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Efficiently producing single-walled carbon nanotube rings and investigation of their field emission properties

Li Song[1,5], Lijie Ci[2], Chuanhong Jin[1], Pingheng Tan[3], Lianfeng Sun[4], Wenjun Ma[1], Lifeng Liu[1], Dongfang Liu[1], Zengxing Zhang[1], Yanjuan Xiang[1], Shudong Luo[1], Xiaowei Zhao[1], Jun Shen[1], Jianjun Zhou[1], Weiya Zhou[1] and Sishen Xie[1,6]

[1] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[2] Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA
[3] Institute of Semiconductors, State Key Laboratory for Superlattices and Microstructures, Chinese Academy of Sciences, Beijing 100083, People's Republic of China
[4] National Centre for Nanoscience and Nanotechnology, Beijing 100080, People's Republic of China
[5] Graduate School of Chinese Academy of Sciences, Beijing 100093, People's Republic of China

E-mail: ssxie@aphy.iphy.ac.cn

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Abstract
Single-walled carbon nanotube (SWNT) rings with a diameter of about 100 nm have been prepared by thermally decomposing hydrocarbon in a floating catalyst system. These rings appeared to consist mostly of SWNT toroids. High resolution transmission electron microscopy showed that these rings were composed of tens of SWNTs with a tightly packed arrangement. The production of SWNT rings was improved through optimizing various growth parameters, such as growth temperature, sublimation temperature of the catalyst, different gas flows and different catalyst components. The growth mechanism of the SWNT rings is discussed. In the field emission measurements we found that field emission from a halved ring is better than that from a whole SWNT ring, which contributed to the better emission from two opened ends of the nanotubes of the halved SWNT ring.

1. Introduction

Carbon nanotubes (CNTs) have been proposed as ideal candidates for the fabrication of nanoelectronic devices [1]. Single-walled carbon nanotubes (SWNTs) are attracting even more interest, due to their being closer to an ideal one-dimensional system. SWNTs have usually been observed to arrange in a regular string-like pattern consisting of several tens of parallel nanotubes [2, 3]. Recently, numerous studies have focused on the role of annular structural deformations on the electronic properties of SWNTs. Theoretical considerations have predicted that the electronic characteristics of carbon nanotubes with an annular geometry could be very useful for investigating interesting physical phenomena such as the Aharonov–Bohm effect and magnetotransport [4, 5]. Many methods have been developed to prepare carbon nanotubes with annular geometry, such as rings and coils. Liu *et al* [6] reported the observation of SWNT toroids ('crop circles') with about 0.01–1% yield in their laser-grown SWNT deposits. The rings obtained in their work typically had a diameter of 300–500 nm and a thickness in the range 5–15 nm. Nagy and co-workers observed a small number of multi-walled carbon nanotube rings of typically 500 nm diameter in the

[6] Author to whom any correspondence should be addressed.

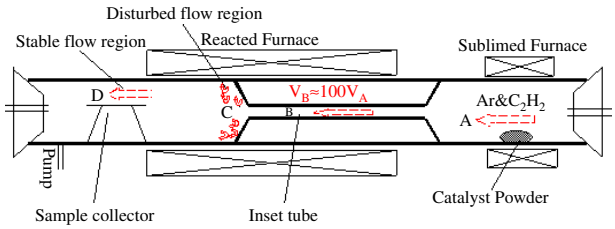

Figure 1. Schematic diagram of the experimental set-up. (This figure is in colour only in the electronic version)

raw material produced catalytically by thermal decomposition of hydrocarbon gas [7]. Colomer *et al* [8] observed rings in a sample obtained by reducing $Mg_{0.9}Co_{0.1}O$ solid solution in an H_2–CH_4 atmosphere. Martel *et al* [9] found that straight SWNTs were induced to organize themselves into rings or coils under ultrasonic irradiation. McEuen's group indicated that rings of carbon nanotubes could be made by evaporating a dilute suspension of bucky tube ropes in dichloroethane on a silica substrate [10]. Most recently, Sano *et al* [11] reported that lightly etched SWNTs could be chemically reacted to form rings with an average diameter of around 540 nm. In most previous work, the rings observed have diameters of greater than 300 nm. Theoretically, rings with radii of curvature much smaller than 100 nm can be generated in principle, although there are no clear experimental observations of such small carbon nanotube rings [12].

In this work we report on the preparation of large scale rings of SWNT bundles in a floating catalyst chemical vapour deposition (CVD) system. The rings obtained have a smaller diameter of about 100 nm, compared with the rings produced in previous works. We found that the production of SWNT rings is related to growth temperature, sublimation temperature of the catalyst, the type of gas flow and different catalyst components or hydrocarbon sources. The results indicated that the production of rings or strings of SWNTs could be selected, depending on the different experimental parameters. We showed that the yield and the quality of SWNT rings could be further increased with better optimized growth parameters. In the field emission measurements we found that field emission behaviour from a halved SWNT ring is better than that from a whole SWNT ring.

2. Experimental section

Our experimental set-up was a two-stage furnace system fitted with an inner quartz tube; the inner tube with a much smaller diameter of 5 mm is inserted in the outer quartz tube (30 mm i.d.), as shown in figure 1. Ferrocene (dicyclopentadienyl iron) and sulfur powder, acting as the catalyst source, were mixed uniformly and ground with a mortar. The catalyst mixture was sublimed in the first furnace at a temperature of 40–70 °C. The sublimed catalyst was carried by a flowing argon (100–1000 sccm) and acetylene (1–5 sccm) mixture into the reaction furnace. The growth temperature of the CNTs was varied from 850 to 1200 °C. The pressure inside the quartz tube was held constant at 1 atm in all our experiments. The products were deposited on the collecting substrate placed at the end of the reaction furnace.

As typical growth parameters, the temperatures of the two furnaces were controlled at 52 and 1100 °C, respectively, and the flow rates of Ar and C_2H_2 gas were about 500 and 1 sccm. Ring growth usually took 1 h. In order to investigate the effect of the experimental parameters, we adjusted different parameter values. While investigating the effect of a certain parameter, the other parameters were used with the above typical values.

Scanning electron microscopy (SEM, S-5200), transmission electron microscopy (TEM, CM200) and micro-Raman scattering spectra (Dilor Superlabram) were performed to characterize SWNT rings samples. Field emission measurements were performed inside a Tecnai G2 TEM with use of a Nanofactory TEM-STM holder [13]. The as-grown SWNT rings assembled directly onto a clean platinum wire by van der Waals force. An electrochemically etched sharp tungsten tip was controlled to move toward and make contact with the selected SWNT ring, which extended out from the edge of the platinum wire. An individual SWNT ring was spot-welded to the tungsten tip by means of a short, controlled electrical pulse, and sometimes a halved SWNT ring was formed with the ring itself broken by the application of a large current. Then the tungsten tip mounted with the SWNT ring was retracted for field emission measurements. The maximum voltage was 140 V and the typical vacuum level was about 10^{-5} Pa.

3. Results and discussions

3.1. General results

Figure 2 reveals the structure of the as-grown samples in our experiments. The SEM image in (figure 2(a)) shows that SWNTs deposited on the silicon substrate are circular. The diameter of most of the rings is about 100 nm, and the thickness of rings ranges from 15 to 30 nm, similar to that of previous SWNT products [14]. The high resolution (HR) TEM image (figure 2(b)) shows that the as-grown ring is made up of SWNT bundles decorated with many small particles. The particles are iron catalysts encapsulated by several graphite layers, confirmed by energy-dispersive x-ray (EDX) analysis. It is also clearly revealed by HRTEM that the nanotube ring is composed of tens of SWNTs in a tightly packed arrangement, as shown by a sectional view of the ring in figure 2(d). From the sectional view, we obtained that the diameter of SWNTs inside the ring bundle is 1–2 nm.

Raman scattering spectra were recorded at room temperature. As-grown samples were excited using the 632.8 nm line of a He–Ne laser with a spatial resolution of less than 2 μm. Figure 3 shows typical Raman spectra of SWNT rings. The tangential mode of the SWNT rings is revealed with several splitting peaks at 1540, 1562 and 1592 cm^{-1}, which are designated as the C–C stretching mode [15]. The detail radial breathing mode (RBM) of SWNT rings is shown in the inset of figure 3. According to the relationship between the RBM frequency and the diameter [16], the diameter of SWNTs inside the ring bundles ranges from 1 to 1.5 nm, which agrees with HRTEM observations.

3.2. The effect of preparation parameters

3.2.1. The growth temperature of the reaction furnace. First, we optimize the growth temperature. After that, it is found that

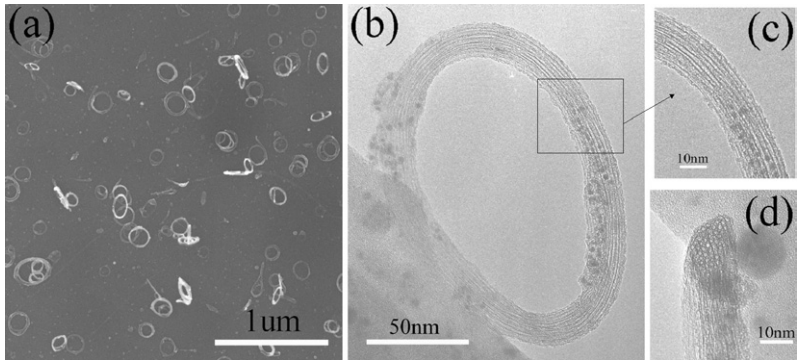

Figure 2. SEM (a) and TEM (b) images of SWNT rings. A high magnification TEM image of ring is shown in (c) and a cross-sectional HRTEM image of an SWNT ring in (d).

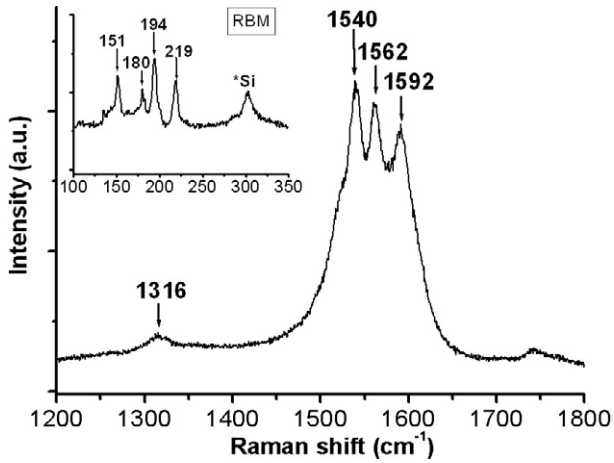

Figure 3. The micro-Raman spectrum of SWNT rings, measured with a laser excitation wavelength of 632.8 nm (1.96 eV).

SWNTs could be better synthesized at a temperature of 1050–1150 °C. A comparison of the results for different growth temperatures is shown in figure 4. At a low temperature below 1000 °C we found that there were few SWNT ring products deposited on the silicon substrate (figures 4(a) and (b)). With the temperature was increased, the rings circles composed of SWNT bundles became plentiful, as shown in figure 4(c). On the other hand, most of the products obtained at temperatures over 1200 °C were amorphous carbon (figure 4(d)), ascribed to the much quicker thermal decomposition of C_2H_2 at higher temperatures [17].

3.2.2. The sublimation temperature of the catalyst. The sublimation temperature of the catalyst was shown to be a crucial factor for producing SWNT rings in our experiments. A comparison of the results is shown in figure 5. We found that when the sublimation temperature was less than 50 °C almost no products could be obtained on the substrate (figure 5(a)). When the sublimation temperature was controlled at 58 °C, SWNT rings were synthesized with a high yield (figure 5(c)). With an increase in the sublimation temperature from 50 to 60 °C, it is found that the relative proportion of ring-shaped SWNTs decreases, as shown in figures 5(b) and (c). When the sublimation temperature was higher than 65 °C, almost all the products are bundles of string-like SWNTs which were entangled with each other (figure 5(d)). This indicates that the production of SWNT rings or strings could be selected depending on the growth parameters. It is known that the supply of iron catalyst is controlled through changing the sublimation temperature of the catalyst. When the sublimation temperature was higher than 65 °C, more sublimed catalyst powder was supplied to the thermally decomposed carbon and more SWNT bundles were produced in the reaction region, which should affect the ring growth process. The optimum sublimation temperature for the growth of nanotube rings is in the range of 52–58 °C.

3.2.3. The total flow of acetylene and argon. The total flow of C_2H_2/Ar is also an important parameter for growth of SWNT rings in our experiments. The results with different gas flow are shown in figure 6. When the total flow is in excess of 800 sccm, most of the products are SWNT strings (figure 6(a)). Upon decreasing the flow rate, a few nanotube rings were deposited on the substrate (figure 6(b)). It is worth noting that plentiful SWNT rings were obtained at a total flow rate of 400 sccm, as shown in figure 6(c). Upon further decreasing the flow rate, the yield of nanotube rings become lower (figure 6(d)). At a low total flow rate below 100 sccm, no SWNT product was deposited on the substrate. Therefore, we found that the optimum total flow is in a range from 400 to 600 sccm. In the meantime, the acetylene could be optionally adjusted in the range of 1–3 sccm while the argon was controlled between 400 and 600 sccm.

3.2.4. The effect of catalyst and carbon source. We also tried to investigate the effect of sulfur in the catalyst. The yield of SWNT rings decreased when we used ferrocene to replace the mixture of ferrocene and sulfur as the catalyst even under the same experimental conditions. It is worth noting that the average diameter of rings (∼70 nm) obtained using ferrocene catalyst was smaller than the average diameter of rings produced using sulfur and ferrocene as the catalyst, as shown in figures 7(a) and (b). We also found that there were fewer impurities observed inside the bundle of SWNT rings, because the amount of sublimed iron catalyst decreased when we used ferrocene as the catalyst without a sulfur promoter [18].

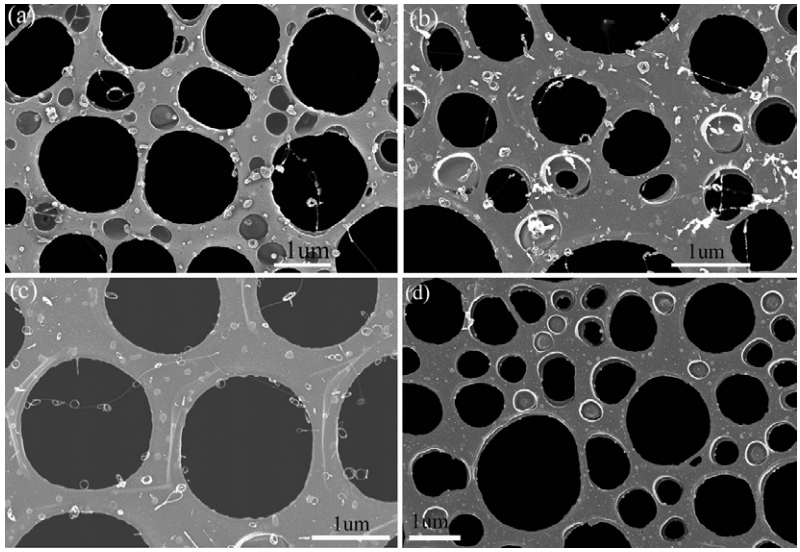

Figure 4. SEM images of SWNT rings synthesized at different growth temperatures and deposited on copper grids. Shown in (a)–(d) are images corresponding to growth temperatures of 900, 1000, 1100 and 1200 °C, respectively. The other parameters were used with the typical values.

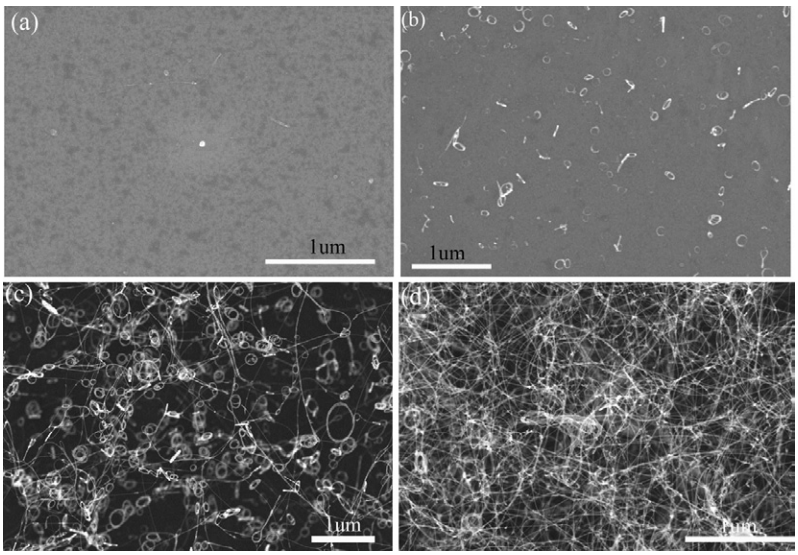

Figure 5. SEM images of SWNT rings synthesized at different sublimation temperatures of the catalyst. Parts (a)–(d) correspond to sublimation temperatures of 48, 52, 58 and 64 °C, respectively. The other parameters had the typical values.

We used methane (CH_4) to replace acetylene as the carbon source in our experiments. The results reveal that SWNT rings also could be synthesized by decomposition of CH_4 in this floating iron catalyst system, although the yield is not satisfactory. The different decomposition temperatures of C_2H_2 and CH_4 contributed to the different yields of as-grown products [19].

3.3. The growth mechanism of SWNT rings

According to previous reports, there are several different formation mechanisms for carbon nanotube rings. Liu *et al* [6] suggested a Kekuléan image of a growing nanotube eating its own tail to explain the formation of SWNT rings in their laser-grown material. Martel *et al* [9] reported that the rings resulted from the folding of nanotubes onto themselves under ultrasonic irradiation. On the theoretical side, carbon rings can be considered either by introducing curvature defects in the helical nanotubes or by bending a straight nanotube elastically so that it closes upon itself [20]. Herein, we suggest that the SWNT rings were formed by the nanotube bundles curling and attaching upon themselves as a result of the growth kinetics and disturbance of the gas flow. The growth kinetics is ascribed to the different growth rates of SWNTs inside the bundles [21, 22]. Based on the conformation of the set-up, the flow would have a disturbed region at the end of the inset tube ('C' region in figure 1), which plays an important role for the formation process of SWNT rings. Therefore, an optimum gas flow (200–600 sccm) may be of advantage for forming an

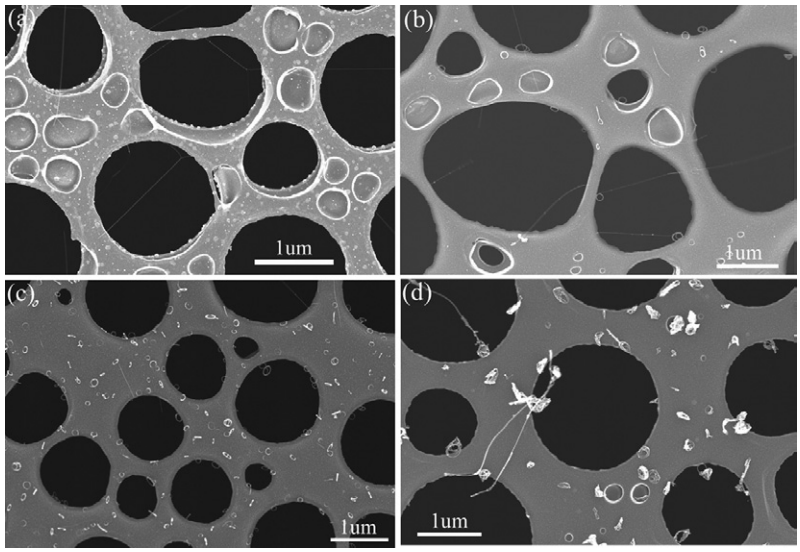

Figure 6. SEM images of SWNT rings synthesized with different total flow rates of acetylene and argon. Parts (a)–(d) correspond to gas flows of 800, 600, 400 and 200 sccm, respectively. The other parameters had the typical values.

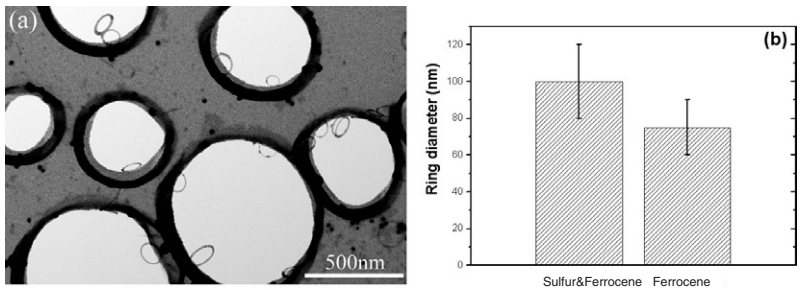

Figure 7. TEM (a) image of SWNT rings synthesized with ferrocene as the catalyst and (b) the distributed histograms of ring diameter before and after removal of sulfur from the catalyst mixture. The other parameters had the typical values.

appropriate disturbed region. Obviously, the different nanotube densities also affect the disturbed region, which agrees with the effect of the sublimation temperature on the formation process of rings in the above experiments. According to elasticity theory [20], the stability condition of rings implies that the radius of rings R should be larger than a critical value $R_c = \pi r^2 Y/4\sigma$, where r is the carbon nanotube radius, Y is the Young's modulus and σ is the surface tension of graphite perpendicular to the basal planes (4.2 J m^{-2}). The above Raman spectra indicated that the diameters of the SWNTs inside the rings ranged from 1 to 1.5 nm (radius: 0.5–0.75 nm). With $Y = 1$ TPa [23], we can calculate that the critical radius of rings is 105 nm for a ring made of a nanotube of radius 0.75 nm and $R_c = 46$ nm for a ring made of a nanotube with a radius of 0.5 nm. This agrees with the value of the ring diameter found in our experiments. As to the effect of sulfur, Cheng *et al* [24] reported previously that the diameter of as-grown nanotubes would increase upon adding sulfur to the catalyst during synthesis of SWNTs in a floating CVD system. Therefore, the diameter of SWNTs decreases when we used ferrocene to replace the mixture of ferrocene and sulfur as the catalyst. SWNTs with a smaller diameter would form smaller SWNT rings, in agreement with our experimental results.

3.4. Field emission of the SWNT ring

For the field emission experiments, SWNT rings adhering to a tungsten tip acted as the cathode and a platinum electrode acted as the anode. Details of the *in situ* TEM set-up have been reported previously [13]. Figure 8(a) shows a typical SWNT ring–tungsten tip and platinum anode geometry, and figure 8(c) shows the corresponding I–V curve and Fowler–Nordheim (F–N) plot for a tip/platinum electrode distance of 0.52 μm. For the whole SWNT ring sample, a field emission current of about 10 nA appears at a voltage of 95 V when the distance between the ring–tungsten tip and the platinum electrode is controlled at 0.52 μm. Moreover, if the distance increased to 3 μm, no emission current could be found, even when loading the maximum voltage of 140 V on the electrodes. Although it is a very crude approximation, the F–N theory is still frequently used as a mathematical interpretation of field emission from different materials [25]. The F–N equation can be given as $I = \alpha E_{\text{eff}}^2 \exp(-\beta/E_{\text{eff}})$, where α is a constant that is related to the geometry of the system, E_{eff} is the effective electric field at the emitting site, and β is a constant which is proportional to the work function. The electric field at the nanotube may be related to the applied voltage V via $E_{\text{eff}} = \gamma V/d$, γ being the field enhancement factor and d the distance between the ring–tungsten tip and the platinum electrode. Assuming that the

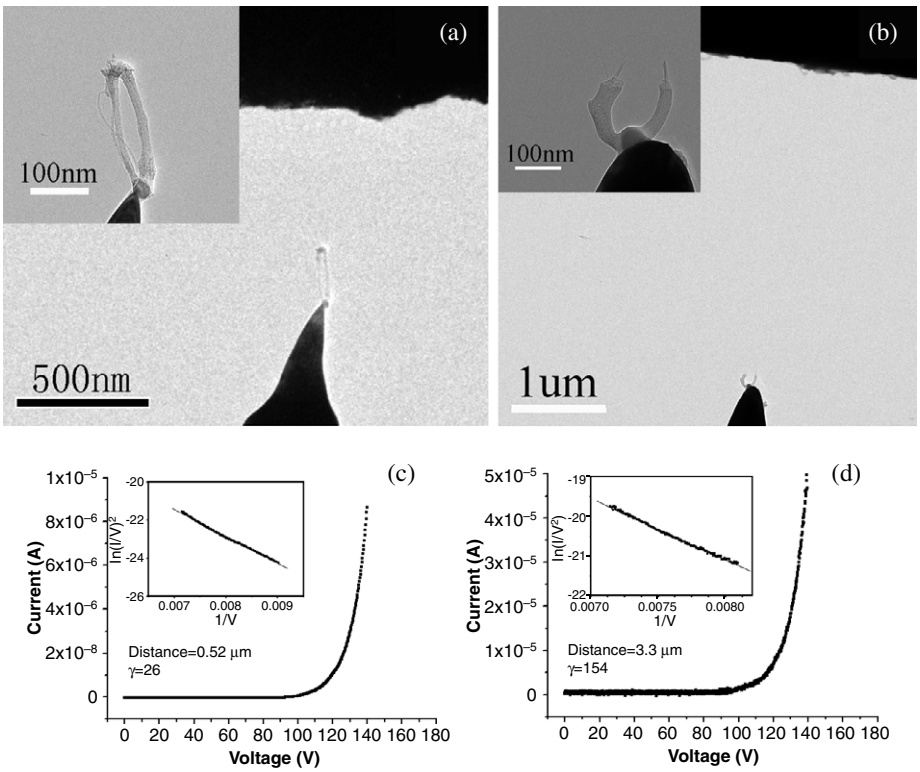

Figure 8. TEM images of the electrode and tip geometry. Part (a) shows a whole SWNT ring–tungsten tip and platinum anode geometry with an electrode distance of 0.52 μm and part (c) shows the corresponding I–V and F–N plots. Part (b) shows a halved SWNT ring–tungsten tip with an electrode distance of 3.3 μm and (d) shows the corresponding I–V and F–N plots.

work function of the SWNTs is the same as that of graphite, i.e. ∼5 eV [26], we obtained a low field-enhancement factor $\gamma = 26$ that may be related to the field emission from the nanotube sidewalls of the ring bundles [27]. On the other hand, a halved SWNT ring with two broken ends was obtained in our experiments, as shown in figure 8(b). Figure 8(d) shows the field emission results performed on the halved ring. For the halved SWNT ring sample, we found that an obvious field current appears at a voltage of 115 V when the distance between the ring–tungsten tip and the platinum electrode is controlled at 3.3 μm. Calculated from the F–N plot, the field enhancement factor γ for the halved SWNT ring is 154, which is consistent with earlier studies on the emission from individual tube tips [28]. The above results indicate that the field emission behaviour from a halved SWNT ring is better than that from a whole SWNT ring. Considering its shape, we believe that the better field emission is related to the two opened ends of the halved SWNT ring. We suggest that the field emission capability from opened SWNT ends is better than that from SWNT sidewalls. However, it looks as if both whole and halved ring samples are not clean but have some tiny tubes extruding from the ring, as shown in the inserts to figures 8(a) and (b). We think that these tiny tubes may also affect the field emission results.

4. Conclusions

In summary, we have successfully prepared small-diameter SWNT rings (diameter about 100 nm) by thermally decomposing hydrocarbons in a floating iron catalyst system. The ring comprises tens of SWNTs with a tightly packed arrangement. To improve the production of rings we optimized various growth parameters. It was found that the optimal reaction temperature is about 1100 °C and the sublimation temperature of the catalyst needs to be controlled at 52–58 °C. A suitable gas flow rate played a key role in producing the rings; it should be controlled in the range of 400–600 sccm. The impurities decorating the inside of the bundles of SWNT rings were decreased remarkably and the diameter of the SWNT rings became smaller when we used ferrocene to replace the mixture of ferrocene and sulfur as the catalyst. Moreover, field emission measurements were performed inside an *in situ* TEM. Compared with the whole SWNT ring, the halved SWNT ring showed a better field emission behaviour due to its opened nanotube ends. This suggests that the field emission capability from opened SWNT ends is better than that from SWNT sidewalls.

Acknowledgments

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