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# Comparison of Microwave-Assisted Synthesis Routes in the Preparation of $SnO_2$ Nanograins by Chemical Precipitation

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**Abstract**

This study considers the effect of microwave treatment in the production of $SnO_2$ nanograins, showing that high-temperature annealing may be omitted in a microwave-assisted process. Tin dioxide nanograins were prepared by chemical precipitation and heated via two microwave-assisted routes – one where precursor precipitates were oven-dried then irradiated, the other where precursor precipitates were irradiated then oven-dried. A third preparation, which served as control, involved subjecting oven-dried precursors to conventional furnace calcination. The placement of the irradiation step in the preparation process was found to affect the crystallite size, degree of particle agglomeration, and moisture content of the final product. Where oven-dried precursors were subsequently microwave-irradiated for ten minutes, tin dioxide nanoparticles registered the highest degree of crystallinity and the smallest particle size. Microwave irradiation was deemed capable of replacing the furnace calcination step in conventional preparation techniques, yielding comparably similar metal oxide products at potentially lower production costs.

**Keywords:** metal oxide nanoparticle preparation, microwave-assisted process, chemical precipitation, nanograins, tin dioxide ($SnO_2$)

## Introduction

Microwave-assisted preparation of metal oxide nanoparticles has gained enormous attention in recent years due to its various advantages over conventional preparation techniques, especially in terms of energy requirement and production speed (Mirzaei & Neri, 2016). The microwave process gives higher energy efficiency due to the direct heating of the target material at a minimal amount of time, as opposed to conventional heat conduction methods that require very high temperatures sustained over very long periods.

The microwave-assisted technique involves direct internal heating of a sample, which overcomes the inherently slow thermal conduction on ceramic powders and thus enabling reactions and diffusion to occur at a shorter time and at lower temperatures (Fall, Esquenazi, Allan & Shulman, 2012). Unlike in a conventional furnace, the temperature of the microwave oven environment is largely immaterial to the process. Inside the microwave,

both the rapid volumetric heating of the sample and the radiant heat prevent losses from the sample surface. This method thus induces a uniform temperature profile, which enables a faster and more uniform heating than is found in conventional methods. There is also no warm-up and cool-down time, thus production time, yield and product performance are improved.

Among the metal oxides used in industry, tin dioxide or tin (IV) oxide ($SnO_2$) finds increasingly more and more cutting-edge applications because of its outstanding electrical and physical properties. Such qualities include a wide band gap value ($E_g$ = 3.6 eV), a large exciton binding energy (130 eV), high conductivity, and high optical transparency (Zhang et al., 2016) – properties that are required in optoelectronic applications like LEDs and electrode materials in solar cells and flat panel displays. Thus, tin dioxide currently finds use as follows: a solid state sensor due to its sensitivity towards different gaseous species, a material in transparent conductive thin film coatings, an oxidation catalyst in industrially important chemical reactions, and a high-capacity anode material in lithium-ion batteries (Singh & Nakate, 2013; Sagadevan, 2015).

Nanoparticles of $SnO_2$ have usually been prepared using various wet or dry techniques such as hydrothermal, solvothermal, gel combustion, evaporation of tin grains in air, chemical vapor deposition, spray pyrolysis, and sol-gel or chemical precipitation methods (Thenmozhi, Manivannan, Kumar & Veerarethinamurugan, 2015). Among these, the wet preparation techniques (e.g., chemical precipitation that forms a separable solid substance from a dissolved solution) are preferred due to inexpensive chemical precursors, low temperature processing, and better product homogeneity (Sagadevan, 2015).

Microwave-assisted synthesis is nothing new. $SnO_2$ has already been prepared previously in conjunction with various wet techniques such as the hydrothermal method used by Blessi, Sonia, Vijayalakshmi & Pauline (2014) and the solvothermal synthesis employed by Zou & Wang (2013). However, very few studies have looked into the influence of the sequence location of microwave treatment during production process on the resulting properties of the material produced.

In many studies, microwave irradiation was applied simply as a pre-treatment prior to calcination (Krishnakumar, Pinna, Kumari, Perumal & Jayaprakash, 2008; Singh & Nakate, 2013; Zou & Wang, 2013) with the aim of achieving a lower calcination temperature and/or a shorter calcination period. Few have asserted the possibility of getting rid entirely of an energy-intensive post-microwave step such as annealing, or showing that the microwave process can serve as the calcination step without compromising product quality. In this study, we endeavor to elaborate the effect of microwave treatment placed at different stages in the production of $SnO_2$ nanograins and show that high-temperature annealing as a final step may be completely omitted in a microwave-assisted process.

## Methodology

Gaber et al.'s (2014) chemical precipitation method for the synthesis of $SnO_2$ was employed. Tin hydroxyl solution (0.1 M) was prepared by diluting 18.96 g of $SnCl_2$ powder with deionized water to produce 1.0 L solution. A 0.14 M tris HCl solution (pH = 8) served as buffer, prepared by diluting 19.94 g tris (hydroxymethyl) aminomethane and 5.83 mL concentrated HCl in deionized water to produce 1.0 L of solution. To induce precipitation, approximately 800 mL of the buffer was poured into the hydroxyl solution to adjust and maintain the pH between 7.0 and 9.0. Precipitates were collected and washed several times with deionized water until chloride ions were no longer detectable by the silver nitrate ($AgNO_3$) test administered.

Collected tin hydroxide precipitates were put into covered crucibles and then used to prepare nanograins of $SnO_2$ via three different dehydration synthesis routes, namely: (1) oven-dried then microwave-assisted (OM), (2) microwave-assisted then oven-dried (MO), and (3) oven-dried then heat-treated in a furnace (OF) which is the traditional method.

Oven-drying at 100 °C was done for about 16 h using an Interlab DSO-500D digital oven. After drying, samples were ground to fine powder. Microwaving was performed for 10 minutes using a domestic microwave oven (American Heritage)

with 800 W and 2.45 GHz output capacity. Heat treatment was performed at 600 °C for 2 h at a ramp rate of 5°C/min in a Carbolite 3216 Muffle Furnace.

The diffraction patterns of all samples were generated using a Shimadzu MAXima_X XRD-7000 X-Ray diffractometer. Surface morphologies were observed by scanning electron microscopy (SEM) using a JSMS310 Scanning Microscope, while the thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) graphs were generated using the TA Instruments TGA Q500 and Nicolet™iS™50 FT-IR Spectrometer, respectively.

## Results and Discussion

*Crystallinity and crystallite size comparisons*

Powder samples obtained from the three synthesis routes – OM, MO and OF – registered diffraction peaks that fit well to the Cassiterite type tetragonal rutile structure of $SnO_2$ crystal (Figure 1). The lack of characteristic peaks in their XRD spectra suggests that high purity $SnO_2$ were produced.

The most crystalline among the samples were those prepared via the OM synthesis route, which registered the narrowest XRD peak that corresponds to a FWHM (full width at half maximum) value of 0.08; samples prepared via MO and OF routes registered FWHM values of 0.12 and 0.20, respectively. This outcome may be explained by looking into the synthesis process. In the OM route, microwave radiation is absorbed and converted to heat more directly by tin hydroxide precursors, as the sample had essentially been rid of water prior to irradiation. This makes for excellent oxide formation by dehydration. In the MO route, microwave radiation is absorbed by both the precipitate precursors and the aqueous components that also use the available heat for the conversion of tin hydroxides to oxides, thus managing to take away some of the heat unto itself. Nevertheless, samples prepared via the MO route were more crystalline than those prepared through the conventional OF method. This could be attributed to the higher reaction temperature that microwave heating provides.

Crystallite size determination was carried out quantitatively using the Scherrer equation. Crystallite sizes so determined were 1.74 nm, 2.89 nm and 33.13 nm for OM, MO and OF samples, respectively. These results show

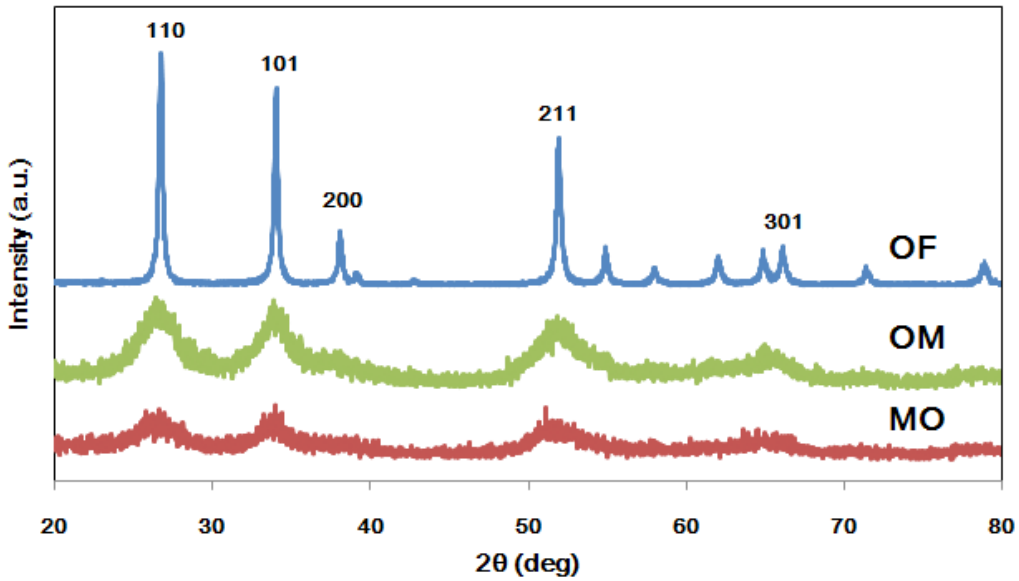


Figure 1. Stacked XRD spectra of the prepared $SnO_2$ powder samples. All three exhibited the Miller indices [110], [101], [200], [211], and [301] which match well with JCPDS card # 41-1445.

that the microwave-assisted process generally produces smaller crystals compared to the conventional process, probably due to the brief period of crystal formation during irradiation compared to furnace calcination. In the OM route where irradiation happens as a final step, crystallite sizes are understandably smaller compared to those prepared via the MO route where irradiation is followed by prolonged low-temperature heating, which somehow affords opportunity for further crystal formation.

*Surface morphologies*

The SEM micrographs of $SnO_2$ samples prepared via the three different routes, including that of an as-dried sample that did not undergo calcination, are shown in Figure 2. The micrographs reveal comparable degrees of particle agglomeration in samples prepared by the OM and OF routes, probably as a consequence of both processes being terminated with high-temperature treatment. Similarly, those terminated with low-temperature treatment as in the MO route or simple oven-drying show essentially the same degree of clustering and wide size distribution. The micrographs also reveal that OM and OF samples produce generally smaller clumps compared to the MO and non-calcined samples – an outcome which may again be linked to where high-temperature treatment is implemented in the preparation process. With regard to agglomerate size, the trend goes toward smaller clumps emerging from heated endings.

*Thermal decomposition behavior*

The thermal behavior of samples prepared via the microwave-assisted routes OM and MO was studied by subjecting these to thermogravimetric analyses. The TGA graphs generated (Figure 3) reveal two stages of decomposition similar to previous reports on $SnO_2$ prepared using traditional methods, although the 100-450 °C range previously reported by Gaber et al. (2014) covering the first stage of calcination where water and hydroxyl molecules are decomposed was reduced to 23-225 °C for the MO route (peaking at 86 °C), and 57-150 °C for the OM route (peaking at 76.5 °C). This means that the samples prepared via the microwave-assisted routes are generally more dehydrated, with

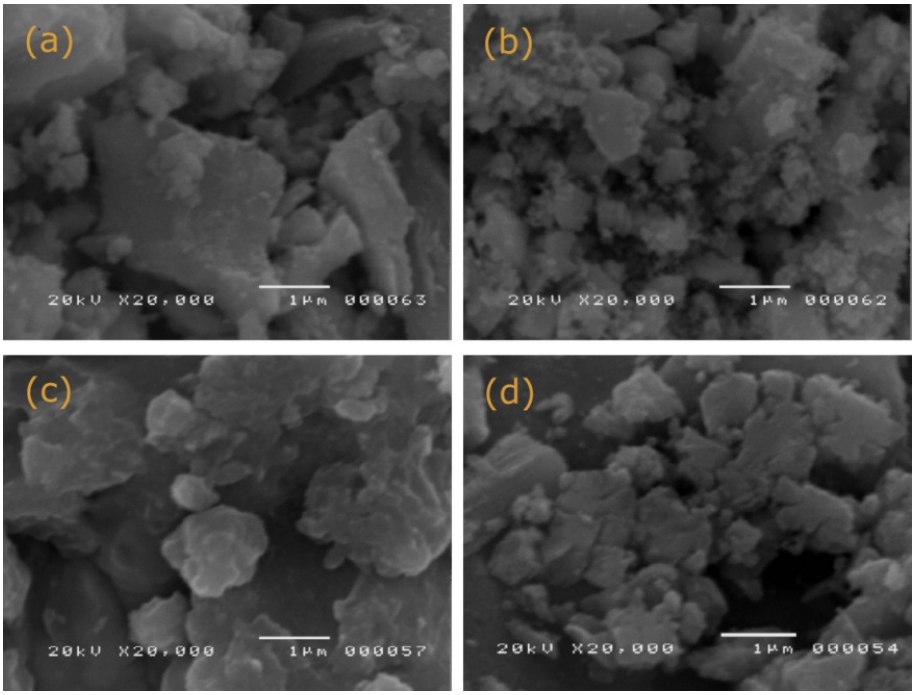


Figure 2. SEM micrographs of samples prepared via (a) simple oven drying, (b) OF, (c) MO, and (d) OM routes, at 20k magnification

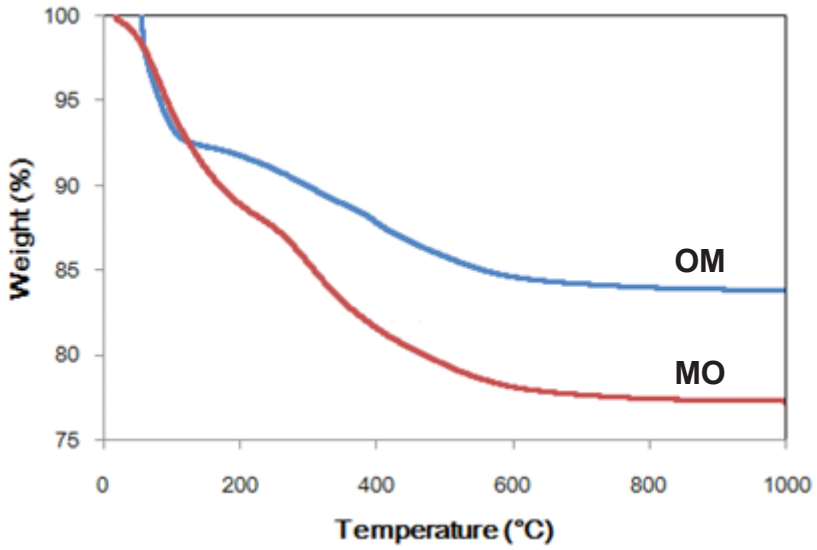


Figure 3. TGA curves of samples prepared via the microwave-assisted routes

OM-samples being the driest due to a very high-temperature finish, however brief. MO-samples tend to remain palpably moist even after 16 h of oven-drying. The resulting weight loss in the first stage of thermal decomposition was approximately 11.8% and 7.7% for MO and OM, respectively.

The second stage of decomposition characterized by the burnout of carbon and the completion of crystallization reactions occur at 225-495 °C (peaking at 302 °C) and 300-540 °C (peaking at 396 °C) for MO and OM, respectively. Weight losses associated to this stage were approximately 11.0% and 8.5% for MO and OM samples, respectively. Altogether, the MO samples registered a weight loss of 22.8% and the OM samples, 16.2%.

*Verification of functional groups*

Fourier transform infrared spectroscopy (FTIR) was employed to determine what functional groups are present in the samples prepared using various routes. The FTIR curves are presented in Figure 4. The strong peaks near the 556 and 656 $cm^{-1}$ regions correspond to the

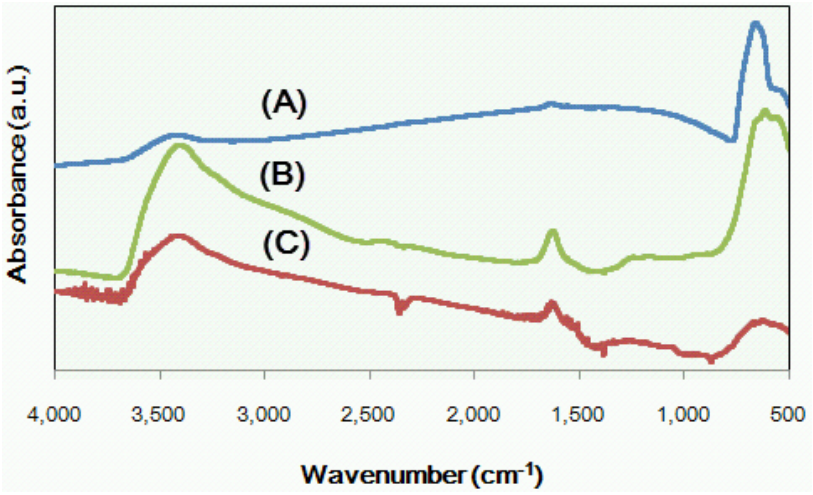


Figure 4. FTIR curve of $SnO_2$ sample prepared via the (A) OF, (B) OM and (C) MO routes.

stretching vibrations of Sn–O bonds (Chen and Gao, 2004). The 556 $cm^{-1}$ absorption band ascribes to the presence of tin hydroxyl groups, while the 656 $cm^{-1}$ band is attributed to the oxide-bridge functional group. As such, the presence of the latter peak means that microwave energy had successfully transformed the tin hydroxyl groups to oxide groups.

Absorbance peaks around 1628 and 3400 $cm^{-1}$ correspond to bending vibrations of absorbed molecular water and the stretching vibrations of –OH groups, respectively. The absorption band at 3419 $cm^{-1}$ may be attributed to the stretching vibration of surface hydroxyl group or adsorbed water which has been observed due to the re-adsorption of water molecules from ambient atmosphere.

## Conclusion

Microwave-assisted synthesis of tin dioxide is highly effective especially if a more crystalline sample is desired. Moreover, this process produces product properties comparable with those prepared by the conventional method of furnace calcination. Switching the microwave irradiation and oven-drying steps leads to three main consequences: (1) a difference in the crystallite size of the sample, (2) a difference in the size of particle aggregates, and (3) a wide gap in moisture content. Tin dioxide produced with microwave irradiation as a final step tends to have smaller crystallite sizes, smaller particle aggregates, and lower moisture content.

Microwave-assisted synthesis is indeed a fast, cost-effective, efficient and precisely controllable alternative to conventional heating methods. Ten minutes of exposure to microwave irradiation can produce highly pure tin dioxide nanocrystals that do not need further high-temperature annealing, thus opening the possibility for efficient production at decreased production costs (energy consumption and sample preparation time).

Further characterization tests using high resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, electrical resistance measurements, etc., are recommended to quantitatively compare other properties of microwave-synthesized $SnO_2$ with those prepared via conventional calcination.

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