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Processing and characterization of Carbon nanotubes decorated with pure electroless nickel and their magnetic properties

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Abstract

In order to obtain a new functional nanomaterial with good magnetic properties, a low cost electroless deposition method was utilized to decorate multi-walled carbon nanotubes (MWCNTs) with pure Ni. In the present study, an inert surface of nanotubes was activated by introducing catalytic nuclei through a two-step sensitization-activation approach. The nanotubes and their coating were characterized by field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDAX), X-ray diffractometry(XRD), transmission electron microscopy(TEM) and vibrating sample magnetometer(VSM). The experimental results showed that multi-walled carbon nanotubes were encapsulated with metallic catalyst and have good particle size. The agglomerated and tangled MWCNTs contain little catalytic impurities. The surface morphologies of coated carbon nanotubes exhibited pure nickel nanoparticles surrounding on bundles of tubes. Magnetic behavior of Ni coated MWCNTs showed ferromagnetism with improved saturation magnetization as compared to pristine MWCNTs. The as coated MWCNTs can be considered as reinforcing nanomaterial in developing composites by aligning them under very low magnetic field.

Keywords: Multi-walled carbon nanotube; Electroless coating; Nickel nanoparticle;X-ray diffraction; magnetic properties

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1. Introduction

Carbon nanotubes (CNTs), since their discovery by Iijima in 1991 have attracted considerable research interest and the subject of numerous studies owing to their excellent mechanical, electrical and thermal properties. The tensile strength and elastic modulus of MWCNTs in axial direction is 150GPa and 900GPa respectively and density is about 1.33-1.4g/cc. Carbon nanotubes are stable in vacuum up to 2800º C and thermal conductivity is as high as 6000W/m K at room temperature and have zero or less coefficient of thermal expansion as reported by Mamalis (2004) and Kalamkarov (2006). However, the potential applications of carbon nanotubes as reinforcing phase in metal and polymer matrix composites are still limited due to their poor dispersion and weak interfacial bonding with the molten metal. Agglomeration and random orientation of CNTs in matrix melt affects most of the properties of CNT composites. Research investigations by Xiaohua et al. (2000) and Miguel et al. (2005) reveals that randomly oriented nanotube embedded in the metal matrix composite show substantially lower electrical and thermal conductivity than expected. Thermal instability of CNTs at high temperature processing condition poses severe challenge to the researchers. Recently, metal coating on carbon nanotubes by electroless deposition method has been investigated by many researchers to improve the oxidation resistance of CNTs and to obtain good wettability with the molten metal which improve the interfacial bonding between matrix and reinforcement[Ang et al.(2000), Susumu et al. (2004) (2012), Kuan et al. (2010) and Xue Ru et al. (2007)]. It is obvious from the geometrical considerations of CNTs that many properties especially mechanical and electrical properties are superior along tube axis than in the direction normal to it. The potential applications of well aligned nanotubes include field emission devices, transistors, diodes, super capacitors, electrochemical sensors and as reinforcement in composites as reported by Konstantin (2009). A variety of techniques for In-situ as well as Ex-situ alignment of CNTs have been proposed by many researchers as most of the CNT mass production techniques results in randomly oriented CNT bundles and these alignment techniques were reviewed by Xiao-Lin et al. (2005). The recent idea about intrinsic ferromagnetism in carbon nanotubes at low temperature has triggered an immense scope for investigating the field assisted alignment behavior of CNTs. Miguel et al. (2005) has demonstrated the alignment behavior of CNTs under low magnetic field by attaching magnetic material on CNT surface. Attachment of magnetic nanoparticles like Co, Ni and Fe on CNT surface by electroless deposition method has been investigated by many researchers [Ang et al. (2000), Susumu et al. (2004) (2012), Kuan et al. (2010), Xue Ru et al. (2007) and Evan et al. (2012)]. Most of the investigations focus on Ni-P (Nickel-Phosphorus) coating on nanotube surface rather than pure Ni. Phosphorus forms brittle interphase inhibiting the mechanical properties of derived CNT composite and moreover its magnetic properties are very poor. Wettability of carbon with Ni is good as compared to Co and Fe and exhibit ferromagnetism at room temperature with high saturation magnetization. In light of this, Susuma Arai et al. (2010) investigated on pure electroless Ni coating on vapour grown carbon fiber (VGCF). It was reported that saturation magnetization of heat treated Ni coated CNTs was increased to a great extent but no evidence for the temperature dependence of magnetization. In light of this, the present research work aims at preparing multi-walled carbon nanubes coated with Ni by electroless deposition technique and to study the morphology and magnetic properties.

2. Experimental

Multi walled carbon nanotubes were procured from M/s. Chengdu Organic chemicals Co. Ltd, China. Table 1 below shows the properties of CNTs as characterized by supplier. In order to impart palladium nuclei on CNT surface for electroless coating, a two-step sensitization-activation process was carried out at room temperature of 25^0 C. Pristine CNTs were sensitized in a solution containing 7g stannous chloride ($SnCl_2$) and 9g hydrochloric acid (HCl) in 100 mL H_2O for about 10 min. The samples were thoroughly washed with distilled water and acetone. The sensitized samples were then activated in a mixed solution containing 0.25g palladium chloride ($PdCl_2$) and 3g hydrochloric acid (HCl) in 1 lit. H_2O for another 10 min. Activated CNTs were then thoroughly cleaned and washed with distilled water and acetone respectively. The palladium coated-CNT particles were immersed in a freshly prepared electroless Ni bath. The bath was stirred continuously by using magnetic stirrer with heater equipment.

Table 1. Properties of CNTs.

Specification	Value
Type	Multi-walled
Purity	>95%
Outer diameter	30-50nm
Inner diameter	5-12nm
Length	10-12µm
Specific surface area(SSA)	600 m^2/g
Electrical conductivity	>100 s/cm
Colour	Black

Table 2 below shows the concentration of chemicals used in preparing electroless bath as reported by Kuan Yu Lin et al. (2010). Chemicals were purchased from M/s. Karnataka fine Chemicals and M/s. Ultra lab products, Bangalore. The ratio of solution volume in mL to mass of CNT in mg was 2. Chemicals were weighed by using electronic balance (Least count 0.01mg). The temperature of the bath was maintained at 40º C. The pH of the bath was adjusted to 5.5 by diluting with HCl. The time of coating was 10 min. The coated CNT particles were then thoroughly cleaned and washed with distilled water and acetone respectively. Ni coated CNTS were finally dried in an oven at 70º C for 3 hours.

Table 2. Composition of electroless nickel bath.

SL.No.	Chemicals	Composition
1	Nickel Chloride, $NiCl_2.6H_2O$	11.9 - 23.7 g/L
2	Borane- Dimethyl Amine, $(CH_3)_2NHBH_3$	7 g/L
3	Sodium Acetate, CH_3COONa	13.2 g/L
4	Do decyl Benzene Sulfonate $C_{12}H_{25}C_6H_4SO_3Na$	0.1 g/L

Characterization of pristine CNTs and coating was carried out using Field Emission Scanning Electron Microscope (FESEM). Micrographs were taken at different magnifications. The elemental composition was studied by using Analytical Scanning Electron Microscope (ASEM) with EDAX (JED-2300) operating at an accelerating voltage of 20kV. Surface morphologies of CNTs were studied for size, type of CNT and its coating by Transmission Electron Microscope (TEM) (JEOL 3010) at an accelerating voltage of 200 kV. Sample preparation for TEM was carried out by dispersing CNTs in toluene and transferring a drop of dispersion on to a copper grid coated with carbon film. Further, the sample was dried at 40º C. Images were captured at three different magnifications by using Gatan digital camera. XRD studies were carried out by using XRDD8ADVANCE, operating at 40kV, 40 mA supply. A scan range (2Θ) of 10 - 90º in step of 0.03 was adopted. Magnetic properties of samples were characterized by using vibrating sample magnetometer (VSM) (Lakeshore7300).

3. Results and discussions

3.1. Morphology and composition

3.1.1 SEM and EDAX

SEM images of Pristine CNTs and electroless Ni coated CNTs at different magnifications are shown in the below Fig.1(a), (b), (c) and Fig. 2 (a), (b), (c) respectively. It is evident from Fig. 1(a), that CNTs were agglomerated. This agglomeration can be attributed to the free static charges at the surface of CNTs. Fig. 1(b) shows the tangled CNTs.

The bright spots in the image suggest metallic catalyst used in synthesis of CNTs by chemical vapour deposition (CVD) method. Further, the diameter of CNTs measured at different location was shown in Fig. 1(c). It was observed that diameter of tube vary from 19.82 - 37.35 nm. Fig. 2 (a) and (b) shows the surface of CNTs decorated with fine metallic nanoparticles by electroless deposition method. Some empty sites were observed at low magnification owing to lack of nucleation sites for Ni $^{2+}$ on CNT surface.

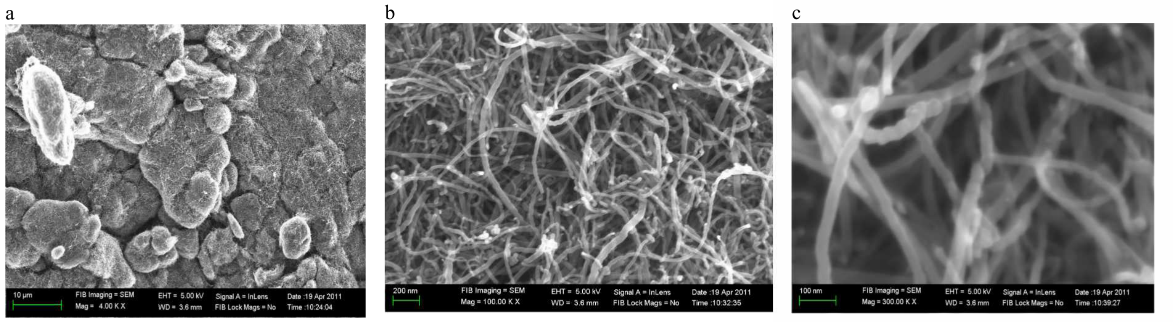

Fig. 1. SEM micrographs of pristine MWCNTs at (a) 4kx; (b) 100kx; (c) 300kx

Since CNT surface is inactive, some nucleation sites have to be developed by activating the surface with palladium (Pd). Defective sites resulting from acidic treatment during purification process themselves acts as sites for nucleation. Further, the coating was not uniform and bumpy in nature as observed in Fig. 2(c) and the reason being coating on agglomerated CNTs.

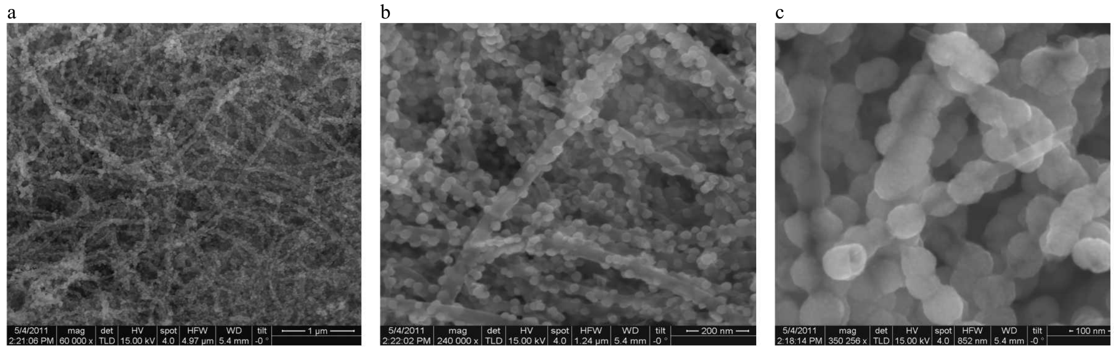

Fig. 2. SEM micrographs of nickel coated MWCNTs at (a) 60kx; (b) 240kx; (c) 350kx

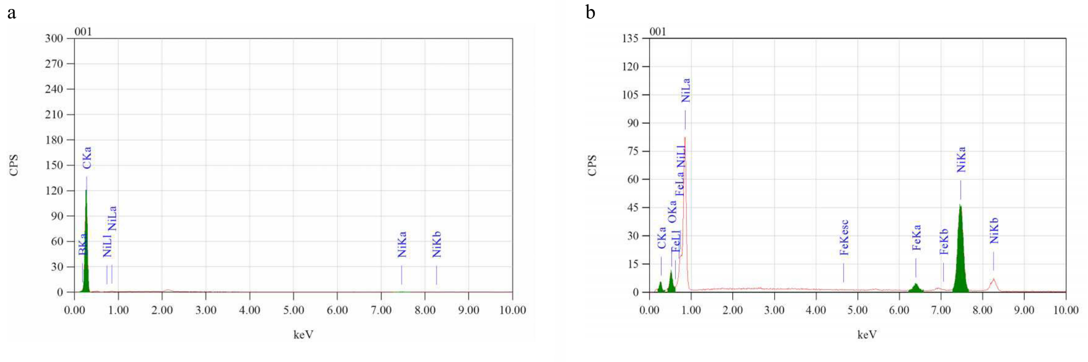

Fig. 3. Energy dispersive spectroscopy of (a) pristine MWCNTs; (b) Nickel coated MWCNTs

Fig. 3(a) and (b) show the EDAX of pristine and decorated CNTs respectively. It was observed that sample contain pristine CNTs with >95% purity and a little amount of Ni. The presence of catalytic nickel particles at the nanotube end cap was evidenced by EDAX. EDAX analytical data from Fig. 3 (b) show 48 wt. % Ni depositions and show no evidence for borane (B) as it is very light to be detected. The absence of chlorine indicates that all $SnCl_2$, $PdCl_2$ and HCl precursors were removed from the process.

3.1.2 TEM

TEM images of MWCNTs at different magnification levels were shown in Fig.4 (a), (b) and (c). It is evident from Fig.4 (a) that CNTs were clustered and tangled due to large radius of curvature and strong Van-der Waals forces between them. The darker contrasts in Fig.4 (b) confirms the presence of particles having higher electron diffraction cross section as compared to carbon and it is catalytic nickel as evidenced by EDAX and SEM. Fig. 4(c) shows concentric multi-walled nanotubes with varying inside diameter ranging from 3-8nm. Fig. 5 (a), (b) and (c) shows the TEM images of elecroless nickel coated MWCNTs at different locations.

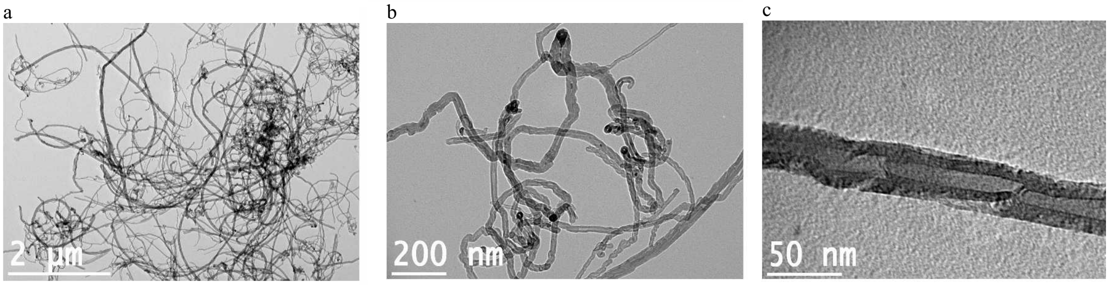

Fig. 4. TEM images of MWCNTs at (a) 2µm; (b) 200nm; and (c) 50nm

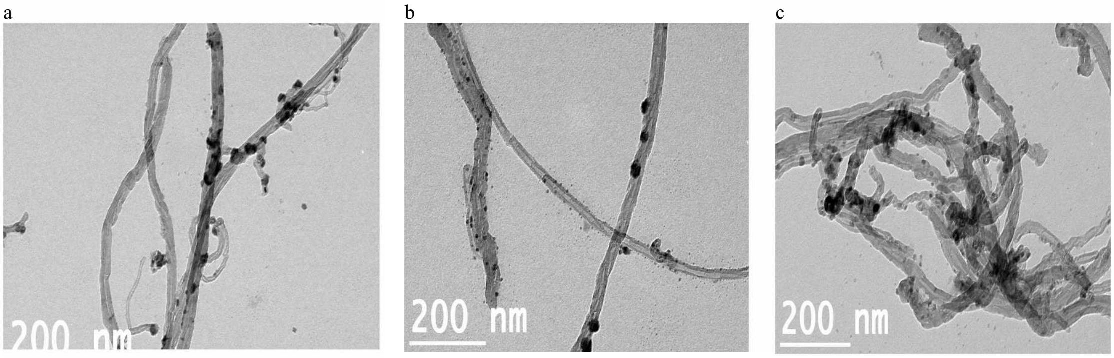

Fig. 5. TEM images of electroless nickel coated MWCNTs at positions (a); (b) and (c)

The Figures clearly shows tiny particles of Ni deposited and distributed unevenly. It was reported by Kuan Yu et al. (2010) that deposition time, temperature and concentration of solution bath plays a critical role in controlling the electroless process. Most of the CNT surfaces were not covered with Ni as observed in SEM and TEM due to lack of activated sites for nucleation. As a result, particles grow on selected sites showing large size. Absence of reducing agent borane (B) and chlorines as observed from EDAX indicates correct concentration of solution bath.

3.1.3 XRD

Fig. 6 (a) and (b) shows the XRD pattern for pristine CNTs and Ni coated CNTs. Fig.6 (a) show two intensity peaks at diffraction angle (2Θ) 25.793° and 42.721° with lattice spacing (d) 3.44513Å and 2.1148Å respectively. Those peaks are associated with (002) and (101) planes of hexagonal graphitic structure respectively. Further, a peak at 44.191° and d spacing of 2.0478Å corresponds to Ni giving conformation to metallic catalyst.

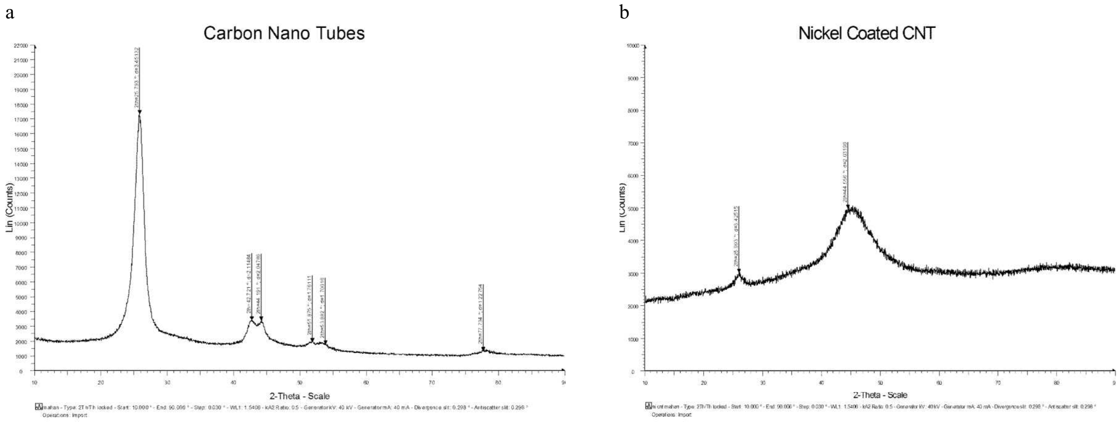

Fig. 6. XRD patterns (a) Pristine MWCNTs; (b) Nickel coated MWCNTs

Fig.6 (b) demonstrates that graphite peaks were suppressed in coated CNTs impressing that CNTs were covered with deposits. Further, increase in diffraction intensity at 44.556° corresponds to (111) plane of face-centered-cubic (FCC) structure of Ni confirms that CNTs were coated with Ni nanoparticles. Broad diffraction peaks indicates the amorphous state of deposits and attributed to the bumpy CNT surface. The higher diffraction intensity indicates large Ni content in the sample. Similar results were observed by Kuan et al. (2010) and Susuma et al. (2012). The investigation results of XUE Ru et al. (2007) suggest that heat treatment of CNTs after electroless deposition transform the amorphous Ni in to crystalline state and make CNT surface smooth. The heat treatment process affects either quality or the morphology of deposits. For better wettability of CNTs, coating should be hard and continuous.

3.2. Magnetic properties of electroless nickel coated MWCNTs

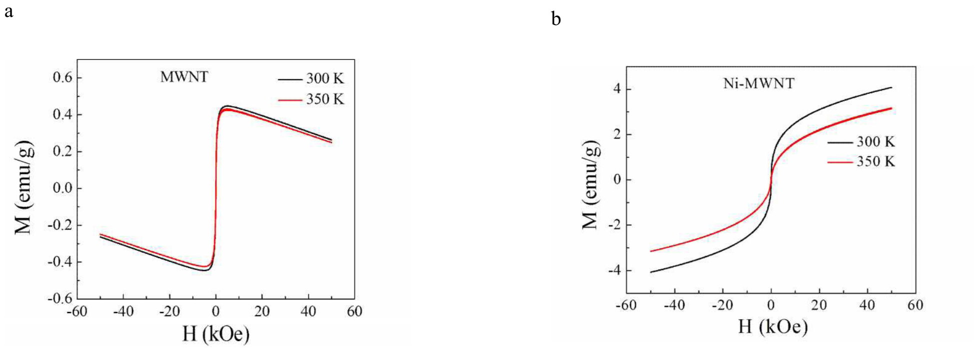

Fig. 7. Magnetization curve for (a) MWCNTs; (b) Ni coated MWCNTs

Fig. 7 (a) and (b) shows the magnetization-field strength (M-H) curves for MWCNTs and Ni coated MWCNTs respectively. It was observed from the above Fig. 7 (a) that the saturation magnetic moment of pristine MWCNTs was 0.45emu/g and 0.4emu/g at 300 and 350K respectively indicates clearly the weak temperature dependence of magnetization. The M-H curve of coated CNTs as shown in Fig.7 (b) is the evidence for the temperature dependant tenfold increase in magnetization of sample. The magnetization data shows superparamagnetic behavior at room temperature and ferromagnetism at fields more than 10kOe. The coercivity (Hc) of both MWCNTs and Ni coated CNTs was observed to be negligible indicating soft magnetic properties of samples. Similar results were observed by Susuma et al. (2010). CNTs can have paramagnetic or diamagnetic response to the applied filed. The recent idea about ferromagnetism in carbon nanotubes creates interest in proper probing of its ferromagnetic properties as intrinsic properties of nanotubes are sensitive to applied magnetic field (H). The magnetic property of MWNT was governed by ferromagnetic (FM) catalyst particle formed during and remains inside the nanotube after synthesis. If the FM particles remain in direct contact with nanotubes, the spin transfer between FM particles and nanotubes alters the CNT magnetism. Some CNTs align themselves by linear orbital anisotropy and torque due to permanent moments. The ferromagnetic particles easy axis lies in the axis of nanotubes and moments associates with permanent moments in CNTs. As a result, application of very low external magnetic field aligns CNTs with their long axis in the direction of field and such behaviour of CNTs was demonstrated by Islam et al. (2005).

4. Conclusions

In the present work, electroless Ni deposition on multi-walled carbon nanotubes (MWCNTs) was investigated and characterized for morphology and magnetic properties by using SEM, TEM, EDAX, XRD and VSM. The following conclusions can be drawn based on results and discussions.

- Multi-walled carbon nanotubes of good particle size ranging from 19.82-37.35nm (OD), 3-8nm (ID) and a few microns in length.
- Tangled and agglomerated MWNTs with >95% purity and encapsulated with Ni catalyst at the tip of tube.
- Pure electroless Ni deposition was successful and total amount of deposition is 48 wt. %.
- Broad diffraction intensity peaks for Ni shows its amorphous state before heat treatment process.
- According to VSM, both CNTs and Ni deposit exhibits soft magnetic properties.
- Superparamagnetic properties at low fields and ferromagnetism at high field strengths were observed.
- Appreciable increase in saturation magnetization (M) of Ni coated CNTs as compared to pristine CNTs.
- Pure electroless Ni coated MWCNTs might be the promising nanomaterial for external magnetic field induced alignment.

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