J Mater Sci (2008) 43:5014–5016
DOI 10.1007/s10853-008-2659-1

LETTER

Synthesis of feather-like carbon nanosheet arrays by radio frequency plasma technique

Xuguang Liu · Dongju Fu · Husheng Jia · Bingshe Xu

Received: 28 March 2008 / Accepted: 14 April 2008 / Published online: 23 April 2008

Abstract Feather-like aligned carbon nanosheet arrays with uniform structures were synthesized from coal by radio-frequency (RF) plasma technique. The morphologies and structures of the products were characterized by FE-SEM, HRTEM, and Raman spectroscopy. The results clearly indicated that the aligned nanosheet arrays with high purity and high packing density could be prepared from coal. The nanosheet arrays consisted of carbon sheets with clear feather configuration, and a narrow length distribution ranging from 20–30 μm. The growth mechanism of the nanosheet arrays was discussed in terms of the chemical structure of coal and RF plasma chemistry.

Since the discovery of fullerenes [1], various novel carbon materials such as carbon nanotubes(CNTs) [2] and carbon nanotrees [3] have attracted much attention. Coal, one of the cheap and readily available carbon sources in nature, has been applied for preparation of fullerenes such as C_{60} [4], CNTs [5], and other carbon materials [6] in the last decade. In our previous work, carbon onions were produced from coal by Radio-frequency (RF) plasma technique [6, 7]. Here, a novel carbon nanosheet arrays with feather-like structure was obtained by adjusting experimental parameters, and its microstructure was also characterized. They are expected to have a great potential in the application of field emission materials, absorption/catalysis materials, and microelectronic technologies.

The coal used in this study was bought from Pingshuo coal mine in Shanxi Province of China. The as-received coal sample was crushed and sieved to 200 mesh, and fully dried at 383 K for 12 h before powder was put into reaction chamber directly as reactants. The device used in this study is SY type 500 W RF plasma reactor. The plasma was activated by a high-frequency coil around a quartz chamber in Ar atmosphere. The RF power was maintained at 380–420 W and the Ar pressure was kept constant at 30 Pa while the flow rate was 22.0 sccm. The experiment lasted for 60 min in Ar atmosphere. The film-like deposits on the chamber wall were characterized by field emission scanning electron microscopy (FESEM, JSM-6700F), high-resolution transmission electron microscopy (HRTEM, JEM-2010), and Raman spectroscopy (JY-T6400).

A series of FESEM images of the deposits on the chamber wall are shown in Fig. 1. It can be seen that two-dimensional carbon nanosheets grow vertically on chamber wall similar to nanotubes arrays [8], forming a unique feather-like nanostructure. From the FESEM image in Fig. 1a, it can be seen that the carbon sheets are arranged in a highly ordered and dense manner. Figure 1b shows a typical FESEM image of integrated carbon nanosheet arrays. The height of the nanosheet arrays, that is, the length of the nano-feather, is around 22 μm (Fig. 1b). At a higher magnification, a feather-like sheet with clearly identified rachis and vane can be clearly seen in Fig. 1c, and the projective angle between vanes and rachis is about

X. Liu · D. Fu · H. Jia · B. Xu
Key Laboratory of Interface Science and Engineering in Advanced Materials of Taiyuan University of Technology, Ministry of Education, Taiyuan 030024, China

X. Liu
College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

D. Fu · H. Jia · B. Xu (✉)
College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China
e-mail: xubs@tyut.edu.cn

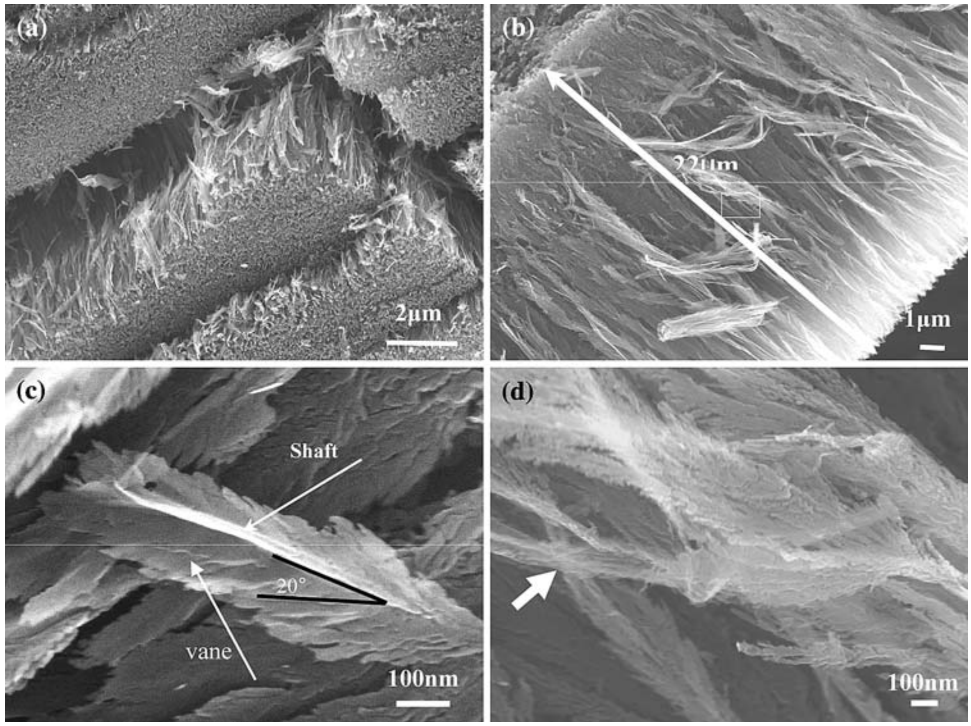

Fig. 1 FE-SEM images of the feather-like carbon nanosheet arrays prepared from coal: (**a**) One side overview of the stacking of the carbon nanosheet arrays; (**b**) Integrated carbon nanosheet arrays observed from another side; (**c**) Feather-like carbon nanosheet; (**d**) Feather-like carbon sheets with barbules

20°. Figure 1d shows the carbon sheets with the thickness of about several tens of nanometers consisting of smaller-size barbules. Moreover, similar products were obtained under the same reaction conditions by changing the coal type from Pingshuo gas coal to Fengfeng rich coal and Zhungeer subbituminous coal. It can be inferred that the coal type has little effect on the structure of the feather-like carbon material.

Figure 2a shows a typical TEM image of many overlapped feather-like sheets with clear rachis. HRTEM characterization, as illustrated in the upper left-hand corner inset, shows that the rachis is composed of well-graphitized shells. We further observed that the vanes of carbon sheets also occur in small feather-like shape and consist of barbules with amorphous carbon (seen in the upper left-hand corner inset of Fig. 2b). It readily developed into well-ordered graphitic carbon via graphitization when further heated at above 1300 K by vacuum heat treatment [9].

The Raman scattering spectra of samples in the range of 1,000–2,000 cm^{-1} are shown in Fig. 3. The G mode at 1,578 cm^{-1}, close to that of HOPG (1,582 cm^{-1}), is regarded as a Raman-allowed Γ-point vibration corresponding to the optical phonon modes of E_{2g} symmetry in graphite. The D band at 1,349 cm^{-1} is related to the defects and disorders in structures on carbonaceous solids. The ratio of the intensities of D-G peak is often used to estimate the degree of perfection of graphene planes [10]. The high value of I_D/I_G, about 1.17, implies the low graphitic degree of carbon. It is also interesting to note that there appears a peak at about 1,618 cm^{-1} (termed as

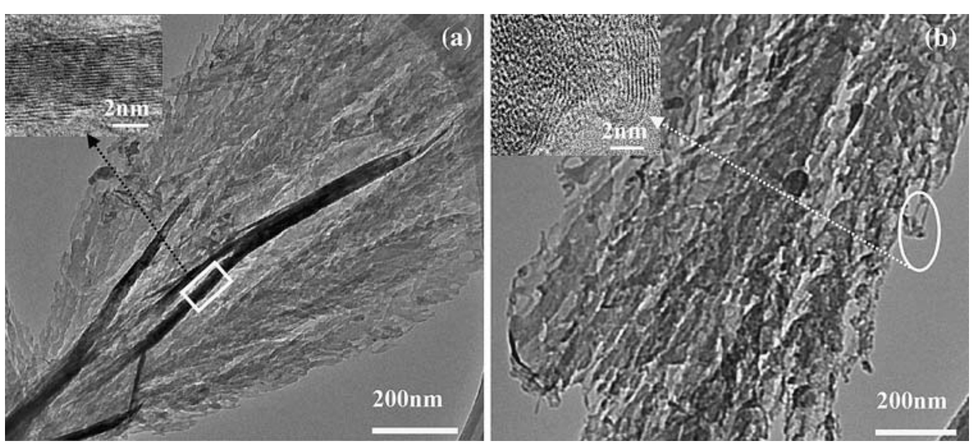

Fig. 2 TEM and HRTEM images of the products from coal: (**a**) TEM image of the carbon sheets with clear rachis and corresponding HRTEM image of the rachis; (**b**) TEM image of vanes and corresponding HRTEM image of part of the vanes

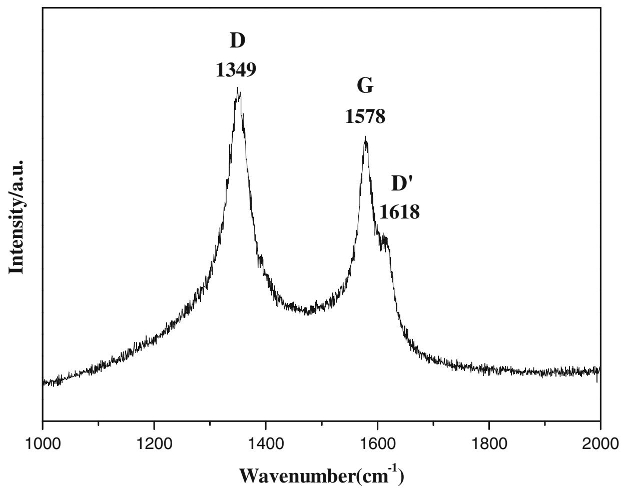

Fig. 3 The one-phonon Raman spectrum of the carbon nanosheet arrays

D́band), which might be attributed to the existence of disorder carbon. This is consistent with the results from HRTEM observation.

Based on the above results, a possible growth mechanism of feather-like carbon nanosheet arrays is proposed. The relatively weak cross-links between adjacent aromatic units in the organic macromolecular structure of coal are broken easily by high energy Ar^+, and a large amount of aromatic fragments are released [11]. Some aromatic fragments can be further decomposed into C_1 or C_2 species under the violent bombardment of high-energy electrons. It is proposed that the carbon species firstly aggregate near nucleation sites and form the rachis of nano-feather with the help of the catalyst particles, which come from some components in coal such as Fe, Si, or Al oxides according to the previous researches [12, 13]. Then, one part of the aromatic fragments nucleate to form vanes on the side of the rachis, and the others assemble to generate smaller barbules along the vanes. When the RF power was improved and kept at 480 W, the smaller aromatic fragments or C_1 and C_2 carbon units act as building blocks in the innermost shell and finally develop carbon onions [7]. Apparently, more work is still needed to clarify the mechanism involved in this process.

In summary, we have prepared a novel feather-like carbon nanosheet arrays from coal in large scale. The packing density of the carbon sheets was high, and the length of carbon feathers is around 22 μm. It is proposed that some components such as Fe, Si, or Al oxides in coal are in favor of the growth of carbon nanosheet arrays.

Acknowledgements We thank Dr Qiangang Fu (Northwestern Polytechnical University) for inspiring discussions. This work was supported by Key Project of National Natural Science Foundation of China (No. 90306014) and Shanxi Scientific Research Foundation for Returned Scholars (No. 200428).

References

1. Kroto HW, Heath JR, Brien SCO et al (1985) Nature 318:162. doi:10.1038/318162a0
2. Iijima S (1991) Nature 354(6348):56. doi:10.1038/354056a0
3. Cho SH, Lee EJ, Lee HM et al (2006) Adv Mater 18:60. doi: 10.1002/adma.200501600
4. Pang LSK, Vassallo AM, Wilson MA (1991) Nature 352:480. doi:10.1038/352480a0
5. Tian YJ, Zhang YL, Wang BJ et al (2004) Carbon 42:2597. doi: 10.1016/j.carbon.2004.05.042
6. Du AB, Liu XG, Fu DJ et al (2007) Fuel 86(1–2):294. doi: 10.1016/j.fuel.2006.05.031
7. Fu DJ, Liu XG, Lin X et al (2007) J Mater Sci 42:805
8. Xiong GY, Wang DZ, Re ZF (2006) Carbon 44:969. doi: 10.1016/j.carbon.2005.10.015
9. Xu BS, Li TB, Hai PD et al (2006) Mater Lett 60:2042. doi: 10.1016/j.matlet.2005.12.106
10. Wang XM, Xu BS, Liu XG et al (2005) Phys B 357:277
11. Pang LSK, Wilson MA (1993) Energy Fuel 7(3):436. doi: 10.1021/ef00039a019
12. Qiu JS, Zhang F, Zhou Y et al (2002) Fuel 81:1509. doi: 10.1016/S0016-2361(02)00069-8
13. Qiu JS, Zhou Y, Wang LN et al (1998) Carbon 36:465