Research Article

INFLUENCE OF SOLVENT ON STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF SNO₂ NANOPARTICLES PREPARED BY DIFFERENT METHODS

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ABSTRACT

This study represents comparisons between the structural, morphologies and optical properties of tin oxide (SnO₂) nanoparticles prepared by two different methods, namely the Sol-gel and the Co-precipitation methods. The characteristics of the particles were analyzed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy Dispersive X ray spectroscopy (EDS). The optical properties were analyzed using UV-vis spectroscopy (UV-vis). Using XRD study recognized the structure of a single phase of SnO₂ nanoparticles of both methods. It has been enormous that solvents played main role in varying the crystallite size of tin oxide nanoparticles in Sol-gel and Co-precipitation methods. From two different types of method, the crystallite size of SnO₂ nanoparticles varies mutually solvent and method. Using the two-different method XRD study showed well crystallized tetragonal SnO₂ can be obtained and the crystal sizes were 16.71, 5.43 and 10.09 nm for the sample of water, methanol and ethanol. In Co-precipitation method the crystal sizes were 18.71, 9.9 and 11.7 nm for the sample of water, methanol and ethanol. In sol-gel method and Co-precipitation X-Ray Diffraction (XRD) patterns showed extremely crystalline single phase tetragonal structure, with a main (110) plane in water and methanol samples and (101) for ethanol samples in the method I. In the Co-precipitation method, with predominant (101) plane in methanol and ethanol sampled and (110) for water samples. With the above analysis, we will discuss that the Co-precipitation may be appreciated for time consuming and high yield of particles.

INTRODUCTION

Tin oxide is a capable efficient material owing to its properties such as strong physical and chemical interaction with adsorbed species, low operating temperature and high degree of transparency in the visible region (Adnan *et al.*, 2010; Zhu *et al.*, 2006). Tin oxide (SnO₂) is an n-type broad band semiconductor (E_g = 3.6 eV at 300 K) and generally used as an foremost functional material for catalyst support and gas sensing material, optoelectronic devices, transparent conductive electrodes, solar cells, (Peaker and Horsley (1971); Drevillon *et al.*, 1989). In the interior the wide family of efficient materials, metal oxides are particularly attractive owing to their applications in sensing, catalysis, energy storage and conversion, optics and electronics (Niederberger, (2007). Titanium oxide (TiO₂), Zinc oxide (ZnO), and Tin oxide (SnO₂) is the centre of exact interest due to their only structural, optical, and catalytic properties (Vij *et al.*, 2012; Das

and Jayaraman (2014); Wang *et al.*, 2015). Above all, the attention in SnO₂ has increased due to its properties like high transparency, little electrical sheet resistance and high chemical strength (Minami, (2000); Young *et al.*, 2002). In addition SnO₂ is also of huge methodical and technological notice due to its multitalented applications in dye-based solar cells, gas sensors, optical devices and electronic devices transparent conducting electrodes etc. (Hieu *et al.*, 2012; Park *et al.*, 2013; Deng and Lee (2008). Owing to the modifications in properties of nanomaterials, in recent times the mind has been unfocused to synthesize and characterize SnO₂ nanoparticles by dissimilar methods. The applications and properties of nanostructured materials are partial intensely by their size, structure, morphology, and chemical composition. Still the achievement in a lot of of these applications relies on the capability in obtaining cost effective, high eminence nano sized materials having standardized grain structures (Henglein, (1989); Alivisatos, (1996); Burda *et al.*, 2005). It is fine known that the

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helpful presentation of SnO₂ is qualified to its, morphology, crystal size, surface properties crystal defects and crystallinity etc. which eventually depends on the investigate methods and preparation situation (Leite *et al*., 2000; Jiang *et al*., 2005). Throughout nanoparticle research, solvent plays a very essential role in a reaction mechanism. Solvent provides a means of temperature control by determining the highest temperature at which reaction will arise (Ungula and Dejene (2015). Before studies also indicated that particle growth and coarsening are powerfully reliant on solvent through the, surface energy, bulk solubility and viscosity (Hu *et al*., 2003). Thus by through dissimilar solvents the control over SnO₂ nanoparticles size and size division could be achieved, which is essential for optical, tailoring, electrical, magnetic and chemical and properties of nanoparticles for exact applications. SnO₂ is an interesting metal oxide because it can exist in diverse convoluted morphologies (Guan *et al*., 2013). SnO₂ has been syntheses by diverse methods such as, hydrothermal methods (Huang *et al*., 2001), solid state synthesis (Gautam *et al*., 2013), chemical vapor deposition (Kennedy *et al*., 2003), colloidal and aerosol routes (Zhang *et al*., 2012) co-precipitation (Nomura *et al*., 2011) and sol-gel method (Kumar *et al*., 2016). In dissimilarity to high temperature production, co-precipitation is one of the favored methods and has recompense such as the option of obtaining metastable materials, achieving better purity and compositional homogeneity of the products at restrained temperatures and the necessity of easy laboratory equipments (Niederberger, (2007). In this, the influences of solvent on the structural, morphological, and optical properties of SnO₂ nanoparticles using two different methods have been reported. In this study, ethanol, methanol, water were used as solvent media. The polar characteristic of solvent was the major factor that affects both growth and nucleation and of SnO₂ nanoparticles, and, as a result, determines the size, shape, and piece ratio of the product (Ungula and Dejene, (2015). Therefore, the mainly significant of this examine paper was to learn the influence of solvent on the structural, morphology, size, and optical properties of synthesized nanoparticles using sol-gel and Co-precipitation method.

MATERIALS AND METHODS

Experimental

All chemical reagents were marketable with AR purity, and used directly without further purification.

Sol-gel method

Two different types of SnO₂ particles were prepared using common Co-precipitation (Nomura *et al*., 2011) and sol-gel (Kumar *et al*., 2016). In a Sol-gel method, SnO₂ nanostructures was prepared by dissolving 0.5 g of SnCl₂.2H₂O was dissolved in 100 ml Methanol. The resulted precursor combination was reserved for stirring on a magnetic stirrer and while stirring into this mixture for 30 minutes. The aqueous ammonia solution was added in drop wise manner (with a rate of 5 drops/minute). On adding of approximately 40-50 drops of aqueous ammonia the sol-gel was produced around within the 15 minutes. The resultant opal gels were washed with ethanol to remove impurities, and dried over 80 C for 5 h in order to remove water molecules. Finally, ash colored tin oxide nanopowders

were formed at 400 C for 2 h. The same procedure was followed for the preparation of tin oxide nanoparticles using ethanol and water as a solvent.

Co-precipitation Method

In Co-precipitation method, SnO₂ nanoparticles was prepared by dissolving 1g stannous chloride dehydrates in 100 ml distilled water. After complete finish, 4ml ammonia solution was added drop wise to the above solution by under stirring. The solution was further stirred for 2 h, and then a few drops of H₂O₂ were added while stirring until the solution changed color. The result was then washed and filtered two times, dried in an oven at 150 °C for 4 h, and calcined at 500 °C for 2 h. In the present study, the calcinations temperature used was 500 °C because the alteration of SnO to SnO₂ occurs at 500-600 °C by direct heating (Allaedini *et al*., 2015). The same procedure was followed for the preparation of tin oxide nanoparticles using ethanol and Methanol as a solvent.
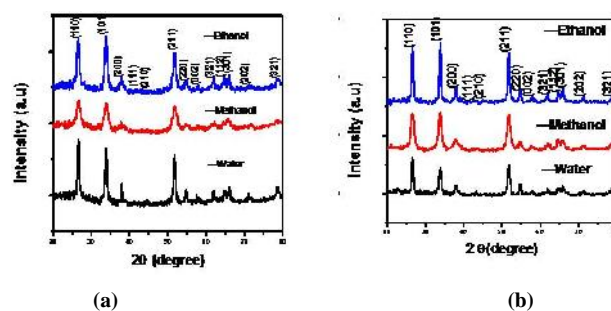
RESULTS AND DISCUSSION

XRD

Fig 1(a), (b) XRD patterns of the synthesized SnO2 using: (a) Sol-gel method, (b) Co-precipitation method

Table 1 Sol-Gel method

Sample	d spacing(hkl)	Crystallite Size (nm)	Lattice parameters			
			Calculated a(Å)	Standard a(Å)	Calculated c(Å)	Standard c(Å)
Synthesis in Water	3.3394 (110)	16.71	4.7226	4.7370	3.1718	3.1850
Synthesis in Methonl	3.3467 (110)	5.43	4.7245	4.7370	3.1704	3.1850
Synthesis in Ethanol	2.6469 (101	10.09	4.7591	4.7370	3.1917	3.1850

Table 2 Chemical Co-precipitation method

Sample	d spacing	(hkl)	Crystallite Size (nm)	Lattice parameters			
				Calculated a(Å)	Standard a(Å)	Calculated c(Å)	Standard c(Å)
Synthesis in Water	3.3484	(110)	18.9	4.7354	4.7370	3.1622	3.1850
Synthesis in Methonl	2.6467	(101)	9.9	4.7582	4.7370	3.1914	3.1850
Synthesis in Ethanol	2.6474	(101	11.7	4.7620	4.7370	3.1925	3.1850

Fig. 1(a) (b) shows the XRD patterns of the prepared SnO₂ nanoparticles using two methods at various solvents (water, methanol, ethanol respectively). All diffraction peaks can be readily indexed to tetragonal SnO₂ phase (JCPDS card No.72-1147). No other peaks were observed such as Sn or any other Sn based oxide, which represents the superior purity of the samples. The diffraction peaks are noticeably broadened, which indicates that the crystalline sizes of samples are extremely tiny. The sharpness and peak intensity increases desponds on

solvents, which reveals that the grain sizes become larger and the crystallinity improved. According to the Debye- Scherer's equation, the crystallite sizes was calculated to be 16.71, 5.43 and 10.09 nm for the samples prepared with water, methanol, ethanol for Co-precipitation method and it was 18.9, 9.9 and 11.7 nm for the samples prepared at various solvents for sol-gel method, respectively). No diffraction peaks due to metallic Sn or other impurities were observed, indicating the single-phase formation of the nanoparticles. In the tetragonal structure of SnO_2 lattice parameters (a = b, and c) have been calculated from the XRD peaks using the equation [27]:

Sem

The SEM image of synthesized SnO_2 nanoparticles using a sol-gel method with different solvents were shown in Fig 2 (a-c), which indicates that SnO_2 nanoparticles have different morphologies with different solvents such as water, methanol and ethanol respectively. Fig2 (a) shows that the SnO_2 nanoparticles have rod like morphology. Also, the rods are highly agglomerated with uniform distribution. Fig.2 (b) shows that most of the SnO_2 nanoparticles have a spherical shape. Here, several particles are combined themselves, which is looking like group of atoms are formed as a molecule. Also, the segregations among the groups of spherical shape nanoparticles. Fig 2(c) shows that the morphology of SnO_2 nanoparticles has a square
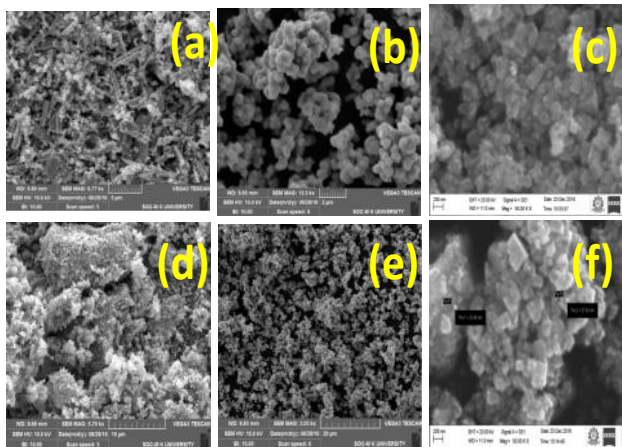

Fig 3 (a-c) shows the SEM images of Sol-gel and (d-f) shows the SEM images of Co-precipitation method

Shape which spreads uniformly throughout the image. Here, the square shaped nanoparticles are highly agglomerated than rod like morphology. The SEM image of synthesized SnO_2 nanoparticles using a Co- precipitation method with different solvents was shown in Fig 2 (d-f), which indicates that SnO_2 nanoparticles have different morphologies with different solvents such as water, methanol and ethanol respectively. Fig 2(d) shows that the morphology of SnO_2 nanoparticles has cluster-like formation. Fig 2 (e) shows that most of the SnO_2 nanoparticles have a spherical shape. Fig.2 (f) shows that the morphology of SnO_2 nanoparticles has a square shape which spreads uniformly throughout the image. The occurrence of chemical elements Sn, O, and Cu can be observed in this graph. The atomic weight percentage is shown in Table 3. It is clear from Table 3 that oxygen has a comparatively large atomic weight percentage showing that SnO_2 was attained. On the other hand, some traces of carbon element were too found,

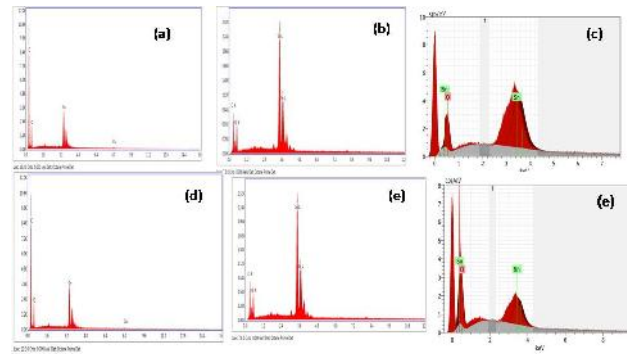which could be credited to the carbon tape of the sample holder.

Fig 3 (a-c) shows the EDX graphs for both the sol-gel (d-e) Co-precipitation methods.

Table 3 Atomic weight percentage result obtained by EDX

Sample	Method	Weight %	Atomic %
Sn	Sol-gel	55.56	27.00
O	Sol-gel	28.05	0.88
C	Sol-gel	17.31	70.86
Sn	Co-precipitation	50.87	22.85
O	Co-precipitation	36.62	0.68
C	Co-precipitation	22.63	65.36

FTIR

The FTIR spectra of tin oxide powder synthesized by the Sol-gel and the Co-precipitation. Methods using different solvents such as water, methanol and ethanol within 400-4000 cm^{-1} are shown in Fig. 4(a, b). For pure SnO_2, the different absorption bands to be found at 672, 1,022, 1,627, 2,926, 3,395 cm^{-1} are observed. Broad absorption bands centered at 673 and 1021 cm^{-1} can be assigned to the stretching vibrations of Sn-O and bending vibrations of O-Sn-O bonds, respectively. From Fig. 4 it is observed that the position of Sn-O is centered at 673, 621, and 619 cm^{-1}, for water, methanol, ethanol respectively, for co-precipitation route and centered at 617, 655 and 612 cm^{-1}, for water, methanol, and ethanol respectively for sol-gel method.
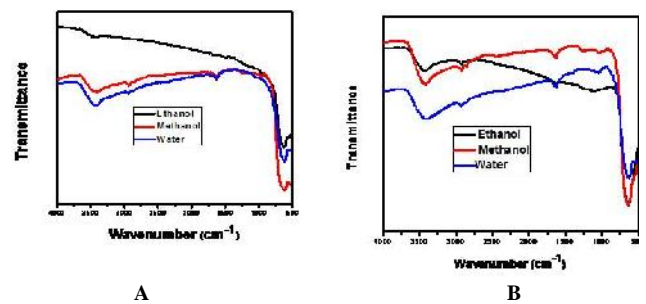

Fig 4 (a, b) shows the FTIR spectrum of SnO2 nanoparticles prepared in different solvents using Sol-gel and Co-precipitation method.

UV-vis absorption spectra of SnO_2 nanoparticles prepared by different solvents using sol-gel method and Co-precipitation method. Fig. 5 (a, b) shows the UV-vis absorption spectra of SnO_2 nanoparticles synthesized by different solvents sol-gel method, Co-precipitation method. In sol-gel method the band gap is established to be 3.67 eV, 3.63 eV, 3.57 eV equivalent to nanoparticles synthesized by different solvent (water, methanol, ethanol), respectively.

UV-visible Analysis

In the Co-precipitation method, the band gap is established to be 3.62 eV, 3.59 eV, 3.52 eV synthesized by different solvent (water, methanol, ethanol), respectively.
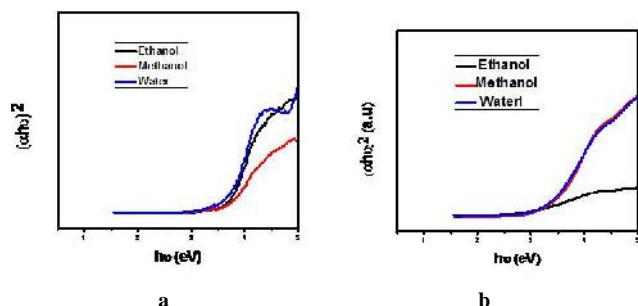

Fig 5 (a, b) shows the UV-vis Absorption Spectra of Sol-gel and Co-precipitation method.

From the result, the optical band gap value is different in different solvents. Using the solvent methanol could be assigned to the difference in a lattice defects and quantum confinement due to decrease in crystallite size i.e. the optical band gap of the nanoparticles was the particle size dependent. As the particle sizes of synthesized samples were larger than the exciton Bohr radius of SnO_2 (2.7 nm), considered under the weak confinement regime (Li *et al.*, 2011). Even in weak confinement regime, the particle size is very important to tune the optical band gap. From the result, the optical band gap of nanoparticle synthesized by sol-gel method and Co-precipitation method will increase with the decrease in particle size (Dijken *et al.*, 2000). Thus, the use of different solvent during synthesis affects the optical properties of SnO_2 nanoparticles.

CONCLUSION

The significance of preparation methods, sol-gel and chemical-precipitation, it was established that the structural, surface morphology and optical properties of SnO_2 NPs considerably depend on the solvent in employment during synthesis. The particle size of SnO_2 NPs synthesized by the sol-gel and the chemical-precipitation methods using different solvents was 16.71, 5.43, 10.09 nm and 18.9, 9.9, 11.7 nm respectively. The X-ray diffraction result established the rutile phase, and the nanoscale character of the SnO_2. In sol-gel method the band gap is established to be 3.67 eV, 3.63 eV, 3.57 eV equivalent to nanoparticles synthesized by different solvent (water, methanol, ethanol), respectively. In the Co-precipitation method, the band gap is established to be 3.62 eV, 3.59 eV, 3.52 eV synthesized by different solvent (water, methanol, ethanol), respectively.

Competing Interests

The authors declare that they have no competing interests.

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