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Anisotropic conductivity of magnetic carbon nanotubes embedded in epoxy matrices

Il Tae Kim^{a,b}, Allen Tannenbaum^{c,d}, and Rina Tannenbaum^{a,e,*}

^aSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^bSchool of Polymer, Textile, and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^cSchool of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^dDepartment of Electrical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

^eDepartment of Electrical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

Abstract

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$)/multi-walled carbon nanotubes (MWCNTs) hybrid-materials were synthesized and their anisotropic electrical conductivities as a result of their alignment in a polymer matrix under an external magnetic field were investigated. The tethering of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on the surface of MWCNT was achieved by a modified sol-gel reaction, where sodium dodecylbenzene sulfonate (NaDDBS) was used in order to inhibit the formation of a 3D iron oxide gel. These hybrid-materials, specifically, magnetized multi-walled carbon nanotubes (m-MWCNTs) were readily aligned parallel to the direction of a magnetic field even when using a relatively weak magnetic field. The conductivity of the epoxy composites formed in this manner increased with increasing m-MWCNT mass fraction in the polymer matrix. Furthermore, the conductivities parallel to the direction of magnetic field were higher than those in the perpendicular direction, indicating that the alignment of the m-MWCNT contributed to the enhancement of the anisotropic electrical properties of the composites in the direction of alignment.

1. Introduction

Carbon nanotubes (CNTs) have been the focus of extensive research in recent years due to their exceptional mechanical, thermal, and electrical properties [1–4]. As a result of their nanoscale dimensions and high surface area, CNTs could be also considered as efficient templates for the assembly of nanoparticles [5]. The alignment of CNTs as fillers in a variety of matrices can be used to reinforce, intensify, and enhance some of the properties of

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Corresponding author: Fax: +1 404 8949140. rinatan@mse.gatech.edu or rinatan@technion.ac.il (R. Tannenbaum).

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the resulting composites as well as introduce various degrees of anisotropy into the properties of the desired nanomaterials [6–7].

The use of composites made from an insulating matrix and highly conductive fillers has significant advantages in a broad range of applications, such as antistatic and electrostatic dissipation, electromagnetic interference (EMI) shielding, and electrostatic painting. Valentini et al. [8] and Tamburri et al. [9] pointed out that functionalized CNTs with amine and -OH or -COOH functional groups showed enhanced conductivity in polymer matrices due to their improved dispersion that was enabled through functionalization. In addition, recently, O'Connor et al. [10] demonstrated a novel liquid phase method to infiltrate MWCNT into the surface layer of polyethylene films, resulting in transparent but conductive polymer composites. Ramasubramaniam et al. [11] observed that homogeneously-dispersed carbon nanotube polymer composites, where the single-walled carbon nanotubes (SWCNTs) were suspended by the attachment of non-covalent functional groups, exhibited dramatic improvements in the electrical conductivity with low percolation threshold.

The electrical properties of composites with an aligned filler phase were superior than those of composites in which the filler phase was randomly distributed. Alignment of CNTs by electric, magnetic, and shear induced field was reported previously by several groups [12–16]. Martin et al. [12] successfully demonstrated the application of AC electric fields allowing both the alignment of carbon nanofibers in epoxy resin and their connection into a network. Zhu et al. [17] studied electric field aligned MWCNT/epoxy composites with a sample size of up to several centimeters using fast UV polymerization, showing significant anisotropic properties for storage modulus and electrical conductivity. Steinert et al. [18] obtained solution cast PET-carbon nanotube composite films by applying a magnetic field, resulting in increased conductivity with the increase of the applied magnetic field. However, due to the low magnetic susceptibility of carbon nanotubes, their alignment by the application of an external magnetic field requires a relatively high magnetic field [15]. This drawback could be solved by enhancing the magnetic susceptibility of carbon nanotubes by tethering magnetic nanoparticles on their surface [19,20].

The decoration of CNT walls with various compounds and structures, such as inorganic nanoparticles, could increase the tunability of their properties, such as electrical and magnetic characteristics [21]. Iron oxide nanoparticles such as magnetite and maghemite have been of technological and scientific interest due to their unique electric and magnetic properties. These nanoparticles can be generated by several methods such as the layer-by-layer technique [22], the hydrothermal method [23], pyrolysis [24], and the magneto-evaporation method [25]. While these nanoparticles have been found useful in various applications such as high-intensity information storage and electronic devices [26–28], they have also proven effective as decorating agent for high surface materials such as carbon nanotubes.

In this paper, we tethered magnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles onto the walls of MWCNT by means of a novel and simple modified sol-gel process using an iron salt as precursor. Subsequently, the magnetic MWCNTs (m-MWCNTs) were introduced into a polymer matrix and aligned by the application of a magnetic field, forming composites with an aligned filler phase. The effective alignment of MWCNT tethered with magnetic nanoparticles requires only a weak magnetic field (as compared with other methods in which alignment is obtained only in high magnetic fields [15]). It is therefore expected that the composites formed in this manner would exhibit anisotropic electrical properties, in accordance with the parallel and perpendicular direction to the magnetic field that has been applied and under which the alignment has taken place. Composites with such anisotropic

electrical properties may be potentially utilized in applications requiring antistatic or electrostatic dissipation.

2. Experimental Section

2.1 Materials

MWCNTs (>99%) produced by chemical vapor deposition followed by HCl mineralization, with 12 nm in diameter and 10 μm in length, were purchased from Aldrich. To activate the surface along the MWCNTs, concentrated sulfuric acid (98%) and nitric acid (70%) were purchased from Fisher Scientific. For the preparation of magnetic carbon nanotubes (m-CNTs), ferric nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was purchased from Acros Organics. Propylene oxide (>99%), absolute ethanol (anhydrous, 200-proof), and sodium dodecylbenzene sulfonate (NaDDBS) were purchased from Aldrich and TCI. In order to make composites with m-CNT, Aeropoxy laminating materials (PR2032 Resin) was used with an appropriate curing agent (PH3660).

2.2 Synthesis of maghemite-MWCNT hybrid materials

Pure-MWCNTs were first dispersed in a solution mixture of concentrated sulfuric acid and nitric acid with the volume ratio of 3:1. The suspension was ultra-sonicated for 3 hrs at room temperature. After that, the concentration of the suspension was diluted up to 50% and filtered with a PTFE membrane (0.45 μm pore size) with the aid of a vacuum pump. Carboxylated MWCNT (MWCNT-COOH) was washed with de-ionized water several times to reach neutral pH and dried under vacuum at 50 $^{\circ}\text{C}$ overnight. The synthesis of maghemite-MWCNT was performed by first adding 0.65 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 20 ml of absolute ethanol (100% purity) and stirring until the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved completely. Subsequently, this iron salt solution was added to a suspension of oxidized MWCNTs with a mass ratio of 4:1 ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: MWCNTs mass ratio of 4:1), stirred, and sonicated for 3 hrs. Twenty ml of 1.2 mM of NaDDBS were added to the solution and stirred for 30 min. Then, 1.2 ml of propylene oxide was added as a gelation agent and stirred for 30 min. The mixture was then placed in a Fisher Scientific iso-temperature oven for drying for 3 days at 100 $^{\circ}\text{C}$. The resulting powder products were washed with water and ethanol several times and dried at 50 $^{\circ}\text{C}$. The calcination of these powders was performed in a furnace under argon atmosphere at 500 $^{\circ}\text{C}$ for 2 hrs. The overall synthesis strategy is shown in Figure 1.

2.3 Fabrication of polymer composites with anisotropic conductivity

Various weight percents of magnetic multi-walled carbon nanotubes (m-MWCNTs) were dispersed in a small amount of ethanol with sonication for 1 hr. Epoxy resin (PR2032) was added to the suspension and mixed with a mechanical stirrer for 30 min in order to obtain optimal dispersion. After that, the nanocomposite solution was sonicated to evaporate entire solvent at 50 $^{\circ}\text{C}$. The curing agent (PH3660) was added into the solution, mixed, and degassed under vacuum. The solution was immediately poured into a mold, and a 0.3 T magnetic field was applied for 1 hr at room temperature, for 1 hr at 60 $^{\circ}\text{C}$, and for another 1 hr at 60 $^{\circ}\text{C}$ without a magnetic field. The nanocomposite was post-cured at 60 $^{\circ}\text{C}$ for 6 hrs in the iso-temperature oven.

2.4 Characterization

The dried samples were ground into a fine powder using a ceramic mortar and pestle. XRD measurements were performed using an X'pert Pro Alpha-1 (wavelength of 1.54 $\text{\AA}$). XRD peaks were collected from $2\theta = 0^{\circ}$ to 90° with a step size of 0.02° . XPS scans of powder samples were taken using a Surface Science Laboratories SSX-100 ESCA spectrometer

using monochromatic Al K α radiation (1486.6 eV). The alignment of the sample was conducted by a magnet (GMW-5403) at 0.3 T, and the experimental apparatus used in this study is depicted schematically in Figure 2(a). The morphology and aligned feature of as-prepared samples were also characterized using SEM (LEO 1530). TEM samples were prepared by placing a droplet of solution onto a TEM grid, and for the observation of aligned features, samples were micro-tomed into 100 nm thick slices using a diamond knife and placed on a TEM grid. These samples were analyzed using a Hitachi HF2000, 200 kV transmission electron microscopy. The electrical conductivity data of as-prepared composites were collected using impedance analyzer (Solartron Instruments SI 1260 with dielectric interface 1296) for the frequency range 0.1 Hz ~ 1 MHz. All the data were collected under an AC voltage of 0.1 V. The setup for electrical measurements of the composites is shown in Figure 2(b). Contact was achieved by silver painting the two ends of the samples, and then using coaxial probes on a probe station attached to the impedance analyzer.

3. Results and Discussion

3.1 The formation of nearly-monodisperse and homogeneously-distributed iron oxide nanoparticles

The novel key step to impart magnetic properties to the carbon nanotubes is composed of a carefully-designed synthesis method, which involves a modified sol-gel process. The formation of γ -Fe₂O₃ is dependent on the presence of propylene oxide, which acts as an oxide-formation promoter. The general mechanism of γ -Fe₂O₃ formation by the introduction of an epoxide to a hydrated iron nitrate solution has been well established [29].

In our system, the homogeneous distribution of the iron oxide nanoparticles on the surface of the MWCNT was achieved due to the electrostatic interactions between negatively charged surface of the MWCNT and the positively charged Fe(III) as shown in Figure 1. Given that the negatively-charged surface sites of MWCNTs are homogeneously distributed, the Fe(III) ions could nucleate accordingly to form well-separated nanoparticles.

The occurrence of gelation upon the addition of propylene oxide to the solution was inhibited by the addition of surface active molecules, NaDDBS. These molecules coordinate to the Fe(III) centers by electrostatic attractions forming a self-assembled protective layer, resulting in the inhibition of gel formation. Therefore, it is appropriate to refer to this method a *modified* sol-gel process. Finally, due to the presence of the NaDDBS molecules, no aggregates of γ -Fe₂O₃ were formed but rather the nanoparticles remained individually isolated and homogeneously distributed.

3.2 Characterization of magnetic carbon nanotubes

Figure 3 shows the XRD patterns of the synthesized γ -Fe₂O₃/MWCNT, demonstrating the high crystalline nature of the nanoparticles. The diffraction peak at 25.98° could be attributed to the graphite structure (002) of MWCNTs. The positions and relative intensities of non-MWCNT related new peaks, after surface modification, in the range of 20° < 2 θ < 80° correspond to the (220), (311), (400), (422), (511), (440), and (533) reflections of maghemite (γ -Fe₂O₃).

X-ray photoelectron spectroscopy (XPS) also confirmed that the iron oxide nanoparticles were formed on the surface of MWCNT. After the formation of surface treated MWCNTs decorated with iron oxide nanoparticles followed by calcination at 500 °C, XPS shows characteristic iron peaks in addition to carbon and oxygen, as shown Figure 4(a). The high-resolution spectrum (Figure 4(b)) indicates that the position of the Fe (2p_{3/2}) and Fe (2p_{1/2})

peaks at 711.3 and 724.4 eV, respectively, are in good agreement with the values reported for γ -Fe₂O₃ in the literature [30], validating the formation of γ -Fe₂O₃ in our samples.

3.3 The characterization of the morphology of γ -Fe₂O₃/MWCNT

Scanning electron microscopy (SEM) images of m-MWCNT confirmed that γ -Fe₂O₃ nanoparticles were attached to the walls of the MWCNT as shown in Figure 5(a), and that the size of the attached iron oxide nanoparticles was about 17 nm (Figure 5(c)). The high-resolution transmission electron microscopy (HRTEM) image of a nanoparticle (Figure 5(b)) illustrates the maghemite interlayer spacing of the (311) lattice plane of approximately 0.25 nm [31]. Furthermore, the inset image of Figure 5(b) shows the electron diffraction patterns of maghemite, indicating the high crystallinity of the maghemite nanoparticles. The homogeneous distribution of the nanoparticles on the surface of the MWCNT was achieved by the electrostatic interactions between the negatively-charged MWCNT and the positively-charged Fe(III) centers (see Figure 1), as well as by the introduction of NaDDBS in order to inhibit the formation of 3D iron oxide networks. The magnetic nature of the as-prepared m-MWCNT could also be easily ascertained by placing an external magnet next to the vial containing the m-MWCNT, as shown in Figure 5(d).

3.4 Alignment of m-MWCNTs in polymer matrix

The SEM images of m-MWCNT hybrid materials are shown in Figure 6(a) and 6(b). When a droplet of dispersed hybrid materials in a water solution was dried under the magnetic field, the surface-modified MWCNT were aligned easily (Figure 6(a)). However, when the nanocomposite solution was dried without applying magnetic field, the surface-modified MWCNT did not exhibit alignment features (Figure 6(b)). The TEM images of composites in which surface-modified MWCNT (m-MWCNT) and unmodified MWCNT were embedded in epoxy matrices are shown in Figure 6(c) through 6(f). We first compared the alignment features of the MWCNT/epoxy nanocomposite and the m-MWCNT/epoxy nanocomposite systems, under the same experimental conditions, i.e. the same strength of the externally-applied magnetic field (0.3 T). Figure 6(c) and 6(d), representing MWCNT/epoxy composites with 0.5 wt% MWCNT and 1.0 wt% MWCNT, respectively, did not reveal any alignment features of filler phase in the polymer matrix under the externally-applied magnetic field. However, in the case of the m-MWCNT/epoxy nanocomposite systems also having 0.5 wt% m-MWCNT and 1.0 wt% m-MWCNT and shown in Figure 6(e) and 6(f), respectively, it is obvious that the m-MWCNTs embedded in the epoxy matrix have indeed aligned parallel to the direction of magnetic field (0.3 T). Comparing the alignment features of aligned m-MWCNT hybrid materials and aligned m-MWCNT/epoxy composites (Figure 6(a), 6(e), and 6(f)), it becomes evident that the m-MWCNT hybrid materials in the absence of a polymer matrix show better alignment, fact which could be attributed to the viscosity of the polymer matrix during processing. Therefore, we can conclude that the m-MWCNT hybrids can be aligned under a relatively weak magnetic field even when embedded in a polymer matrix. This alignment is expected to directly affect the anisotropic conductivity of the resulting epoxy composites, as will be shown in the subsequent section (Figure 7 and 8). The bundling of the m-MWCNTs in the polymer matrix, as observed in the inset in Figure 6(e), may be attributed to the anisotropic nature of the dipolar interactions of the iron oxide nanoparticles near the ends of the carbon nanotubes, i.e. the near-linear stacking of the north and south poles of the m-MWCNT in the polymer matrix, resulting in their observed end-to-top connectivity [22,32].

3.5 The anisotropic conductivity of polymer composites

The electric conductivities of the m-MWCNT/epoxy composites were measured at a series of different frequencies, from 0.1 Hz to 1 MHz. Figure 7 shows various conductivities of a series of m-MWCNT/epoxy nanocomposite samples containing various degrees of loading

(weight percent) of m-MWCNT in the polymer matrix. At the same magnetic field (0.3 T), the conductivity increased with increasing m-MWCNT mass fraction in the composite. In the case of 0.1 wt% filler content, the nanocomposite exhibited dielectric behavior because the low fraction of m-MWCNT made it difficult to form interconnected m-MWCNT networks that would have facilitated electron flow. However, for m-MWCNT contents of 0.5 wt% and higher, the samples exhibited increased conductivity as a function of increased fraction of the m-MWCNT moiety. Percolation theory predicts a critical concentration or percolation threshold where the material converts from a capacitor to a conductor [33,34]. In order to determine the percolation threshold of this aligned system, the volume conductivity data could be fitted to a power law in terms of volume fraction of m-MWCNT.

$$\sigma_c \propto (v - v_c)^t \quad (1)$$

Where σ_c is the composite conductivity, v is the m-MWCNT volume fraction in the composite, v_c is the critical volume fraction, and t is the critical exponent. We assumed that the density of m-MWCNT is the same as that of unmodified-MWCNT (2.1 g/cm³), since both mass and volume of m-MWCNT increase similarly. Figure 8 inset shows the plot of σ_c as a function of $v - v_c$ for the parallel measurements. The linear fit to the data generated a straight line with $v_c = 0.2$ vol% (corresponding to 0.4 wt%), which gives a good fit.

When we compared the results of samples in which conductivity was measured in the direction of the m-MWCNT alignment (parallel to the magnetic field) and perpendicular to the m-MWCNT alignment (perpendicular direction to the magnetic field) for the same mass fraction of m-MWCNT, we observed that the conductivity measured parallel to the magnetic field was higher than that measured perpendicular to the magnetic field, indicating a cooperative effect due to the alignment of the magnetic carbon nanotubes in the polymer matrix, as was previously shown in Figure 6(e) and 6(f). Figure 8 shows the variation of the conductivities measured at a frequency of 0.1 Hz as a function of m-MWCNT mass fractions in the epoxy nanocomposite for both the parallel and perpendicular directions with respect to the magnetic field. The measured conductivities are summarized in Table 1.

We would like to note that for a 3.0 wt% m-MWCNT sample, even though the conductivity in the parallel direction was somewhat larger than that in the perpendicular direction (see Figure 7 inset and Figure 8), the values obtained were, nevertheless, quite similar. This is most likely due to the following factors: (a) We assumed that the viscosity of the composite solution containing 3.0 wt% m-MWCNT is higher than for other compositions, as evidenced by the superior alignment of a similar mass concentration of m-MWCNT in the absence of a polymer matrix to that of m-MWCNT/epoxy composites, as discussed in a previous section. The introduction of higher mass loadings of the carbon nanotubes into the polymer solution causes the viscosity of the system to further increase, fact which could then handicap the alignment process. Therefore, we can conclude that when the magnetic field was applied to the 3.0 wt% m-MWCNT sample, the alignment of the decorated carbon nanotubes was not as effective as in the less concentrated samples, and hence, the differences between the conductivities in the parallel and the perpendicular directions were not as pronounced, mainly due to the higher viscosity of the solution. (b) In addition, the conductivity of 3.0 wt % m-MWCNT sample (measured in either direction) was not much higher than the conductivity of the 1.0 wt% m-MWCNT sample (see Figure 8). Tethered iron oxide (maghemite) nanoparticle has high resistivity [35]. Hence, the higher viscosity of the 3.0 wt % m-MWCNT sample may have lead to the formation of iron oxide rich regions, resulting in a decrease of the conductivity.

4. Conclusions

In this study, we developed a novel method to form magnetic carbon nanotubes using a simple modified sol-gel technique as well as achieved m-MWCNT/epoxy composites having magnetic field induced anisotropic electrical conductivities. The modified sol-gel technique for the tethering of maghemite nanoparticles to the surface of acid-activated MWCNTs generated nearly-monodispersed and homogeneously spaced $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, which in turn, imparted magnetic properties to the $\gamma\text{-Fe}_2\text{O}_3$ /MWCNT hybrid materials. Due to the acquired magnetic property of the m-MWCNTs, they could be aligned either alone or embedded in a polymer matrix by the application of only a relatively weak magnetic field. Conductivity measurements performed on m-MWCNT/epoxy composites, showed that the conductivity of the m-MWCNT/epoxy composites increased with increasing m-MWCNT contents with low percolation threshold ($\sim 0.4\text{--}0.5$ wt% m-MWCNT loading). Moreover, the conductivity measured in the direction parallel to the magnetic field was higher than that measured in the direction perpendicular to it. However, the alignment of a nanocomposite sample having a loading of 3.0 wt% m-MWCNT was not as effective as samples with lower nanofiller content because of the higher solution viscosity in the more concentrated samples. This hurdle could, in principle, be overcome by applying a stronger magnetic field. In summary, our facile magnetic functionalization method could be effectively applied for the development of conductive films, composites with conductive polymers, and bio-based composites with aligned features.

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References

1. Lourie O, Cox DM, Wagner HD. Buckling and collapse of embedded carbon nanotubes. *Phys Rev Lett*. 1998; 81(8):1638–1641.
2. Lukic B, Seo JW, Bacsa RR, Delpeux S, Beguin F, Bister G, et al. Catalytically grown carbon nanotubes of small diameter have a high Young's modulus. *Nano Lett*. 2005; 5(10):2074–2077. [PubMed: 16218740]
3. Yu MF, Files BS, Arepalli S, Ruoff R. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Phys Rev Lett*. 2000; 84(24):5552–5555. [PubMed: 10990992]
4. Treacy MMJ, Ebbesen TW, Gibson JM. Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature*. 1996; 381(6584):678–680.
5. Grzelczak M, Correa-Duarte MA, Liz-Marzan LM. Carbon nanotubes encapsulated in wormlike hollow silica shells. *Small*. 2006; 2(10):1174–1177. [PubMed: 17193585]
6. Garmestani H, Al-Haik MS, Dahmen K, Tannenbaum R, Li D, Sablin SS, et al. Polymer-mediated alignment of carbon nanotubes under high magnetic fields. *Adv Mater*. 2003; 15(22):1918–1921.
7. Kimura T, Ago H, Tobita M, Ohshima S, Kyotani M, Yumura M. Polymer composites of carbon nanotubes aligned by a magnetic field. *Adv Mater*. 2002; 14(19):1380–1383.
8. Valentini L, Armentano I, Puglia D, Kenny JM. Dynamics of amine functionalized nanotubes/epoxy composites by dielectric relaxation spectroscopy. *Carbon*. 2005; 43(2):323–329.

9. Tamburri E, Orlanducci S, Terranova ML, Valentini F, Palleschi G, Curulli A, et al. Modulation of electrical properties in single-walled carbon nanotube/conducting polymer composites. *Carbon*. 2005; 43(6):1213–1221.
10. O'Connor I, De S, Coleman JN, Gun'ko YK. Development of transparent, conducting composites by surface infiltration of nanotubes into commercial polymer films. *Carbon*. 2009; 47(8):1983–1988.
11. Ramasubramaniam R, Chen J, Liu HY. Homogeneous carbon nanotube/polymer composites for electrical applications. *Appl Phys Lett*. 2003; 83(14):2928–2930.
12. Martin CA, Sandler JKW, Windle AH, Schwarz MK, Bauhofer W, Schulte K, et al. Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites. *Polymer*. 2005; 46(3):877–886.
13. Nagahara LA, Amlani I, Lewenstein J, Tsui RK. Directed placement of suspended carbon nanotubes for nanometer-scale assembly. *Appl Phys Lett*. 2002; 80(20):3826–3828.
14. Chen XQ, Saito T, Yamada H, Matsushige K. Aligning single-wall carbon nanotubes with an alternating-current electric field. *Appl Phys Lett*. 2001; 78(23):3714–3716.
15. Camponeschi E, Vance R, Al-Haik M, Garmestani H, Tannenbaum R. Properties of carbon nanotube-polymer composites aligned in a magnetic field. *Carbon*. 2007; 45(10):2037–2046.
16. Camponeschi E, Florkowski B, Vance R, Garrett G, Garmestani H, Tannenbaum R. Uniform directional alignment of single-walled carbon nanotubes in viscous polymer flow. *Langmuir*. 2006; 22(4):1858–1862. [PubMed: 16460118]
17. Zhu YF, Ma C, Zhang W, Zhang RP, Koratkar N, Liang J. Alignment of multiwalled carbon nanotubes in bulk epoxy composites via electric field. *J Appl Phys*. 2009; 105(5):054319-1-6.
18. Steinert BW, Dean DR. Magnetic field alignment and electrical properties of solution cast PET-carbon nanotube composite films. *Polymer*. 2009; 50(3):898–904.
19. Korneva G, Ye HH, Gogotsi Y, Halverson D, Friedman G, Bradley JC, et al. Carbon nanotubes loaded with magnetic particles. *Nano Lett*. 2005; 5(5):879–884. [PubMed: 15884887]
20. Kim IT, Nunnery G, Jacob K, Schwartz J, Liu X, Tannenbaum R. Synthesis, characterization and alignment of magnetic carbon nanotubes tethered with maghemite nanoparticles. *J Phys Chem C*. 2010; 114(15):6944–6951.
21. Kuang Q, Li SF, Xie ZX, Lin SC, Zhang XH, Xie SY, et al. Controllable fabrication of SnO₂-coated nanotubes by chemical vapor multiwalled carbon deposition. *Carbon*. 2006; 44(7):1166–1172.
22. Correa-Duarte MA, Grzelczak M, Salgueirino-Maceira V, Giersig M, Liz-Marzan LM, Farle M, et al. Alignment of carbon nanotubes under low magnetic fields through attachment of magnetic nanoparticles. *J Phys Chem B*. 2005; 109(41):19060–19063. [PubMed: 16853457]
23. Jia BP, Gao L, Sun J. Self-assembly of magnetite beads along multiwalled carbon nanotubes via a simple hydrothermal process. *Carbon*. 2007; 45(7):1476–1481.
24. Sun ZY, Liu ZM, Wang Y, Han BX, Du JM, Zhang JL. Fabrication and characterization of magnetic carbon nanotube composites. *J Mater Chem*. 2005; 15(42):4497–4501.
25. Youn SC, Jung DH, Ko YK, Jin YW, Kinri JM, Jung HT. Vertical Alignment of Carbon Nanotubes Using the Magneto-Evaporation Method. *J Am Chem Soc*. 2009; 131(2):742–748. [PubMed: 19072279]
26. Sun SH, Murray CB, Weller D, Folks L, Moser A. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices. *Science*. 2000; 287(5460):1989–1992. [PubMed: 10720318]
27. Yi DK, Lee SS, Ying JY. Synthesis and applications of magnetic nanocomposite catalysts. *Chem Mater*. 2006; 18(10):2459–2461.
28. Pu HT, Jiang FJ. Towards high sedimentation stability: magnetorheological fluids based on CNT/Fe₃O₄ composites. *Nanotechnology*. 2005; 16(9):1486–1489.
29. Walker JD, Tannenbaum R. Characterization of the sol-gel formation of iron(III) oxide/hydroxide nanonetworks from weak base molecules. *Chem Mater*. 2006; 18(20):4793–4810.
30. Sun ZY, Yuan HQ, Liu ZM, Han BX, Zhang XR. A highly efficient chemical sensor material for H₂S: alpha-Fe₂O₃ nanotubes fabricated using carbon nanotube templates. *Adv Mater*. 2005; 17(24):2993–2997.

31. Hyeon T, Lee SS, Park J, Chung Y, Na HB. Synthesis of Highly Crystalline and Monodisperse maghemite Nanocrystallites without a Size-Selection Process. *J Am Chem Soc.* 2001; 123(51): 12798–12801. [PubMed: 11749537]
32. Butter K, Bomans PH, Frederik PM, Vroege GJ, Philipse AP. Direct observation of dipolar chains in ferrofluids in zero field using cryogenic electron microscopy. *J phys: Conds Matter.* 2003; 15(15):S1451–S1470.
33. Weber M, Kamal MR. Estimation of the volume resistivity of electrically conductive composites. *Polym Compos.* 1997; 18(6):711–725.
34. Ounaies Z, Park C, Wise KE, Siochi EJ, Harrison JS. Electrical properties of single wall carbon nanotube reinforced polyimide composites. *Compos Sci Technol.* 2003; 63(11):1637–1646.
35. Mei Y, Zhou ZJ, Luo HL. Electrical resistivity of rf-sputtered iron-oxide thin-films. *J Appl Phys.* 1987; 61(8):4388–4389.

Figure 1. Schematic illustration of the overall strategy for the synthesis of maghemite-MWCNT hybrid materials via a modified sol-gel process.

Figure 2.

The schematic illustration of the alignment of m-MWCNT in an epoxy matrix and the measurement of the resulting electrical properties. (a) The application of a magnetic field to the m-MWCNT/epoxy nanocomposite solution, and (b) The measurement of electrical conductivity of the resulting nanocomposite material.

Figure 3.
The XRD patterns of maghemite/MWCNT hybrid structures formed from an initial $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: MWCNTs mass ratio of 4:1, and calcinated at 500 °C.

Figure 4.
(a) The XPS survey spectrum of maghemite/MWCNT hybrid structures, and (b) The high resolution XPS spectrum of Fe(2p) bands of the maghemite/MWCNT hybrid structures.

Figure 5.

(a) SEM image of maghemite/MWCNT hybrid structures; (b) High resolution TEM image of maghemite. Inset shows diffractions of a single maghemite nanoparticle; (c) Size distribution of the as-prepared iron oxide nanoparticles in the maghemite/MWCNT hybrid structures; (d) The photograph of m-MWCNT hybrid materials in the presence (left image) and in the absence (right image) of a magnet.

Figure 6.

(a) SEM image of aligned m-MWCNT hybrid materials parallel to the direction of magnetic field; (b) SEM image of m-MWCNT hybrid materials that were not subjected to a magnetic field; (c) TEM image of MWCNT/epoxy composites with 0.5 wt% filler loading; (d) TEM image of MWCNT/epoxy composites with 1.0 wt% filler loading; (e) TEM images of m-MWCNT/epoxy composites with 0.5 wt% filler loading. Inset shows the end-to-top connectivity between two m-MWCNTs under an external magnetic field; (f) TEM image of m-MWCNT/epoxy composites with 1 wt% filler loading.

Figure 7.

The conductivity of m-MWCNT/epoxy composites as a function of frequency for different mass fractions of m-MWCNT as measured in the direction parallel to the magnetic field and perpendicular to the magnetic field (inset shows magnified region of a nanocomposite with a 3.0 wt% filler loading).

Figure 8.

The conductivity of m-MWCNT/epoxy composites as a function of different mass fractions of m-MWCNT measured in the direction parallel to the magnetic field and perpendicular to it. Inset: Percolation equation fit to the experimental conductivity data of obtained parallel to the direction of the magnetic field.

Table 1

The conductivities of m-MWCNT/epoxy composites in the directions that were parallel and perpendicular to the externally-applied magnetic field as a function of m-MWCNT mass loading.

m-MWCNT loading (wt%)	Conductivity (S/m)		Conductivity ratio of // and $\perp$
	Parallel (//)	Perpendicular ($\perp$)	
3.0	1.0×10^{-6}	8.5×10^{-7}	1.2
1.0	4.1×10^{-7}	1.0×10^{-7}	4.1
0.5	1.6×10^{-8}	5.3×10^{-9}	3.0
0.1	6.0×10^{-11}		1.0