Carbon submicrotubes synthesized on carbon microfibers

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Abstract

Carbon submicrotubes were synthesized on carbon microfibers by floating catalyst method, and carbon nanotubes were also observed to grow on the rough surface of carbon submicrotubes. The morphology, microstructure and composition of the obtained products were characterized by field emission scanning electron microscopy, high-resolution transmission electron microscopy, Raman spectroscopy and energy dispersive X-ray spectroscopy. The growth of carbon submicrotubes on carbon microfibers was attributed to the pretreatment of carbon microfibers, which gave rise to catalyst areas, while the secondary growth of carbon nanotubes could be related to the defects of hexagonal graphite on the surface of carbon submicrotubes.
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1. Introduction

As a special type of one-dimensional materials, organic submicrotubes with hollow structures and sizes between nanoscale and microscale have attracted a great deal of interest due to their unique extraordinary mechanical, electrical and optical properties and potential applications in optoelectronics [1–4]. Similar to carbon nanotubes (CNTs), carbon submicrotubes are hollow and are composed of graphitic structures. Carbon submicrotubes have shown the same exceptional properties as CNTs [5–12]. It is well known that carbon microfibers are conducting and chemically stable, therefore they can be used as a substrate for growing carbon submicro- and nano-tubes. The composites that are composed of submicro- and micro-scale carbon are expected to exhibit more unique properties than that of materials composed of carbon microfibers or submicrotubes only. Moreover, CNTs can also be grown on carbon submicrotubes. It is very interesting to synthesize and characterize these carbon-based composites due to potential applications in optoelectronics and other fields.

In the past, CH_4 (C_2H_2)–H_2, CH_4 (C_2H_2)–H_2–N_2 or CH_4 (C_2H_2)–H_2–Ar gas system was used to prepare carbon nanomaterials (including CNTs etc) by chemical vapor deposition method and catalysts (Fe, Co and Ni, etc) were needed to be sputtered onto a substrate before the deposition [13–16]. However, C_2H_2–N_2 gas system and ferrocene catalyst precursor were simultaneously used to grow carbon nanomaterials without the predeposition process of catalyst by floating catalyst method.

In this paper, we report the synthesis of carbon submicrotubes on carbon microfibers and of CNTs on these carbon submicrotubes using the floating catalyst method that was used to prepare CNTs [17,18]. We study the morphology, composition and microstructure of carbon submicrotubes by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. Finally, we discuss the formation mechanism of carbon submicrotubes on carbon microfibers, and propose a secondary growth mechanism of CNTs on carbon submicrotubes.

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2. Experimental details

2.1. Pretreatment of carbon microfibers

The carbon microfibers used in the experiment are polyvinyl alcohol (PVA)-based activated carbon fibers with a diameter range from 3 to 6 μm. They were prepared from PVA fibers by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences. The pretreatment process of carbon fibers was carried out as follows:

(1) Carbon microfibers were cleaned ultrasonically in acetone and ethanol, consecutively, for 10 min, and were then dried at room temperature.
(2) Carbon microfibers were boiled in a solution of sulfuric acid and nitric acid ($V_{H_2SO_4}$:V_{HNO_3} = 1:3) for 30 min to activate the surface of the carbon microfibers, then they were rinsed for three times with deionised water and dried at room temperature.
(3) A solution of ferrocene and acetone was prepared. First 0.1 g ferrocene was dissolved in 100 ml acetone. The solution was magnetically stirred for 30 min to completely dissolve the ferrocene. Then the activated carbon microfibers were immersed into the solution for about 12 h. Finally, the carbon microfibers were taken out and dried at room temperature.

2.2. Synthesis of carbon submicrotubes

The growth of carbon submicrotubes was carried out in a double-temperature zone tubular furnace with a horizontal quartz tube at atmospheric pressure by floating catalyst method. The schematic diagram of the floating catalyst set-up is shown in Fig. 1. First a quartz boat with carbon microfibers was pushed into the center of the quartz tube (high temperature zone) and ferrocene was placed at the front of the quartz tube (low temperature zone). The two temperature zones were controlled by temperature controllers 1 and 2, respectively. Then the quartz tube was heated under N_2 flow with a rate of 50 sccm to remove oxygen in it. When the temperature in the middle of quartz tube reached 1023K, C_2H_2 was introduced into the tube. The flow rate of C_2H_2 was 50 sccm, and simultaneously the flow rate of N_2 was increased to 200 sccm. In the process, the sublimed ferrocene particles were introduced into the reaction chamber by
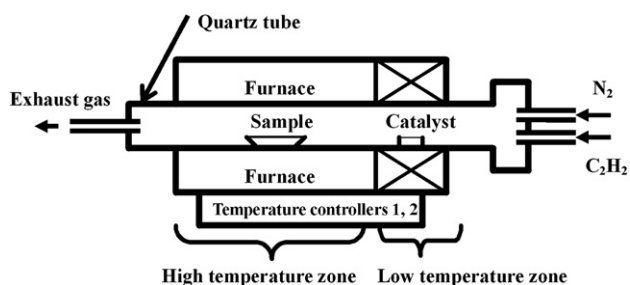

Fig. 1. Schematic diagram of the floating catalyst set-up for the growth of carbon submicrotubes.

C_2H_2 and N_2 gas flow. The carbon submicrotubes were grown on the carbon microfibers, when ferrocene molecules decomposed into Fe clusters and fell onto the surface of carbon microfibers at the high temperature of 1023 K. After about 30 min, C_2H_2 gas and power supply were shut off. Finally, the system was cooled down to the room temperature in N_2 ambient with a flow rate of 50 sccm. The purities of both C_2H_2 and N_2 employed in the experiment are higher than 99.5%.

2.3. Characterization

The morphology, microstructure and composition of carbon submicrotubes on carbon microfibers were characterized by using a field emission scanning electron microscope (Hitachi S-4800 and Philips XL30 (with EDX accessory)), a high-resolution transmission electron microscope (Tecnai F 30) and a Raman spectrometer (Jobin Yvon HR800) with the laser wavelength of 488.0 nm from an Ar^+ laser. The composition of a single carbon submicrotube was determined by EDX, which was equipped with a standard Si (Li) detector and calibrated with the pure elements Cu and Al prior to the analysis. During the observation, the field emission scanning electron microscope was operated under accelerating voltages of 15 and 20 kV, and the high-resolution transmission electron microscope was operated under an accelerating voltage of 300 kV. During the EDX measurement, the system was operated under an accelerating voltage of 20 kV and the collection time for EDX spectrum was 100 s. The HRTEM sample was prepared by scratching a few carbon submicrotubes from carbon microfiber surfaces, then dispersing them ultrasonically in ethanol for 20 min, and finally dropping a few droplets onto a carbon-coated copper grid.

3. Results and discussion

3.1. Morphology and composition analysis

Fig. 2 shows the SEM images of carbon submicrotubes grown on carbon microfibers. As seen in Fig. 2(a), a number of carbon submicrotubes are grown on the surface of carbon microfibers, which have a diameter of about 4 μm. The length of carbon submicrotubes ranges from 5 to 8 μm, their diameter is around 400 nm and Fe particles with a diameter of about 800 nm also exist at the end of carbon submicrotubes. It can also be noted that some carbon submicrotubes are not linked directly with carbon microfibers but with carbon submicrotubes, perhaps resulting from the deposition process of floating catalysts. Some new carbon submicrotubes were found to grow on the carbon submicrotubes because the catalysts were deposited on the walls of carbon submicrotubes grown on the microfibers during the preparation of the submicrotubes. Fig. 2 (b) shows the image of disordered carbon submicrotubes, this disorder being natural for a thermal CVD process. It can be seen that the root of carbon submicrotubes is twisted as pointed to Fig. 2(b) by arrows. Fig. 2(c) is an enlarged image of the rectangle shown in Fig. 2(a). It can be observed that the top of the tubes is caped by a big Fe particle. As seen in Fig. 2(d), the
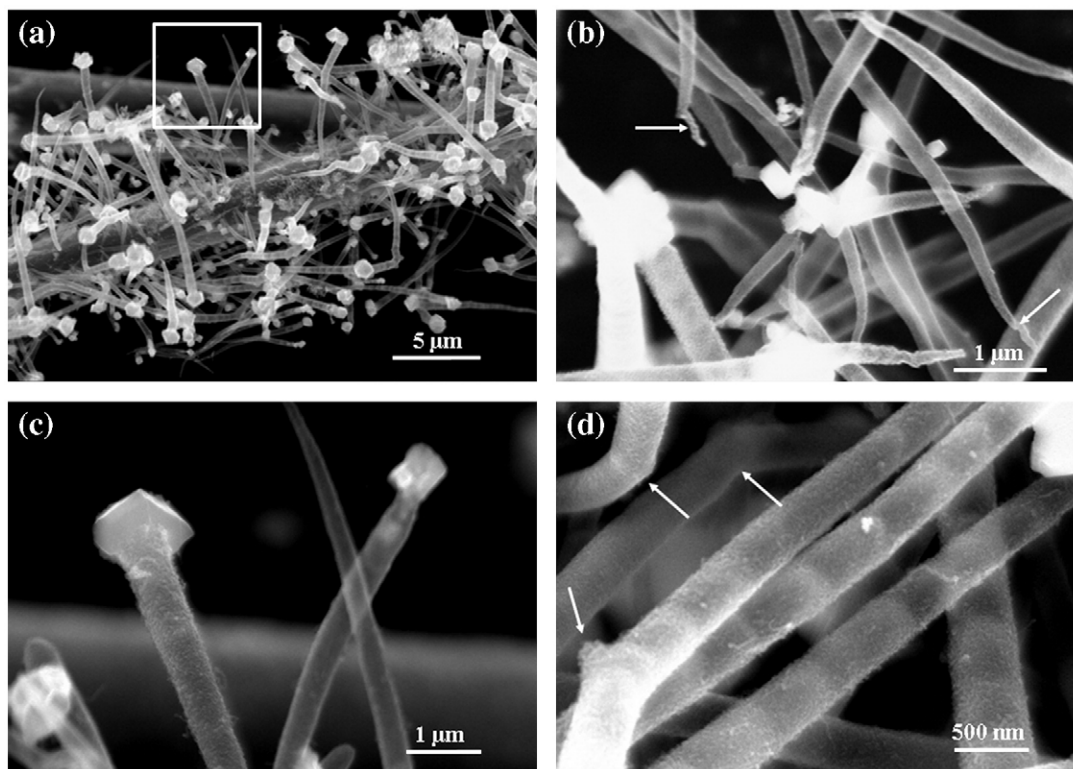
Fig. 2. SEM images of low-resolution (a), disordered distribution (b), local enlargement of (a) (c), and curve structure (d) of carbon submicrotubes grown on carbon microfibers.

carbon submicrotubes exhibit distinct bamboo-like structures and the diameter is mostly constant. Most of carbon submicrotubes are straight, but a few are curved.

Fig. 3 shows typical SEM images of a single carbon submicrotube at different positions. As seen from the open end of a carbon submicrotube in Fig. 3(a), the inner wall is smooth, but the outer wall is rough. Fig. 3(b) shows the image of the middle part of a carbon submicrotube. As seen from the SEM image of the close end of carbon submicrotube in Fig. 3(c), the top of carbon submicrotube is hemispheric, and the diameter of the top is larger than that of the middle part. Moreover, a Fe particle covers the top of carbon submicrotube. In addition, a few CNTs are found to grow on the outer wall of carbon submicrotubes as shown by arrows in Fig. 3(a), (b) and (c). The SEM images show that the outer walls of carbon submicrotubes on carbon microfibers are very rough and a few CNTs were grown on the submicrotubes. In order to further explore the growth mechanism of carbon submicrotubes, the sample was treated by sputtering Au. The surface morphology of the sample is shown in Fig. 3(d). It was found that some small particles with a diameter of about 25 nm were grown on the surface of carbon submicrotubes.

Further, the composition of carbon submicrotubes was determined by EDX. Fig. 4 shows EDX spectrum of a single carbon submicrotube that corresponds to the one in Fig. 3(d). This shows that carbon submicrotube consists of C, Fe and O besides Au which was brought by the treatment of the sample. Fe and O might come from the catalyst and its oxidation.

3.2. Microstructure analysis

In order to further understand the microstructure of carbon submicrotubes, HRTEM studies of the carbon submicrotubes were made. As seen in Fig. 5, the small particles on the surface of carbon submicrotubes have a graphitic structure, similar to CNTs. Fig. 5(a) shows the HRTEM image of the outer layers of a carbon submicrotube. The outer wall of carbon submicrotube is not smooth and the structure defects are also present. However, as shown in Fig. 5(b), the inner layers of carbon submicrotube have a well graphitic structure. Most of layers are parallel to the axial direction, but several are perpendicular to the axial direction of carbon submicrotube as shown in Fig. 5(b) by arrow 1. In Fig. 5(c), some CNTs with about 15 layers grown vertically on the outer wall of the carbon submicrotube are depicted. It can be noted that the growth of CNTs on the submicrotubes was carried out without the link of catalyst. However, it has been reported that the presence of catalysts on CNTs is a prerequisite for the growth of new CNTs on CNTs [19]. Moreover, the curvature structure of CNTs is suggested to be related to many defects such as pentagons and heptagons in hexagonal graphite structure [20–22]. Our results indicate that the rough surface of carbon submicrotubes, resulting from the defects of hexagonal graphite, may provide the growth sites of CNTs.

Fig. 6 shows the Raman spectrum of carbon submicrotubes grown on carbon microfibers. Two strong peaks at about 1352 and 1582 cm^{-1} are clearly observed in the spectrum, which are
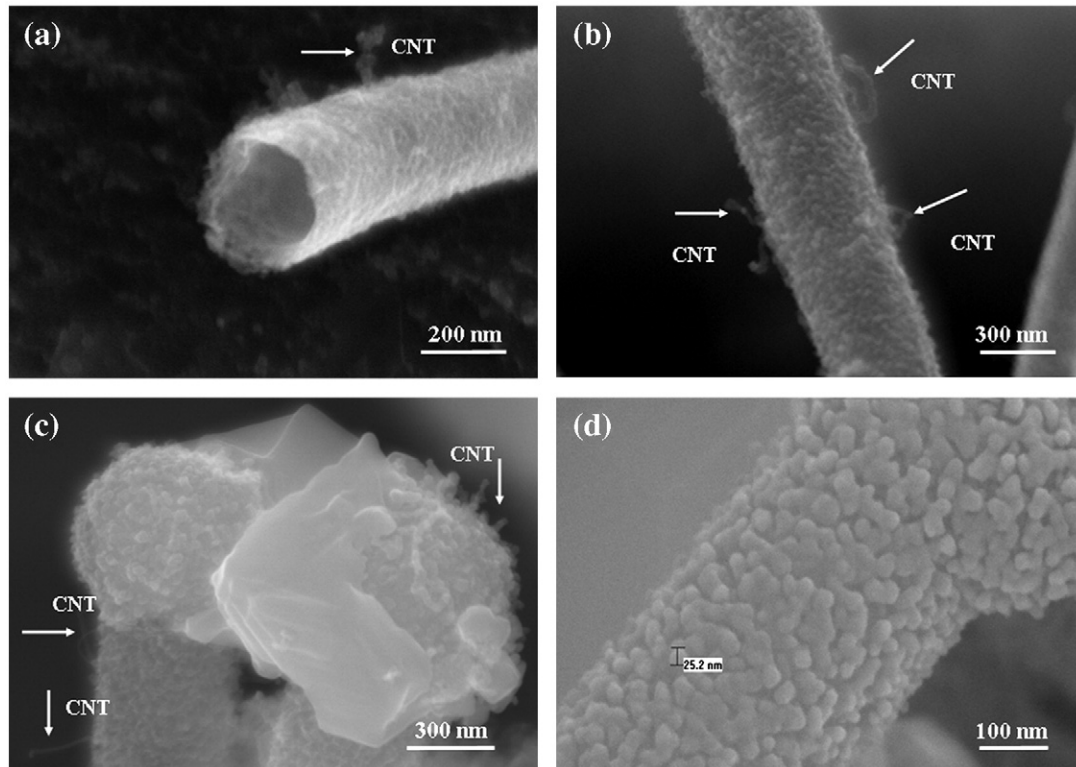
Fig. 3. SEM images of a single carbon submicrotube at different positions: open end (a), middle part (b), close end (c), and part near close end sputtered with Au (d).

commonly known as the D and G bands of graphite, respectively. The peak at around 1582 cm^{-1} corresponds to an E_{2g} mode of graphite, which is due to the sp^2-bonded carbon atoms in a two-dimensional hexagonal graphitic layer [23]. The D band at around 1352 cm^{-1} is associated with the presence of other carbonaceous impurities and defects in the hexagonal graphitic layers [24]. The result indicates that carbon submicrotubes have a graphitic structure, and that many defects and carbonaceous impurities are present in the submicrotubes, which is in accordance with the SEM and HRTEM. The ratio of the intensity of the D and G peaks is known to be correlated to the quality of graphitic structure: the higher the I_D/I_G ratio, the higher the defects. The I_D/I_G ratio of carbon submicrotubes is estimated to be about 1.223. The high D peak indicates that carbon submicrotubes have more defects than CNTs. Liu et al. [25] have suggested that CNTs should be grown at the defects of hexagonal graphite on the basis of the defect growth model of CNTs. The Raman spectrum of carbon submicrotubes shows the presence of the large surface defects in carbon submicrotubes, which is favorable for the secondary growth of CNTs.

In the experiment, carbon submicrotubes were synthesized by floating catalyst method, which has been used by others to prepare CNTs [26,27]. Therefore, the formation mechanism of carbon submicrotubes should be similar to that of CNTs. It is well known that the size of catalyst greatly affects the diameter of CNTs. It has been shown that when the size of the catalyst increases, the size of the CNTs increases as well [28]. In the floating catalyst process, on the one hand, ferrocene molecules are decomposed rapidly at high temperature and the decomposed Fe atoms assemble to form Fe clusters. If the

concentration of catalyst is high, the Fe clusters coalesce into bigger Fe clusters. When the concentration of catalyst is sufficiently high, the size of the Fe particles is compatible with efficient catalysts of carbon submicrotubes growth. On the other hand, carbon microfibers were treated in a solution of ferrocene/ acetone before the experiment, resulting in the presence of ferrocene molecules on the carbon microfibers. At high temperature, the Fe particles resulting from the decomposition of ferrocene also provide catalyst sites for growing carbon submicrotubes. Moreover, the surface of carbon microfibers has also been activated by boiling in a solution of H$_2$SO$_4$/HNO$_3$, leading to the formation of surface defects. The activated surfaces were suitable for depositing Fe clusters and the surface defects may become the growth sites of carbon submicrotubes.
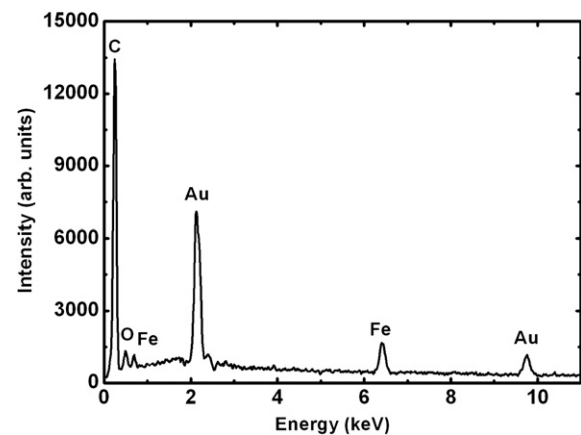

Fig. 4. EDX spectrum of a single carbon submicrotube.

Furthermore, the synthesized carbon submicrotubes are shown to have morphologies similar to carbon nanofibers [29]. Carbon nano-rods were suggested to be the structural unit of carbon nanofibers, and single carbon nano-rods assemble into a multi-wall CNT with 4–5 nested graphitic sheets [30]. In Fig. 5(b), it is found that the inner wall of a carbon submicrotube has a structure similar to CNTs, but the outer wall is covered by graphitic nanoparticles (Fig. 5(a)). Similarly, the outer wall of carbon submicrotubes can be considered to be
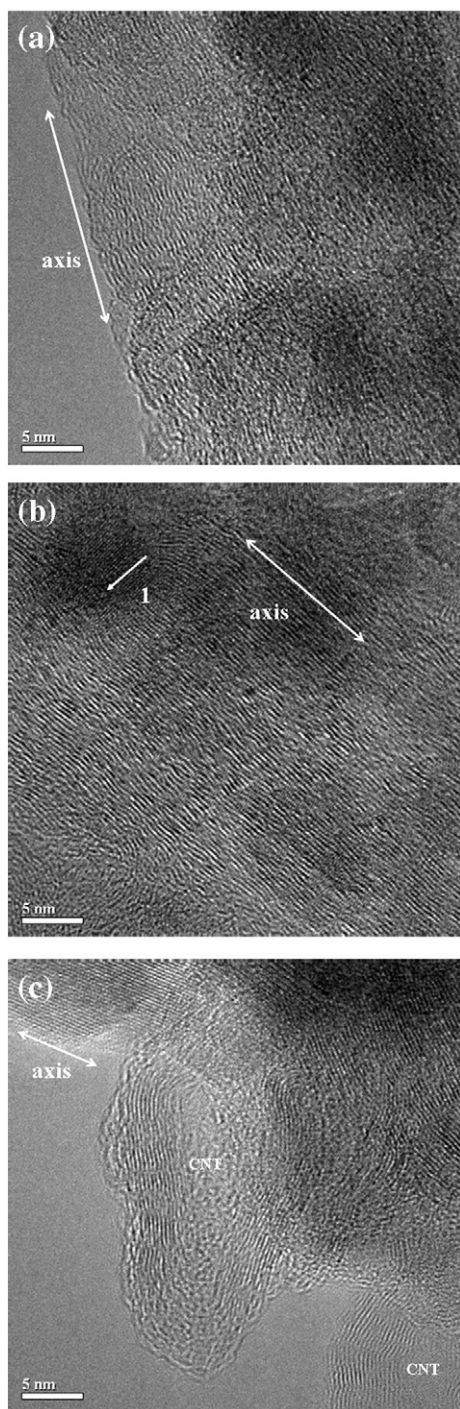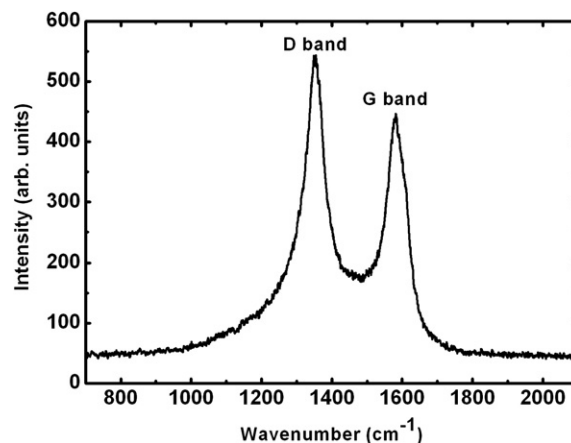

Fig. 6. Raman spectrum of carbon submicrotubes on carbon microfibers.

the assembly of carbon nanoparticles with a diameter of about 25 nm consisted of tens of graphene sheets, and the inner wall of carbon submicrotubes is considered to be the assembly of CNTs. We suggest that carbon submicrotubes prepared in this experiment consist of CNTs and carbon nanoparticles, and that the carbon nanoparticles assembled on the outer wall of the carbon submicrotubes may be related to the secondary growth of CNTs.

4. Conclusions

In summary, carbon submicrotubes were synthesized on carbon microfibers by the floating catalyst method. The results indicated that the growth of carbon submicrotubes was related to the pretreatment of carbon microfibers giving rise to catalyst areas, and the secondary growth of CNTs on carbon submicrotubes makes it possible for the synthesis of carbon microfibers, submicro- and nano-tubes composites. The formation mechanism of carbon submicrotubes and the secondary growth mechanism of CNTs, need to be further investigated. Because of the large hollow-structure and good electronic conductivity of graphite structure, the carbon submicrotube composites could be a good electrode material and so on. In addition, composite materials could be produced if the hollow carbon submicrotubes are filled with other nanomaterials.

Acknowledgment

Fig. 5. HRTEM images of a single carbon submicrotubes: the outer layers (a), the inner layers (b), and the outer layers with CNTs (c).

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