Modification of photoluminescence characteristics of single-walled carbon nanotubes by ZnS intercalation

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ABSTRACT

Commercially available high purity SWCNT samples were further rigorously purified by high temperature oxidation, acid treatment etc. By a wet chemical process, SWCNT bundles were intercalated with freshly prepared ZnS nanoparticles of a size range 1.00-2.50 nm. Characteristization by SEM, HRTEM, FTIR and UV-Vis-NIR spectroscopy clearly showed thin SWCNT bundles intercalated with ZnS nanoparticles. Photoluminescence study of the intercalated SWCNT-ZnS hybrid structure showed luminescence of two distinct types, one is for the low excitation wavelength range, covering a large part of the visible spectrum with maximum emission in the violet-blue-yellow region. The other is for the higher excitation wavelength range and the photoluminescence spectrum mostly covers the UV-violet region.

***Keywords*: Modified SWCNT, Photoluminescence, ZnS nanocrystals**

1 INTRODUCTION

Fascinating optical properties of modified single-walled carbon nanotubes (SWCNTs) have attracted the attention of scientists for quite sometime now. Bandgap fluorescence from micelle coated semiconducting SWNTs has been observed by O'Connell et. al.[1]. At pH <5, they reported emission in the range of 550-900 nm covering a region of visible to NIR, and also another range of 800-1600 nm for E_{11}^{s} and E_{22}^{s} transitions. Sergei Lebedkin et. al. [2] investigated FTIR luminescence mapping of dispersed single-walled carbon nanotubes and concluded that below $\lambda_{exc} \sim 500$ nm, a rich pattern of PL peaks corresponding to E_{33}^{s} and E_{44}^{s} excitations are observed. Lain-Jong Li and R.J. Nicholas[3] studied bandgap-selective chemical doping of semiconducting SWNTs. Manashi Nath et. al.[4] studied optical properties of SWCNTs intercalated with CdSe, CdS and ZnSe nanoparticles at different loadings and observed luminescence in the blue-violet region of the visible spectrum. C. Subramaniam et. al.[5] showed that SWCNT bundles emitted visible fluorescence in the presence of noble metal nanoparticles. Solution properties [6] of single walled carbon nanotubes were studied by a team under Robert C. Haddon and his collaborators. Optical properties studied by several groups showed interesting results[7-16]. Real-time observation of non-linear coherent phonon dynamics in single walled carbon nanotube was made by A. Gambetta et al.[17]. Werner J. Blau, et al.[18] worked on linear and non-linear spectroscopic studies of phthalocyanine carbon nanotube blends. Synthesis and study of optical properties of ZnO and CNT based coaxial heterostructures was done by D.S. Kim, et al.[19]. Masao Ichida, et al.[20] made a study on the coulomb effects on fundamental optical transition in semiconducting SWCNTs. Here we report a study of photoluminescence of Zns-SWCNT coaxial heterostructure for a wide range of excitation wavelength from 220 nm to 400 nm. A broad emission in the visible region covering a range upto 650nm with peak emission at 425 nm was observed under UV excitation of 330 nm. Two types of typical emission patterns have been detected, one for 220 - 250 nm and another for 260 - 400 nm excitation ranges. The characteristic PL emissions as reported in the present article can be explained by considering the modification of the energy band structure of SWCNT due to wrapping by the ZnS nanoparticles. The goal of the present work has been to improve and tune the visible luminescence characteristics of SWCNT for possible applications in biological imaging, sensors and fabrication of nanoelectronic devices.

2 EXPERIMENTAL DETAILS

We started with the purification of commercially available SWCNT (1-2 nm outer diameter, length: 1-3 µm) of purity >95% which involved high temperature oxidation, acid treatment, ultrasoniction and filtration. Pristine SWCNT samples were characterized by SEM/EDAX, XRD, HRTEM and UV-Vis-NIR spectroscopy. Through a simple chemical wet process, SWCNTs were intercalated with as-prepared ZnS nanoparticles. Chemicals of Merck (GR grade) were used. Firstly, we took 20 ml of zinc nitrate solution and 10 ml of saturated solution of sodium sulphide in methanol. To the freshly prepared zinc nitrate solution, 9.4 mg of pure SWCNT was added and stirred vigorously using a magnetic stirrer upto 1 hr and then sodium sulphide solution was added to the zinc nitrate solution containing SWCNTs dropwise till the pH became 8. Ultrasonication of the solution was done for 1 hr using (250W, Piezo-U-Sonic) Ultrasonicator, followed by filtration using Millipore filtration apparatus to separate the precipitate from the mixture. The precipitate was washed with methanol followed by de-ionized water to remove excess sodium particles. This process was carried out at room temperature. Characterization of the as-prepared sample for its optical as well as nanostructural properties was made. To study the optical property of Zns-intercalated SWCNTs, the dried sample was dispersed in DMSO and its optical absorbance characteristics studied using UV-Vis-NIR (Techomp-UV 2300) spectrophotometer. Photoluminescence spectrum of the sample was studied using FL Spectrofluorimeter (HITACHI, F-2500). The coating of SWCNT bundles by ZnS nanoparticles was confirmed by HRTEM micrograph (JEOL JEM 2100) using an operating voltage of 200 kV. For compositional analysis of the sample, FTIR (Nicolet, iS10) and SEM/EDAX (HITACHI S-3000N) were used. FTIR analysis confirmed the presence of sulphur compound with SWCNTs.

3 RESULTS AND DISCUSSIONS

SEM/EDAX observation of modified SWCNT samples show the presence of ZnS nanocrystallites forming thick layers around SWCNT bundles. Fig 1(a). shows the SEM micrograph of SWCNT bundles in ZnS nanoparticles envelope.

Fig.1(a)

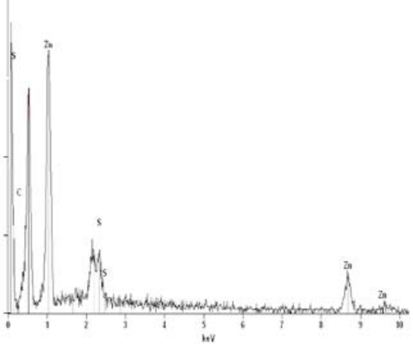

Fig.1(b)

Fig.1(a). SEM micrograph of SWCNT bundles in ZnS envelope. Fig. 1(b). EDAX analysis of ZnS-intercalated SWCNT.

The presence of ZnS has been revealed from EDAX analysis of intercalated SWCNT. Fig 1(b) shows the EDAX spectrum of ZnS-intercalated SWCNT. X-ray diffraction spectrum of the modified SWCNT is shown in Fig 1(c).

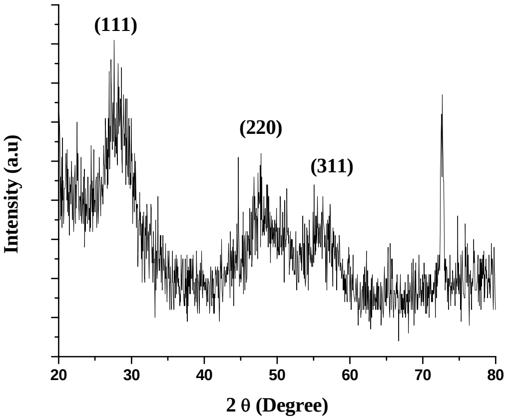

Fig.1(c)

Fig.1(c). XRD pattern of ZnS nanoparticles-intercalated SWCNT

From XRD (using Philips, PANalytical X-Pert Pro diffractometer) pattern, it is revealed that the ZnS nanocrystallites which intercalated SWCNT are of cubic fcc structures. The other subsidiary peaks are due to SWCNT. HRTEM micrograph of the sample is shown in Fig 2.

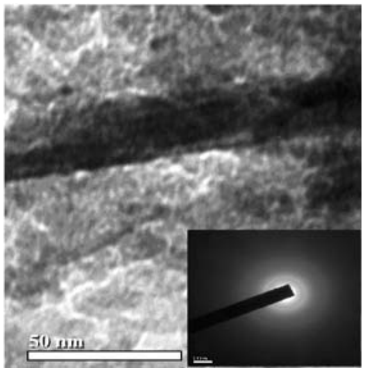

Fig 2.

Fig.2. HRTEM micrograph showing SWCNT bundles intercalated with ZnS nanoparticles. The inset of Fig.2. shows the SAED of the intercalated SWCNT sample.

The corresponding selected area electron diffraction (SAED) is shown in the inset of Fig2. The uniform bright rings suggest that the nanocrystals have preferential instead of random orientation. The average size of the ZnS nanoparticles is found to fall in the range 1.00-2.50 nm, whereas, the average size of the SWCNT bundles fall in the range 3.50-6.00 nm. Fig3. shows a comparison of the FTIR spectrum of pristine SWCNT and that of ZnS-intercalated SWCNT. The stretches at 1124 nm and 1386 nm confirmed the presence of sulphur compound bondings which are absent in the case of pristine SWCNT.

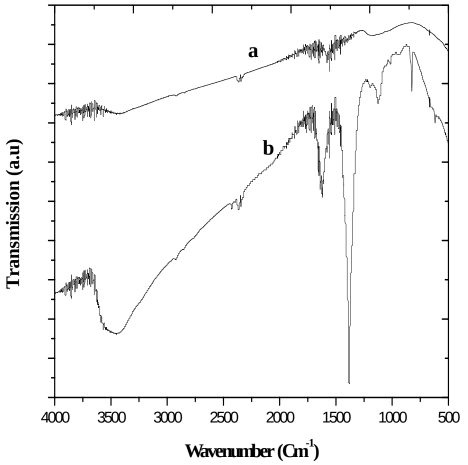

Fig 3. FTIR spectra of (a) pristine SWCNT,(b) ZnS-intercalated SWCNT

The absorbance pattern of ZnS-interclated SWCNT has a red shift when compared to that of pristine SWCNT as shown in Fig 4.

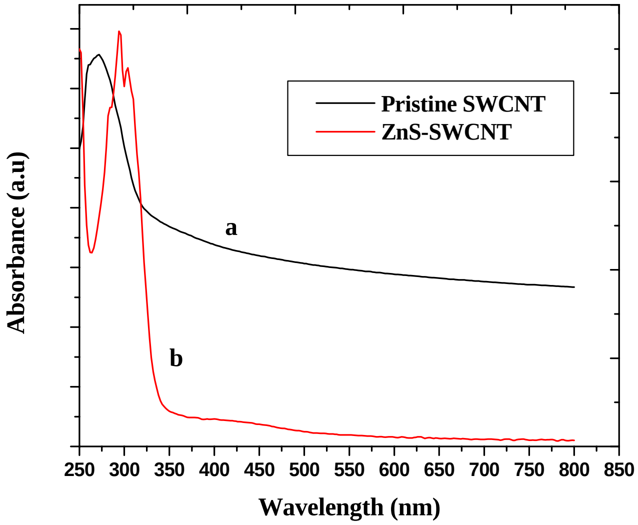

Fig.4. Absorbance spectra of (a) pristine (b) ZnS-intercalated SWCNT

Fig 5(a). shows the PL spectra of pristine SWCNT and ZnS-intercalated SWCNT at an excitation wavelength of 330 nm. Fig. 5(b) and 5(c) exhibit the two typical patterns of PL spectra for two different ranges of wavelength.

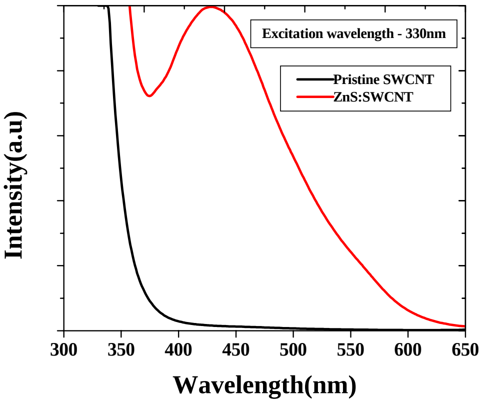

Fig.5(a)

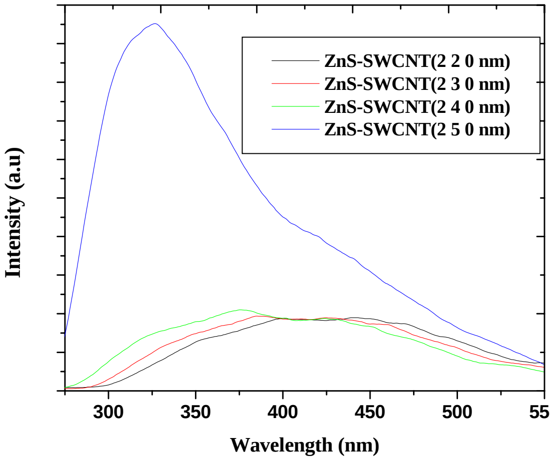

Fig.5(b)

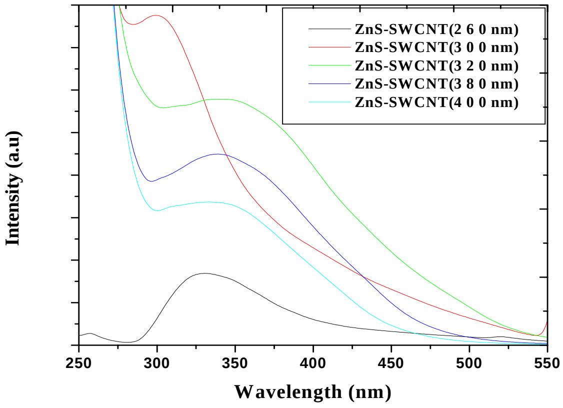

Fig.5(c)

Fig5(a).PL spectra of pristine SWNT and ZnS-intercalated SWNT at excitation wavelength of 330 nm.
(b) first range of PL emission(220-250 nm wavelength).
(c) second range of PL emission (260-400 nm wavelength)

To study the optical characteristics, the nanopowders were well dispersed in DMSO and taken in a quartz cuvette. Characteristic UV-Vis-NIR absorbance was observed with a strong absorbance peak at 277 nm for ZnS-intercalated SWCNT while at about 272 nm for that of pristine SWCNT. The photoluminescence (PL) study of ZnS-intercalated SWCNT showed a broad emission in the visible region covering a range upto 650 nm with peak emission at 425 nm under UV excitation of 330 nm. Also, two types of typical emission patterns have been noticed, one for 220-250 nm and another for 260-400 nm excitation ranges. This may be due to the influence of both metallic as well as semiconducting nanotubes. The PL emission characteristics signify the modification of the energy bands structure of SWCNT due to the intercalation by ZnS nanoparticles. When SWCNT intercalated by ZnS nanoparticles is irradiated by UV light, the valance band electrons of ZnS get excited and move towards the conduction bands forming electron-hole pairs. Due to strong interfacial connection between ZnS nanoparticles and SWCNTs, the excited e^- of the conduction band of ZnS nanoparticles can migrate to SWCNTs, which are relatively good electron acceptors. So, recombination of the electron-hole pairs is retarded, which results in the promotion of photocatalytic activity in Zns nanoparticles [21], as well as modification of energy band structure.

4 CONCLUSION

Synthesis of ZnS nanoparticles and SWCNT coaxial heterostructures have been achieved following a simple chemical process. Average size of ZnS nanocrystals is nearly 2nm. These nanocrystals wrapped around the thin SWCNT bundles as confirmed by HRTEM micrographs. Two distinct patterns of photoluminescence spectrum have been achieved when excited by UV radiations.

5 ACKNOWLEDGEMENT

Authors acknowledge with thanks the support from Dr. D. Sukul and Dr. A. K. Patra of Department of Chemistry, NIT Durgapur, for PL and FTIR characterization. We are grateful to Technical Education Quality Improvement programme(TEQIP), National Institute of Technology, Durgapur and Government of India for financial support. We also extend our thanks to Central Research Facility, IIT Kharagpur, for making available the HRTEM facility.

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