25 September 1998

ELSEVIER

Chemical Physics Letters 294 (1998) 593–598

CHEMICAL PHYSICS LETTERS

High yield of single-wall carbon nanotubes by arc discharge using Rh–Pt mixed catalysts

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Received 11 June 1998; in final form 28 July 1998

Abstract

Single-walled carbon nanotubes (SWNT) were produced using binary mixtures of the platinum-group metals as catalysts by arc evaporation in helium gas. Transmission electron microscopy and Raman scattering spectroscopy revealed that the production yield of SWNTs was remarkably enhanced when a Rh–Pt mixture was used as a catalyst. The density of SWNTs in raw soot was as high as that obtained from Fe–Ni and Y–Ni. The distribution of diameters of SWNTs was narrow (1.28 ± 0.07 nm). The merit of this catalyst is that it is free from magnetic metals. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

An electric arc discharge between carbon electrodes is used widely for synthesizing fullerenes, nanotubes and other fullerene-related materials. Single-wall carbon nanotubes (SWNT) were discovered in 1993 in the course of synthesis of carbon nanocapsules entrapping magnetic nanoparticles such as iron [1], cobalt [2] and nickel [3]. The diameters of SWNTs produced from the iron-group metals were in the range between 0.7 and 3 nm, and the lengths were more than 10 μm. After this discovery, some rare-earth metals [4–6] and platinum-group metals [7–10] were also found to catalyze the formation of SWNTs. Moreover, it was demonstrated that the yield of SWNTs was enhanced when some catalytic metals were used as binary mixtures. Typical examples of effective mixtures were Fe–Ni [11,12], Y–Ni [13] and Co–Ni [14]. By using a Y–Ni binary metal, the density of SWNTs in raw soot was reported to reach 70–90 % [13]. Laser evaporation of carbon was also employed for synthesizing SWNTs; Co–Ni binary metal was the most effectual catalyst, and a yield of 70–90% was reported [14].

We studied previously the catalytic activities of a series of elemental metals within the platinum-group (i.e. Ru, Rh, Pd, Os, Ir, Pt) and reported that Rh, Pd and Pt assisted the formation of SWNTs, whereas for other metals the catalytic activities were hardly observable [7].

In the present study, we examined the effect of mixing of metals within the platinum group on the formation of SWNTs. The mixtures studied were all the binary combinations of Ru, Rh, Pd and Pt. Os

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PII: S0009-2614(98)00921-X

and Ir were excluded because they are refractory. The production yield and structures of SWNTs were studied by transmission electron microscopy (TEM) and Raman scattering spectroscopy.

2. Experimental

The method to produce SWNTs [7,15] was a dc (direct current) arc discharge between two electrodes in a stainless-steel chamber filled with helium gas. The anode was a graphite rod (6 mm diameter, 50 mm length) in which a hole (3.2 mm diameter, 30 mm deep) had been drilled and filled with a mixture of metal and graphite powders. The mixing ratios of the metals and graphite are listed in Table 1. The cathode was a pure graphite rod (13 mm diameter, 30 mm length). The purity of the graphite rod and powder was 99.998% and the purity of the metal powders was 99.9% or higher.

The arc discharge was generated in helium gas (purity 99.99%) of 600 Torr and sometimes also 50 and 1520 Torr. The discharge current was 70 and 100 A. Since the anode was preferentially consumed by evaporation, the arc gap between the electrodes was kept constant (1–2 mm) by manually advancing the consumed anode. After evaporation for 1–3 min, the following carbonaceous materials were formed: (1) soot deposited on the inner wall of the reaction chamber, (2) a cylindrical hard deposit at the end of the cathode, (3) rubbery soot around the root of the cylindrical hard deposit. These carbonaceous materials were separately collected from the three regions. Hereafter, we call the first carbonaceous material (1) 'chamber soot', the second one (2) 'cylindrical hard deposit' and the last one (3) 'cathode soot'. For the chamber soot, we collected samples only from those deposited on the ceiling of the chamber.

Recovered soot materials were examined by TEM, Raman scattering spectroscopy and X-ray diffraction (XRD). For preparing samples for TEM, soot materials were ground by a mortar and pestle and then dispersed under ultrasonic agitation in ethanol. The suspension was dropped on holey carbon grids and allowed to dry. A transmission electron microscope (Philips CM120) was operated at 120 kV. Raman scattering spectra were measured in a backscattering geometry at room temperature using an Ar-ion laser

Table 1
Densities of SWNTs in raw soot obtained from binary mixtures of metals

Mixtures[a]		He pressure (Torr)	Density of SWNTs[b]		
			Chamber soot	Cylindrical hard deposit	Cathode soot
Ru/Pd/C	(1:1:1)	50	no	no	no
		600	no	no	low
		1520	no	no	very low
Rh/Pd/C	(1:1:1)	50	no	no	very low
		600	no	no	medium
		1520	no	no	low
Ru/Rh/C	(1:1:1)	50	no	no	very low
		600	very low	no	very low
		1520	no	no	very low
Ru/Pt/C	(5:5:2)	600	very low	no	very low
Rh/Pt/C	(9:1:2)	600	low	no	high
	(1:1:1)	600	medium	no	very high
	(5:5:2)	50	very low	no	low
		600	low	no	very high
		1520	no	no	very low
	(1:9:2)	600	low	no	high
Pd/Pt/C	(1:1:1)	600	very low	no	medium

[a] Weight ratios of metals and carbon powders packed into a hole of the graphite anode are shown in parentheses.
[b] Densities in raw soot are graded into five classes: very high ($>20\%$), high ($\sim 20\%$), medium ($\sim 10\%$), low ($\sim 1\%$), very low ($<1\%$).

(488 nm). XRD was performed with a powder X-ray diffractometer with a CuK_{α} source.

3. Results and discussion

The abundance of SWNTs produced from mixed catalysts of Pt-group metals studied is summarized in Table 1. The density of SWNTs was estimated by TEM observation. SWNTs were found predominantly in the cathode soot, but only a trace, or no trace, of SWNTs were observed in the chamber soot and cylindrical hard deposits. The yield of SWNTs depended not only on the catalysts but also on the helium pressure. SWNTs were produced at a higher density by using a Rh–Pt mixture at 600 Torr of helium. The yield was strongly affected by the mixing ratio of Rh and Pt; the highest yield was obtained with a mixture of 1:1 weight ratio. The content of carbon powder packed in the hole of the anode was not sensitive to the density of SWNTs. A similar effect of the mixing ratio on the yield was also observed for the Fe–Ni system [12].

Fig. 1 shows a typical TEM picture of SWNTs in the cathode soot obtained from the Rh–Pt catalyst. Bundles of SWNTs are entangled with each other, exhibiting 'highway junction'-like patterns. Dark spherical particles with diameters of 10–20 nm were Rh–Pt alloy with the fcc structure, as revealed by electron diffraction and XRD. The composition of alloy particles was estimated to be Rh–54 atom% Pt from the measured lattice constant ($a = 0.386$ nm). The length of SWNTs exceeds 10 μm. Similar growth morphology is commonly observed for samples containing long SWNTs at high density, e.g. soot samples obtained from Y–Ni and Fe–Ni catalysts, which are known to be the most efficient catalysts for yielding SWNTs by arc evaporation [11–13].

Raman scattering spectroscopy also exhibited the presence of SWNTs at high density. Fig. 2 shows spectra in the optical-mode region of graphite

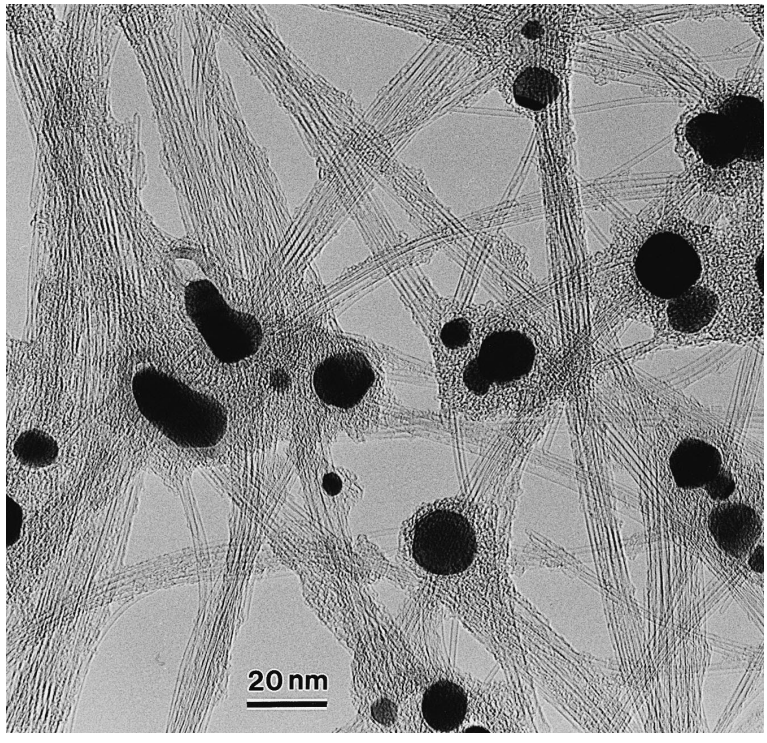

Fig. 1. TEM picture of single-wall carbon nanotubes grown in soot around the root of a cylindrical hard deposit. Rh–50 wt.% Pt catalyst was used.

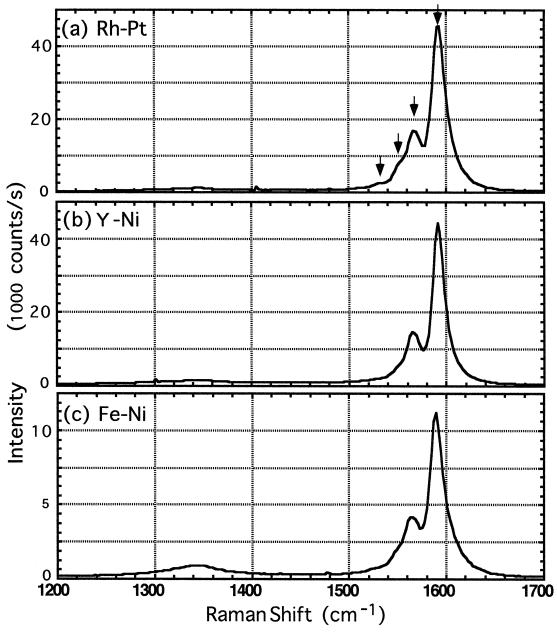

Fig. 2. Raman scattering spectra in a frequency region of the optical modes of SWNTs obtained from as-prepared soot (raw soot) containing SWNTs produced from (a) Rh–Pt, (b) Y–Ni and (c) Fe–Ni catalysts. Prominent peaks centered at 1580 cm^{-1} are due to the E_{2g} (stretching) mode. A weak broad hump observed at 1340 cm^{-1} is due to amorphous carbon.

(1200–1700 cm^{-1}) recorded from the cathode soot obtained from three catalysts. The three samples in Fig. 2 were prepared under the optimal conditions for the respective catalysts; see Ref. [13] for Y–Ni and Ref. [12] for Fe–Ni. Peaks centered at 1580 cm^{-1} have been assigned to the E_{2g} (stretching) mode of graphite [16,17]. Splittings of the E_{2g} mode observed for the three samples are characteristic of SWNTs [16–19]. The sample obtained from Rh–Pt exhibits the splitting most clearly, as indicated by the arrows in Fig. 2a, suggesting the narrow distribution of the diameters of the SWNTs [17]. A broad hump, slightly observed at 1340 cm^{-1}, resembles the hump observed commonly in graphitic materials of small sizes or with structural imperfections [20]. Therefore, the observed hump is attributed to other carbonaceous materials (e.g. amorphous carbon) synthesized together with SWNTs. The ratio of the peak height at 1580 cm^{-1} to that at 1340 cm^{-1} reflects the abundance of SWNTs in the soot [13,16,17]. The measured average ratios are approximately 50 for Rh–Pt, 40 for Y–Ni and 13 for Fe–Ni, showing that the Rh–Pt mixture is equally or more effective for producing SWNTs than other well-known mixed catalysts, Y–Ni and Fe–Ni. Thus, the density of SWNTs in the cathode soot produced from Rh–Pt is expected to be at least 50%, which is comparable to that obtained from the Y–Ni catalyst.

Fig. 3a shows the histogram of the diameters of SWNTs obtained from the Rh–Pt catalyst at 600 Torr of helium, as measured by TEM. The distribution is narrow, though exceptionally thick tubes (2.5–2.6 nm in diameter) are present as a minority. A mean diameter of about 1.28 nm with a standard deviation of only 0.07 nm, is obtained when the thick tubes are disregarded. The narrow distribution of diameters was also confirmed by Raman scattering in the 'breathing modes' region, as shown in Fig. 4. The spectrum was obtained from as-prepared soot containing SWNTs with laser excitation at 488 nm. Resonance Raman spectra recently reported [21] show

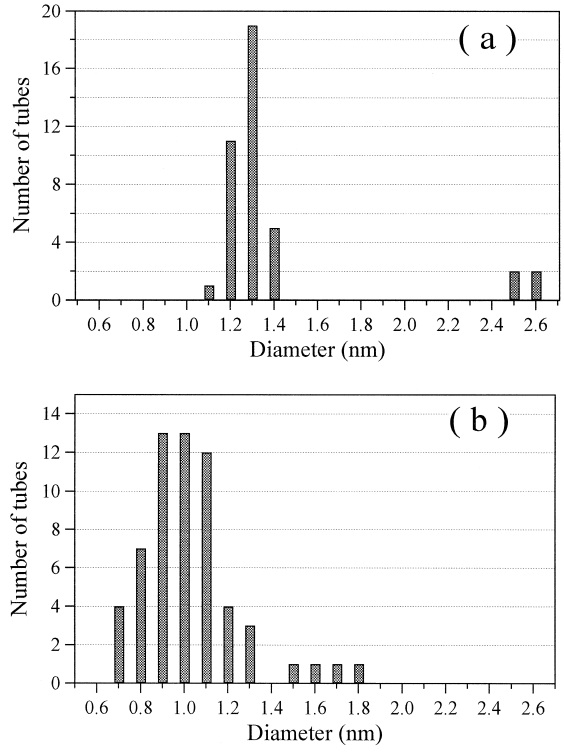

Fig. 3. Histogram of diameters of SWNTs in the cathode soot produced from the Rh–Pt catalyst at (a) 600 Torr and (b) 50 Torr of helium.

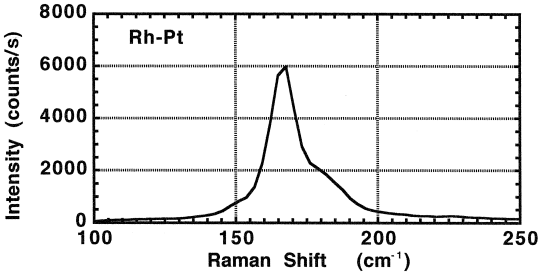

Fig. 4. Raman scattering spectrum in the frequency region of so-called 'breathing modes' of SWNTs. The spectrum was obtained from cathode soot containing SWNTs produced from Rh–Pt catalysts. One prominent peak at 167 cm^{-1} and a shoulder at 185 cm^{-1} are observed. The diameters of SWNTs corresponding to these Raman shifts are 1.33 and 1.21 nm, respectively.

that all the 'breathing modes' lying in the range of 170–200 cm^{-1} are on resonance at 488 nm and exhibit nearly equal intensities. In the spectrum obtained with 488 nm excitation (Fig. 4), only a prominent peak at 167 cm^{-1} accompanying a hump around 185 cm^{-1} is observed. This suggests that the diameters of the SWNTs are restricted to only a few values. Raman shifts originating from the 'breathing modes' of SWNTs are sensitive to the diameters of the SWNTs; they are approximately proportional to the inverse of the diameter of the SWNT [18,19]. The observed Raman shifts at 167 and 185 cm^{-1} correspond to diameters of 1.33 and 1.21 nm, respectively, which is consistent with the TEM observation (Fig. 3a).

The diameters of SWNTs obtained from the Rh–Pt catalyst depended on the pressure of helium gas in the reaction chamber. Thinner SWNTs were obtained at lower helium pressure, though the yield of SWNTs decreased. Thin SWNTs with diameters of 0.7–1.3 nm were obtained at 50 Torr of helium, as shown in Fig. 3b. The pressure dependence of the diameters of SWNTs was observed for other catalysts such as Fe–Ni [22]. Details of the pressure dependence will be published elsewhere.

4. Conclusion

Using the binary Rh–Pt catalyst, we were able to synthesize SWNTs in a high density. The density in raw soot was comparable with that prepared from Y–Ni. The distribution of the diameters, centered at 1.28 nm, was very narrow with a standard deviation of only 0.07 nm. The catalysts used so far to synthesize SWNTs with high yields contained ferromagnetic metals. In contrast, the Rh–Pt mixture is free from magnetic metals. Therefore, the SWNT samples produced from the present mixture should be more suitable for studies of the electric and magnetic properties of SWNTs.

Acknowledgements

This work was supported by the Yazaki Science and Technology Foundation, the Aichi Science and Technology Foundation and the Research Foundation for the Electrotechnology of Chubu.

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