Change of magnetic behaviour of nitrogenated carbon nanotubes on chlorination/oxidation

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Abstract: The magnetic effects of chlorine and oxygen functionalised NCNTs have been studied. The diamagnetic behaviour of non-functionalised NCNTs changes to paramagnetic behaviour on Cl-functionalisation; on O-functionalisation NCNTs become ferromagnetic. A prominent cusp-like behaviour is observed at around $\approx 45$ K in $M_{FC}$ and $M_{ZFC}$ measurements, further confirming the ferromagnetic behaviour of O-functionalised NCNTs; but Cl-functionalised NCNTs do not shows any cusp-like behaviour indicating formation of paramagnetic behaviour. The change of magnetic behaviour occurs owing to formation of different bonding with carbon/nitrogen and/or Fe-catalyst atoms that is verified with theoretical calculation. The initial computational results show that the differential bonding patterns of the Cl-functionalised and the O-functionalised NCNTs are the main cause for the different magnetic behaviour in these systems.

Keywords: magnetisation; nitrogenised carbon nanotubes; NCNTs; functionalised with oxygen (NCNTs:O); functionalised with chlorine (NCNTs:Cl); density functional theory; DFT.
1 Introduction

Carbon nanotubes (CNTs) display excellent electrical, thermal and mechanical properties [1,2] and large specific surface area, which are highly desirable for their enormous potential applications particularly for nanoelectronics. CNTs containing nanomagnetic-materials are able to form a perfect spin-transport medium, since electron transport in them is one-dimensional and ballistic with a long spin relaxation time and weak
spin-orbital effects. Even pure CNTs, which are non-magnetic materials, are characterised by a giant magneto-resistance [3,4]. On the other hand, it is quite obvious that modification of CNTs would lead to significant differences in their electronic structure and other different properties [5–7]. Owing to very large magnetic shape anisotropies, the encapsulation of magnetic phases in CNTs could provide a feasible approach to achieve magnetic order stabilisation against thermal fluctuations in systems having extremely reduced dimensions. Also, the ferromagnetic nanoclusters are expected to have much better magnetic properties than bulk metals owing to their single domain nature [8].

Therefore, it is desirable to produce CNTs not only with magnetic material inside the tubes in a specific and controlled way but also further modification with specific species. Beyond the geometrical advantage of a quasi-one-dimensional CNT design, the carbon shells can provide an effective protection against oxidation. The growing of CNTs is however a catalysed-determined process. The most used catalyst materials are the Fe, Co, and/or Ni. All these metals show over a wide temperature range ferromagnetic properties. Hence, alternative techniques have to be developed in order to either remove completely the catalyst material from the nanotubes or to apply nonmagnetic catalysts. Various purification methods have been employed to remove magnetic impurities, such as chemical treatment, microwave heating, mechanical filtration, and heat treatment in a vacuum or oxidative environment [9–12]. However, a graphitic coating commonly found around ferromagnetic catalyst particles shields the particles from acid dissolution. Attempts to remove this graphitic coating often result in damage or destruction of SWNTs [12]. Although some groups applied magnetics filtration, the efficiency was low such that ferromagnetism still dominated the magnetic moment of the sample for fields of order a few Tesla [13–16]. To circumvent this problem, other researchers synthesised nanotubes using non-ferromagnetic catalysts such as Rh/Pd or Rh/Pt [17]. Lipert et al. [18] shows two different ways to obtained CNTs having diamagnetic behaviours (nonmagnetic).

In this present work, we prepared the MW-NCNTs and studied their magnetic properties after functionalisation with chlorine and oxygen plasma atmosphere. We observed that at room temperature non-functionalised MW-NCNTs show diamagnetic behaviours, whereas chlorine and oxygen functionalised MW-NCNTs are para and ferromagnetic, respectively. To have an idea about the nature of bonding and its possible influence on the magnetic behaviour, we have also carried out computational calculations on some model systems. Thus, the purpose of this work is to study magnetic characteristics of multi-walled NCNTs functionalised with chlorine and oxygen as a function of the magnetic field and temperature.

2 Experimental details

In this process, we synthesised vertically oriented nitrogenated multiwall carbon nanotubes (MW-NCNTs) by the microwave plasma-enhanced chemical vapour deposition (PECVD) process on silicon substrates pre-coated with an e-beam evaporated thin Fe catalytic layer [19]. Then, obtained N-CNTs were chlorinated in an inductively plasma coupled reactor in flowing Cl-gas [20]; oxidation was performed under air-atmospheric plasma conditions using a dielectric barrier discharge system [21].

The dia/para/ferromagnetic behavioural change M-H loops and \( M_{FC}/M_{ZFC} \) measurements
were measured at 5 K and 300 K, respectively using quantum design superconducting quantum interference device (SQUID) magnetometer. The details preparation and different characterisation of functionalised (Cl/O)/non-functionalised of MW-NCNTs could be found elsewhere [19–23]. The computational calculations were carried out using DFT based B3LYP method and 6-31G (d) basis set combination implemented in Gaussian 09 software program [24]. To generate the model we have used a small portion of a carbon nanotube and the dangling bonds were then saturated with hydrogen. This model was then used to get the N-doped CNTs and further chlorine and oxygen functionalised N-doped CNTs systems.

3 Results and discussion

Figures 1(a)–(c) show the scanning electron microscopy (SEM) images of N-CNT, N-CNT:Cl, and N-CNT:O, respectively. The cross sectional SEM images of N-CNT:Cl(O) show that the vertical alignment of the chlorine-plasma treated one is destroyed but the oxygen-plasma treated N-CNTs exhibit stronger vertical alignment. The densities, lengths and diameters are changed on chlorine-plasma/oxygen-plasma treatment as described in our previous reports [19–22].

Figure 1 Scanning electron microscopy of (a) MW-CNTs (b) chlorine functionalised NCNTs and (c) oxygen functionalised NCNTs
The magnetisation M-H hysteresis loop of NCNTs obtained at 300 K and 5 K is shown in Figure 2(a). The spectral features behaviour unambiguously implies a pure diamagnetic behaviour, although the nanotubes have contribution of strong magnetic Fe-particles as a catalyst in the NCNTs. Lipert et al. [18] observed the similar diamagnetic behaviour of Fe-based MWCNTs, after post annealing process at very high temperature ~2500°C. They have claimed that the ferromagnetic behaviour changed into diamagnetic owing to complete evaporation of Fe-catalyst particles from the CNTs at this high temperature annealing. Lipert et al. [18] also observed the diamagnetic behaviour for the CNTs synthesised using non-magnetic Re as a catalyst. In our case, we are expecting the diamagnetic behaviour of NCNTs may be due to presence of non-magnetic bonding that dominates the Fe-catalyst in the NCNTs structure. Furthermore, the oxygen
functionalsied NCNTs shows strong ferromagnetic behavioural M-H hysteresis loop (opposite trend of pure NCNTs) unlike non-functionalised NCNTs as shown in Figure 2(c). Del Bianco et al. [25] observed the ferromagnetic behavioural M-H loop for the core interface of oxygen passivated Fe-nanoparticles. In our case, we also expect that the ferromagnetic behaviour may occur owing to oxygen passivation with the NCNTs on oxidation (oxygen plasma treatment). In case of chlorine-plasmatreated NCNTs shows the M-H loops in Figure 2(b) are not like either pure NCNTs or NCNTs:O; but inter-phase of those two (dia- and ferro-) indicating possible paramagnetic behaviour. We are expecting these magnetic behavioural changes to occur owing to formation of different bonding with carbon/nitrogen/Fe-catalyst on chlorine/oxygen-plasma functionalisation process.

However, we also further characterised the thermal evolution of the magnetisation of MW-NCNTs (:Cl/O) with temperature (T) dependent magnetisation (M) by the zero-field-cooling (M_ZFC) and field-cooling (M_FC) procedures in an applied magnetic field of 1000 Oe in between 5 K and 300 K. Figure 3(a) shows the M-T curve of N-CNTs; whereas N-CNT:Cl and N-CNTs:O shown in Figure 3(b) and (c), respectively. It is found that the \(M_{ZFC}\) curve gradually deviates from the \(M_{FC}\) curve with decrease of temperature at about ~255 K (for MW-NCNTs), ~200 K (for CNTs:Cl) and ~300 K (for CNTs:O); when the applied magnetic field is 1000 Oe. Upon further cooling, the \(M_{ZFC}\) plot exhibits a cusp centred at about ~45 K for the MW-NCNTs and NCNTs:O; but not in NCNTs:Cl. This variable temperature magnetic data of NCNTs and NCNTs:O clearly indicate that the Fe/N-CNTs exhibit ferromagnetic behaviour at below room temperature, which is attributed to the uncompensated surface spin states or ferromagnetic Fe clusters, although M-H curve of non-functionalised NCNTs shown in Figure 2(a) is completely diamagnetic in behaviour. It is believed that this ferromagnetic performance of the Fe/N-CNTs:O comes from the ferromagnetic Fe clusters with formation of different bonding with carbon/nitrogen and the uncompensated surface spin states. In case of NCNTs:Cl the \(M_{ZFC}\) and \(M_{FC}\) curves coincide up to ~200 K as shown in Figure 3(b), when measured at an applied magnetic field 1000 Oe and they split below that temperature. A similar behaviour has been observed by Del Bianco et al. [25] to occur in oxygen passivated Fe-nanoparticles. In that case, the anti-ferromagnetic character of \(\text{Fe}_2\text{O}_3\) was in the origin of the low temperature irreversibility. This low temperature ferromagnetic phase magnetisation is correlated to the fact that at lowest temperature and after \(M_{ZFC}\) process, the moments of magnetic particle Fe are not fully aligned with the applied field. Furthermore, no cusp is observed in the \(M_{ZFC}\) plot in N-CNT:Cl indicating non-ferromagnetic in nature. In case of N-CNT:O, it is found that the \(M_{ZFC}\) curve gradually deviated from the \(M_{FC}\) curves with decrease of temperature at about 300 K as shown in Figure 3(c), when measured at an applied magnetic field of 1000 Oe. A similar behaviour has been observed by Zhang et al. [26] for CoO/CNTs core-shell nanostructures, when they have measured at an applied magnetic field 100 Oe between 2 K and 300 K. In our present case, it is also further observed upon further cooling that the \(M_{ZFC}\) plot exhibits a cusp centred at about ~45 K and the \(M_{FC}\) data sequentially increases indicates ferromagnetic behaviour at this temperature compared to NCNTs and NCNTs:Cl. It is believe that the ferromagnetic behaviour in NCNTs:O comes from the ferromagnetic Fe-clusters and uncompensated surface spin states owing to formation of different bonding with carbon/nitrogen/Fe-catalyst.
To identify the bonding features of pure NCNTs and Cl/O functionalised NCNTs (NCNTs:Cl and NCNTs:O); computational calculations were carried out using DFT based B3LYP method and 6-31G (d) basis set combination implemented in Gaussian 09 software program [24]. To generate the model we have used NCNTs and two most stable complexes of

- NCNTs with Cl$_2$
- NCNTs with O$_2$ that are shown in Figure 4(a)–(c).

The hydrogen atoms in these models saturate the dangling bonds of carbon atoms, so that these carbon atoms mimic those in NCNTs, NCNTs:Cl and NCNTs:O. For the N-doped model system, we got a very stable chemically bonded singlet structure. This N-doped system then used to study the interaction of Cl$_2$ and O$_2$ in their ground states. Fundamentally, when a singlet molecule (like Cl$_2$) reacts with another system with singlet electronic configuration gives a singlet product, and when a triplet molecule (like O$_2$) reacts with a singlet system gives a triplet product. So we have analysed nature of bonding in those two different products

- singlet NCNTs with Cl$_2$
- triplet NCNTs with O$_2$. 

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**Figure 3** $M_{\text{FC}}$ and $M_{\text{ZFC}}$, M-T spectra of (a) NCNTs (b) chlorine functionalised NCNTs and (c) Oxygen functionalised NCNTs (see online version for colours)
Analysis of the results shows that Cl\textsubscript{2} reacts with NCNTs and the product obtained is in singlet state as shown in Figure 4(b). It can be seen that the Cl atoms are now dissociated and the nature of interaction between the NCNTs and the Cl-atoms are physisorption in nature. It is also interesting to note that the physisorption site for the Cl-atom is very specific and it prefers to stay above the C-atom of the NCNTs and not above the N-doped site. As the product is in singlet configuration, the electrons spins will be perfectly paired, but the electrons in both the Cl-atoms will precess in the presence of the magnetic field as they are almost in unbound states. The two magnetic vectors coming from the both the Cl-atoms will lie in the same plane with a well defined phase relationship. It is well known that the condition for an effective transition from the singlet state to the triplet state is that the local fields must differ (even slight difference is effective) at the two electrons. Owing to the curved nature of the NCNTs, it can be easily expected that the electron on each Cl-atom must experience a slight difference in the local fields. As the two electrons are in the influence of different local fields, one of the electron vectors will precess at a greater rate than the other when a magnetic field is applied. This leads to periodic transition from singlet to triplet configuration. Such a behaviour will lead to the paramagnetic behaviour of a material system and in this light we think the Cl-doped system’s paramagnetic behaviour can be explained.

**Figure 4** The most stable model complexes of (a) NCNTs, (b) chlorine functionalised NCNTs and (c) oxygen functionalised NCNTs (see online version for colours)
Analysis of the results shows that O₂ reacts with NCNTs and the product obtained is in triplet state as shown in Figure 4(c). We did not carry out a complete potential energy search to ascertain if there are any other stable minima with other spin multiplicities or not. From the Figure 4(c) it can be seen that in the O₂ doped case, O₂ is chemically bound to the nanotube and not like the earlier case of Cl₂ doping. This stable chemically bound state in the O₂ case may be freezing the spins of the two unpaired electrons and parallelising the orientations of the two spin vectors. Only such phenomena can lead to a permanent magnet-like behaviour of the material system. In view of the experimental findings we can explain that the O-functionalised NCNTs to show the ferromagnetic type of behaviour it should definitely have a stable chemically bound state and spin bound conditions as shown here in this work. In light of such chemical structural feature with a spin bound triplet state only, one can explain why the O-functionalised NCNTs are ferromagnetic in nature.

4 Conclusion

Room temperature and below room temperature magnetic behaviours have been studied for the NCNTs and functionalised NCNTs with chlorine and oxygen. The interaction between Fe-nanoparticles and the NCNTs plays a critical role for the diamagnetic behaviour of the Fe-catalyst based NCNTs at room temperature. NCNTs:O show ferromagnetic nature at room/below room temperature and is owing to ferromagnetic Fe-clusters and the uncompensated surface spin states owing to formation of different bonding with carbon and/or nitrogen. It is believe that these magnetic/non-magnetic NCNTs (:Cl/O) may show promising applications in biomedicine/bio- and nanoelectronics applications. From the computational results we considered that the differential bonding patterns of the Cl-functionalised and the O-functionalised NCNTs are the main cause for the different magnetic behaviour of these systems.

Acknowledgements

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References

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