Chapter 4

Synthesis and Properties of MWCNT Based Magnetic Heterostructures and Their Possible Applications

This chapter discusses the fabrication of Multiwalled Carbon Nanotubes (MWCNTs) using template assisted Chemical Vapour Deposition and their subsequent hybridisation with magnetic materials such as Cobalt, Nickel and Iron Oxide. Cobalt and Nickel were electrodeposited inside aligned MWCNTs employing different precursors for electrodeposition. These hybrid structures were then subjected to detailed structural, morphological and magnetic investigations. The veracity of the mobility assisted growth mechanism inside carbon nanotubes is also tested. Nickel filled MWCNTs were subjected to microwave absorption studies in the S-band using cavity perturbation technique and the results were compared with that of bare MWCNTs and Ni NWs. Aqueous ferrofluids based on Iron Oxide are synthesized using a controlled co-precipitation technique. Carbon nanotubes are filled with aqueous Ferrofluids using the principle of nanocapillarity. Structural, morphological and magnetic properties of these nanocomposites are analysed using FESEM, TEM, SAED, Micro-Raman and SQUID magnetometer.

*A part of the work discussed in this chapter has been reported in
1. “Nanotechnology” (2009, 20, 055607)
3. “Nanotechnology” (2009, 20, 285702)
4.1 Introduction

The landmark paper on carbon nanotubes (CNTs) by Iijima in 1991 and the subsequent successful synthesis of CNTs in bulk triggered a multitude of research activities on CNT based materials. CNTs and CNT based materials are appealing to both engineers and scientists because of their superlative physicochemical properties. The unique and interesting electronic, mechanical, optical and structural properties of carbon nanotubes made them extremely promising for applications in materials science and medicine. CNTs assume significance not only because of their unique electrical and optical properties but they are also ideal templates for the synthesis of various other nanostructures. The formation of tubular structures, ranging from a few nanometers to few tens of nanometers in diameter suggests the possibility of engineering these nanostructures on scales considerably larger than those to the fullerenes and immense research is underway in these tubular carbon nanostructures all over the world. Moreover, these excellent quasi-one-dimensional nanostructures provide a unique platform for studying the physics at low dimensions.

The combination of magnetic materials and CNTs is emerging as an interesting area of advanced research. Nanocomposites consisting of carbon nanotubes (CNTs) and magnetic materials have been attracting the interest of many researchers and considerable amount of research is underway in this area, especially on the synthesis and properties. Numerous attempts were made earlier to fill CNTs with metallic elements or compounds. The application potential of these metal encapsulated composites extend to various fields like spin polarized transportation, magnetoresistive random access memory, nano-electronic devices and radar absorbers. The microwave absorbing properties of CNT-metal composites are of importance because of its usefulness in military and business fields. A good electromagnetic absorber should possess the required dielectric...
permittivity and appropriate magnetic permeability in a given frequency of operation leading to perfect impedance matching. Due to the modification of their electronic structure, metal incorporated CNTs are found to be good microwave absorbers. Embedding metallic inclusions in MWCNTs will also provide encapsulation and passivation leading to long term stability.

The filling of CNTs is accepted as an ingenious idea right from the early days of CNT research and attempts for complete filling of CNTs are an ongoing research activity rewarded only with partial success. The confined existence of particles inside CNTs might introduce interesting new properties which are unseen in these systems previously. Moreover filling of CNTs leads to confinement of particles and confinement of nanoparticles leads to possible quantum mechanical effects. Various chemical and physical methods are in vogue for filling of CNTs. Immediately after the theoretical prediction of capillary filling of CNTs by Pederson and Broughton, attempts were made to fill CNTs by capillary action of molten metals. However attempts to completely fill CNTs were in vain or have met with only partial success.

Electrodeposited metal nanowires are increasingly becoming popular, and they are a hot topic of research due to their application potential in ultrahigh density magnetic recording, ultrafast optical switching, and microwave devices. Metal nanotubes are another interesting system of current research where they can find enormous applications in hybrid nanostructures for possible energy storage devices, cell separation and diagnosis. Electrodeposition of metals inside CNTs has not yet been perfected due to the buckling and bending of carbon nanotubes during electrodeposition. Electrodeposited ferromagnetic fillings inside the carbon shell are protected against oxidation and hence ensure long term stability. Moreover, decoration of CNTs with magnetic nanoparticles, such as coating or loading CNTs with γ-Fe₂O₃, NiFe₂O₄, and Fe₂O₄ impart new optical,
magnetic and electrochemical properties to CNTs.\textsuperscript{[9]} The hybrid magnetic nanostructures based on CNTs can find applications ranging from electromagnetic devices to biomedical fields such as magnetically guided drug delivery systems and agents for hyperthermia.\textsuperscript{[36]}

With the growing demand for good electromagnetic shields and absorbers the attention of scientists turned towards CNT based microwave absorbers. Isolated metallic soft magnetic materials have an upper hand over traditional ferrite based microwave absorbers because of their higher Snoek’s limit in the GHz frequency regime.\textsuperscript{[37,39]} Filling of CNTs with 3d transition metals like Ni/Fe/Co will render them useful for applications such as electromagnetic interference shields and microwave absorbers. Due to the suppression of eddy current, isolated metallic particles having sizes less than their skin-depth can exhibit enhanced microwave absorption.\textsuperscript{[40]} Che \textit{et al.}\textsuperscript{[41]} reported the microwave absorption of iron encapsulated carbon nanotubes and the enhanced microwave absorption of this system is attributed to the better impedance match between the dielectric loss and magnetic loss. Researchers adopted catalytic pyrolysis or wet chemical routes for the synthesis of MWCNTs-metal composites.\textsuperscript{[38,42]} Template assisted electrodeposition is an alternative to such techniques and it is an efficient and simple method for metal filling of MWCNTs.

The S band of the electromagnetic spectrum is extensively employed in weather radars, communication satellites, direct broadcast satellites, mobile satellite services and also in emerging WiMAX technology.\textsuperscript{[43-45]} Ni is employed as a filler in MWCNT due to its large resonance line width and it can be used for large band width microwave absorbers \textsuperscript{[46]} and literature reports on the microwave absorbing properties of Ni-MWCNT composite is rather scarce or seldom reported. The evaluation of complex dielectric permittivity of MWCNTs, Ni nanowires (Ni NWs) and Ni filled MWCNTs thus assume significance.
Synthesis and properties of...

Nanocapillarity is the spontaneous penetration of fluids into wettable capillaries, and can be effectively utilized for filling large area of CNTs.\cite{29} This technique received the much needed fillip when open ended aligned CNTs were prepared.\cite{47} Potential applications of filled CNTs with different materials are in areas such as nanofluidic devices and functional devices like nanoexplorers and cell manipulators. The lack of complete understanding of liquid flow through nanochannels has propelled further activities on filling of CNTs by capillarity and their further characterizations.\cite{48-49} It must be noted here that the melting of materials often results in loss of useful physical properties of materials. Filling of CNTs with colloidal suspensions was thought of as an alternative to filling of CNTs with molten materials.

Ferrofluids (FF) are colloidal suspensions of magnetic particles and they display novel magnetic and magneto optical properties. The condition for arresting both agglomeration arising out of magnetic dipolar interaction and sedimentation due to gravity necessitates the size of magnetic particles inside the suspension to lie within 10nm.\cite{50} These nanometer sized magnetic particles in a ferrofluid are to be coated with an organic hull thus preventing them from agglomeration. The size constraint leads to interesting applications for ferrofluids under the action of an applied magnetic field. FFs can either be synthesized using hydrocarbon carriers or they can be aqueous based. Hydrocarbon based FFs are noted for their extensive applications in various engineering fields.\cite{51} The magneto optical and viscous properties of these FFs are utilized in making devices like heat sinks, damping arrestors and optical switches and can be used as magnetic inks in high speed printing technology.\cite{52} Aqueous magnetic fluids find innumerable applications in therapy, diagnostics and as nanoprobes for biological applications.\cite{53}

The absence of any natural magnetic ordering in CNT and the growing demand for structured nanomagnets in fields such as NEMS (Nano Electro Mechanical Systems),\cite{29} medicine and in defence persuaded
hybridization of CNT with magnetic materials. Use of FM melts to fill CNT is not practical because of the high melting point of FM metals and the interaction between their melts and carbon. Attempts to fill CNTs with magnetic oxides (ferrites) by employing physical methods such as vigorous stirring with salts and other chemical means did not realise the desired objectives. This persuaded researchers to seek alternatives and filling MWCNTs with FF was proposed as a viable alternative. Fabrication of CNT- FM composites can be achieved if FM particles can be dispersed as colloidal suspensions in a carrier fluid. Fortunately, FFs offer this platform and can be effectively utilized for this purpose.

In addition to a plethora of applications that can be perceived with FF filled CNTs, they are ideal templates for investigating the magnetic properties at the fundamental level. Confinement of ultrafine magnetic particles will give rise to volume effects and will induce shape anisotropy. Complex interplay between various interactions like exchange interaction, dipolar interaction, shape anisotropy along with various other surface effects will provide a unique opportunity to probe these interactions from a fundamental perspective. FFs are interesting because of the possibility of manipulating the interparticle interaction via dilution. For example, it would be interesting to explore the phenomena of confinement of superparamagnetic iron oxide nanoparticles (SPIONs) inside MWCNTs. FF filled CNTs can serve as potential nanoprobes for biological applications and as agents for magnetic hyperthermia. The ease with which CNTs can be functionalized provides further leverage to target CNTs to a specific site by the application of an external magnetic field. So yet another motivation of the present study is to explore these possibilities by the synthesis of a CNT-SPION composite.
4.2. Experimental

4.2.1 Synthesis of MWCNTs

MWCNTs were synthesized by template assisted chemical vapour deposition (CVD) over nanoporous alumina template (99.9% pure, Whatman). Acetylene ($C_2H_2$) was used as the precursor for pyrolysis and argon as a carrier gas. The temperature for pyrolysis was optimized at 650 °C for the formation of nanotubes. The flow rate of acetylene (10 sccm) and argon (70 sccm) were optimized during the CVD process to obtain MWCNTs with a maximum inner diameter of~150nm. The resultant nanotubes were plasma etched for removing the amorphous carbon content using a Radio Frequency (RF) plasma unit (Harrick PDC-32G, plasma power 18 W) and then used for further characterization. Figure 4.1 shows the schematic of template assisted CVD set up.
The resulting carbon nanotubes have an average length of ~ 60 μm. The FESEM images of MWCNTs are shown in Figure 4.3.

4.2.2. Metal filling inside MWCNTs
Nickel and Cobalt are electrodeposited inside MWCNTs using potentiostatic electrodeposition (as explained in Chapter 2 and Chapter 3). Different precursors are employed for electrodeposition. Schematic of electrodeposition is depicted in Figure 4.2.

![Figure 4.2: Schematic of electrodeposition inside MWCNTs.](image)

Initially, the Ag coated AAO templates are subjected to Chemical Vapour Deposition (CVD) in order to grow MWCNTs inside the nanopores. These AAO templates are used as working electrode for electrodeposition and electrodeposition was carried out inside the AAO templates containing MWCNTs.

4.3 Results and discussion
The FESEM images (both lateral and top) of as synthesised MWCNTs are shown in Figure 4.3.
The quality of formed multiwalled carbon nanotubes is tested using Micro Raman analysis. The spectrum (Figure 4.4) is characteristic of the order G ($E_{2g}$ mode in the graphite structure of carbon, $1600 \text{ cm}^{-1}$) and the disorder D ($1343 \text{ cm}^{-1}$) peaks exhibited by graphite.\(^{[55]}\) The G-band corresponds to the tangential stretching mode of highly oriented pyrolytic graphite and can be used to assess the degree of crystallinity /graphitisation. The D-band originates from the disorder in the sp\(^2\) hybridised carbon atoms and is characteristic of lattice distortions in the curved graphite sheets and/or tube ends.

Figure 4.3: FESEM images of MWCNTs, (a) lateral view, (b) top view.

Figure 4.4: Micro Raman spectrum of MWCNT (excitation: 514.5 nm).
It is assumed that extend of graphitization is taken as a yard stick for good quality CNTs. This is found from the relative intensities of G and D peaks from the Raman spectra (relatively high intensity ratio of G to D (~ 1.2)) it is to be concluded that the formed carbon nanotubes are of high purity.\[56]\]

4.3.1. Ni filled MWCNTs

Nickel has been electrodeposited inside MWCNTs using Nickel sulphate hexahydrate as precursor. FESEM images of Ni filled MWCNTs are shown in Figure 4.5.

![Figure 4.5: FESEM image of Ni filled MWCNT (Nickel sulphate hexahydrate): (a) a bundle of Ni filled MWCNTs, (b) a single Ni filled MWCNT over a silicon substrate, (c) EDS of Ni filled MWCNTs.](image-url)
EDS of Ni filled MWCNT indicates the presence of elemental Ni. AFM and MFM studies are carried out on this single Ni filled MWCNT and is shown in Figure 4.6.

Figure 4.6: AFM, MFM images of a Ni filled MWCNT over a silicon substrate (Nickel sulphate hexahydrate).

The MFM phase contrast image is shown in Figure 4.6.b. The phase contrast clearly reveals the presence of ‘magnetic’ Ni particles inside the MWCNTs. Particle size of the filled Ni particles calculated from MFM image correlates well with the FESEM image (Figure 4.5) that they have an average size of ~ 70 nm. Room temperature M(H) characteristics of Ni filled MWCNTs have been plotted using a SQUID magnetometer and is shown in Figure 4.7. Magnetic field has been applied parallel to the nanotube.

Figure 4.7: Room temperature M(H) curve for Ni filled MWCNTs.
Though the particle size inferred from MFM and FESEM are higher than the critical particle size of nickel (~20 nm), the M(H) curve exhibit a superparamagnetic behaviour for Ni filled MWCNTs (H_c~0 Oe, M_r~0 emu). This may be due to the agglomeration of nickel nanoparticles and the actual particle size can be less than that inferred from FESEM and MFM. Micro-Raman studies have been carried out on Ni filled MWCNTs after each hour of electrodeposition and is plotted in Figure 4.8.

![Figure 4.8: Micro-Raman studies on Ni filled MWCNTs (Nickel sulphate hexahydrate).](image)

It is noted that the intensity of the D peak is getting enhanced after each hour electrodeposition and the ratio I_G/I_D was decreased to a value of ~ 0.6 after 5 hour electrodeposition from I_G/I_D=1.2 for pristine one. Moreover, the D peak getting broadened with electrodeposition and G peak slightly shifted to lower frequencies. This is thought to be because of the strain developed due to the introduction of metal particles and hence the number of defects also gets enhanced.[57]
4.3.2. Co filled MWCNTs

Cobalt is electrodeposited inside MWCNTs using cobalt acetate and Cobalt sulphate heptahydrate. The morphology is different in this case and is shown in Figure 4.9 and Figure 4.12. As in the case of Co NTs (discussed in Chapter 3), Cobalt acetate after electrodeposition inside MWCNTs give rise to Co-axial nanotubular structure with MWCNTs. The bright open ended FESEM image indicate the formation co-axial structure and is named after this as Co-in-Carbon nanotube. EDS indicates the presence of elemental cobalt. This is further verified using TEM elemental mapping and is shown in Figure 4.10.

![Figure 4.9: (a) FESEM image, (b) EDS of Co filled MWCNT (using Cobalt acetate).](image)

Figure 4.9: (a) FESEM image, (b) EDS of Co filled MWCNT (using Cobalt acetate).
The uniform mixing of green (carbon) and red (cobalt) indicates the co-axial structure of the resultant nanostructure after electrodeposition.

Figure 4.10: (a) TEM image Cobalt-in-Carbon nanotube, (b) elemental mapping of Cobalt-in-Carbon nanotube (red color indicates Cobalt and Green color indicates Carbon).

Figure 4.11: The room temperature M(H) behaviour of the cobalt-in-carbon nanotubes for field parallel to the nanotube.

Figure 4.11 depicts the room temperature magnetic hysteresis for Co-in-Carbon nanotubes. The very high value of the coercivity (Hc ~550 Oe) indicates that the easy axis of magnetisation is parallel to the tube axis and is
arising out of the very high shape anisotropy due to the very high aspect ratio of these tubular structures (aspect ratio~330).\textsuperscript{58-59} Since the coercivity value for bulk cobalt is only 10 Oe, the very high value obtained here can arise only from the uniaxial shape anisotropy, in the nanowire or nanotube form of cobalt.

The FESEM image shows the open ends of the nanostructure, which confirm the nanotube structure of the prepared sample. This further verifies the general mobility assisted growth mechanism that was discussed in chapter 3, in that the hydration layer in the cation and mobility of the cation determine the resultant morphology of one dimensional nanostructures after electrodeposition. The mobility assisted growth mechanism during electrodeposition seems to be valid in other nanopores such as carbon nanotubes too.

This is further tested by the electrodeposition of Cobalt using cobalt sulphate heptahydrate. As in the case of Co NWs, this gives in to a nanowire inside MWCNTs (Figure 4.12).
Figure 4.12: FESEM image (Top), and EDS (Bottom) of Co filled MWCNT (using cobalt sulphate heptahydrate).

EDS indicates the presence of elemental Cobalt. The presence of Copper and Silver seen in the spectrum are from the copper tape and silver back coating respectively. Micro-Raman studies have been carried out on Co filled MWCNTs (using cobalt sulphate heptahydrate) and is shown in Figure 4.13.
Figure 4.13: Micro-Raman Co filled MWCNTs (using cobalt sulphate heptahydrate).

The gradual decrease in G-band (1600 cm\(^{-1}\)) with electrodeposition time is evident from the spectrum and this can be attributed to defects with introduction of metals in to the carbon nanotubes.

4.4 Microwave absorption studies using cavity perturbation method
Cavity perturbation method is widely used to measure the complex dielectric permittivity and magnetic permeability of materials. Cavity is a rectangular box made of a non-magnetic metal with dimensions appropriately chosen to have resonance of electromagnetic waves in the frequency range of interest and connected to a vector network analyser through coaxial cables. The length (l), breadth (a), and height (b) of a cavity are so chosen to have a predetermined TE mode to sustain in the cavity. The schematic of a cavity resonator is shown in figure 4.14.
Samples whose complex dielectric permittivity and magnetic permeability are to be measured are usually made in the form of thin rods of very small volume in comparison to the volume of the cavity so that it must produce only negligible effect on the field configuration in the cavity. The sample is inserted through a non-radiating hole made on the cavity wall, generally along the broad side length. The cavity perturbation technique is based on the change in the resonant frequency and quality factor of the cavity due to the insertion of a sample in to it at the position of electric field maximum or magnetic field maximum, depending upon the nature of the parameter to be studied.

Complex dielectric permittivity and permeability measurements of MWCNTs, Ni NWs and Ni filled MWCNTs were carried out using a vector network analyzer (Rohde & Schwaz ZVB4). 0.01 wt% solutions of MWCNT, Ni NW and Ni filled MWCNTs were prepared using a mixture of toluene and ethyl alcohol (1:2) after extensive sonication. These solutions were carefully filled in a capillary tube of known dimensions (measured using a travelling microscope) and inserted in to a rectangular cavity (waveguide-WR284) with a narrow line slot having dimension 3mm x180mm for permittivity measurements, (figure 4.15).
The cavity was perturbed for different TE_{10m} modes. During the insertion of the sample, the resonant frequency and the quality factor changes and from this change in resonant frequency and quality factor the dielectric permittivity and dielectric loss of the material were evaluated using the formulae:\(^{[60]}\)

\[
\varepsilon_1 = \frac{V_s (f_c - f_s)}{2V_c f_s} + 1 \tag{4.1}
\]

\[
\varepsilon_2 = \frac{V_s}{4V_c} \left( \frac{1}{Q_s} - \frac{1}{Q_c} \right) \tag{4.2}
\]

where \(V_s\) and \(V_c\) are the volume of the material and cavity respectively, \(f_s\) and \(f_c\) are the resonance frequencies with and without the material while \(Q_s\) and \(Q_c\) are the corresponding quality factors of the sample and cavity, given by

\[
Q_s = \frac{f_s}{f_s - f_c}, \quad Q_c = \frac{f_c}{f_c - f_s}. \tag{4.3}
\]

Figure 4.16.a and 4.16.b show the variation of \(\varepsilon_1\) and \(\varepsilon_2\) with frequency. The real part of dielectric permittivity is found to be 11 and 14
for MWCNT and Ni nanowire respectively. There is a large increase in the permittivity ($\varepsilon$) for Ni filled MWCNT when compared to pristine MWCNT and Ni NW. Ni filled MWCNTs exhibited an enhanced permittivity ($\varepsilon_r$ of 33.7 at 3.6GHz. The real part of dielectric permittivity decreased from 39 to 33.7 for Ni filled MWCNT in the frequency range of 2.4-3.6GHz.

The Ni filled MWCNTs also exhibited an increase in dielectric loss with an increase from 0.3 to 19.7 compared to that of pure MWCNTs.

![Variation of permittivity with frequency](image)

Figure 4.16: Variation of (a) $\varepsilon_1$ and (b) $\varepsilon_2$ with frequency.

The cavity perturbation technique which was employed for the evaluation of complex dielectric permittivity can also be used for determining the complex magnetic permeability of magnetic materials.\cite{61} When the material is introduced at the position of minimum electric field in a rectangular cavity (TE$_{10n}$ mode), the real ($\mu_1$) and the imaginary ($\mu_2$) parts of the permeability are given by:\cite{62}

$$\mu_1 = 1 + K \frac{(f_c - f_s)}{f_s} \frac{V_c}{V_s}$$ \hspace{1cm} 4.4

$$\mu_2 = K \left( \frac{1}{Q_s} - \frac{1}{Q_c} \right) \frac{V_c}{V_s}$$ \hspace{1cm} 4.5
where \( K \), the geometrical factor dependent on the guided wave length \( (\lambda_g) \) and width of the cavity \( (a) \) by the relation,
\[
K = \frac{(\lambda_g^2 + 4a^2)}{8a^2}
\]
\[4.6\]
For the \( TE_{10n} \) mode, \( \lambda_g = \frac{2L}{n} \), where \( L \) is the length of the cavity and \( n=1,2,3,4 \).

Figure 4.17.a and 4.17.b depict the variation of \( \mu_1 \) and \( \mu_2 \) with frequency in the S band. The permeability of both the samples, Ni NWs and Ni filled MWCNTs, decreases with increase in frequency and is in agreement with other reports\,[63]. Unfilled MWCNTs exhibited negligibly small complex permeability values.

In pure MWCNTs, the energy loss of the electromagnetic waves can be attributed to their dielectric loss,\,[64] which arises out of their semi metallic nature and in turn their conductivity. When EM radiation is incident on metallic surfaces, the electric field will induce two types of electrical currents within the material. They are the conduction current induced due to the presence of free electrons in the metal and the displacement current due to bound charges. The conduction current will contribute to the imaginary
part of the permittivity (dielectric loss), whereas the displacement current will contribute to the real part of the permittivity. The later is due to polarization effect, which mainly involves the unpaired point defects. So the increase in the real part of the complex permittivity can be mainly ascribed to the dielectric relaxation and space charge polarization effects. The increase in the imaginary part of the complex permittivity can be attributed to the increase in electrical conductivity. They are governed by the relation

\[ \sigma' (\omega) = \omega \varepsilon' (\omega) \]

where \( \sigma' (\omega) \) is the real part of the conductivity, \( \omega \) is the angular frequency and \( \varepsilon' (\omega) \) is the imaginary part of the permittivity.\(^{[65]}\)

In metal filled MWCNTs, the presence of a larger number of MWCNT – metal interfaces gives rise to enhanced interfacial electric polarization. Interfacial polarization aids the microwave absorption due to the interaction of microwave radiation with charge multipoles at the interfaces.\(^{[66-67]}\) In ferromagnetic metals, an additional effect known as magnetic resonance will also contribute to the microwave absorption. This magnetic resonance absorption occurs due to the coupling of microwave field to the internal magnetic moments. Moreover, if the impregnated metals are in the nanometric regime, quantum size effects will also play a major role leading to an increase in their energy level spacing and they increase the microwave absorption. From FESEM (Figure 4.5) and MFM (Figure 4.6.b) studies it is evident that there is a larger number of Ni – MWCNT interfaces in Ni filled MWCNT sample. Besides, the magnetic contrast in the MFM (Figure 4.6.b) proclaims that filled Ni nanoparticles are magnetic. The permeability values, \( \mu_1 \) and \( \mu_2 \) (Figure 3a and 3b) of Ni NWs and Ni filled MWCNTs are comparable with that of Fe filled MWCNTs \(^{[41]}\) and other reported values of magnetic nanowires such as Co\(_{44}\)Fe\(_5\)B\(_2\).\(^{[62]}\) This indicates that the magnetic loss can also contribute to the microwave absorption in Ni NWs and Ni filled MWCNTs. So, both the interfacial polarization and
magnetic loss are contributing to the enhanced microwave absorption in the Ni filled MWCNTs. The average particle size of Ni particles inside MWCNTs is ~70 nm. Since the skin-depth of Ni at 1GHz is ~ 0.5 μm (500 nm), there will be suppression of eddy currents in filled Ni nanoparticles. This also contributes to the enhanced microwave absorption of these composites. Defects in MWCNTs can also modify the dielectric permittivity due to multiple scattering and interfacial electric polarizations, which provides an additional impetus to the absorption mechanism. So Micro-Raman studies were conducted (at 514.5 nm) to identify the presence of defects in Ni filled MWCNTs and the result is shown in Figure 4.18.

Comparatively higher value of the relative intensity ratio of order (G) and disorder (D) peaks (I_G/I_D) ~1.2 indicates the extent of graphitization in pure MWCNT. But, the I_G/I_D is much lower (~0.7) for Ni filled MWCNTs. The reduction in the value of I_G/I_D along with a broad D peak (at ~ 1340 cm\(^{-1}\)) in Ni filled MWCNT reveal the presence of defects in filled MWCNTs.

![Micro-Raman spectrum of pure MWCNT and Ni filled MWCNT](image)

Figure 4.18: Micro-Raman spectrum of (a) pure MWCNT, (b) Ni filled MWCNT.

This is further confirmed by the shifting of G peaks to a lower value in Ni filled MWCNT (1584 cm\(^{-1}\)) compared to that of pure (1605 cm\(^{-1}\)). This
is thought to be due to strain and uneven curving of the graphite layers in the presence of metals.\textsuperscript{43} Though these defects do not alter the bandgap of MWCNTs, and so is the conductivity, however, they can act as polarization centers and thereby increase the $\varepsilon_r$ value.\textsuperscript{46} This gives credence to the belief that addition of defects in MWCNTs by filling of metals can significantly contribute to better microwave absorption characterizations.

4.5 MWCNT-SPION nanocomposites

4.5.1. Synthesis of Aqueous FF (AFF)

AFFs were synthesized by a controlled co-precipitation technique. Initially, nanosized iron oxide particles were prepared by chemical co-precipitation method with ferric chloride ($\text{FeCl}_3$) and ferrous sulphate ($\text{FeSO}_4.7\text{H}_2\text{O}$) in the molar ratio 2:1. Aqueous ammonia was added to this solution aided by constant stirring at room temperature by maintaining the pH at 10. The resultant blackish Iron Oxide precipitate was collected and dispersed in a 3 molar citric acid solution. The resultant mixture was maintained at 90°C for half an hour and the residue was collected and dispersed in water by extensive sonication. By this technique, highly viscous ferrofluids with high shelf life and high thermal stability could be prepared.

4.5.2. Synthesis of MWCNT-SPION composite

For this, one drop of AFF ($\sim3\mu\text{L}$) was placed over MWCNT. The fluid infiltrated in to the nanotubes instantaneously. A magnetic field ($\mu_0\text{H} \sim 1\text{T}$) was applied along the tube axis to enhance the infiltration process. The carrier fluid was evaporated off at room temperature. Subsequently, the surface of CNT was etched by sonicating with ethanol in order to remove the surface layer. Alumina template was removed (for certain studies like SEM,
TEM, EDS) by dissolving the template in a 3molar sodium hydroxide (NaOH) solution and the residue was magnetically separated.

AFF prepared by co-precipitation exhibits high thermal stability and offered high shelf life. The fluid spiked even under small applied magnetic fields and this is an indicator of the fact that the FF synthesized by this method yielded high quality FF. Figure 4.19 shows the schematic of the infiltration processes.

Figure 4.19: Schematic illustration of MWCNT filling by AFF.(a) Infiltration, (b) AFF filled MWCNT.

Figure 4.20.a and 4.20.b depict the FESEM images of AFF filled MWCNTs after the removal of the alumina template. The energy dispersive spectrum (EDS) of the MWCNT-SPION composite is displayed in Figure 4.20.c. Evidence for the presence of element iron emanating from iron oxide can be clearly seen in the spectrum.
Figure 4.20 (a), (b) FESEM, (c) EDS images of AFF filled MWCNT.
Figure 4.21: (a),(b) TEM images of AFF filled MWCNT, (c) TEM image of AFF of SPION, (d) Selected Area Electron Diffraction (SAED) image of AFF filled MWCNT.

The TEM characterization was carried out after removing the alumina template using 3M NaOH and the residue was magnetically separated. Two sets of samples were prepared for TEM analysis (in order to verify the filling of SPION particles inside MWCNTs) by dispersing the residue in ethanol and sonicating the residue for few minutes. This solution was drop casted over TEM copper grid. TEM images derived from two different parts (Figure 4.21.a. and Figure 4.21.b.) of the sample reveal filling of CNTs with FF. The average size of the SPIONs is found to be ~12nm (Figure 4.21.c). The SAED images (Figure 4.21.d) are indicative of superimposition of several planes. They correspond to polycrystalline planes of graphite, (110) and (112), and nanocrystalline planes from iron oxide, (440). The size distribution of SPIONs is depicted in figure 4.22. The distribution is Gaussian and centred at ~11.7 nm.
4.5.3. Magnetisation Studies

The AFM/SFM studies are conducted on both unfilled as well as filled MWCNTs and the results are shown in figure 4.23 and 4.24.

Figure 4.22: Particle size distribution from TEM.

Figure 4.23: (a) AFM image of open ended MWCNTs (Left), (b) MFM image (Right).

Figure 4.24: (a) AFM image of FF filled MWCNT (Left), (b) MFM image (Right).
The open ended pores of MWCNTs are clearly seen from the AFM image of unfilled MWCNTs (figure 4.23.a). There is no magnetic phase contrast visible in unfilled MWCNTs (figure 4.23.b). But, the open ended pores of MWCNTs are found to be filled in the case of FF filled MWCNTs as it is inferred from AFM image (figure 4.24.a). Moreover, a magnetic phase contrast is clearly visible in the MFM image of FF filled MWCNTs (figure 4.24.b), indicating that the sample is magnetic.

The magnetic properties M(H) studies have been carried out using a SQUID magnetometer. Room temperature hysteresis loop of the composite is shown in Figure 4.25. Hysteresis loop is typical of a superparamagnetic material with near zero coercivity (Hc) and negligible remanence (Mr).

![Figure 4.25: M(H) curve for MWCNT-SPION composite at room temperature.](image)

Fitting the Langevin function with the experimentally observed M-H curve is considered as a sure test for superparamagnetism (SPM). The Langevin function can be written as

$$L(x) = \coth x - \frac{1}{x}$$  \hspace{1cm} 4.7
However, if due weightage is not given to the size distribution, this fitting can be erroneous and can be misleading. So, after providing due weightage for size distribution the Langevin function is modified as

\[ L(x) = \frac{1}{2bx} \int_{x(1-b)}^{x(1+b)} L(x')dx' \]

where \( b \) is the width of the size distribution. This modified function in Equation 8 is used to simulate the magnetisation curve and is shown in Figure 4.26.

![Graph showing Langevin function fit to experimental curve](image)

**Figure 4.26: Langevin function fit (dotted line) to the experimental curve.**

The function fit is in agreement and it reaffirms the fact that the MWCNT-SPION composite exhibits SPM. It is to be noted here that the magnetic response of AFF filled MWCNT originates from the SPIONs.

A better understanding of these spatially constrained SPION particles can be arrived at by a temperature dependent magnetisation study. The magnetisation of CNT-SPION composite is recorded at 6K and is
Synthesis and properties of... depicted in Figure 4.27. It is noteworthy that they exhibited enhanced coercivity (~150 Oe) and nonzero remanence.

Figure 4.27: M(H) curve for MWCNT-SPION composite at 6K.

In order to probe the magnetic phase transitions emerging at low temperatures, Zero field cooling-Field cooling (ZFC-FC) measurements were carried out under an applied magnetic field of 300 Oe. The results are shown in Figure 4.28.a

Figure 4.28: ZFC-FC curves for (a) MWCNT-SPION composite, (b) bare (CA coated) SPION.
ZFC curve shows a blocking behaviour\textsuperscript{[70]} at $\sim 110$K. The blocking temperature $T_B$ is related to the size of the superparamagnetic particle by the relation,\textsuperscript{[71]}

\[ KV = 25k_B T \]

where $k_B T$ is the thermal energy, $K$ anisotropy constant (for magnetite $1.35 \times 10^4 J/m^3$) and $V$ the volume of the particle. The blocking temperature $T_B$ calculated for 12nm magnetite particles is $\sim 40$K. The deviation can be attributed to the clustering of SPION particles.\textsuperscript{[72]} TEM pictures also provide proof for clustering of SPION particles within MWCNT.

This implies that magnetic properties of an ensemble of single domain particles follows that of single particles and particle-particle interaction is not strong enough to prevent collective behaviour of the system at these temperatures.

It is to be noted here that FC and ZFC measurements carried out on these samples exhibit anomaly near room temperature. Above room temperature they show a ferromagnetic like behavior up to 400K. Here ZFC measurements were carried out by cooling the sample in zero field up to 6K and then moment is measured while warming in a field of 300 Oe. In FC measurements, the sample is cooled in a field of 300 Oe up to 6K and the moment is evaluated while warming upto a temperature $\sim 400$K. ZFC and FC possess different ground states and similar variation in ZFC and FC above room temperature indicates that the transition is reversible and intrinsic. This observation points to the fact that there is a ferromagnetic like moment ordering due to possible exchange interaction taking place between constrained superparamagnetic particles. Figure 4.28.b depicts the ZFC-FC curves for bare SPION at a lower field (100 Oe). Though there is a
bifurcation temperature higher than that of MWCNT-SPION (it is expected since the present experiment is carried out at lower magnetic field and hence the blocking will be shifted to higher temperatures\textsuperscript{[73]}, there is no increase in magnetisation at elevated temperatures. It is known that magnetic relaxation and blocking play a major role in fine particle system when they are randomly oriented.\textsuperscript{[67]} Once the temperature is increased above room temperature, thermal energy wins over the electrostatic polar repulsive energy between each nanoparticle, which keeps the particles away from agglomeration in the case of a ferrofluid. However, when the nanoparticles are constrained to small volumes, the role of interparticle interaction cannot be ignored and this may initiate an exchange interaction between the nanoparticles.

![Figure 4.29: ZFC-FC curves for MWCNT.](image)

Recently, immense interest has been shown on organic magnetism and induced magnetism in carbon nanotubes and lot of work, both in theoretical and experimental, are underway all around the world.\textsuperscript{[24]} In order to investigate any magnetic ordering in synthesised MWCNTs, ZFC-FC
measurements on bare MWCNTs are conducted. Figure 4.29 shows the ZFC-FC curve for bare MWCNT. ZFC-FC curves do not exhibit any magnetic phase transition indicating that the anomalous transition undergone in the case MWCNT-SPION composite is not emanated from MWCNT. In order to probe the origin of enhancement in magnetisation with temperature for MWCNT-SPION composite a detailed thermomagnetisation and field dependent studies are needed and will be carried out later.

Conclusion

MWCNT based various hybrid magnetic nanostructures of Nickel and Cobalt were fabricated using electrodeposition. The mobility assisted growth mechanism suggested for the growth of 1-D nanostructures inside AAO template is verified in the case of MWCNTs. A novel and high coercivity nanostructure called Co-in-Carbon nanotube has been synthesized using cobalt acetate as precursor for electrodeposition. Introduction of defects in MWCNTs by the addition of metals is studied using micro-Raman studies.

Microwave absorption properties of Ni filled MWCNTs are studied using cavity perturbation technique. Ni filled MWCNTs are found to be acting as a good electromagnetic absorber in the S band. They exhibited enhanced microwave absorption than bare MWCNTs and Ni NWs. Moreover, Ni filled MWCNTs exhibited better microwave absorption characteristics than that reported for Fe filled MWCNTs and they find applications as magnetodielectrics for microwave devices such as phase shifters, modulators and power absorbing terminals.

MWCNT-SPION composite was prepared by employing nanocapillarity of ferrofluids. Magnetisation studies of MWCNT-SPION conducted at room temperature and low temperature suggest that the embedded iron oxide nanoparticles exclusively contribute to the magnetic properties of the composite. Anomalous ZFC-FC curves exhibited by this
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system above room temperature are probably due to the enhanced interparticle exchange interaction. This kind of MWCNT-SPION composite can be envisaged as good agents for drug delivery and can be easily navigated through blood stream with augmented heating for hyperthermia.
References

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