

Formation of Magnetic Semiconductor Carbon Nanotubes via Iron Incorporation

Abstract

This article reports the synthesis of iron (Fe) encapsulated carbon nanotubes (CNTs) that could lead to formation of magnetic semiconductors, by the arc discharge method. Morphology of the samples were studied from transmission electron microscope (TEM) and scanning electron micrograph (SEM) imaging, and data recording by x-ray diffractometer (XRD) and energy dispersion x-ray (EDX) equipments is used for the identification of the sample constituent. TEM images of metal added samples indicate that defects are completely removed after mono acidic treatment and open air oxidizing at 400°C for 15minutes leaving nano sized carbonaceous skeins attached on the surface of carbon nanotubes and catalyst particles encapsulated. This formation is recognized as a phenomenon at certain temperature limit. From the SEM analysis a new phenomenon of spherical structure with diameter nearly $15\mu\text{m}$ to which bundles of CNTs and carbonaceous impurities are attached is observed. EDX examination shows that the carbon weight % is dominating the composition as expected along with oxygen and iron perhaps forming FeO during the reaction, as also revealed from XRD analysis, indicating success in metal incorporation. This envisages that there would be formation of magnetic semiconductors, as can be verified with further experiments, where iron ions may take carbon sites in the CNTs with semiconducting behavior and iron filling otherwise.

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Keywords: Arc discharge, carbon nanotubes, defects, FeO, iron encapsulation.

1. Introduction

Carbon nanotubes are a front line research topic since last two decades [1, 2]. Their discovery was in electric arc discharge experiments for fullerene synthesis [1]. Carbon Nanotubes, CNTs, have been produced mainly by various methods involving gas solid reactions such as arc discharge, laser ablation, catalytic chemical vapor deposition (CVD) and plasma assisted deposition [3].

The quality and quantity of the nanotubes is understood as to depend on the type of the discharge method, the environment, annealing temperature, annealing duration, refluxing

temperature, refluxing duration, system geometry, the electric current and voltage applied, and type of acids used for the reflux [4–6]. Experimental works have been reporting that these tubes can be of either with metallic [7] or semiconducting character [8, 9]. Theoretical electronic band structure calculations have also predicted that the chirality (n,m) indices and diameter determine whether a SWNT has a metallic or semiconducting behavior [10, 11].

Because of their unique properties, CNTs are attractive materials for a wide range of applications

such as biosensors [12, 13], fillers [14], gas and energy storage [15], efficient source of electron field emitters [16], that enabled fabrication of field-effect transistors based on individual single- and multi-wall with analyzed performance [8,17,18], chargeable batteries [19], and semiconductor devices [20]. Moreover, for their gate effect narrow diameter SWCNTs are required for applications in carbon nanotube-based field effect transistors [8] than larger diameter MWNTS in some semiconductor devices, where band gap of semiconducting CNTs is understood to decrease with increasing diameter [19]. This novel functionality can bring dynamism combined with magnetic ions such as iron, nickel and chromium integrating semiconductivity and storage facilities in a single crystal.

The effect of metal added CNTs was studied systematically by plasma-enhanced hot-filament chemical vapor deposition and known to determine the diameter of the nanotube diameter [21]. Iron catalyzed production of CNTs have been investigated using different incorporation mechanisms and technique [6, 22] for both quantity and quality improvement. In the present work, iron incorporation was done through powder mixing in which preparation and characterization is carried out in two phases. Sample preparation by the arc discharging process and purification of the pristine sample by acidic treatment and open air oxidizing for the removal of unwanted impurities followed by characterization using various mechanisms.

2. Experimental Details

In sample preparation we used carbon graphite rods commercially available. These rods were cut into pieces and drilled from one end forming a well structure. A mix of graphite and iron powder of 1:1 molar ratio is stuffed in to each well and mounted horizontally on the electrodes of the arc used as anode and cathode, few millimeters apart in a chamber of deionized water cover, as shown in fig.1, before the process [23].

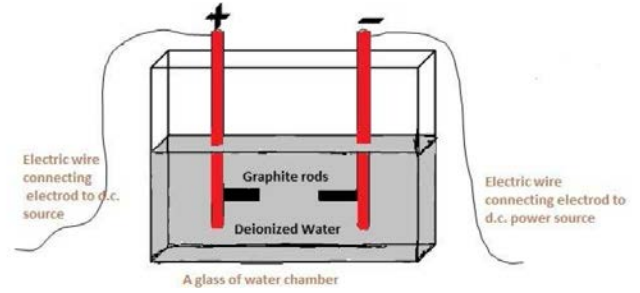


FIG. 1: The schematic diagram of the arcing equipment locally devised [23].

A d.c of 50-200A driven by a 40V potential creating a high temperature discharge between the electrodes was applied. After frequent arcing, soot is formed in the water. The soot of water is then transferred into a bigger beaker after the removal of the chamber from the setup. Six hours later, the surface water was decanted and the remaining crude made dry in an oven for about 12 hours at 100°C. Finally, the sample was tested for the purity by powder x-ray diffractometer, XRD Cu-K α_1 , X'Pert PRO PANalytical.

The CNTs collected in the form of soot were purified by refluxing in a strong oxidant 8M Nitric acid (HNO_3) for the removal of catalyst metal for 24 hours. Subsequently, filtration with a 0.25 μm filter membrane with the aid of a pump and thoroughly washing with distilled water until the pH value reaches neutral was done. Finally, the samples were dried in an oven at 100°C followed by open air oxidizing for 15min at 400°C in a furnace for the removal of impurities/amorphous carbon and other unreacted reagents [6, 24]. Ultimately, the product was analyzed by XRD, TEM, HR-TEM, EDX, SEM and scanning tunneling microscopy (STM).

3. Results and Discussion

The XRD measurement of the pristine sample shows that there are no apparent peaks attributed as introduced by defects, as can be seen from left panel of fig.2. However, the XRD plot of the as prepared sample from iron doping in the Fe:C 1:22 molar ratio prepared from previously purchased graphite rods of the same company indicated that

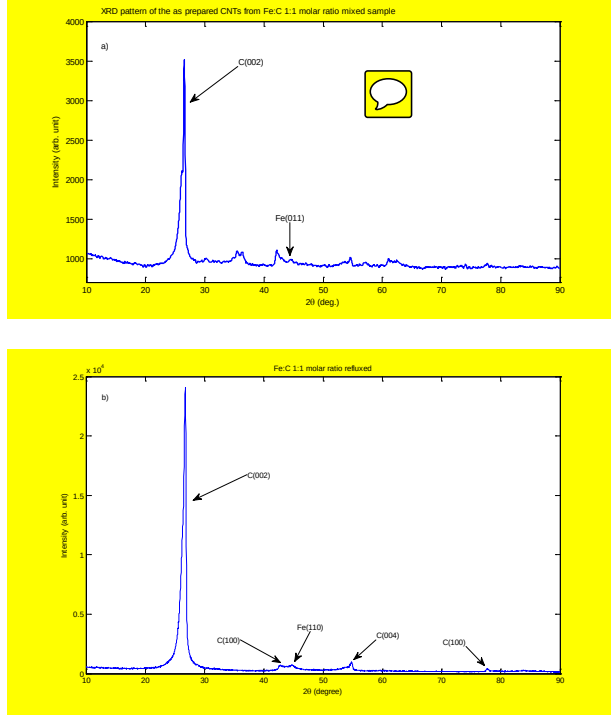


FIG. 2: XRD pattern of CNTs from Fe:C 1:1 molar ratio as prepared, 2a, and post purification, 2b, with their corresponding planes[25].

impurities can be introduced industrially during preparation of the sample source. This was revealed from fig. 3 and other reports [25] directing to preferably use the later with increased molar ratio (1:1) in order to prevent degradation especially on mass production. This suggests that quality of the source material can persuade the purification rate as well.

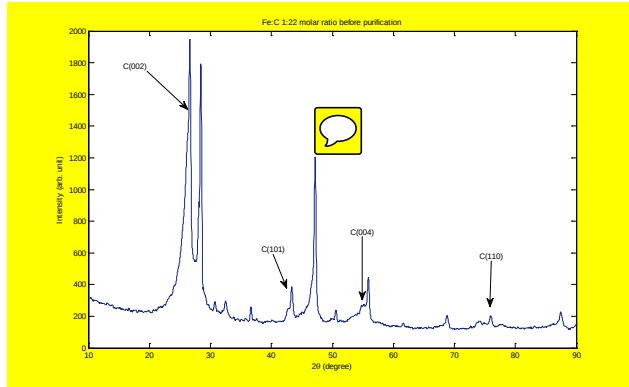


FIG. 3: XRD pattern of as prepared CNTs from Fe:C 1:22 molar ratio. The diffraction peaks emerged at 26.42° corresponds to C(002) plane, 43.43° corresponds to C(101) and so on have resemblance with that of graphite. The remaining peaks reveal the existence of

any other kind of ingredient including iron nano particles in the sample.

The XRD measurement data plotting of purified sample shown in the right panel of fig. 2 indicates that there are few remnant iron nano particles after purification and the product is of, 97.35%, carbon content attributed as of CNTs at large, as can also be seen from table III and fig. 6. The relatively small diffraction peaks associated with Fe phase suggested the presence of well crystallized iron grains with certain amount of size [26]. Peak positions in both panels of fig. 2 are the same except that there are slight shifts and change in intensity in which those of graphite and Fe are dominating, and perhaps some of them might have been overwhelmed by noise before purification.

Table I demonstrates the inter planar spacing between the diffraction fringes calculated from the XRD patterns shown in the left panel of fig. 2, applying the famous Braggs' equation, $n\lambda = 2d \sin\theta$, signifying the decrease of the spacing with increase in Braggs' angles.

TABLE I: Inter planar spacing calculated post purification.

2θ	hkl	Inter planar spacing, $d(\text{\AA})$
26.61°	002	3.3471
42.86°	100	2.1082

Scherrer's formula [27] $t = \kappa\lambda/\beta\cos\theta_B$, is applied in order to estimate thickness t of the nanotubes, where κ is the shape factor approximated to 0.9. $\beta = 2\Delta\theta \times \pi/180^\circ$ is the line broadening at half the maximum intensity (at full width half of maximum intensity, FWHM), λ is the x-ray wave length and θ_B is the Bragg's angle. In accordance with this, table II is calculated for peaks indicated in the XRD data plots shown in fig. 2; illustrating the size decrement of both carbon and iron particles contrary to the line broadening after the sample is purified perhaps due to the removal of certain portion during acidic treatment and open air annealing.

TABLE II: Particle size calculated pre and post purification.

Pristine CNTs from 1:1 molar ratio mixed sample				
	$2\theta(deg.)$	$\Delta 2\theta(deg.)$	hkl	$t (A^0)$
Fe	44.29	1.6976	011	50.5039
C	26.456	0.62514	002	130.4913

For CNTs from 1:1 molar ratio post purification				
	$2\theta(deg)$	$\Delta 2\theta(deg)$	hkl	$t (A^0)$
Fe	44.65292	1.75263	011	48.9815
C	26.61034	0.72724	002	112.2068

In this study, the TEM images where collected after sonication of the samples for 5 days suspended in ethanol using a device of power 2keV model HITACHI 7500, maximum magnification of 6×10^6 times and resolution $0.2A^0$.

According to fig. 4 most of the CNTs have cone shaped tips in agreement with previously obtained results [1], and also cut slantly from one end. Those open at the middle along their length are found in bundle with some roped creating graphitic nano ribbons and also layered over one another (as in fig. 4a and c), as for the case of SWNTs [28]. There are others with striped surfaces closed from both ends standing separately (as shown in fig. 4d). Gloomy spot like particles (shown in fig. 4a, b and c) are observed on the surface of the tubes as well. There are bean shaped nano rings of inner diameter 5nm-8nm with thickness 3nm located scattered elsewhere on the surface of graphene sheets and also attached to sides of some of the CNTs, oriented parallel and perpendicularly, as in figs. 4b. This situation is confirmed by high resolution transmission electron microscopy (HR-TEM) images, detected by apparatus operating at 200keV accelerating voltage, and shown as in fig. 5b. Speculations from further scrutiny indicate that the surface attached systems are CNTs of hexagonal structure with multilayered rings, as shown in fig. 5a too.

Both fig. 4 and fig. 5 reveals that there are CNTs longitudinally cut open from center, **with some observed to have** multilayered structure and parallel to the axial direction exhibiting a good crystallinity.

Fig. 5b shows the 3D scanning transmission electron microscopy, STEM structure of graphene sheet with attachment of CNTs and fullerene on the surface. Moreover, the presence of Fe in the sample and acidic treatment is understood as increasing mass production of CNTs in comparison to their absence at the temperature limit the experiment is carried out, perhaps reducing breakages [25].

Incorporation of iron nano particles into CNTs from inside is illustrated, as in fig. 5c and d, indicating such carbon nanotube composite can be engineered for the purpose of data storage beside optical and transport facilities. Perhaps, the merging could follow substitutional or interstitial scheme where the later could degrade ferromagnetism. The substitutional method may well assist introduction of magnetic spins leading the CNTs, of specially,

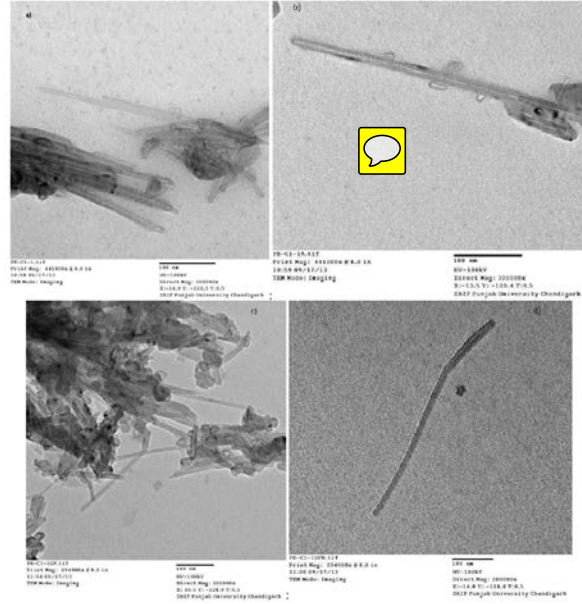


FIG. 4: TEM images of CNTs prepared from Fe:C 1:1 molar ratio, after purification.

semiconducting nature to acquire magnetic semiconductor property. In this situation carbon of four valence electrons could be replaced by iron of two valence electrons with six localized d sub shell electrons ($3d^6$) forming sp^3 hybridization. This would introduce holes for ferromagnetic mediation of the localized spins, **following Dietl model [29], establishing exchange energy explained** by the well-known Heisenberg mathematical expression $H = \sum_{ij} J_{ij} S_i \cdot S_j$ where J_{ij} is exchange energy of magnetic spins S localized at cites i and j . This can

also ascertain a new scheme and a useful motivation for systematic study of properties of carbon nanotube coated iron in analogy with the gold coating iron nano clusters, aiming at understanding the magnetic properties of core-shell structure used in biomedical applications [30].

According to Energy dispersive X-ray spectroscopy (EDS) analysis, weight percentage content of the iron particles in the purified product is about 0.29, as also can be seen from Table III. Fig. 6 shows profile of EDS chemical characterization of the sample illustrated in table III in which copper, Cu is introduced due to copper grip on which the sample was deposited. Morphology of the sample was also analyzed from scanning electron microscope (SEM; using a JEOL JSM 6490 instrument) images.

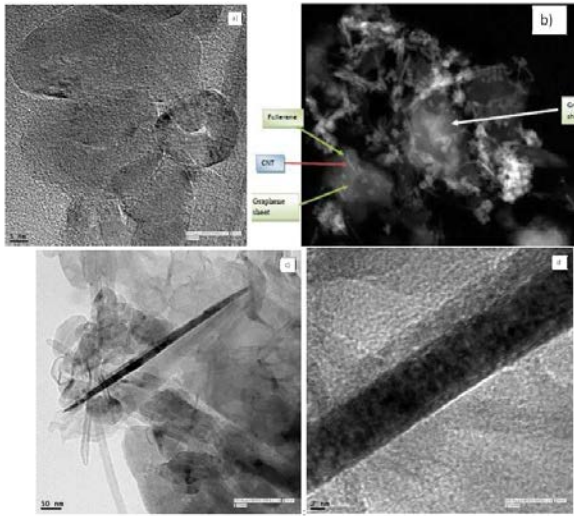


FIG. 5: HR-TEM and STEM images of CNTs prepared from Fe:C 1:1 molar ratio after purification a) HR-TEM images of high magnification of the nano-rings/fullerene attached to each other b) STEM 3-D images of graphene sheet c) distribution of CNTs and fullerene on the surface of graphene sheet d) magnified form of panel c, showing morphology of CNT filled with iron particles.

Though SEM with high resolution is powerful instrument for imaging of fine structure of materials and nano particles fabricated by the nanotechnology, the low magnification device available was used. As shown in figs. 7, the CNTs are found in filament-like structures that are dense perhaps, bundled by van der Waals attractions being agitated thermally and/or depending on where in the reactor they were deposited in

agreement with previous results [23]. Few of these tubes are found attached on the surface of a carbonaceous system that formed spherical structure of about $15\mu\text{m}$ in diameter, attributed as a new phenomenon.

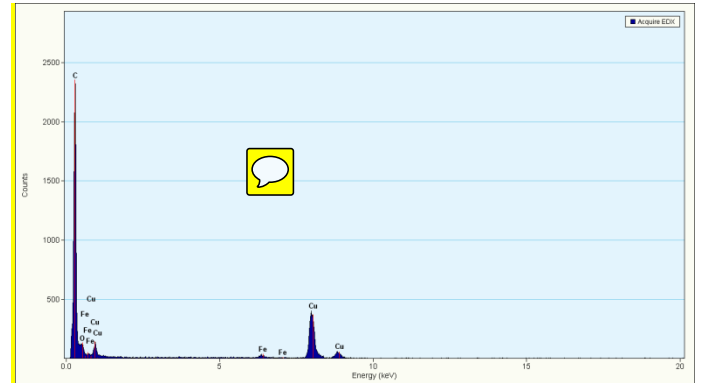


FIG. 6: EDS analysis of CNTs prepared from graphite-iron C:Fe 1:1 molar ratio mix post purification.

TABLE III: Energy dispersive X-ray spectroscopy (EDS) elemental analysis of the sample.

Quantification Results					
Correction method: None					
element	Weight %	Atomic %	uncert. %	Detector correction	K-factor
C(K)	85.92	95.72	0.61	0.26	3.940
O(K)	2.08	1.74	0.08	0.49	1.974
Fe(K)	0.26	0.06	0.02	0.99	1.403
Cu(K)	11.72	2.46	0.14	0.99	1.667

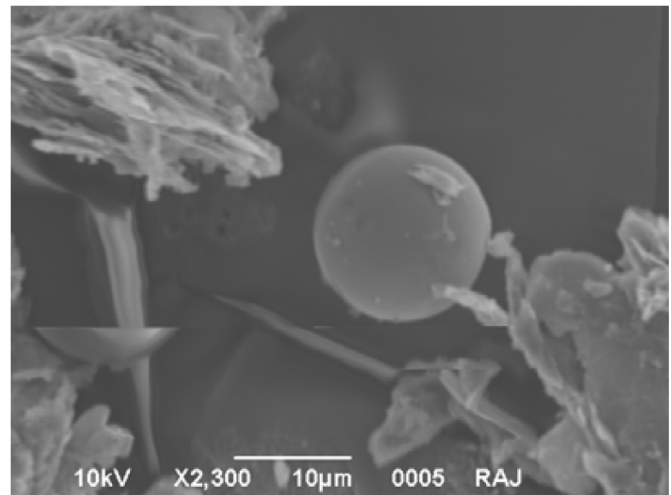


FIG. 7: CNTs after acid treatment with 8 M HNO_3 . Large bundles of CNTs and carbonaceous impurities are observed with attached spherical phenomena.

4. Conclusions

The possibility of incorporation of metal iron in to CNTs and the formation of magnetic semiconductors is suggested for nanotubes of semiconducting behavior. Production of Fullerene is identified as a phenomenon of attachment on the surface of CNTs at $400^{\circ}C$, the maximum annealing temperature limit considered in this experiment. Iron encapsulation was done by powder mixing mechanism at Fe:C 1:1 molar ratio. After acidic treatment the remaining product is found to be more of CNTs, fullerene, few graphene sheets and other carbonaceous impurities. Calculations from the XRD data indicated that particle size decreases with increase in diffraction angle contrary to the line broadening. According to the TEM images most of the CNTs have cone shaped tips and cut slantly from one end. Those open at the middle along their length are found in bundle with some roped and layered over one another. The EDX analysis show that there are carbon, oxygen and iron contents remaining in the sample after purification, perhaps forming FeO during the reaction indicating that iron is successfully incorporated as well. Such carbon nanotube composite can be engineered for the purpose of data storage beside optical and transport facilities.

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