A Simple Route to Form Straw-like Carbon Microbundles

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Novel straw-like carbon microbundles (CMBS) were obtained by simple solvothermal route at 500 °C for 48 h. In this process, magnesium acetate and polyethylene glycol may play an important role in determining the straw-like morphology. The products were characterized with X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Those CMBS have diameter in the range of 0.8–1 μm and lengths up to tens of micrometers. This provides a simple preparation method and technology of carbonaceous materials with different morphology and size.

In recent years, carbon materials attract worldwide scientists' interests due to their unique structures, special chemical and physical properties, including the capability for the storage of a large amount of hydrogen,[1] conductive and high-strength composites,[2] nanotweezers,[3] semiconductor devices,[4] separation technology,[5,6] and field emission displays.[7] The preparation and properties of these carbon materials have attracted considerable attention, because their applications significantly depend on the shape and size of the particles. Since the discovery of carbon nanotubes,[8] therefore, more efforts have been made to produce novel kinds of them such as carbon onions,[9] carbon cubes,[10] carbon micro-trees,[11] carbon cones,[12] carbon micro-coils,[13] and hollow carbon calabashes.[14]

However, to our knowledge, there are few reports of carbon microbundles (CMBS) with straw-like morphology. In this paper, we have demonstrated a simple and convenient solvothermal route to the production of novel uniform straw-like CMBS by using magnesium acetate, polyethylene glycol, and absolute ethanol as reactants in an autoclave at 500 °C for 48 h. The yield of CMBS was estimated through SEM observations of the as-prepared samples to be about 90%.

All the chemical reagents were A.R. grade and used without further purification. In a typical procedure, 3 g of $Mg(CH_3COOH)_2 \cdot 4H_2O$ and 10 mL of polyethylene glycol were put into beaker with 40 mL absolute ethanol, then supersonicated for 10 min to form a homogeneous solution. The resulting solution was transferred into a stainless steel autoclave of 60 mL capacity. The autoclave was sealed and maintained at 500 °C for 48 h, and then cooled to room temperature naturally. A dark precipitate was collected and washed with absolute ethanol, dilute HCl aqueous solution, distilled water and absolute ethanol, respectively. The obtained sample was then dried in a vacuum at 60 °C for 1 h.

Structure characterization was performed by X-ray powder diffraction (XRD) pattern on MSAL-XD2 X-ray diffractometer with Cu Kα radiation (40 kV, 20 mA, and $\lambda = 1.54051$ Å). The morphologies of the sample were characterized with Philips XL-30 scanning electron microscopy and Philips TECNAI-10 transmission electron microscopy. The Raman spectrum of as-prepared samples was recorded at ambient temperature on Renishaw RM2000 Raman microspectrometer with an argon-ion laser at an excitation wavelength of 785 nm.

Figures 1a and 1b show the X-ray diffraction pattern of the as-prepared samples before and after HCl acid treatment, respectively. A scanning rate of $0.08^\circ\ s^{-1}$ has been used to record the pattern in the range of 10–80°. The sharp diffraction peaks with high peak intensity in this Figure 1a were indexed as crystalline hexagonal $MgCO_3$ (JCPDS card No. 86-0175), while the broad peaks with low peak intensity could be indexed as carbon; Figure 1b includes two peaks both indexed as low crystalline carbon indicating that crystalline $MgCO_3$ was removed after the acid treatment process. No characteristic peaks of impurities were detected in the pattern. The cell parameter calculated from this pattern were $a = 2.450$ Å and $c = 6.812$ Å, in agreement with that found in the literature (JCPDS Card. No. 75-1621).

Figures 2a–2d show typical SEM and TEM images of straw-like CMBS prepared by solvothermal route at 500 °C for 48 h. Figure 2a indicates a large amount of CMBS appears as a sheaf of straw tied in the end, forming the straw-like microstructure of carbon. It is interesting to note that most of the resulting products in Figures 2a–2d are straight, straw-like morphology and generally have both open ends. The CMBS have diameter in the range of 0.8–1 μm and lengths up to tens of micrometers. High-magnification SEM image (Figure 2c) indicates that typically CMBS has open end with a wall thickness in the range of 200–300 nm. The TEM image presented in Figure 2d shows that the straw-like CMBS are hollow structure. It is worth noting that some unformed tubes can be seen from Figure 2e, which are made of a lot carbon spheres and amorphous graphite. In addition, some carbon spheres also are been observed in Figure 2a. Owing to these appearances of tube are similar to the straw-like CMBS. Therefore, we consider that the growth mechanism of straw-like CMBS may be related to carbon sphere. However, the exact formation mechanism still needs further research.

It is well known that Raman spectroscopy is one of the powerful techniques for characterizing carbon materials. The micro-Raman spectrum of the CMBS is shown in Figure 3. The peak at 1585 cm^{-1} (G) corresponds to an E_{2g} mode of graphite, related

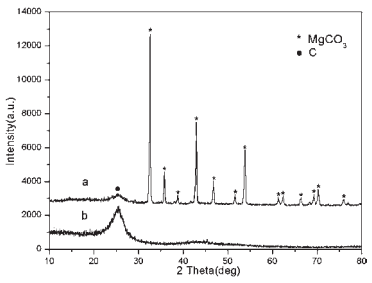

Figure 1. X-ray diffraction of the sample before and after HCl acid treatment, respectively.

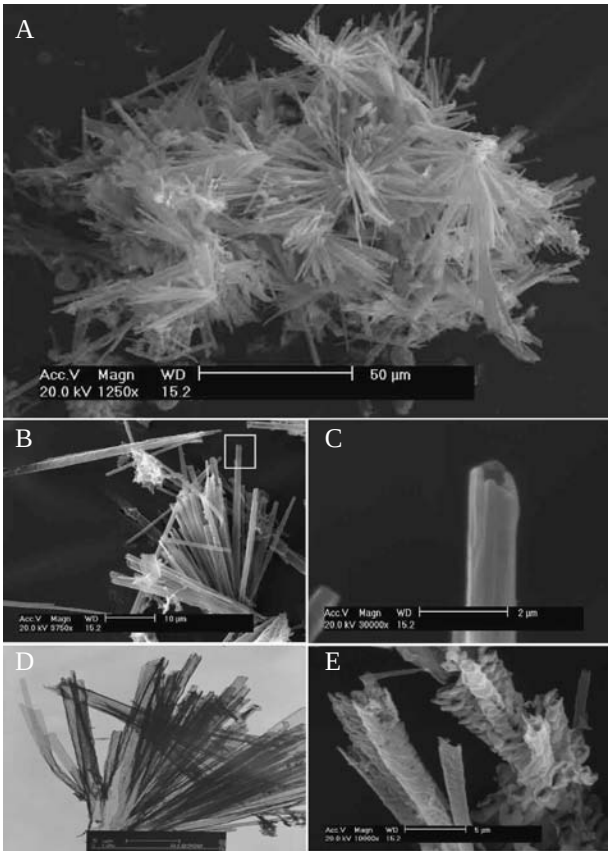

Figure 2. Typical SEM and TEM images of sample: (A) low-magnification SEM image of straw-like CMBS, (B) high-magnification SEM image of straw-like CMBS, (C) the Figure (B) area of rectangle is shown enlarged, (D) TEM image of straw-like CMBS, and (E) SEM image of the unformed straw-like CMBS.

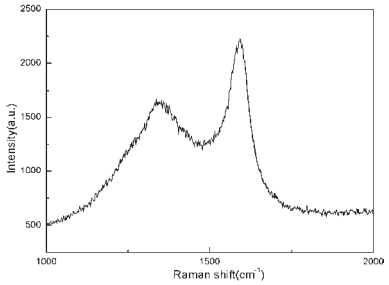

Figure 3. Micro-Raman spectrum of the as-prepared sample.

to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer. The peak at 1345 cm^{-1} (D) is associated with vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite.[15] The D- and G-bands of carbon show an intensity ratio of $I_D/I_G = 0.75$, this ratio indicates the lower graphitic degree in the as-prepared CMBS prepared via solvothermal route.

In this experiment, temperature and time are important factors influencing the yields of CMBS, which were proven in our contrast experiments. When the temperature is lower than 500 °C, such as 300 and 400 °C, there is no CMBS in the as-prepared sample. If the temperature is raised to 600 °C, a large amount of amorphous carbon, few CMBS, are obtained. Meanwhile, we find that a particular period of reaction time (48 h) appears to be optimum to give a large quantity of CMBS than other reaction times (10, 24, and 36 h). Therefore, the most favorable temperature is 500 °C, and the optimal reaction time is 48 h. In addition, the effects of magnesium acetate and polyethylene glycol are also considered. Magnesium acetate may be played an important role in producing CMBS, because no CMBS are obtained when there is no magnesium acetate in the reaction process; when there is no polyethylene glycol, only a great lot of carbon microspheres can be observed, that is, polyethylene glycol may act as template during the formation of the straw-like CMBS.

In summary, novel straw-like CMBS with a diameter in the range of 0.8–1 µm and lengths up to tens of micrometers can be formed by simple solvothermal route at 500 °C for 48 h. Magnesium acetate and polyethylene glycol may play an important role in determining the straw-like morphology; the exact formation mechanism still needs further research. These novel structure materials may find a range of potential applications such as catalysis, separation technology, and hydrogen storage.

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