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CHARACTERISTIC OF FIELD EMISSION FROM CARBON NANOTUBES SYNTHESIZED FROM DIFFERENT SOURCES

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Abstract. The field emission of carbon nanotubes (CNTs) synthesized from different sources is investigated. Comparisons are made between graphite with Ni metal as catalyst and polycyclic aromatic hydrocarbon as precursor in arc discharge. Key parameters are also evaluated to obtain high quality and high yield CNT for application of field emission display. Cathode deposits are examined using SEM and HRTEM to determine microstructure. Raman spectroscopy is also used to study carbon structure. Electron field emission characteristic is measured with the diode method. Microstructural investigation provides evidence that both metal catalyst and precursor not only can be used to synthesize CNTs but also to enhance their production rate. From field emission measurement, the lowest onset field is about 1.0 V/mm and can be attributed to highly sharp tips and high density of CNTs. Based on microstructure characterization and field emission measurement, influence on field emission of CNT synthesized from different sources is discussed.

1. INTRODUCTION

The allotropes of carbon materials include graphite, diamond, fullerene [1], and carbon nanotube (CNT) [2]. The high aspect ratio and small tip radius of curvature of CNT make it especially suitable as a source for field emission [3,4]. In this paper, arc discharge method, using graphite rods with Ni metal as catalyst and polycyclic aromatic hydrocarbon as precursor, was adopted to synthesize CNT to potentially improve CNT-FED applications.

2. EXPERIMENTAL METHODS

Carbon nanotube (CNT) was produced in a vertical arc furnace, as shown in Fig. 1. The arc discharge system used in synthesizing of CNT is described in detail elsewhere [5,6]. Major experimental parameters are shown in Table 1. Microstructural characterization was carried out using SEM and HRTEM. Raman spectroscopy was used to confirm formation of graphitic CNT.

Field emission property was investigated using diode type measurement shown in Fig 2. Emission current vs. applied field (I-V) was characterized by varying potential from 0 to 1000 V at a constant gap of 200 mm. Emission I-V data was measured with an electrometer (Keithley 6517A) and recorded by a personal computer under 10^{-6} torr vacuum. CNT bundles were directly attached to a double-sided Cu tape adhered to a thin rolled Cu foil of cathode surface. The stainless steel spindle of digital micrometer was used as an anode.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Typical SEM micrographs of cathode deposits are shown in Fig. 3. Dense, fibrous CNTs can be seen at longitudinal cross-section of specimen G-1 (Fig. 3(a)). Fiber-like CNTs distributed randomly and carbon nanoparticles are observed clearly at transverse cross-section surface of specimen Ni/G-1 (Fig. 3(b)). An individual CNT is several microns long. Similar to specimen Ni/G-1 in Fig. 3(b), random fiber-like CNTs appear for specimen PAH/G-1 (Fig. 3(c)). CNT can thus be synthesized using pure graphite, Ni catalyst, and PAH precursor.

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Table 1. Major experimental parameters of CNT synthesized by the arc discharge method.

Group	Specimen	Materials	Experimental Parameters
G	G-1	graphite	He: 300mm Hg flow rate: 5 l/min reaction time: 5min
Ni/G	Ni/G-1 Ni/G-2	graphite + 5 % wt. Ni powder	He: 300~500 mm Hg flow rate: 5~10 l/min reaction time: 10~15min
PAH/G	PAH/G-1 PAH/G-2	Graphite + pyrene coating	He : 300~500 mm Hg flow rate: 5~10 l/min reaction time: 2~3min

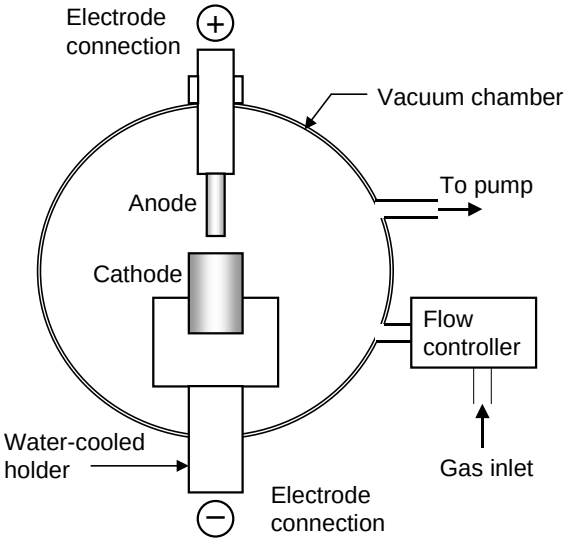

Fig. 1. Schematic diagram of apparatus used for synthesizing CNT

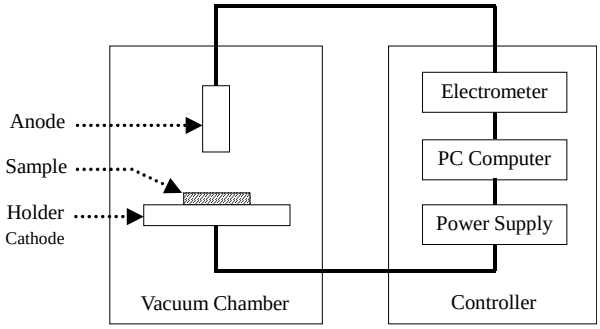

Fig. 2. Schematic diagram of field emission measurement system

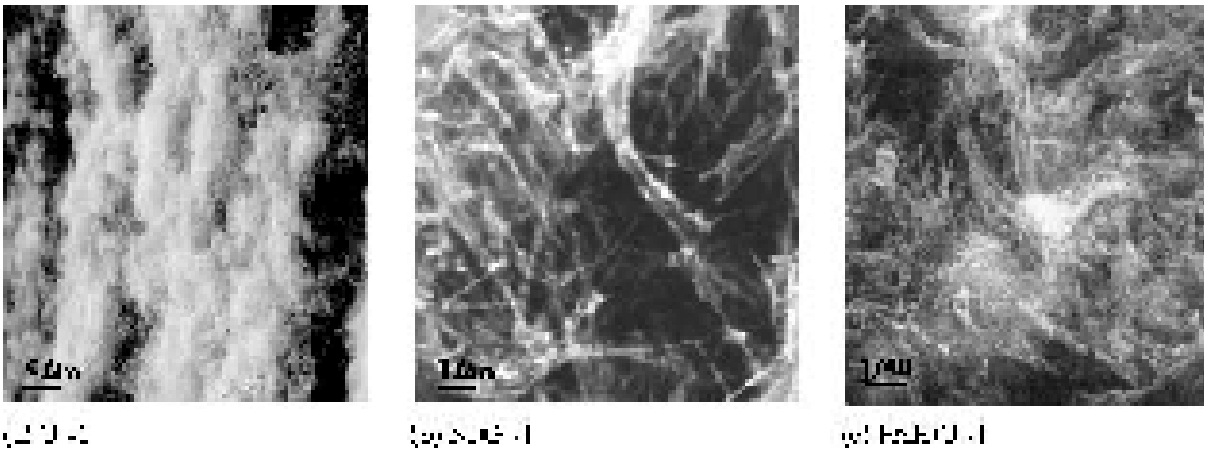

Fig. 3. SEM micrographs of CNT specimens

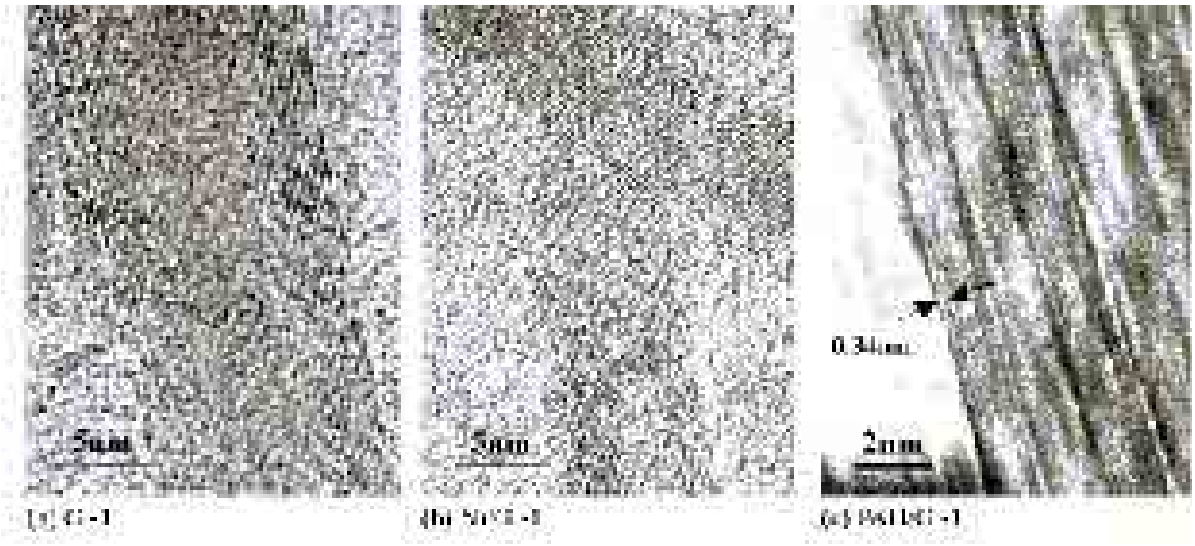

Fig. 4. HRTEM micrographs of CNT specimens.

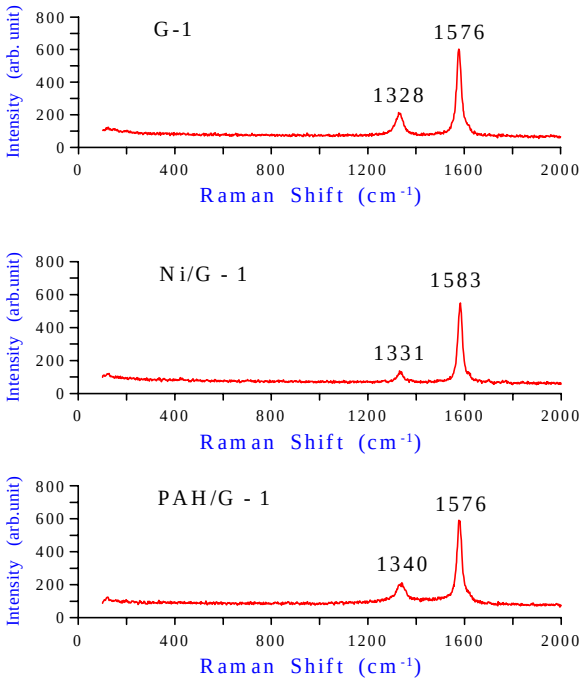

Fig. 5. Raman spectra of CNT specimens

Fig. 4 shows typical HRTEM micrographs of CNT specimens. HRTEM images clearly exhibit characteristic features of multiwalled carbon nanotubes (MWNT). The CNT core is hollow with multiple layers parallel to CNT axis on the wall. The inner and outer diameters are about 4 and 13 nm, 3 and 6 nm, and 1.5 and 4.5 nm for G-1 (Fig. 4(a)), Ni/G-1 (Fig. 4(b)) and PAH/G-1 (Fig. 4(c)), respectively. The distance between parallel straight lattice fringe in wall is about 0.34 nm. The spacing in-layer structure is very even. One of the CNTs is closed at the end with cap as shown in Fig. 4(b).

Raman spectra of the CNT are shown in Fig. 5. This figure shows typical twin peaks at 1328-1340 cm^{-1} (D-band) and 1576-1583 cm^{-1} (G-band). These bands are characteristic of disordered and graphitic carbon structures. Raman spectrum illustrates a stronger peak at about 1580 cm^{-1} indicating formation of well-graphitized CNT. This feature may be assigned to MWNT [7]. The degree of CNT graphitization is high and is in good agreement with HRTEM result.

Ni catalyst and PAH precursor are found to increase yield of CNT. Furthermore, pyrene can serve as building block for CNT formation. High temperature graphitization processes induced by arc plasma enables hydrocarbon acted as carbon source and changes aromatic species into layered graphite structure of CNT.

Fig. 6 shows field emission characteristic of CNT specimens. In general, the current density exhibits a sharp onset at very low electric field and increases exponentially with increasing electric field. Results of I-V measurement are shown in Table 2. All I-V curves behave with typical field emission characteristics. Field emission values of the present study are comparable with those found from the arc discharge method as shown in Table 3 [3,12,13]. Based on the I-V curves, the PAH/G group has a minimum E_{on} value and the minimum E_{on} is 1.2 V/μm at 1 nA or 1.4 V/mm at 10^{-5} A/cm^2. This observation can be attributed to highly sharp tips and high density of CNTs. A similar trend can also be observed in the threshold value E_{th}. Accordingly, CNT synthesized

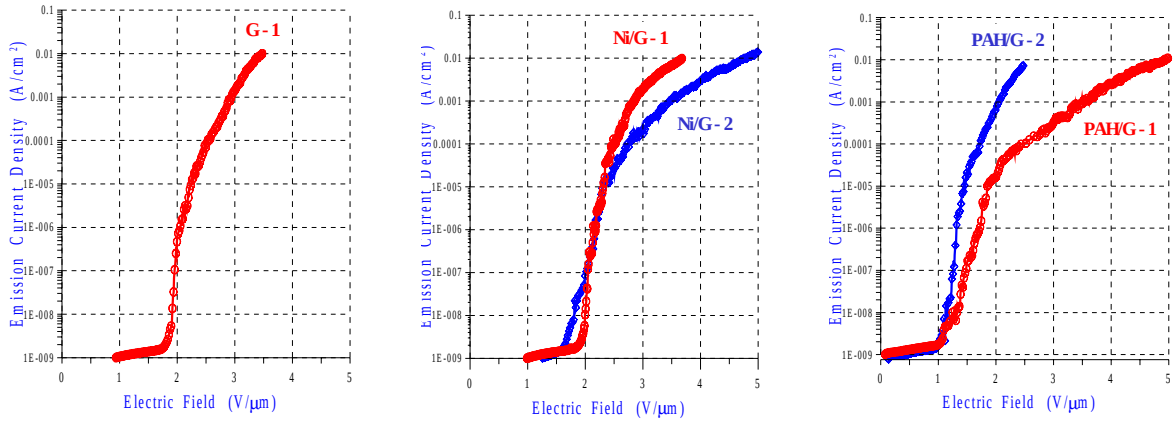

Fig. 6. Field emission characteristics of CNT specimens

Table 2. Results of I-V measurement of CNT specimens

Group	Specimen	Turn on Voltage at 1nA	E_{on}(V/μm) at 10^{-2}mA/cm^2	Threshold Voltage E_{th}(V/mm) at 10mA/cm^2
G	G-1	1.9	2.2	3.5
Ni/G	Ni/G-1	2.0	2.3	3.7
	Ni/G2	1.9	2.4	4.8
PAH/G	PAH/G-1	1.4	1.8	5.0
	PAH/G-2	1.2	1.4	2.5

Table 3. Characteristics of materials used in field emitter.

Materials	Si	SiC	SiCN	DLC	CNT
Morphology	Dia. 1μm	Nanowire Dia. 20nm	Nanorod Dia. 20~50nm	Film	SWNT, MWNT Dia. 1.6~ nm
Turn on Voltage (at 10^{-2}mA/cm^2)	N/A	20 V/μm	10 V/μm	5–8 V/μm	0.8 – 3 V/μm
Current Density	1500 A/cm^2 at 10 kV	10 mA/cm^2 at 30 V/μm	4.5 mA/cm^2 at 36.7 V/μm	1.02 mA/cm^2 at 21.6V/μm	1mA/cm^2 at 3V/μm
Enhancement Factor	N/A	N/A	N/A	N/A	1000 ~ 33000
Work Function	1.7~4.7 eV	N/A	N/A	N/A	3.7 – 5.0 eV
Ref.	[8]	[9]	[10]	[11]	[3,12,13,14]

from PAH precursor is shown to have the most attractive field emission property.

4. CONCLUSIONS

The CNT can be synthesized from three sources: pure graphite, graphite coated with Ni catalyst, and PAH precursor, respectively. Random fiber-like CNTs with length of several mm are found in SEM micrographs. HRTEM images clearly show the characteristic feature of multiwalled carbon nanotube (MWNT). The inner and outer diameters of MWNT are in the range from 1.5 nm to 13 nm. Raman spectrum shows a stronger peak at about 1580 cm^{-1} in-

dicating formation of well-graphitized CNT. High degree graphitization is in good agreement with HRTEM observation. I-V curves behave with typical field emission characteristics. CNT synthesized from PAH/G group not only has the smallest diameter but also has the minimum E_{on} value indicating PAH/G has the most attractive field emission property.

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