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Preparation of CN_x/Carbon Nanotube Intramolecular Junctions by Switching Gas Sources in Continuous Chemical Vapour Deposition

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ABSTRACT

Nitrogen-doped carbon nanotubes (CN_x)/carbon nanotube intramolecular junctions were prepared by a simple continuous chemical vapour deposition (CVD) method at 650 °C. The catalyst was obtained by calcination of a layered double hydroxide precursor containing Fe and Mg. By switching between hexane and ethylenediamine repeatedly in the CVD process, multiple intramolecular junctions composed of CN_x with a bamboo-like structure and empty hollow carbon nanotubes were observed, and such different structures at both sides of the junctions indicated some interesting properties and offered potential applications for future nanodevices.

KEYWORDS

Nitrogen-doped carbon nanotubes, junction, chemical vapour deposition.

1. Introduction

Carbon nanotubes (CNTs) are considered potential materials for future miniaturized electronics due to their unique electrical, and excellent thermal and mechanical properties.[1,2] In recent years, dramatic advances in the application of CNTs in nanoelectronics have been accomplished. CNTs could be metallic or semiconducting depending on their intrinsic diameter and helicity.[3] Doping CNTs with different elements is a possible method to control the electronic properties of nanotubes in a well-defined way. Research into CNTs doped with nitrogen,[4] boron,[5] potassium[6] and rubidium,[7] or CNTs encapsulated with gallium[8] and filled with iron oxide[9] has been extensively reported. Among these doped CNTs, the nitrogen-doped carbon nanotubes (CN_x) are usually thought to be n-type tubes.[10]

Connecting different types of CNTs to form intramolecular junctions is one of the crucial issues for the development of carbon-based nanodevices.[11] These intramolecular junctions can serve as functional components in the circuit such as rectifiers, switches, amplifiers, photovoltaic devices, etc. Because of their importance, much attention has been focused on this topic and significant progress has been achieved in the synthesis, properties, and applications of the intramolecular junctions of CNTs. The intramolecular junction composed of CN_x and CNTs (CN_x/C) has proved to be a high performance, field-effect, transistor with reproducible rectifying behaviour.[12–14] Another kind of junction composed of boron carbonitride nanotubes (BCNs) and CNTs (BCN/C) has also been observed to have typical rectifying diode behaviour.[15] Recently, different CNTs intramolecular junctions were fabricated.[12–24] ^{12}C-^{13}C multi-walled carbon nanotubes (MWCNTs) intramolecular junction arrays were prepared by a ^{13}C-ethylene isotope labelling method.[16] MWCNTs/MWCNTs junctions were obtained in porous anodic aluminum oxide templates,[17] by arc-discharge[18] or two-step plasma-enhanced CVD methods.[19] MWCNTs/single-walled carbon nanotubes junctions were grown by switching carbon sources between ethyne and methane in a two-step thermal CVD process.[20] CN_x/C and BCN/C junctions were fabricated by introducing different doping sources midway into the CVD process.[12–15,21–24] During the course of CN_x/C junction growth, microwave plasmas[21] and higher growth temperature (950 °C)[13,23] are often required, which limits the large scale preparation of CN_x/C junctions. In this paper, we report a simple method for synthesis of massive CN_x/C intramolecular junctions at 650 °C in a continuous CVD process.

2. Experimental

2.1 Preparation of Catalyst

The catalyst was obtained from layered double hydroxide (LDH) containing Fe and Mg, and the LDH precursor was prepared using a coprecipitaion reaction. A solution containing $Mg(NO_3)_2$ $6H_2O$ and $Fe(NO_3)_3$ $9H_2O$ was added to another solution containing NaOH and Na_2CO_3. The resulting slurry was aged, filtered, washed and dried to form the LDH precursor. The mixed oxides used to grow nanotubes were obtained by calcination of the LDH precursor at 600 °C for 4 h in air. Details have been published before.[25,26]

2.2 Preparation of CN_x/C Intramolecular Junctions

The preparation of CN_x/C intramolecular junctions was carried out in a horizontal furnace with a quartz tube. A thermocouple connected to the program temperature controller was inserted in the middle of the horizontal furnace. About 0.20 g of catalyst was transferred to a quartz boat, inside a quartz tube, and placed in the middle of a furnace, which was heated under a flowing Ar (200 mL min^{-1}) at a rate of 5 °C min^{-1}. On reaching 400 °C, Ar was replaced with H_2 (120 mL min^{-1}). On reaching 650 °C, hexane was pumped into the furnace at a rate of 0.2 mL min^{-1} with a mixture of Ar and H_2 (Ar, 400 mL min^{-1}; H_2, 100 mL

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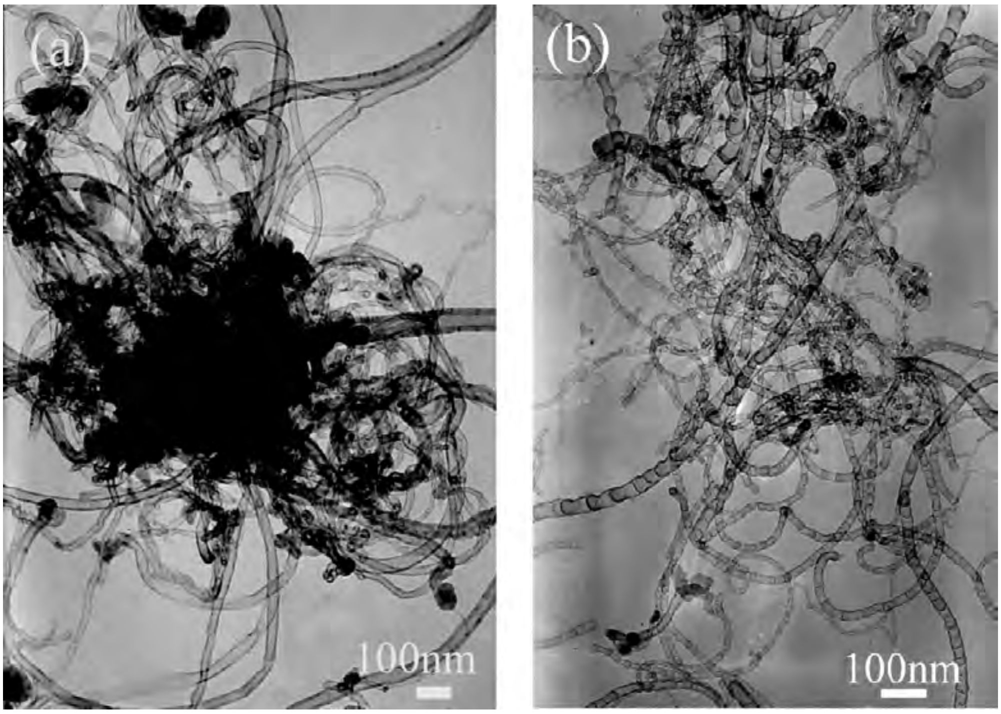

Figure 1 TEM images of MWCNTs (**a**) and CN_x (**b**).

min^{-1}). After 2 min, ethylenediamine, instead of hexane, was feed into the furnace for 2 min. This cycle of hexane/ethylenediamine was repeated for about 10 min, when the furnace was allowed to cool to room temperature under Ar. The furnace took about 8 h to cool. The products were collected in the quartz boat in which the catalyst was placed.

The pure CN_x and CNTs were also prepared according to the above procedure except only ethylenediamine or hexane were used respectively, rather than a mixture of the two.

2.3 Characterization

The morphologies of the samples were observed through transmission electron microscopy (TEM, JEM1200EX, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) using an accelerating voltage of 100 kV, a beam current of 10 A and EDS acquisition time of 100 s. High-resolution electron microscopy (HRTEM) images were taken on a JEM2010 with an accelerating voltage of 120 kV. All samples were suspended in ethanol and a drop of the suspension was deposited on a copper grid and the solvent evaporated.

3. Results and Discussion

From our previous work,[25] the catalyst used to grow nanotubes was α-Fe (bcc) nanoparticles supported on MgO. Figures 1(a) and 1(b) show the TEM images of the pure CNTs and CN_x. Under these experimental conditions, the prepared CNTs are all multi-walled, i.e. MWCNTs. These MWCNTs demonstrate a typical tubular structure with hollow cores. The grown CN_x have obvious bamboo-like morphology with transverse carbon bridges forming a compartment, which can be clearly observed in Fig. 1(b). The N-doped content of these tubes, which is defined by the N/(N+C) atomic ratio, was determined by X-ray photoelectron spectroscopy to be about 6.3 %.[26]

The HRTEM image of one CN_x/C intramolecular junction within an individual tube is indicated in Fig. 2. A remarkable characteristic of the resulting CN_x/C junction is that this tube consists of two sections: one segment with an empty, hollow, cylinder-like structure is MWCNTs obtained from the decomposition of hexane, and the other segment with a curved compartment, bamboo-like structure is CN_x resulting from ethylenediamine. Though these two sections have different structures, both tubes have similar diameters of about 50 nm. As the gas source switches from hexane to ethyenediamine, the tube growth turns from MWCNTs to CN_x. These two different structured tubes can be successfully connected together to form intramolecular junctions. They are called intramolecular junctions because these junctions exist in a molecule or are formed by chemical bonds. The MWCNTs segment could be metallic or semiconducting,[3] while the CN_x segment is usually thought to be an n-type tube,[10] so the CN_x/C intramolecular junctions can produce diodes with a rectifying behaviour.

Figure 3 shows the HRTEM images of two CN_x/C intramolecular junctions within an individual tube. In Fig. 3(a), the tube consists of an empty, hollow, cylindrically structured MWCN in the middle and bamboo-like structured CN_x at the two ends. Similarly, with Fig. 2, the diameters of these three segments are almost unchanged. As far as we know, a tube with this special structure has not been seen elsewhere. This special structure can be labelled as a CN_x/C/CN_x intramolecular junction. The applications of this special structure needs to be further

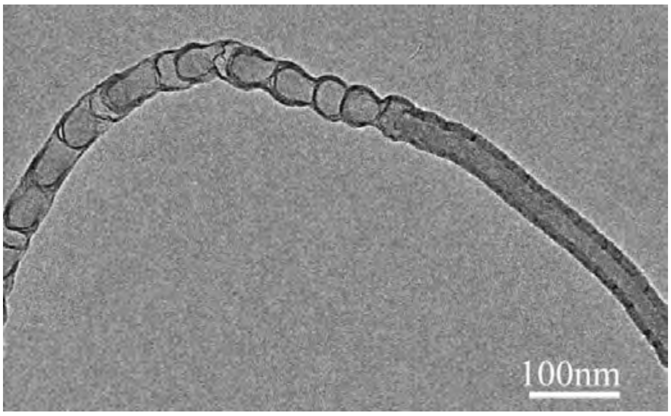

Figure 2 HRTEM image for one junction within an individual tube.

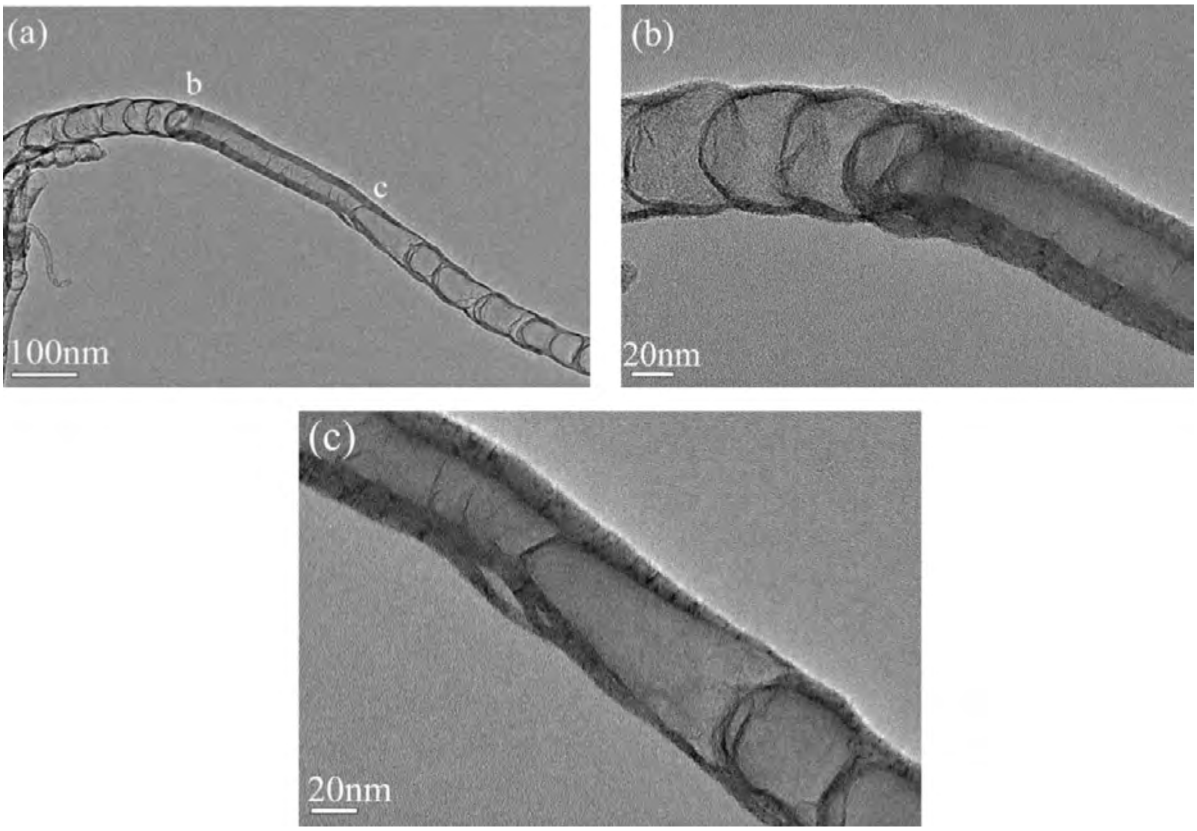

Figure 3 HRTEM images for two junctions within an individual tube: (**a**) $CN_x/C/CN_x$ junction; (**b**) and (**c**) high-magnification images of two junctions in (a).

investigated. High-magnification images of the $CN_x/C/CN_x$ junction are shown in Fig. 3(b) and 3(c), which correspond to the 'b' and 'c' marked in Fig. 3(a). Both images indicate the detailed structures of two CN_x/C intramolecular junctions.

In all the products, a large number of tubes have one or two CN_x/C intramolecular junctions, while a few tubes have three or more junctions. The TEM image of three CN_x/C intramolecular junctions within an individual tube is demonstrated in Fig. 4. The empty hollow cylinder structure MWCNTs (marked 'a' and 'c') and bamboo-like structure CN_x (marked 'b' and 'd') are grown alternatively when switching between hexane and ethyenediamine repeatedly. This structure can be labelled as $C/CN_x/C/CN_x$ intramolecular junction. A black particle indicated by an arrow lies at the interface of the junction between 'b' and 'c' segments. In order to investigate this junction more fully, a TEM, equipped with EDS was used. The EDS of the part indicated by an arrow in Fig. 4 is shown in Fig. 5. The results demonstrate that this section of the tube is made up of C (96.38%, atomic), Fe (2.01%), Cu (1.49%) and a little Si (0.12%). The large amount of C comes from the nanotube; Cu results from the copper grid and the small amount of Si may be from the quartz boat. Thus the EDS results confirm that the black particle is the Fe catalyst. From this we conclude that the catalyst cannot only lie at the tip or the bottom of the tubes, but can also appear in the middle during the growth process of the tubes. The phenomenon has been observed previously in preparing CN_x/C intramolecular junctions via the CVD method by pyrolysis of ferrocene and melamine.[23] It should be pointed out that no catalyst is necessary for connecting CN_x and MWCNT segments. As shown in Figs. 2 and 3, no catalysts can be found at or near the interface of these junctions.

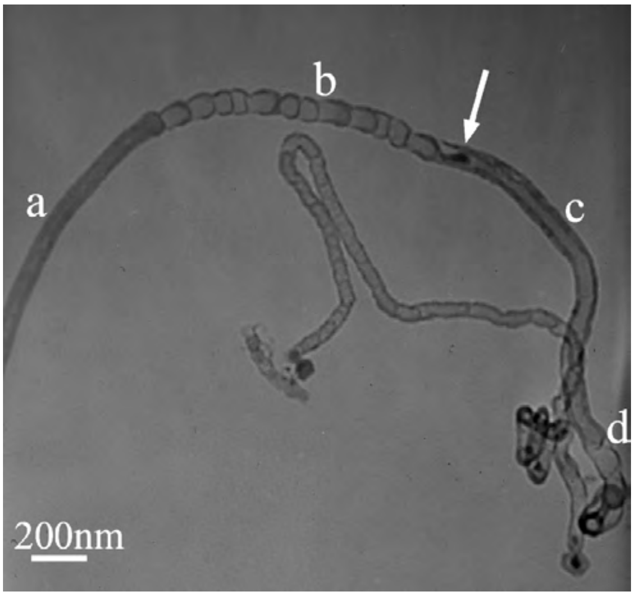

Figure 4 TEM image for three junctions within an individual tube.

4. Conclusions

We report a simple method for the synthesis of massive CN_x/C intramolecular junctions at a relative low temperature (650 °C). Hexane and ethylenediamine were used as C and N sources during the growth progress. The intramolecular junctions are connected together by bamboo-like structured CN_x and empty, hollow MWCNTs. Because of their special and excellent properties, devices based on intramolecular junctions can be used as building blocks in future molecular electronics or nanoelectronics, or they can be integrated and work as functional components in traditional semiconductor circuits. The electrical characterization measurements still need to be carried out with these

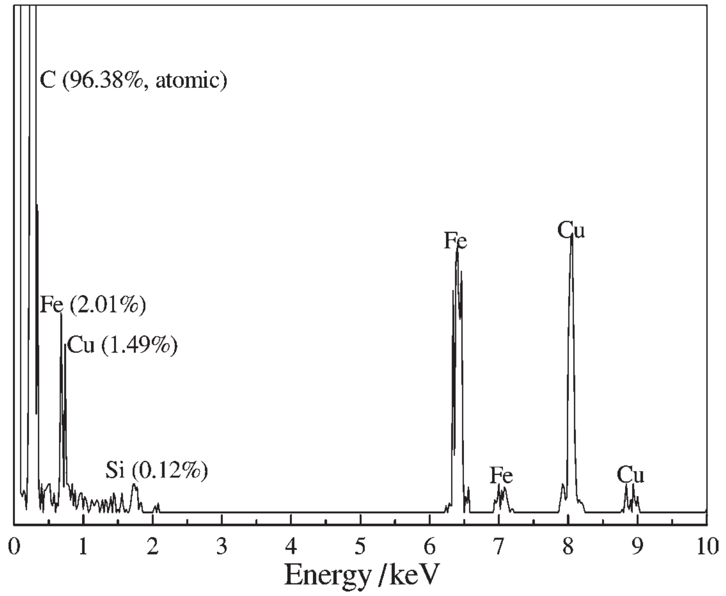

Figure 5 EDS of the region indicated by an arrow in Fig. 4.

products although there are many problems. On the other hand, the results of this work provide a clear picture of the growth process of CNTs in CVD and represent a step forward toward fully understanding the growth mechanism of nanotubes.

Acknowledgements

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