Journal of Ovonic Research Vol. 7, No. 5, September - October 2011, p. 93 - 98

ENHANCED SURFACE MODIFICATION OF MWCNT: INDIUM AND VANADIUM DOPED SnO_2 COMPOSITE BY SOL-GEL ROUTE AND SONICATION

J.SURYAKANTH, V.ARIVAZHAGAN, M.MANONMANI PARVATHI, S.RAJESH*

Department of Physics, School of Science and Humanities, Karunya University, Coimbatore-641 114, Tamil Nadu, India

In this study, Nanocrystalline Indium and Vanadium doped SnO_2 multiwalled Carbon nanotube composite is prepared by simple sol-gel process. The Nanocomposite produced was Ultrasonicated for five minutes. The impact of Ultrasonication on the surface modification of MWCNT, structural and optical properties was analysed. The sample was characterized by X-ray diffraction, scanning electron microscopy, UV-visible absorption and Laser Raman Spectroscopy studies. A comparative study was done between the as-prepared and Ultrasonicated sample. The X-ray diffraction revealed the improved crystallinity of the Ultrasonicated sample. The UV-Visible spectrum gave the size dependent absorption and transmittance in the visible region. The SEM images show that ultrasonication enhances the full coverage of the MWCNT and very less agglomeration on the surface. The percolation was not much pronounced on the samples sonicated after five minutes.

(Received September 8, 2011; accepted September 20, 2011)

Keywords: MWCNT, Vanadium and Indium dopant, sol-gel, Ultrasonication

1. Introduction

Carbon nanotubes are a promising material due to its electrical, chemical, mechanical properties and hence it is actively studied. It is given more significance due to their application in the various fields of nanoscience and nanotechnology [1, 2].The surface modification of MWCNT by Metal Oxide Semiconductors like SnO_2, In_2O_3, and ZnO has proved their significance in various potential applications. Among these metal oxides SnO_2 is a very important n-type semiconductor with a direct band gap of 3.6eV between the oxygen 2p valence band and tin states at the bottom of the conduction band. It is a semiconducting material used as a catalyst for Oxidation of Organic compounds, as a gas sensors[3] Rechargeable Li-batteries[4] and Optical devices [5].The Hybrid of SnO_2 and CNT could express not only the properties of CNT and Nanocrystal but also other novel properties. Mixing SnO_2 with CNT could promote direct and efficient charge transfer between metal oxide and CNT and hence improves the material efficiency leading it to be utilized as chemical sensors [5] and biosensors [6]. In this present work, we have prepared a hybrid of MWCNT and SnO_2 by sol-gel route method [7]. The Nanocomposite was doped with Vanadium and Indium for selectivity of certain industrial gases. The prepared sample was Ultrasonicated. A comparative study was made between the as-prepared and Ultrasonicated sample by X-ray diffraction, SEM, UV-Visible and Laser Raman Spectrometer.

* Corresponding author: drsrajesh@karunya.edu

2. Experimental

The surface of the multiwalled carbon nanotubes was modified using Indium and Vanadium doped Tin oxide by sol-gel chemical route technique. Multiwalled carbon nanotubes were purchased from Aldrich (0.D 10-15nm, 1.D-2-6nm, length 0.1-10μm, purity >90%) chemicals and used without further purification. Tin (II) chloride ($SnCl_4.2H_2O$), Indium(III)chloride($InCl_3$) and Vanadium(II)Chloride (VCl_2) were taken as starting precursor for the source of Tin, Indium, Vanadium. Tin (II) chloride of 0.5mg was dissolved in 10ml of isopropyl alcohol and the same concentration of Indium (III) chloride and Vanadium (II) Chloride (VCl_2) were taken. Then 80% of Stannous chloride solution along with 20% of Indium chloride and Vanadium(II)Chloride solution were mixed together and stirred using magnetic stirrer for 2 hours. Viscous sol was attained after 24 hours of aging. Multiwalled carbon nanotubes of 0.13g were mixed well with the 1.5ml of prepared precursor solution. Then the mixer was divided into two samples, one out of them was ultrasonicated for 5 minutes and the other sample was used as-prepared sample. Then the two samples were annealed to 500°C in the furnace for 1 hour. After the heat treatment the as-prepared and sonicated sample were used for various characterizations. The structural properties of the samples were studied using X-ray Diffractometer (Shimadzu 6000). The morphological studies of the samples were analyzed by FE-SEM (JSM 6390 LV) .The UV-NIR spectrophotometer (JEOL) was used to analyze the absorption and transmittance spectra of the samples. The spectroscopic studies were done by Laser Raman spectrometer (HORIBA JOBIN).

3. Result and discussion

3.1. Structural studies of MWCNT: Indium and vanadium doped SnO_2 composite

The X-ray diffractogram of Indium and Vanadium doped Tin oxide on multiwalled carbon nanotubes are shown in figure 1. The polycrystalline nature of the particles was observed from large number of peaks in as-prepared and sonicated samples. The high intense peak at (1 1 0), (1 0 1) and (2 1 1) planes corresponds to Tin oxide nano particles. The intensity of the peak is comparatively high for Tin oxide particle on Multiwalled CNT than other medium or substrates [8]. This happens due to flexibility of carbon nanotubes. The structure (tetragonal) of the coated layer from the peak position and the plane orientation were compared with JCPDS (PDF no 88-0287) and were in good agreement with the experimental values. The crystalline nature improved on ultrasonicated sample. The full width half maximum of the relative intense peak (FWHM) of as-prepared was more when compared to sonicated sample. The sonicated sample had the crystalline size of 5nm, from which it was evident that the sonicated MWCNTs surface was well coated by precursors. However, the relative split of high intense peaks at their edges showed that the doped materials were lodged well on Tin oxide lattices. The particle size coated on the surface of multiwalled carbon nanotubes were calculated using Debye Scherer's formula [9] and is tabulated in table 1. The lattice constant of the samples with tetragonal structure were calculated and were in good agreement with the already reported values. Crystalline size (D), lattice constant (a), full width half maximum of the diffracted peaks (FWHM), interplanar distance (d) of both the samples (as-prepared and sonicated).

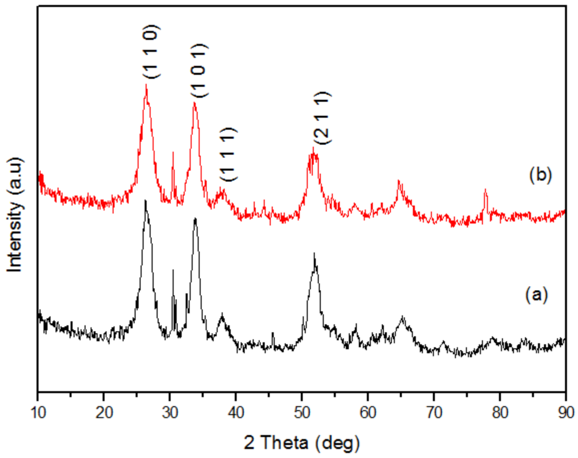

Fig.1..XRD spectrum of MWCNT: Indium and vanadium doped SnO_2 composite for as-prepared (a) and sonicated sample (b).

Table.1. Structural parameters Crystalline size (D), lattice constant (a), full width half maximum of the diffracted peaks (FWHM), interplanar distance (d) of as-prepared and sonicated MWCNT: Indium and vanadium doped SnO_2 composite.

Treatments	h k l	2θ(deg)	d(A°)	FWHM	D (nm)	a(A°)
As-prepared samples	1 1 0 1 0 1 2 1 1	26.3504 33.6909 51.6098	3.37855 2.65812 1.76955	2.21030 1.81820 2.30540	3 4 3	a=4.8 c=3.2
Sonicated samples	1 1 0 1 0 1 2 1 1	26.3956 33.7312 51.7539	3.37387 2.65504 1.76496	1.92880 1.56830 1.96500	4 5 4	a=4.7 c=3.1

3.2. Morphological studies

The FE-SEM images of Indium and vanadium doped SnO_2 coated multiwalled carbon nanotubes are shown in figure 2. The diameter of the MWCNT had increased, which was evident that the mixed particles were well coated on MWCNT. The surface modification of the carbon nanotubes of as-prepared sample is shown in fig 2 (a).

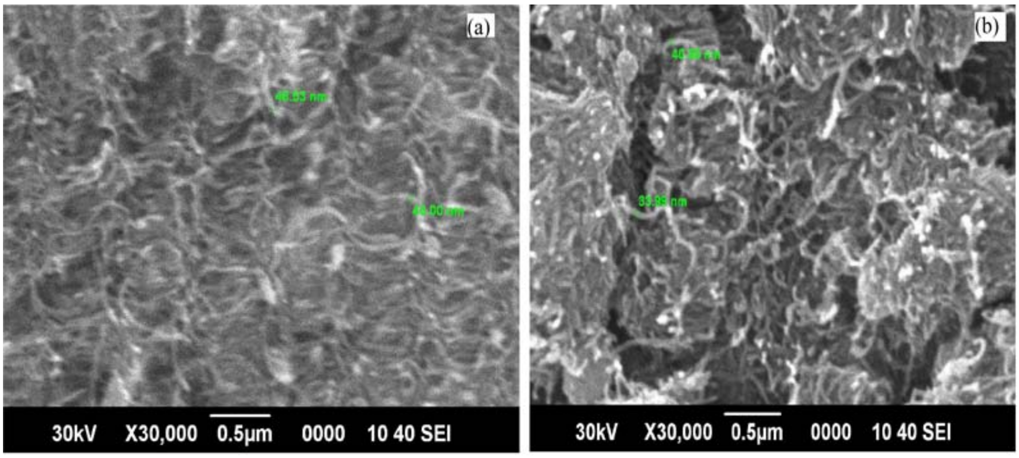

Fig.2. FE-SEM of as-prepared (a), sonicated (b) MWCNT: Indium and vanadium doped SnO_2 composite

The figure 2(b) indicated the field emission scanning electron microscope image of sonicated sample. The sample prepared by sonication treatment had the diameter of 33-40nm.

3.3.UV-Vis studies of surface modified MWCNT: Indium and vanadium doped SnO_2 composite

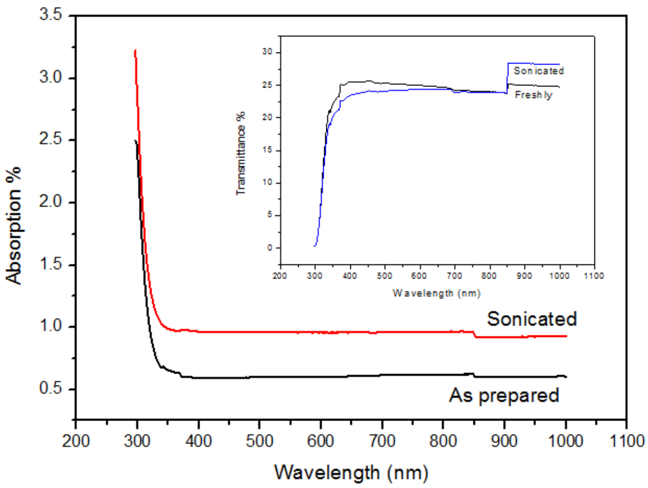

Fig.3. Absorption and transmittance spectra of MWCNT: Indium and vanadium doped SnO_2 composite.

The UV – Visible spectroscopic studies of the In/V doped SnO_2 coated multiwalled carbon nanotubes were analyzed by a wavelength of 200-1100nm to see the absorption edge and the transmittance spectra. The absorption shift towards red wavelength clearly indicated the presence of crystal formed on the surface of multiwalled carbon nanotubes[10]. The absorption edge starts around 300nm and the inset of the transmittance spectra of sonicated sample was around 25 %.

3.4. Spectral studies of MWCNT: Indium and vanadium doped SnO_2 composite

The spectral studies of the two samples were done using Laser Raman spectrometer. Laser Raman spectrums of the prepared samples are shown in fig.4. There were three well resolved peaks appearing in both the samples. The intensity of sonicated sample was high when compared to that of as-prepared sample. The 'G' active mode of multiwalled carbon nanotubes were observed at $1580cm^{-1}$[11] in both the samples and the G' mode was observed with less intensities around $2200cm^{-1}$. This mode corresponds to the planar vibrations of carbon atoms and present in graphite like materials. There was no more split in G mode which indicated the multiwalled nature of carbon nanotubes. The peak observed at 1350cm^{-1}[11] clearly indicated the D mode of the multiwalled carbon nanotubes that arises due to the stretching modes of carbon nanotubes. The peaks corresponding to stretching mode for double coordinate Tin oxide were also seen in the spectrum around at 850cm^{-1}. The full width of the peak was broader than the other two peaks, which was evident that the coated layer had undergone hybridization.

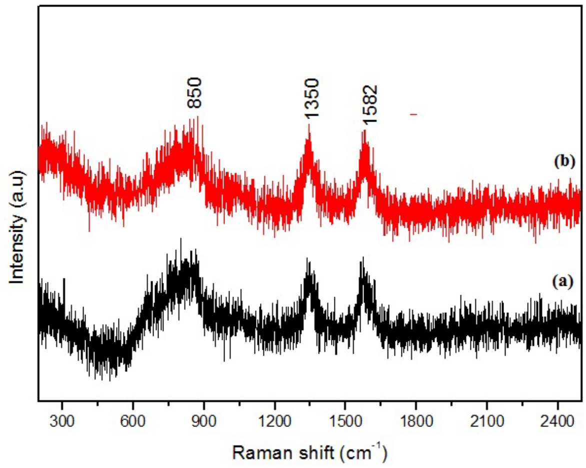

Fig.4. Laser Raman spectrum of as-prepared (a) and sonicated (b) MWCNT: Indium and vanadium doped SnO_2 composite.

It also indicated that the material coated on the multiwalled carbon nanotube were very thin and it will lead the sample to have high selectivity and flexibility, making itself a significant material for gas sensing applications. When this nature increases, the electrical and thermal properties of the material increases. All the above Raman modes could be observed as stokes and antistokes scattering. The ratio of I_G/I_D for the as-prepared and ultrasonicated samples was found to be 1 and 0.83 respectively. The explanation for the observed I_G/I_D ratio variation in composite samples might be due to variation in the atomic order of crystallinity of MWCNT [12]. It was reported in the literature that I_G/I_D value of SnO_2/MWCNT composite decreased after SnO_2 was deposited on the exterior surface of MWCNTs, which was attributed to the interaction between SnO_2 and the surface group of MWCNT [12, 13].

4. Conclusion

The surface modification of the multiwalled carbon nanotubes was successfully done using Indium and Vanadium doped SnO_2 by sol-gel route and sonication. The polycrystalline nature of both the samples with tetragonal structure was evident from X-Ray diffraction. The particle size coated on the surface of MWCNT was calculated and ranges from 3nm-5nm. The crystalline nature of ultrasonicated sample had improved, which was evident that the coated layer was well formed on the surface of MWCNT. The morphological studies of the samples indicated that Indium and Vanadium doped SnO_2 was uniformly coated on the surface of carbon nanotubes. The absorption shift towards greater wavelength indicated the formation of Nanocrystal on the surface of MWCNT. Laser Raman spectroscopic analysis indicated the standard G and D stretching modes. The shift in Raman spectrum around 850cm^{-1} indicated the surface defects of the carbon nanotubes due to Tin oxide hybridization, which will provide high sensitivity and selectivity making itself suitable for gas sensing application.

Acknowledgement

The authors thank STIC-SAIF, Kochi for providing FE-SEM testing facilities. The authors are also grateful to DRDO centre for life sciences, Bharathiar University for providing Laser Raman Spectroscopic facilities.

References

[1] T.W Ebbesen, Annu.Rev.Mater.Sci **24**, 235 (1994).
[2] R.H.Baughman,A.A.Zakhidov,W.A de Heer,Science **297**,787 (2002).
[3] N.Barsan,M.Schweizer- Berberich,W.gopel, Fresenius.J.anal.chem.**365**.287 (1999).
[4] Park-Min-sik, Wang Guo-Xiu, Kang Yong-Mook, Wexler David, Dou Shi-Xue, hua-Kun-Liu, Angew chem. Int.Ed **46**,750 (2007).
[5] J.kong, M.G.Chapline, H.J.Dai, Adv.mater.**17**, 2458 (2005).
[6] R.J.Chen, Y.G.Zhang, D.W.Yang, C.M.Lieber, Nature **399**,48 (1999).
[7] Shek ch,lai jkl,lin gm,ananostruct.mat.**11**,887 (1999)
[8] V.Arivazhagan, S.Rajesh, Journal of Ovonic research **6**, No. 5, September-October 221 (2010)
[9] Jagriti pal,pratima chauhan, mat. Char. **609**, 1512 (2009)
[10] J.Suryakanth,v.Arivazhagan M.Manonmani Parvathi,S.Rajesh J.optoelect. and biomat. **3**(2), 31 (2011).
[11] Yanbao.f,ruobiao.m, ye.s, zhuoc,xiahua.m, mat. Lett.**63**,1946 (2009)
[12] Matusmura Y, Wang S, Mandorij. J.Electrochem Soc **142**, 914 (1995)
[13] Park Ms, Needham SA, Wang GX, Kang YM, Park JS, DouSX, chem.Mater **19**, 2406 (2007).