PREPARATION AND APPLICATIONS OF THIN-WALLED CARBON NANOTUBES FILLED WITH MAGNETIC NANOWIRES

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Introduction

As a group of nanocomposites, carbon nanotubes (CNTs) filled with ferromagnetic metals (M-CNTs) can combine the electrical property of CNTs with the magnetic property of metals, and show potential applications in diverse areas, for example in magnetic data storage, microwave absorption, tumor therapy and probes for magnetic force microscopy (MFM), etc. Up to now, several methods have been proposed to synthesize M-CNTs. Despite of the great progress, these methods still have shortcomings as poor growth control and complicated procedure. Particularly, the filling efficiency of metal into CNTs in previous reports seems very low, which can be seen from the following two facts: 1) the sidewalls of CNTs are very thick (8~40 nm) and, 2) most of the metal encapsulates exist in the form of particles or short rods (length <500 nm). Such low filling efficiency significantly hinders their practical applications in above-mentioned areas. Therefore, it is crucial to develop a highly efficient and well-controlled method to prepare thin-walled CNTs filled with long ferromagnetic nanowires.

In this contribution, we summarized our recent progress [1-8] in the synthesis of open-ended, thin-walled CNTs filled with long ferromagnetic nanowires by using chlorine-contained benzene as precursor. The applications in field emission and microwave absorption of as-synthesized M-CNTs are also demonstrated.

Experimental

The experimental setup and procedure can be found in our previous work [2, 6] in detail. In a typical procedure for the synthesis of FeNi-filled CNTs (FeNi-CNTs), ferrocene and nickelocene powders were first dissolved in trichlorobenzene (TCB, $C_6H_3Cl_3$) to form a solution with a concentration of 0.06 g/ml. Then, the temperature of chemical vapor deposition (CVD) furnace was raised to 860 ºC and kept constant. Next, the solution was fed into the CVD system by a syringe pump. At the same time, a mixture of Ar and H_2 was flowing through the system at 2000 sccm and 300 sccm, respectively. After the CNTs grew for a certain time, the solution supply was terminated and the CVD system was cooled to room temperature naturally. FeCo-filled CNTs (FeCo-CNTs) and FeCoNi-filled CNTs (FeCoNi-CNTs) were synthesized in the same way, by using TCB precursor and combination of multiple metallocenes (i. e. ferrocene, cobaltocene, nickelocene).

Results and Discussion

Fig. 1(a) and (b) are the TEM images of as-grown FeNi-CNT products by using TCB as precursor. It can be seen from Fig. 1(a) that most of the CNTs are filled with long continuous metal nanowires. The length of the nanowires encapsulated in CNTs is up to ~4 μm, which is increased to an order of magnitude compared with previous reports (lengths <500 nm) [9]. Fig. 1(b) is a high-magnification TEM image, from which we can see the filling of nanowires in CNTs more clearly. The upleft inset of Fig. 1(b) is a HRTEM image. Fig. 1(b) shows that the typical walls of CNTs is ~4 nm, which is thinner than that of previous report (~8 nm) [10]. The upright inset of Fig. 1(b) is a SAED pattern of the rectangular part, which also proves the formation of γ-FeNi alloy structure.

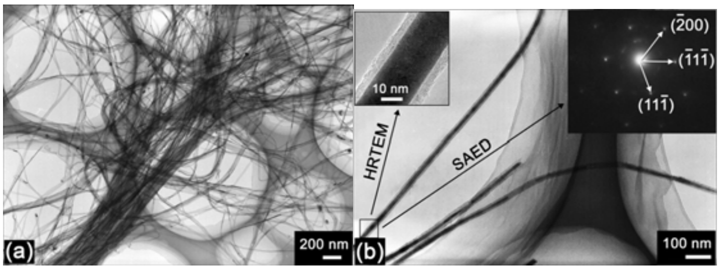

Fig. 1 Morphology of thin-walled CNTs filled with long FeNi nanowires by using TCB as precursor. (a) Typical TEM image; (b) high-magnification TEM image and corresponding HRTEM image (upleft inset) and SAED pattern (upright inset) [7].

Size-dependent etching effect of Cl radicals on the CNT sidewalls has been proved by theoretical calculation [2]. Fig. 2 is our calculation model, which is based on a model proposed by Park et al. [10], but different from their model because no trace of Cl can be detected in the final FeNi-CNT product. In other words, the Cl radicals will etch the C atoms away instead of grafting onto the sidewalls of CNTs. Detailed calculation can be found in our recent work [2].

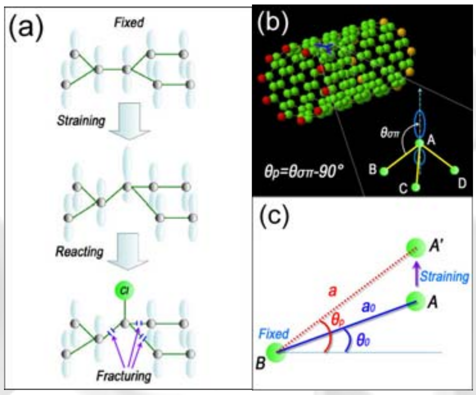

Fig. 2 (a) The etching effect of Cl on a graphene sheet; (b) pyramidal angle θ_p is defined by the angle between the π orbital and σ bond minus 90°; (c) relationship between pyramidal angles θ_p, θ_0 and bond lengths a, a_0 [2].

Previous work has found that the CNT tip-cap closing is more likely to occur for small-diameter nanotubes because the energy barrier to go from an open to a closed cap increases with the diameter of the nanotube [11]. Consequently, the thin-walled CNT is easier to form open-ended tip structure than the thick-walled one when they have the same outer diameters. Our experimental results are in good agreement with this viewpoint (see Fig. 3). The open-ended tip structure of the thin-walled CNT is also favorable to the continuous filling of FeNi particles to form long nanowires.

By using Cl-contained precursor and combination of single or multiple metallocenes, thin-walled CNTs filled with other ferromagnetic metal (eg. Fe [1], FeCo, FeCoNi [3]) nanowires can also be successfully prepared. This synthesis strategy (see Fig. 4) will pave the way to the future practical applications of ferromagnetic metal-filled CNTs.

As-synthesized thin-walled M-CNTs exhibit remarkably enhanced field electron emission performance with a low turn-on field of 0.3 V/μm and better field-emission stability [2]. Furthermore, our work also demonstrates that M-CNTs are promising to be used as lightweight and wide-band microwave absorbers [3]. The relationships between microwave frequency and reflection loss of different coatings were measured at 2~18 GHz and shown in Fig. 5, which demonstrates that the microwave reflection losses are remarkably enhanced after only 1.3 wt% M-CNTs were added into the epoxy matrix. It can be seen that the reflection losses in S-band (2~4 GHz), C-band (4~8 GHz) and X-band (8~12 GHz) are enhanced in the order of FeCoNi-CNTs< FeNi-CNTs< FeCo-CNTs, which can be attributed to their difference in magnetic property [3]. An important feature of the present work is that the mass percentages of M-CNTs are only 1.3 wt%, which is much less than ferrite absorbers (e.g. 70-80 wt%). In other words, the areal density of coatings is mainly dominated by the matrix materials, not by the absorbers. Thus, as-prepared M-CNTs are promising to be used as lightweight and wide-band microwave absorbers.

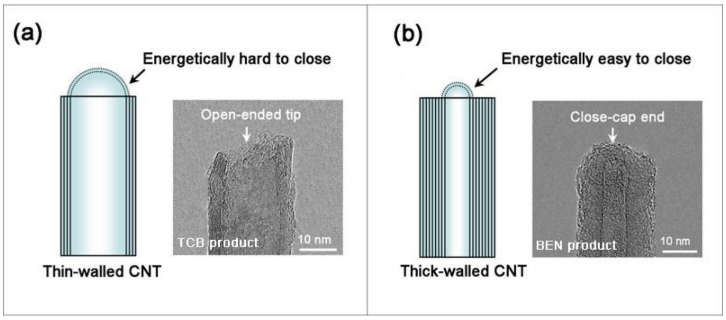

Fig. 3 Tip structure difference between the thin-walled CNT and thick-walled CNT with the same outer diameters. (a) The thin-walled CNT from TCB is energetically hard to form close-cap end, thus open-ended tip structure will be obtained; (b) thick-walled CNT from BEN tends to form close-cap end. Inset in each figure is the corresponding HRTEM image of CNT tip [2].

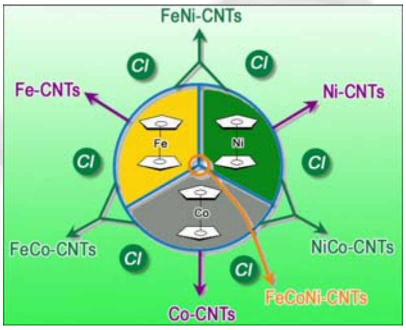

Fig. 4. General synthesis strategy of different ferromagnetic-filled CNTs by using Cl-contained precursor and combination of single or multiple metallocenes.

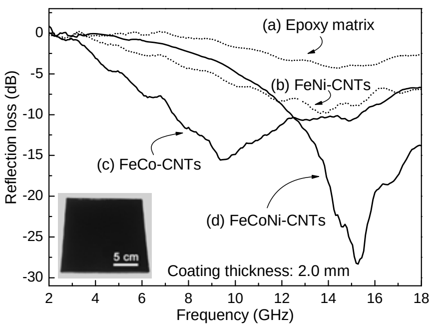

Fig. 5 Electromagnetic wave reflection loss of (a) epoxy matrix and coatings by dispersing 1.3 wt% (b) FeNi-CNTs, (c) FeCo-CNTs, (d) FeCoNi-CNTs into epoxy matrix; the coating thickness and area are 2.0 mm and 180 mm 180 mm, respectively. Inset is the photo of FeCo-CNTs (1.3 wt%) coating[3].

Conclusions

An efficient method for in-situ synthesis of open-ended, thin-walled CNTs filled with long continuous ferromagnetic (Fe, FeNi, FeCo, FeCoNi, etc.) nanowires was proposed. The key feature of this method is to use Cl-contained benzene (e.g. TCB) as carbon precursor. The resulting products exhibited much enhanced field emission and good microwave absorption performance. It is promising to find practical applications in low-energy consumption field-emission displays and lightweight microwave absorbers in the aircrafts.

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