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'Pulsed' CVD growth of single-walled carbon nanotubes

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The potential for using single-walled carbon nanotubes (SWNTs) as building blocks for nanoelectronic devices has been recognized since their discovery in 1993 [1–4]. However, such usage has been limited because the controlled growth of carbon nanotubes with defined atomic structures and electrical properties is not currently possible. Recently, a few attempts have been made to obtain and study nanotube products with various types of junction structures. For example, intramolecular junctions have been fabricated with mechanical manipulation [5], electron irradiation [6] or occasionally observed and studied in chemical vapor deposition products [7,8]. These junction structures show diode-like and rectifying behavior and thus will offer great potential and new possibilities for the use of SWNTs in nanoelectronics devices. To be different from the normal chemical vapor deposition (CVD), we describe here a novel approach, 'pulsed' CVD—intermittent feeding of the carbon source, for the controlled growth SWNTs. The results indicate that this approach provides a higher yield and high purity of SWNTs products compared with normal CVD process. Most interestingly, the intermittent feeding of the carbon source interrupted the growth of SWNTs, and thus introduced more pentagon–heptagon pair defects in the structure of individual SWNTs, forming intramolecular junctions.

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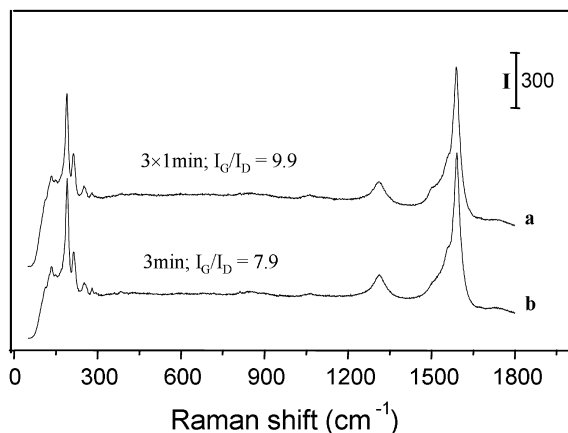*E-mail addresses:* jzhang@chem.pku.edu.cn (J. Zhang), lzf@chem.pku.edu.cn (Z. Liu).

The procedure of normal and pulsed CVD was described as follows. MgO supported Fe catalyst [9] was inserted into a tube furnace and heated to 850 °C in 300 sccm Ar flow. Methane was then fed in at a flow rate of 50 sccm for a desired time, after which the system was cooled down to room temperature. For pulsed CVD process, methane gas was introduced for several times, each lasting 1 min and separated by 1-min intervals, during which the system was kept at 850 °C. The as-prepared materials were treated with 37% HCl to remove the catalyst, and then dispersed in 1,2-dichlorobenzene or 1,2-dichloroethane. The morphology of the SWNTs was characterized by AFM, STM, SEM and TEM. Carbon yield was measured by heating the as-prepared soot in air at 900 °C and measuring the weight loss relative to the weight of the remainder.

Fig. 1 shows the Raman spectra of SWNTs grown by pulsed CVD (3×1 min) and normal CVD (3 min). For SWNTs, four Raman bands are strongly enhanced. Three of them are located around 1600 cm^{-1} and the fourth strong band appears around 200 cm^{-1}, which is unique to SWNTs indicating the SWNTs' prepared by the two methods show the same characteristics. The only difference is the ratio between I_G and I_D, which is shifted from 9.9 for pulsed CVD to 7.9 for normal CVD, indicating that a high purity of SWNTs products can be obtained in pulsed CVD.

Fig. 2 shows the relationship between the yield of SWNTs and growth time using normal and pulsed CVD processing methods, respectively. Initially, the yield of

Fig. 1. Raman spectroscopy of SWNTs grown by pulsed CVD (3×1 min) (a), and normal CVD (3 min) (b).

Fig. 2. The yield of SWNTs grown with normal CVD and pulsed CVD.

carbon deposits increased rapidly with growth time under normal CVD processing, but slowed down remarkably after 2–3 min, approaching plateau values. The maximum yield was around 17% after 1 h. In contrast, the weight gain of carbon deposits obtained by pulsed CVD processing was clearly greater than that obtained by normal CVD processing for the same times. For example, when 1+1+1
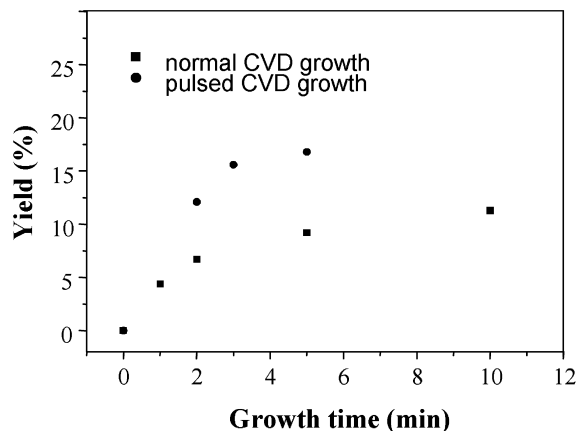
min pulsed CVD processing was used, the resulting yield (16.5%) approached that of the maximum value obtained by normal CVD processing, despite the fact that the total time for the pulsed CVD processing was only 3 min, indicating that pulsed CVD processing was more favorable for the growth of SWNTs. However, when methane gas was intermittently injected for >5 times (1+1+1+1+1+
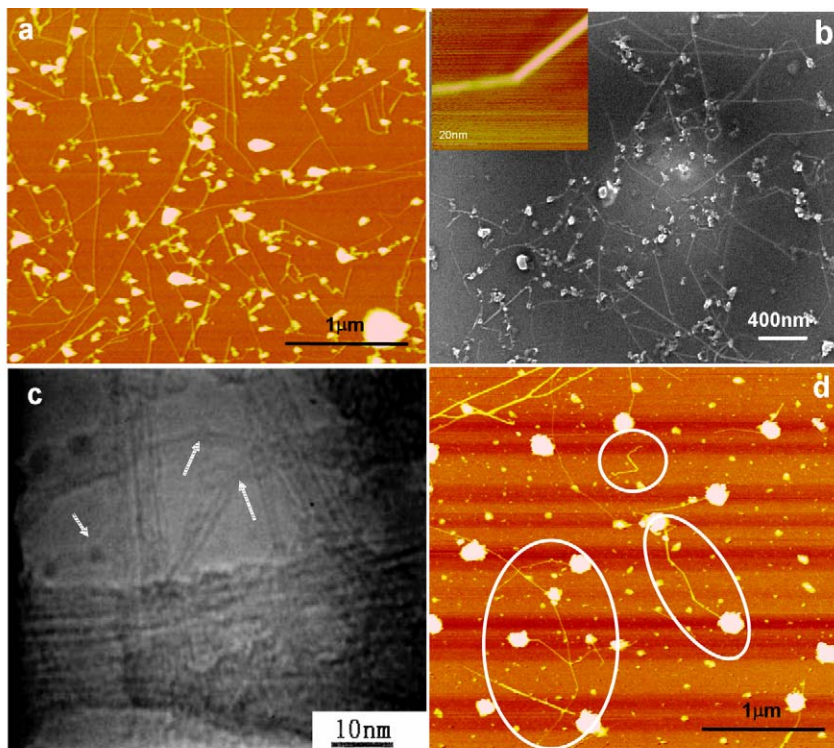

Fig. 3. AFM, SEM STM and TEM images of SWNTs grown by pulsed CVD with two 1-min pulses ('1+1 min') (a–c), and three 1-min pulses ('1+1+1 min') (d).

1 min), no further increase was found in the yield, suggesting that the pulsed CVD method rapidly reached equilibrium for SWNT growth. It was also observed that shorter pulsed CVD processing times (1+1 min) produced a greater effect on the yield compared with longer times (e.g. 2+2 min). This suggested that the growth of SWNTs was a rapid process. In additional, SWNTs products obtained by the pulsed CVD processing showed a higher purity compared with the normal (uninterrupted) CVD methods performed for similar time periods.

Most interestingly, we found the intramolecular junctions were formed during the pulsed CVD processing. Fig. 3 shows typical AFM, SEM and TEM images of SWNTs obtained by pulsed CVD processes. When two 1-min pulses were used (named '1+1 min'), the morphology of SWNTs was obviously different from that of SWNTs produced by the normal CVD process, with many bends and kinks observed in individual SWNTs (Fig. 3a and b). Compared with the normal CVD, the effect of intermittent injection of methane seemed to induce a different growth mode for the SWNTs. Increasing the number of pulses of methane (e.g. three 1-min pulses, named '1+1+1 min') increased the number of kink sites on individual SWNTs (Fig. 3d). It should be noted that increasing the pulse number to more than three had little more effect than that seen in the 1+1+1 min processing (data not shown). This may well be related to the yield of SWNTs obtained by pulsed CVD.

Why is the pulsed CVD process more favorable for the growth of SWNTs, with different morphologies compared to the normal processing methods? This can be explained from an understanding of the CVD growth mechanism for SWNTs [10,11]. Using MgO as the support material for the catalytic growth of SWNTs offered the advantage of evenly dispersing the metal particles over the support materials. In this way, the metal particles could be maintained as small nuclei, avoiding their aggregation into larger metal clusters. As a result, when hydrocarbon molecules passed over the catalyst, individual SWNTs formed as protrusions from almost every metal particle. When the carbon source (in our case methane gas) was intermittently switched on ('pulsed CVD processing'), a nanotube would be expected to protrude from a metal particle during the first injection of methane. During the interval period, due to the absence of further hydrocarbons, the supply of dissolved carbon atoms could conceivably be exhausted locally, leading to the metal particle recovering its fresh catalytic interface. Upon injection of the next pulse of the carbon source, hydrocarbon molecules could be catalytically dissociated and dissolved into the metal particles once again. Two possible mechanisms could now operate: (1) the original carbon nanotube extrusion could continue to grow out in the same direction, in which case, interconnection with the graphene structures of first tube would unavoidably create some topological defects resulting in the formation of kinks on tubes (intramolecular

junctions) and/or (2) extrusion could occur in a different direction, in this case the interconnection with the first tube would be directly achieved by the metal particle (metal particle bridged heterojunctions). Using HRTEM (Fig. 3c), we found evidence of both types of junctions following pulsed CVD growth. Besides, STM images also confirmed the formation of junctions along the tube axis (inset of Fig. 3b). We conclude therefore, that SWNT junctions resulting by the pulsed CVD method are of two distinct types, reflecting their intramolecular junctions induced by topological defects and metal particle bridged heterojunctions.

In summary, intermittent injection of a carbon source was investigated as a process for the CVD growth of SWNTs. It was found that the products of pulsed CVD processing were remarkably different from normal CVD processing in two major aspects. First, pulsed CVD processing provides a higher yield and high purity of SWNTs products compared with normal CVD processing. Second, pulsed CVD processing appears to be an effective means of preparing SWNTs with special structures, notably intramolecular and heterojunctions. The overall number of junctions created appeared to be related to the number of pulses used in the processing. Finally, this methodology could be extended to the pulsed injection of different kinds of carbon source as a means to customizing and generating SWNTs with specific structural features.

Acknowledgements

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