

Synthesis and Characterization of Nickel Doped Tin Oxide Nanoparticles by Hydrothermal Method

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Abstract Present paper deals with the synthesis of nickel doped tin oxide by sol-gel method. As we increase the doping of nickel the decrease in bandgap take place.

Keywords: *sol-gel, nanotechnology, hydrothermal*

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1. Introduction

Metal oxide nanoparticles have attracted considerable attention because of their outstanding properties such as high stability, high active surface area, quantum confinement and large band gap. The majority of properties of nanomaterials depend on the shape and size of the nanocrystals. Tin oxide (SnO_2) is an n-type wide band gap (3.5-3.8eV) semiconductor, which has been studied with great attention due to its high transparency in visible region, high reflectivity in infrared region, enhanced gas sensing properties, and small electrical resistance in comparison to other semiconductor nanomaterials. The physical properties of semiconductor could be tailored by doping with transition-metal ions, such as Mn, Co, Fe, Ni, etc. The experimental efforts on transition-metal doped SnO_2 were accelerated on finding high-temperature ferromagnetism with large magnetic moment in transparent Co-doped SnO_2 . Some reports on various techniques are available in literature for the synthesis of Ni-doped SnO_2 such as sol-gel, polymeric precursor, pulsed laser deposition, spin coating, hydrothermal, co-precipitation method, solid-state reaction, flash evaporation technique, etc. Ni-doped SnO_2 showed decrease in band gap with increasing Ni doping levels and exhibited room-temperature ferromagnetism. In consistent results on structural, optical and magnetic properties could be seen, which might be due to the dependence of the properties on the synthetic procedure and growth conditions. Ni-doped SnO_2 is used in very diverse range of application, such as sensors, electrode materials, electrochemical generation of ozone, etc. Needle shaped Ni-doped SnO_2 nanocrystals showed gas sensing properties synthesized by sol-gel chemical precipitation method. Ni-doped SnO_2 hollow nano-fibers prepared by electro-spinnig have potential for the application in high sensitive. More recently, Ni-doped SnO_2 nanospheres have been synthesized by hydrothermal method, which could be used as anode material for lithium

ion batteries. Also this, Ni-doped SnO_2 anode also show electro catalytic activity for ozone evolution. It is well-known that the band gap of semiconductors can be tuned by controlling the size of the particles, which increases with decrease in the particle size due to the quantum size effects. The size of the nanoparticles can be controlled by the soft chemical synthesis methods. Therefore, we have chosen the oxalate precursor mediated modified solvothermal method to synthesize Ni-doped SnO_2 nanoparticles at very low temperature (500°C). This method is cost effective since the chemical synthesis requires the use of inexpensive chemicals and a simple refluxing glass assembly instead of an expensive autoclave. Also, the oxalate precursor helps in the synthesis of pure and homogeneous oxide nanoparticles at low decomposition temperature. In addition, polymeric citrate precursor route is insensitive to the presence of moisture and it does not require any inert atmosphere as well as even without careful control of the gel processing time, a high degree of homogeneity may be obtained in nano products. Recently, this method has used for the successful synthesis of Mn-and Co-doped SnO_2 nanoparticles with controlled morphology.

2. Synthesis Techniques

Sol-gel method is the most easiest and common method for synthesis of nanoparticle in which we used bottom up approach to synthesis nanomaterial using several chemicals. Nickel doped Tin oxide is synthesized by chemical reduction of its chlorides as explain below.

2.1. Doping by Solvothermal Method

The synthesis of SnNiO_2 was carried out by the thermal decomposition of oxalate precursor at 500°C using modified solvothermal method. Molar quantities of 0.1M aqueous solutions of tin chloride dehydrate and nickel chloride hexahydrate with continuous stirring. A light

green suspension was immediately formed. Approximately, 75 mL of ethanol was also added to the reaction mixture to make low boiling a zeotropic solution. The mixture was refluxed for 12h at $\sim 70^\circ\text{C}$ in a closed environment so that the volume of reaction mixture remains constant. The product was well separated by centrifugation, washed with acetone and then dried at 60°C in oven.

2.2. Solid State Reaction Method

Ni doped SnO_2 powders at 3, 5, 7, 10, and 15 at % of Ni were set by a standard solid-state reaction method. Commercially available SnO_2 and NiO_2 (M/S Sigma-Aldrich, 99.99% pure) were accurately weighed in required proportions using microbalance and were mixed and ground thoroughly using an Agate mortar and pestle to change to very fine powders. The grinding of the mixture was permitted out for 16h for all the Ni doped SnO_2 powder samples. The ground powder samples were loaded into a small one end closed quartz tube of diameter of 10 mm and length of 10 cm, which was enclosed in a bigger quartz tube of diameter of 2.5cm and length of 75cm with provision to allow unwanted vapors to get away from the reaction chamber, and evacuated at 2×10^{-3} mbar using a rotary pump. The complete setup was placed in horizontal tubular microprocess or controlled furnace and passionate for several hours at different temperatures. The firing temperature and firing periods were optimized at 800°C and 10h through trial-and error procedures. X-ray diffraction was used to establish structural aspects. The diffused reflectance spectra were record during UV-Vis-NIR Spectrophotometer (JASCO V-670). Magnetic measurements were carried out at room temperature using vibrating sample magnetometer (LakeShore-7404).

2.3. Doping of Nickel in Tin Oxide via Sol-gel Route

Nickel nanoparticles are synthesized by sol-gel route in which the nickel chloride is chemically reduces to nanosize by the bottom up approach. In this process nickel chloride is firstly dissolves in water and stirrer for 4 hr continuously by 600 rpm and then add PEG 400 (polyethylene glycol) drop wise then again stirrer for 6 hr to remove the chloride ions from the solution. After removing chloride solution will kept in dust free environment then again tin nanoparticles are synthesized by same method then we add both solution in same ratio and stirring for 12 hr. After the 12 hr continuous steering both the solution are mixed together then we add ammonia drop wise to agglomerates particle to gives the powder form which can be filtered out and annealed at 600°C then the final nickel doped tin oxide nanoparticles are formed.

3. Result and Discussion

3.1. SEM Analysis

Nickel doped tin oxides are synthesized by sol gel chemical route and the morphology and microscopic structure are characterized by using Scanning electron microscope (SEM) as shown below:

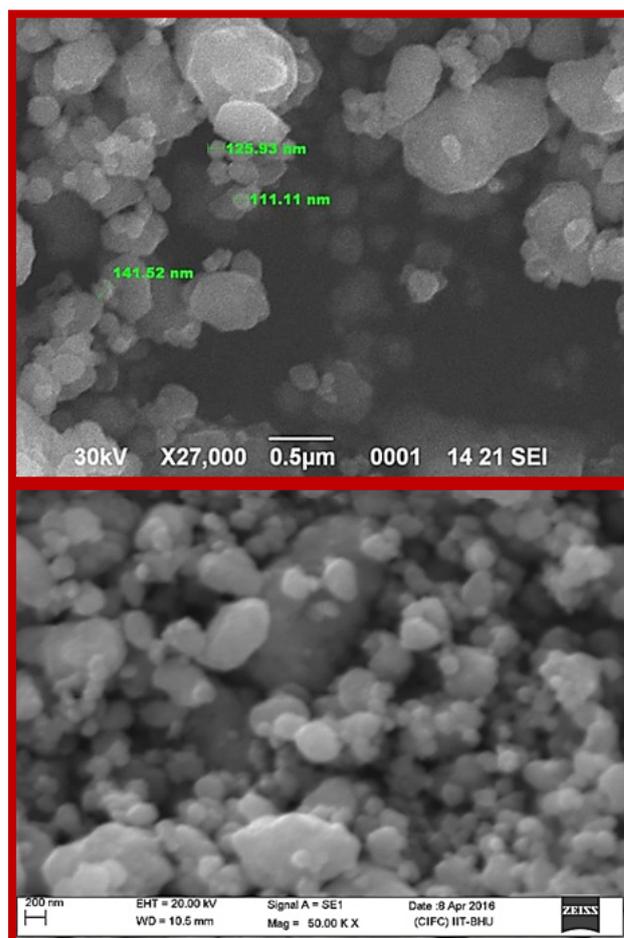


Figure 1. SEM analysis of Ni doped SnO_2 nanoparticle at different scale

After characterizing the Ni doped tin nanoparticles we found that the size of nanoparticles varies from 110nm to 140 nm in which the high porosity are found so these type of nanoparticles are used in different application like solar cell and sensor. The morphology will contain two different type of chemical structure because of doping material so the particles are agglomerates and found the cluster in such case.

3.2. EDX Analysis

After SEM characterization for finding the purity or contents of materials in the prepared sample we analyzed the EDX data the peaks of data gives the amount of material content inside the nanoparticles. On analyzing the EDX data we found that there are two highest peaks are found in which confirms the presence of Sn nanoparticles in the sample and the Cl peaks are found because of reacting with the atmosphere and the another peaks shows the presence of Ni nanoparticles and the Pt peak are found for preparing of sample for SEM analysis. Now the EDX data are shown below in Figure 2.

3.3. UV Visible Spectroscopy

The band gap and absorbance spectra of carbon nanotubes are measured by using ultra volatile spectrometer (Evolution 202). In this uv spectra molecule absorbs energy by the rotational, translational or ionization of molecule depending on the frequency of electromagnetic

radiation. Excited molecules are unstable and quickly drop down and again give off the energy that they received from the electromagnetic radiation. The wavelength and intensity of the electromagnetic radiation absorbed can be recorded to get a spectrum.

For direct band gap material the transition probability near the fundamental edge is approximately constant therefore, the dependence of absorption coefficient on the incident photon energy is given by

$$\alpha h\nu = \text{const} (h\nu - E_g)^{1/2}$$

Where, $h\nu$ is the incident photon energy and E_g is the direct optical band gap of the sample. Value of the band gap (E_g) was obtained by extrapolating the linear part of the $(\alpha h\nu)^2$ versus $h\nu$ plot (known as Tauc plot) to energy ($h\nu$) axis. Band gap values of a material strongly depend on the carrier concentration, which in turn depends on the deposition conditions.

As Figure 3 the band gap are calculated by using Tauc plot between energy and the absorbance the tangent of the curve will give the band gap of the material. In such case the band gap was calculated as 5.8 eV which confirms that the doping of materials are found in such case.

3.4. FTIR

The IR spectra are analysed between absorption and wavelength these vibrational spectra give peaks due to resonance of vibration and stretching of atoms and bonds between them. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)].

Difference in the energy state = energy absorbed

$$E_1 - E_0 = hc / \lambda$$

Where,

h is the Planck's constant

c is the velocity of the light

λ is the wavelength of the light

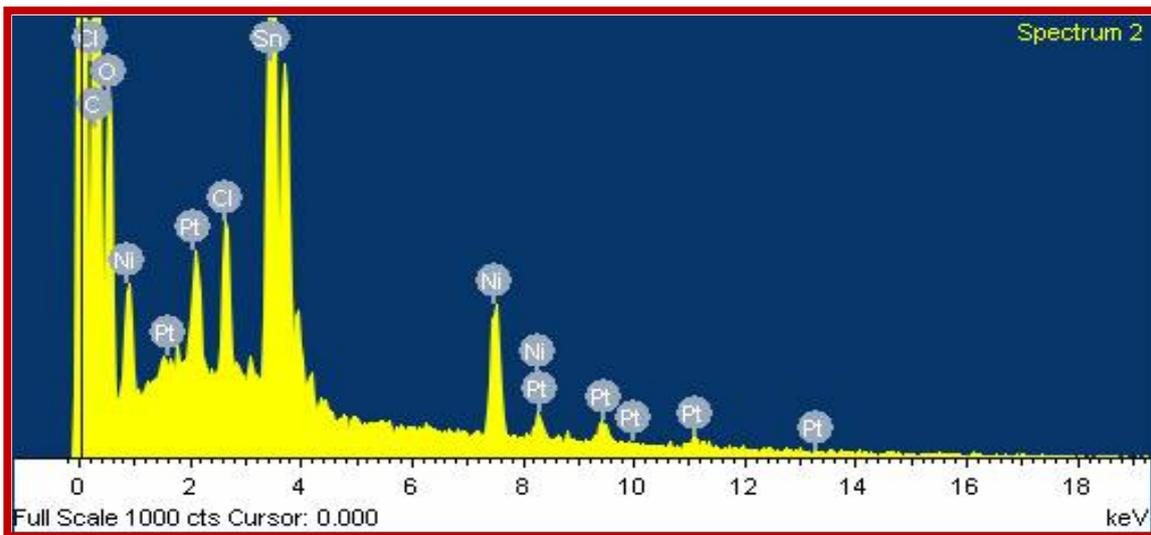


Figure 2. EDX of Ni doped Sn nanoparticle

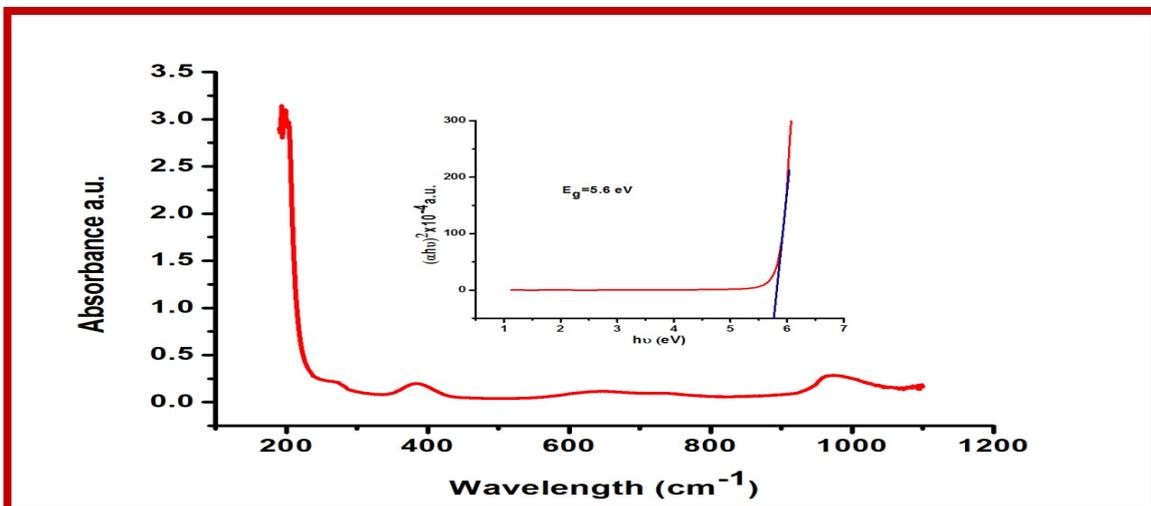


Figure 3. Tauc plot of Ni doped SnO₂ nanoparticle using absorbance spectra of UV

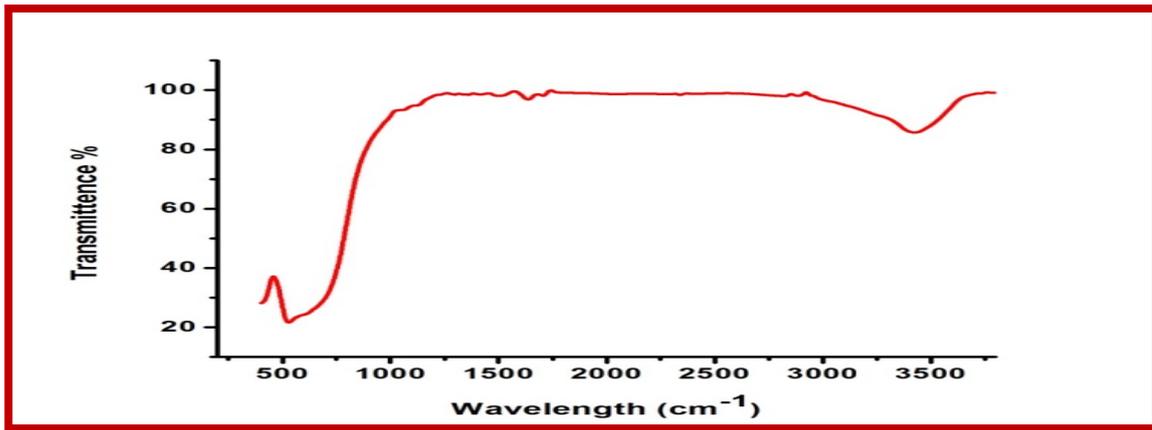


Figure 4. FTIR transmission spectra of Ni doped SnO₂ nanoparticle

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

3.5. Particle Size

The particle size of CNT are analyzed by using nano zeta sizer in which the size of particle are measured by the brownian moment of collidal particle so for finding size of particle firstly we prepare a dispersed solution of CNT in sulfuric acid then it placed in side the chamber. (Figure 5)

Laser of wavelength 625 nm will strike on the solution and then scattering phenomenon is occurred which are detected by the detector placed from 90° from the sample then the average particle size is detected. Some particles

are large and some are very small so due to this the average particle size are found to be 160 nm.

3.6. XRD Analysis

The XRD pattern of CNT are analysed by using powder XRD method using CuK α as source in which they gives a highest peak at 26.58 degree on calculating the crystal size of CNT by debye sherrer formula we found that the size is about 33.4 nm which is similar as the diameter of CNT.

The particle size was calculated by using formula

$$D = \frac{n\lambda}{\beta \cos\theta}$$

Where D is the crystalline size and λ is the wavelength β is FWHM and θ is the measured angle.

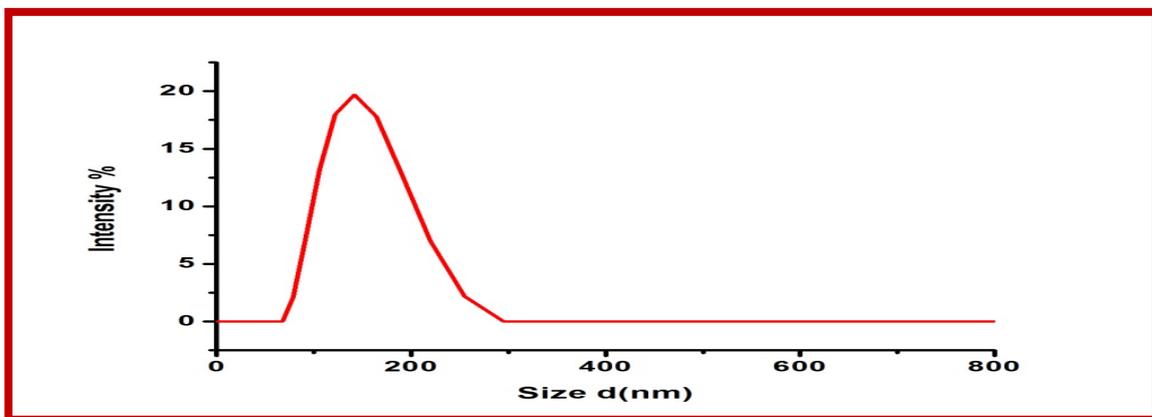


Figure 5. Average particle size of Ni doped SnO₂ nanoparticle

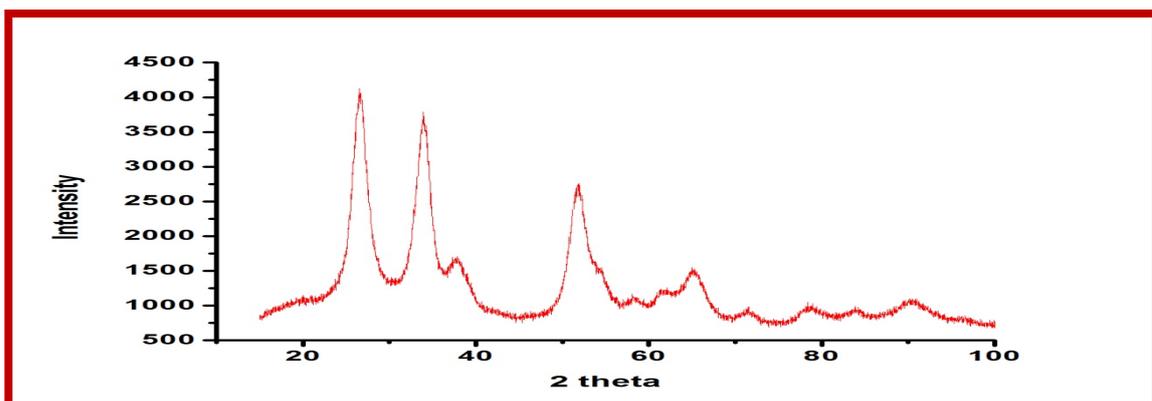


Figure 6. XRD analysis of Ni doped SnO₂ nanoparticle by using CuK α as source

The above XRD data confirms the doping of Ni in SnO₂ because of having both peaks the first two higher peak confirms the Sn and another peak shows the Sn have different miller indices.

4. Conclusion

The Ni doped SnO₂ nanoparticles are synthesized by so many different rout but the best way to synthesized nanoparticle at room temperature via chemical rout is Sol-Gel. The nanoparticle were characterized by SEM, FTIR, EDX, XRD, UV-Visible spectroscopy which shows the surface morphology, vibrational peak, crystalline size and the band gap of materials. The wide band gap of nanoparticles is used in so many applications.final

References

- [1] Hornyak, Gabor L., et al. *Introduction to nanoscience*. CRC press, 2008.
- [2] Pillai S O. *Solid State Physics: Structure and Electron Related Properties*. Wiley Eastern Limited, 1994.
- [3] "Nickel – Handbook of Mineralogy" (PDF). *Hand book of mineralogy.org*. Retrieved 2016-03-02.
- [4] J. Zhang and L. Gao, *J. Solid State Chem.* 177 (2004) 1425.
- [5] M. Batzill and U. Diebold, *Progress in surface Science.* 79 (2005) 47.
- [6] H. Zhang, N. Du, B. Chen, T. Cui and D. Yang, *Materials Research Bulletin.* 43, (2008), 3164.
- [7] J. Pena, J. Perez-Pariente and M. Vallet-Regi, *J. Mater. Chem.* 13, (2003), 2290.
- [8] H. Zhu, D. Yang, G. Yu, H. Zhang and K. Yao, *Nanotechnology* 17, (2006), 2386.
- [9] F. Du, Z. Guo and G. Li *Materials Letters* 59, (2005), 2563.
- [10] S. V. Manorama, C. V. Gopal Reddy and V. J. Rao, *Nanostruct. Mater.* 11, (1999), 643.
- [11] L. Fraigi, D.G. Lamas and N.E.W. Reza, *Nanostruct. Mater.* 11, (1999), 311.
- [12] D. Davazoglou, *Thin Solid Films.* 302 (1997) 204.
- [13] 13 Y. Liu, F. Yang and X. Yang, *Colloids and Surfaces A.* 312, (2008), 219.
- [14] Deshpande NG, Gudage YG, Sharma R, Vyas JC, Kim JB, et al. Studies on tin oxide-intercalated polyaniline nanocomposite for ammonia gas sensing applications. *SensActuat B- Chem* 138, (2009), 76-84.
- [15] Krivetskiy V, Ponzoni A, Comini E, Badalyan S, Rumyantseva M, et al. A selectivity modification of SnO₂- based materials for gas sensor arrays. *Electroanalysis* 22, (2010), 2809-2816.