SYNTHESIS AND CHARACTERIZATION OF SnO_2 NANOPARTICLES

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Abstract

Tin Oxide, SnO_2 nanoparticles have been synthesized by sol-gel auto combustion method in this work from $SnCl_4.5H_2O$, NH_4OH and distilled water. After preparation the powder has been calcined at five different temperatures (400°C, 500°C, 600°C, 700°C and 800°C) for 1 hour. Then, the phase analysis identification has been conducted by X-ray Diffraction Analysis (XRD). Besides, Fourier Transform Infrared Spectroscopy (FTIR) analysis has been conducted after synthesis. FTIR spectrum shows the molecular vibration of SnO_2 nanoparticles. Moreover, the microstructure of the sample has been characterized by Scanning Electron Microscope (SEM).

Keywords: SnO_2 nanoparticles, XRD, FTIR, SEM.

Introduction

One of the most intriguing materials, Tin oxide ,SnO_2has been investigated because of its potential application in transparent conductive electrode for solar cells, a gas sensing material for gas sensors devices, transparent conducting electrodes, photochemical and photoconductive devices in liquid crystal display, gas discharge display, lithium-ion batteries, etc.

Moreover, nanometer-sized materials have recently attracted a considerable amount of attention due to their novel electrical, physical, chemical, and magnetic properties. These properties strongly depend on the size, structure and shape of the nanoparticles. Many processes have been developed to the synthesis of SnO_2 nanoparticles, e.g., spray pyrolysis, hydrothermal methods, chemical vapor deposition, thermal evaporation of oxide powders and sol–gel auto-combustion method.

In this research work, the synthesis and characterization of SnO_2 nanoparticles by Sol-gel Auto-combustion method was studied because this process has a potential synthesis technique in the production of nanometer scaled oxide powders.

Experimental Details

The chemical reagents used for nanoparticle synthesis were Tin (IV) Chloride pentahydrate, ($SnCl_4.5H_2O$),Ammonia solution (NH_4OH) and Distilled water. In the preparation of SnO_2, 20 g of $SnCl_4.5H_2O$ has been weighed with CENT-O-GRAM (OHAUS) sliding balance and 20 ml of Distilled water has been weighed with graduated cylinder. After complete dissolution, 20 g of ammonia solution was added to the above solution by drop wise under stirring with magnetic stirrer. When mixing, the reaction takes place and gradually turned into gel type. Then, the mixture has been heated with Temperature Controlled Hot Plate up to 300°C. At 150°C, it started to boil. At 200°C, it changes into dry-gel. Auto-combustion takes place at 300°C and it takes for6 hours. The combustion has finished after 6 hours. SnO_2 powder comes out from the experiment. Then, this powder has been grounded with mortar and pestle to become the fine powder. After that, the SnO_2 powders were calcined at five different temperatures (400°C, 500°C, 600°C, 700°C and 800°C) for 1 hour in the furnace. Then, the phase analysis identification has

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been conducted by X-ray Diffraction Analysis (XRD) in order to determine the crystallite sizes of SnO_2 nanoparticles. Besides, Fourier Transform Infrared Spectroscopy (FTIR) analysis has been conducted after synthesis. FTIR spectrum shows the molecular vibration of SnO_2 nanoparticles. Moreover, the microstructure of the sample has been characterized by Scanning Electron Microscope (SEM).

(a) $SnCl_4.5H_2O$

(b) Distilled Water

(c) NH_4OH solution

Figure 1 Starting Materials

(a) Magnetic Stirrer with Variable Power Supply

(b) Sliding Balance (CENTOGRAM – OHAUS)

(c) Temperature Controlled Hot Plate

(d) Mortar and Pestle

(e) Furnace

(f) Dropper

(g) Graduated cylinder

Figure 2 Synthesis Equipments

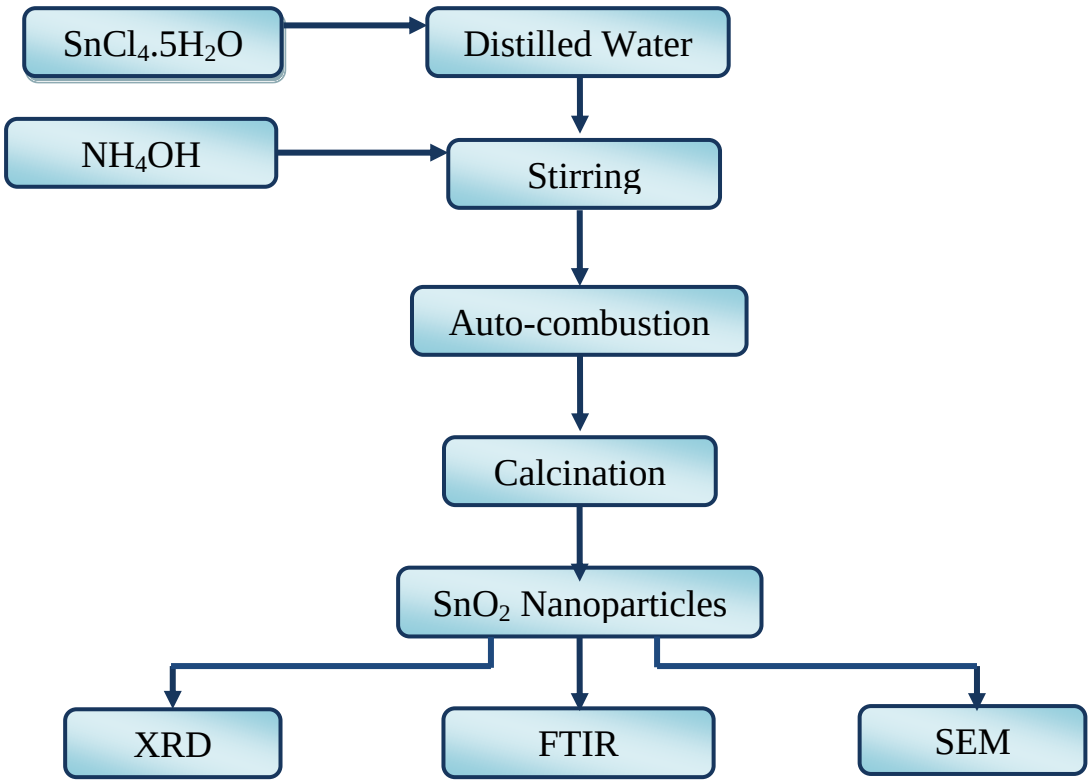


Figure 3 The Flow Chart of the Synthesis Procedure of SnO_2 nanoparticles

Synthesis Technique

X-ray Diffraction Technique (XRD)

X ray diffraction (XRD) technique is a technique which is commonly used in material characterization. This technique provides the peak position, intensity, width, shape and all-important information about the structure of the materials. From the XRD patterns, lattice constants have been calculated by the equation:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (\textit{for Tetragonal})$$

where, d_{hkl} = the lattice spacing between (hkl) planes.

For a polycrystalline powder, if the individual crystal is less than 100nm in size, the crystallite size can be estimated using the *Scherrer equation*:

$$L = k\lambda/B\cos\theta$$

where, B = peak width measured at half intensity (radian),

λ = the wavelength (Å)

k = particle shape factor (for spherical particles, k = 0.9)

L = diameter of the crystallites (Å).

In the Universities Research Center, University of Yangon, the materials can be examined by using Rigaku Multiflex 2kW Powder X-ray Diffractometer (XRD).

(a) External view (b) Internal view

Figure 4 Rigaku Multiflex 2kW Powder X-ray Diffractometer

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. The infrared absorption or transmission spectra of the SnO_2 nanoparticles were measured by using Fourier Transform Infrared Spectrometer (FTIR – 8400 Shimadzu), shown in figure (5). In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

Figure 5 Fourier Transform Infrared Spectrometer (FTIR – 8400 Shimadzu)

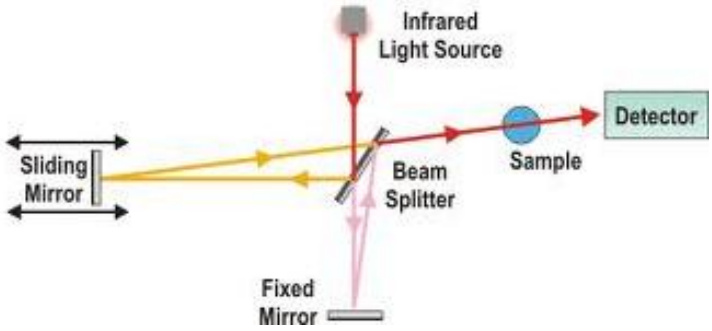


Figure 6 Schematic diagram of FTIR analysis

Scanning Electron Microscope (SEM)Technique

The Scanning Electron Microscope (SEM) is a microscope that used electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time.

The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of sample was relatively easy since most SEMs require the sample to be conductive. The combination of higher magnification larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research area today. The purpose of using SEM is to characterize the grain, pore and the surface morphology of the SnO_2 nanoparticles.

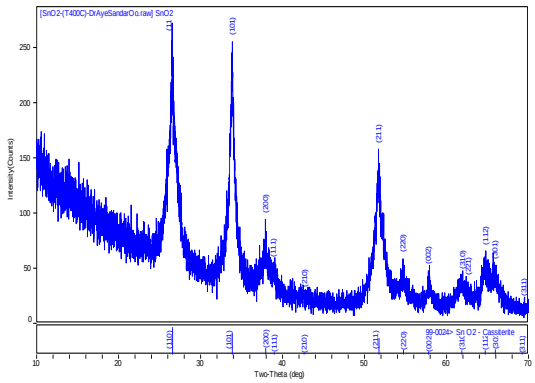
(a) Operation system of SEM (b) Sample holder of SEM

Figure 7 Scanning Electron Microscope (SEM)

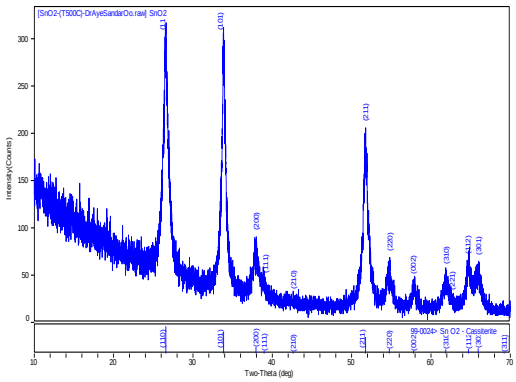
Result and Discussion

X-ray Diffraction Analysis

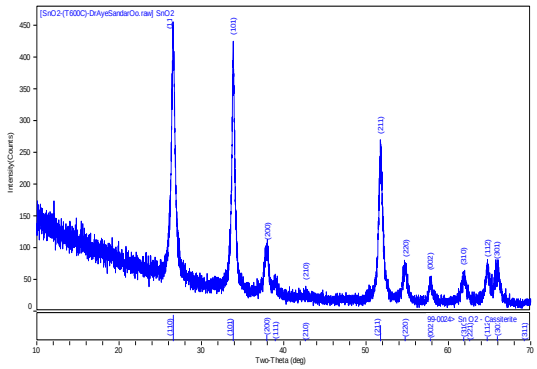
The structural properties of SnO_2 nanoparticles have been characterized by X-ray diffractometer (model RIGAKU MULTIFLEX) using CuK_α radiation (40 kV,50 mA) over a 2 θ range from 10^o to 70^o on a powder type XRD with λ = 1.54056 Å. The XRD spectrum of SnO_2 is shown in Figure (8 (a-e)).It was observed that all peaks are perfectly matched with the tetragonal structure of SnO_2 with the standard library file (ICDD_PDF # 99_0024) which indicating the present structure is found to be of SnO_2, which exist in the tetragonal phase. The lattice parameters of the crystal were obtained from the data of XRD spectrum. The peaks were occurred at (110), (101), (200), (211), (220), (002), (310), (112) and (301) the crystal planes from the XRD patterns. No other additional peaks were observed. This showed that the samples have no more impurity after calcination. The typical XRD pattern of synthesized SnO_2 nanoparticles confirmed that the crystalline phase of SnO_2 was tetragonal without any impurities. Moreover, the average crystallite sizes were found to be round about 18 nm to 32 nm. Besides, the smallest crystallite size of SnO_2 is 18.65 nm and the crystallinity was the most perfect for the sample annealed at 500^oC since there was no additional diffraction peaks were observed in its diffraction pattern.



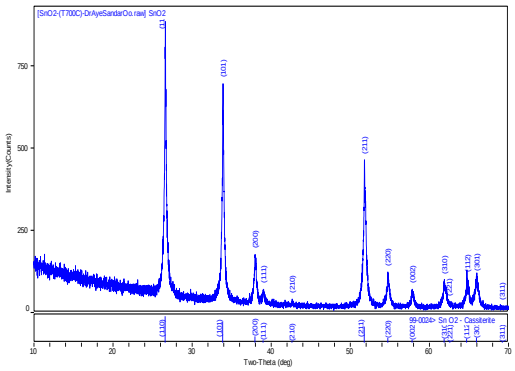
(a) 400^{o}C



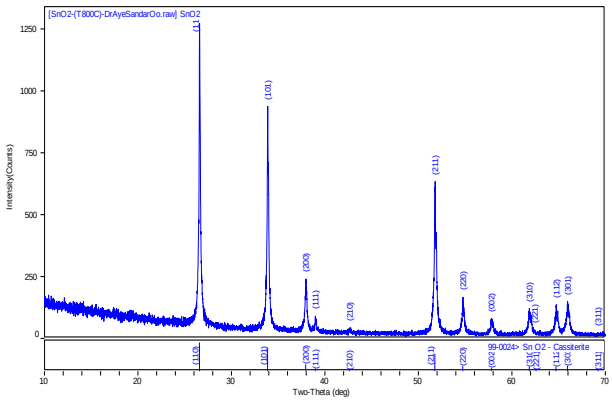
(a) 500^{o}C



(c) 600^{o}C



(d) 700^{o}C



(e) 800^{o}C

Figure 8 (a-e) XRD patterns of SnO_2nanoparticles with different temperatures

Table 1 The crystallite size of SnO_2 with different temperature

Temperature (^oC)	Average Lattice Parameter (Å)		Average Crystallite Size (nm)
	a = b	c	
400	4.7440	3.1920	22.54
500	4.7343	3.1852	18.65
600	4.7377	3.1842	20.71
700	4.7333	3.1854	24.70
800	4.7364	3.1863	32.85

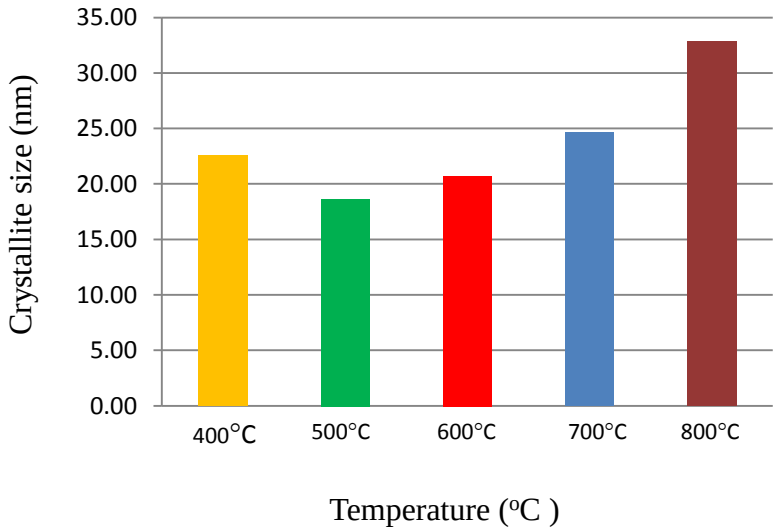


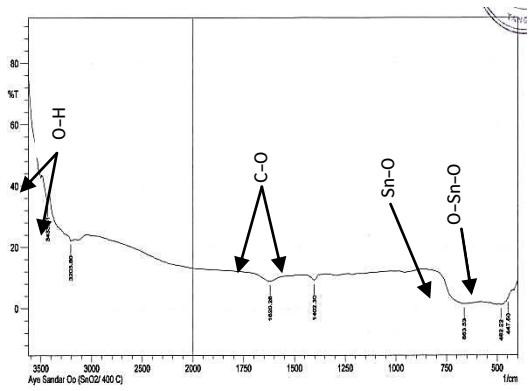
Figure 9 Graph of the crystallite size of SnO_2 with different temperatures

Fourier Transform Infrared Spectroscopic Analysis

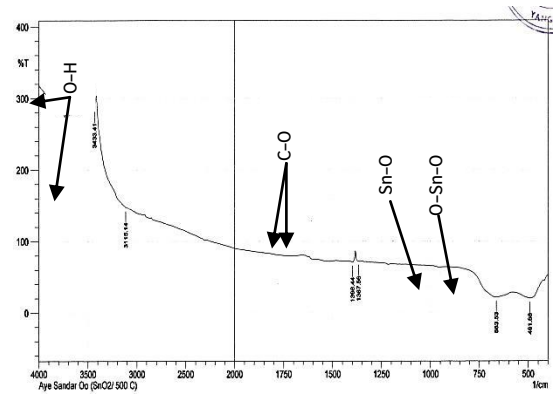
FTIR spectra of SnO_2 nanoparticles that calcined at five different temperatures(400°C, 500°C, 600°C, 700°C and 800°C) are shown in Figure (10 (a-e)) respectively. Infrared transmittance spectra demonstrate the vibration bands due to Sn-O bonds and O-Sn-O bonds in its structure. The frequencies of FTIR vibration band for SnO_2nanoparticles with different temperatures are shown in Table (2). The observed bands in the range of 2312.73cm^{-1} –3444.98 cm^{-1} in the SnO_2 nanoparticles have been assigned to the hydroxyl group (O-H) stretching vibrations, over 1200 cm^{-1} to 1600 cm^{-1} is showed that the carboxylate groups(C-O). Moreover, FTIR spectra attributed to O- Sn-O bonds and Sn-O bonds stretching vibrations in the range of 447.50 cm^{-1} to 569.02 cm^{-1} and 617.24 cm^{-1} to 663.53 cm^{-1}. Therefore, the selected region of the recorded FTIR spectra have been confirmed the tetragonal structure of SnO_2.

Table 2 The molecular vibration in FTIR spectra of SnO_2 nanoparticles with different temperatures

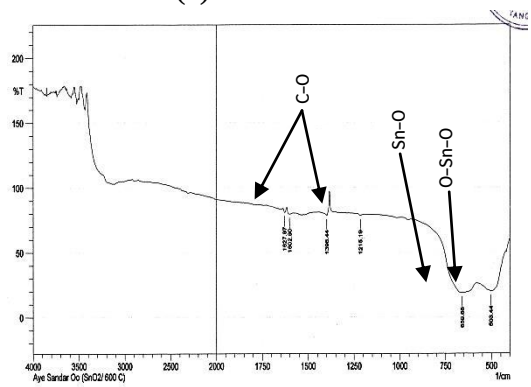
Temperature (^oC)	O-Sn-O Stretching (cm^{-1})	Sn-O Stretching (cm^{-1})	Carboxylate Stretching (cm^{-1})	Hydroxyl Stretching (cm^{-1})
400	447.50-482.22	663.53	1402.30-1620.26	3205.80-3433.41
500	491.86	663.53	1367.58-1398.44	3115.14-3433.41
600	503.44	659.68	1215.19-1627.97	-
700	472.58-569.02	653.89	1396.51-1660.77	-
800	503.44	617.24-646.17	1338.64-1629.90	2312.73-3444.98



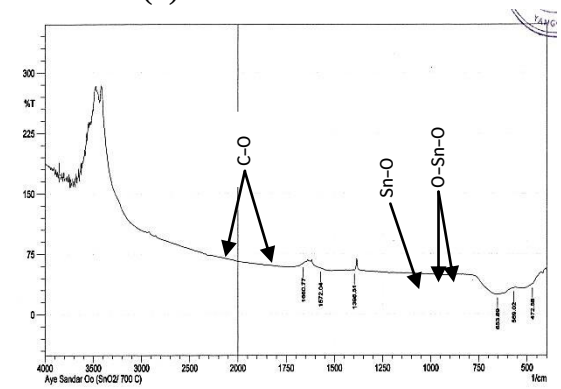
(a) 400^{o}C



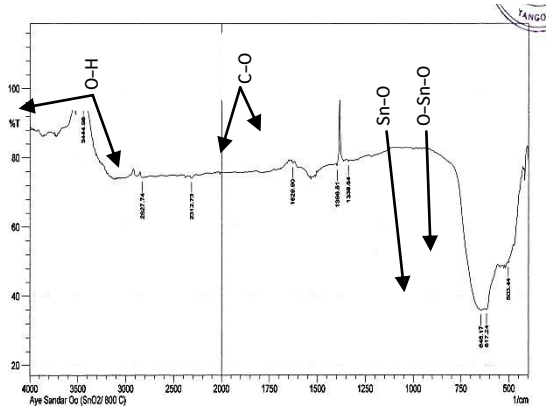
(b) 500^{o}C



(c) 600^{o}C



(d) 700^{o}C



(e) 800^{o}C

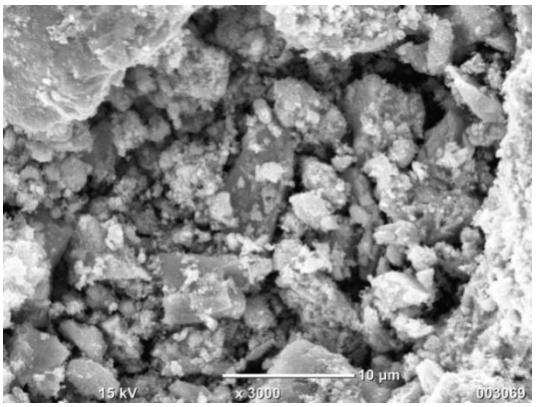
Figure 10 (a-e) The FTIR spectra of SnO_2 nanoparticles at five different temperatures

Morphological Investigation

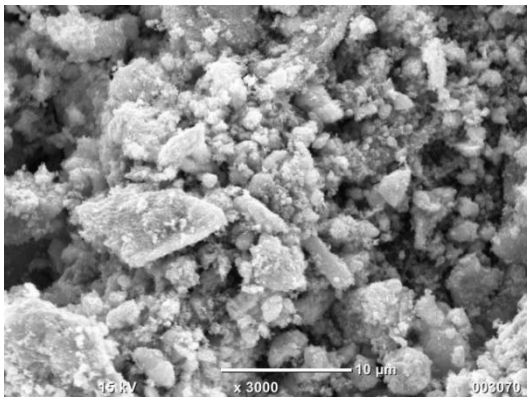
In this research, the SEM micrographs ofSnO_2 nanoparticles was investigated by SEM (Type: JEOL) are shown in Figure (11 (a-e)). SEM micrograph indicates the morphological feature of the SnO_2 nanoparticles and the average grain sizes are shown in Table (3). According to observation, the SEM micrographs of the SnO_2 nanoparticles found to be non-uniform shape because of different temperatures. At the higher temperature, 700^{o}C and 800^{o}C, has the smallest grain size and are composed of agglomerated particles. If the grain size is smaller, the more contact between each other is larger, which can be used as a conducting devices. At the lower temperature, (400^{o}C, 500^{o}C, 600^{o}C), the grain sizes are bigger than that of higher temperature and with more pores which is suitable for sensing devices.

Table 3 Average grain size of SnO_2 nanoparticles

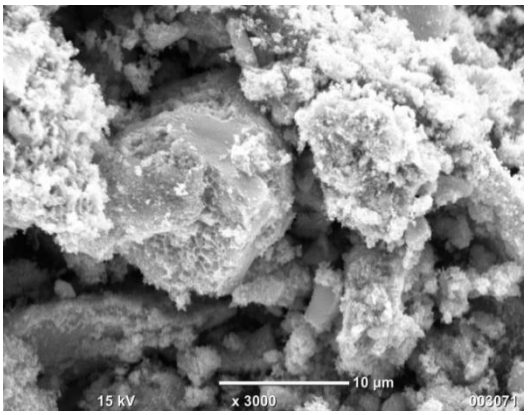
Temperature (^{o}C)	Average grain size (μm)
400	2.00
500	1.33
600	1.67
700	1.20
800	0.95



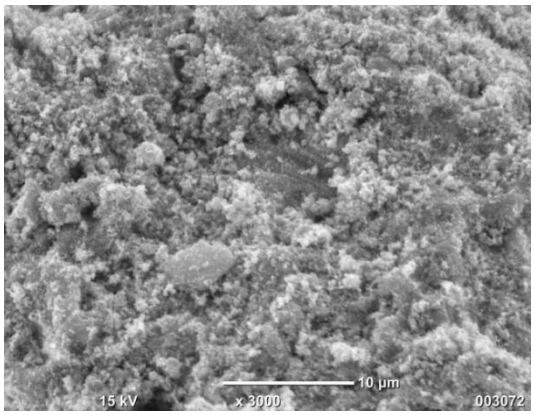
(a) 400^{o}C



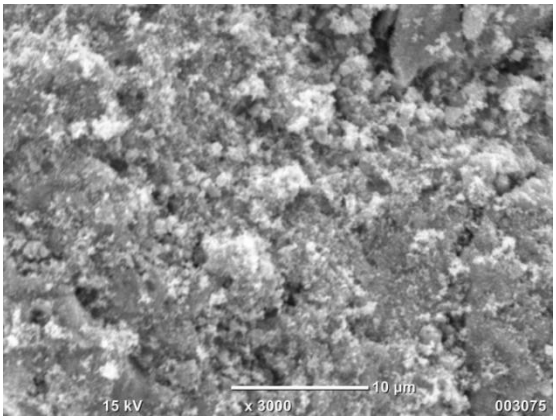
(b) 500^{o}C



(c) 600^{o}C



(d) 700^{o}C



(e) 800^{o}C

Figure 11 (a – e) The SEM micrographs of SnO_2 nanoparticles at five different temperatures

Conclusion

To be concluded, the aim of this research is to produce the SnO_2 nanoparticles easily. The method, Sol-gel Auto-combustion, used in this research is cost effective and easy way to make the process of SnO_2 nanoparticles. The typical XRD pattern of synthesized SnO_2 nanoparticles confirmed that the crystalline phase of SnO_2 was tetragonal structure without any impurities. Moreover, the average crystallite sizes of SnO_2 are in the range of 18 nm to 32 nm. FTIR spectra attributed to O- Sn-O bonds and Sn-O bonds stretching vibrations in the range of 447.50 cm^{-1} to 569.02cm^{-1} and 617.24 cm^{-1} to 663.53 cm^{-1} and confirming the SnO_2 spectra. The SEM micrographs of the SnO_2 nanoparticles found to be non-uniform shape because of different temperatures. According to observation, SnO_2 nanoparticles is the potential application in transparent conductive electrode for solar cells, a gas sensing material for gas sensors devices, transparent conducting electrodes, photochemical and photoconductive devices, gas detection, lithium-ion batteries, etc.

Acknowledgement

The authors would like to acknowledge Professor Dr Kay Thi Thin, Pro Rector, Meiktila University, for her kind permission to carry out this work and Dr Daw Hla Win, Professor, Department of Physics, Meiktila University, for her valuable advice.

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