Fe_3O_4-modified Carbon Nanotubes: A Facile and Efficient Method to Orientate Alignment in Magnetic Field

Yan Shan and Lian Gao*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050 P. R. China

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The orientation of carbon nanotubes (both SWNTs and MWNTs) has been demonstrated in magnetic field through modification with magnetic particles Fe_3O_4. The process of Fe_3O_4-modified CNTs composites is that acid-treated CNTs were refluxed in 2-pyrrolidone containing ferric triacetylacetonate at the solution's boiling point with the protection of nitrogen gas. The composites are ideal materials to help the CNTs to be aligned in magnetic field.

Carbon nanotubes (CNTs) are ideal building blocks for the bottom-up assembly of integrated nanodevices because of their unique one-dimensional nanostructure and remarkable electronic properties.[1] Many electronic devices using CNTs such as light-emitting diodes, field-effect transistors, and sensors show good prospects.[2,3] Field-effect transistors with individual p-type semiconducting SWNTs show a higher field-effect mobility and transconductance per unit channel width than comparable devices composed of silicon.[4] However, the problem of how to assemble and integrate SWNTs into nanodevices on a large scale with precise control of the density, position, and orientation is a big challenge to the mass production of these devices.

Some CNT devices have been fabricated using chemical vapor deposition in which the catalytic material is deposited at prepatterned sites prior to growth,[5] but control is difficult and the temperatures required place limits on the substrates that can be used. Another method is to use an atomic force microscope tip to position individual CNTs from a random assembly into the desired location of the electrodes.[6] This latter method is effective but is too expensive and lengthy for mass production. A solution-based method is a simple, low cost, and promising way to assembly of CNTs into integrated devices over a large area, and much effort has been made to improve it, but in spite of this, an easier and more efficient method is still needed.

This work shows that it is possible to orientate CNTs from solution using a permanent magnet if the CNTs are modified with Fe_3O_4 nanocrystals. The method was suggested by Li[7] using the following process. First, the MWNTs were treated by concentrated nitric acid at 140 °C for 6 h, rinsed with distilled water, and dried at 100 °C for 12 h. Second, 50 mg of MWNTs was dispersed in 40 mL of 2-pyrrolidone containing 1 mmol of ferric triacetylacetonate ($Fe(acac)_3$). Third, the solution was purged with nitrogen to remove oxygen and heated to 245 °C. After refluxing for 30 min, the sample was cooled to room temperature. The resultant black precipitate was washed with acetone several times and then dried for characterization.

Figure 1 shows the XRD pattern of the product. The diffraction peaks show that the sample is a mixture of magnetite Fe_3O_4 and MWNTs. The peak at $2\theta = 26°$ corresponds to the (002) reflection of the MWNTs, and all the other peaks are due to

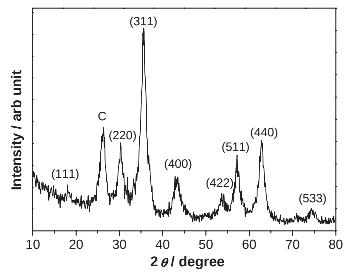

Figure 1. XRD pattern of MWNT/Fe_3O_4 composites.

magnetite Fe_3O_4, (JCPDS card 79-0419). The broad Fe_3O_4 peaks indicate that the nanoparticles are small, with an average size of about 8 nm calculated by the Scherrer equation.

Figures 2a and 2b are TEM images of the product with different magnifications. They clearly show that nearly all the MWNTs are homogeneously coated with a layer of nanoparticles, and no free nanoparticles are found. It is estimated that the ratio of the Fe_3O_4-coated MWNTs is about 95%. The EDS analysis of the coating layer reveals Fe, O, C, and Cu (from the support grid) signals, as shown in the inset of Figure 2b. The corresponding selected area electron diffraction patterns (Figure 2c) taken from the nanoparticles on the wall of MWNTs exhibit six rings corresponding to the (111), (220), (311), (400), (511), and (440) planes of Fe_3O_4. Combining the results of EDS, SAED and XRD, we can confirm that the nanoparticles on the surface of the MWNTs are Fe_3O_4. It can also be seen from the TEM images that the average size of the Fe_3O_4 is about 9 nm, which is nearly consistent with the XRD results calculated from the Scherrer equation.

The magnetic properties of the MWNTs, MWNT/Fe_3O_4 composites, and Fe_3O_4 were investigated with a vibration sample magnetometer (EG&G VSM Model 155). Figure 3a shows the room-temperature magnetization of MWNTs, Fe_3O_4-modified MWNTs and Fe_3O_4 prepared by the same method. The MWNTs show no magnetic property, while Fe_3O_4/MWNT composites exhibit the same superparamagetic characteristics as Fe_3O_4, whose saturation magnetization is 20 emu/g. The pure

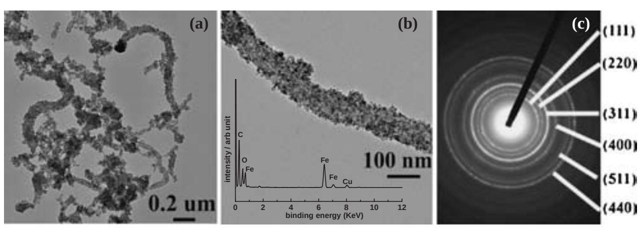

Figure 2. TEM images (a), (b), and SEAD pattern (c) of MWNTs/Fe_3O_4 composites showing a large quantity of Fe_3O_4-coated MWNTs, inset of (b) is the EDS spectrum of the Fe_3O_4-coating layer.

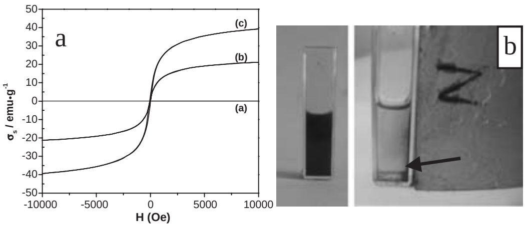

Figure 3. a: Room-temperature magnetization curves of (a) MWNTs, (b) Fe_3O_4/MWNTs composites, and (c) pure Fe_3O_4; b: the response of Fe_3O_4-coated MWNTs in an alcohol solution to a magnet.

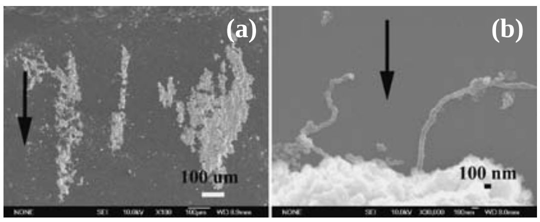

Figure 4. SEM images at (a) low and (b) high magnifications of MWNT/Fe_3O_4 on a glass slide in a magnetic field after their dispersion solvent evaporated. The arrows in both pictures indicate the direction of applied magnetic field.

Fe_3O_4 particles exhibit a magnetic coercivity of 45 Oe, and their saturation magnetization is 39.26 emu/g. The lower saturation magnetization of the MWNT/Fe_3O_4 composites may be due to the different size of Fe_3O_4 in the two samples.[7] It has been reported that the nanocrystals growing on the MWNTs often have smaller size than those synthesized without MWNTs.[8] The average size of the pure Fe_3O_4 is 15 nm (not shown), while in the MWNT/Fe_3O_4 it is 9 nm, so the two samples show different magnetic properties. The digital images in Figure 3b show changes of a Fe_3O_4-coated MWNT alcohol solution before and after in a magnetic field. They clearly show that the solution becomes clear and clear, and the Fe_3O_4-coated MWNTs are attracted to the side near the magnet as the arrow shown in Figure 3b.

To further probe the alignment process, a drop of MWNT/Fe_3O_4 alcohol dispersion was allowed to evaporate on a glass slide in the presence of a permanent magnet. The nanotubes were aligned in the field and became immobilized as the solvent evaporated (Figure 4). It is found that the MWNT/Fe_3O_4 composites align parallel to the magnetization direction on a large scale. Figure 4b is a higher magnification image, which clearly shows the individual MWNTs aligned in the field. Inevitably, not every MWNT aligns parallel to the direction of the applied magnetic field, because on the one hand, the MWNTs we used are warped and not straight, on the other hand, the magnetic field is not large and homogeneous enough, the closer the MWNTs are to the magnet, the better the alignment.

We prepared Fe_3O_4-modified SWNT composites using the same procedure as for MWNTs. Figures 5a and 5b show TEM images of Fe_3O_4-modified SWNTs with different molar ratios. It is surprising to find that the Fe_3O_4 nanoparticles are attached to the tips of the SWNTs, which is a perfect structure for SWNTs to be used in nanodevices. It has been reported that the physical properties of CNTs can be dramatically influenced by surface modification with selected organic, inorganic, and biological species.[9] Here, the Fe_3O_4 is located at the tips of the tubes acts only as a directional guide, and does not destroy the intrinsic properties of the tubes. The Fe_3O_4-modified SWNTs have the same changes in response to the magnet as MWNTs (Figure 3b), but because of the smaller number of attached Fe_3O_4 particles, it took more time for them to move towards the magnet. Figure 5c gives the SWNTs aligned in magnetic field after the dispersion solvent evaporated.

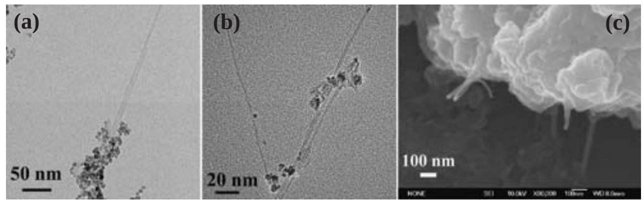

Figure 5. (a), (b) TEM images of Fe_3O_4-modified SWNTs with different molar ratio: (a) Fe:C = 50:1, (b) Fe:C = 20:1, and (c) SEM image of SWNTs (Figure 5a) aligned on the glass slide in magnetic field.

These Fe_3O_4-modified SWNTs can be easily integrated into nanodevices in a magnetic field. First, they have magnetic properties, which show a good response in a magnetic field. Second, the intrinsic properties of the tubes are not destroyed, and the Fe_3O_4 only acts as a directional guide, which could be easily removed by acid after assembly into nanodevices. Third, because the intrinsic properties of the nanotubes are not destroyed, one should be able to fabricate different devices depending on the different properties of the SWNTs (semiconductor or metallic). In addition, the method used to orient the SWNTs is low cost and can be scaled up.

The reason why Fe_3O_4 nanoparticles are selectively attached to the tips of SWNTs while coated on the wall of MWNTs can be explained as follows. After acid treatment, MWNTs became more hydrophilic, and there are many -COOH, -CO groups produced on their surface.[10] While for SWNTs, because of their more perfect structures than MWNTs, the functional groups will be produced at their tips. Fe_3O_4 is water-soluble and iron(III) ions can coordinate with carbonyl groups,[11] causing the Fe_3O_4 nanocrystals to distribute on the surface of the MWNTs and precipitate on the tips of the SWNTs.

In summary, Fe_3O_4-modified CNT (SWNT and MWNT) composites were successfully prepared, and the alignment of CNT in magnetic field were demonstrated.

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References

1 R. H. Baughman, A. A. Zakhidov, W. A. Heer, *Science* **2002**, *297*, 787.
2 A. P. Graham, G. S. Duesberg, R. V. Seidel, M. Liebau, E. Unger, W. Pamler, F. Kreupl, W. Hoenlein, *Small* **2005**, *1*, 382.
3 S. Saito, *Science* **1997**, *278*, 77.
4 M. D. Lay, J. P. Novak, E. S. Snow, *Nano Lett.* **2004**, *4*, 603.
5 N. R. Franklin, H. Dai, *Adv. Mater.* **2000**, *12*, 890.
6 J. Lefebvre, J. F. Lynch, M. Llaguno, M. Radosavljevic, A. T. Johnson, *Appl. Phys. Lett.* **1999**, *75*, 3014.
7 Z. Li, H. Chen, H. Bao, M. Gao, *Chem. Mater.* **2004**, *16*, 1391.
8 J. L. Jiang, L. Gao, *Chem. Lett.* **2004**, *33*, 1114.
9 L. Fu, Z. M. Liu, Y. Q. Liu, B. X. Han, J. Q. Wang, P. A. Hu, *Adv. Mater.* **2004**, *16*, 350.
10 S. C. Tsang, Y. K. Chen, P. J. F. Harris, M. L. Green, *Nature* **1994**, *372*, 159.
11 D. M. L. Goodgame, D. J. Villiams, R. E. P. Winpenny, *Inorg. Chim. Acta.* **1989**, *166*, 159.

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