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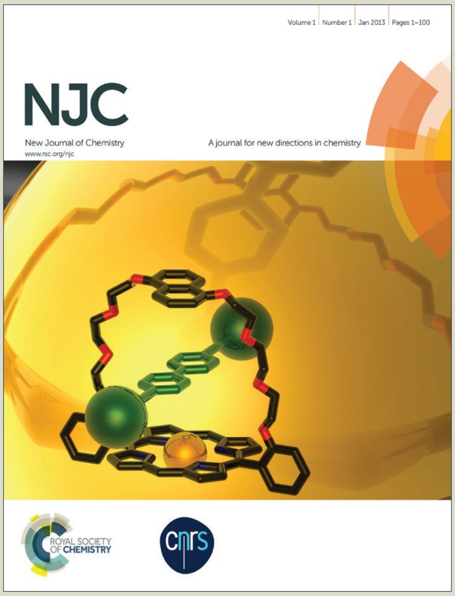

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In-situ growth of silicon carbide-carbon nanotube composites

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Abstract:

Carbon nanotubes (CNTs) have great potential for a variety of applications out of which composite reinforcement is the most promising one. Silicon carbide (SiC) with its unique properties is expected to enable significant enhancements in the existing properties of CNTs to a far-ranging variety of applications and systems. In this report SiC- CNT composite through the novel route of d.c. arc discharge technique using silicon powder as filler in a graphite anode has been prepared. Structural characterizations of this composite were studied using X-ray diffraction, Raman spectroscopy and transmission electron microscopy technique and further the spectroscopic characteristics were investigated using photoluminescence spectrometer. XRD results confirm the formation of SiC along 111 plane (35.6°, d spacing 0.25 nm) which agreed with the d spacing values calculated from the fringes of HRTEM images. Further, the shifting in the Raman peak of SiC confirms successful synthesis of SiC-CNT composites.

Keywords:

CNT, SiC, dc-arc discharge, Raman spectroscopy

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Introduction:

Carbon nanotubes (CNTs) exhibit fascinating electrical, thermal, optical properties, and remarkable mechanical stability, which makes these unique one-dimensional nanostructures promising candidates for use in a variety of devices and composites[1]. Silicon carbide (SiC) is a promising material for power electronics because of its wide band gap[2] (2.0 eV< Eg < 7.0 eV) and high thermal conductivity. In recent years, SiC has received much attention because of its potential for high-power devices. The unique material properties of SiC, high electric breakdown field[3], high saturated electron drift velocity, and high thermal conductivity[4] of this material makes it tremendous potential in the power device arena[5]. Recently various diverse methods of production of different forms of SiC have emerged like Zhang et al[6] reported a work of synthesis of SiC nanoribbons with tens to hundreds of microns in length. Further the mechanical properties of crystalline silicon carbide nanowires, synthesized with a catalyst-free chemical vapor deposition method, were characterized with nanoscale tensile testing and mechanical resonance testing methods inside a scanning electron microscope[7]. The Young's modulus values from tensile tests were in good agreement with the ones obtained from the mechanical resonance tests.

The current work is focused on the synthesis and characterization of SiC-SWCNT composites. SiC with its excellent oxidation, creep and carburization resistance, is often used as reinforcing component together with other ceramic materials[8]. Oxidation of SiC results in a dense SiO_2 layer at the surface and prevents further oxidation of the material. On the other hand CNTs, besides having outstanding mechanical properties, are also known for thermal stability (up to 2000 K in inert atmosphere[9]). The combination of these two materials in a composite is envisaged to yield high strength material with good oxidation resistance.

Single walled carbon nanotubes have the most unique combination of properties and hence have become a highly active focus of the research world. Jiang et al . reported production of SWCNT fibers from SWCNT polyelectrolyte dispersions stabilized by crown ether in dimethyl sulfoxide and coagulated into aqueous solutions that has shown high tensile strength upto 124 MPa and a Young's modulus of 14 GPa[10]. In recent years carbon nanotuboids(CNTDs) can be used for achieving highly concentrated dispersions of SWCNTs and can also be used as an important intermediate for covalent chemical modification[11]. In another work the solubility of SWCNT polyelectrolytes $[K(THF)]_n$SWCNT in dimethyl sulfoxide (DMSO) was determined. Small-diameter SWCNTs were found to be preferentially functionalized when the SWCNT polyelectrolytes were dispersed in DMSO[12]. Although individual CNTs possess excellent electronic and mechanical properties, extensive research is also being done in CNT networks[13] which are an emerging class of materials with applications ranging from sensors to storage to biomedical.

There are several studies for the synthesis of SiC-CNT composites. Wang et al. [14] fabricated SiC–CNT composite using the high pressure reactive sintering technique. Samples were synthesized at high pressures (2 and 8 GPa) and temperatures (1770 and 1970 K). These composite structures were studied using X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and Raman spectroscopic technique. This composite produced at high pressure have pronounced nanocrystalline structure (the mean crystallite size of the SiC matrix was 32–37 nm) and very promising mechanical properties: fracture toughness of 6.8–7.1 MPa $m^{0.5}$ and Vickers hardness of 20–21 GPa. Govindaraajan et al.[15] reported spark plasma sintering of SiC and multi-walled carbon nanotube (MWCNT) reinforced zirconium diboride ultra-high temperature ceramic matrix composites. The SiC and CNT reinforcement improved the indentation fracture toughness of the composites. Kamalakaran, et al.[8] reported the spray pyrolysis of SiC/ferrocene slurry in xylene, at 1050 °C that resulted in the formation of free-standing flakes consisting of carbon, silicon carbide and CNTs. Carbon–carbon (C–C), carbon–silicon carbide (C–SiC) and silicon carbide–silicon carbide (SiC–SiC) composites are promising for high-temperature applications. Wang et al [16] reported a rapid, low temperature microwave-induced reaction to create a nanoscale silicon carbide (SiC)–SWCNT composite. SWCNTs incorporated into ceramic matrices are known to impart enhanced mechanical, thermal and electrical properties to the formed composites. Selective growth of CNTs on SiC substrate will create some new applications in composites and electronic devices by combining their mechanical and physical properties. Lijie, et al [17] successfully grew MWCNTs on SiC whiskers using a conventional xylene–ferrocene chemical vapor deposition process. Xie et al[18] synthesized CNTs/SiC composites by pyrolysis of methane over SiC supported nickel catalysts. The composites show good microwave absorption ability in the frequency range of 2–18 GHz. Katja et al [19] for the first time, used electrophoretic deposition to deposit MWCNTs onto SiC fibres (SiC_f) to form an effective CNT interphase layer for SiC_f/SiC composites. Similarly CNTs were introduced into the carbon fiber reinforced silicon carbide matrix (C_f/SiC) composite via the infiltration slurry during the precursor infiltration and pyrolysis by Yu et al[20]. Attributed to the introduction of the small quantity of CNTs, both flexural strength and fracture toughness of the

C_f/SiC composite was increased by 25%. The room temperature thermal conductivity was also increased by 30%. Hence different kinds of properties can be altered depending on the amount of CNT, SiC, added, the synthesis route, and can be used in varied applications. The aim of the current work is to demonstrate the feasibility of in situ incorporation of CNTs with SiC. As it is clear from the above reports that different researchers have tried different routes to develop SiC-CNT composites, but there is still scope to explore novel techniques.

Experimental part:

Raw Materials:

SiC-SWCNT was synthesized using the conventional d.c arc discharge technique which is generally used to grow SWCNTs[21]. It consists of two electrodes i.e cathode and anode. A high density solid graphite (purity: 99.9%) of 10 mm (dia.) was used as the cathode. The anode was graphite tube (8 mm OD, 6.5 mm ID.) filled with a mixture of a silicon and graphite along with the catalysts. Hence the anode was filled with silicon + graphite (50% + 50%) and catalysts mixed with graphite in the specific ratio; Graphite + Nickel +Cobalt +Yttrium (95%+2%+2%+1%).

Methodology:

The above mentioned composition of the materials was finely ball milled for 24 hours at 250rpm speed. This filler material was filled inside the hollow electrode by careful stacking to avoid any voids. This anode was then inserted into the electrode holder inside the arcing chamber. The chamber was pumped down to a vacuum of 10^{-4} mbar using a diffusion pump backed by a rotary pump. The arcing was done with current of 100A and the cathode was constantly moved towards anode to maintain a constant distance of ~1-2 mm between the electrodes; thereby maintaining a constant potential difference of 30 V. The whole procedure was carried out in an inert atmosphere of flowing helium gas and maintaining the chamber at constant pressure of 400 torr. Arcing continued for nearly 20 minutes until the whole electrode was consumed. After the arcing procedure, the material developed got deposited at various places inside the chamber. This material deposited inside the chamber was collected and characterized. Fig 1 shows the schematic of this whole procedure.

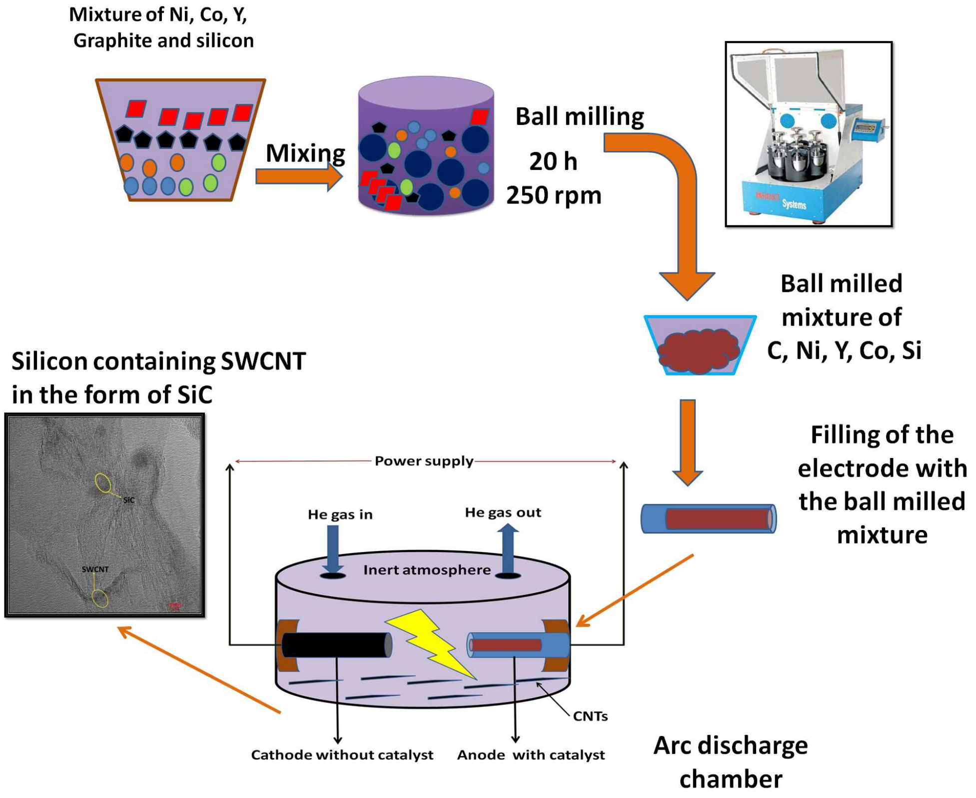

Fig 1 : Schematic for the synthesis of SiC based SWCNT

Characterization:.

TEM, X-ray diffraction (XRD), Photoluminescence spectroscopy and Raman spectroscopy were used to characterize the structure of the SiC–CNT specimens. This material was characterized for its structural properties using Renishaw inVia Reflex Raman spectrometer, UK (with an excitation source of 514.5 nm and 2.5mW power). The morphological study was carried out by using HRTEM (Technai G30-stwin) operating at 300 kV. The XRD patterns were recorded using a Bruker D8 Advance X-ray diffractometer in the diffraction (2Θ) range of 10– 70 ° (slit width of 0.1 mm) using the Cu Ka line (1.54 Å) as radiation source. Photoluminescence characterization were carried out using a photoluminescence spectrometer (Edinburgh, FLSP-920), where a Xenon flash lamp acts as source of excitation.

Results and Discussion:

The main finding of the work is the successful synthesis of SiC-SWCNT composite by the novel route of d.c. arc discharge technique. The composite mainly consists of nanotubes of the diameter nearly 1.25nm. The resultant composite is thoroughly analyzed, first by Raman spectrometer to view the structural properties and then by XRD. The HRTEM images were also analyzed to reconfirm the properties of the composite.

Figure 2(a) shows the Raman spectroscopy analysis of the as produced material. The G-band and D-band are clearly visible. The Raman analysis shows the presence of SiC peaks at 814cm^{-1} as shown in the inset of fig.2(c). Similarly the significant RBM bands are visible at 180.8cm^{-1} , 169 cm^{-1} , 163 cm^{-1} (fig 2(b)). The diameter of the tubes are estimated to be in the range of 1.25 to 1.39nm[22]. The quality factor I_G/I_D is obtained as 1.48. SiC has main Raman peaks centered at 796 and 973 cm^{-1} which correspond to the transverse optic (TO) and longitudinal optic (LO) modes, respectively. Therefore this shift in the peak from 796 to 814cm^{-1} confirms[23] the formation of composite material of SiC and SWCNT.

XRD pattern of the sample is shown in figure 3 where three main peaks at 2θ value of 35.6°, 60.0°, and 71.7° were identified as the (111), (220), and (311) orientations, respectively, of the cubic structure of *â*-SiC [24]. Now by using the Bragg's equation, we can determine the value of d-spacing. Taking λ=1.54Å as the wavelength, $2\theta = 35.6^0$, we obtain the value of 0.25nm by calculating using the following equation:

$n\lambda=2d \sin\theta$ ………………. (2)

Figure 4(a) shows the HRTEM images of the SiC/SWCNT composite. Figure 4(b) shows the HRTEM image of SiC in which the lattice fringes separated by a distance of 0.25 nm indicate that SiC is growing along the [111] direction. The interspacing obtained from the HRTEM images very well agrees with the value of d-spacing obtained from XRD data using the peak of SiC at 35.6^0. Figure 4(c) shows the HRTEM image of the SWCNT ropes formed during the arc discharge procedure.

Photoluminescence (PL) is a powerful optical probe for the determination of electronic energy band structure and surface defect analysis. Figure 5(a) exhibits the comparative excitation spectra of composite as well as pristine SWCNT at 398 nm emission wavelength of SiC-SWCNT composite and Figure 5(b) represents the comparative steady state photoluminescence emission spectra of composite composite as well as pristine SWCNT upon 252 nm wavelength at room temperature. When SiC –SWCNT composite is formed, SiC gets attached along the SWCNT particles thereafter interface is formed and hence this leads to creation of defect sites. SWCNT has its own characteristic PL, but it is enhanced due to the defect sites. Because, in general the, probability of a material to exhibit luminescence depends on the intrinsic band edge structure and other internal or external factors (intrinsic/extrinsic defects)[25-28]. In present investigation, we have explored only defect induced plasmonic emission of this nanostructure excluding band gap related PL[29]. The possible origin of luminescence can be further accredited to the photons generated at the recombination of electron and holes at the interface of SiC-SWCNT during UV excitation. It is well established that the available delocalized π electrons can be easily excite by UV wavelength in range of 240-290 nm[26]. In the present investigations, the PL emission depends upon the presence of delocalized π electrons in the excited state and their relaxation to ground state, whereas the excess excitation energy is being trapped into the associated defects, which are related to interface formation between the SiC and SWCNTs during UV excitation (252 nm). Furthermore, it is still need to re-ignite the research work on exact mechanism of PL to establish exact cause. In spite of playing role to induced defects on SWCNTs surface, SiC possess many superb properties, such as high hardness, high thermal conductivity, low coefficient of thermal expansion, and excellent resistance to erosion and corrosion. It also exhibits interesting electronic and optical properties, which vary with the size of particles. SiC being a promising new generation replacement for high[30] efficiency batteries[30, 31] and photovoltaic devices [31], and SWCNT being a flexible[32] and resilient high strength conducting material, this nanocomposite of SiC-SWCNT can be applied in various fields.

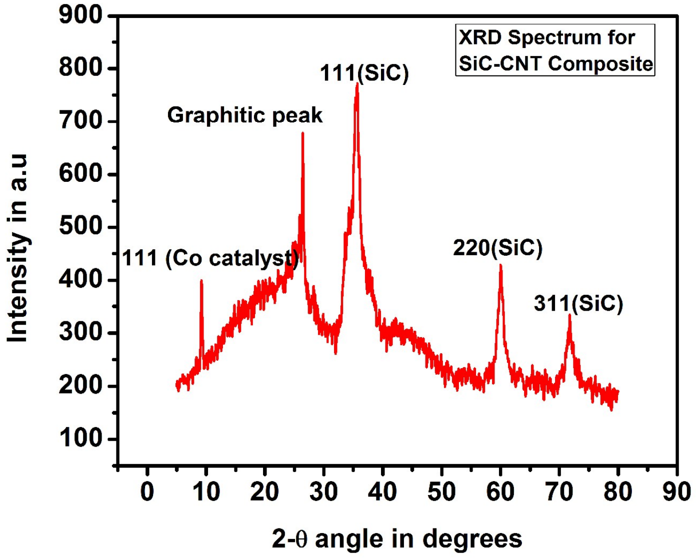

Fig 2: XRD results SiC-CNT

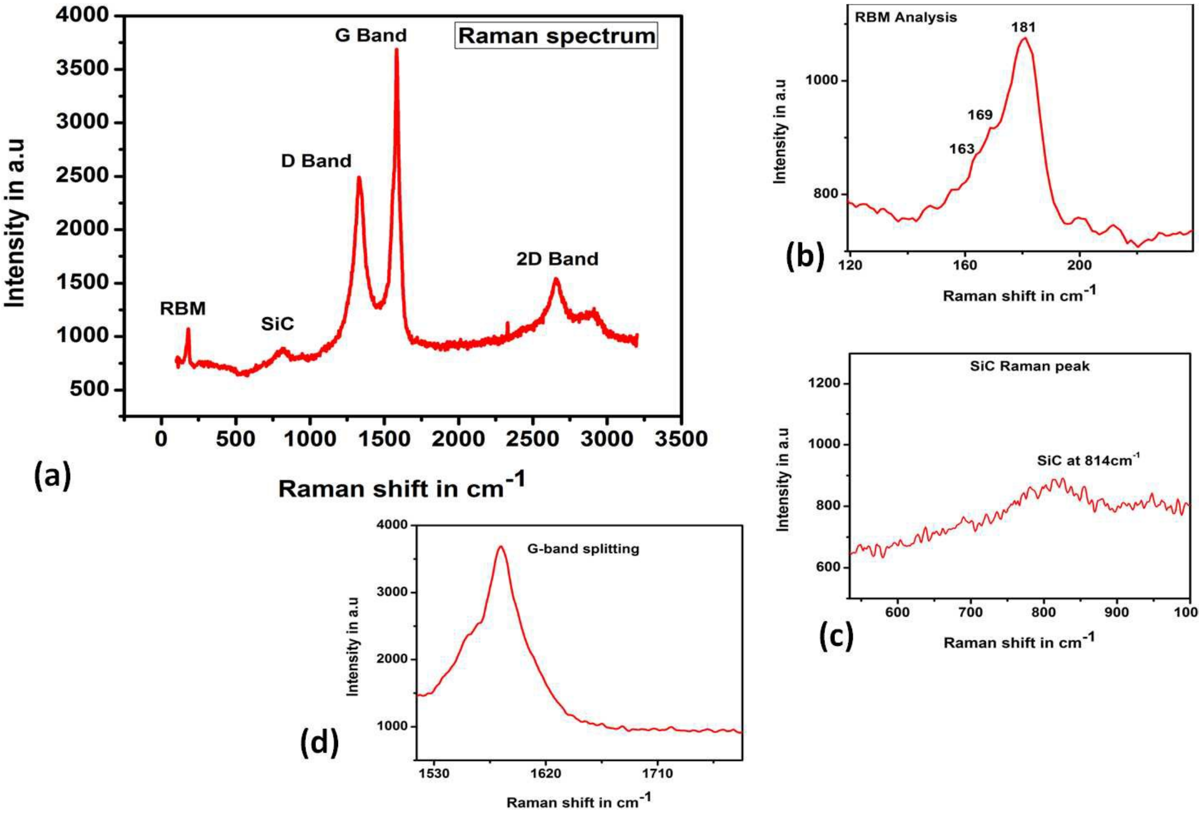

Fig 3: (a) Raman spectroscopy analysis of SiC/SWCNT .

The inset shows the peak of RBM peak(b), SiC(c) and the G-band splitting(d)

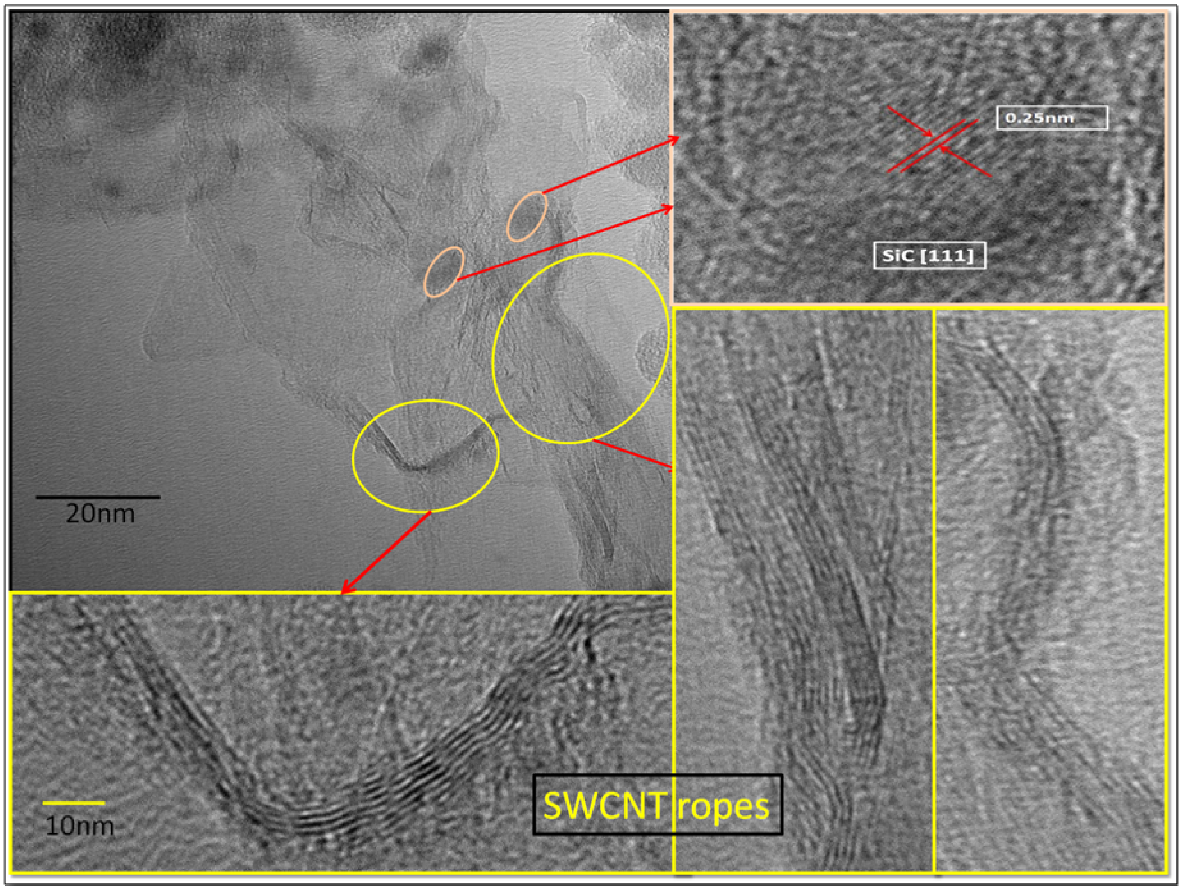

Fig 4: HRTEM image of SiC/SWCNT composites

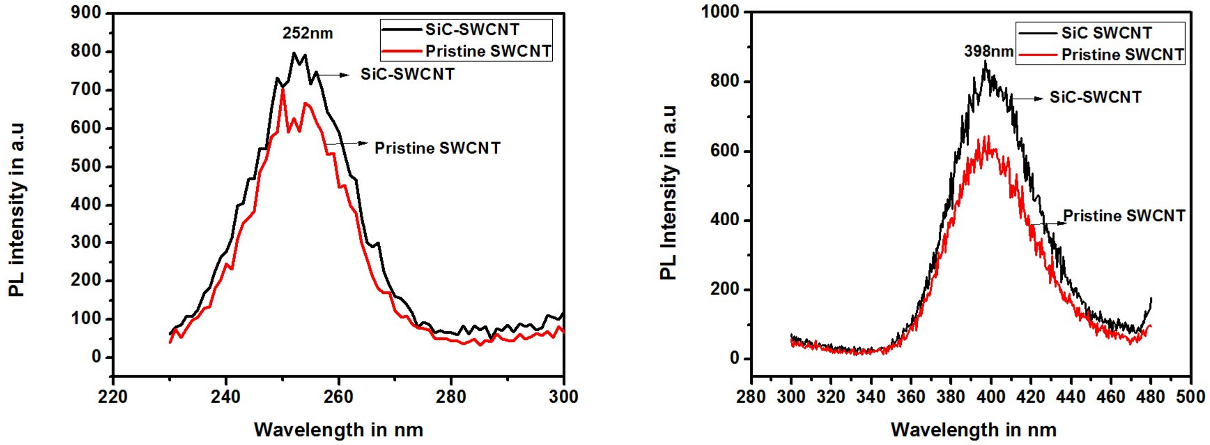

Fig 5: PL spectra of the pristine SWCNT and SiC/SWCNT composite, where Fig. 5(a) exhibits the excitation spectrum at 398 nm emission wavelength and Fig. 5(b) represents the emission spectrum upon 252 nm wavelength.

Conclusion:

Hence in the present work Silicon carbide (SiC) containing single walled carbon nanotubes were grown using the d.c. arc discharge technique. The presence of SiC was confirmed by the X-ray diffraction analysis showing the peaks of SiC and the High resolution transmission electron microscopy images showing the same lattice fringe distance as calculated from the X-ray diffraction analysis. The Raman spectroscopy also shows the peaks of SiC and the signatory Radial Breathing Mode peak for single walled carbon nanotubes thereby confirming the presence of SiC as well as single walled carbon nanotubes in SiC- single walled carbon nanotube composites. Owing to the enormous and all fields applications of SiC and high flexibility, strength and resilience of single walled carbon nanotubes, these SiC- single walled carbon nanotube composites have promising applications in the field of microelectronics, power generation and storage, and high strength composites.

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Graphical abstract

In-situ growth of silicon carbide- carbon nanotube composites

Santwana Pati[1,4], Bhanu Pratap Singh[1,4*], Devendra Kumar Saket[1], Bipin Kumar Gupta[2], Vidya Nand Singh[3], Sanjay R. Dhakate[1]

SiC-single walled carbon nanotubes composites were prepared through the novel route of d.c. arc discharge technique using silicon powder as filler in a graphite anode and confirmed by X-ray diffraction, Raman spectroscopy and transmission electron microscopy technique