

SWCNT/Inorganic polymer nanocomposite: a new class of transparent conductor and UV-Vis photo – generator

S. Bose*, S. Balaji**, R. Debnath*

*School of Laser Science & Engineering, Jadavpur University, Jadavpur,
Kolkata – 700 032, India. saptasree.bose@gmail.com; drdebnathr@gmail.com

**Central Glass and Ceramic Research Institute, Jadavpur
Kolkata- 700 032, India. bvhsbalaji@gmail.com

ABSTRACT

Synthesis and optical, electronic and optoelectronic properties of a photo-active SWCNT/(Pb, Zn)-phosphate glass composite have been reported. Absorption spectrum of SWCNTs of the composite differs significantly from that of its film which has been attributed to the host related internal stress induced conformational deformations and subsequent modulation of their band structure. Conductivity studies show that incorporation of SWCNTs in the glass increases the conductivity of the latter by almost hundred thousand times. UV-Vis light-induced ESR spectrum of the composite exhibits an enhancement of the conduction electron-signal of its SWCNTs with concomitant appearance of a new signal at the lower field region which owes its origin to the (Pb⁺³) holes. A phenomenon of charge separation in the system due to light induced release of electrons from the Pb⁺² – sites of the host and capture of those electrons by the SWCNTs is thus observed. The material is prospective for use both as transparent conductor and solar photo-current generator.

Keywords: SWCNTs/phosphate glass composite, SWCNT – band structure, increased conductivity, Photo-induced charge separation, solar photo-current converter.

1 INTRODUCTION

Single walled carbon nanotubes (SWCNTs) have electronic conduction and electron acceptor properties. Reports of preparing SWCNT based semitransparent conductor [1] and designing of SWCNT/organic polymer composite based photovoltaic cells are known [2,3]. Since a commercial sample of carbon nanotubes always contains a mixture of semiconducting and metallic varieties and the metallic nanotubes are ~ 6 times better conductor [1] than the semiconducting species, preparation of optically transparent metallic SWCNT rich conducting composites is challenging.

In the context of designing of SWCNT/organic conjugated polymer based photovoltaic cell, one major problem that needs to be overcome is that the organic conjugated polymers are chemically unstable and prone to photo-degradation. Efforts are being made worldwide to search for alternative photo-generators which have better photo-

stability and higher UV-visible light absorption efficiency (η_A). Photo-sensitive inorganic polymers are potential candidates for this purpose. With the reported knowledge in mind that the interstitial Pb⁺² ions in a silicate or phosphate glass are sensitive to high energy irradiation like UV, X-ray, γ -ray [4,5] and can produce (Pb⁺³)-holes and free electrons in the matrix, in the present work we have synthesized a transparent SWCNT/(Pb, Zn)-phosphate glass composite and studied its optical, electrical and optoelectronic properties. The results show that the composite has prospect of being used as optically transparent large-area efficient conductor as well as a solar photo-current converter.

2 EXPERIMENTAL

The SWCNT - glass composite was prepared by melting a mixture of carboxylic acid functionalized SWCNT (a precursor of SWCNT, Sigma Aldrich) and a (Pb, Zn)-phosphate glass in an atmospheric controlled furnace. Details of the method are discussed elsewhere [6, 7]. To make a comparative study of the optical and electronic properties of the composite with those of the pristine SWCNT-film, a film of the same SWCNTs was also prepared. The presence of pure SWCNTs in the composite and in the film was ascertained from transmission electron micrographs (TEM) as well as from respective absorption spectrum.

TEM of the composite were recorded in a transmission electron microscope (JEM-2011, JEOL, Japan). The absorption spectra were recorded at 300K in an UV-Vis-NIR absorption spectrophotometer (Shimadzu, Japan). The Electron Spin Resonance spectra of the composite with and without UV-Vis light illumination were recorded at 300K in an X-Band ESR Spectrometer (JEOL Japan). A 150W Xenon-lamp was used to illuminate the sample.

The electrical conductivity and resistivity were studied by using a Pico-ammeter (Keithley, USA). Electrical measurements at varied temperature were made by using a thermostat. To study photo conductivity, a 150W Solar Simulator (Sciencetech Inc, Canada) was used to illuminate the sample. The light from the source was guided on to the sample by using an optical grade UV-silica core/PCS clad waveguide. Temperature of the sample in each case was kept unchanged during illumination.

3 RESULTS AND DISCUSSIONS

The TEM of the composite is shown in Fig.-1. The micrograph shows the existence of randomly oriented both isolated and SWCNT-bundles in the matrix. A simple calculation based on the diameter distribution data (~ 1.3 - 1.5nm) of the SWCNTs used, indicated that the sample were a mixture of (10, 10), (11, 11) arm chair metallic, (18, 0) zigzag quasimetallic, (17, 0), (19, 0) zigzag semiconducting and other semiconducting nanotubes of different chiralities.

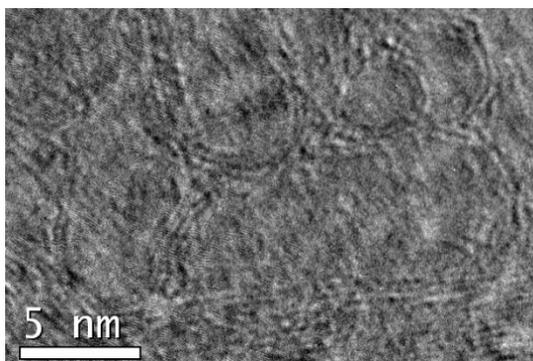


Fig.1, HRTEM of the composite

3.1 Absorption spectra

The Fig.2 shows the absorption spectrum of SWCNT in the composite along with that of the base glass vis-à-vis that of the SWCNT-film.

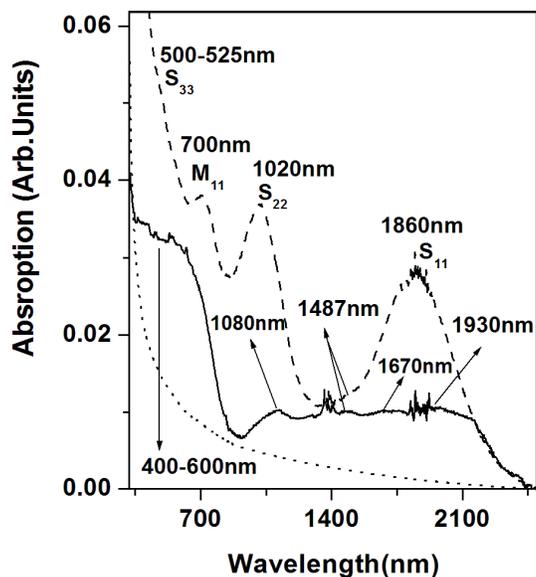


Fig.2, Absorption spectrum of the SWCNTs of the composite (—); that of the host glass (....); Spectrum of a mat of the SWCNT sample (- - -).

The spectrum of the SWCNT- film exhibits two broad absorption bands peaking respectively at around 1860 (0.66eV) and 1020nm (1.2eV), and a relatively narrow band

with maximum at around 700nm (1.77eV). The spectrum also shows a high energy absorption shoulder at around 500-525 nm (2.48 – 2.36eV) on the tail of the strong π – plasmon absorption of the nanotubes. The absorption bands observed in the spectrum of the SWCNT- film are, in fact, the average absorption characteristics of different types of SWCNTs present in the film. The two low energy bands and the high energy absorption shoulder are assigned [8] respectively as the transitions across the band gaps of the first, second and third pairs of one dimensional van Hove singularities (VHS) of the density of states of different semiconducting SWCNTs, which are marked respectively as S_{11} , S_{22} and S_{33} . The band observed at around 700nm (1.77eV) is attributed [8] to the first order metallic/quasi-metallic transitions of the SWCNTs. Surprisingly, the corresponding absorption bands of the SWCNTs of the composite, exhibit a drastic change in their features in respect of energy as well as relative intensities. The S_{11} semiconducting band in this case, suffers a broadening concomitant with a significant lowering of its intensity. Interestingly, within this new broad band, a number of poorly resolved weak bands [0.64eV (~1930nm) and 0.74eV (~1670nm)] distributed respectively on the lower and higher energy side of the peak position 0.66eV (1860nm) of the S_{11} band of the SWCNT film, are discernible. Similar broadening and lowering of intensity are observed also in the case of the S_{22} band, but the shift in this case only to the lower energy 1.15eV (~1080nm) side. The semiconducting S_{33} absorption shoulder after suffering a loss in intensity is found to mingle with the M_{11} metallic band which also has suffered a shift to higher energy without making any significant loss in its relative intensity. The S_{33} band and the shifted metallic band on mingling together have actually created a broad absorption region ranging 400-600nm (3.10 – 2.06eV).

The spectrum of the composite thus shows that the band gap energies of its nanotubes have suffered a change. While the first order metallic bands of the metallic nanotubes experience a phenomenon of opening a gap at their Fermi energy, the semiconducting tubes suffer both an increase and decrease of their band gaps.

Stress induced deformation and consequent modulation of band structure of SWCNTs are well known [9, 10, 11]. Considering the fact that the present composite was synthesized by rapidly quenching a melt of mixture of the glass and the SWCNTs from 1033-1043 K to 300 K, generation of different types of stress inside the composite is expected. The linear thermal expansion coefficient of the glass component of the composite is $12.80 \times 10^{-6} \text{ K}^{-1}$. The inter-tube space corrected radial expansion coefficient of SWCNT in the temperature region 300K to 800 K, is known to be negative and has the value [12] $\sim -7 \times 10^{-6} \text{ K}^{-1}$. Calculation of the volume strain of the SWCNTs/SWCNT-bundles of the composite yielded a value $(\Delta V/V) \approx -0.022$. The bulk modulus of SWCNT being 35GPa [13], the value of the compressive stress in the composite is $\sim 0.77 \text{ GPa}$. Thus the SWCNTs in the composite are under a

compressive stress from all its circumferential sides and suffer from strains like polygonization, radial compression etc. Ijima et al [11] studied in details stress induced polygonization of 1.4 nm diameter SWCNTs and calculated a compressibility factor for such tubes $(1/V)dV/P = 0.024 \text{ GPa}^{-1}$. Calculation of the compressibility factor of the SWCNTs ($d \sim 1.3 - 1.5 \text{ nm}$) of the present composite yielded a value of $\sim 0.028 \text{ GPa}^{-1}$ which is quite in agreement with the value reported by Ijima et al [11].

3.2 Conductivity properties

The phenomenon of conformational modulation and subsequent change in the band structures of the SWCNTs of the composite is however, further evident from their electrical properties. The glass component of the composite is an insulator, so any electrical conduction through the composite, should occur by its SWCNT-network only. Fig. 3 shows the conductance vs. voltage curve of the composite vis-à-vis that of the SWCNT-film.

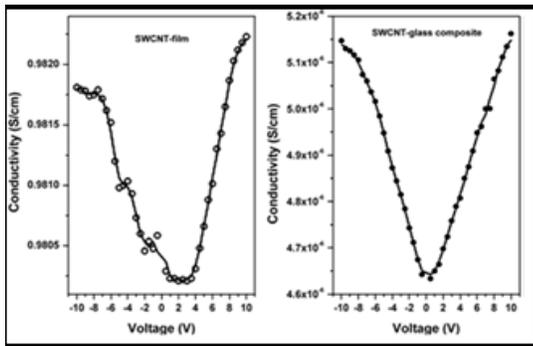


Fig.3, Conductance vs. voltage curve of the composite (•••) vis-à-vis that of the SWCNT-film (o o o o o)

The curve of the composite exhibits a feature which is similar to the feature reported [14] in case of small-band gap metallic (quasimetallic) SWCNTs. The similar curve for the SWCNT-film shows a characteristics which is known [14] for semiconducting SWCNTs. Actually a small band gap nanotube shows only a moderate off state dip in the conductance when the Fermi-level is tuned into its band gap. This is because, its band gap is comparable to the thermal energy, $E_{\text{gap}} \sim k_B T$. Such a characteristic is clearly discernible in the conductance behavior of the composite. A semiconducting tube, on the other hand, shows a broad region of near-zero conductance because its $E_{\text{gap}} \gg k_B T$, - a characteristic which is evident in the conductance behavior of the SWCNT-film. The results clearly show that the band structures of the major fraction of the SWCNTs in the composite have changed to quasimetallic type, making the composite a good electrical conductor.

3.3 (I-V) Characteristics

The (I-V) - characteristic of the composite has also been studied vis-à-vis that of the SWCNT-film (shown in Fig.4).

The composite exhibits a non-Ohmic behavior in its electronic conduction. In spite of the fact that the host component of the composite (phosphate glass) is basically an insulator ($R = \text{few hundred Giga Ohm}$), conductivity of the composite becomes hundred thousand times ($R = \text{micro Ohm}$) higher than that of the glass. The composite thus shows a prospect of its use as a transparent conductor.

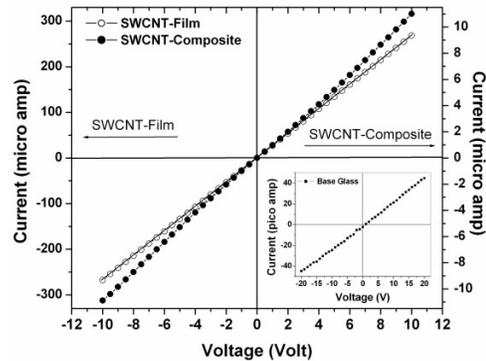


Fig. 4, I-V characteristics of the composite vis-à-vis that of the SWCNT film; **Inset:** I-V characteristics of the host glass

3.4 Light induced ESR spectrum

Fig. 5 shows the ESR spectra of the composite with and without illumination of UV-Vis-light. The composite in absence of light gives a spectrum which exhibits a broad ESR signal with 'g' tensor $g_1 = 2.21$ and a line width $\Delta H_{\text{pp}} = 125 \text{ mT}$. Overlapping with this broad signal a sharp signal with $g_2 = 2.0024$ and $\Delta H_{\text{pp}} = 2.8 \text{ mT}$, is also noted. The value of 'g' tensor ($g_1 = 2.21$) and the line-width of the broad signal suggest [15] that the signal is associated with the paramagnetic Ni - nanoclusters that was probably used by the manufacturer for the synthesis of the SWCNT product of our study.

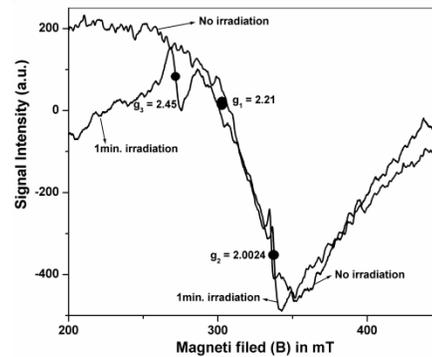
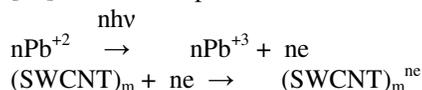


Fig5. ESR spectra of the composite with (—) and without (---) illumination of UV-Vis light.

It is well known that the ferro-magnetic catalysts which are normally used for synthesis of SWCNTs always remain as contaminant with the product. These impurities cannot be removed from the sample even after soft-bake acid-purification [16]. The value of the g tensor ($g_2 = 2.0024$) and the narrow line width ($\Delta H_{\text{pp}} = 2.8 \text{ mT}$) of the

overlapping sharp signal, on the other hand, suggest that the signal should be associated with the surface lying conduction electrons of the SWCNTs [16]. Upon UV-Vis light illumination, the composite exhibits a dramatic change in its ESR spectrum. Within a moment of illumination, the intensity of the conduction electron- signal of the SWCNTs becomes almost double to its dark value, showing clearly that the SWCNTs of the composite gain in population of their conduction electrons upon UV-Vis illumination. Concomitant with the above phenomenon, a new signal with g tensor ($g_3 = 2.45$) and line-width $\Delta H_{pp} = 9$ mT, appears in the low field region of the spectrum. The values of the magnetic parameters of the new signal ($g_3 = 2.45$ and $\Delta H_{pp} = 9$ mT) indicate that the signal owes its origin to Pb^{+3} holes (natural abundance of ^{204}Pb , ^{206}Pb and ^{208}Pb together is 79% and each having $I = 0$) which are generated in the system as a result of UV-Vis irradiation [4, 5].

It is well known that in a low Pb-containing phosphate and silicate glass, most of the Pb^{+2} ions remain into the network structure (P-O-Pb-O-P)/(Si-O-Pb-O-Si) of the glass [17]. However, in case of a high Pb-containing glass the picture changes. A large fraction of the Pb^{2+} ions of such glass remains in the interstices of the glass-structure. These interstitial Pb^{+2} ions are very sensitive to radiations ranging from γ -ray to UV-Vis light [4, 5] and generate Pb^{+3} holes and free electrons in the matrix by the action of the incident photons. These irradiation generated electrons, in a normal case, are captured by the network Pb^{+2} ions [(P-O-Pb-O-P)/(Si-O-Pb-O-Si)] of the glass itself and create trap centers of the type (P-O-Pb-O-P)/(Si-O-Pb-O-Si) [17]. However, in presence of an added strong electron scavenger like fullerene or a similar species in the glass the irradiation generated electrons are mainly captured by the added scavenger [5, 18] and the formation of (P-O-Pb-O-P) like trap centers in the matrix is inhibited. We indeed, did not observe any signal due to the (P-O-Pb-O-P) type trap centers in the light induced ESR spectrum of our composite. The observed enhancement of intensity of the conduction electron - signal of the SWCNTs upon UV-Vis light illumination of the composite, to the contrary, shows that the irradiation generated electrons are in fact, captured by the SWCNTs. The process of capture of the photo-generated electrons by the SWCNTs however, rapidly reaches a saturation level and thereafter no light induced increase in intensity of the signal of the conduction electron is observed. The result indicates that the light induced forward electron transfer from interstitial Pb^{+2} ions to the neighbouring SWCNTs and its back transfer reach an equilibrium within a short period of time and an equilibrated charge separated state is created in the system [18]. The related photo-induced reactions are as follows:



The glass component of the composite is found to function as an efficient photo-carrier generator under the influence

of UV-Vis light while the incorporated SWCNTs act as a good acceptor of these photo-generated carriers. The composite thus also has the prospect of being used as a UV-Vis light sensor and an efficient photo-generator.

4 CONCLUSIONS

A novel photoactive SWCNTs/(Pb, Zn)-phosphate glass composite has been prepared. Our results show that the band structures of the SWCNTs of the composite change to a quasimetallic type due to internal stress induced various structural deformations and subsequent band structures modulation. Photo-effect studies show that the glass component of the composite functions as an efficient photo-carrier generator under the influence of UV-Vis light and the incorporated SWCNTs act as a good acceptor of these photo-generated carriers. The composite has potential prospect for use as transparent conductor as well as a UV-Vis - photocurrent converter.

ACKNOWLEDGEMENT

S. Bose and R. Debnath express their gratitude to CSIR, India respectively for awarding a research fellowship to SB and sanctioning grant-in-aid under the Emeritus Scientist Scheme to RD. They also thank Sri D Misra, Director, School of Laser Science and Engineering, Jadavpur University, Kolkata, India, for extending co-operation.

REFERENCES

- [1] A. A. Green, M. C. Hersam, *Nano Lett.* 8 1417, 2008
- [2] E. Kymakisa, G. A. Amaratunga *J. Appl. Phys. Lett.* 80 112, 2002
- [3] S. Ren, M. Bernardi et al, *Nano Lett.* 11, 5316, 2011
- [4] D. L. Griscom *J. Non-Cryst. Solids*, 40, 21, 1980
- [5] R. Sahoo, R. Debnath *Adv. Mater.* 15, 287, 2003
- [6] S. Balaji, R. Debnath, *Nanotechnol.* 22, 415706, 2011
- [7] S. Balaji, S. Bose, R Debnath, *J. Phys. D: (Appl. Phys.)* 45, 325106, 2012
- [8] G. L. Wilder, C. Venema et al *Nature*, 391, 59, 1998
- [9] X. Blasse, L. X. Benedict et al, *Phys. Rev. Lett.* 72, 1878, 1994
- [10] S. Kazaoui et al, *Phys. Rev. B* 62, 1643, 2000
- [11] J. Tang, Lu-C. Qin et al, *Phys. Rev. Letts.* 85, 1887, 2000
- [12] Y. Maniwa et al, *Phys. Rev. B* 64, 241402, 2001
- [13] S. M. Sharma et al, *Phys. Rev. B* 63, 205417, 2001
- [14] M. J. Biercuk, et al, *Topics Appl. Phys.* 111, ed A. Jorio, G. Dresselhauss, M. S. Dresselhauss (Berlin: Springer) p 455, 2008
- [15] N. Guskos, et al, *Rev. Adv. Mater. Sci.* 23, 113, 2010
- [16] W. D. Rice, R. T. Weber et al, *ACS Nano*, 6, 2165 2012
- [17] T. V. Bocharova, G. O. Karapetyan, *Glass Phys. Chem.* 31, 738, 2005
- [18] A. Kongkanand, P. V. Kamat, *AcsNANO*, 1, 13, 2007