

of DWNTs. In contrast, the Lorentzian bands related to the inner tubes appear to a slight downshift (4 cm^{-1}) from 1582 cm^{-1} to 1578 cm^{-1} , which indicates the occurrence of charge transfer from Cs to the inner wall of DWNTs. One simple possibility for above different downshift of Raman peaks can be attributed to a different filling level between Cs encapsulation in and intercalation around DWNTs. Furthermore, the process of intercalating Cs in relatively narrow channels between nanotubes can easily reach a saturation phase compared to the case of filling Cs inside nanotubes, which may also be responsible for the great shift of G-band for outer tubes of Cs-filled DWNTs.

In summary, the filling of Cs in DWNTs has successfully been realized for the first time by a plasma-ion irradiation method. The presence of Cs in DWNTs has been confirmed by TEM observation and Raman spectra. These Cs-filled DWNTs are expected to be useful in the fabrication of nano-sensors and electronic devices.

Acknowledgements

The authors would like to thank Prof. K. Tohji and Mr. K. Motomiya for their technical support. Part of this work

has been carried out at the laboratory for Nanoelectronic and Spintronics, Research Institute of Electrical Communication, Tohoku University. This work was supported by Tohoku University 21st Century Center of excellence (COE) Program, Japan, and JSPS-CAS Core-University Program on Plasma and nuclear Fusion.

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Flower-like carbon materials prepared via a simple solvothermal route

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Received 25 September 2005; accepted 6 February 2006

Available online 6 March 2006

Keywords: Graphitic carbon; Chemical treatment; Scanning electron microscopy; Raman spectroscopy

Nowadays, shape and size control of carbon materials is important for practical applications, so the preparation of various morphologies of carbon materials has attracted considerable attention, such as carbon cubes [1], carbon micro-trees [2], carbon cones [3], gypsum flower-like carbon [4]. However, there are no reports of flower-like carbon materials (FCMs) that are produced here by a simple solvothermal route. The yield of FCMs was estimated through SEM observations of the as-prepared samples to be not less than 80%. In a typical procedure, 3 g of $\text{Mg}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ and 10 mL of polyethylene glycol were put into a bea-

ker with 40 mL absolute ethanol, and sonicated for 10 min to form a homogeneous solution. The resulting solution was transferred into a stainless steel autoclave of 60 mL capacity, which was sealed and maintained at $600\text{ }^\circ\text{C}$ for 24 h, and then it was allowed to cool to room temperature. A dark precipitate was collected and washed with absolute ethanol, dilute HCl aqueous solution and distilled water, respectively. The obtained sample was then dried in a vacuum at $60\text{ }^\circ\text{C}$ for 1 h.

The morphologies of the sample were characterized with scanning electron microscopy (SEM, PHILIPS XL-30S), transmission electron microscopy (TEM, PHILIPS TECNAI-10), and high-resolution transmission electron microscopy (HRTEM, JEOL-2010 using an accelerating voltage of 200 kV). The Raman spectrum was recorded at

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ambient temperature on a Renishaw RM2000 Raman micro-spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-prepared samples before and after HCl acid treatment. The sharp diffraction peaks with high peak intensity in curve: (a) were indexed as crystalline hexagonal MgCO_3 (JCPDS File No. 08-0479), while the broad low intensity peaks were produced by disordered carbon; curve: (b) includes three peaks that could both be indexed as low crystalline carbon. The crystalline MgCO_3 was removed after the acid treatment. No peaks for impurities were detected.

Fig. 2 shows typical SEM images of the FCMs prepared by solvothermal route at 600 °C for 24 h. Fig. 2(a) indicate a large amount of the FCMs appears as the flower-like microstructure of carbon. It is interesting to note that most of the resulting products as shown in Fig. 2 is the typical morphology, generally consist of undulated flakes. SEM image (Fig. 2b) indicates that typically FCMs is made up of many flakes and is very like a flower for bloom. The FCMs have diameters in the range of 8–10 μm .

Fig. 3(a)–(c) shows the TEM and HRTEM images of the typical FCMs. The graphite flakes of many similar flower petals can be observed clearly. It is worth noting that some rumples can be seen in flakes (Fig. 3b), and a further clear magnified image of part flake is shown (Fig. 3c). The SAED pattern (Fig. 3d) of these carbon flakes shows clearly hexagonal dots, indicating that the FCMs have a hexagonal crystalline carbon structures. The energy-dispersive X-ray (EDX) analysis (Fig. 3e) on the FCMs shows it consists of carbon. The peaks of O may origin from the absorbed water molecules and the Cr may come from stainless steel autoclave.

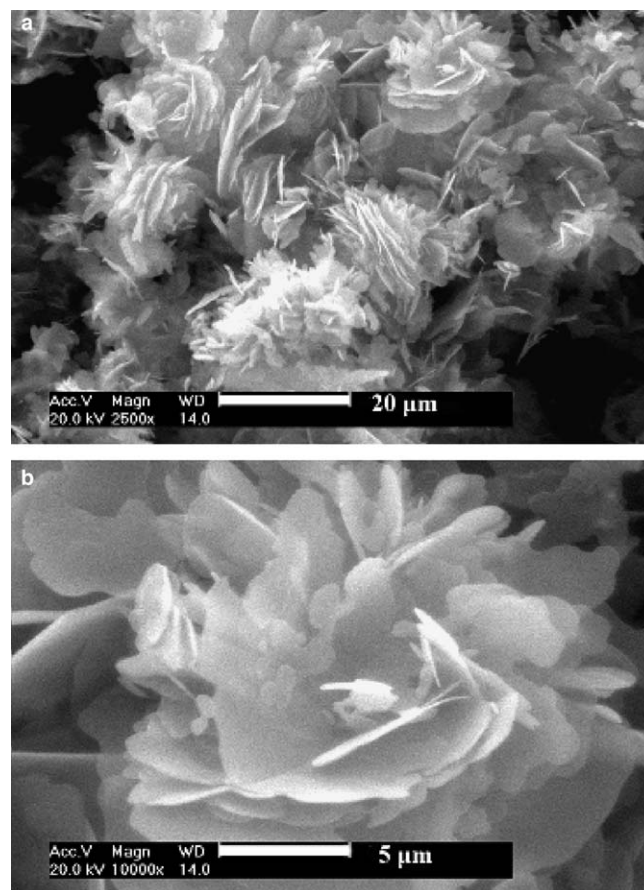


Fig. 2. Typical SEM and TEM images of FCMs: (a) SEM image of sample, (b) the Figure (a) area of single FCMs is shown enlarged.

A typical Raman spectrum of FCMs is shown in Fig. 4, in which a broad peak at 1339 cm^{-1} as well as a sharp absorption peak at 1592 cm^{-1} can be clearly seen. The peak at 1339 cm^{-1} is usually associated with vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered carbon and is labeled as the D-bands. The peak at 1592 cm^{-1} (G-bands) corresponds to an E_{2g} mode of carbon closely related to the vibration in all sp^2 -bonded carbon atoms in a two-dimension hexagonal lattice, such as in a graphene layer [5].

To determine the influence of different reaction conditions, we carried out the comparative experiments and found that temperature and time are important factors influencing the yields of FCMs. When the temperature is lower than 500 °C, such as 300 and 400 °C, there are no FCMs in the products. If the temperature is raised to 500 °C, large amounts of straw-like carbon, few FCMs, are obtained. When the temperature reaches 600 °C, many of the FCMs were acquired. Meanwhile, we find that a particular period of reaction time (24 h) appears to be optimum to give a large quantity of FCMs than other reaction times (10 and 36 h). Therefore, the most favorable temperature is 600 °C, and the optimal reaction time is 24 h. In addition, magnesium acetate may play an important role in producing FCMs, because no FCMs are

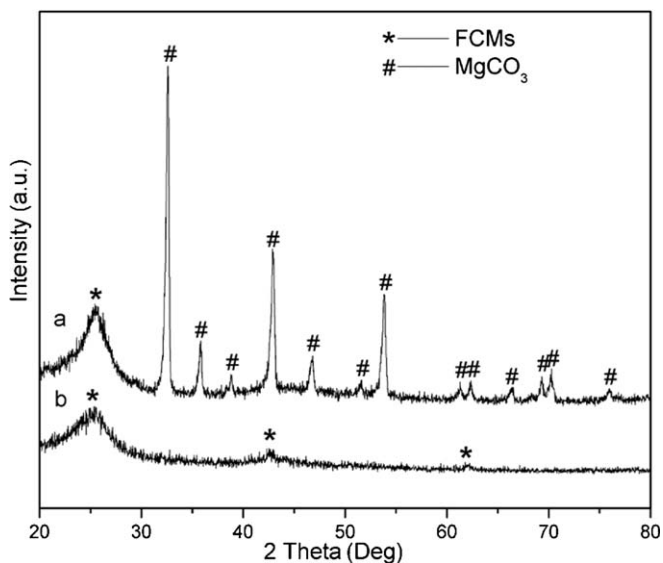


Fig. 1. X-ray diffraction of the samples before and after HCl acid treatment.

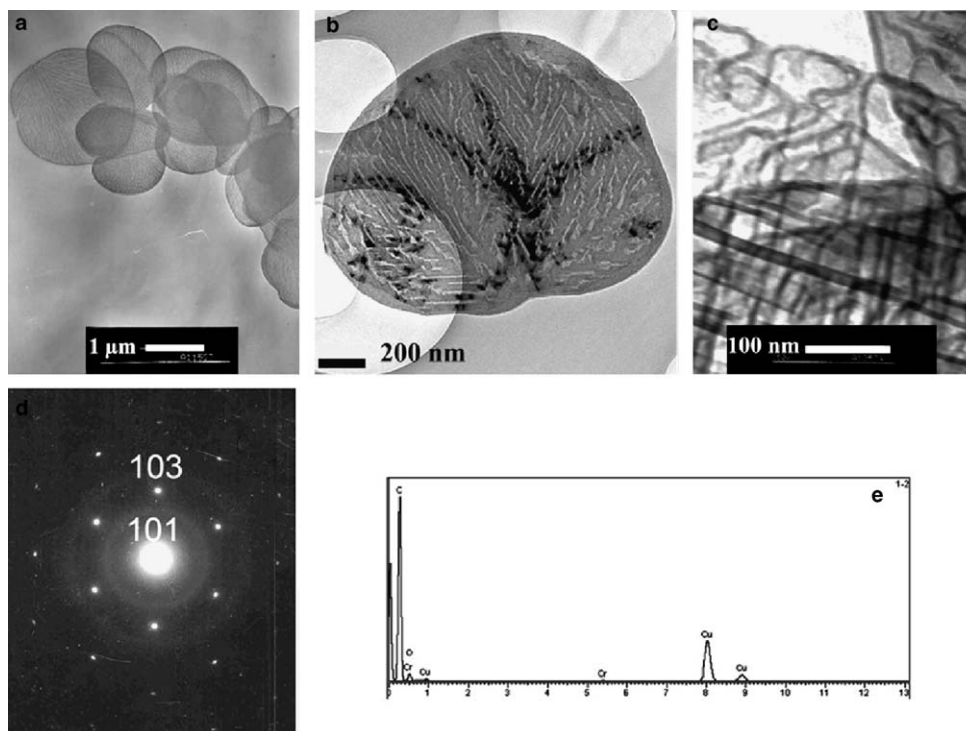


Fig. 3. TEM and HRTEM images (a, b and c), the SAED pattern (d) and EDX spectrum (e) of the as-prepared FCMs.

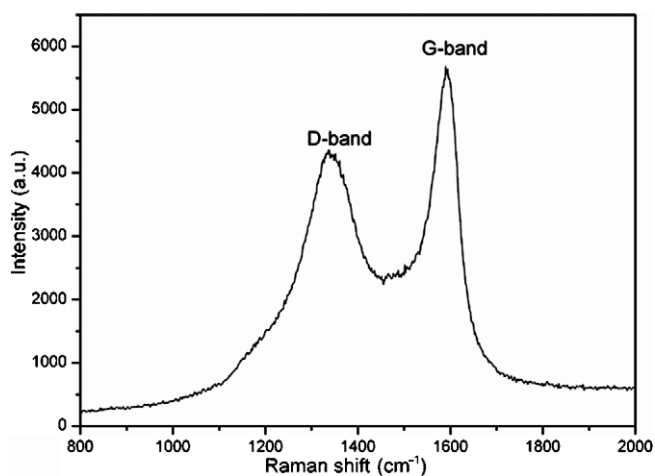


Fig. 4. Raman spectrum of the as-prepared FCMs.

obtained when there is no magnesium acetate in the reaction process, as we replaced the magnesium acetate by zinc acetate with other conditions of the reaction unchanged, the products were mainly carbon micro-spheres. It indicated that magnesium acetate played a key role in the formation of FCMs. When there is no polyethylene glycol, only carbon micro-spheres can be observed, that is, polyethylene glycol may act as a template during FCMs formation.

The formation mechanism of FCMs may be very complex. Here it can be determined that the effect of polyethylene glycol on the formation of FCMs is quite great and it

or its intermediate produced in heating process should play a key role for the novel structure and shape of FCMs. Further work is under way.

In summary, novel FCMs with diameters in the range of 8–10 μm can be formed by a simple solvothermal route at 600 $^{\circ}\text{C}$ for 24 h. Owing to their unique morphology, the FCMs may have potential applications in electrode materials and microreactors.

Acknowledgments

This work was financially supported by the Science and Technology Project of Guangdong Province (2KM02304G and 2005A11001001) and Qian Bai Shi Project of Guangdong Province (Q02059).

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