all the remaining solution was used, and the color can be seen in Figure 9.



Fig. 9: SnO_2 solution on day 8 (final day) of the experiment (left). Sample produced more product after centrifuging than any previous days (right)

To identify the size of the SnO_2 particles, and whether the particles had increased in size from day 6 to day 8, TEM was also performed on the day 8, dried sample. The results produced from this test can be seen in Figure 10. This TEM shows much larger particles than what can be seen in Figure 7 previously.

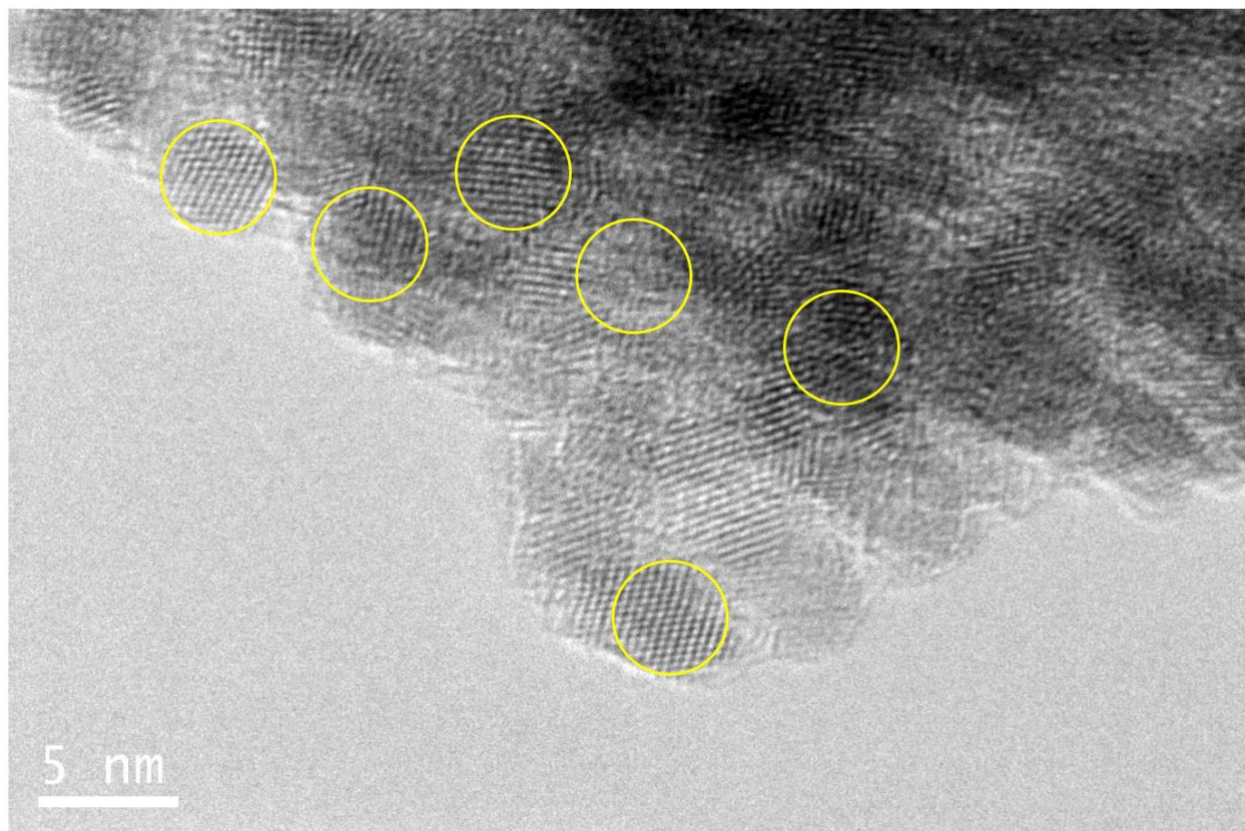


Fig. 5: TEM of day 8 sample. Yellow circles indicate fringe interplanes.

XRD was done on the samples from days 4, 6, and 8 to determine if any SnO_2 nanoparticles were present in the samples. When compared to the standard SnO_2 XRD (Figure 11), the peaks present in the XRD graphs confirmed that SnO_2 was present in each of the three days that were analyzed (Figure 12).

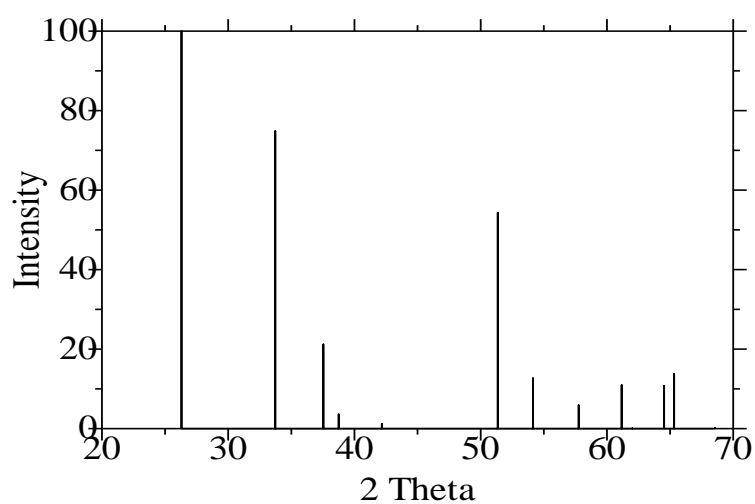


Fig. 11: SnO_2 standard XRD graph.

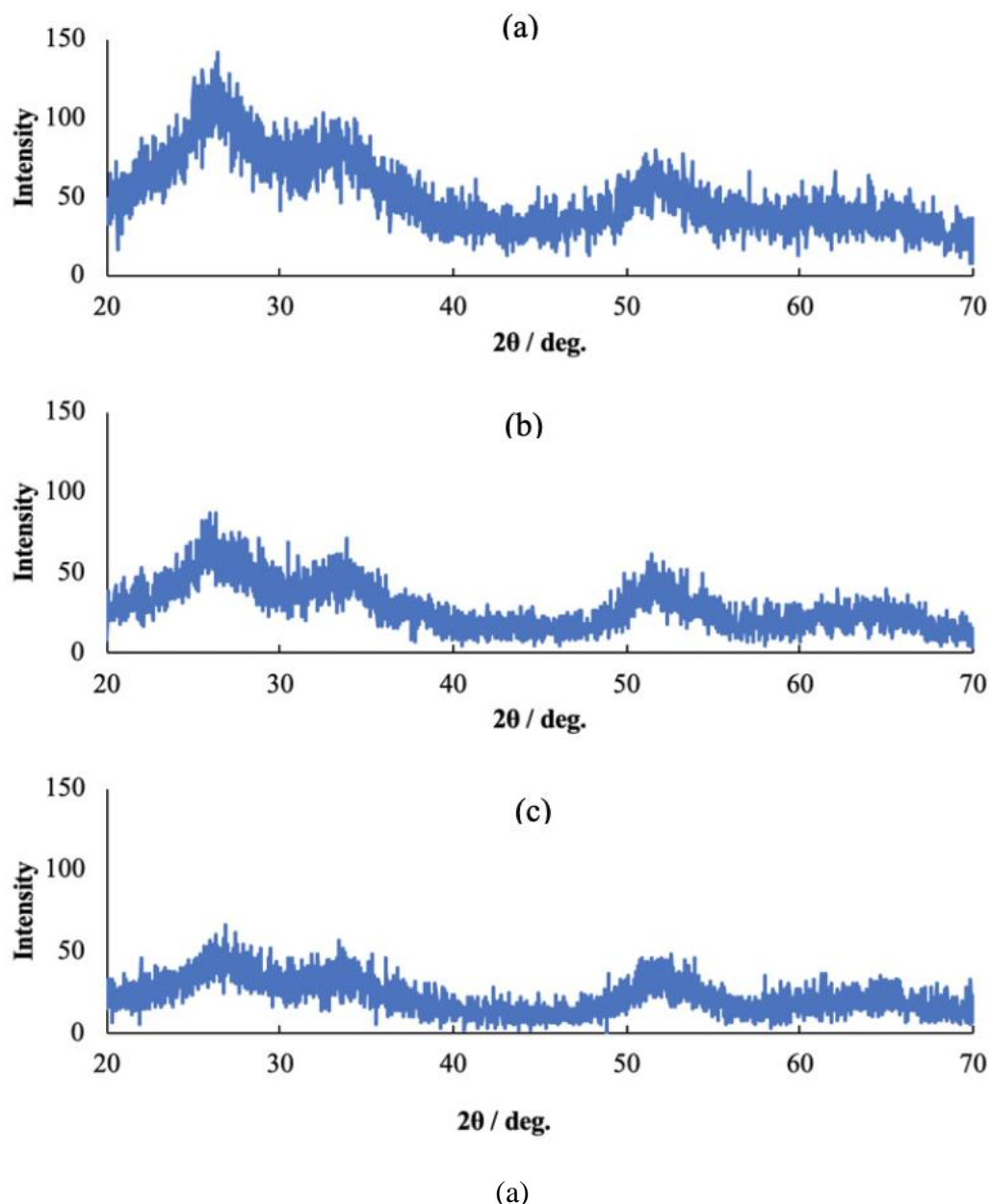


Fig. 12: Combined XRD taken a different sampling days, (a) after 4 days, (b) after 6 days, and (c) after 8 days.

4. CONCLUSIONS

We demonstrated that the low-temperature synthesis of SnO_2 , using freeze drying, was effective for obtaining crystalline SnO_2 nanoparticles, as verified by XRD. From the results of this experiment it can be concluded that the SnO_2 particles were present from the first day of sampling. Furthermore, the nanoparticles continued to gradually grow larger over the life of the experiment which allows the control of the particle's sizes. Currently, studies are on the way to determine the optimum size (synthesis time) to produce PSCs with the highest efficiency.

(b)

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(c)

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