Synthesis and Characterization of SnO_2 Quantum Dots

A PROJECT REPORT

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY

in

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Submitted By

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CANDIDATE'S DECLARATION

I, VARSHA MISHRA, Roll No. 2K16/NST/10, student of M. Tech. Applied Physics, hereby declare that the project Dissertation titled **"Synthesis and Characterization of SnO_2 Quantum Dots"** which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in the partial fulfillment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associate ship, Fellowship or other similar title or recognition.

Place: Delhi **Varsha Mishra**
Date: **2K16/NST/10**

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CERTIFICATE

I hereby certify that the Project Dissertation titled **“Synthesis and Characterization of SnO_2 Quantum Dots”** which is submitted by Varsha Mishra, Roll No. 2K16/NST/10 of Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi
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ABSTRACT

Quantum dots are nanostructures having attractive physical and chemical characteristics. Quantum dots are not easily obtainable as the materials tend to agglomerate. The cost for the preparation of SnO2 nanoparticles in industrial scale is a challenging job in material production. Therefore simple method, cheap starting materials and other suitable parameters are the main necessity for the synthesis of SnO2 nanoparticles. In this work, Tin Oxide (SnO2) quantum dots have been successfully synthesized via a simple and low cost method which is the sol-gel method using methanol as solvent. Ethylene glycol, water and ethanol can also been used as solvents for synthesizing tin oxide (SnO_2) quantum dots. The sol-gel thus obtained was washed and calcinated at 200º C, 300º C and 400 °C to obtain the SnO2 nanopowder. The SnO_2 nanopowder thus synthesized was analysed using X- Ray Diffraction (XRD), Scanning Electron Microscopy (SEM). Energy Dispersive X-Ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR). The size of the nanoparticles was found to be 2.5 nm, 4.5 nm and 8 nm for the calcinations temperature of 200º C, 300º C and 400 °C. The size of nanoparticles formed at 200º C that is 2.5 nm is less than the bohr exciton radius for SnO_2 which is 2.7 nm. The synthesized quantum dots can be used in magnetic data storage and magnetic resonance imaging, as catalysts, energy-saving coatings and anti-static coatings, as electrodes and anti-reflection coatings in solar cells, gas sensors, optoelectronic devices and resistors, liquid crystal displays and lithium ion battery anode material.

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CHAPTER-1

INTRODUCTION

1.1. Nanotechnology and it’s applications

Nanotechnology is the study of structures with size ranging between 1 nanometer and 100 nanometer and can be applied across all the other fields of science. A particle whose diameter is of 100 nanometers or less is called a nanoparticle. Professor Norio Taniguchi coined the term nanotechnology. Some of the applications of nanomaterials are listed below:

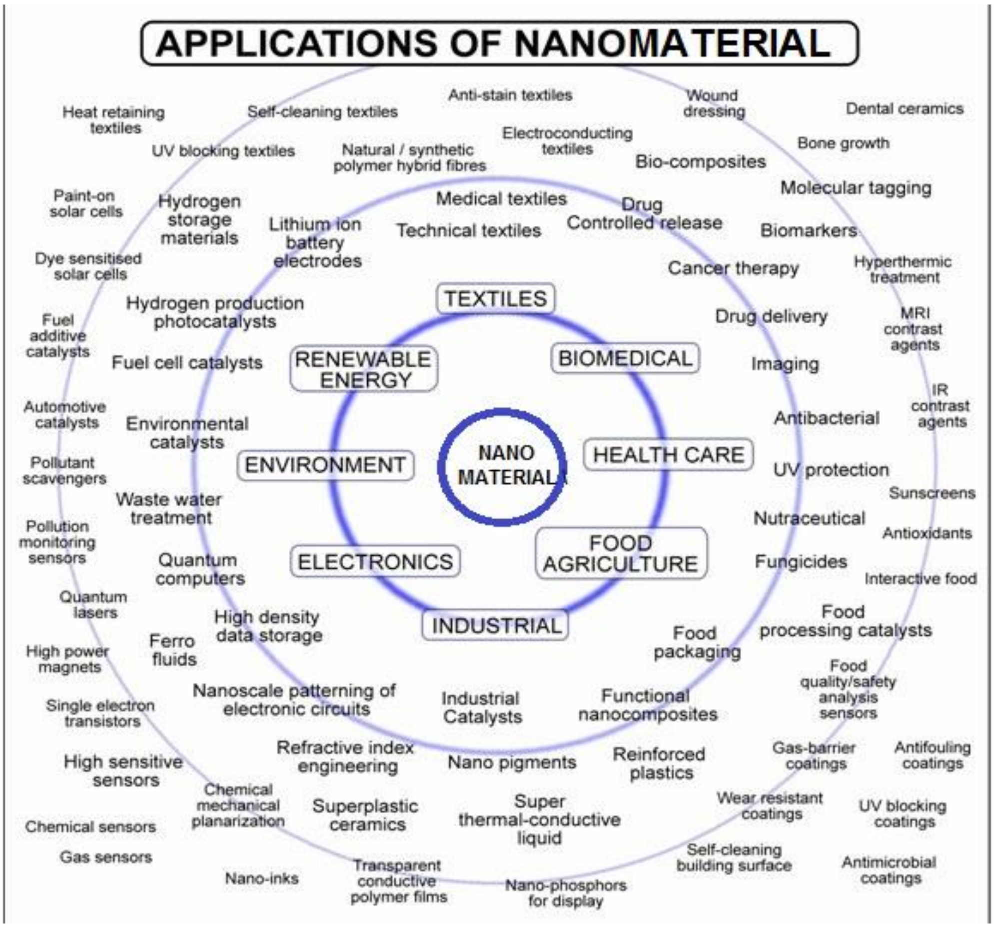


Fig. 1.1. Applications of nanomaterial (Source: Source: enteknomaterials.com)

1.2. Quantum Dots

1.2.1. Definition

Nano materials are materials whose scale ranges from 1 to 100 nanometer in size [1]. 3D or 3 dimensional nanomaterials are those that having all of their three dimensions in nanometer range. 2D or 2 dimensional nanomaterials are those that have two out of three dimensions in the nanometer range. 1D or 1 dimensional nanomaterials are thise that have one out of three dimensions in the nanometer range and then comes the 0D or zero dimensional nanomaterial that has all of its three dimensions in the nanoscale range [2]. quantum dot can also be called as zero dimensional semiconducting nanomaterial.The confinement takes place because of the production of electrostatic potential due to impurity, strains, doping etc or because of the interface of different semiconducting materials, semiconducting surface or their combination [3]. Though a quantum dot is a crystal even then its behavior is similar to an individual atom so it is also called artificial atom.

1.2.2. Uses

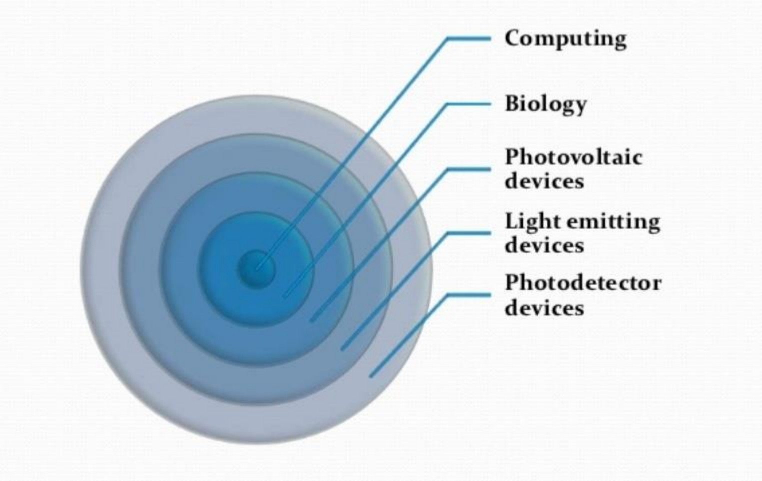


Figure 1.2. Applications of quantum dot (Source: slideshare.net)

1.3. Tin Oxide (SnO_2)

Tin dioxide (tin(IV) oxide) or stannic oxide, is an inorganic compound with the formula SnO_2 also called as Cassiterite in it's mineral form which is the main ore of tin [4]. Tin Oxide is a colourless, amphoteric and diamagnetic solid and the most important material in tin chemistry.

The chemical information of tin oxide are given below.

Table 1.1 Chemical data for SnO_2

Chemical Data	
Chemical symbol	SnO_2
Group	Tin 14, Oxygen 16
Electronic configuration	Tin [Kr]$4d^{10}$ $5s^2$ $5p^2$, Oxygen[He] $2s^2$ $2p^4$

Table 1.2. Chemical composition of SnO_2

Chemical Composition	
Element	**Content (%)**
Tin	78.80
Oxygen	21.20

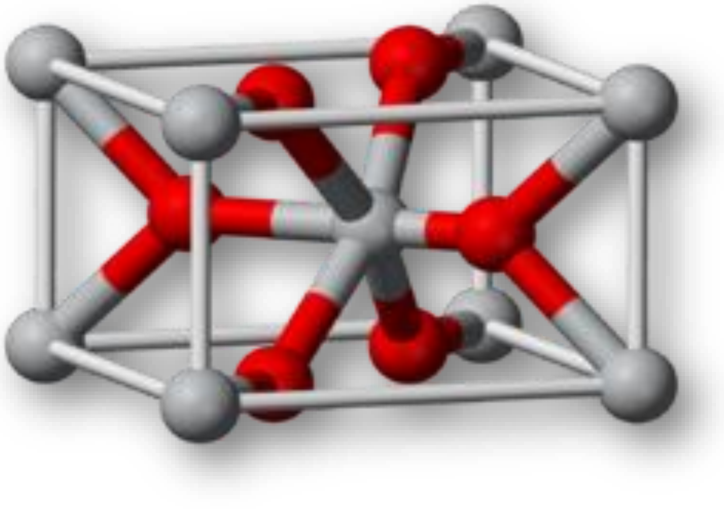


Fig. 1.3. Structure of SnO_2: Red denotes oxygen, White denotes tin.
(Source: chemistry.stackexchange.com)

Fig. 1.4. Tin oxide (SnO_2) powder (Source: chemistry.stackexchange.com)

Some applications of tin oxide are as follows:

- Due to its magnetic properties it is used in Magnetic data storage and in magnetic resonance imaging.

- As a catalysts, in energy-saving coatings and in anti-static coatings.
- As electrodes like anode material in lithium ion batteries.
- In anti-reflection coatings used in solar cells.
- In making gas sensors [5], [6], optoelectronic devices and resistors [7].
- Making of liquid crystal displays (LCD).

Nanomaterial's properties vary from that in their bulk state. A large number of efforts are being made towards the development of nanometer sized materials in order to understand their basic functioning, the various effects imposed by their size, the quantum effect and how to effectively use these materials by finding all possible uses by knowing their properties. Materials of nanometer size along with semiconductor materials have a large potential in industrial applications. Metal oxide semiconductors are of low cost and can serve as effective gas sensing materials. What makes tin oxide (SnO_2) stand apart from other metal oxides is its gas sensitivity, transparent nature and high conductivity, gas sensitivity, transparent nature and high conductivity.

SnO_2 is an n-type semiconducting compound having a wide energy band gap of 3.6 eV [8] which has attracted the attention of researchers to find its all possible usage in the fields of science and engineering like in making transparent conducting films [9], monitoring the environment, in making bio-chemical sensor [10], lithium ion rechargeable batteries, as catalytic materials [11], in dye-sensitized solar cells [12] and ultrasensitive gas sensors.

There are a number of processes that have been developed to effectively manufacture SnO_2 in nanostructured form. Some important ones are spray pyrolysis, chemical vapor deposition [13], hydrothermal method [14], solvothermal, evaporating tin grains in air, thermal evaporation of tin oxide powder , rapid elemental tin oxidation, the sol-gel method [15], etc.

Quantum dots (QDs) are semiconducting inorganic nanocrystals whose dimensions are small or equal to the exciton Bohr radius of the material, such that there is confinement in nanosized region for both the carriers and excitons in the 3D. Because of this there is unsual transformation in structure, electronic states become discrete and optical properties change. Further blue shift takes place in quantum dots. Surface atoms play a pivotal role as QD have surface-to-volume ratio value high with less surrounding coordinate atoms that ae taken as defects when contrasted with bulk atoms. Additional electronic states are formed in the band gap due to these defects, that have the property to mix with intrinsic states of the material and thus have effect on energy level spacing and properties related to optics for quantum dots. Therefore, quantum dots show a wide spectrum of properties added with a wide range of applications in opto-electronics, telecommunications, optical-sensors and laser. Exciton Bohr radius of SnO_2 is approximately 2.7 nm [16].

1.4. Literature Review

There is an increase in research on tin oxide as it has a large number of applications like in photovoltaic device [12], gas sensor [5],[6], as electrode, in liquid crystal displays (LCD), photo sensor, resistors [7], as a catalyst [11] etc. Tin oxide is crucial material because of its transparent nature in visible spectrum, as it possesses interactions on adsorbed species which are both physically and chemically strong, it operates at a low temperature and has high thermal stability which is as high as upto 5000^{o}C. Tin occurs in two oxidation states +2 and +4, therefore two types of oxides are possible in nature which are stannous oxide (SnO) and stannic oxide (SnO_2). Between the two oxides, SnO_2 is more stable than SnO.

The magnetic, optical, catalytic and electronic properties of nanomaterials have a strong dependence on theie size, structure and shape, which makes their behavior different from their bulk form. The decrease in particle size leads to a change in semiconductor band structure. As the band gap increases and band edges splits into decreases energy levels.

On comparing to the bulk SnO_2, the sensor that works based on SnO_2 quantum dot has shown a better response on getting exposed to H_2S. Chen et al showed that tin oxide nanocomposites have notable potential in developing advanced materials that can serve numerous functionality [17]. Tin dioxide (SnO_2) is an important material because it has high mobility of electron and its band gap is wide. SnO_2 quantum dots and graphene composites have been successfully created by making use of facile ultrasonic method. In this method, SnO_2 nanoparticles are placed such that they prevent the restacking of graphene nanosheets during the reduction process. Upon calcination, the SnO_2 nanoparticles gets distributed uniformly on the graphene which further enables the production of SnO_2 quantum dots.

Green synthesis of SnO_2 quantum dots (QDs) has been made possible by using microwave heating method which uses amino acids such as asparitic and glutaimic acid. This method results producing spherical SnO_2 QDS which have their average diameter within the range of tin oxide’s bohr exciton radius. A simple hydrothermal process was demonstrated by Zhu et al [18] for the synthesis of SnO_2 quantum dots (QDs), which used hydrazine hydrate as the mineralizer instead of NaOH which gave the diameter of the SnO_2 nanoparticles in the range of 2.3–3.1 nm , with most of the nanoparticles having smaller diameter than the exciton Bohr exciton radius of SnO_2 (2.7 nm) and the band gap of the SnO_2 quantum dot has been shown to be 3.88 eV.

The SnO_2 nanoparticle based gas sensors have stable response, smaller size, economical, reliable,small size, good mechanical strength and faster response [19]. It also has a strong physical and chemical interaction with adsorbed species and its thermal stability in air is up to $5000^{o}C$. These changes in the properties of SnO_2 due to gas adsorption are related to the nonstoichiometry, average coordination number per grain and the neck size effect in the functional material.

Solution-processed SnO_2 colloidal quantum dots (CQDs) have emerged as an important new class of gas-sensing materials due to their potential for low cost and high-throughput fabrication. The design strategy is based on the synergetic effect from highly sensitive SnO_2 CQDs and excellent conductive properties of multiwalled carbon nanotubes (MWCNT) to overcome the transport barrier in CQD gas sensor [20]. The attachment and coverage of SnO_2 CQDs and MWCNTs at room temperature. Compared to the pristine SnO_2 CQDs, the sensor based on SnO_2 quantum dot/ MWCNT nanocomposite exhibits higher response upon exposure to H_2S.

CHAPTER 2

EXPERIMENTAL METHOD

All the chemicals that were used were of analytical grade. In this synthesis we took 0.5 g of tin chloride ($SnCl_2.2H_2O$) and dissolved it in 50 mL of methanol while stirring magnetically for 1 hour. After $SnCl_2$ source gets completely dissolved, 2 mL of NH_3 solution was added dropwise to the main solution and the final pH of the solution was adjusted to be 9. The solution was then heated at 90^oC and this temperature was maintained for 4 hours. During the process tin hydroxide precipitate was formed. The precipitate formed during the process was separated by centrifugation by centrifuging at 5000 rpm for 10 minutes and was washed repeatedly with water and ethanol to remove the byproducts. The tin oxide was obtained after the calcination of the precipitate at 200^oC, 300^oC and 400^oC for 2 hours.

The chemical reaction mechanism involved in the synthesis SnO_2 Quantum Dot is:

$SnCl_2 + 2CH_3OH \rightarrow Sn(OH)_2 + 2CH_3Cl$

$Sn(OH)_2 + 2CH_3Cl + 2NH_4OH \rightarrow Sn(OH)_2 + 2NH_4Cl + 2CO_2 + 4H_2$

$Sn(OH)_2 \rightarrow SnO + 2H_2O$

$2SnO + O_2 \rightarrow 2SnO_2$

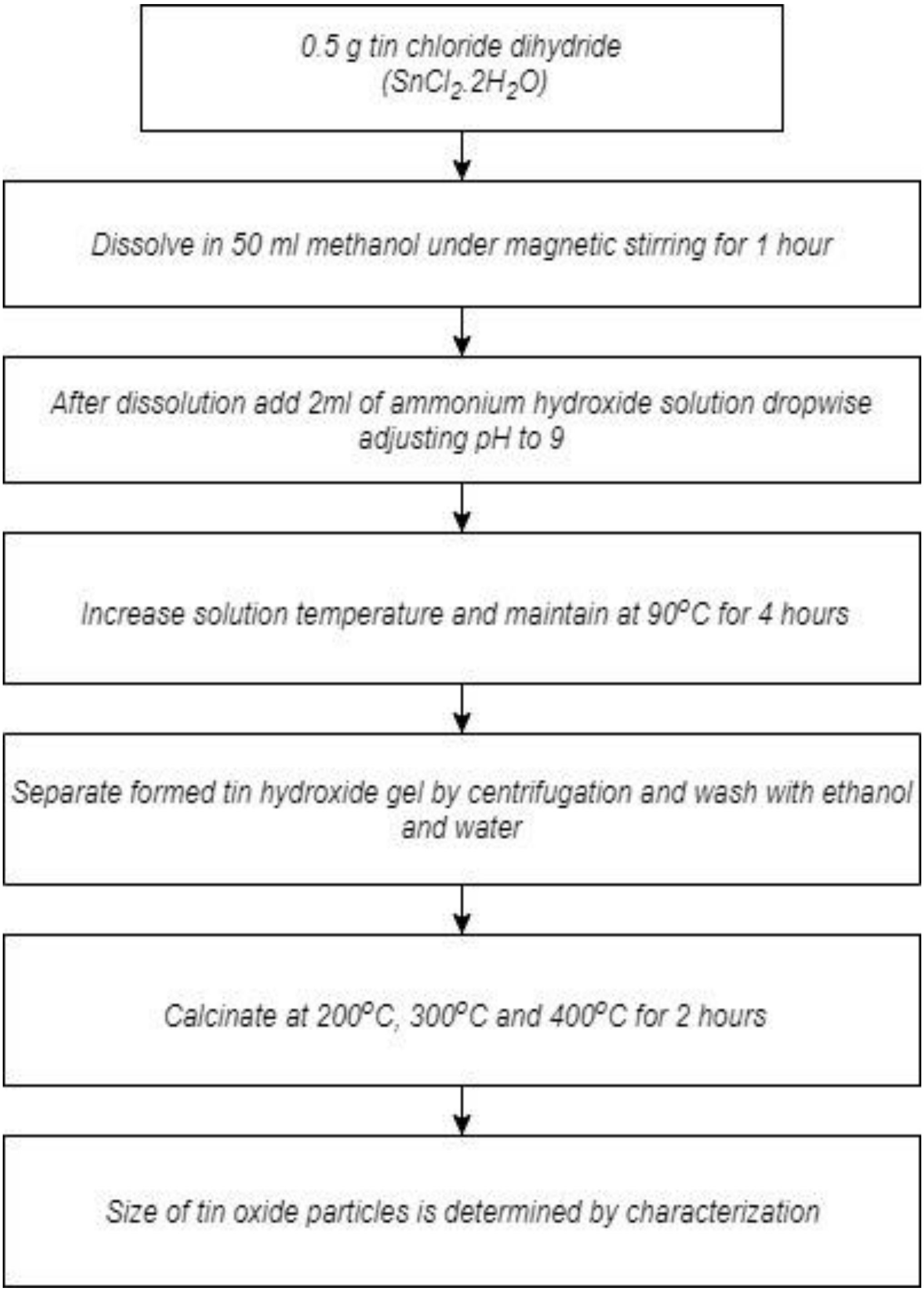


Fig. 2.0. Experimental procedure flowchart

CHAPTER 3

RESULTS AND DISCUSSION

3.1 XRD ANALYSIS

The XRD patterns for the nanoparticles produced at 200^o C (Fig. 3.1) shows peaks produced shows diffraction peak at 2θ values of 26.60^o for plane (110), 34.22^o for plane (101), 51.74^o for plane (211), and 65.30^o for plane (112) which follows the tetragonal rutile structure of SnO_2 nanoparticles. The SnO_2 quantum dot synthesized at 300^o C (Fig. 3.2) shows diffraction peak at 2θ values of 26.91^o for plane (110), 34.09^{o}for plane (101), 38.02^o for plane (200), 52.12^o for plane (211), 54.9^o for plane (220), 58.07^o for plane (002), 62.1^o for plane (310) and 65.81^o for plane (301) which is in agreement with the structure of SnO2 nanoparticles. Further the XRD pattern of SnO_2 quantum dot formed at 400^{o}C (Fig. 3.3) shows diffraction peaks at 2θ values of 26.8^o for plane (110), 34.13^o for plane (101), 39.28^o for plane (200), 52.05^o for plane (211), 55.04^o for plane (220), 58.13^o for plane (002), 62.23^o for plane (310), 65.01^o for plane (112) and 66.18^o for plane (301). The XRD pattern is confirming the structure of SnO_2 nanoparticles formed at the calcination temperature of 200^{o}C, 300^{o}C and 400 ^{o}C.

As it can be seen that peaks are getting sharper as we have increased the calcination temperature from 200^{o}C to 400 ^{o}C and the full width half maximum (FWHM) has been brought down to a lower value on increasing the temperature. This accounts for the fact that there is an increase in particle size and crystallinity on increasing the calcination temperature from 200^{o}C to 400 ^{o}C. Debye-Scherrer equation could be used to calculate the average size of SnO_2 nanoparticle which has been formed at different calcination temperatures. The Debye-Scherrer equation is given as :

$$D = \frac{k\lambda}{b\cos\theta} \tag{3.1}$$

where D is the crystallite size, λ is the X ray wavelength (Kα(Cu)= 0.154056 nm), b is the full width half maximum (FWHM) of the diffraction peak, θ is the Bragg diffraction angle and k is the shape factor which has a value of 0.96. The average size of SnO_2 nanoparticles formed at 200ºC, 300ºC and 400ºC was then determined from the Debye-Scherrer equation and was found out to be 2.5 nm, 4.5 nm and 8 nm, respectively. This increase in size could be associated to the fact that at high temperature, the neighbouring particles cluster up and this leads to an increase in the grain size of SnO2 nanoparticle. This shows that the size of SnO_2 nanoparticle increases on increasing the calcinations temperature. Hence, it is obvious that the size of SnO_2 nanoparticles can be changed by controlling the temperature of the reaction.

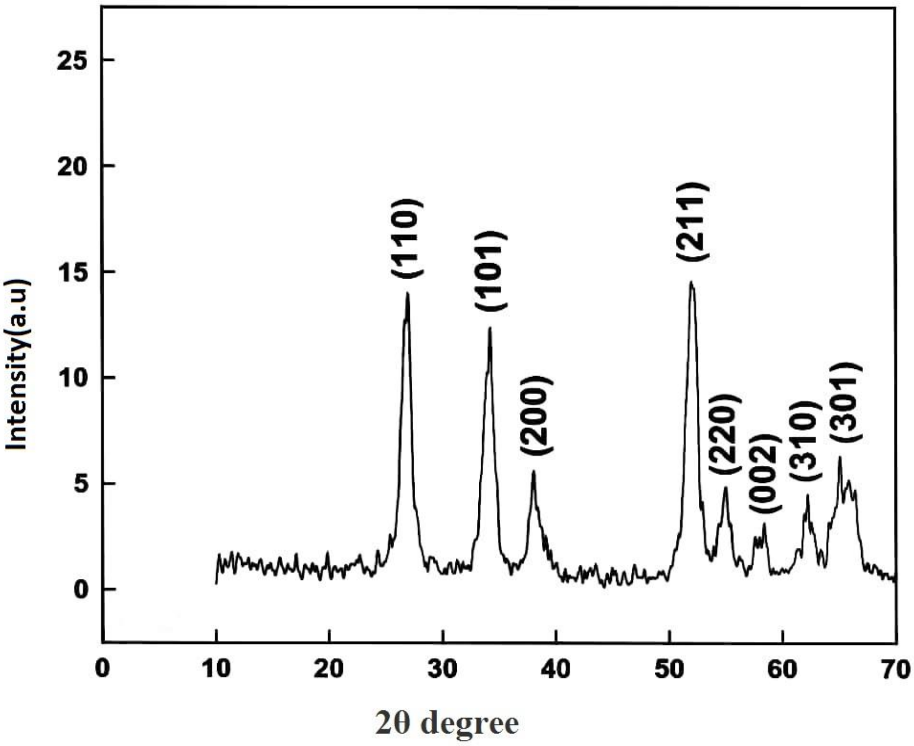


Fig. 3.1. XRD pattern of SnO_2 nanoparticles at 200º C

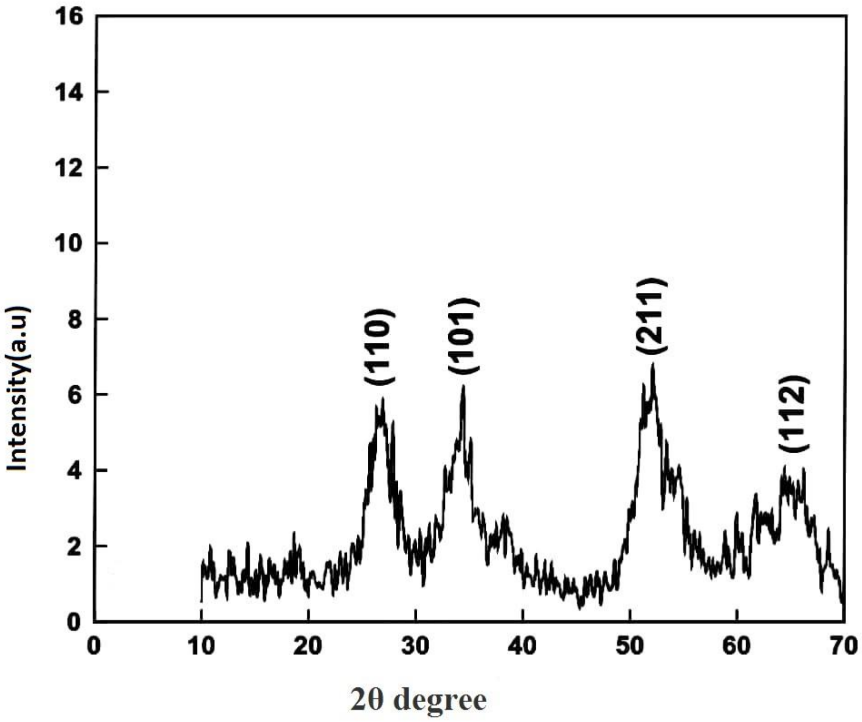


Fig. 3.2. XRD pattern of SnO_2 nanoparticles at 300^O C

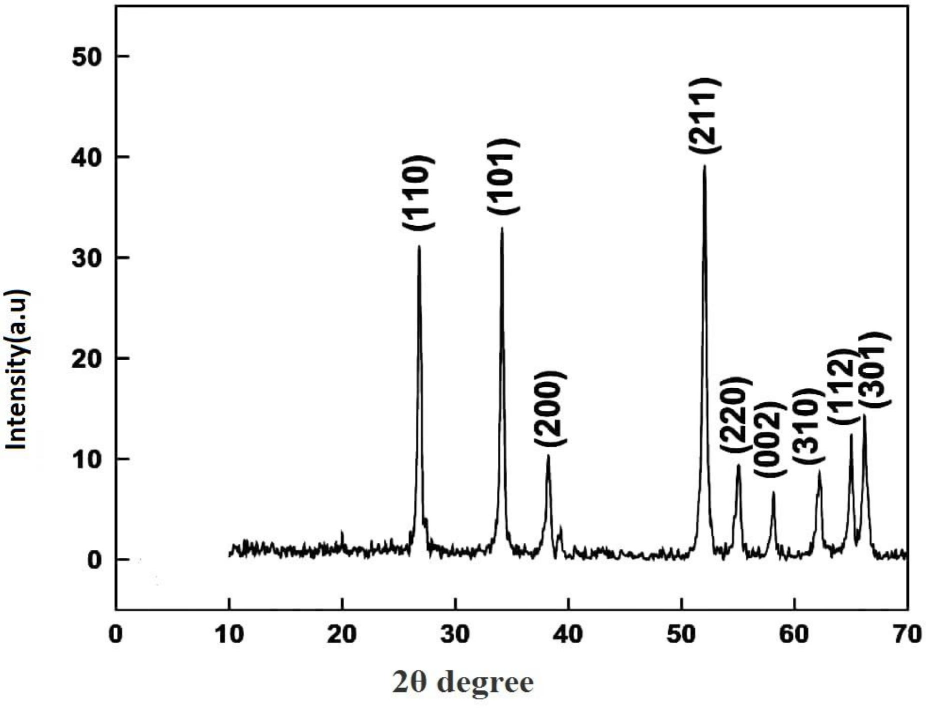


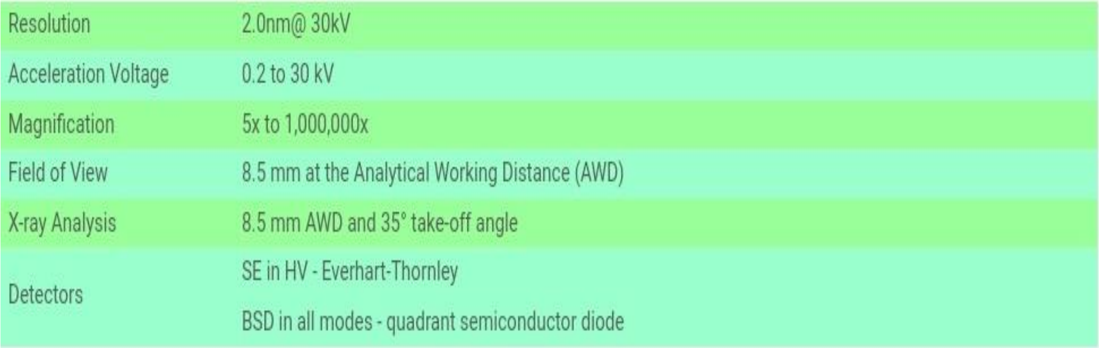
Fig. 3.3. XRD pattern of SnO_2 nanoparticles at 400^O C

3.2. SEM ANALYSIS

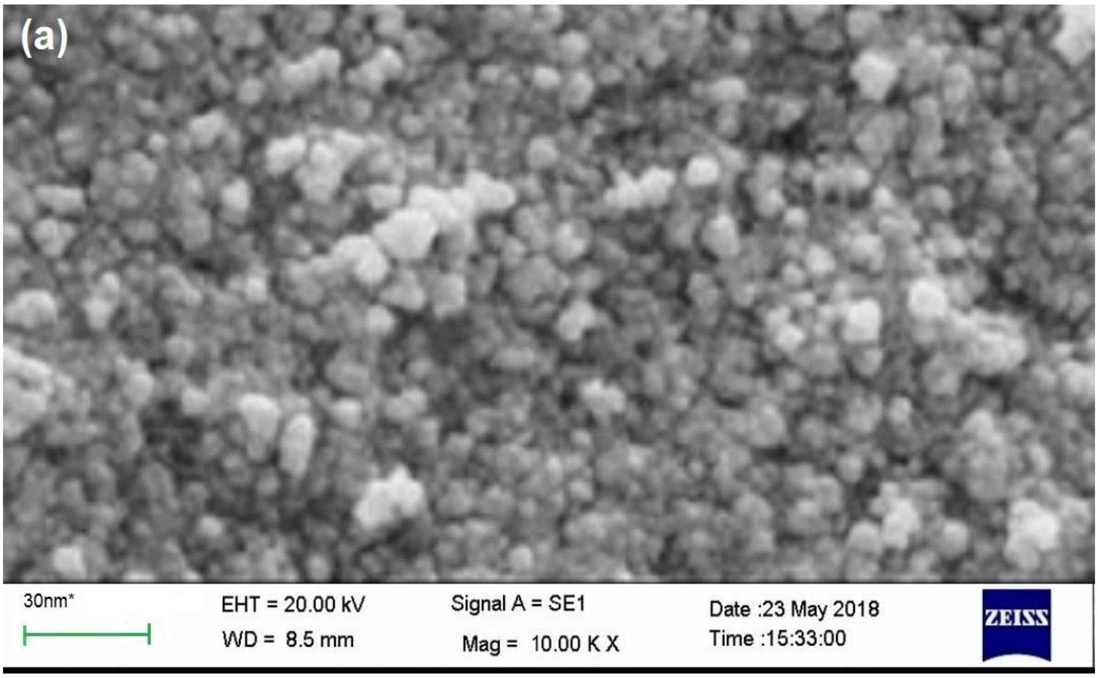
SEM analysis (Scanning Electron Microscope used was CARL ZEISS EVO 50V as shown in Fig. 3.4) shows that spherical structures of SnO_2 have been synthesized at 200ºC (Fig. 3.5), 300ºC (Fig. 3.6) and 400ºC (Fig. 3.7). The size of particle synthesized was found out by debye- scherrer formula to be 2.5 nm for particle synthesized at 200ºC which is within the quantum range as its size is less than the bohr exciton radius of 2.7 nm. Thus quantum dot of SnO_2 have been formed.

Fig. 3.4. Scanning Electron Microscope, CARL ZEISS EVO 50V (Source: iitk.ac.in)

The various specifications of the SEM (Fig. 3.4) used for analysis are:



Resolution	2.0nm@ 30kV
Acceleration Voltage	0.2 to 30 kV
Magnification	5x to 1,000,000x
Field of View	8.5 mm at the Analytical Working Distance (AWD)
X-ray Analysis	8.5 mm AWD and 35° take-off angle
Detectors	SE in HV - Everhart-Thornley
	BSD in all modes - quadrant semiconductor diode



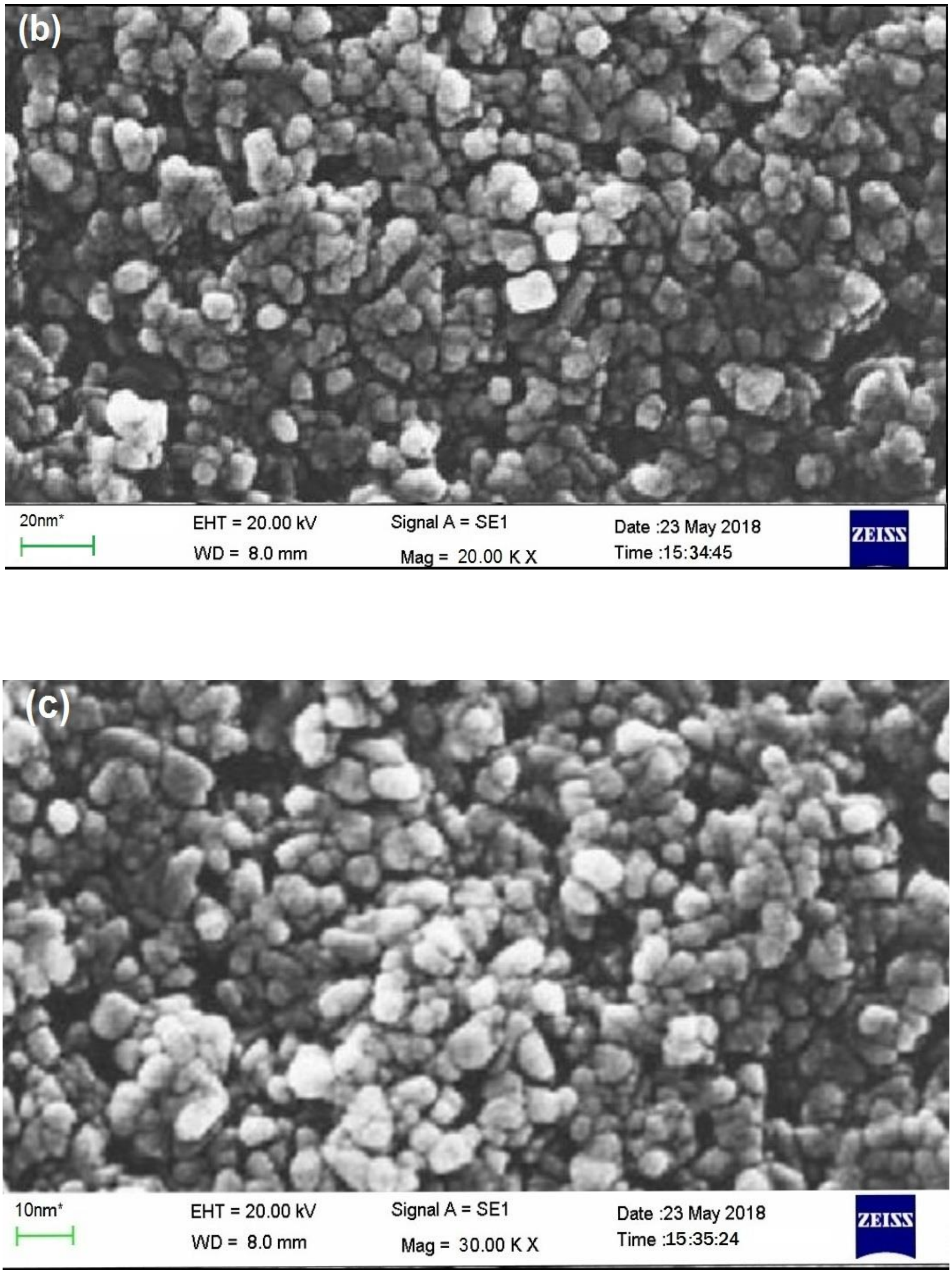
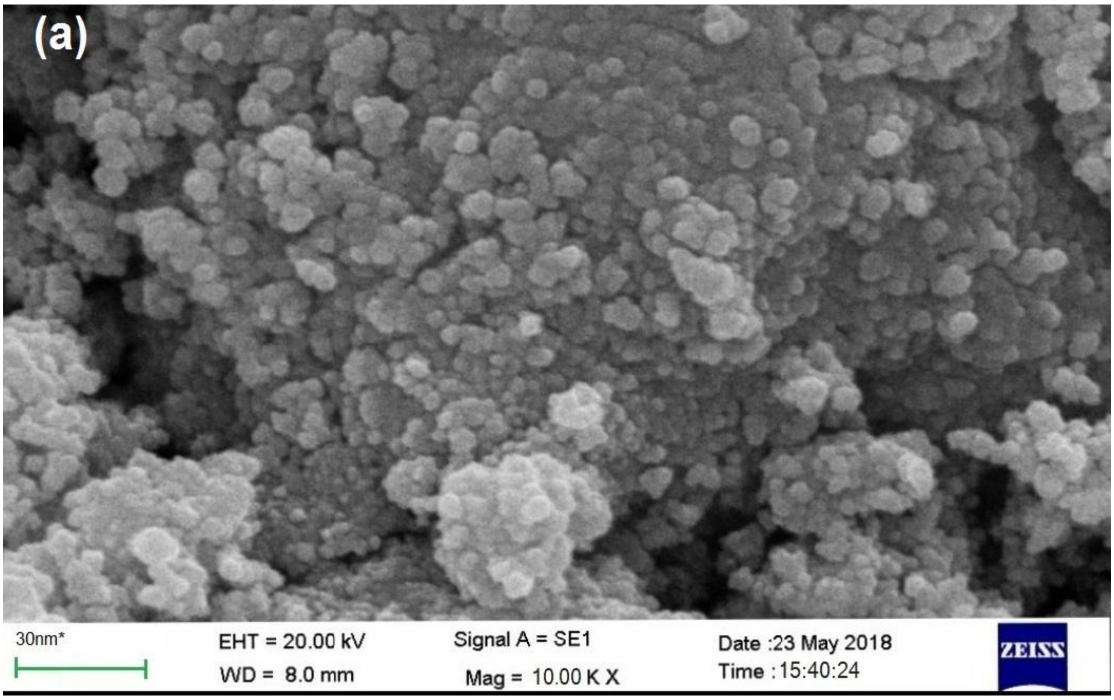


Fig. 3.5. SEM images of SnO_2 nanoparticles at 200°C


(a)
30nm*
EHT = 20.00 kV
WD = 8.0 mm
Signal A = SE1
Mag = 10.00 K X
Date :23 May 2018
Time :15:40:24
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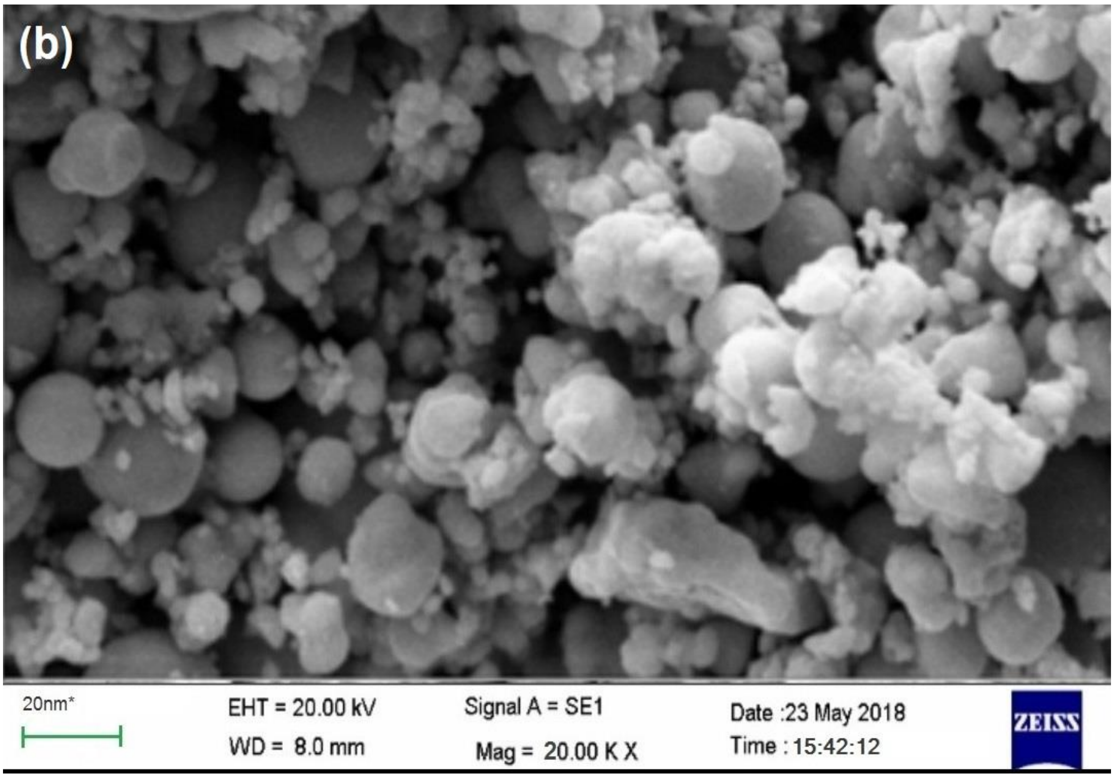
(b)
20nm*
EHT = 20.00 kV
WD = 8.0 mm
Signal A = SE1
Mag = 20.00 K X
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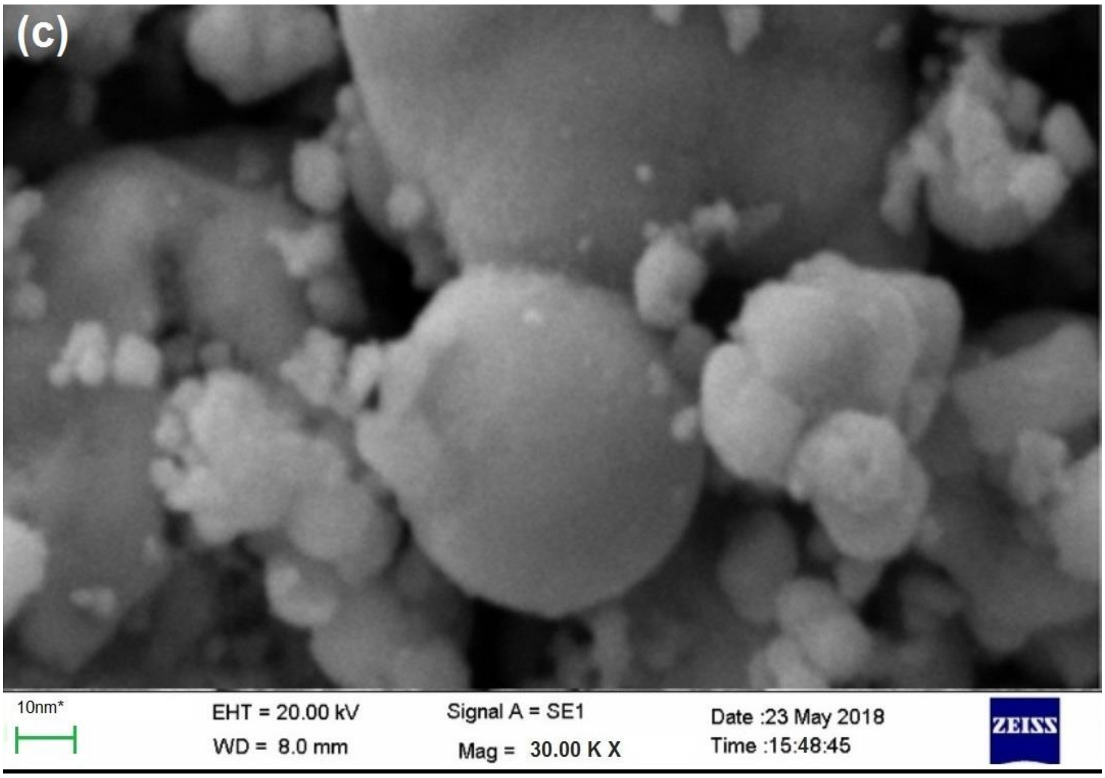
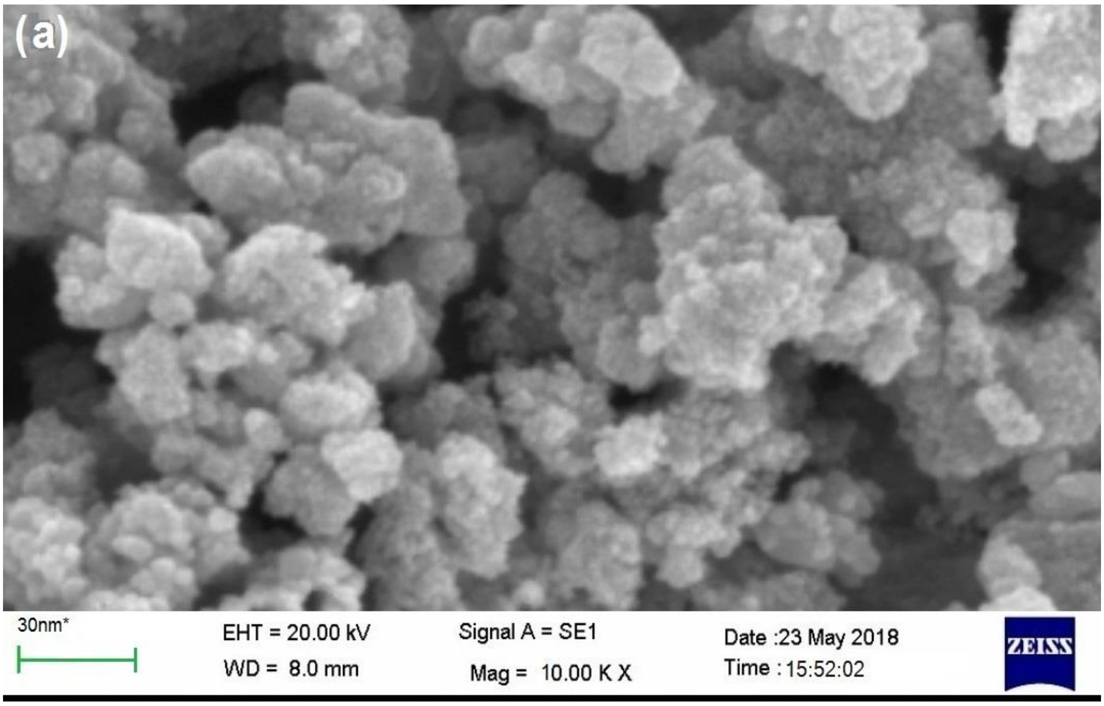


Fig. 3.6. SEM images of SnO_2 nanoparticles at 300ºC



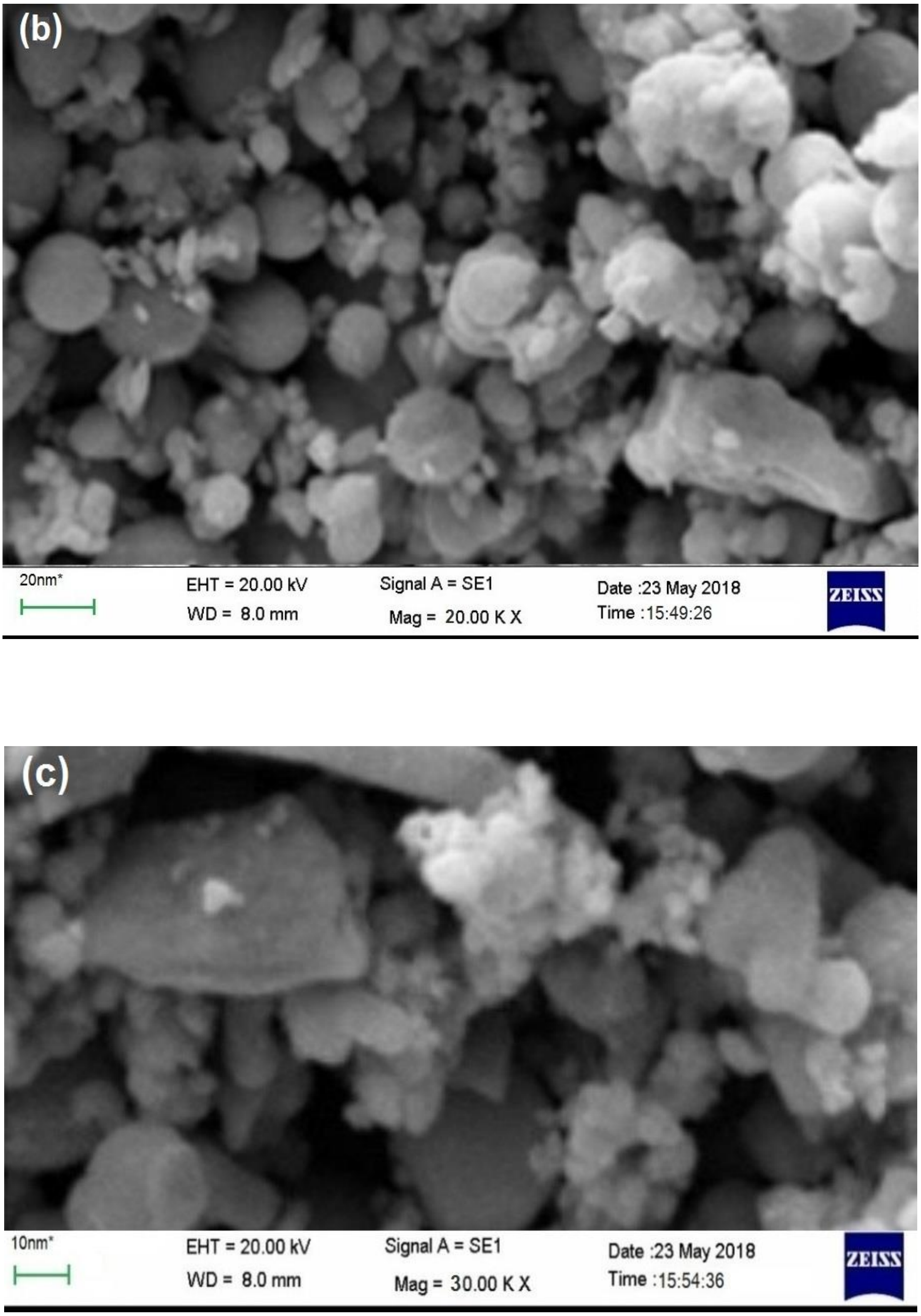


Fig. 3.7. SEM images of SnO_2 nanoparticles at 400°C

3.3 EDX ANALYSIS

EDX analysis is done to get information about the elemental composition of a sample as well as the composition in terms of weight percentage of the elements present in the sample (The EDX analysis of this study was done at Indian Institute of Technology, Kanpur) The results are as given below in Fig. 3.8, Fig. 3.9 and Fig. 3.10.

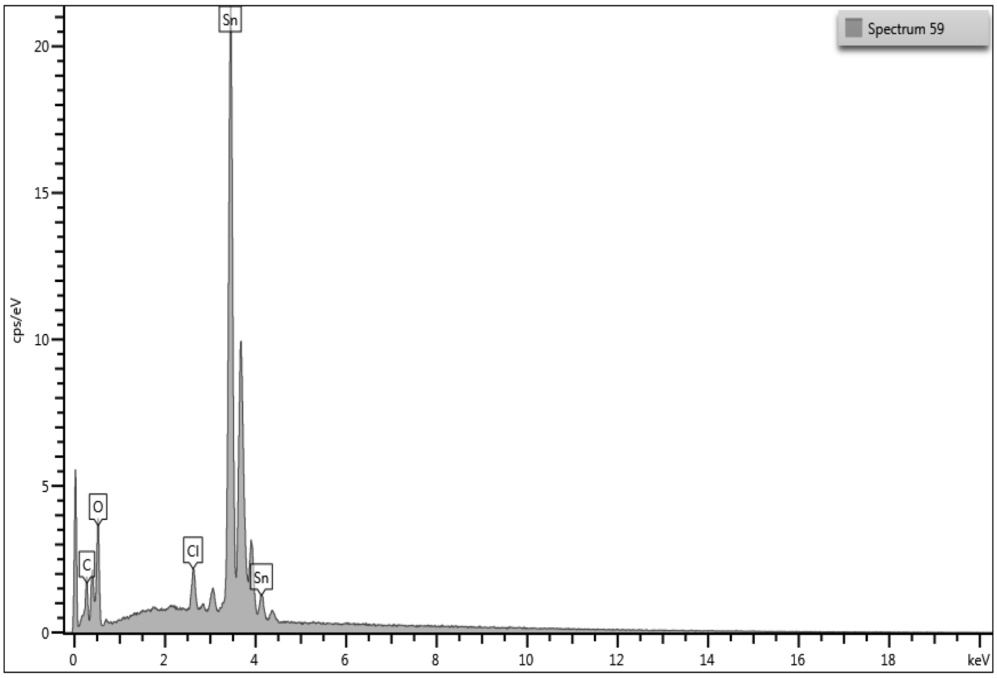


Fig. 3.8. EDX spectra of SnO_2 nanoparticles at 200ºC

Table 3.1. Elemental composition of SnO_2 nanoparticles at 200ºC

Element	Weight %
C	2.26
O	17.81
Cl	1.69
Sn	78.24
Total	100.00

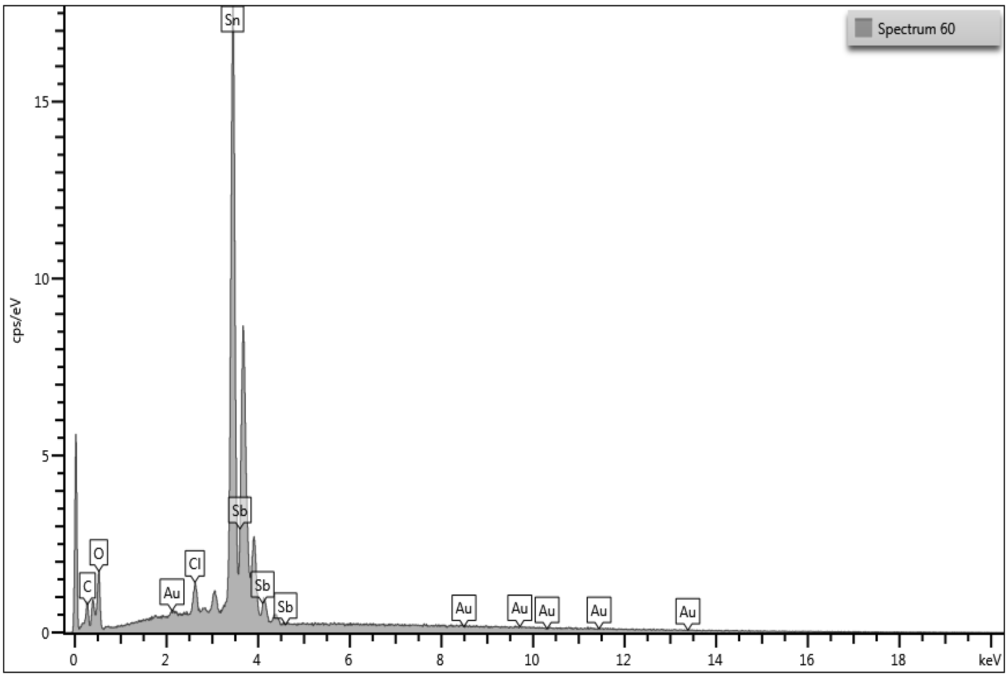


Fig. 3.9. EDX spectra of SnO_2 nanoparticles at 300ºC

Table 3.2. Elemental composition SnO_2 nanoparticles at 300ºC

Element	Weight %
C	1.28
O	16.17
Cl	1.21
Sn	79.77
Sb	0.87
Au	0.63
Total	100.00

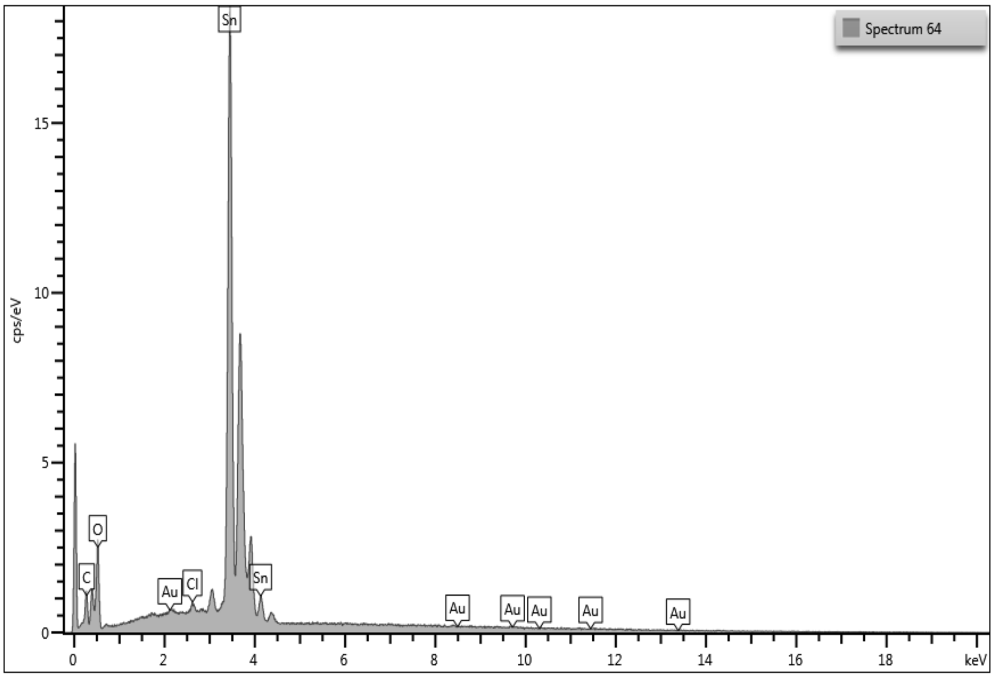


Fig. 3.10. EDX spectra of SnO_2 nanoparticles at 400^oC

Table 3.3. Elemental composition SnO_2 nanoparticles at 400^oC

Spectrum Label	Spectrum 64
C	1.36
O	16.65
Cl	0.33
Sn	81.24
Au	0.42
Total	100.00

It can be seen from the EDX analysis data as shown in Table 3.1, Table 3.2 and Table 3.3 that the ratio of Tin (Sn) and Oxygen (O) is quite consistant with the amount of Tin and Oxygen that is supposed to be present in an SnO_2 sample that is 78.80% of Tin and 21.20% of oxygen.

3.4 FTIR ANALYSIS

FTIR (Fourier Transform Infrared Spectroscopy) gives us the information about the various bonds present in a given sample with special emphasis on the presence of covalent bond. From the FT-IR spectra observed from the SnO_2 nanoparticles at 200ºC (Fig. 3.11), 300ºC (Fig. 3.11) and 400ºC (Fig. 3.11) we find that the peaks are observed in the range 655-615 cm^{-1} is due to presence of Sn-O-Sn stretching vibration mode of surface bridging oxide bond. Band close to 525-535 cm^{-1} is due to Sn –O bond vibration of Sn-OH group. We also see a peak at 3660-3670 cm^{-1} is due to presence of –OH group. Further on increasing calcinations temperature from 200ºC, 300^0C and 400ºC the intensity close to 620 cm^{-1} increases while intensity close to 525cm^{-1} decreases that means increment in temperature leads to conversion of Tin(II) hydroxide (SnOH) to Tin oxide (SnO_2). (The FT-IR study was conducted at Central Instrumentation Facility, Jamia Milia Islamia using Bruker TENSOR 37 FTIR Spectrometer as shown in Fig. 3.14).

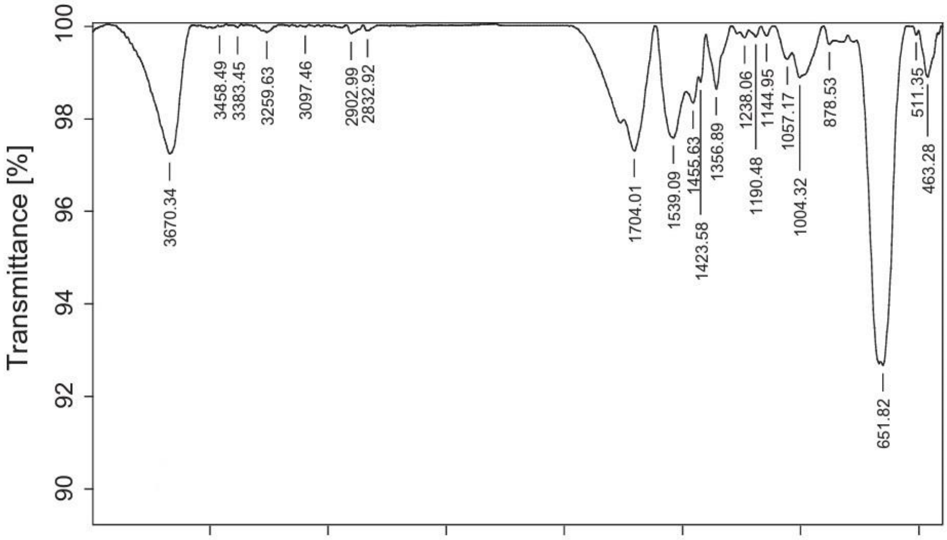


Fig. 3.11. FTIR spectra of SnO_2 nanoparticles at 200ºC

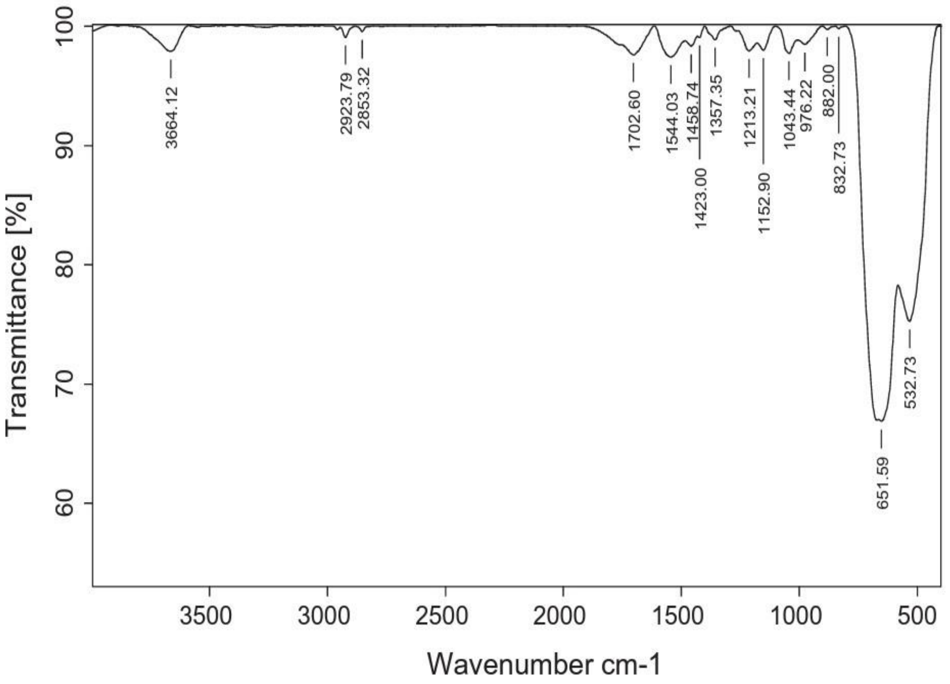


Fig. 3.12. FTIR spectra of SnO_2 nanoparticles at 300°C

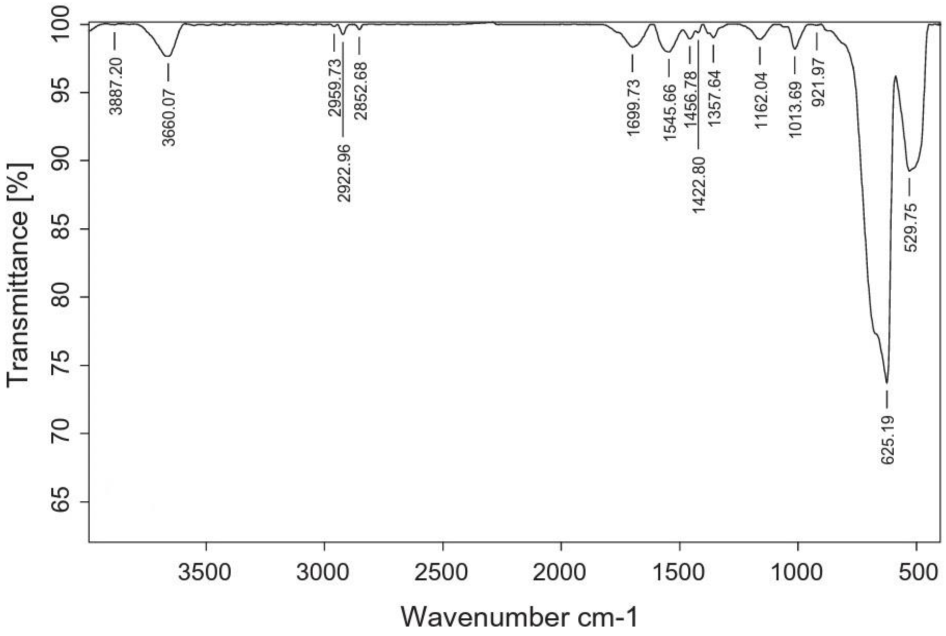


Fig. 3.13. FTIR spectra of SnO_2 nanoparticles at 400°C

Fig. 3.14. FTIR Spectrometer (Source: chem.ch.huji.ac.il)

CHAPTER 4

CONCLUSIONS

In the above study we have synthesized SnO_2 nanoparticles by sol-gel method which is a practical and economical method for synthesis and found that on increasing the calcination temperature from 200^oC to 400^oC the size of the particles changes being 2.5 nm for 200^oC, 4.5 nm for 300^oC and 8 nm for 400^oC as calculated by the debye-scherrer formula from the XRD data. From the above characterization techniques we have also found that the synthesized SnO_2 nanoparticles are spherical in shape as seen from the SEM images. The characteristic peaks in the XRD pattern gives characteristic diffraction peaks in agreement with the rutile structure of SnO_2. EDX data suggests that the composition of prepared nanoparticles is similar to the pristine SnO_2 particles. The particles obtained at 200^oC with size 2.5 nm are smaller than Bohr exciton radius for SnO_2 which is 2.7 nm which confirms the quantum confinement of the nanoparticles prepared at 200^oC. Such quantum dots could be further used in Li-ion batteries, catalytic reaction, sensing, solar cell and so on.

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