FUNCTIONALISATION OF MWCNT WITH SnO_2 THROUGH SOL-GEL ROUTE

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The surface modification of the multiwall carbon nanotubes (MWCNT) coated with Tin oxide by sol-gel route was investigated and various treatments such as microwave irradiation, sonication were employed and the structural, morphological and photoluminescence analysis were studied. X -ray diffraction pattern exhibits the tetragonal structure with (1 1 0),(1 0 1), (2 1 1) strong peaks. The microwave assisted samples had well grown structure. The surface morphology of SnO_2 coated MWCNTs shows the modified surface of the CNTs. The room temperature photoluminescence analysis shows blue and green emission peaks. The calculated stokes shift lies between 2.5-3.5 eV which shows the band gap value of Tin oxide.

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1. Introduction

Semiconductor Metal Oxide (SMO) gas sensors are of prime importance because of their advantages of more robust nature, its less sensitive to moisture and temperature, faster response time,recovery time and simple interface towards electronics devices[1]. SMO gas sensors based on pellets or thick film technology are normally not chosen for the fabrication of intelligent Microsystems due to processing incompatibility and also due to high consumption of high power. Hence thin film SMO gas sensors are been regarded as the next generation gas sensing elements. In recent years, novel gas sensing materials with unusual properties are developed from the ideas of nanotechnology which is very promising with SMO gas-sensing materials. Since SMO's principle of gas detection is based on variations of the depletion layer at the grain boundaries, due to the presence of either reducing or oxidising gases. As a result, the adsorbed gas leads to a variation in the height of the energy barriers of free charge carriers (e.g. electrons in SnO_2) [2]. When particle size decreases, the ratio of the depleted volume to the whole bulk grain volume increases greatly, this is related to the surface to volume ratio. It is recognized that SnO_2 semiconductor thin film can have maximum gas sensitivity only if the nanocrystalline size within the film is comparable with its space-charge layer thickness (3nm for SnO_2, [3]). Qin Kaung et al reported controllable SnO_2 coated multiwall carbon nanotubes by chemical vapour deposition [4]. M.Parthibavarman et al observed the improved crystallinity on microwave assisted synthesis SnO_2 nanoparticles [5] .In this present work, it is reported that the surface modification of the multiwall carbon nanotubes is done by coating Tin oxide by sol-gel method and structural, morphological and photoluminescence properties of fresh, microwave irradiated and sonicated samples is discussed.

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2. Experimental

The sol-gel chemical route technique was utilised for the modification of surface of multiwall carbon nanotubes using Tin oxide. Multiwall carbon nanotubes were purchased from Aldrich (0.D 10-15 nm, 1.D-2-6 nm, length 0.1-10 μm, purity >90%) chemicals and used without further purification. Tin (II) chloride ($SnCl_4.2H_2O$) was taken as precursor for the source of Tin. 0.5mg of Tin (II) chloride was dissolved in 10ml of isopropyl alcohol and well stirred using magnetic stirrer for a period of 2 hours and allowed to age for 24 hours. Multiwall carbon nanotubes of 0.13 g were mixed well with the 1.5 ml of prepared precursor solution. Then the mixer was divided into three samples, out of them one sample was treated with microwave, one sample was ultrasonicated for 5 minutes and the other sample was used as a fresh sample. Then the three samples were annealed to 500°C for a period of 1 hour. After the heat treatment the freshly, microwave assisted and sonicated samples were used for various characterization studies. The structural properties of the samples were analysed under X-ray Diffractometer (Shimadzu 6000). The surface morphological studies carried out using FE-SEM (JSM 6390 LV). Photoluminescence characterization was done by Fluoromax-4 spectrometer in which Xenon is used as source at room temperature.

3. Result and discussion

3.1. Structural studies of SnO_2 coated -MWCNTs

The structural analysis of surface modified multiwalled carbon nanotubes coated with SnO_2 were studied using X-ray diffraction with range of angle between 10°-90° is shown in fig.1. The relatively strong peaks observed at (1 1 0), (1 0 1) and (2 1 1) plane confirms tetragonal structure and is in good agreement with standard JCPDS data (card no: 88-0287).

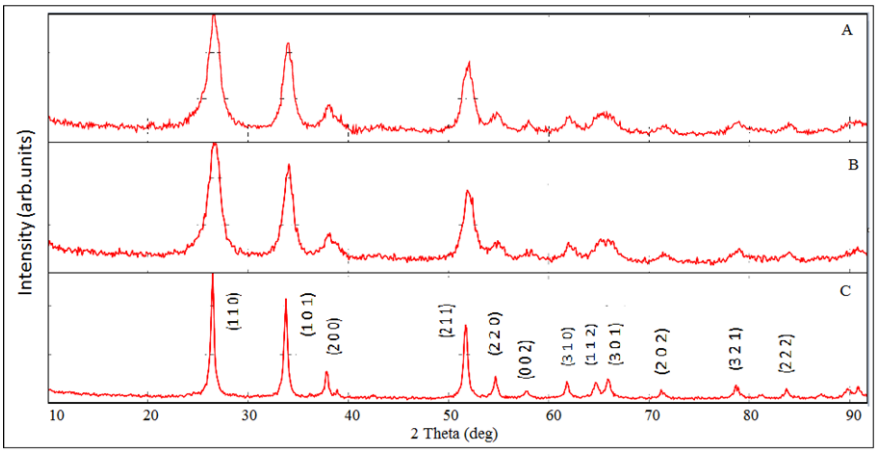

Fig.1. XRD pattern of Freshly (A), Sonicated (B) and Microwave assisted (C) SnO_2 coated-Multiwall carbon nanotubes.

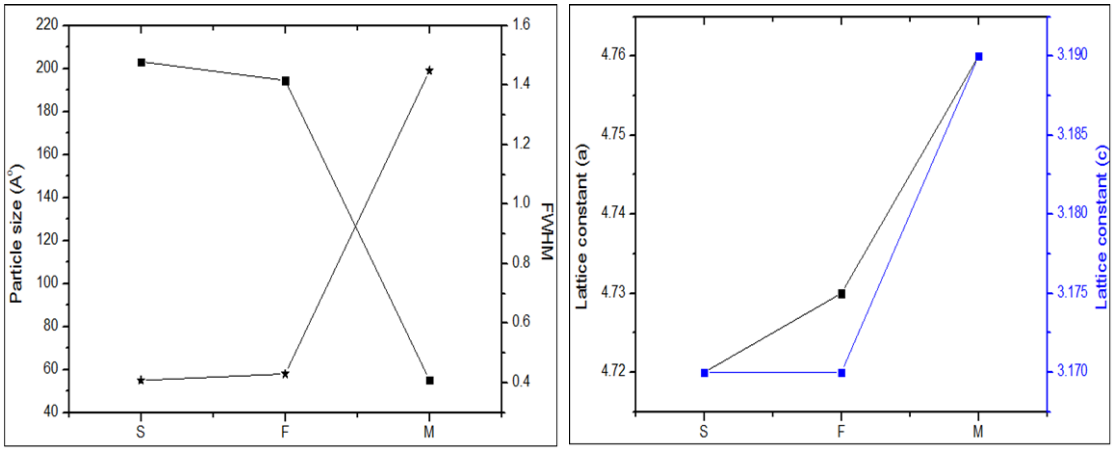

Fig.2. Variation of Particle size and FWHM (2a) and Lattice constant (2b)

The freshly and sonicated sample have broad full width half maximum (FWHM) while the sample prepared with microwave irradiation have low FWHM. This reveals that the surface of the carbon nanotubes of microwave assisted sample is well modified than those sample prepared by sonication and fresh nature. M.Parthibavarman et al observed the improved crystallinity on microwave assisted synthesis SnO_2 nanoparticles [5] and the similar effect were observed in this work. Fig.2a shows the variation of FWHM and crystalline size as a function of freshly, sonicated and microwave assisted samples.

Table.1. Structural parameters of SnO2 coated-MWCNTs

Treatments	2θ (deg)	Lattice spacing (d)	FWHM	Crystalline size (A°)	Lattice constant	
					a	C
Freshly	26.6127 33.9947 51.9180	3.34684 2.63506 1.75977	1.41550 1.20560 1.34800	57 68 65	4.73	3.17
Microwave	26.4578 33.7568 51.6829	3.36683 2.65308 1.76722	0.04094 0.41600 0.42380	199 199 208	4.76	3.19
Sonicated	26.6471 33.9210 51.9849	3.34259 2.63324 1.75766	1.47850 1.29940 1.39380	55 61 63	4.72	3.17

The calculated lattice constant of SnO_2 on MWCNTs are (a=4.73, c=3.17), (a=4.72,c=3.17) and (a=4.76, c=3.19) for freshly, sonicated and microwave assisted samples respectively ,while the standard values are (a=4.73, c=3.18) and this indicates that there is no strain induced between the surface of the CNTs and the coated SnO_2 layer. The variation of lattice constant a and c as a function of various treatments are shown in fig.2b

The crystalline size of the SnO_2 coated-multiwall carbon nanotubes were calculated using Debye Scherer's formula given by,

$$\mathbf{D} = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

Where λ is the wavelength of X-ray used, β is the full width half maximum of the peak and 2θ is the angle between the incident and scattered X-rays.
The lattice constant of SnO2 on MWCNTS were calculated using the relation,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

Where h,k,l are the Miller indices, a and c are the constant and d is the glancing angle.

The structural parameters crystalline size, Lattice constant is calculated using the equations (1 and 2) and tabulated in table 1. It is observed from the table, the particle size on freshly prepared and sonicated samples are equal (6 nm) whereas the particle size of microwave assisted sample was observed to be 20 nm and this clearly confirms that the SnO_2 is well coated on the surface of Multiwall carbon nanotubes.

3.2. FT-IR analysis

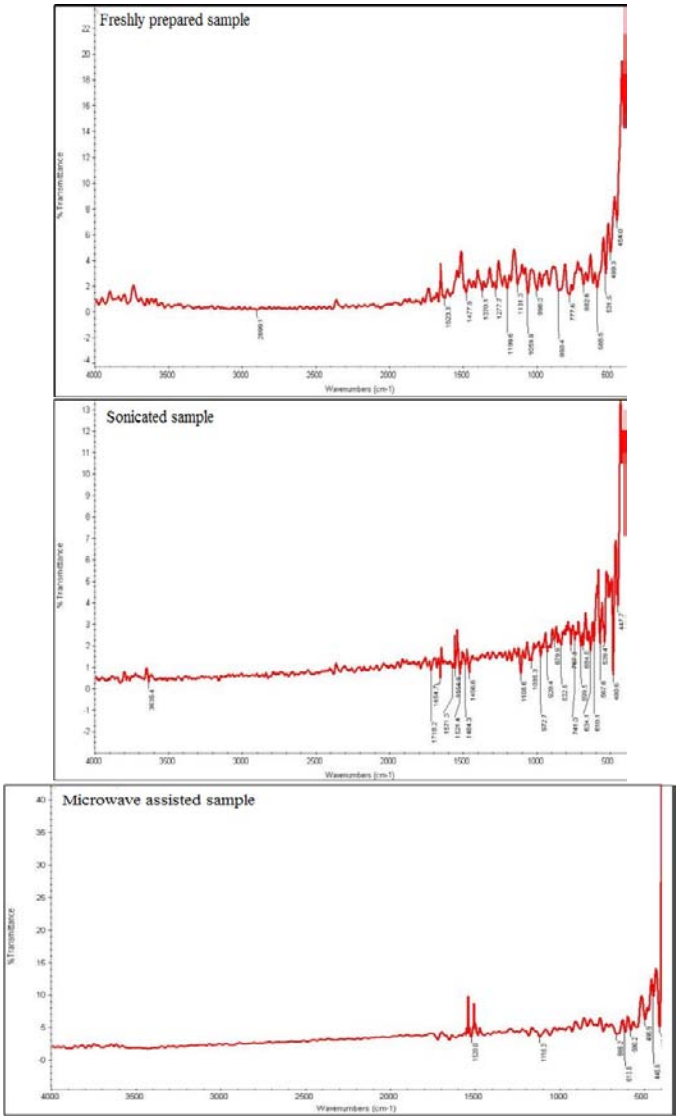

Fig.3. FT-IR spectra of SnO2 coated multilwall carbon nanotubes.

The FT-IR spectrum of freshly, sonicated and microwave assisted samples are shown in

fig. 3 .The various transmittance peaks in the wave number range of 500 to 4000cm^{-1} were analysed. The peaks around 615cm^{-1}corresponds to Sn-O stretching modes and the presence of vibrations due to inorganic tin compounds on the surface of multiwall carbon nanotubes. The spectrum confirms the resistance in them of rutile like features.

3.3. Surface morphology on MWCNTs coated with SnO_2

The surface morphological analysis of SnO_2 coated multiwall carbon nanotubes using scanning electron microscope leads to the view of modification occurred on the surface of carbon nanotubes. Scanning electron microscopy images of freshly, sonicated and microwave assisted samples are shown in fig.4.

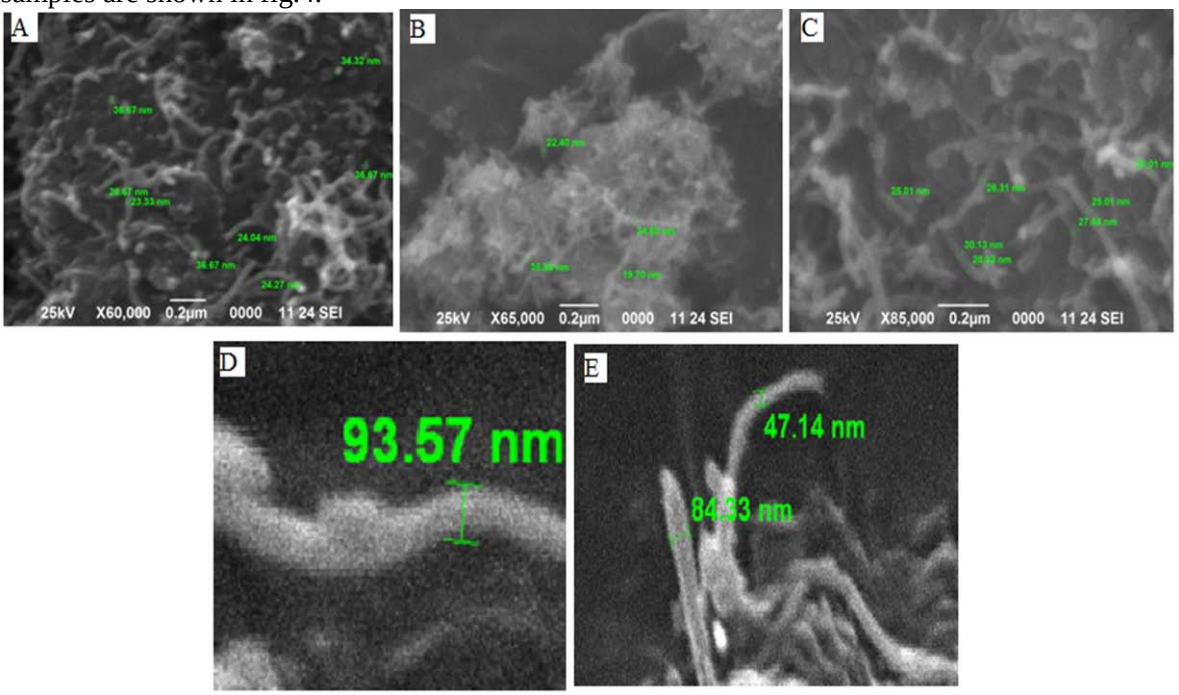

Fig.4.SEM images of SnO_2 coated-MWCNT's.A) freshly, B) microwave assisted, C) Sonicated samples. D and E show the FE-SEM of microwave assisted samples.

The freshly prepared SnO_2 coated on MWCNTs were well resolved and have the diameter distribution ranging from 20-39nm are shown in fig.4A. Fig.4B shows the SEM images of microwave assisted CNTs and 4E and 4D shows the FE-SEM images of microwave assisted CNTs. The diameter of the CNTs 21-25nm and 31-35 nm has increased due to impact of microwave irradiation as shown in the FE-SEM image(fig.4E) (diameter =93 nm), which confirms that the surface of the MWCNTs were well modified because of microwave irradiation. The treatments by sonication are shown in fig.4C and the diameter of the CNTs ranges from 20-29nm and 40-49nm. It is concluded from the scanning electron microscope images that the diameter of SnO_2 coated MWCNTs has increased from its original surface due to sonication and microwave irradiation .

3.4. Photoluminescence analysis

The room temperature photoluminescence studies of SnO_2 coated multiwall carbon nanotubes were carried out using Xenon source. Fig (5-7) shows the PL spectra of freshly, sonicated and microwave assisted SnO_2: CNTs.

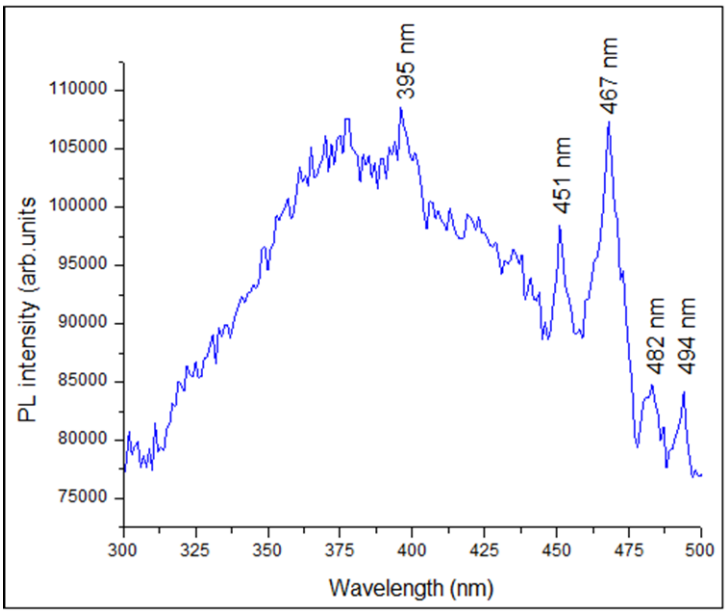

Fig.5. PL spectra of freshly prepared SnO_2: CNTs at room temperature

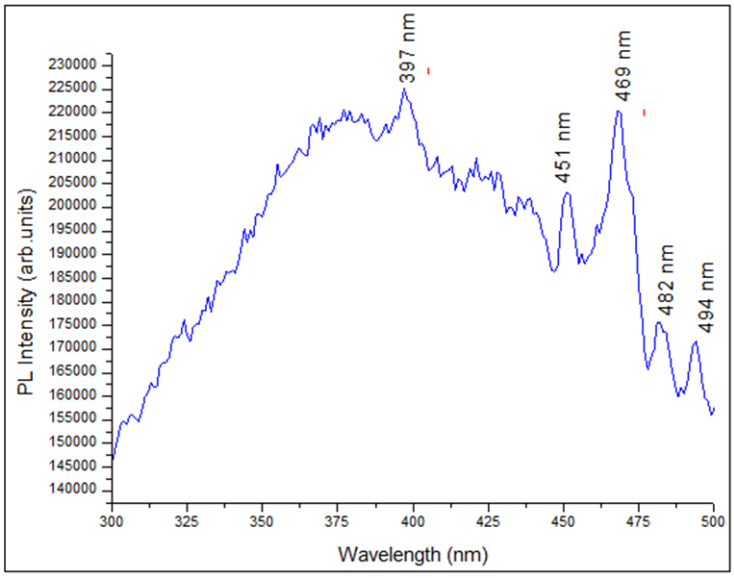

Fig.6. Microwave assisted SnO_2 coated MWCNTs of PL spectra at room temperature.

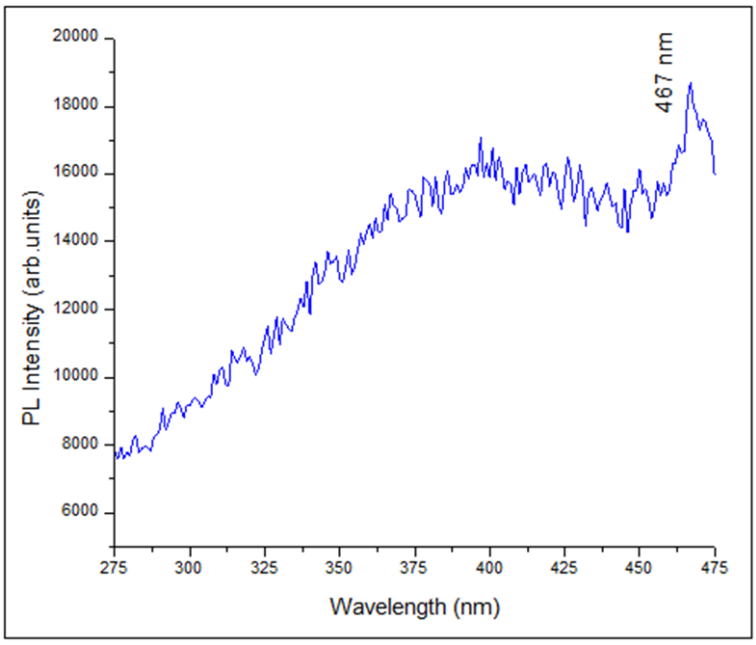

Fig.7. PL spectra of sonicated SnO_2: CNTs at room temperature.

All the SnO_2: CNTs were excited at the wavelength of 275nm and the emission bands lies in the visible region as shown in fig (5-7). The strong blue emission band centred at 467nm was observed and this is due to band to band transitions. The emission peaks centred at 391nm and 451nm exhibits the inter band transitions. The inter band transitions occurred at 484nm and 494nm. The shift in emission band centred at 469nm and 397nm from the freshly prepared samples were observed in microwave assisted samples. This shift toward green emission bands due to well growth of SnO_2 on MWCNTs as in XRD was observed. However, the inter band transitions occurring in microwave assisted samples is same as that of freshly prepared samples. The sample prepared by sonication has the emission peaks centred at 467nm as freshly prepared samples and were not well resolved. The emission peaks in all the spectra lies in the range of 2.5eV-3.1eV which is the band gap value of Tin oxide (2.5-3.5 eV). The PL intensity is high on microwave assisted samples and more small peaks indicate that the splitting of energy levels in the conduction bands. The stokes shift was calculated from the excited and emission peaks which ranges from 0.042-1.03eV.

5. Conclusion

It is concluded that, the surface of the multiwall carbon nanotubes were modified coated with SnO2 by sol-gel chemical route. The various treatments by microwave and sonication were done and investigated was that the CNTs coated with SnO_2 show good crystallinity which were exhibited from X-ray spectrum. The crystalline size of 6nm was observed on freshly and sonicated samples while 20 nm was observed on microwave assisted samples. The scanning electron microscopy gives the clear view on how the surfaces of the CNTs were modified with Tin oxide. The room temperature photoluminescence spectrum show that the blue emission bands and the emission energies were in well agreement with band gap values of Tin oxide.

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