Chemistry Letters Vol.33, No.5 (2004)

Preparation of Carbon Spheres Composed of Entangled Fibers at Low Temperature

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(Received October 20, 2003; CL-030992)

In this paper, we report a new mild reaction route to prepare carbon spheres composed of entangled fibers. The reaction was carried out at 250 °C for 24 h using sodium and polytetrafluorethylene as reactants and benzene as solvent. A possible formation mechanism is proposed.

Since the discovery of carbon nanotubes by Iijima,[1] there has been intense interest in carbon materials. Carbon nanotubes and other carbon structures have a wide range of applications including conductive and high-strength composites,[2] gas storage media,[3] templates,[4] semiconductor devices,[5] and field emission displays.[6] Different carbon morphology and structures, such as C_{60},[7] nanofibers[8] have been synthesized via various methods.

Carbon spheres represent a special class of materials, which are of interest in the fields of medicine, pharmaceutics, materials science, and paint industry. They have been found to have diverse applications, including encapsulation of products (for the controlled-release of drugs, cosmetics, inks, and dyes), as well as protection of light-sensitive components, catalysis, coatings, composites, and fillers.[9,10] They were synthesized from a water-in-oil emulsion, followed by heat-treatment at various temperatures;[11] or via mixed-valent oxide-catalytic carbonization process at 900–1050 °C under the action of MnO_2 catalyst; or annealing products of sodium and hexachlorobenzene in nitrogen flow above 1400 °C;[12] or taking medial-reduction using Na_2CO_3, CCl_4, and Mg at 450 °C.[13]

To get high quality of materials at mild condition is always our desire. Recently, the chemical solution routes are emerging as an effective, convenient, less energy-consuming synthetic method. We synthesized carbon spheres composed of entangled fibers at 250 °C using sodium and polytetrafluorethylene as reactants.

All reagents were commercially available and used without further purification. In a typical experiment, metallic Na (0.200 g) and microsize polytetrafluorethylene powder (0.217 g) were added into a stainless steel reactor of 50-mL capacity, then 40-mL C_6H_6 was filled in. The reactor was maintained at 250 °C for 24 h. Then the reaction resultants were collected, washed with absolute ethanol and dried in vacuum at 40 °C for 4 h.

The obtained samples were characterized via X-ray powder diffraction (XRD) using Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 0.15406$ nm), the scanning rate of $0.05^\circ s^{-1}$ was applied to record the pattern in the 2θ range of 10°–70°. Figure 1 shows the XRD pattern of as-prepared products, which may be indexed as (002) peak and (10) band of hexagonal graphite structure (JCPDS 41-1487). The (002) peak is strong while (10) band is weak and widened.

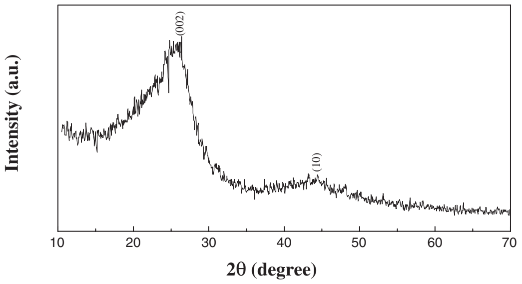

Figure 1. XRD pattern of as-prepared products.

The scanning electron microscopy (SEM) image was obtained on a Hitachi X-650 scanning electron microanalyzer. The transmission electron microscope (TEM) images and selected-area electron diffraction (SAED) pattern were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

Figure 2a shows a SEM image of as-prepared products, which take the morphology of sphere. The carbon spheres are

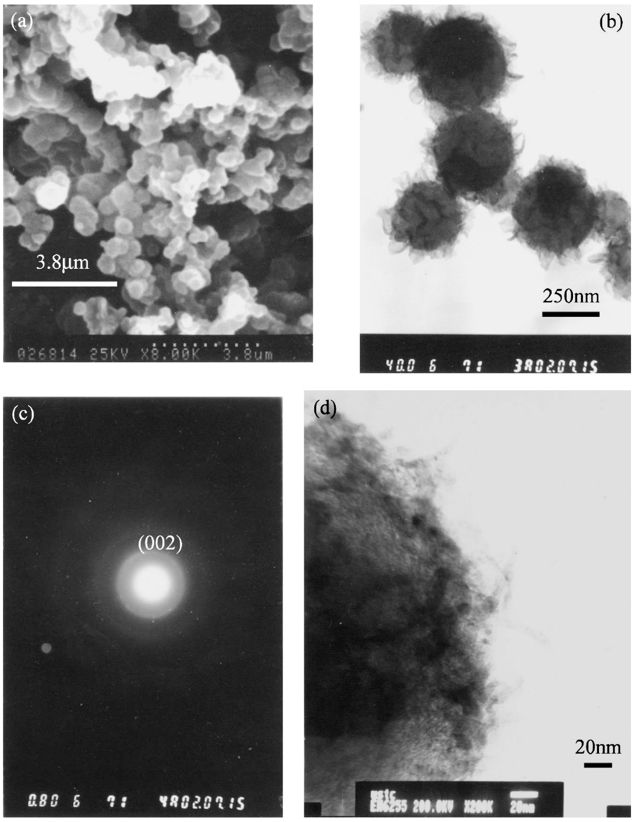

Figure 2. (a) SEM image of products showing the morphology of sphere in large scale; (b) TEM image of products showing carbon sphere with entangled fiber on the surface; (c) SAED of carbon sphere; (d) TEM image of sphere with large magnification indicating that spheres are composed of entangled carbon fibers.

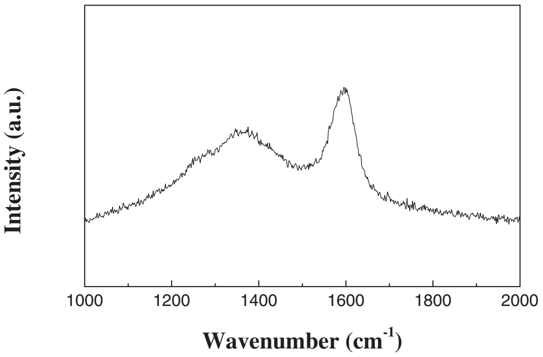

Figure 3. Raman spectrum of products which shows G-and D-graphite peaks at 1365 and 1594 cm^{-1}.

in large scale and uniform. Figure 2b is a typical TEM image. The carbon spheres are 300–400 nm in diameter with entangled fibers on the surface. Figure 2c is the SAED pattern of the sphere. The diffraction ring can be indexed as (002) reflections of graphite. Figure 2d is the close TEM examination of sphere with large magnification. It indicates that the spheres are made of entangled carbon fibers. The fibers are less than 10 nm in diameter.

The carbonaceous products were used directly to record the Raman spectrum (Figure 3) at room temperature using a confocal laser Raman microspectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. There exist two strong peaks at 1594 and 1365 cm^{-1}. The peak at 1594 cm^{-1} may be a mixture of E_{2g} (ca. 1580 cm^{-1}) and D'band (ca. 1620 cm^{-1}), the E_{2g} mode is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice. The peak at 1365 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite.[14] This peak is quite broad and it means that in the basal plane there exists 2-D disorder, which is to be expected because of the low reaction temperature.

The mechanism for the formation of carbon spheres with entangled fibers is proposed. The reaction might take place as follows:

$$(C_2F_4)_n + Na \rightarrow C + NaF$$

As sodium is liquid and polytetrafluorethylene is solid at reaction condition, it is supposed that the reaction produces carbon on the surface of polytetrafluorethylene powder; the newly produced carbon grows into the shape of fiber as the reaction proceeds into the core of polytetrafluorethylene powder. The metal sodium deprives all fluorine atoms from polytetrafluorethylene and leaves carbon sphere with entangled fibers.

The crystallinity of as-prepared carbon spheres made of entangled fibers is not high, but they may find application in the fields such as controlled release, catalysis, composites, and fillers because the internal vacancies in the carbon sphere provides the space for guest to occupy. This route is very easy to maintain and control. As wet chemical method can be applied to a greater variety of materials and has relative higher yields than other methods, it may provide a new method to produce other carbonaceous materials.

The project was supported by Excellent Scholar Foundation of Anhui Province Education Administration and Starting Foundation of Anhui Normal University for Doctors.

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