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Structural Investigation and Electrical Properties of Nickel Doped Tin Oxide Nanoparticles

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Abstract

In this research, preparation of tin oxide and nickel doped tin oxide nanoparticles from tin (II) chloride were carried out by co precipitation method. The structural and morphological properties of these nanoparticles were investigated by using X-ray diffraction(XRD), thermogravimetric-differential thermal analysis(TG-DTA), scanning electron microscopy(SEM), field emission electron microscopy(FESEM),and Fourier transform infrared spectroscopy(FT IR).Effects of calcination temperatures (200,300,400,500 and 600^{0}C) on crystallite size of the tin oxide nanoparticles were studied. Calcination of tin oxide and nickel doped tin oxide nanoparticles showed amorphous nature at 200 and 300^{0}C.After calcination at 400,500 and 600^{0}C, tin oxide and nickel doped tin oxide nanoparticles showed crystalline nature. It was found that the optimum temperature was 500^{0}C. Average crystallite sizes of tin oxide nanoparticles were found to be 33.53nm, 27.55nm and 35.10nm at 400,500 and 600^{0}C respectively. Average crystallite sizes of nickel doped tin oxide nanoparticles were found to be 33.19nm, 23.57 nm and 32.22nm for 1% nickel doping,19.62nm, 19.44nm and 32.05nm for 2% nickel doping at 400,500 and 600^{0}C respectively. Characteristic peaks at Miller Indices of (110), (101), (200), (211), (220), (310), (112) and (301) of the tin oxide nanoparticle samples are well matched with standard library of PDF 77-0447 of cassiterite tin oxide. The morphology of pure tin oxide and nickel doped tin oxide nanoparticles gave spherical shape according to scanning electron microscope (JOEL-JSM 5610 Japan) and field emission scanning electron microscope (Agilent 8500 FE SEM). Electrical properties of pure tin oxide and nickel doped tin oxide nanoparticles have been investigated. The lower resistivity and the higher conductivity of nickel doped tin oxide were observed compared to pure tin oxide nanoparticles.

Key words : tin oxide nanoparticles, nickel doped tin oxide nanoparticles, co-precipitation method electrical properties

Introduction

Cassiterite is the best-known tin mineral. It has been used as the chief ore of tin from early history throughout the ages, and remains so even today. Many of the economical cassiterite deposits exist in placer stream deposits where this very heavy mineral collects as rounded waterworn pebbles. The name cassiterite is derived from the Greek "kassiteros", meaning tin (Hall, *et al.*, 2004).

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Tin oxide (SnO_2) is an industrially important material which is used in numerous applications where the specific electrical, optical, and mechanical properties of SnO_2 are highly desirable (Adan *et al.*, 2010). For example, SnO_2 is used extensively as the active material in gas sensors, as well as in systems where optical or electrical coatings are required, such as in low-emissivity architectural glass, solar cells, liquid crystal displays, and photodetectors, video touch screens, plastic coating for light or colour, optoelectronic devices,and lithium batteries, etc., Tin oxide (SnO_2) is an n-type wide band gap (3.6 eV) semiconductor (Gnanam and Rajendran, 2010).

Semiconductors are solids whose conductivity lies between the conductivity of conductors and insulators. Due to exchange of electrons to achieve the noble gas configuration semiconductors arrange as lattice structure. Unlike metals, the conductivity increases with increasing temperature. Increasing temperatures leads to broken bonds and free electrons are generated (Nath *et al.*, 2008).

Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. Resistivity is commonly represented by the Greek letter ρ (rho). The SI unit of electrical resistivity is the ohm·metre (Ω·m) although other units like ohm·centimetre (Ω·cm) are also in use. Electrical conductivity or specific conductance is the reciprocal of electrical resistivity, and measures a material's ability to conduct an electric current. It is commonly represented by the Greek letter σ (sigma), but κ (kappa) (especially in electrical engineering) or γ (gamma) are also occasionally used. Its SI unit is siemens per metre (S/m) and CGSE unit is reciprocal second (s^{-1}) (Johari *et al.*, 2012).

The main aim of this study was to prepare tin oxide and nickel doped tin oxide nanoparticles from tin (II) chloride by using co-precipitation method and to characterize the prepared tin oxide nanoparticles by XRD, SEM, FE-SEM. and FT IR techniques and also to study the electrical properties (resistivity and conductivity) of prepared tin oxide and doped tin oxide nanoparticles thin film on glass surface by using Multimeter (Fluke 289) .

Materials and Methods

Preparation of Nickel Doped Tin Oxide

Tin (II) chloride dihydrate was dissolved in distilled water and hydrochloric acid (conc.) solution was added until the solution is clear and heated at sand bath. This solution was mixed with nickel chloride hexahydrate solution. The sufficient amount of aqueous ammonia was added into this mixture solution and stirred for 2 h. The solution was filtered .Then the pH was adjusted to pH 9.5. The precipitate was collected, washed with distilled water and dried in an oven. The precursor nickel doped tin oxide was obtained. The precursor nickel doped tin oxide was calcined at different temperatures 400°C, 500°C and 600°C for 6 h.

Determination of Electrical Properties

A given amount of nanopowder (1.5g) was made into a pellet.Silver plate (electrical and thermal conducting paste) was used to interface or homogeneously contacted between surfaces of crystal and electrodes. Electrical property such as resistance values of tin oxide and nickel doped tin oxide nanoparticles obtained from tin (II) chloride were measured by Fluke 289 Multimeter (Johari *et al.*, 2012).

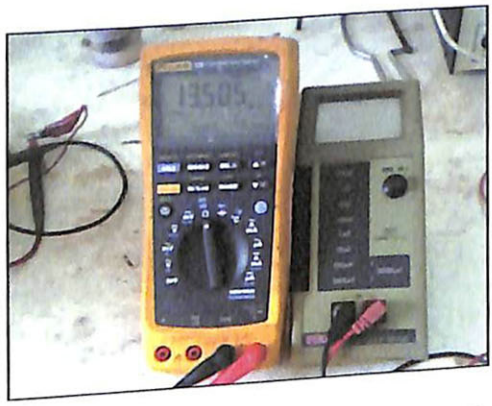


Figure 1 Fluke 289 Multimeter for measurements of resistance and conductivity

Results and Discussion

Characterization of Pure Tin Oxide Nanoparticles by XRD Analysis

X-ray diffraction is used to determine crystallinity of polymeric materials. XRD uses the total X-ray scattering both the crystalline and amorphous phases to determine the crystallinity. According to the XRD analysis, pure tin oxide nanoparticles were well matched with standard library of PDF 46-1088 of hydrated tin oxide and PDF 77-0447 of cassiterite tin oxide, respectively. Eight characteristic peaks at Miller Indices of (110), (101), (200), (211), (220), (310), (112) and (301) were observed. These values are well matched with standard PDF data of tin oxide. The peak positions 2θ values of pure tin oxide in XRD patterns are 24.939, 32.334, 36.364, 50.164, 53.201, 60.363, 63.066 and 64.488. D-spacing (Å) of pure tin oxide nanoparticles are 3.567, 2.766, 2.468, 1.817, 1.720, 1.532, 1.472 and 1.443. All of the peaks can be indexed to be pure tin oxide structure of tetragonal. The average crystallite size of pure tin oxide nanoparticles prepared from tin (II) chloride are 33.53 nm, 27.55 nm and 35.10 nm at 400°C, 500°C and 600C° respectively (Table 1).

Table 1. XRD Data of Tin Oxide Nanoparticles from Tin (II) Chloride (pH = 9.5)

Sample	Temperature (°C)	Crystallinity	Average crystallite size (nm)
1	200	Amorphous	-
2	300	Amorphous	-
3	400	Crystalline	33.53
4	500	Crystalline	27.55
5	600	Crystalline	35.10

Time=6 h

Characterization of Nickel Doped Tin Oxide Nanoparticles by XRD Analysis

The X-ray diffraction pattern of the 1%, and 2% nickel doped tin oxide samples are shown in Figures 1, 2, 3, and 4. It was found that x -ray diffractogram of nickel doped tin oxide nanoparticles showed four

characteristic peaks and its relative Miller Indices of (110, 101, 211, 220, 112 and 301) were observed. The peak position of 2 θ value of nickel doped tin oxide in x-ray diffractograms are 26.741, 34.077, 51.901, 54.877, 64.886 and 65.939. D-spacing (Å) of nickel doped tin oxide nanoparticles are 3.330, 2.628, 1.760, 1.671, 1.435 and 1.415. All diffraction peaks are well assigned to tetragonal crystallite phase of nickel doped tin oxide with the reference pattern JCPDS 78-0643. It was observed that nickel doping does not change the tetragonal structure of pure tin oxide. It was noted that the intensity of the nickel doped tin oxide peaks decreased with increasing nickel concentration. Furthermore, the full width at half maximum values of nickel doped tin oxide nanoparticles became smaller and two theta values increased when compared to pure tin oxide nanoparticles. After doping 1 % and 2 % nickel on tin oxide, the average crystallite sizes of nickel doped tin oxide nanoparticles were found to be 33.19nm, 23.57nm and 32.22nm for (1%), and 19.62nm, 19.44nm and 32.05nm for (2%)at 400°C, 500°C and 600°C respectively (Table 2). It was noted that the crystallite size of nickel doped tin oxide decreases gradually as the nickel concentration increases. The crystallite sizes (D) were calculated by using the Scherrer equation.

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta}$$

where, D_{hkl} is the average dimension of the crystallites, k=0.9, λ is the wavelength of the x-ray diffraction (0.15405nm), θ is the Bragg angle for the crystal planes (hkl) and β_{hkl} is the broadening (Full-width at half-maximum FWHM) of the peak.

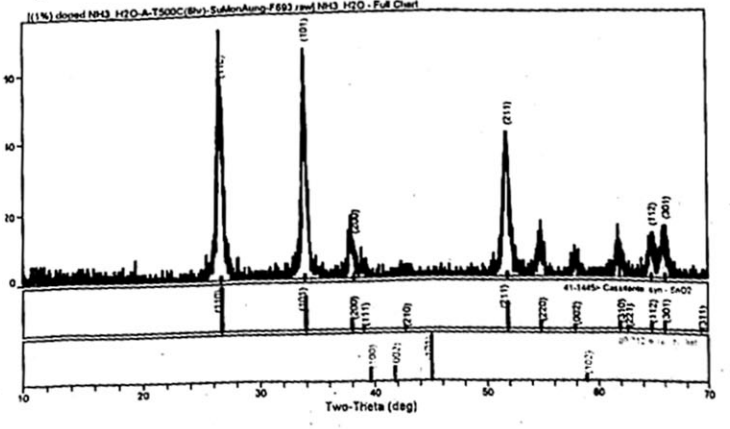


Figure 1 X-ray diffractogram of 1% nickel doped tin oxide nanoparticles at 500°C

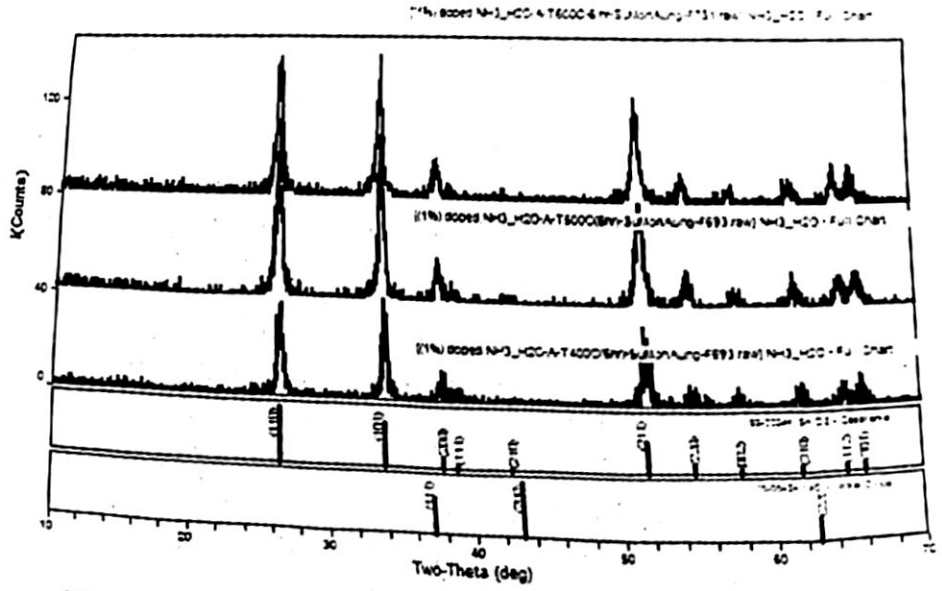


Figure 2 XRD diffractograms of 1% nickel doped tin oxide nanoparticles at different temperatures (400, 500 and 600°C)

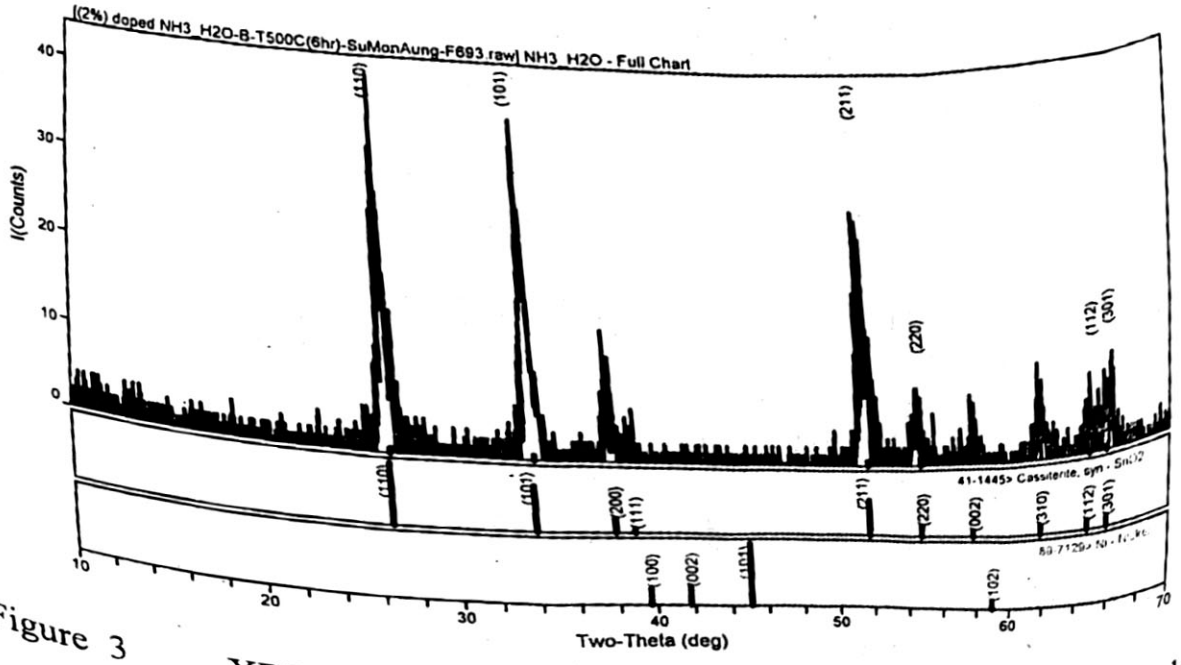


Figure 3 XRD diffractograms of 2% nickel doped tin oxide nanoparticles at 500°C

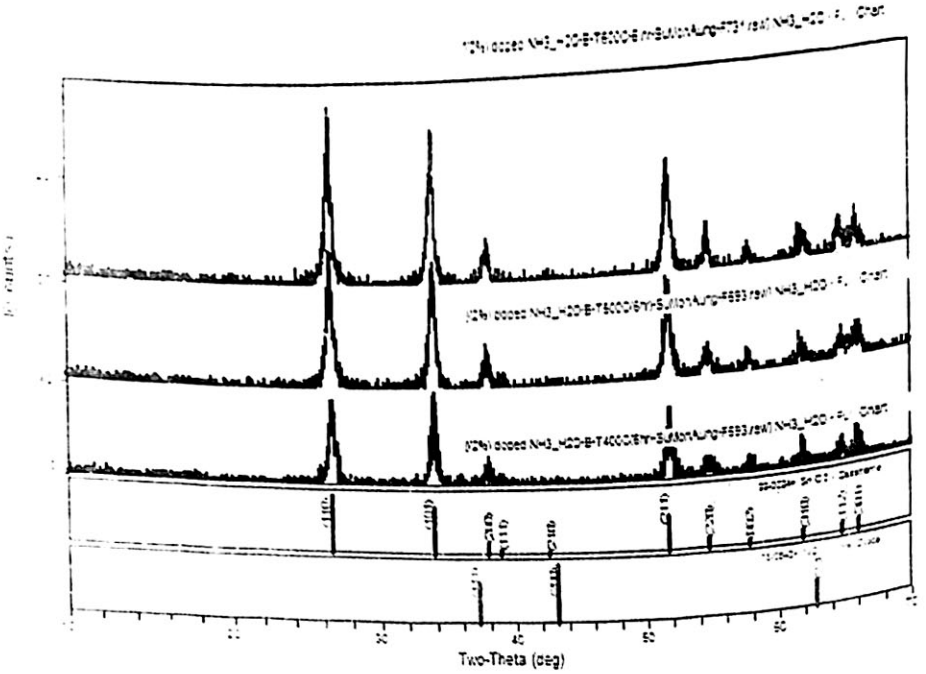


Figure 4 XRD patterns of 2% nickel doped tin oxide nanoparticles at different temperatures (400, 500 and 600°C)

Table 2 Various Sizes of Nickel Doped Tin Oxide Nanoparticles with Temperature

Sample	Average crystallite size (nm)
	33.19
1%	23.57
	32.22
	19.62
2%	19.44
	32.05

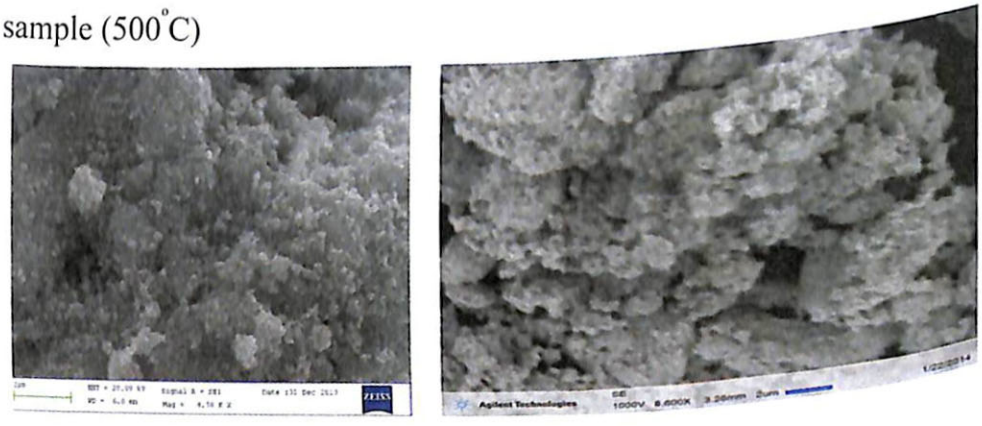
Morphological Analysis of Pure Tin Oxide and Nickel Doped Tin Oxide by Scanning Electron Microscope and Field Emission Electron Microscope

The Agilent 8500 FE SEM has been optimized for low-voltage imaging, extremely high surface contrast and resolution typically found only in much larger and more expensive field emission microscopes. Scanning electron microscope and field emission electron microscope images of pure tin oxide and nickel doped tin oxide nanoparticles are shown in Figures 5 (a) and

(b), Figures 6(a) and (b) and Figures 7(a) and (b) respectively. It was found that the particle sizes of pure tin oxide nanoparticles were in the range of 19.27 nm to 48.19 nm. For 1 % and 2% nickel doped tin oxide nanoparticles, the particle sizes were in the range of 15.03 nm to 27.06 nm and 10.87 nm to 19.57 nm respectively.

(a) (b)

Figure 5 (a) SEM and (b) FE SEM micrographs of calcined pure tin oxide sample (500°C)



(a) (b)

Figure 6 (a) SEM and (b) FE SEM micrographs of calcined 1 % nickel doped tin oxide sample(500°C)

(a) (b)

Figure 7 (a) SEM and (b) FE SEM micrographs of calcined 2% nickel doped tin oxide sample(500°C)

Electrical Properties (Resistivity and Conductivity) by Fluke 298 Multimeter

In the present work, electrical measurements were carried out by using Fluke Multimeter. On the basis of the results obtained from this experiment, electrical resistivity of nickel doped tin oxide was found to decrease with increase in electrical conductivity. Measurements of resistivity and conductivity are characteristics of electrical properties. The lower resistivity for nickel doped tin oxide nanoparticles was observed compared to pure tin oxide nanoparticles. On the other hand, the conductivity of nickel doped tin oxide nanoparticles was higher than that of pure tin oxide nanoparticles. Variations of electrical resistivity and conductivity with temperature are shown(Tables 3 and 4).Among the temperatures studied, the lowest electrical resistivity and the highest conductivity were observed at 500^0C.

Table 3 Resistivity of Prepared Pure Tin Oxide and Nickel Doped Tin Oxide Nanoparticles

No	Temperature(°C)	Resistivity (Ω m)	
		Pure SnO_2	Ni doped SnO_2
1	400	$4.9117 \times 10^{+4}$	$4.6806 \times 10^{+4}$
2	500	$2.4693 \times 10^{+4}$	$2.3147 \times 10^{+4}$
3	600	$1.2828 \times 10^{+7}$	$1.0500 \times 10^{+7}$

Table 4 Conductivity of Prepared Pure Tin Oxide and Nickel Doped Tin Oxide Nanoparticles

No	Temperature(°C)	Conductivity ($S\ m^{-1}$)	
		Pure SnO_2	Ni Doped SnO_2
1	400	2.03×10^{-5}	2.13×10^{-5}
2	500	4.04×10^{-5}	4.32×10^{-5}
3	600	7.79×10^{-8}	9.52×10^{-8}

Conclusion

In this research, tin oxide nanoparticles and nickel doped tin oxide nanoparticles from tin (II) chloride were prepared by co-precipitation method. Effect of calcinations temperature (200, 300, 400, 500 and 600°C) on average crystallite size of tin oxide nanoparticles was investigated. For calcination at 200 and 300°C, tin oxide nanoparticles showed amorphous nature. After calcinations at 400, 500 and 600°C, tin oxide and nickel doped tin oxide nanoparticles showed crystalline nature. By using the Scherrer equation, average crystallite size of pure tin oxide nanoparticles were observed as 33.53 nm, 27.55 nm and 35.10 nm at 400, 500 and 600°C. Average crystallite size of nickel doped tin oxide nanoparticles were found to be 33.19nm, 23.57nm and 32.22nm for (1%), 19.62nm, 19.44nm and 32.05nm for (2%) at 400, 500 and 600°C respectively.

According to SEM and FE SEM images of pure tin oxide and nickel doped tin oxide nanoparticles appeared spherical shape. Particle sizes obtained from SEM and FE SEM images are comparable with crystallite sizes calculated from XRD spectra. It was found that the particle sizes of pure tin oxide were in the range from 19.27nm to 48.19nm. The particle size of nickel

doped tin oxide nanoparticles were from 15.03 nm to 27.06 nm for (1%), 10.87 nm to 19.57 nm for(2%) Ni doped SnO_2, respectively. It indicated that the average crystallite size of the nickel doped tin oxide nanoparticles was smaller than that of pure tin oxide nanoparticles. In this work, electrical properties for pure tin oxide and nickel doped tin oxide nanoparticles were studied. The resistivities of pure tin oxide and nickel doped tin oxide nanoparticles were found to be 4.9117×10^4, 2.4693×10^4 and $1.2828 \times 10^7(\Omega)$ and 4.6806×10^4, 2.3147×10^4 and $1.0500 \times 10^7(\Omega)$ at 400,500 and 600°C. The conductivity of pure tin oxide and nickel doped tin oxide nanoparticles found to be 2.03×10^{-5}, 4.04×10^{-5} and $7.79 \times 10^{-8}(Sm^{-1})$ and 2.13×10^{-5}, 4.32×10^{-5} and $9.52 \times 10^{-8}(Sm^{-1})$ at 400,500 and 600°C respectively. It was noticed that the minimum resistivity and maximum conductivity of nickel doped tin oxide nanoparticles were observed at 500°C. SnO_2 is a very promising material for a number of applications like gas sensing, optoelectronic device applications and dilute magnetic semiconductors when doped with transition metals.

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