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LETTER

Growth of oriented vapor grown carbon fibers on pyrolytic carbon films without catalyst

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Vapor-grown carbon fibers (VGCFs) have been of great interest to scientific and industrial communities for many years due to their unique crystalline structure as well as excellent physical and chemical properties [1–3]. They have potential applications as fillers in composites, super-high hydrogen storage materials, and good electrode materials [4–8]. VGCFs are usually prepared by the decomposition of hydrocarbons, such as benzene and methane, using ultra-fine transition metal particles or their alloys as a catalyst at a growth temperature of 600–1300 °C [9–11]. However, these methods sustain the disadvantage of introducing catalyst particles, which can make the synthesis process more complex, and the existence of catalyst must influence the properties of the products. Moreover, the mesoporous template or the d.c. bias was generally needed to enhance the growth of the oriented carbon nanotubes and carbon nanofibers [12, 13]. Recently, Lin et al. [14] prepared multi-walled carbon nanotubes on a porous carbon surface using carbon black as a substrate by the decomposition of diluted ethylene. Rantonen et al. [15] synthesized needle-shaped carbon filaments at low temperature by ultraviolet laser irradiation under near- and supercritical conditions without catalyst. These reports showed that the growth of carbon filaments without the aid of catalysts is possible. In this paper, microwave-assisted CVD method was used to prepare oriented VGCFs on pyrolitic carbon films by direct pyrolysis of methane without the use of any catalysts. The influence of reaction time (2, 10, 25, and 30 min) on the morphologies and structures of products at 1100 °C was also discussed.

The experiments were carried out in a vertical quartz tube heated in a home-made microwave furnace. The schematic of the experimental device is shown in Fig. 1. Carbon source gas is introduced into the gap between quartz tube and microwave absorbing materials, and then conducted out of microwave furnace via gas outlet. The silver-gray pyrolytic carbon films were deposited on the inner wall of quartz tube with a gas residence time of 0.1 s at 1000 °C for 60 min by the microwave chemical vapor infiltration technique, and then used as the substrate. The reaction was conducted at 1100 °C with the flow of mixture gas CH_4/N_2 (1:1 vol), for 2, 10, 25, and 30 min, respectively. After the reaction, the furnace was cooled down to room temperature in the atmosphere of N_2. A layer of black filament-like substance deposited on the surfaces of the substrate was collected for analysis.

The morphology and structure of products were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4700), and Raman spectroscopy (Renishaw Invia Reflex). The elemental composition of the materials was analyzed by an energy-dispersive X-ray (EDX) analysis technique attached to the scanning electron microscopy.

Figure 2 shows typical FESEM images of oriented VGCFs with a uniform diameter of about 50 μm when the reaction time is 30 min. Figure 2a shows a side view of VGCFs formed on pyrolytic carbon film. It shows that the

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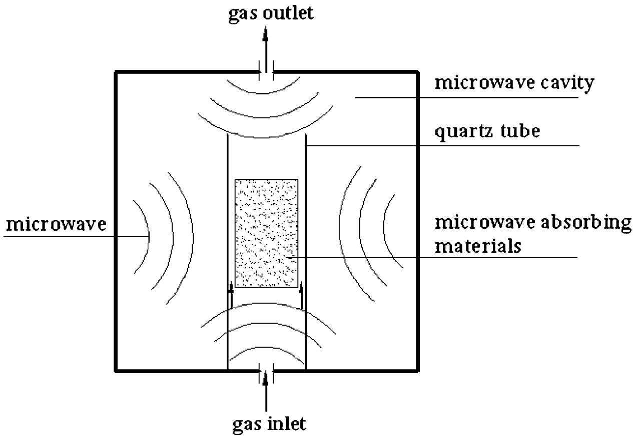

Fig. 1 Schematic of the experimental apparatus

VGCFs with rough surface is densely packed and oriented on the pyrolytic carbon substrates. The growth of the oriented VGCFs may be related to the generated micro-plasmas during microwave heating, which were also mentioned by other researchers [16, 17]. The great bombardment energy of the N_2 microplasmas promotes the oriented growth of VGCFs. Some fibers aggregate into branched structure when the fibers grow above a certain critical height (arrow in Fig. 2b). Branched structures have been mainly attributed to the strong interaction between each fiber by the pyrolytic carbon deposition condition during the growth process. The length of most fibers, which was estimated from Fig. 2a and b, is approximately in the range of 0.2–1 mm. For single VGCF, the diameter is increasing along the fiber axes, as shown in Fig. 2c. Moreover, most of the fibers have a semispherical tip, but some fiber tips appear as cauliflower-like structure (Fig. 2d).

The chemical compositions of the as-prepared VGCFs are determined using energy-dispersive X-ray analysis of SEM. In the samples, only carbon element and trace of gold coming from thin Au films sputtered on the SEM samples (as shown in Fig. 3) are observed, and no evidence is found for any other metal impurity.

Figure 4a shows the cross-section of a broken fiber. It can be seen that the fiber consists of a central filament and an external deposit of pyrolytic carbon with the annular structure of a tree. Moreover, the texture of zones A and B of pyrolytic carbon surrounding the primary fiber is very different. This may be related to the local conditions during the deposition. Figure 4b shows a FESEM image of cracked end of a fiber. In the image, it can be observed that the primary fiber is pulled out and the annual growth layer is very clear. Simultaneously, it also can be noted that surface morphology of each layer with shingle-like structure is similar (arrow in Fig. 4b), which will help us in understanding the growth mechanism of VGCFs.

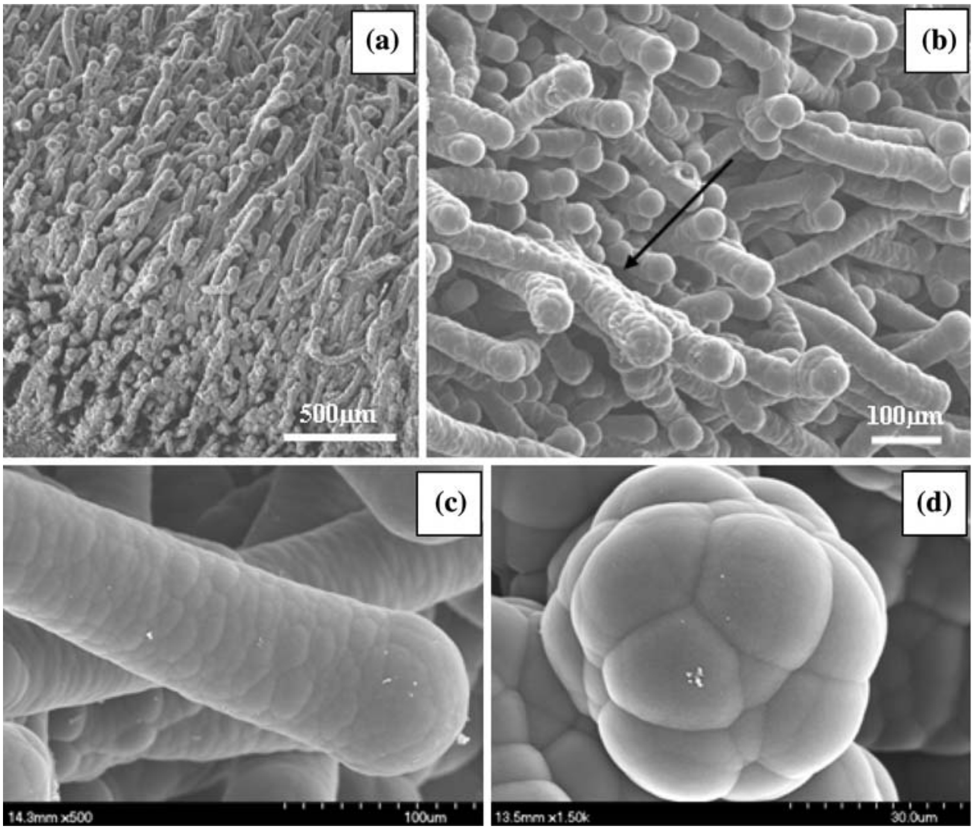

Fig. 2 FESEM image of oriented VGCFs grown on pyrolytic carbon film after deposition for 30 min. **a** Side-view SEM image of oriented VGCFs, **b** top-view SEM image of oriented VGCFs (branched structure as *arrow*), **c** a fiber with increasing diameter along the fiber axes, and **d** a fiber tip with cauliflower-like structure

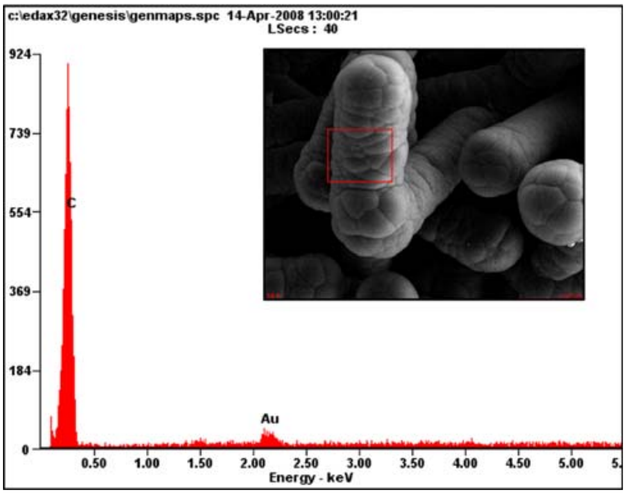

Fig. 3 EDS spectrum of the as-prepared VGCFs

In order to understand well the growth process of VGCFs, the reaction time was varied from 2 to 30 min with the other reaction conditions being kept the same. Figure 5 shows FESEM images of the products synthesized at different reaction times. The products gradually varied from carbon nodules to individual straight fibers, and then crisscross fibers with increasing reaction time. The surface morphology of pyrolytic carbon film before deposition is relatively clear, as shown in Fig. 5a. Figure 5b shows the surface morphology of pyrolytic carbon film after deposition for 2 min. It can be seen that no filaments are formed but many spherulitic carbon nodules emerge out of the surface, and some nodules are aggregated together. These nodules might provide nuclei sites for subsequent outward growth of VGCFs. With the deposition time exceeding 10 min, some VGCFs grow out from the surface. Compared with Fig. 2a, the FESEM image in Fig. 5c illustrates a transition to shorter, more conical, less branched structure, and the VGCFs are relatively straight with a smooth surface. With the deposition time being increased to 25 min, the diameter, length, and density of fibers are rapidly increased due to a higher growth rate, as shown in Fig. 5d. Compared with Figs. 2a and 5d, the shape of the fibers with big tips has no obvious changes, though the diameter of the fibers is slightly decreased when the reaction time is extended to 30 min. It may be due to the volume shrinkage of carbon layers resulting from the continuous improvement of the degree of graphitization.

Based on the above findings, we regard that the spherulitic nodules deposited on the films would play important roles in the growth of fibers. These carbon nodules act as nuclei sites and induce growing up of fibers in microwave field. Therefore, the fibers grow from their bases, and then the fibers thicken and lengthen by direct deposition of layer-like pyrocarbons. Moreover, the deposition mechanism of pyrolytic carbon follows lamellar growth pattern, as shown in Fig. 4. This may be similar to the reported carbon micro-trees prepared by a flash CVD method without any help of metal catalysts, which involves fast resistive heating of graphite electrodes in an atmosphere of methane and helium [18, 19]. During growth, some spherulitic nodules emerged out of the new graphitic surface and served as the nuclei for subsequent outward growth of the carbon micro-trees. In our experiment, VGCFs are also obtained by microwave-assisted pyrolysis of methane without any catalyst, which has the potential advantages of uniform, rapid, and volumetric heating. The deposition of carbon by two methods was carried out under similar conditions (using rapid heating and cooling cycles). So we suggested microwave field might enhance the growth of fibers, but more work is required to clarify this point.

Raman spectroscopy is one of the most effective tools for distinguishing different carbon phases, as each phase displayed its own Raman bands. Figure 6 shows a representative Raman spectrum of the VGCFs in the range of 1000–2000 cm^{-1}. There exist two strong peaks centered at 1584 and 1348 cm^{-1}, which are attributed to the Raman-active E_{2g} in-plane vibration mode (G-band) and the Raman-inactive A_{1g} in-plane breathing vibration mode (D-band), respectively. The peak at 1584 cm^{-1}, compared with that of HOPG (1582 cm^{-1}), the position has been

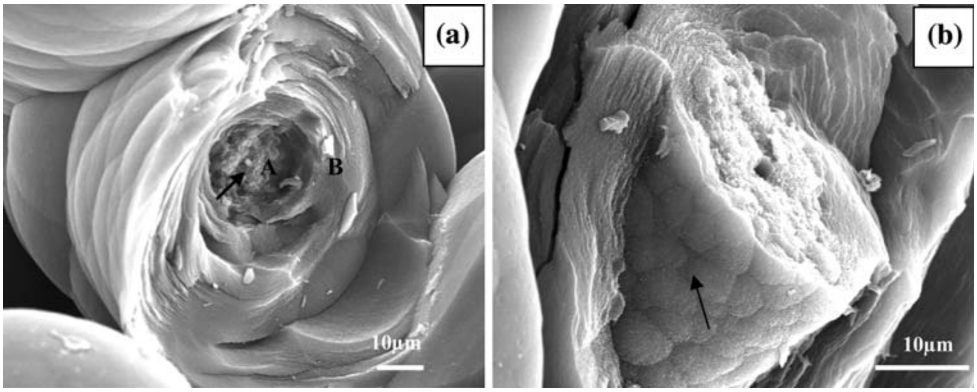

Fig. 4 FESEM image of **a** fracture morphology of a fiber and **b** cracked end of a fiber

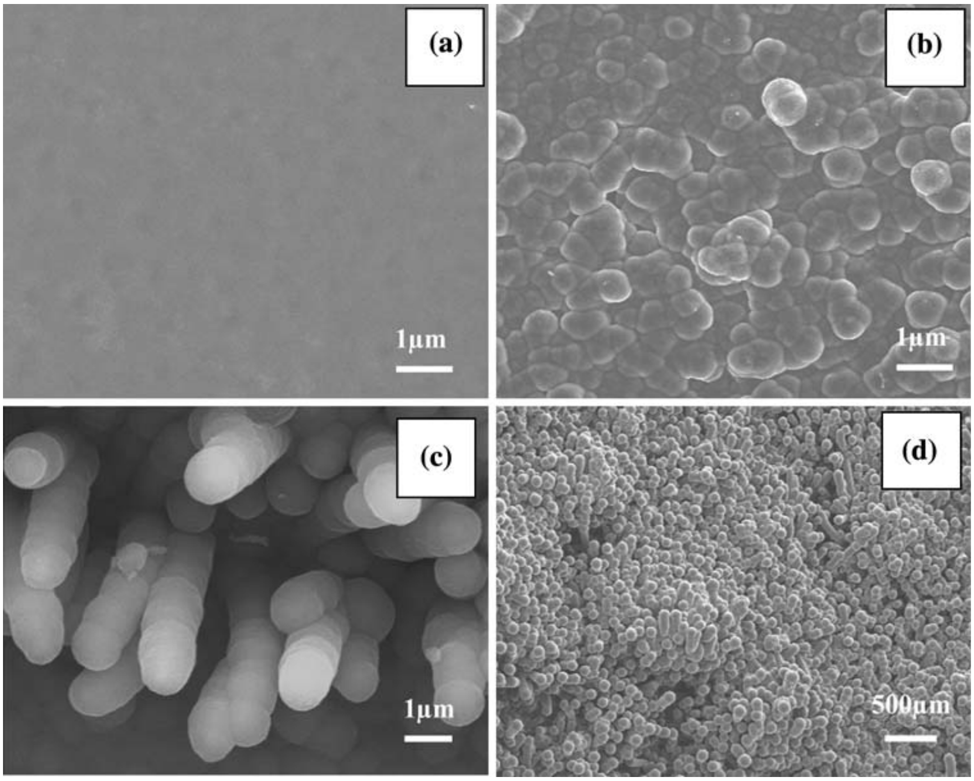

Fig. 5 FESEM images of the VGCFs synthesized at different times: **a** 0 min, **b** 2 min, **c** 10 min, and **d** 25 min

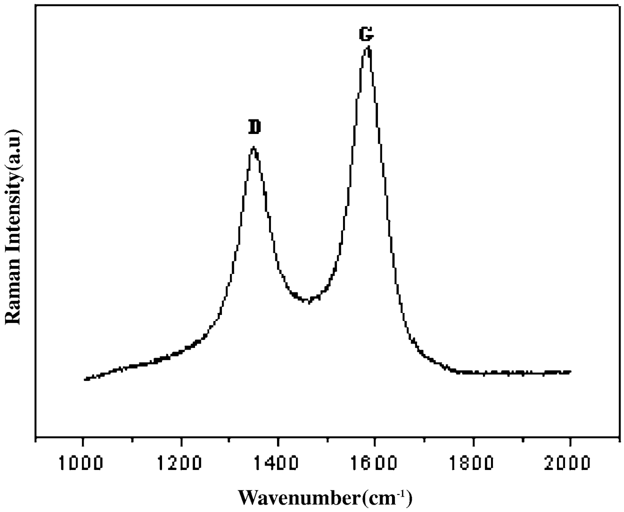

Fig. 6 Raman spectrum of the as-prepared VGCFs

shifted upward slightly, indicating that VGCFs prepared by the technique exhibit relatively high degree of graphitization [20]. The D-band is related to the defects and disorders in structures on carbonaceous solids. The weak D-band (about 1348 cm^{-1}) demonstrates that the samples contain very small amount of amorphous carbon materials, revealing that high-purity VGCFs are prepared in our method. The ratio of the intensities of D–G peak is often used to estimate the degree of perfection of graphene planes [21]. The I_D/I_G value for the VGCFs is 0.65, and low I_D/I_G ratio indicates a low degree of disorder or plane defects in the structure of VGCFs.

In summary, oriented VGCFs with high purity were prepared without any catalyst by direct microwave-assisted pyrolysis of methane, at 1100 °C. The fibers are made up of central filaments and external deposits of pyrolytic carbon with the annular structure of a tree. Raman spectroscopy indicated that the VGCFs possess relatively high degree of graphitization. The influence of reaction time on VGCFs was obvious. The samples gradually varied from carbon nodules to straight fibers, and then criss-cross fibers with increasing reaction time. It was assumed that microwave field might catalyze the formation of VGCFs.

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