Alignment of Carbon Nanotubes under Low Magnetic Fields through Attachment of Magnetic Nanoparticles

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Received: August 10, 2005; In Final Form: September 3, 2005

The alignment of multiwalled carbon nanotubes (MWNTs) has been accomplished through deposition of uniform layers of magnetite/maghemite nanoparticles (diameter = 6−10 nm) and use of an external magnetic field. The coating of CNTs with magnetic nanoparticles was performed by combining the polymer wrapping and layer-by-layer (LbL) assembly techniques. The particle-coated MWNTs are superparamagnetic and can be aligned at room temperature on any substrate by deposition from an aqueous solution in an external field B = 0.2 T. The volume magnetization of the particle coated MWNTs is found to be enhanced by 17% compared to the pure particles in a powder indicating that either the adsorption process onto the CNTs changes the particle magnetization, or the MWNTs carry an intrinsic magnetization due to remaining Ni used as a catalyst for the growth process.

Carbon nanotube (CNT)-based materials have been the focus of intense research since their discovery[1] because of their unique structure-dependent electrical, mechanical, and optical properties.[2−4] Many of the potential applications of CNTs are based on their electronic properties,[5] which can be tuned through control of their diameter and helicity or through the introduction of defects.[6] The application of these materials in such different fields as composites and biotechnology[7] has been shown to be strongly dependent on the development of strategies for functionalizing, processing, and/or assembling carbon nanotubes. Recently, several methods have been reported for the attachment of nanoparticles of various nature onto CNTs,[8−12] and special attention has been directed to synthesizing and assembling CNT-based magnetic composites, by filling the CNTs with magnetic wires[13] and nanoparticles[14] or by coating them with a magnetic shell.[15] As an example, Gao et al.[16] reported the incorporation of CNTs on a magnetic matrix increasing the electrical conductivity of the composite. However, a better adhesion and distribution of CNTs in the matrix remains to be achieved.

The layer-by-layer (LbL) assembly technique has been widely used for the deposition of nanoparticles onto both macroscopic substrates and spherical colloids.[17] However, the assembly on more complicated geometries has been very limited, and only recently, mono- and multilayers of metallic nanoparticles onto carbon nanotubes have been accomplished by combining LbL and the so-called polymer wrapping technique.[12] The polymer wrapping technique[18] comprises the functionalization of the CNTs through noncovalent attachment of macromolecules producing individual and well-redispersed CNTs in aqueous solution. This stabilization is based on the thermodynamic preference of CNT−polymer interactions with respect to CNT−water interactions, suppressing the hydrophobic surface of the CNTs.

Another important limitation for some potential applications of CNTs comes from the fact that randomly oriented nanotubes embedded in bulk samples have exhibited substantially lower electrical and thermal conductivities than expected.[19,20] To overcome this limitation, assemblies of aligned nanotubes have been proposed to reach the individual properties of CNTs in a bulk material.[21−32] An alternative method for CNT alignment has been proposed, based on their anisotropic magnetic susceptibilities,[33] by using a high external magnetic field. With this method, CNTs both in dispersion and embedded in polymeric matrixes have been aligned.[34,35]

Herein, we report a simple procedure for the alignment of CNTs under relatively low magnetic fields, based on the assembly of magnetite/maghemite nanoparticles onto the surface of the CNTs. The assembly of a compact layer of magnetic nanoparticles onto CNTs was carried out by following the procedure reported in our previous work.[12] The method combines the polymer wrapping and LbL self-assembly techniques

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SCHEME 1. (a) Schematic Illustration of the Experimental Process for the Deposition of Magnetite Nanoparticles Based on Polymer Wrapping (1) and LbL Assembly (2, 3). (b) Schematic Illustration of the Alignment of Fe_3O_4/γ-Fe_2O_3-Coated CNTs Under an External Magnetic Field.
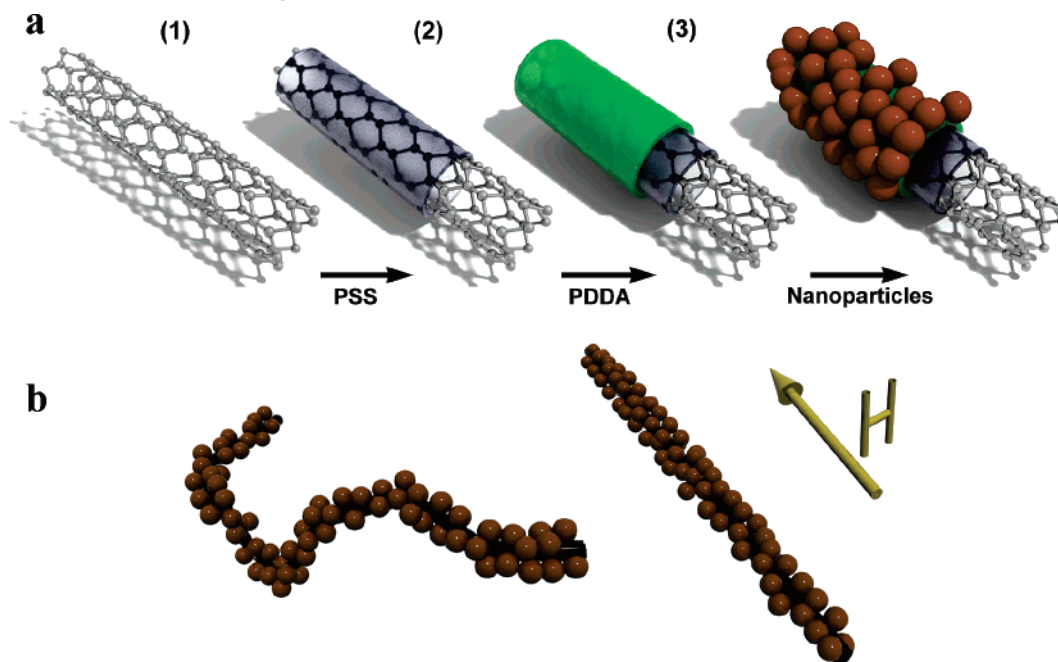
allowing the noncovalent attachment of nanoparticles onto the carbon nanotubes and thus leaving intact their structure and electronic properties (Scheme 1a). Scheme 1b outlines the alignment of the nanotubes in the presence of an external magnetic field, upon assembly of magnetic nanoparticles onto the CNT surface.

Poly(sodium 4-styrene sulfonate) (PSS) was used as a wrapping polymer providing remarkably stable aqueous dispersions of multiwalled carbon nanotubes (MWNTs). Because of the high density of sulfonate groups on the negatively charged polyelectrolyte PSS, it acts as a primer onto the CNTs surface for the subsequent, homogeneous adsorption through electrostatic interactions of the cationic polyelectrolyte poly(dimethyldiallylammonium chloride) (PDDA), which in turn provides a homogeneous distribution of positive charges. These positive charges ensure the efficient adsorption of negatively charged magnetic nanoparticles onto the surface of CNTs by means of electrostatic interactions. Although the adsorption of nanoparticles (diameter $D = 6-10$ nm) onto CNTs is often problematic because of the extremely high curvature ($D_{MWNT} = 15-30$ nm), which hinders the formation of dense coatings, the LbL self-assembly technique overcomes these difficulties, since the interactions responsible for the assembly are mainly electrostatic.[36]

The magnetic nanoparticles prepared in aqueous solution (basic pH) are negatively charged and therefore are electrostatically attracted to the positively charged PDDA layer adsorbed onto the CNTs. The pH for the most efficient adsorption of the Fe_3O_4/γ-Fe_2O_3 nanoparticles on polyelectrolyte was found to be $11.9-12.0$, while at higher pH values, no adsorption was observed. A uniform coating of magnetic particles onto the CNTs was achieved, as shown in the transmission electron microscopy (TEM) images of Figure 1a,b. Long (>5 μm) CNTs are completely covered with a dense layer of magnetic nanoparticles, and no free nanoparticles were found in the whole grid. On the other hand, aqueous dispersions of magnetite/maghemite-coated CNTs were found to be very stable for several days or even weeks in the case of dilute solutions (Figure 1c) when (after centrifugation/washing) tetramethylammonium hydroxide (TMAOH) was added to the solution. Since the early work by Massart,[37] TMAOH has been a popular stabilizer for the preparation of aqueous ferrofluids, mainly comprising iron oxide nanoparticles. The stabilization of the magnetic CNTs in water takes place through the formation of a double layer, with negative hydroxide ions fixed on the surface of the nanoparticles and positive tetramethylammonium as counterions in the basic environment. The magnetic response of these magnetic CNTs was easily and quickly visualized by holding the sample close
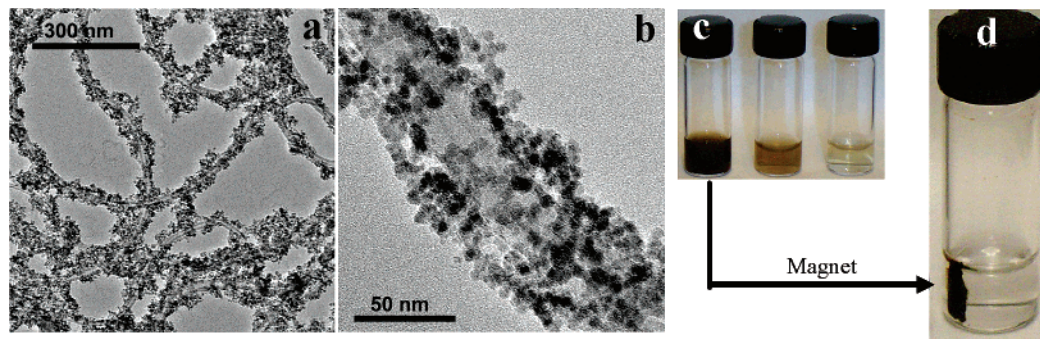

Figure 1. TEM images at lower (a) and higher (b) magnifications of iron oxide-coated CNTs and photographs of dispersions in aqueous solution with different concentrations (c) and manipulated by an external magnetic field (d).
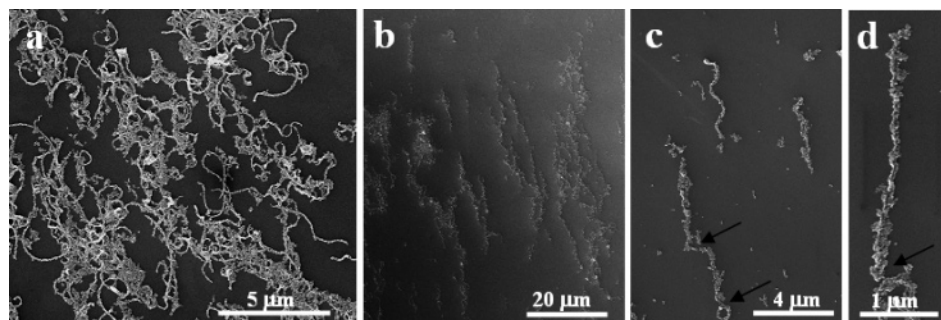
Figure 2. SEM images of Fe$_3$O$_4$-coated CNTs in the absence (a) and presence (b,c,d) of an external magnetic field.
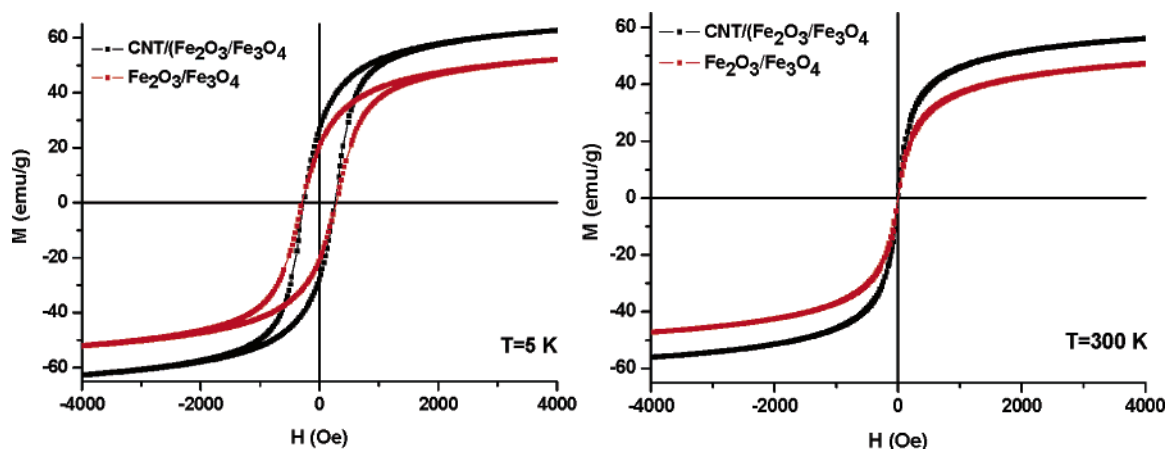

Figure 3. Magnetic hysteresis cycles for Fe$_3$O$_4$/γ-Fe$_2$O$_3$-coated CNTs (black lines) and Fe$_3$O$_4$/γ-Fe$_2$O$_3$ nanoparticles (red lines), showing M−H data at 5 K (a) and 300 K (b).

to a small magnet as shown in Figure 1d, since all CNTs were driven toward the magnetic source.

When a drop of the dispersion was dried on a Si wafer without an external field, the magnetic CNTs were found randomly oriented on the silicon substrate (Figure 2a), as previously reported for the deposition of CNTs on a polyelectrolyte-functionalized substrate.[38] However, the magnetic CNTs can be oriented in the plane of a silicon wafer by using an external magnetic field (which was applied parallel to the substrate). The magnetite/maghemite-coated CNTs were aligned as long-chain structures by means of magnetophoretic deposition on a silicon substrate at 300 K,[39] since magnetic CNTs suspended in a liquid align parallel to the direction of the applied magnetic field. Figure 2b−d shows the typical behavior of a suspension of magnetic CNTs deposited onto a substrate under a magnetic field of 0.2 T.

In zero field, the magnetic moments of the iron oxide nanoparticles randomly point in different directions, resulting in a vanishing net magnetization. However, if a sufficiently large homogeneous magnetic field is applied, the magnetic moments of the nanoparticles align in parallel, and the resulting dipolar interactions are sufficiently large to overcome thermal motion and to reorient the magnetic CNTs favoring the formation of chains of aligned carbon nanotubes. These chainlike structures are formed by connecting the magnetic CNTs in line, touching each other in a head-to-tail fashion, i.e., north to south pole (at positions indicated by arrows in Figure 2c,d).

This behavior has been reported for different magnetic nanoparticle systems and takes place because of the anisotropic nature of the dipolar interaction; since the north and south poles of the dipolar nanomagnets attract each other, while particles coming close to each other side by side with the magnetization direction parallel will repel each other, thus favoring the formation of nanoparticle chains.[40] Therefore, at first glance,

one could find it astonishing that some magnetic CNTs were found connected in chains which are parallel (Figure 2b). This can be explained by either capillary and van der Waals forces or the fact that long magnetic chains whose end points are not next to each other will also attract each other, forming double or triple chains which are parallel and close to each other but are offset to each other along the long axis.

Magnetic properties of magnetite/maghemite nanoparticles and magnetic CNTs were recorded in a Quantum Design vibrating sample magnetometer (VSM). Figure 3 shows hysteresis curves collected at 5 K (Figure 3a) and 300 K (Figure 3b). Both iron oxide nanoparticles and magnetic CNTs show the same superparamagnetic behavior, i.e., the same coercive field (H_c = 280 Oe at 5 K) and no remanence or coercitivity at room temperature. At first sight, magnetic CNTs seem to have a larger magnetic moment per gram of sample (see Supporting Information for details). The saturation magnetization of the original Fe$_3$O$_4$/γ-Fe$_2$O$_3$ nanoparticles, whose relative concentration cannot be quantified because of the similarity of γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ X-ray diffraction spectra (see XRD data in Supporting Information), presents a lower value than the bulk magnetization of γ-Fe$_2$O$_3$ (60−80 Am^2/kg), which was reported to be dependent on the particle size and on the different degree of vacancy ordering of the particles, which is directly related to the sample preparation method.[41] Nevertheless, when assembled onto the surface of MWCNTs, the saturation magnetization is increased by 17% compared to the initial particle powder and agrees rather well with the bulk magnetization of γ-Fe$_2$O$_3$. This 17% increase may vary and could be even higher because of the different amount of magnetic material per gram of sample, since in the case of iron oxide-coated CNTs, the organic polyelectrolytes and CNTs should also be taken into account. The origin of this magnetization increase is not clear and needs further investigation. Furthermore, the presence of nickel traces

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from the catalytic Ni surfaces used to grow the CNTs should also be taken into account. The error bar of the sample weight (less than 0.1 mg) could represent a maximum deviation of 1% on the magnetization, far away from the obtained 17%.

In summary, we have achieved the effective magnetic functionalization of CNTs by coating with iron oxide nanoparticles using the polymer wrapping and LbL assembly techniques. Upon such functionalization, the alignment of CNT chains in relatively small external magnetic fields was demonstrated. The resulting magnetic CNT structures are excellent candidates to be used as building blocks for the fabrication of novel composite materials with a preferential orientation of the magnetic CNTs.

Supporting Information Available: Synthetic procedures for Fe_3O_4/γ-Fe_2O_3 nanoparticles and Fe_3O_4/γ-Fe_2O_3-coated CNT; XRD spectra of Fe_3O_4/γ-Fe_2O_3 nanoparticles; saturation magnetization measurements (calculation details). This material is available free of charge via the Internet at http://pubs.acs.org.

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