SYNTHESIS OF SWNTS & MWNTS FROM CAMPHOR AND THEIR FIELD EMISSION STUDY

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Introduction

Camphor ($C_{10}H_{16}O$), well known for its medicinal uses in the Eastern countries, is relatively less known in Europe and America. It is the crystallized latex of *cinnamomum camphora* tree abundantly grown in almost all sub-tropical countries and also thriving in Egypt, Canary Islands, Argentina, Europe, Florida, California, Formosa, etc. Against the conventional use of petro-hydrocarbons (such as, methane, acetylene, benzene) for carbon nanotube (CNT) synthesis by CVD, we adopted novel use of this tree product and succeeded in growing single-wall, multiwall and aligned carbon nanotubes incorporating floating catalyst method [1-3]. By changing the catalyst and rather using a supported catalyst method, now we are able to control their diameter distribution with improved yield and quality. Thermal decomposition of camphor over Fe-Co impregnated zeolite powder yields nanotubes at a temperature as low as 550°C. Though the highest yield of multiwall tubes (MWNTs) is obtained at 650°C (~30 mg per 15 min pyrolysis), single-wall nanotubes (SWNTs) grow in the higher temperature range of 850-950°C.

Field emission investigation of vertically aligned nanotubes (ANTs) grown from camphor on various substrates exhibit an appreciable current density of 10-20 mA/cm^2 at a low applied field of 6-8 V/µm even at an ordinary vacuum of 10^{-5}–10^{-6} torr; i.e., ultra-high vacuum is not required. Utilizing such an encouraging emission efficiency of these nanotubes, a model field emission microscope has been fabricated and informative emission patterns are being observed on a fluorescent screen.

Experimental

Commercial camphor was used as a carbon source without further purification. Two kinds of catalyst and support were used. In the first kind, desired quantities of iron acetate and cobalt acetate (0.1–0.5 g each) were dissolved in 20 ml ethanol and 1 g zeolite powder was added to it. The mixture was sonicated for 10 min, dried at 80°C for 24 h and ground into fine powder to be used as ready support for CNT growth. A 90 cm long quartz tube (inner diameter: 26 mm) was used as a CVD reactor kept horizontally inside two adjacent electric furnaces. Camphor (typically 200 mg, put in the first furnace zone) was vaporized at 225°C and pyrolyzed over catalyst-pregnated-zeolite (typically 40 mg, placed in the second furnace zone) at desired temperature (500-1000°C) under an argon flow of 100 ml/min. After such a15-min pyrolysis, the furnaces were allowed to natural cooling under argon flow and then blackened zeolite was collected, weighed and characterized.

In the second kind, 200 mg camphor, mixed with 1–2 wt% ferrocene, was coevaporated in the first furnace at 200°C and pyrolyzed over quartz plates (1 cm × 1 cm) placed in the second furnace at 850°C. Such a 15-min reaction under a mild argon flow of 75 ml/min resulted in vertically aligned CNTs ideally suitable for field emission investigation. Two types of field emission set-up were realized. In parallel plate device, vertically aligned nanotubes on quartz substrate were readily used as cathode, whereas a stainless steel rod (1.5 mm φ) held vertically 500 μm above the CNT film served the purpose of anode. Negative high tension (1–5 kV, in steps of 20 V) was applied to the CNT film at 10^{-5}–10^{-6} torr and corresponding anode current was measured precisely. In the second type of field emission experiment, an extremely small pinch of the aligned CNT was picked up by fine tweezers under an optical microscope and stuck to a tungsten hairpin to be used as field emitter. In this case, a phosphor-coated indium tin oxide plate (10 cm × 10 cm) held 1–5 cm in front of the CNT emitter served the purpose of electron collector as well as image display screen.

Results and Discussion

In presence of Fe-Co binary catalyst impregnated in zeolite nanopores, camphor vapor was able to form CNTs at all temperatures from 550°C to 1000°C. Careful TEM investigation followed by diameter distribution analysis of as-grown nanotubes revealed that temperature is a decisive factor in diameter control. The diameter distribution was found to increase with increasing growth temperature. CNTs grown at 550°C were found within a narrow diameter range of 5–14 nm, while high temperature (850°C) samples contained MWNTs of diameter 10–50 nm. However, the best yield (>90%)of MWNTs was obtained at 650°C, as shown in Fig. 1a, depicting clear tubes of fairly uniform diameter ~10 nm. EDX analyses of as-grown CNTs indicate negligible Fe and Co contents (~0.2–0.3 wt%) against C (99.5 wt%). SWNTs could be observed in the temperature range of 850–1000°C only, with a maximum yield of ~20% at 900°C, as shown in Fig. 1b. Although the present 20% yield of SWNTs sounds to be low, their diameter is fairly uniform: 1.3 nm (±0.3 nm). However, growing SWNTs from camphor pyrolysis below 850°C still remains a challenge, and we are striving for the same.

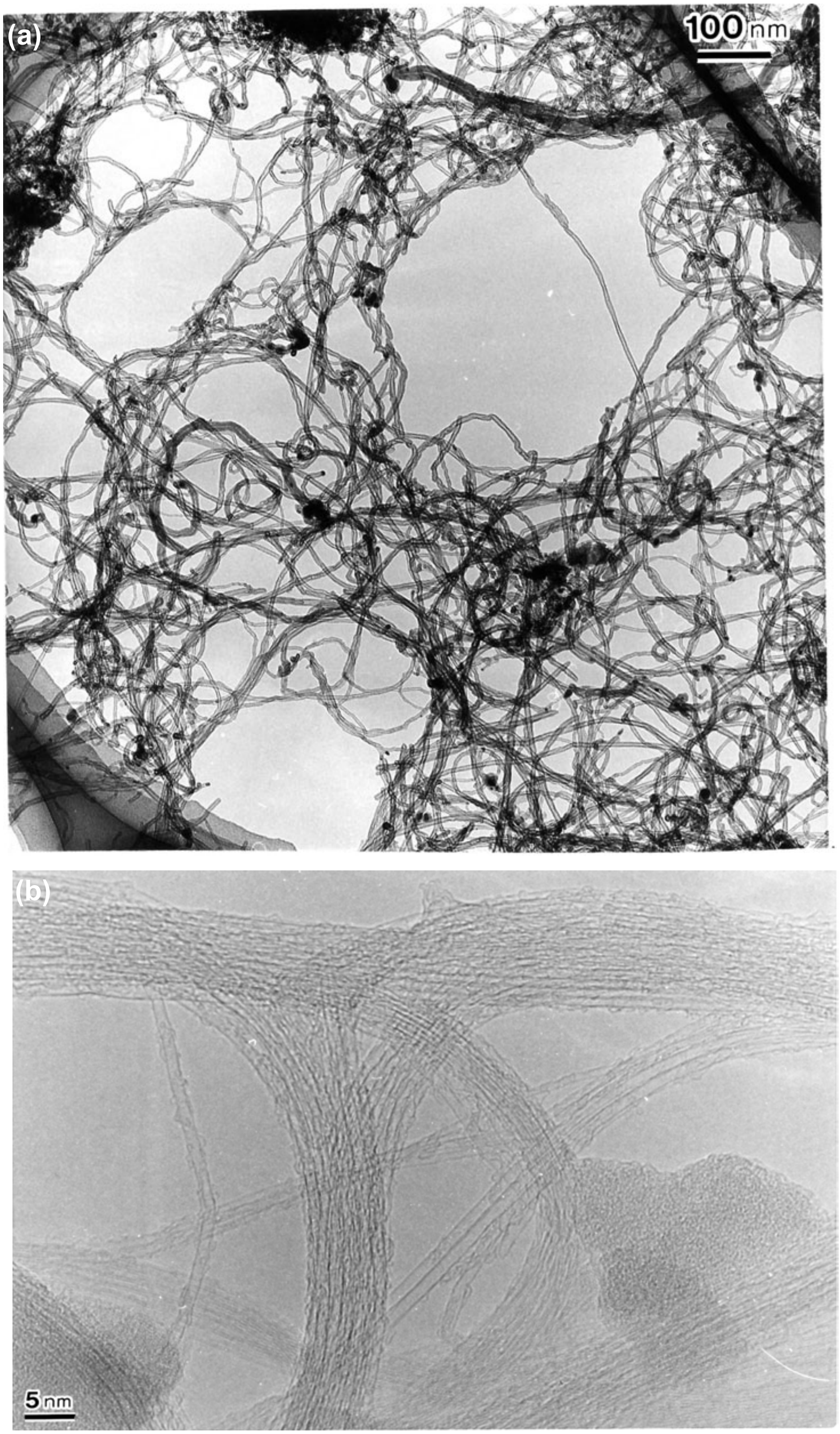
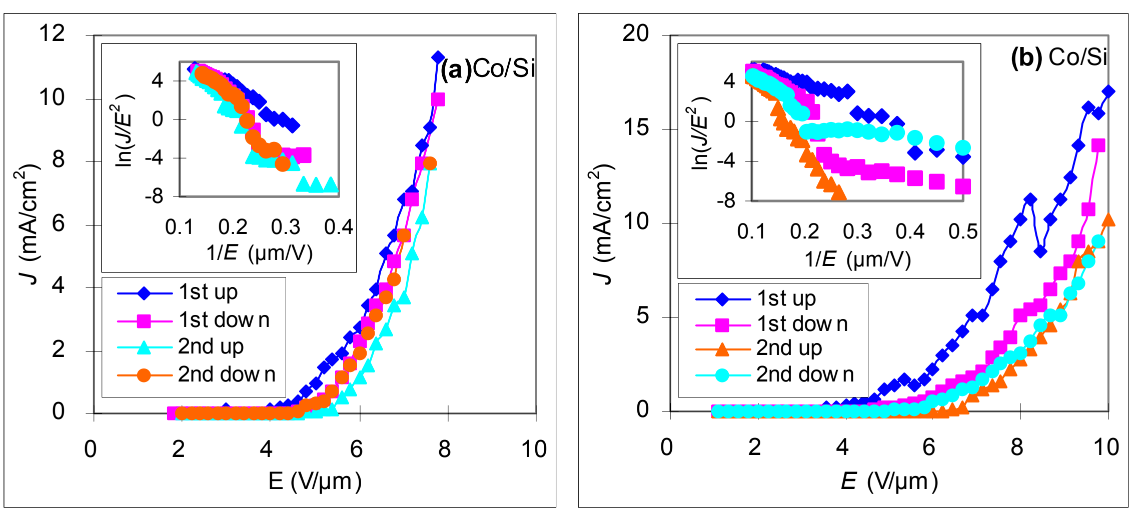


Figure 1. TEM images of (a) MWNTs and (b) SWNTs grown at 650°C and 900°C, respectively, using zeolite support

On the other hand, pyrolysis of coevaporated camphor-ferrocene mixture yielded vertically aligned CNTs on quartz, silicon and cobalt-coated-silicon substrates [4]. As-grown CNTs on all those substrates were found to be good field emitters capable of emitting a current density of mA/cm^2 order. Highly dense deposit of ANTs on quartz substrate resulted a low current density (1.3 mA/cm^2) due to field screening effect, whereas less dense ANTs on silicon substrate gave medium range current density (4 mA/cm^2). It was also observed that a thin coating of cobalt on silicon substrate before CNT deposition overrides the underlying resistive SiO_2 layer, thereby increasing the emission current up to 14 mA/cm^2 [4]. Hence in the present study, we attempted to see the effect of different metal coatings (cobalt and nickel) on the field emission from CNTs grown on them. It may be noted that as-deposited cobalt and nickel films on silicon substrate do not serve as a catalyst, and no CNT is grown on them unless 1–2 wt% ferrocene is coevaporated with camphor. In this report, we present the field emission results of four samples of ANTs grown on cobalt-coated and nickel-coated silicon substrates using different ferrocene concentrations.

As-grown ANTs on these substrates were directly suitable for field emission investigation without any post-deposition treatment/processing. Field emission current was measured as a function of applied voltage at a fixed separation (500 μm) between cathode (nanotube deposit) and anode (stainless steel rod). Figure 2 shows the field emission *J-E* curves obtained from the four ANT samples, and their characteristic features are summarized in Table 1. It is encouraging that the turn-on field (corresponding to an emission current of 1 μA/cm^2) for camphor-grown CNTs is pretty low: 1–3 V/μm, while the maximum current density goes up to 22.6 mA/cm^2 at 6–10 V/μm. It is also noted that a slight increase in the catalyst concentration during the CNT growth enhances its emission efficiency. The field enhancement factor (β), as calculated from the slope of the Fowler-Nordhiem plots, is fairly high in all the four cases. So far as the stability of these CNTs is concerned, there was a slight decrease in the emission current in the second cycle of voltage application, whereafter, quite reversible *J-E* curves were obtained without any hysteresis up to eight cycles measured.



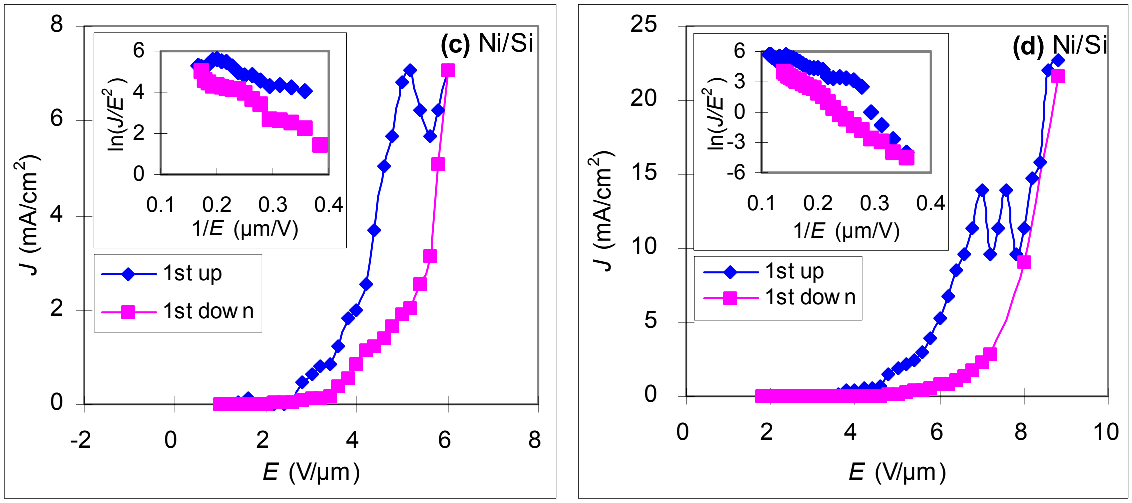


Figure 2. Field emission *J-E* curves and corresponding F-N plots (inset) obtained from the four ANT samples

Table 1
Field emission characteristics of different ANT samples

Substrate	Fe:Camphor	Turn-on field*	Maximum current density	β
(a) Co/Si	1.0 : 100	2.0 V/µm	11.3 mA/cm^2 at 7.8 V/µm	839
(b) Co/Si	1.5 : 100	2.4 V/µm	17.0 mA/cm^2 at 10 V/µm	971
(c) Ni/Si	1.5 : 100	1.0 V/µm	7.1 mA/cm^2 at 6.0 V/µm	1624
(d) Ni/Si	2.0 : 100	3.0 V/µm	22.6 mA/cm^2 at 8.8 V/µm	655

* corresponds to an emission current density of 1 µA/cm^2

ANTs grown on large area substrates as described above are useful for flat panel display devices. However, another important application of CNT field emitters is realized in an electron microscope that uses a single CNT as a field emission electron gun to produce a highly coherent electron beam. In order to investigate the suitability of our CNTs for such an advanced application, an extremely small pinch of as-grown ANTs was picked up by micromanipulator and mounted to a fine tungsten hairpin. Applying a high negative voltage to such an emitter in a vacuum chamber as shown in Fig. 3a, the emission pattern was directly observed on a fluorescent screen. A typical emission pattern, reflecting 4-fold symmetry of an individual nanotube emitter, is shown in Fig. 3b. Each bright spot corresponds to the presence of a pentagon at the nanotube tip. This suggests a nanotube structure as sketched in Fig. 3c. Similar emission patterns were observed by Fransen et al. (2-fold and 4-fold symmetries) [5] and Saito et al. (5-fold symmetry) [6] in ultra-high vacuum (10^{-8}–10^{-9} torr) conditions. However, the encouraging aspect of the present report is that such emission patterns are always observed at an ordinary vacuum of 10^{-5}–10^{-6} torr, which certainly attributes to better tube quality of camphoric nanotubes from the FE perspectives. More careful experiments are going on to estimate the tube chirality by FEM study.

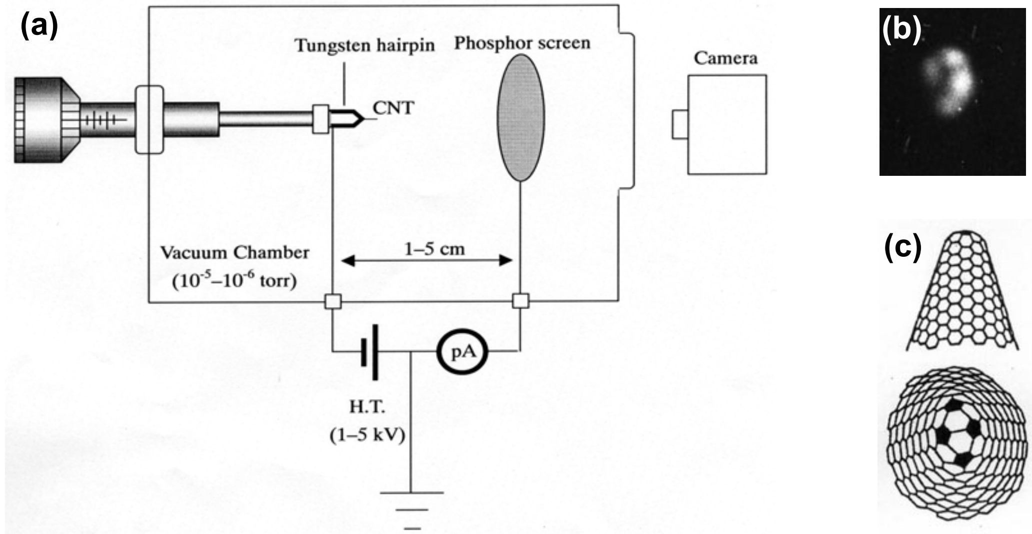


Figure 3. (a) Schematic diagram of the FEM set-up; (b) Emission pattern reflecting four-fold symmetry of an individual CNT tip; (c) Speculated structure of the corresponding CNT tip

Conclusions

We have presented the preliminary results of field emission from camphor-grown CNTs which suggest that as-grown CNTs are promising for further investigation for advanced application.

References

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