MAGNETICALLY ANISOTROPIC NANO-PILLARS: MICRO-STRUCTUREING OF NANOCOMPOSITES USING OSCILLATING MAGNETIC FIELDS

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ABSTRACT

Nanoparticles (carbon, ceramic, metal, etc.) implementation is a powerful reinforcement option for composites; organization of these nanoparticles within matrices can be tailored for desired functionalities (mechanical, electrical, thermal, thermoelectrical, etc.). When properly implemented, these nanoparticles will reinforce mechanical strength against fracture and erosion, and serve as conductive networks for defect sensing, lightning/EMI shielding, and deicing. Yet, development and application of these multi-functional nanocomposites in bulk have stagnated, because bulk manufacturing methods for nanocomposites with highly organized micro-structures are missing. In this work, we investigated scalable patterning of carbon nanotube (CNT) pillars using oscillating magnetic fields, in order to achieve bulk 1D-patterned nanocomposites in future. Particle structuring within matrices, before curing, using external fields has balanced benefits of scalability and micro-structure quality. Magnetically anisotropic nano-pillars were fabricated by e-beam coating multi-walled CNTs with ferromagnetic metal, iron (Fe). Multi-walled CNTs are a convenient structural component, for their unique, tailorable dimensions, and for multi-functional properties such as high strength and thermal/electrical transport properties. The Fe coatings on CNTs were evaluated for their dimensions and textures using electron microscopy and atomic force microscopy, and for their chemical states using X-ray photoelectron spectroscopy (XPS). Their anisotropic magnetic properties were characterized using alternating gradient force magnetometry. The preliminary assembly of the Fe-coated CNTs was conducted using permanent magnets; the results indicated that CNT alignment along the magnetic fields. In future, this magnetic method to pattern nano-pillars will be evaluated for its capability and scalability in terms of magnetic field strength, assembly time, and maximum sample size. In addition, nanocomposites will be fabricated and characterized using polymer matrices, and CNT micro-structures and nanocomposite properties will be compared to obtain further knowledge on multi-scale structure-property relationships.

1 INTRODUCTION

Carbon nanotubes that are coated with ferromagnetic metal layers are studied in this work to provide magnetic nano-pillars with high aspect ratio: a structural component that can provide nanocomposites with magnetic anisotropy due to their size scale and periodic micro-structures. Micro-structuring of magnetic materials have been recently investigated to achieve organized magnetic domains and thus unique properties, mainly for data storage applications. Magnetic domains, including anisotropy, can be tailored by controlling magnetocrystalline formation and domain shapes using high pressure, heat, or

mechanical deformation [1, 2]. Specifically, structuring in nano scale can form single magnetic domains, resulting in extremely high coercivity or magnetostrictive responses [3, 4]. Here, the authors fabricate magnetic nano-pillars by coating CNTs with ferromagnetic metals to be used as a novel structural component. These highly anisotropic magnetic nano-pillars are expected to align and assemble to form organized micro-structures using oscillating magnetic fields in a scalable manner [5-8]. Beyond magnetic applications, these magnetic nano-pillars can provide multi-functional nanocomposites. Nanocomposites with organized nano-particles have been investigated as novel materials with improved mechanical, thermal, electrical, and smart properties, but scalable manufacturing of these nanocomposites is currently difficult due to poor dispersion and particle position control, especially with metal matrices [9]. The magnetic metal-coated CNTs, to be presented in this work, can provide a solution to scalable manufacturing of nanocomposites with tailored micro-structures. CNTs are highly sought nano-particles due to their stiffness, strength, and conductivities. These magnetic CNT rods can be organized using magnetic fields in uncured polymer matrices, and then cured to form nanocomposites.

2 MATERIALS AND METHODS

2.1. Preparation of Metal-Coated CNTs

Magnetic nano-pillars were prepared in three steps as illustrated in Figure 1: synthesis of directional multi-walled CNTs on the substrates, controlled laying of the CNTs on a substrate using capillary forces, and then deposition of ferromagnetic metals on the CNTs using electron-beam (e-beam) evaporation. CNTs were synthesized on Silicon (Si) wafer substrates using atmospheric chemical vapor deposition (CVD). Si wafers were deposited with patterned layers of diffusion barrier (aluminum oxidized in the air, ~30 nm thick) and catalyst (iron, ~30 nm thick), using photolithography using image reversal photoresist (AZ 5214 E), e-beam evaporation of metal layers (0.5 A/sec rate, 5×10^{-8} Torr base pressure), and metal lift-off processes. The prepared substrates were die-sawed into 4 mm × 4 mm square pieces, and placed inside a purged tube furnace (2 inch diameter), and supplied with heat (720 ^{o}C), ethylene gas (C_2H_4, carbon source gas, 500 sccm) and argon gas (Ar, carrier gas, 500 sccm) to vertically grow CNTs (> 50 μm long). CNTs were grown only on the pattered areas where catalyst was deposited. The pattern was selected as periodic winglet shapes (see Figure 1, 100 μm long, 5 μm wide, and 25 μm apart), so that grown CNTs will lay horizontally due to capillary forces when solvent vapors were applied [10]. Finally, a ~50-nm-thick iron (Fe) were deposited as ferromagnetic metal on the laid CNT layers. Other methods to deposit thin material layers on CNTs exist, and their resulting coatings are more conformal: atomic layer deposition [11], electro-plate deposition, and electroless deposition [12]. However, these methods are currently limited only with certain material types or involve with wet processes. Thus, e-beam evaporation, a dry directional process, was selected for faster results and proof of concept for this work, although coating might not be conformal. In addition to the CNT samples, baseline samples were prepared and inspected as reference samples. The baseline samples were prepared in the same way as the metal-coated CNT samples but without CNTs: Si wafer samples, without CNTs, deposited with the original catalyst layers (~30nm-thick aluminum oxide and ~30nm-thick Fe) and the ferromagnetic metal layer (~50nm-thick Fe). The fabricated nano-pillars were visually and quantitatively inspected for their coating quality using scanning electron microscopy (SEM), metal layer thickness using atomic force microscopy (AFM), and CNT-metal bonding using X-ray photoelectron spectroscopy (XPS).

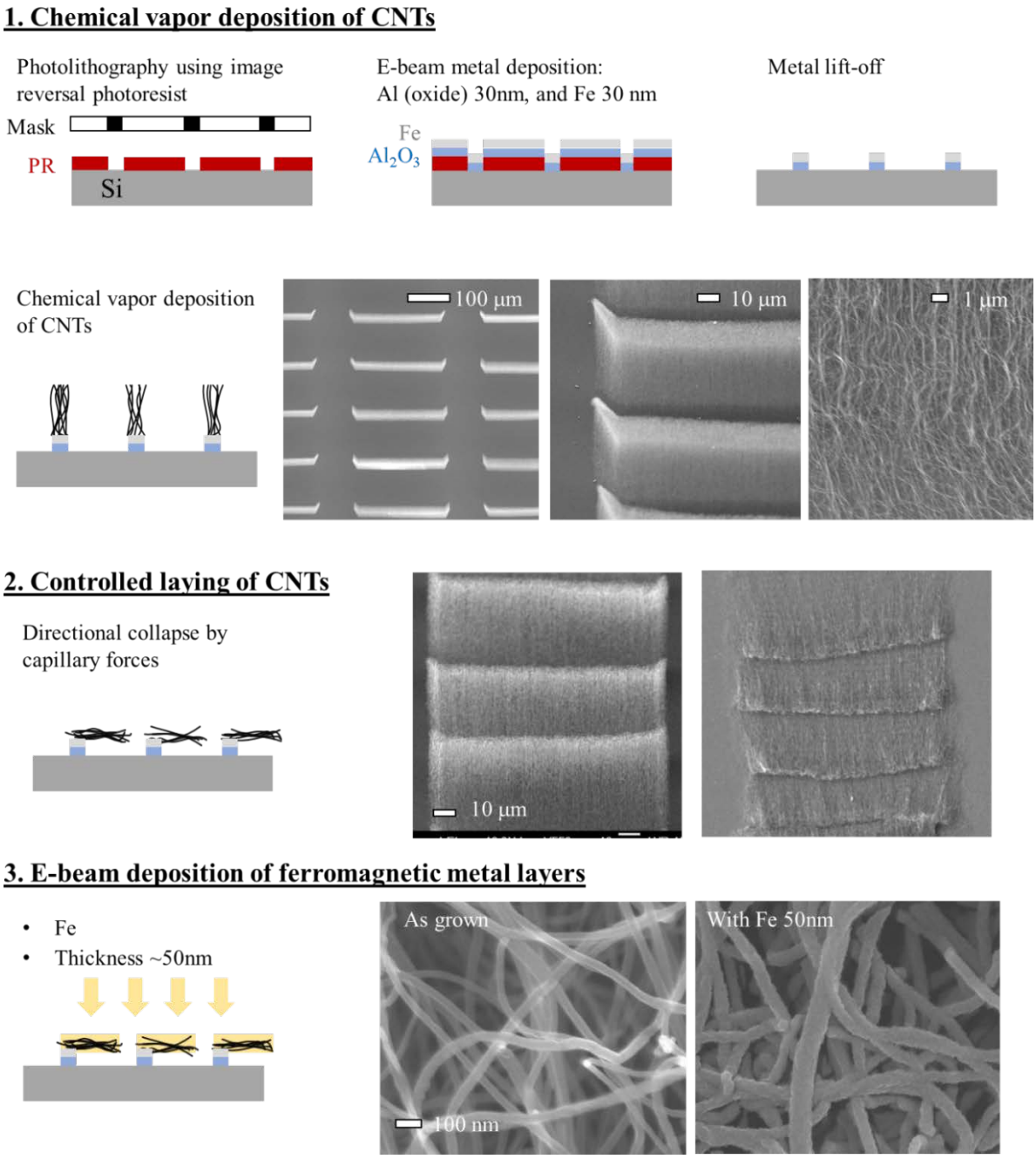

Figure 1. Cross-section schematics and scanning electrode microscopy (SEM) images of samples at each fabrication stage.

As shown in Figure 1 (bottom right), surface metal coating appeared to bond well with CNTs when visually inspected using SEM (JEOL JSM-6700 Field Emission SEM, ~5-10 keV). The Fe layer deposited on CNTs were estimated as ~18.3±5.3 nm (vs. Si surface roughness of ~1.7±1.2 nm) by comparing the CNT diameters measured before and after the Fe deposition using AFM (Veeco Dimension 5000, 3 μm scan length, 256 lines × 256 lines, 4.8 μm/s). This estimated metal layer thickness is smaller than but on the same order as the targeted thickness of metal deposition (~50 nm). The chemical states of the deposited metal were inspected using XPS (Surface Science M-probe, spot size 250 μm × 1000 μm, 0.065 eV step, averaged over 20 scans). Two samples prepared under the same conditions were measured at two spot locations each. The measured data were calibrated to the carbon

1s peak (284.6 eV). All these samples were kept in an oven (~ 75 °C) overnight to eliminate moisture before measurement. The measurement data about the oxygen peaks are summarized in Figure 2. CNT samples showed stronger metal carbonate peaks than metal oxide peaks, while baseline samples showed comparable metal carbonate and metal oxide peaks; this results indicate that metal carbonate was formed at the metal-CNT boundaries.

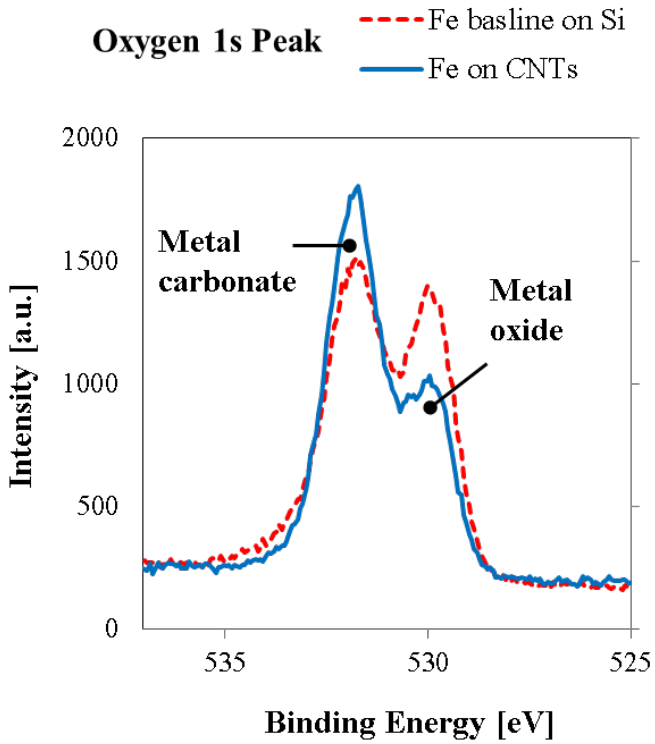

Figure 2. Oxygen 1s peak of baseline (Fe on Si) and CNT (Fe on CNTs) samples measured using XPS.

2.2 Magnetic Property of Metal-Coated CNTs

Metal-coated CNT samples on a Si substrate and baseline samples were characterized (see Figure 3) for their magnetic properties using alternating gradient magnetometer (AGM, Micromag 2900 Series, Lake Shore Cryotronics, Inc.) with high sensitivity (10^{-8} emu). Magnetic measurement with the AGM is ideal for small, weak magnetic samples (thin films, particles, etc.) with which closed magnetic circuits are difficult to be created. The AGM device applies an alternating magnetic field on magnetic samples with a gradient coil system. The magnetic samples respond to the magnetic fields and oscillate, and their oscillations, and thus magnetic moments, will be detected by piezoelectric bimorph sensors. In order to capture the nature of magnetic anisotropy, the angle between the CNT alignment direction on the samples and the applied magnetic field (H) direction was varied from 0, 30, 45, 60, and 90 degrees. All the samples were demagnetized before measurement.

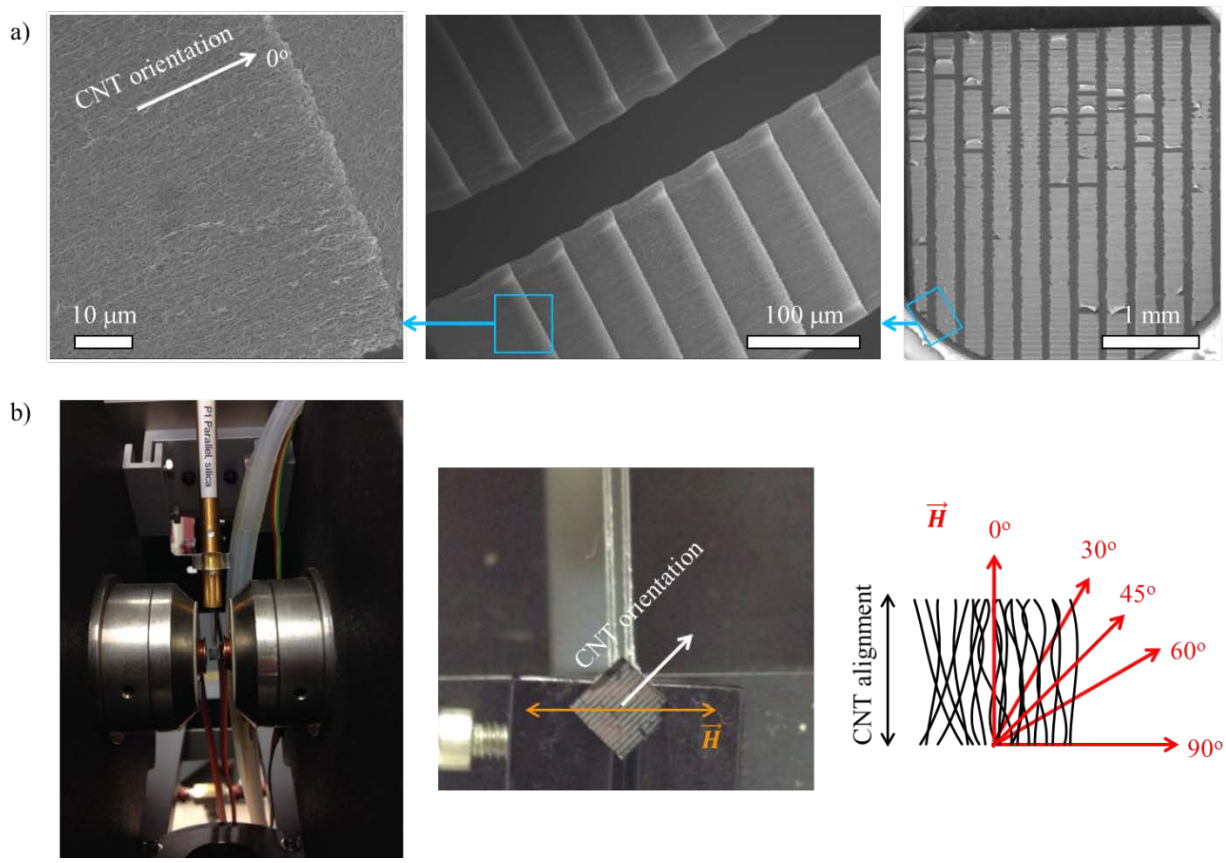

Figure 3. AGM experimental setup to explain sample mounting to vary the angle between the CNT alignment direction and the applied magnetic field: a) SEM images of the CNT samples showing CNT alignment direction, and b) digital images (left) and a schematic (right) showing how the CNT samples are mounted against the applied magnetic field.

3. Results and Discussions

3.1. Magnetic Property of Fe-Coated CNTs

The magnetic hysteresis plot (magnetic field vs. magnetic moment), coercivity, and squareness (Mr/Ms, normalized remanence) from measurements are summarized in Figure 4. The magnetic hysteresis plots (Figure 4a) of both the baseline and CNT samples showed ferromagnetic behavior. When compared, the CNT samples show more hysteresis (higher coercivity and remanence) and lower saturation than the baseline samples; these differences can be attributed to the Fe-layer textures and discontinuities introduced due to non-flat CNT surfaces. In addition, the initial demagnetization portion of magnetic hysteresis consists of two overlapping slopes, indicating that the Fe layers on CNTs consist of two magnetic phases.

In Figure 4b and 4c, squareness and coercivity of the CNT samples are plotted as a function of the CNT alignment angle against the applied magnetic field (*H*), and also compared with those of the baseline samples and the literature value; both plots clearly indicated the magnetic anisotropy of the CNT samples [13]. When CNTs are aligned against H, the squarereness of the CNT samples were measured to be ~0.4, higher than the baseline and literature values of bulk Fe. As the angle increases, the remanence decreases and reached the baseline value when the CNT alignment is perpendicular to H. The coercivities measured about the CNT samples (see Figure 4c) also shows the decreasing trend (from ~100 Oe down to ~50 Oe) with the increasing angle difference, but the coercivity value of the CNT

samples whose CNT direction is perpendicular to *H* is still larger than the baseline sample value (~11 Oe), indicating potential existing of magnetic domains aligned perpendicular to the CNT alignment angle. The coercivities measured in this work are also compared with those of Fe in various forms from the literature: bulk Fe (~0.15-5 Oe), textured thin film (400-nm-wide Fe stripe in the <110> direction on the Si (111) plane, -2 to 8 Oe [13]), and randomly oriented CNTs coated with iron oxide nanoparticles (6-10 nm diameter) (no remanence or coercivity observed at room temperature [14]). The Fe-coated CNT samples fabricated in this work have larger coercivities, indicating potential contributions for data storage applications.

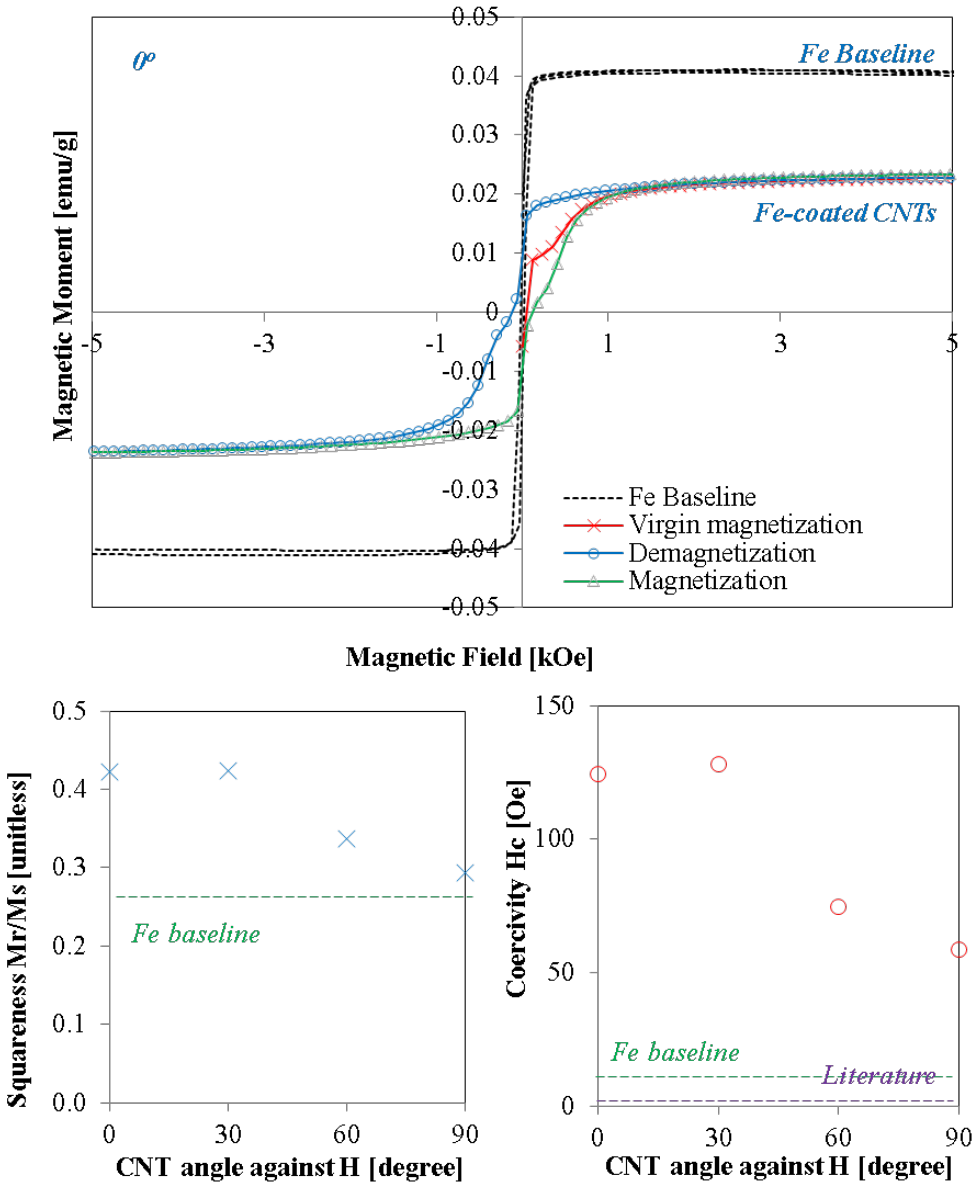

Figure 4. Measured magnetic properties of Fe-coated CNT and baseline samples: a) magnetic hysteresis where CNTs are aligned along the magnetic field, and b) squareness/remanence and c) coercivity as a function of the CNT alignment angle against the applied magnetic field.

3.2. Magnetic Assembly of Fe-Coated CNTs

Fe-coated CNTs were dispersed in isopropyl alcohol (IPA) and applied with small magnetic field (~10mT) using permanent magnets (see Figure 5). Visual inspection of this very preliminary trial showed indication of potential alignment of the fabricated magnetic nano-pillars, although further quantitative and control experiments are necessary to confirm the above.

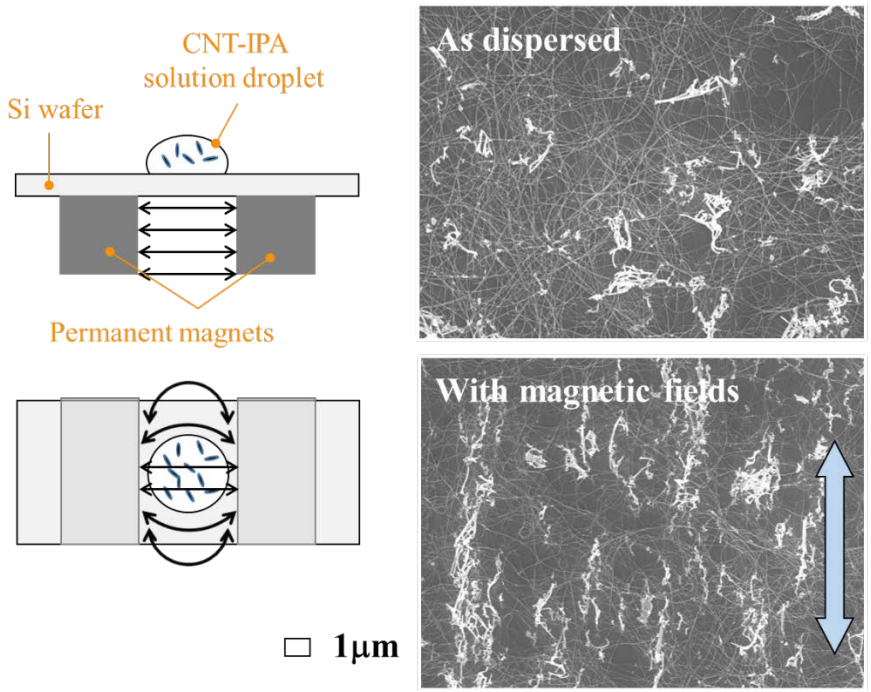

Figure 5. Preliminary trial to magnetically assemble CNT nano-pillars: (left) schematic of magnetic field application, and (right) SEM images of CNTs before and after the magnetic field application.

4. Conclusions

Magnetic nano-pillars were prepared by (partially) coating aligned CNTs with iron, and magnetic domain texturing and anisotropy were confirmed through measurement of CNT samples as a function of alignment angle (between CNTs and *H*). When compared with bulk and textured thin layers of Fe in the literature, the Fe-coated CNT samples in this work showed much higher coercivity (~50-100 Oe), due to their aligned micro-texturing from the CNT substrate template and also due to very small film thickness (~18 nm). These magnetic nano-pillars can be potentially used for magnetic data recording (high coercivity), and also for magnetostrictive sensors (high aspect ratio). Immediate next steps is further evaluation of magnetic assembly behavior within polymer matrices for its capability and scalability in terms of magnetic field strength, assembly time, and maximum sample size. With fabricated nanocomposites, CNT micro-structures and nanocomposite properties will be compared to obtain further knowledge on multi-scale structure-property relationships.

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REFERENCES

1. Advanced Magnetic Nanostructures. New York, NY: Springer; 2006.
2. Martín JI, Nogués J, Liu K, Vicent JL, Schuller IK. Ordered magnetic nanostructures: fabrication and properties. Journal of Magnetism and Magnetic Materials. 2003;256(1–3):449-501.
3. Park JJ, Reddy M, Mudivarthi C, Downey PR, Stadler BJH, Flatau AB. Characterization of the magnetic properties of multilayer magnetostrictive iron-gallium nanowires. Journal of Applied Physics. 2010;107(9):09A954.
4. McGary PD, Tan L, Zou J, Stadler BJH, Downey PR, Flatau AB. Magnetic nanowires for acoustic sensors (invited). Journal of Applied Physics. 2006;99(8):08B310.
5. Erb RM, Libanori R, Rothfuchs N, Studart AR. Composites Reinforced in Three Dimensions by Using Low Magnetic Fields. Science. 2012;335(6065):199-204.
6. Erb RM, Segmehl J, Charilaou M, Loffler JF, Studart AR. Non-linear alignment dynamics in suspensions of platelets under rotating magnetic fields. Soft Matter. 2012;8(29):7604-9.
7. Wirtz D, Fermigier M. One-dimensional patterns and wavelength selection in magnetic fluids. Physical Review Letters. 1994;72(14):2294-7.
8. Zhang YD, Budnick JI. Dynamic alignment of magnetic materials. Applied Physics Letters. 1997;70(9):1083-5.
9. Bakshi SR, Lahiri D, Agarwal A. Carbon nanotube reinforced metal matrix composites - a review. International Materials Reviews. 2010;55(1):41-64.
10. De Volder M, Tawfick SH, Park SJ, Copic D, Zhao Z, Lu W, Hart AJ. Diverse 3D Microarchitectures Made by Capillary Forming of Carbon Nanotubes. Advanced Materials. 2010;22(39):4384-9.
11. Andrew SC, Christopher AW, Alan WW, Steven MG. Atomic layer deposition on gram quantities of multi-walled carbon nanotubes. Nanotechnology. 2009;20(25):255602.
12. Chen X, Xia J, Peng J, Li W, Xie S. Carbon-nanotube metal-matrix composites prepared by electroless plating. Composites Science and Technology. 2000;60(2):301-6.
13. dos Santos MC, Geshev J, Schmidt JE, Teixeira SR, Pereira LG. Origin of the magnetization reversal of an Fe thin film on Si(111). Physical Review B. 2000;61(2):1311-4.
14. Correa-Duarte MA, Grzelczak M, Salgueiriño-Maceira V, Giersig M, Liz-Marzán LM, Farle M, Sierazdki K, Diaz R. Alignment of Carbon Nanotubes under Low Magnetic Fields through Attachment of Magnetic Nanoparticles. The Journal of Physical Chemistry B. 2005;109(41):19060-3.