

PROCESSING OF MULTI-WALLED CARBON NANOTUBES TO ACHIEVE MAGNETIC ADDITIVES FOR POLYMER NANOCOMPOSITES

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INTRODUCTION

Carbon nanotubes (CNTs) and CNT-polymer nanocomposites are rigorously investigated as novel coating and interlayer materials in aerospace and other applications because of their tailorable, multi-functional properties [1]. Carbon nanotubes exhibit high mechanical strength, high currently carrying capacity, high thermal stability, and low weight [2, 3]. Owing to these high mass-specific properties, CNTs and their nanocomposites are sought as lighter alternative materials with additional functions for aerospace and other applications. For example, if CNTs are embedded properly within fiber-reinforced plastics of airplanes, conductive CNT networks can potentially add functions such as shielding against lightening or electromagnetic interferences, and system health monitoring. In addition, mechanical CNT network can potentially improve fracture toughness and prevent delamination.

However, bulk application of CNT-polymer nanocomposites is currently limited due to lack of capability to properly organize CNTs. Organizations of CNTs within polymer matrices, micro-structures, are critical in determining properties of the nanocomposites and thus efficacy of CNT implementation. Due to inter-particle forces (van der Waals, etc.) and their morphology with high aspect ratios, CNTs tend to agglomerate and results in non-homogeneous distributions and imperfect organizations. The properties of such nanocomposites are much smaller than theoretically predicted values [4, 5].

In this study, we plan to provide a capability to more accurately organize multi-walled carbon nanotubes (MWCNTs) within nanocomposite using externally applied magnetic fields, by processing MWCNTs to make them magnetic nano-additives. Application of magnetic fields is a promising scalable method of delivering bulk nanocomposites while structuring micro-structures of nano-additives within uncured polymer matrices [6, 7]. If magnetized, CNTs can be aligned along the external magnetic fields, or in future potentially patterned using oscillating magnetic fields applied in multiple directions.

METHODOLOGY

Approach to fabricate magnetic CNTs in this work consists of three steps, as summarized in Figure 1.

First, MWCNTs were grown in-house by chemical vapor deposition (CVD) process [8].¹ CVD synthesis of MWCNTs was selected in this study, as the focus of this study is mass production of nanocomposites with structural CNTs. Substrates were prepared by depositing an aluminum oxide diffusion barrier (30 nm) and an iron catalyst layer (1 nm) on a silicon wafer. The CNTs are grown on the substrate with argon to provide an inert environment, ethylene as the carbon source gas, and hydrogen as a reduction gas (750°C, atmospheric pressure). After 15 minutes of growth, the MWCNTs were observed to grow vertically aligned, and to have 35 ± 10 nm diameter and ~ 200 μm length (see Figure 2).

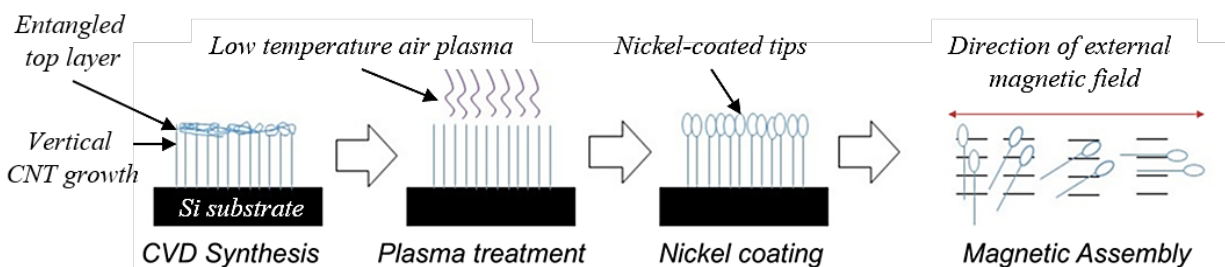


Figure 1. Schematic explaining the production process for magnetic carbon nanotubes.

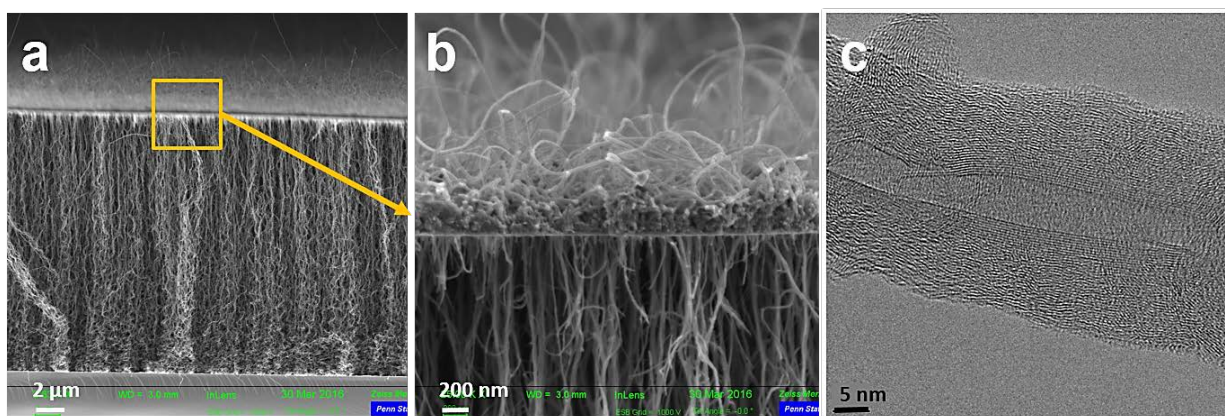


Figure 2. Electron microscopy images of CVD-grown MWCNTs: (a) SEM image of cross-section of vertically aligned CNT bundles, (b) SEM image of directionally-grown individual CNTs, and (c) TEM image of an individual MWCNT.

Second, MWCNTs were functionalized with oxygen plasma using a plasma asher (Harrick PDC-32G Basic Plasma Cleaner), in order to clean the CNT surfaces and to functionalize the surface to enhance suspension of CNTs within matrices. Compared to acid treatment, plasma treatment is a less polluting, less damaging, and scalable functionalization method. In addition, a wide range of functional groups can be provided by modulating the parameters such as power, gases, treatment time, and pressure [9,10]. In this work, oxygen was selected as the treatment gas in order to eliminate amorphous carbon and to attach oxygen-containing groups (hydroxyl, carbonyl, and carboxyl). These surface modifications can decrease CNT agglomeration in a solvent (isopropyl

alcohol, IPA) and potentially enhance bonding with the applied Ni-coatings. Treatment time (2, 4, 6, 8, and 10 mins) and power settings (low 6.8W, medium 10.5W, and high 18W) were varied in order to optimize CNT dispersion. The degree of functionalization and dispersion are being evaluated both qualitatively and quantitatively. The treated CNTs were dispersed within IPA using an ultrasonicator, and images of settlement behaviors were observed and recorded over time. In future, the treated CNTs will be characterized using X-ray Photoelectron Spectroscopy (PHI VersaProbe II Scanning XPS Microprobe) for the functional group peaks around C1s peak.

Third, after functionalization, the CNTs were deposited with a thin ferromagnetic layer of nickel (Ni, ~20-100 nm) using e-beam evaporation (Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System). In future, their anisotropic magnetic properties will be characterized using vibrating sample magnetometer (MicroSense EZ VSM) [11, 12]. The Ni-coated CNTs were dispersed in DI water, and were assembled under the 100 G DC magnetic field in order to demonstrate preliminary magnetic assembly.

RESULTS AND DISCUSSION

First, elimination of amorphous carbon was visually observed. As grown, the CNTs have thin layers on top consisting of entangled CNTs and amorphous carbon (Figure 3a). Plasma treatment eliminated these top layers and exposed the CNT tips, ready for Ni coating (Figure 3b).

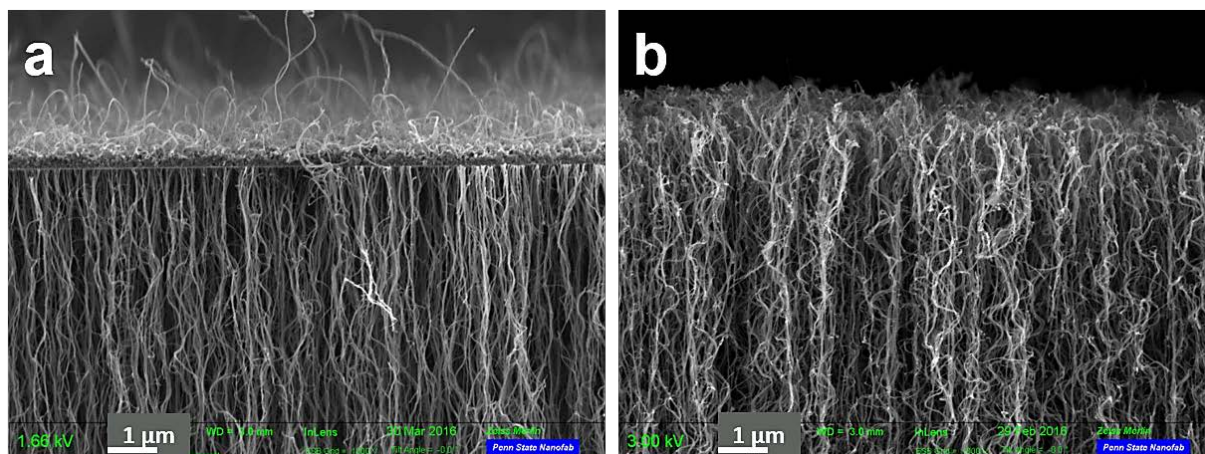


Figure 3. Cross-sectional SEM images of (a) as-grown MWCNTs with top layer of entangled CNTs, and of (b) plasma-treated MWCNTs with exposed CNT tips.

Second, the functionalization condition was optimized as 8 min-low condition for best CNT dispersion within IPA. Settlement behaviors of dispersed CNTs in IPA have been recorded over time; the effects of power setting (see Figure 4) and of treatment time were inspected. In addition, immediately after dispersion, droplets of CNT-IPA solution were deposited and dried on silicon wafers, and these CNTs were inspected under SEM for their dispersion degree (see Figure 5); as-grown, pristine CNTs stayed as bundles after dispersion, while functionalized CNTs showed better dispersion as expected. As shown in Figure 4, best CNT dispersion was observed with the lowest power setting. This can potentially because that more hydroxyl functional groups have been attached to MWCNT surfaces than carbonyl or carboxyl functional groups when the power setting is low, as observed with previous studies with plasma treatment of MWCNTs with oxygen [11]

and oxygen/argon mixture [10]. Another potential factor is that higher power might have damaged CNTs and formed larger carbon compounds. About the effect of treatment time, CNT dispersion was observed to be optimal when proceed for 8 mins. This behavior again can be due to hydroxyl functional group; less hydroxyl functions were observed on MWCNTs as the plasma treatment time increases [11]. Currently, XPS characterization and Raman spectroscopy of these functionalized CNTs are on-going to quantitatively evaluate the types of function group attached and degradation of carbon structures due to plasma treatment.

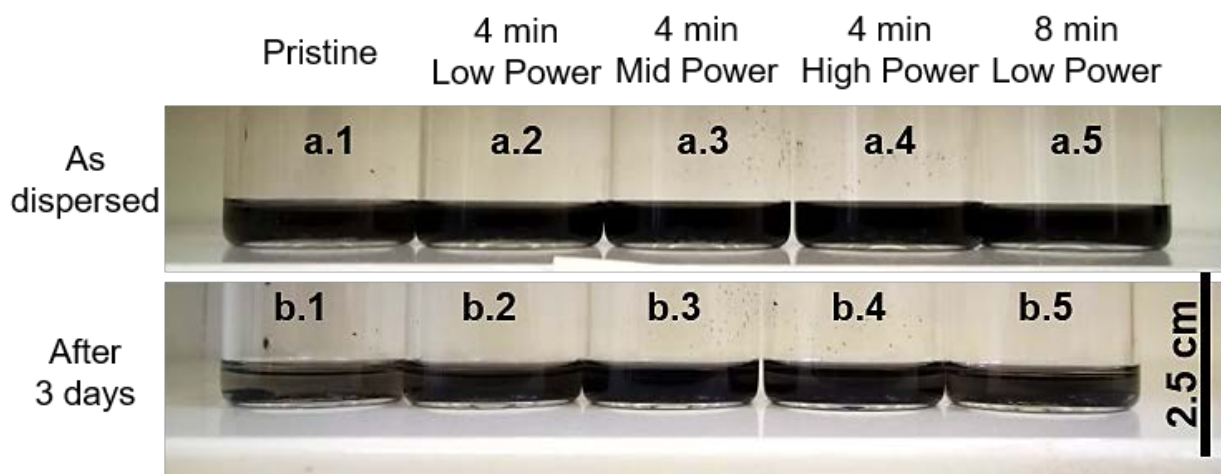


Figure 4. Digital images showing the effect of plasma treatment power setting on CNT dispersion in IPA: as dispersed (top), and after 3 days (bottom). The functionalized conditions of these CNTs are pristine, 4 min low power, 4 min medium power, 4 min high power, and 8 min low power from left to right.

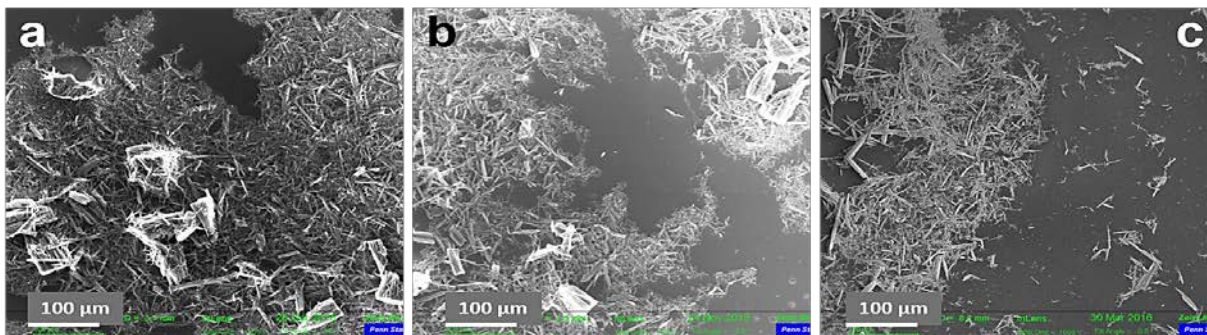


Figure 5. SEM images of dispersion of CNTs in IPA; (a) pristine, (b) with 4 min. low power functionalization, and (c) with 8 min. low power functionalization

Third, preliminary assembly of Ni-coated MWCNTs were experimentally confirmed. As shown in Figure 6, although not conformal, Ni-coating deposition on the CNT tips were observed in SEM images. When applied with the small magnetic fields (~ 100 G), the Ni-coated CNTs showed relative alignment within the time of 5 min (see Figure 7). Further studies are necessary in order to enhance uniform coating and stronger adhesion of the magnetic layers on CNTs, and to study the assembly behaviors of CNTs with high anisotropy in terms of morphology and magnetic orientations.

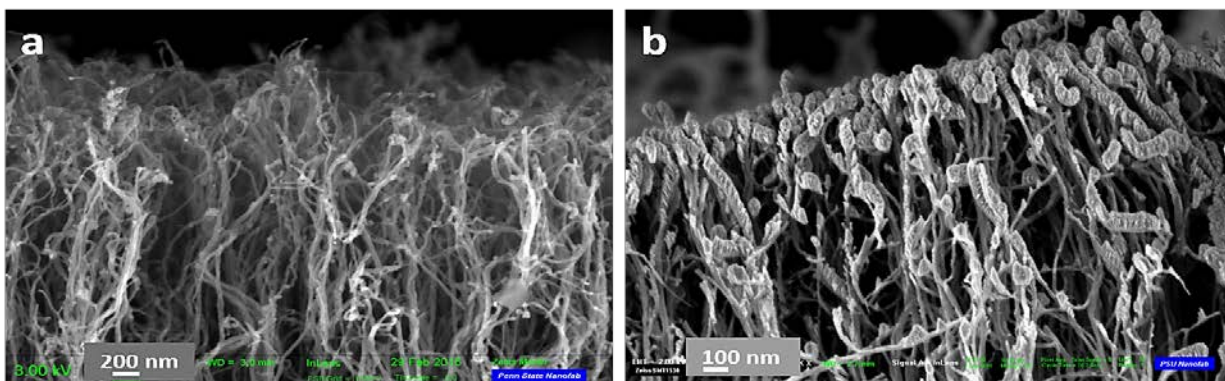


Figure 6. SEM images of CNT tips (a) before coating (b) after 100 nm. Nickel coating using e-beam deposition

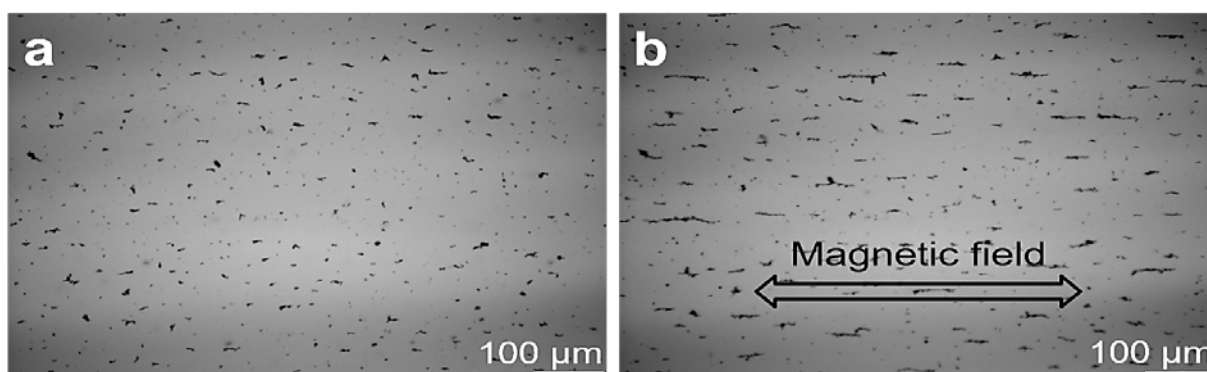


Figure 7. Optical microscope images of dispersed and assembled MWCNTs with 100 nm. Nickel coating (a) before and (b) after application of external unidirectional magnetic field (100 G).

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REFERENCES

1. Ajayan P. M. (1999). "Nanotubes from Carbon", *Chemical Reviews* 1999 99 (7), 1787-1800.
2. Breuer O. and U. Sundararaj (2004), "Big returns from small fibers: a review of polymer/carbon nanotube composites", *Polymer composites* 25(6): 630-645.
3. Coleman, J. N., et al. (2006), "Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites", *Carbon* 44(9): 1624-1652
4. Thostenson, E. T. and T.-W. Chou (2006), "Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites", *Carbon* 44(14): 3022-3029
5. Schadler, L. S., Giannaris, S. C. and Ajayan, P. M. (1998), "Load transfer in carbon nanotube epoxy composites", *Applied Physics Letters*, 73, 3842-384.
6. Erb, R. M., et al. (2012), "Composites Reinforced in Three Dimensions by Using Low Magnetic Fields", *Science* 335(6065): 199-204.

7. Spencer M. P. and Yamamoto N. (2016), "Nanoparticle Alignment using Oscillating Magnetic Fields for Scalable Nanocomposite Manufacturing", 57th AIAA/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, American Institute of Aeronautics and Astronautics.
8. Hart A. J. and Slocum A. H. (2006), "Rapid Growth and Flow-Mediated Nucleation of Millimeter-Scale Aligned Carbon Nanotube Structures from a Thin-Film Catalyst", *The Journal of Physical Chemistry B* 2006 110 (16), 8250-8257.
9. Changlun Chen, Bo Liang, Akihisa Ogino, Xiangke Wang, and Masaaki Nagatsu (2009), 'Oxygen Functionalization of Multiwall Carbon Nanotubes by Microwave-Excited Surface-Wave Plasma Treatment', *The Journal of Physical Chemistry C* 2009 113 (18), 7659-7665.
10. Felten, A., et al. (2005), "Radio-frequency plasma functionalization of carbon nanotubes surface O₂, NH₃, and CF₄ treatments", *Journal of Applied Physics* 98(7): 074308 (2005),
11. Namiko, Y. et al. (2016), "Magnetically anisotropic additive for scalable manufacturing of polymer nanocomposite: iron-coated carbon nanotubes", *Materials Research Express* 3(2): 025004
12. Qunqing Li, Shoushan Fan, Weiqiang Han, Chenhang Sun and Wenjie Liang (1997), "Coating of Carbon Nanotube with Nickel by Electroless Plating Method", *Japanese Journal of Applied Physics* Vol. 36, Part 2, No. 4B,