

Preparation, characterization and growth mechanism of platelet carbon nanofibers

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Abstract

The synthesis of platelet carbon nanofibers (PCNFs) on a silicon substrate using chemical vapor deposition method is reported. Scanning electron microscope, high-resolution transmission electron microscopy, and Raman spectroscopy were used to characterize the nanofibers. It is found that these platelet nanofibers are of the order of 10 μm long, and most have a nearly rectangular transverse section with several hundreds nm wide and several tens of nm thick. Structure analysis reveals that the carbon layers of platelet nanofibers are parallel to each other, and have a uniform (002) orientation that is perpendicular to the fiber axis. Many faults and nanodomain have been found in the nanofibers. It is suggested that the PCNF grow in tip growth mechanism by the precipitation of carbon from the side facet of catalyst flakes.

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1. Introduction

Since the discovery of C_{60} [1] and carbon nanotubes (CNTs) [2], much effort has been made to study carbon nanomaterials. With the changing of preparing conditions, the carbon nanomaterials obtained from the catalytic decomposition of CO or hydrocarbons exhibits a wide variety of morphologies, including tubes [2], onions [3], cones [4–6], discs [5], earthworms [7], cubes [8,9] and so on. Many investigations have been carried out to study the morphologies, microstructures, and growth mechanism of these materials, especially for the carbon nanotubes. However, few attentions have been paid to platelet carbon nanofibers. In fact, platelet carbon nanofibers were firstly reported in 1970s [10], but the novel material was not

thoroughly studied by the limitation of analytical instruments at that time. In 1990, Murayama [11] obtained these filaments again and investigated their structure. Later, bi-directional growth PCNFs [12] were found from the interaction of a powdered catalyst containing a large fraction of iron with a CO/H_2 mixture at 600 °C. Up to now, platelet carbon nanofibers are all found as a byproduct of carbon nanofilaments (carbon nanofibers) obtained by the catalytic decomposition of CO, and the gain of PCNFs had been more a matter of serendipity than design. So the repeatable and bulk preparation of PCNFs remains a challenging issue.

In this paper, we report the synthesis of large amounts of platelet carbon nanofibers on silicon substrate by a thermal chemical vapor deposition (CVD) technique. Based on the systematically study on the morphology and microstructure of these nanofibers and catalyst substrates, the growth mechanism of PCNFs has been presented. Furthermore, potential usages of PCNFs are discussed.

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2. Experimental

The $10 \times 10 \text{ mm}^2$ n-type Si(111) slices with a resistivity of 4–4.8 $\Omega \text{ cm}$ were prepared as substrates. Original silicon slices were ultrasonic cleaned in a 99.7% alcoholic solution. And 5 nm thickness of Fe film was deposited on the Si substrates by a metal vapor vacuum arc (MEVVA) ion deposition system. Before deposition, substrates were bombarded by Fe ion to get clean surfaces. Synthesis of PCNFs was carried out in a horizontal thermal CVD system. Si substrates coated with Fe film were placed in a quartz boat, and transferred into the middle of reaction chamber. The reaction zone was heated up to 580 °C in N_2 gas environment. H_2 gas was introduced to reduce the Fe catalyst for 30 min. Then the NH_3 was introduced and the substrates were pretreated in NH_3 gas environment at 730 °C for 15 min to activate and refine the catalyst particles. Thereafter, mixtures of C_2H_2 and H_2 gas with a ratio of 75/400 sccm was introduced into the reaction chamber for 60 min for the growth of PCNFs. After experiments, the samples were furnace cooled slowly in a H_2 gas environment. The purities of the gas employed in the experiments were all higher than 99.95%.

Morphologies of PCNFs and catalyst substrates were examined using a field emission scanning electron microscope (FESEM) XL30S—FEG. Microstructure of PCNFs was analyzed by a high-resolution transmission electron microscopy (HRTEM) H-9000 at 300 kV. TEM specimens were prepared by dispersion of a small mass of the carbon deposit in ethanol, and a droplet of the resulting suspension was applied to a holey carbon support film. Raman spectrum was recorded to evaluate the structure and

crystallinity of PCNFs by a Jobin Yvon-spex T6400 microscope Raman spectrometer with 532 nm He–Ne excitation laser.

3. Results and discussion

While the samples have been taken out of the reaction chamber, it can be found that there are black films covered on the silicon substrates. Fig. 1 shows the SEM images of the film. It can be seen from Fig. 1(a) that the film is composed of aggregated nanofibers. We call them platelet carbon nanofibers. The fibers are of several tens μm long, zigzag, and most of them have a bright ellipsoidal particle on their tip. The particle has the nearly same width as that of the PCNFs. EDX analysis (Fig. 1(b)) indicates that the particle contains of C and Fe element. Fig. 1(c) and (d) show the size and morphology of a typical PCNF. The fiber has a rectangular transverse cross-section with several 100 nm width and 20–30 nm thickness, as Fig. 1(c) shows. Ratio of surface area/mass of these novel materials reaches $100 \text{ m}^2 \text{ g}^{-1}$. The fibers are flat along the width direction, but are zigzag in their length direction. Fig. 1(d) is the high-resolution SEM images of a fiber. The fiber has a corrugated surface along the length direction and looks like a washboard. Meanwhile, it has a ragged edge.

Fig. 2 is the high-resolution transmission electron micrograph of a typical PCNF. The inset is the selected area electron diffraction (SAED) pattern of the fiber. Electron diffraction pattern shows (002), (004) diffraction spots and (100), (110) diffraction rings. The orientation pointed out by (002) spots is consistent with the growth direction of the fiber, which means that the fiber grows along the

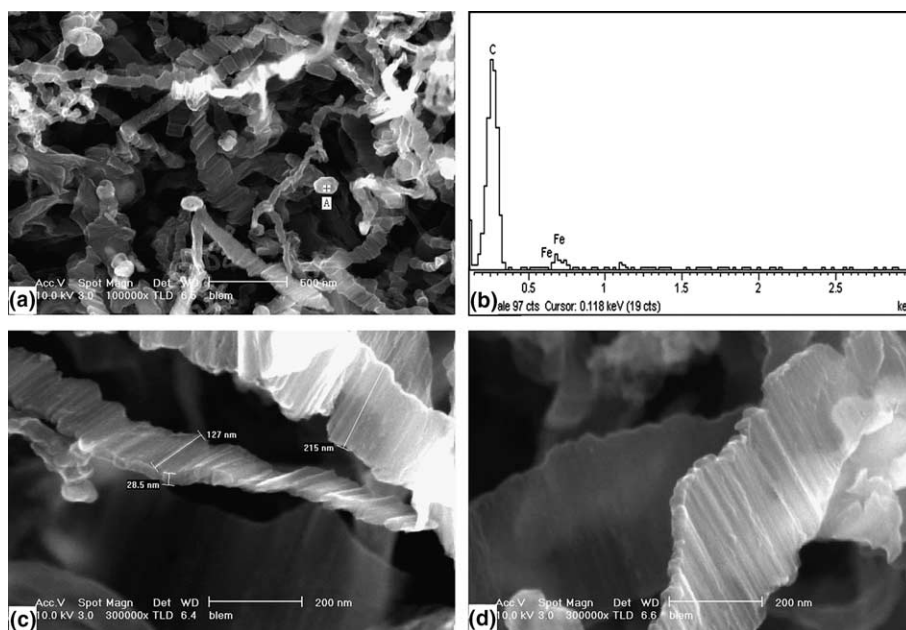


Fig. 1. SEM images of platelet carbon nanofibers film. (a) SEM image of PCNFs film (b) Energy dispersive X-ray spectrometry (EDXS) of a light particles (indicated by 'A' in (a)) on the top of a fiber. (c) The size of a typical PCNFs, which shows the width (100–300 nm) and thick (~ 30 nm) of the fiber (d) surface morphology of a PCNF.

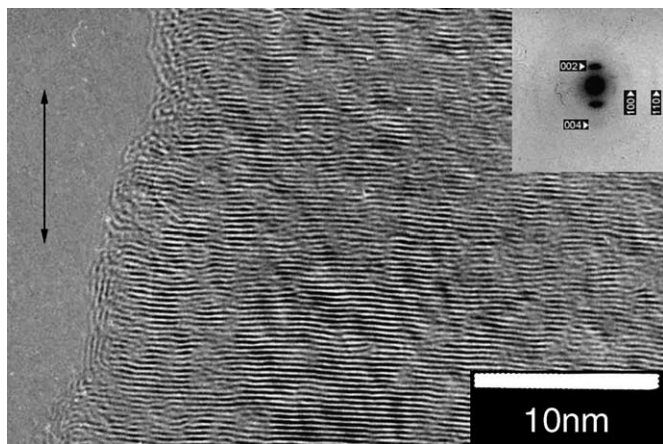


Fig. 2. HRTEM image of a typical PCNF. The inset is the selected area electron diffraction (SAED) pattern of the fiber. The arrow shows the growth direction of the fiber.

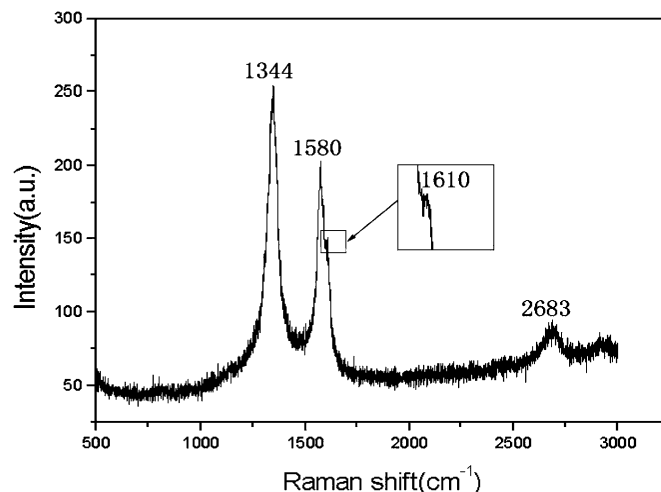


Fig. 3. Raman spectra of PCNFs, obtained with an excitation wavelength of 532 nm. The inset shows details of the shoulder band D' (1610 cm⁻¹).

(002) direction by stacking carbon layers. Semilunar (002) spot indicates the existence of texture and the direction relaxation of (002) carbon layers. (100) and (110) diffraction rings reveal the existence of nanodomain in the fiber. These results are consistent with HRTEM observation. Different from the hollow structure of carbon nanotubes, the fiber has a solid structure. Carbon layers of the fiber have been stacked along the growth direction of fiber with an average d_{002} of 0.337 nm. The carbon layers are folded every several layers at the edge of fiber. In addition, the fiber has an accidented surface. It can be observed that carbon layers are discontinuous throughout the fiber and have been divided into many nanoorder domains by a large number of faults.

Raman spectroscopy is a useful nondestructive method for the structural characterization of different carbon materials. In this paper, the samples contain some Fe and amorphous impurities, which dilutes the signal of nanofibers. Nevertheless, structure information can still be extracted. Fig. 3 shows the Raman spectra of PCNFs. The main features in the Raman spectrum are the D (1344 cm⁻¹) and G bands (1580 cm⁻¹) and the corresponding second order band at around 2683 cm⁻¹. Different from the Raman spectrum of highly oriented pyrolytic graphite (HOPG) or carbon nanotubes (CNTs), PCNFs have a shoulder band D' (1610 cm⁻¹) and a stronger D band. The D band is explained in terms of the relaxation of the wave vector selection rules resulting from finite crystal size effects [13]. The D' band is assigned to disorder-induced symmetry breaking by the microscopic defects [14]. Consequently, Raman spectrum of PCNFs also indicates the existence of nanodomain and faults in PCNFs. Moreover, the intensity ration of D and G band I_D/I_G is 1.77, much high than that of HOPG or CNTs. It further suggests that the graphitization degree of PCNFs is not as high as that of HOPG or purified CNTs.

Most of the highly ordered graphitic materials so far prepared have graphite layers that are oriented parallel to

their surfaces. However, the graphite layers of PCNFs are oriented perpendicular to their large surface. The alignment and crystalline perfection of the carbon platelets are two parameters that are governed by the nature and shape of the catalyst particle and precipitating faces [15,16]. So the shapes of catalyst particles are carefully observed.

Fig. 4 is the SEM image of a Fe catalyst film which was sintered at 580 °C and then etched by NH₃ at 730 °C. Besides the granular catalyst particles with different size, there are some catalyst flakes. These flakes are of several tens nm thickness and 100–300 nm width, consistent with the dimensions of fibers. It is well-known that continuous Fe film will agglomerate into catalyst particle film while it was sintered at 580 °C. Therefore, catalyst flakes must be formed in the subsequent etching procedure. During the NH₃ etching, the polycrystalline Fe particles are preferentially etched at grain boundaries [17]. If grains in a Fe

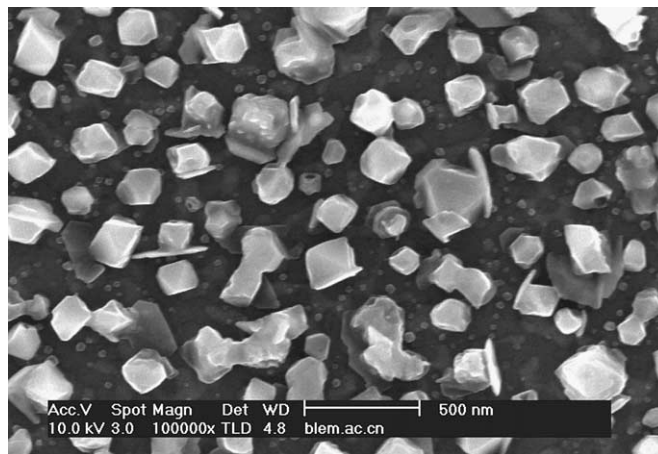


Fig. 4. The morphology of etched catalyst substrate. Some catalyst flakes (several tens nm thickness and 100–300 nm width) adhere to the granular catalysts.

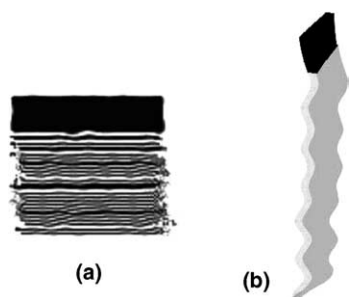


Fig. 5. The schematic diagram of growth mechanism of a platelet carbon nanofiber (on the top of the fiber, black part indicates the catalyst flake), (a) front view: carbon layers precipitate from the edge of catalyst flake, (b) side view: the zigzag growth of the fiber.

catalyst particle has suitable shape and orientation, the grain is prior etched by NH_3 along grain boundaries and some special crystal planes (for example, the high-energy plane), the catalyst flakes may develop.

Filamentary carbon usually grows by the generally accepted mechanism firstly proposed by Baker et al. [18]. We suggest that PCNFs grow in a “tip growth mechanism” similar with that of carbon nanofibers. Fig. 5 shows the schematic diagrams of growth mechanism of PCNFs. The catalyst particles contain six well-defined crystallographic faces. Five faces are capable of decomposing hydrocarbons and only one face is available for precipitating carbon. This face controls both the shape of fiber and the geometric alignment of the graphite layers. The continuous precipitating of graphite layers takes place on the single wider and thinner facet of catalyst flakes, which makes the carbon layers pile up layer-by-layer and forms the platelet carbon nanofibers. Since the ratio of the areas of the decomposing to precipitating faces in the catalyst flakes is higher than that in the catalyst particles of nanotubes, PCNFs grow much faster than CNTs. This is why we do not find any CNTs on the sample surface, as shown in Fig. 1(a). Since the width of fibers is about 10 times larger than its thickness, it is difficult to keep the balance precipitating of carbon atom through out the whole face. Any perturbation of carbon atom concentration will give rise to the discontinuous of carbon layers and form stacking faults and nanodomains in PCNFs, as shown in Fig. 5(a). In a similar way, due to the ribbon-like shape of PCNFs, rigidity in their thickness direction is much lower than that in their width direction. Growth direction of PCNFs will be changed by the inhomogeneous precipitation of carbon layers, which leads to the zigzag morphology of PCNFs, as shown in Fig. 5(b). Inhomogeneous precipitation of carbon layers will generate the washboard surfaces and nonuniform widths of PCNFs, too.

According to above discussion, the shape and nature of catalyst particles are the key factors that influence the morphology and the crystalline perfection of platelet carbon nanofibers. Mass production of PCNFs on large area Si substrate can be realized by the careful control of catalyst flakes preparation processing parameters, such as thickness

of Fe film, etching temperature, etching time, NH_3 concentration, etc.

In contrast to carbon materials with perfect structure, such as carbon fibers and carbon nanotubes, platelet carbon nanofibers have many defects and relatively lower strength. But these novel materials have a large surface area ($\sim 100 \text{ m}^2 \text{ g}^{-1}$) and numerous edges of graphite layers on the surface. Therefore, PCNFs might have some special usages. For example, it can be used as the anode material of secondary lithium battery [19]. The special structure of PCNFs makes lithium ions easy to intercalate into the (002) carbon layers interstices and escape from it. PCNFs anode will not only provides the high revisable specific energy capacity, but also improves the cycling performance of the secondary battery. Besides the anode of secondary battery, the large surface area and opening structure made PCNFs have potential applications for catalyst carriers [20,21], absorbents, gas storages, and so on. Further study on the application of PCNFs will be carried out on the base of mass production.

4. Summary

Platelet carbon nanofibers were produced from the interaction of iron catalyst with $\text{C}_2\text{H}_4/\text{H}_2$ at 730°C . The obtained carbon nanomaterials are one kind of ribbon-like carbon filament with the dimensions of several tens μm length, several hundreds nm width and several tens nm thickness. According to HRTEM and Raman spectrum analysis, carbon layers of nanofibers have a uniform orientation that is perpendicular to the fiber axis. The orientation is confirmed to be (002) direction. The degree of graphitization of PCNFs is not as high as that of HOPG. Many nanodomain and stacking faults exist in carbon layers. The alignment and crystalline perfection of the PCNFs are governed by the nature and shape of the catalyst flakes. The growth of carbon nanofibers is believed to be the result of the diffusion and precipitation of carbon from the side facet of catalyst flakes. Because of the special structure of PCNFs, they will have many potential applications, such as the anode material of secondary lithium battery, catalyst carriers, absorbents or gas storages, and so on.

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