

Direct Synthesis of Carbon Nanotubes on Organic Polymer Substrates

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Introduction

Carbon nanotubes (CNTs) are materials of increasing concern due to their excellent electronic properties and physical and chemical stability. Various methods for the synthesis of CNTs have been reported: arc-discharge, laser ablation, chemical vapor deposition, flame synthesis and the high pressure CO(HIPCO) process. However, none of them are able to synthesize CNTs at low temperature, so that the incorporation of CNTs with low melting point materials, such as organic polymers, has been severely limited. Therefore, the strategy frequently used is to separate the synthesis of CNTs from the fabrication of devices. However, it is very difficult to handle CNTs in the post-processing steps, due to the extremely small size of CNTs. A much better strategy is to synthesize CNTs *in situ* at the exact location of the devices. This strategy has been successful only with high melting point materials.

We report here the CNTs synthesis by selective heating of catalyst particles with microwave. Compared with conventional heating methods, microwave heating, where the microwave energy is delivered to the materials through molecular interaction with the electromagnetic field, has the potential advantages of uniform, rapid, and volumetric heating.

Experimental

Sodalime glass, Teflon and polycarbonate(PC) were used as substrates in our experiments. The melting points of them were 500°C, 330°C, and 130°C, and their thicknesses were 3mm for glass and 2mm for the others. An organic metal compound, cobalt naphthenate (6wt% aqueous solution), was painted on the upper side of the substrates and then dried.

To prepare cobalt sulfide catalysts, 1 gram of cobalt black was mixed with 10ml of Nafion solution (5wt% aqueous solution) and sonicated for 10 minutes. The mixture was then painted on a Teflon sheet to form a catalyst film. After drying overnight at 110°C, the substrate was sulfided with a 10vol% H₂S/H₂ mixed gas at 300°C for 10 hours. Cobalt sulfide particles formed on the substrate.

The flexible CNTs emitters were fabricated and the field emission was measured. The organic polymer substrate was the 280 μ m thick Teflon sheet and the roughness was about 60nm. A thin layer of Cr electrode was deposited onto the substrate by a magnetron sputter. The sputtering chamber was evacuated to a pressure lower than $\sim 1 \times 10^{-6}$ Torr. Argon gas was introduced into the sputtering chamber and the gas pressure in the chamber was kept at 2.1×10^{-2} Torr during the sputtering. DC power was fed to generate plasma and the thickness of Cr layer was 150nm. Cobalt sulfide catalysts were electrochemically synthesized. The Cr-deposited substrate was immersed in a mixture of 0.1M CoSO₄ and 0.5M Na₂S₂O₃ (volume ratio = 1:1) in ethylene glycol solution and CoS_x was deposited at the potentiostatic condition of -1.5 V for 10minutes.

The catalyzed substrate was inserted in a quartz reactor and microwaves were irradiated on it with a flowing reactant gas. C₂H₂ was used as a carbon source and mixtures of C₂H₂ and H₂ or He were also used. Fig. 1 shows the schematics of the synthesis apparatus.

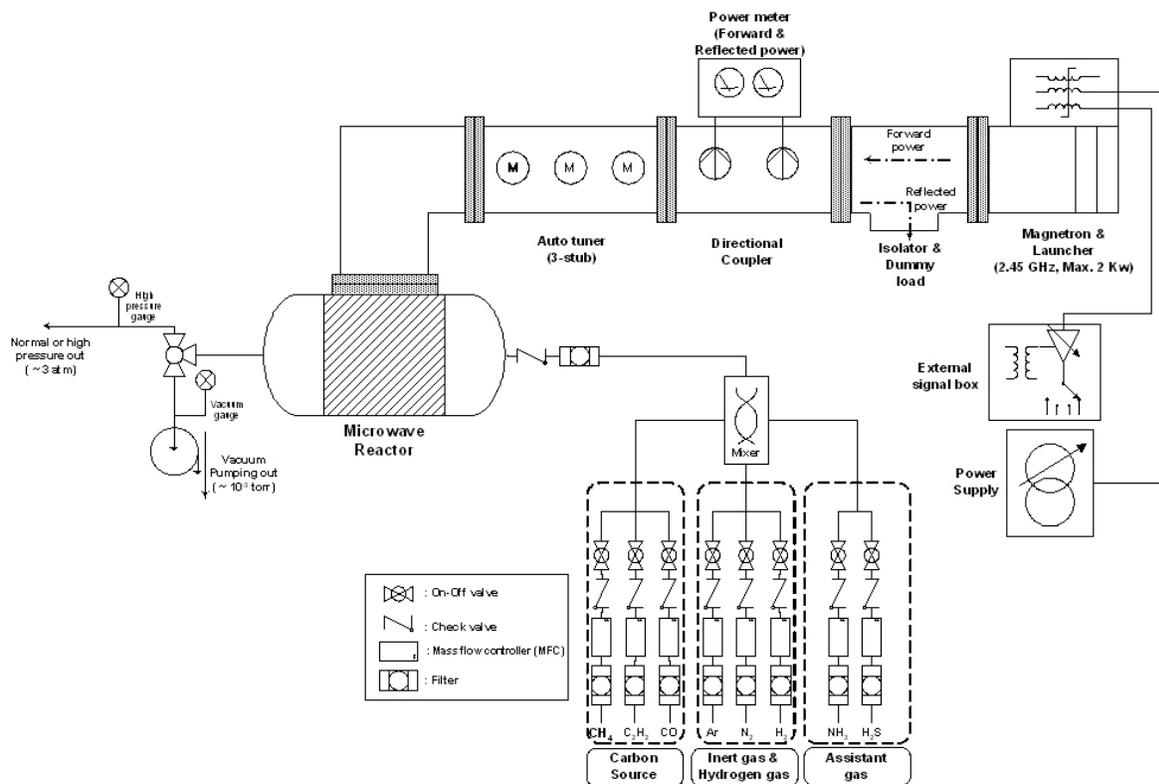


Figure 1. Schematics of the microwave synthesis apparatus

The field emission current for CNTs on CoS_x/Cr/Teflon was measured. The Cr layer was used as the cathode and the glass coated with indium tin oxide (ITO, 150nm, polished) was used as the anode. The space between the field emitter arrays (FEA) and the anode was

200 μm . Field emission current was measured by electrometer (Keithley6485) at a pressure of $\sim 1 \times 10^{-7}$ Torr.

Results and Discussions

CNTs were directly synthesized on organic polymer substrates by selective heating of catalysts using microwave radiation. Since the microwave energy is selectively absorbed by the catalysts, not by the substrates, local heating occurs, resulting in the CNT synthesis even on the organic polymer substrates. Degradation of the substrate material was minimum. Various shapes of carbon nanotubes and carbon fibers were observed as well as amorphous carbons. (Fig. 2)

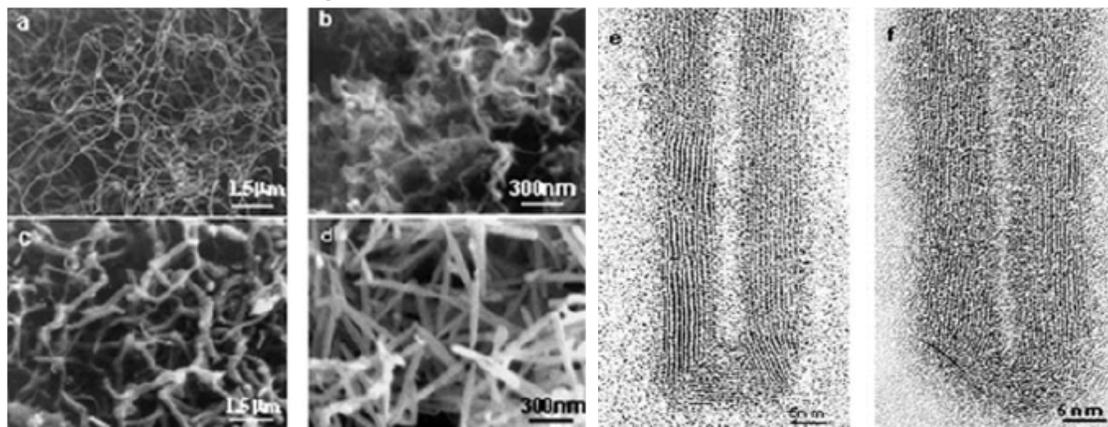


Figure. 2. CNTs grown on low melting point substrates. (a) cobalt naphthenate on glass, (b) cobalt naphthenate on Teflon, (c) cobalt naphthenate on polycarbonate, (d) CoSx on Teflon, (e) wall structure of the CNT shown in (c), (f) wall structure of the CNT shown in (d)

Figure 2 also shows the microscopic structure of the synthesized CNTs. These HR-TEM photographs show that they are well-graphitized multiwalled carbon nanotubes (MWNTs). Since graphite can absorb microwave energy very efficiently and be heated to 1000 $^{\circ}\text{C}$ in a few tens of seconds, the synthesized MWNTs are likely to go through high temperature annealing. We may take advantage of this self-annealing property of microwave synthesis of CNTs to get high crystallinity.

Flexible field emitters of carbon nanotubes were fabricated based on these findings. The fabrication process includes (1) sputter deposition of Cr layer on organic polymer substrate, (2) electrodeposition of catalysts, and (3) in situ synthesis of carbon nanotubes by microwave irradiation.

Figure 3 shows the field emission current density from the field emitter as a function of applied electric field, and the inset is the Fowler-Nordheim plot. This I-V curve was obtained

after sweeping the voltage several times. Field emission didn't occur on CoS_x/Cr/Teflon even though CoS_x had many edge sites, which supports that CNTs are responsible for the electron emission. In case of CNTs on CoS_x/Cr/Teflon, the turn-on field (E_{to}) at the emission current density of $1 \mu\text{A}/\text{cm}^2$ was $7.6\text{V}/\mu\text{m}$, and applied field was $9.7\text{V}/\mu\text{m}$ at the emission current density of $10 \mu\text{A}/\text{cm}^2$. The work function of the CNTs in our sample was taken to be that of graphite, 5eV . The slope of FN plot was 9718, and the field enhancement factor β calculated from the slope of the FN plot, was about 1649.

In our work, E_{to} is relatively higher than those previously reported for CNT emitters, and the emission current density is low. The existence of CoS_x catalyst layer in our field emitter structure may play a role of a resistive layer, thus have a negative effect on electron transport from Cr electrode to CNTs. The existence of resistive layer is known to be beneficial to the uniform electron emission. Further investigation on field emission measurements is on going. This novel method is an important advancement to the fabrication of flexible field emission displays (FEDs)

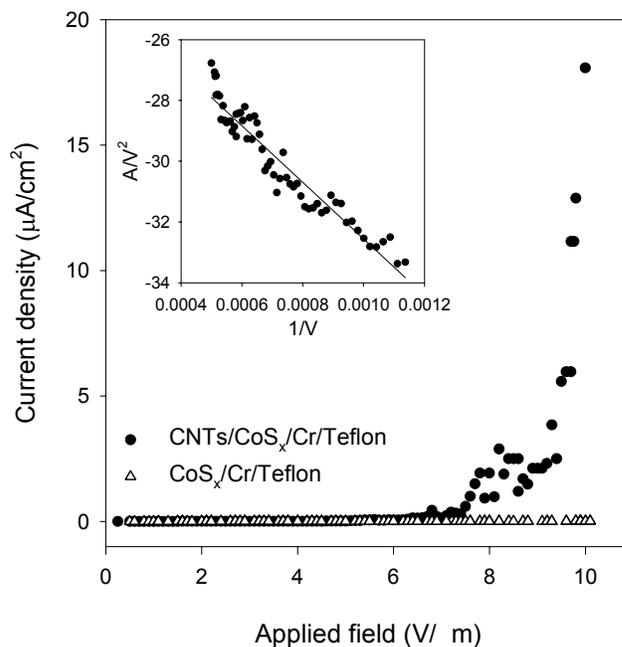


Figure 3. Field emission current from the flexible field emitters. (Inset) Fowler-Nordheim plot for CNTs grown on CoS_x/Cr/Teflon

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