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Purification and Characterization of Carbon Nanotubes and the Formation of Magnetic Semiconductors for the Spintronic Application

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Abstract: This article reports the synthesis of carbon nanotubes (CNTs) encapsulating iron (Fe) that would lead to formation of magnetic semiconductors, employing the arc discharge method. Morphology of the samples is studied from transmission electron microscope (TEM) imaging. Data is recorded by x-ray diffractometer (XRD) and identification of the sample constituent by energy dispersion x-ray (EDX). TEM images of metal added samples indicated that defects are completely removed after mono acidic treatment and open air oxidizing at 400^0C for 15 minutes, leaving nano sized carbonaceous attached on surfaces of carbon nanotubes and catalyst particles encapsulated. This formation is recognized as a phenomenon at certain temperature. EDX examination shows that there is oxygen constituent remaining after purification along with iron and carbon, perhaps forming FeO during the reaction with water, indicating success in metal incorporation. This envisages that there would be formation of magnetic semiconductors where iron ions may take carbon cites in the CNTs of semiconducting characteristics, as can be revealed from experiments. This suggests that magnetic carbon nanotubes can be used for the spintronic application.

Keywords: Arc Discharge, Carbon Nanotubes, Defects, FeO, Magnetic Semiconductors

1. Introduction

Carbon nanotubes are a front line research topic since last two decades [1, 2]. Their discovery was in electric arcdischarge 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 electronicband 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]. Thisnovel functionality can bring dynamism combined with magnetic ions such as iron, nickel and chromium integratingsemiconductivity 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, samples are prepared with the arc discharge method in a de-ionized water environment from low cost and locally devisable benefits point of view. Iron incorporation was done through powder mixing in which characterization is carried out in two phases. Pre- and post purification using various techniques.

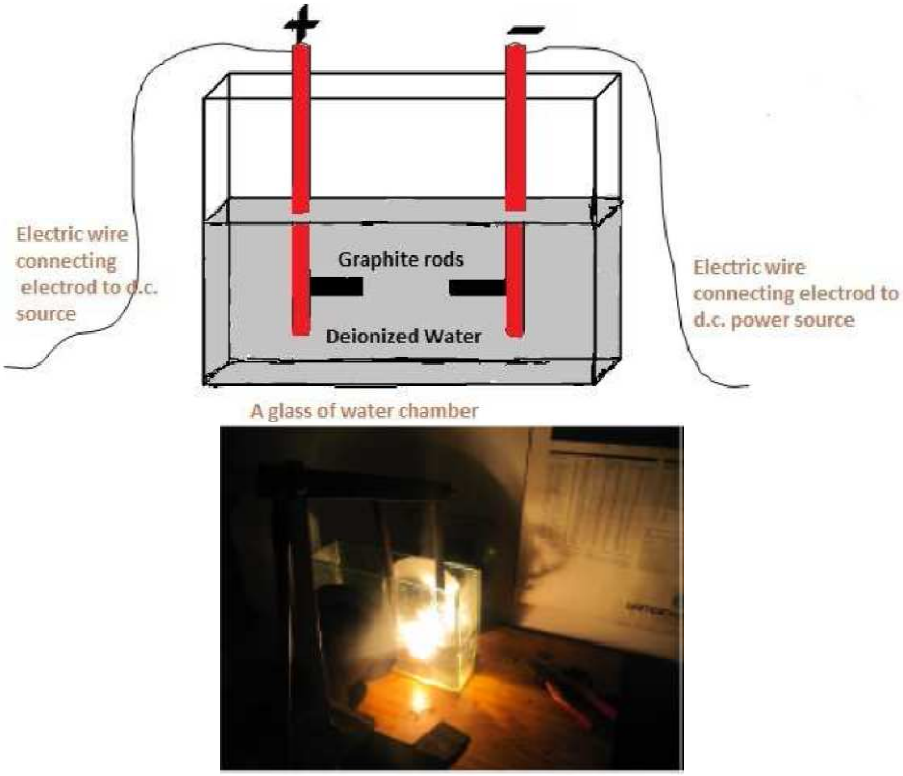

Fig. 1. *The schematic diagram of the arcing equipment locally devised [23].*

2. Experimental

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].

A d.c of 50-200Adriven by a 40Vpotential 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 100^0C. Finally, the sample was tested for the purity by powder x-ray diffractometer, XRD Cu-Kα_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 0.25μmfilter 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 100^0cfollowed by open air oxidizing for 15min at 400^0Cin 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, and EDX.

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 fig.2a. 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 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.

The XRD measurement data plotting of purified sample shown in fig. 2b indicates that there are few remnant iron nanoparticles after purification and the product is of carbon

content attributed as of CNTs at large, as can also be seen from table I. 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 in which those of graphite and Fe are dominating, and perhaps some of them might have been overwhelmed by noise before purification

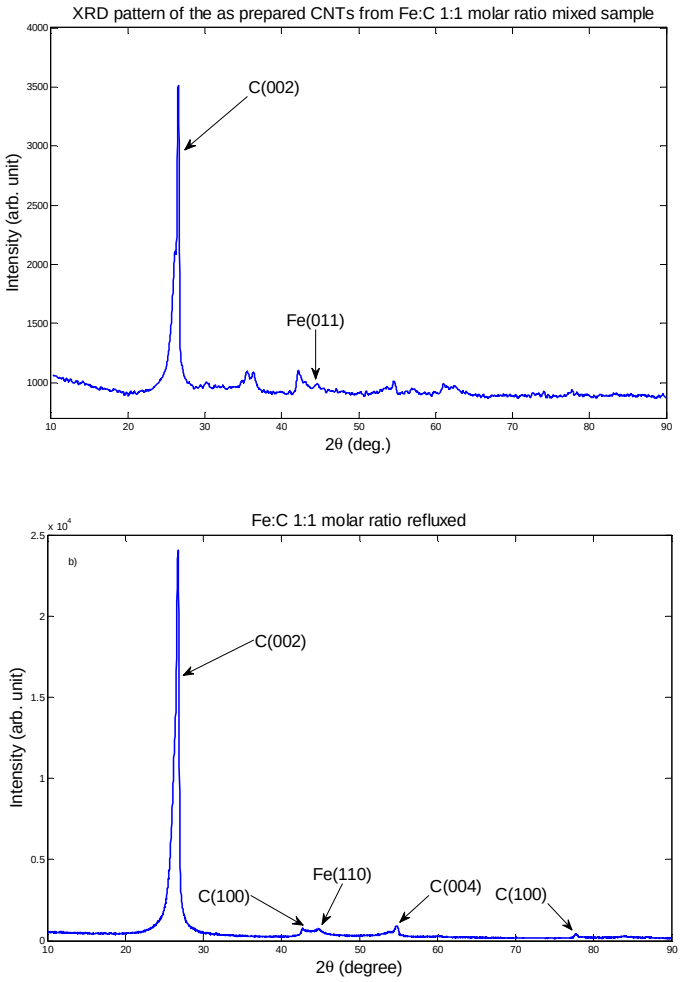

Fig. 2. *XRD pattern of CNTs from Fe:C1:1 molar ratio as prepared (a) and post purification (b) with their corresponding planes[25].*

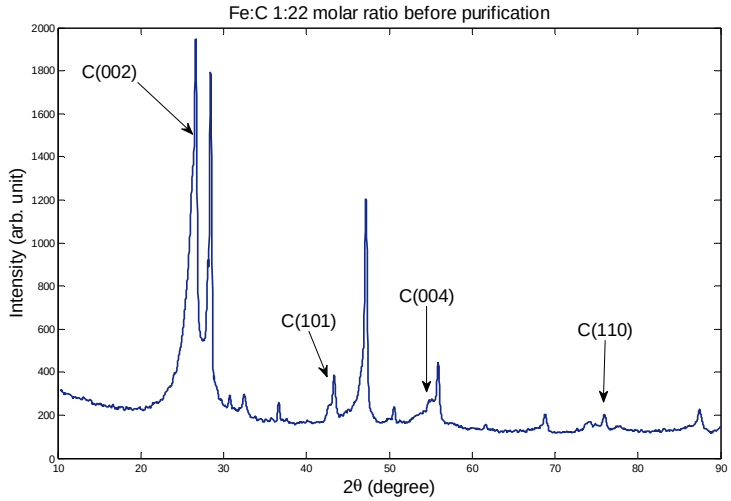

Fig. 3. *XRD pattern of as prepared CNTs from C:Fe 22:1. The diffraction peaks emerged at 26.42^o corresponds to C(002) plane, 43.43^0 corresponds to C(101) and so on have resemblance with that of graphite. The remaining peaks reveal the existence of any other kind of ingredient including iron nano particles in the sample.*

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

According to fig. 4 most of the CNTs have cone shaped tips in agreement with previous 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-8nmwith thickness 3nmlocated scattered elsewhere on the surface of graphene sheets and also attached to sides of some of the CNTs, oriented parallel and perpendicularly, as in fig. 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.

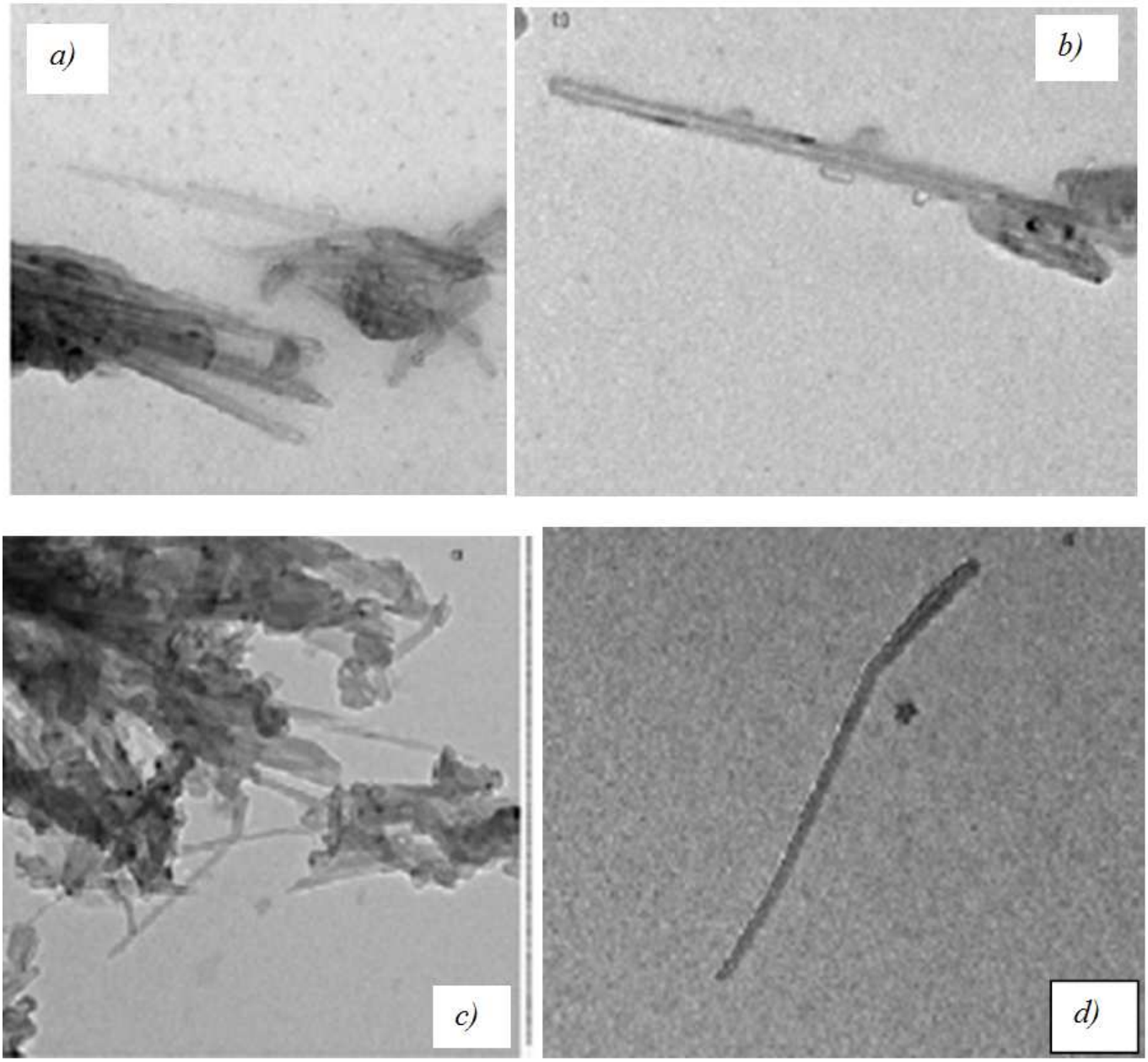

Fig. 4. *TEM images of CNTs prepared from Fe:C 1:1 molar ratio, after purification.*

Both fig. 4 and fig. 5 reveals that there are CNTs longitudinally cut open from center and 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, thepresence 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].

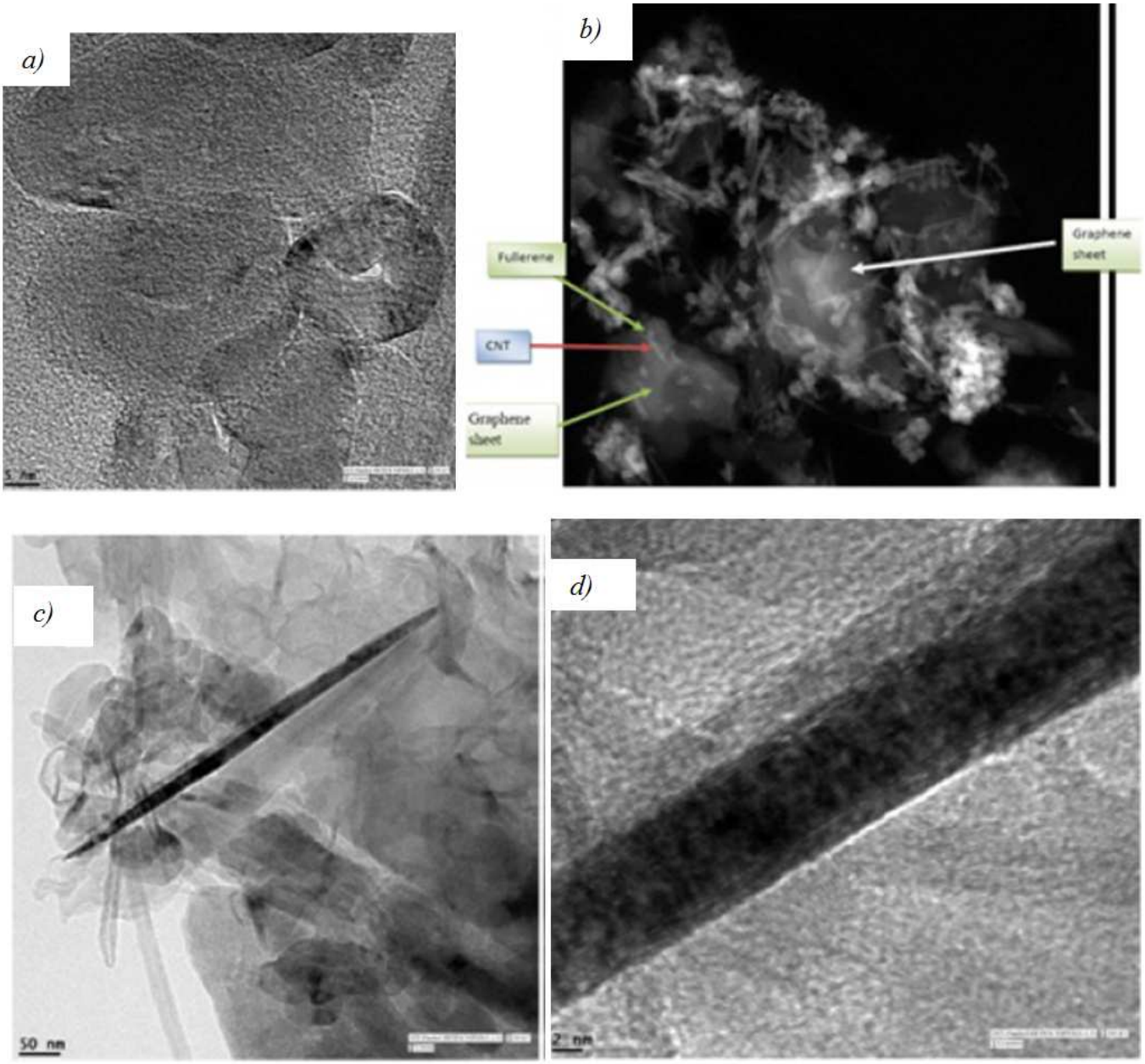

Fig. 5. *HR-TEM and STEM images of CNTs prepared from Fe:C 1:1 molar ratio after purification a) HR-TEM images of high magnification of the nano-rings/fullerene attached to each other b) STEM 3-D images of graphene sheet c) distribution of CNTs and fullerene on the surface of graphene sheet d) magnified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

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 semiconductor CNTs 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 $H = \sum_{ij} J_{ij} S_i . S_j$ 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 I where copper, Cu is introduced due to copper grip on which the sample was deposited.

Table I. *Energy dispersive X-ray spectroscopy (EDX) elemental analysis of the sample.*

Quantification Results **Correction method: None**					
elements	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

4. Conclusions

Preparation of CNTs in de-ionized water and purification through acidic treatment is done successfully. Their morphology is studied applying the transmission electron microscopy and elemental analysis by the x-ray diffractometer. Production of Fullerene is identified as a Phenomenon of attachment on the surface of CNTs at 400^0C, the maximum annealing temperature limit considered in this experiment. Iron encapsulation is 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. 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 XRD and EDX analysis show that there are carbon, oxygen and iron contents remaining in the sample after purification, perhaps forming FeO as well during the reaction, indicating that iron is successfully incorporated. Such carbon nanotube composite can be engineered for the purpose of data storage beside optical and transport facilities.

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