GROWTH AND CHARACTERIZATION OF ELECTROSPUN SnO_2NANOFIBERS BY ELECTROSPINNING TECHNIQUE*

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Abstract

Tetragonal tin oxide (SnO_2) nanoparticles of the range 80 nm have been successfully synthesized by a direct precipitation from an aqueous solution in the presence of stannous chloride dehydrate ($SnCl_2.2H_2O$) and ammonium hydroxide. The final products was ground into a fine powder and then annealed at 650˚C for 6 h. Characterization of the materials was carried out using technique such as scanning electron microscope and the optical studies were carried by UV-Vis absorption. SnO_2 nanofibers were fabricated by home-made electrospinning with vertical experimental set up. The electrospinning solution was prepared by homogeneous viscous solution of tin acetate in polyvinyl alcohol (PVA). The electrospinning were under taken by applying a DC voltage of 20 kV to the tip of a syringe and maintaining the tip to collector distance (TCD) of 5 cm, 7 cm, 10 cm and 12 cm. The spinning or running time interval was set to 4 h. The green nanofibers were calcined at 600˚C for 1 h. The XRD analysis revealed that nanofibers were phase pure and all materials exhibited a tetragonal rutile structure of SnO_2. The nanofibers treated at 600˚C was examined by field emission scanning electron microscope (FESEM).The functionalize sample surface at a nanometer range of SnO_2nanofibers were examined by Atomic Force Microscopy (AFM). The SEM and AFM shows cylindrical fibers with diameter in the range of 47 – 100 nm. In general, average diameter of the fibers decreased with decrease in TCD.

Keywords: Tin acetate, polyvinyl alcohol, Nanofibers, TCD, Electrospinning

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Introduction

Nano-sized tin oxide (SnO_2) is an interesting semiconducting material with a wide band gap and one of the most widely used due to its chemical and mechanical stabilities [H. Kose et al and Lucky M Sikhwivhilu et al]. Tin oxides (SnO_2) are widely used 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 and many other application [Asama. N. Naje et al, Nehru L.C. and V. Senthilkumar et al]. Many process have been developed to the synthesis of tin oxide (SnO_2) nanostructures, for example, spray pyrolysis, hydrothermal method, evaporation tin grain in air, chemical vapor deposition (CVD), thermal evaporation of oxide powders, rapid oxidation of elemental tin, the sol-gel method and etc. [Ganesh E Patil]. One-dimensional nanostructure, tin oxide nanowirs, nanobelts, nanorods and nanofibers, with a high surface to volume ratio has attracted special attention in the last years. Currently, there are three techniques available for the synthesis of nanofibers: electrospinning, self-assembly and phase separation. Of these, electrospinning is the most widely studied technique and also seems to exhibit the most promising results. Moreover this technique also has important advantages such as simplicity, low cost, and easy mass production. It is one of the most useful methods for the fabrication of 1-D composite nanofibers by electro stretching [Jose Pedro Santos et al and Rajesh Vasita et al]. Electrospinning is a very simple and popular technique for fabrication of sub-micron to nanometer range fibers. It is one of the simplest method to form continuous one-dimensional nanofibers under the electrostatic force of the charges on the surface of a liquid droplet in a sufficiently high electric field, which is applied between the capillary nozzle and the metal collector [M. Chandraiah et al and Zunxian Yang et al]. In this research SnO_2nanopowders were prepared by precipitation method and the resulting powders were characterized by UV-Vis and FESEM. Then SnO_2 nanofibers were prepared by electrospinning homogeneous viscous solution of tin acetate in polyvinyl alcohol (PVA). The SnO_2 nanofibers were also characterized by XRD, FESEM and AFM.

Experimental Procedure

Sample Preparation of SnO_2Nanopowder

In this research, Stannous chloride dehydrate ($SnCl_2.2H_2O$) was used as starting materials. The block diagram of sample investigation was described in figure 1. All chemicals were analytically pure and directly used as received without further purification. Distilled water was used as a solvent. SnO_2nanopowders have been prepared by using precipitation method. SnO_2nanopowders were prepared by means of dissolving of 2 g (0.1 M) stannous chloride dehydrate ($SnCl_2.2H_2O$) in 100 ml distilled water. 10% ammonium hydroxide was slowly added to the solution for complete precipitation of tin hydroxide in the pH range 7.5 - 9.Then the solution was put into thermostat water bath, in which the temperature was kept about 80 ˚C, for 15 minutes until white depositions came out. Then the precipitate was centrifuged and washed several time with distilled water to reduce the amount of ammonium chloride. The resulting gels was filtered and dried at 100 ˚C for 3 h. The obtained powder was collected and grounded in an agate mortar and it is referred “as – prepared”. The color of the as-prepared sample is gray. Finally the as-prepared sample was heated in a muffle furnace at 650 ˚C for 6 h in an atmosphere, then the color turned into white. Optical absorption spectra of the sample were taken with UV-1800 UV-Vis Spectrometer. Field emission scanning electron microscopy (FESEM) was employed for morphological study using JEOL JSM-5610. Atomic force microscope (AFM) (Bruker N8 Rados) was used to examine the surface morphology.

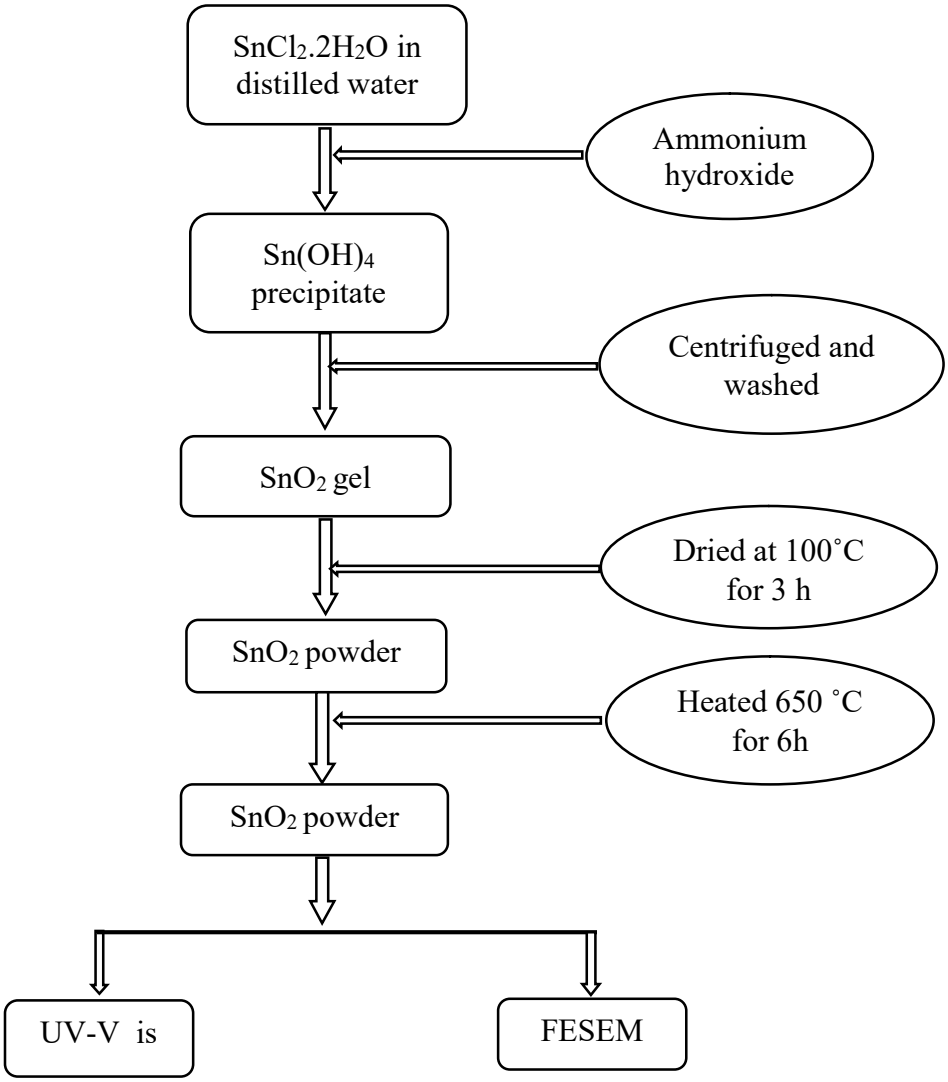

Figure 1. Block diagram of preparation for SnO_2 powder

Sample Preparation of SnO_2Nanofibers

In this study, the flow chart of experimental procedure is shown in figure 2. Tin dioxide (SnO_2), Poly Vinyl Alcohol (PVA) and distilled water were chosen as the starting chemicals and solvent. SnO_2 nanofibers were prepared by sol-gel process. 1 g of SnO_2 was dissolved in 2 ml of acetic acid with constant stirring for 10 min to obtain a clear solution of tin acetate in the pH range 1-2. This solution was mixed with 4 ml of 10 % PVA solution. The solution was stirred for 4 h by a magnetic stirrer and a viscous sol-gel was obtained with viscosity in the range of 1100-1180 cP. The solution gel was expected to be viscous enough for electrospinning. Nearly 5 ml of the viscous solution was taken in a 20 ml syringe. The distance of 5 cm, 7 cm, 10 cm and 12 cm were maintained between the collector plate and the tip of the needle. Al-substrate was then struck on the collector.

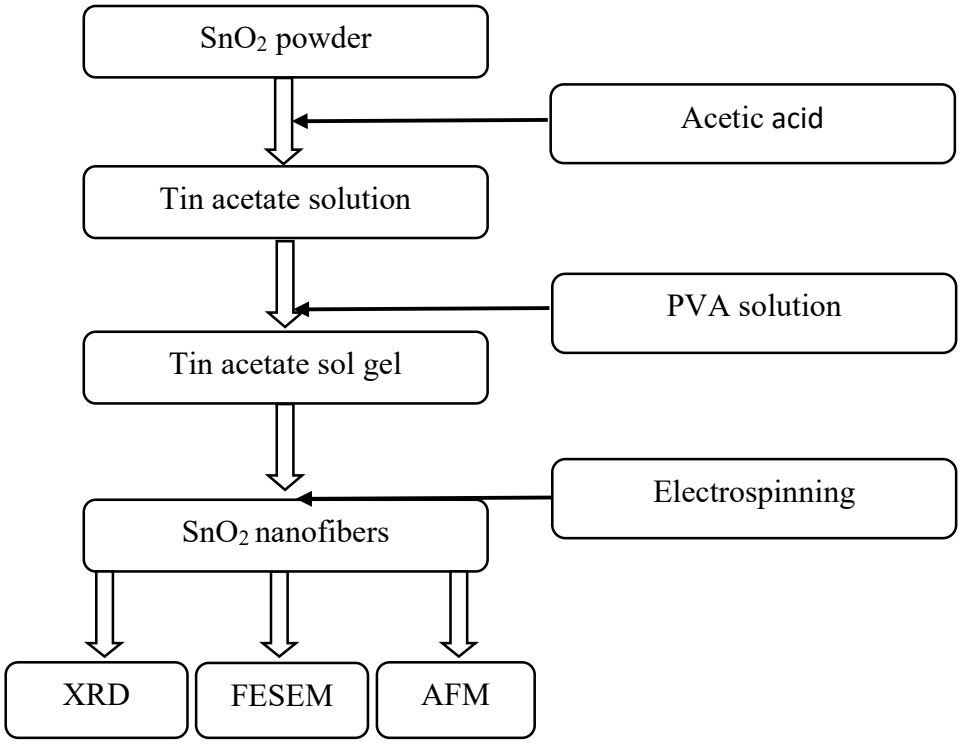

Figure 2. The flow chart of experimental procedure for SnO_2 nanofibers

Electrospinning Setup

The home-made electrospinning device consisted of a syringe, stand, high voltage DC source and a ground collector plate. The high voltage source was taken from 21" fly pad (219 x 6M, Toshiba) indirectly and the output voltage is 20 kV. The positive terminal of the DC source was connected with a needle and the Al-substrate (collector) was connected with the negative terminal to ground it. When the voltage was applied a stream of solution came out through the needle which was subdivided into a number of nano to submicron sized jets and were deposited in the form of nanofibers on the collector pate. The green nanofibers were calcined at 600 ˚C for 2 h. A typical electronspinning set up is shown in figure 3. The electrospinning conditions are mentioned in table 1. The morphology of the fibers was measured by field emission gun-scanning electron microscope (FESEM).

Table 1. The elctrospinning conditions of SnO_2 sample

Syringe capacity	**20 ml**
Tip to collector distance (TCD)	5 cm, 7 cm, 10 cm and 12 cm
Voltage	20 kV
Running Time	5 hr
Colling time	5 hr
Annealing temperature	600 ˚C
Annealing time	2 h

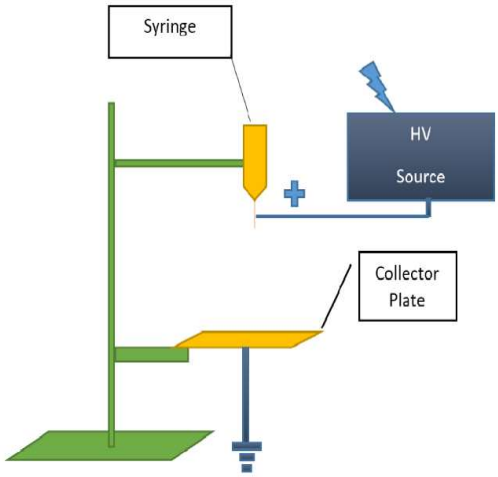

Figure 3. Schematic drawing of the electrospinning process set up

Results and Discussion

Characterization of tin oxide nanofiber by XRD analysis

According to the XRD analysis, pure tin oxide nanofiber were matched with standard library of PDF 77-0447 cassiterite tin oxide. The X-ray diffraction (XRD) pattern of SnO_2 nanoparticles fiber from $SnCl_2.2H_2O$ is shown on figure 4. There are four peaks and all of the peaks can be indexed to be pure tin oxide structure of tetragonal due to the lattice parameters agreement with the literature. The average crystallite size is 31.5 nm.

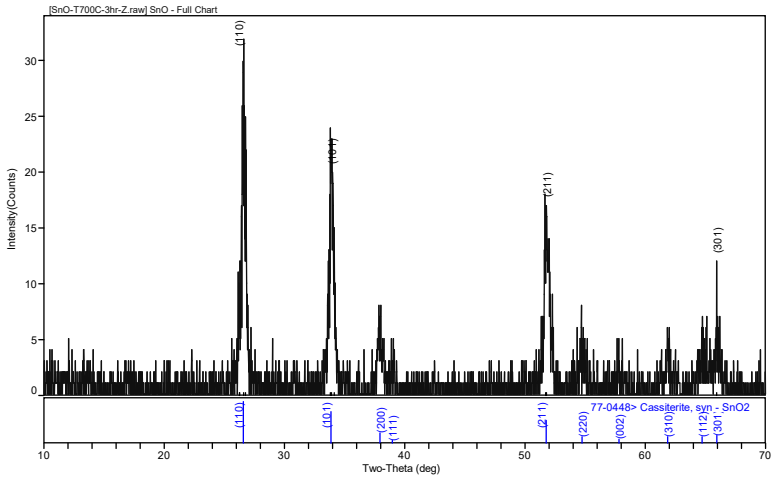

Figure 4. XRD diffractorgram of tin oxide nanofiber

UV-Visible analysis of SnO_2nanopowder

The UV-Vis spectra of SnO_2 powder was recorded with respect to the glass substrate placed in the reference beam using beam spectrometer in the range 190 to 1100 nm. The absorption spectrum of SnO_2 deposited on glass substrate is shown in figure 5. The figure shows high absorption coefficient in the UV region. It's transparent coefficient also in the UV region. The optical band energy (E_g) of the semiconductor is calculated from the relation.

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n$$

where α is the absorption coefficient, A is a constant (independent from υ) , n is the exponent that depends upon the quantum selection rules for the

particular material, h is the planck's constant and E_g the energy band gap. A plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ shows intermediate linear region, the extrapolation of the linear part can be used to calculated the E_g from intersect with $h\upsilon$ axis. The resultant values of E_g for SnO_2 is found to be about 3.82 eV. The value may be related to the formation of nanostructures of SnO_2 and the bulk SnO_2, these value show a good agreement with the values published by other researchers.

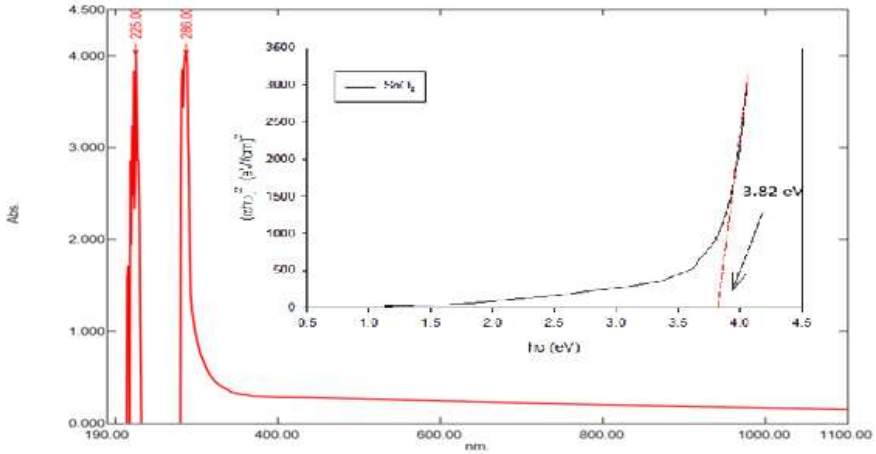

Figure 5. The absorption spectrum of SnO_2 powder

Characterization of tin oxide nanoparticles and nanofibers by FESEM

The SnO_2 powder was obtained from directed precipitation method. Figure 7 shows the FESEM analysis of the SnO_2 powder. The grain sizes were calculated by using well known bar code system. Bar code size was 1 μm. According to the calculation the grain size is 80 nm. The powders morphology was spherical in shape and then the surface was rough.

The SnO_2 fibers on aluminum foil were carried out to examine by FESEM image. In order to study the morphology and the nano structural properties of fabricated SnO_2 nanofibers for different tip to collector distance (TCD) 5 cm, 7 cm, 10 cm and 12 cm are shown in figure 8 (a) (b), figure 9 , figure 10 (a) (b) and figure 11 (a) (b). According to the FESEM analysis SnO_2nanofibers from all TCD distance reveal the retention of cylindrical shape but with surface roughness. And then, the fibers form TCD 5 cm and

TCD 7 cm are straighter and smaller diameter than TCD 10 cm and TCD 12 cm. But most of the fibers of TCD 10 cm TCD 12 cm are uniform but TCD 5 cm and TCD 7cm are not. The average diameter of the SnO_2nanofibers of TCD 5 cm are 47 - 80 nm, TCD 7 cm are 50-75 nm, TCD 10 cm are 80-85 nm and TCD 12 cm are 100 nm – 102 nm. So, tip to collector distance (TCD) 5 cm is the best position to produce nanofibers because its fibers diameter are the smallest in all position. The fibers diameter for all TCD position are listed in table 2.

Table 2. The fibers diameter for all tip to collector distance (TCD) position

Sample	Fiber diameter (nm)
TCD 5 cm	47
TCD 7 cm	50
TCD 10 cm	80
TCD 12 cm	100

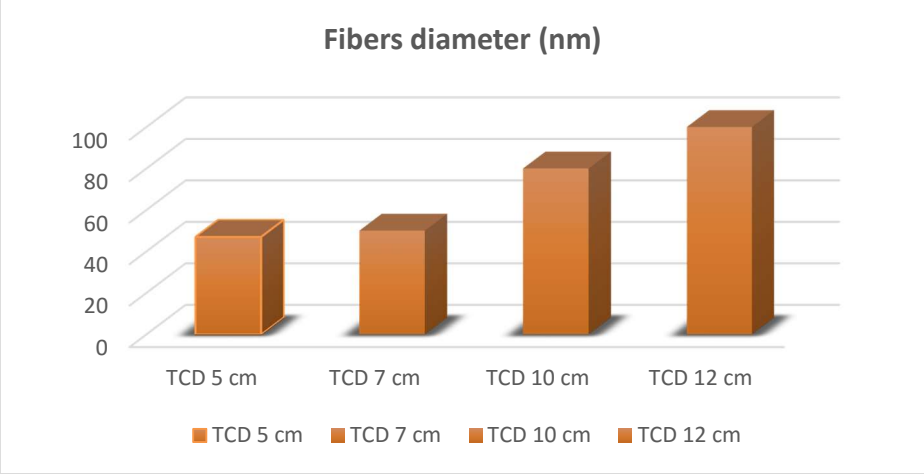

Figure 6. Tip to collector distance (TCD) dependence of fiber diameter

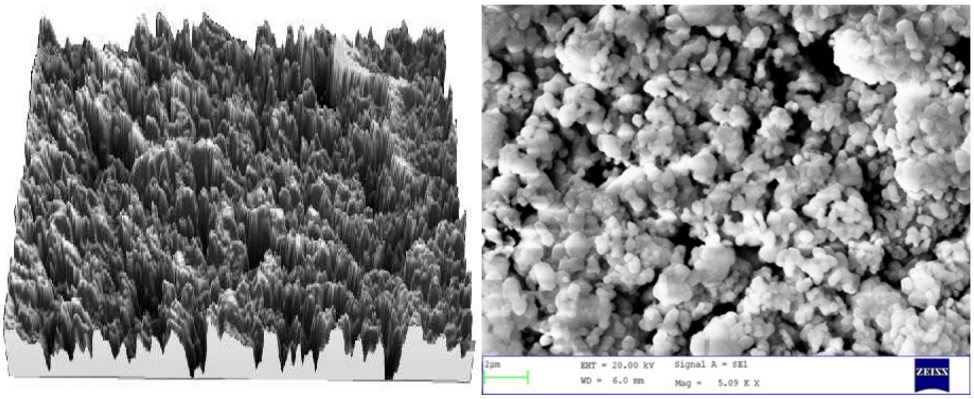

Figure 7. FESEM image of SnO_2nanopowder

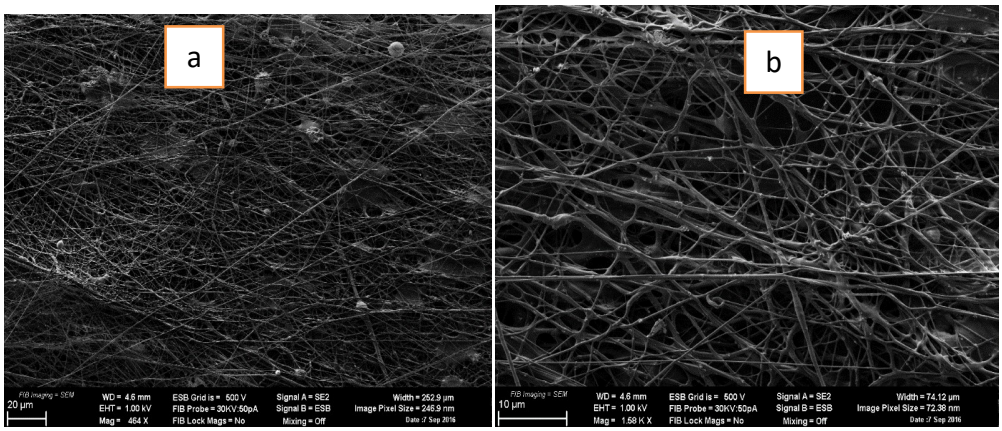

Figure 8. The FESEM photograph of SnO_2 nanofibers for 5cm (TCD) (a) 20µm (b) 10µm

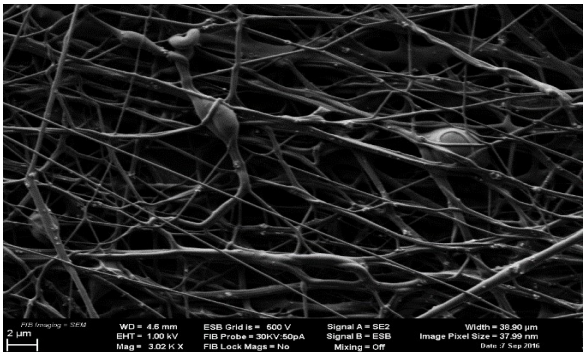

Figure 9. The FESEM photograph of SnO_2nanofibers for 7cm (TCD)

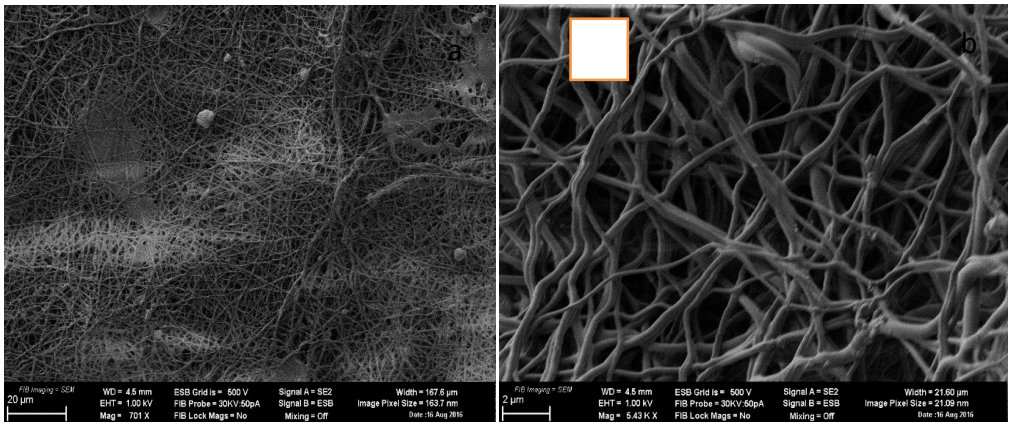

Figure 10. The FESEM photograph of SnO_2 nanofibers for 10cm (TCD)(a) 20 µm (b) 2 µm

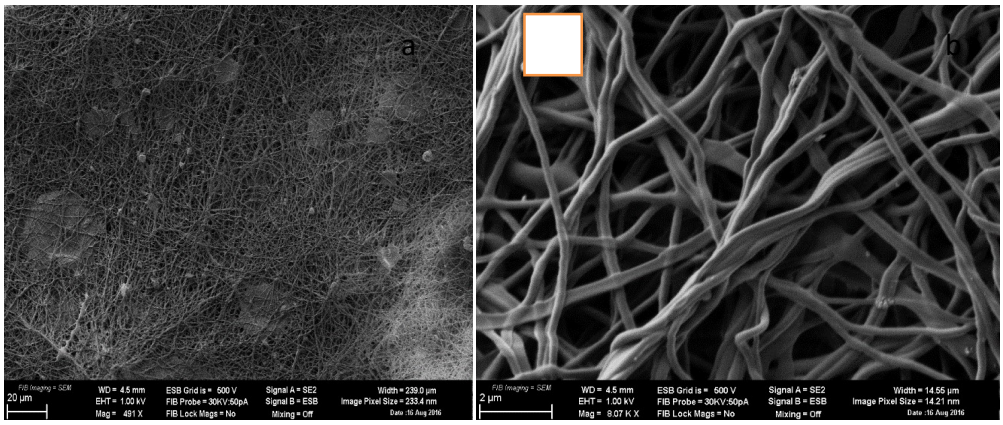

Figure 11. The FESEM photograph of SnO_2 nanofibers for 12cm (TCD) (a) 20 µm (b) 2 µm

Characterization of tin oxide nanofibers by AFM analysis

Atomic force microscope (AFM) is a technique for analyzing the surface of a rigid material all the way down to the level of the atom. AFM uses a mechanical probe to magnify surface features up to $1x10^8$ times, and it produces 3-D images of the surface. The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. The AFM image of TCD 5 cm, 7 cm and TCD 10 cm

are shown in figure 12, 13 and 14. Fiber diameter is estimated from fiber height to avoid tip-convolution effects. According to the line profile, the average fibers diameter for TCD 5 cm are 40 nm – 70 nm and TCD 10 cm are 84 nm – 95 nm.

Table 3The comparison of fibers diameter between the FESEM and AFM results

TCD (cm)	Fiber diameter (nm)	
	FESEM	AFM
5	47 - 80	40 - 70
10	80 - 85	84 - 95

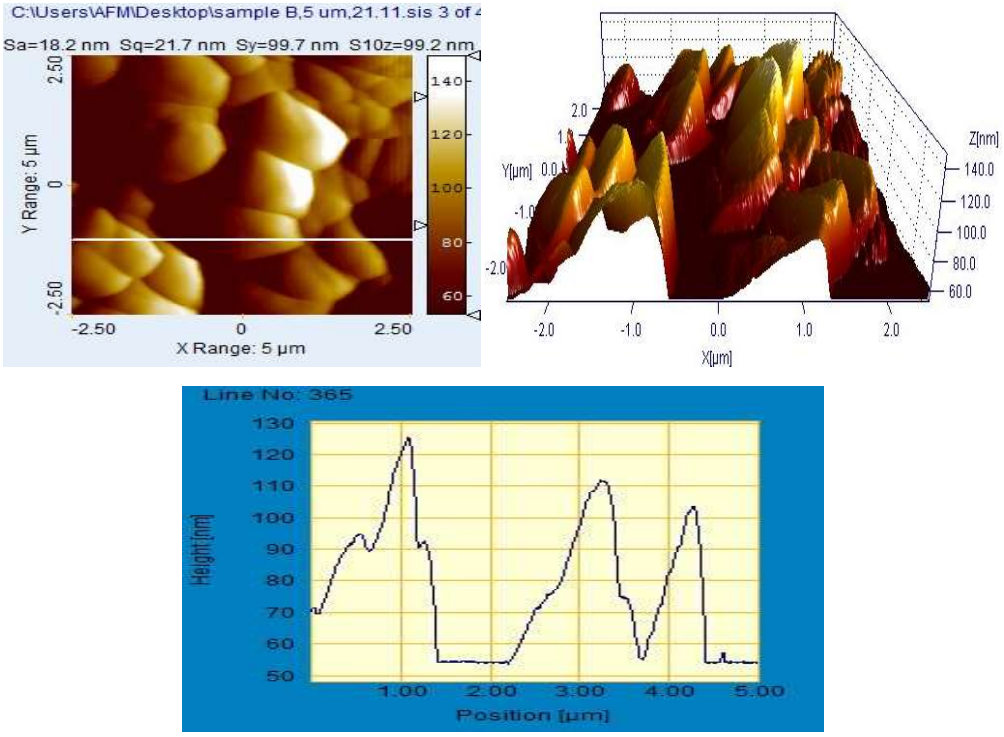

Figure 12. The amplitude, the 3D image and line profile for TCD 5 cm

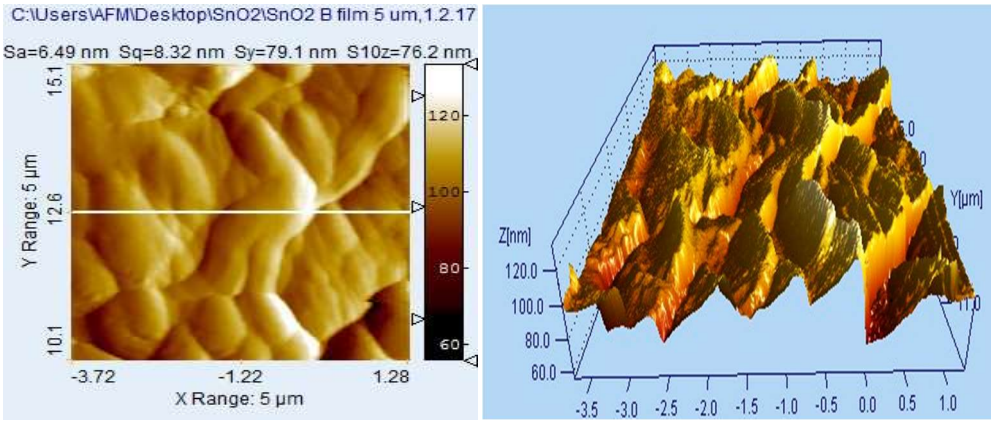

Figure 13. The amplitude and the 3D image for TCD 7 cm

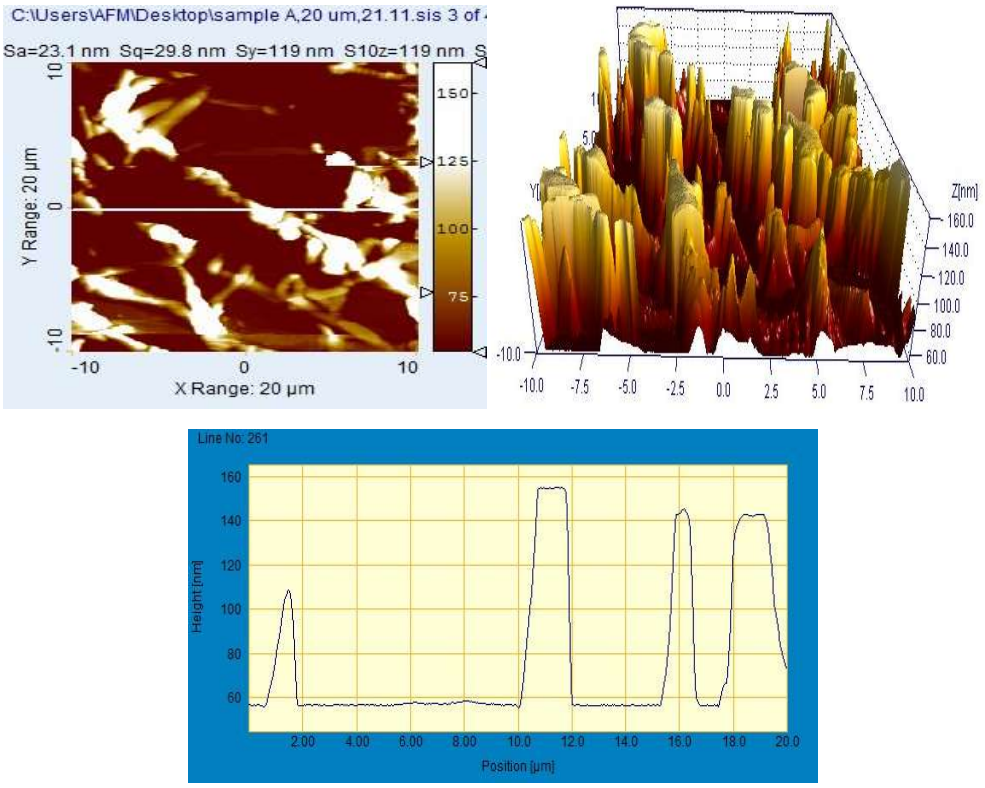

Figure 14. The amplitude, the 3D image and line profile forTCD 10 cm

Conclusion

Tin oxide powders were prepared by direct precipitation method from starting material $SnCl_2.2H_2O$. According to the XRD and SEM analysis the resulting SnO_2 powder was indicated the good crystalline nature of the powder. The SEM images indicated the presence of predominantly spherical shape having grain size 80 nm. The optical absorption spectrum showed the sharp absorption edge at 225 nm and 286 nm. And then SnO_2 nanofibers were fabricated by home-made electrospinning with vertical experimental set up. Moreover the tip to collector distance (TCD) was changing in 5 cm, 7 cm, 10 cm and 12 cm. According to the FESEM image the structural properties of fibers are changing depending upon the (TCD). The SnO_2nanofibers from all TCD distance reveal the retention of cylindrical shape but with surface roughness. And then, the fibers form TCD 5 cm and TCD 7 cm are straighter and smaller diameter than TCD 10 cm and TCD 12 cm. But most of the fibers of TCD 10 cm TCD 12 cm are uniform but TCD 5 cm and TCD 7cm are not. The average diameter of the SnO_2nanofibers of TCD 5 cm are 47 - 80 nm, TCD 7 cm are 50 - 75 nm, TCD 10 cm are 80-85 nm and TCD 12 cm are 100 nm – 120 nm. The fiber diameter is influenced by the tip to collector distance (TCD). Moreover the AFM profiles reveal the fibers diameter of TCD 5 cm are 40 nm – 70 nm and TCD 10 cm are 84 nm – 95 nm. So, tip to collector distance (TCD) 5 cm is the best position to produce nanofibersbecauseits fibers diameter are the smallest in all position. This home-made high voltage power supply and electrospinning set-up are quite simple, easily made and low cost than the others but it can produce fine nanofibers.

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