Synthesis of Carbon Hollow Spheres by a Reaction of Hexachlorobutadiene with Sodium Azide

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Carbon hollow spheres with an average size of about 250 nm in diameter were successfully synthesized by a reaction of hexachlorobutadiene (C_4Cl_6) with NaN_3 at 400 °C. The X-ray powder diffraction (XRD) and Raman results reveal the graphite structure of the as-prepared sample. The thermal stability of the as-prepared sample was also investigated. The possible mechanism has been proposed.

There has been a lot of research works focused on carbon materials since the discovery of fullerenes by Kroto et al. in 1985.[1] The subsequent studies indicated that carbon can exist as a number of novel structures, such as carbon nanotubes,[2] carbon onions,[3] and graphitic cones.[4] Various techniques or methods have been tried to produce these new carbon materials, including laser vaporization, arc discharge, and electron irradiation, because of to their wide range of applications in semiconductor device, gas storage, nanotweezers, and electronics.[5–8]

As a kind of highly curved graphitic network structure, carbon spheres have attracted relatively less interest than other carbon materials. However, the applications of carbon spheres are no lesser. Carbon spheres can be used as lubricating materials, special rubber additives and so forth.

Previously, carbon spheres have been synthesized by various methods. For example, carbon hollow spheres with several micrometers in diameter have been formed from C_{60} fullerene powder after shock compression up to 57 GPa.[9] Wang et al. produced graphitic carbon solid spheres via a mixed-valent oxide-catalytic carbonization (MVOCC) process at 900–1050 °C.[10] Hu et al. synthesized hollow carbon spheres by a self-assembly approach using hexachlorobenzene and Na, followed by annealing above 1400 °C to remove NaCl generated during the reaction.[11] Complicated processes or hazardous experimental conditions are necessary for the above methods.

Herein, we reported a novel direct chemical route to synthesize carbon hollow spheres by a reaction of hexachlorobutadiene (C_4Cl_6) with NaN_3 at 400 °C. The reaction was carried out in an autoclave and can be described as follows:

$$C_4Cl_6 + 6NaN_3 \rightarrow 4C(\text{carbon hollow spheres}) + 6NaCl + 9N_2$$

In a typical procedure, an appropriate amount of anhydrous hexachlorobutadiene (0.01 mol) and NaN_3 (0.06 mol) were put into a stainless autoclave with a glass tube liner of about 50-mL capacity. The autoclave was sealed and maintained for 5 h at 400 °C, then cooled to room temperature. The product was washed successively with absolute ethanol, dilute hydrochloric acid, and distilled water to remove NaCl and other impurities. After drying in vacuum at 60 °C for 4 h, the final black powder product was obtained.

The morphology of the as-prepared samples was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. Raman spectra were measured on a LabRAM HR Raman spectrophotometer. The 5145 Å laser was used as an excitation light source. X-ray powder diffraction (XRD) measurement was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Thermogravimetric analysis (TGA) profile was collected with a Shimadzu-50 thermoanalyzer apparatus under air flow.

Figure 1 shows the XRD pattern of the sample. Two peaks could be indexed to the hexagonal graphite phase (002) and (101) planes. The *d* spacing of (002) plane is calculated from $2\theta = 26.07°$ to be 3.4150 Å, which is a little larger than the reported value of graphite ($d = 3.3756$ Å, JCPDS card, No.41-1487). This suggests that the spacing between the sp^2-carbon layers in the carbon hollow spheres is increased. The (002) peak is broadened. This may originate from the existence of a distribution of the spacing between the sp^2 carbon layers due to the different diameters of carbon hollow spheres.

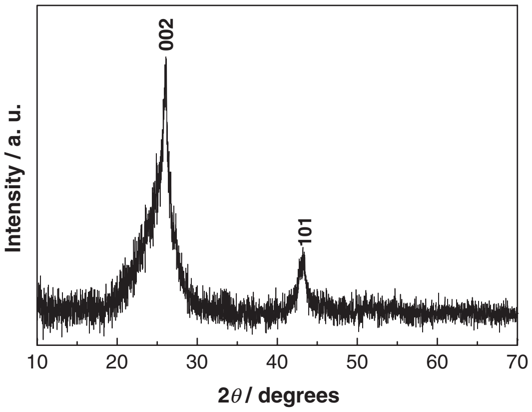

Figure 1. XRD pattern of the as-prepared sample.

Further evidence for the graphite structure of the sample can be obtained through Raman spectroscopy. Figure 2 shows the room-temperature Raman spectrum of the as-prepared sample. Two strong peaks at 1343 and 1574 cm^{-1} can be observed clearly. The peak at 1574 cm^{-1} has been attributed to Raman G mode, which is associated with the vibration of sp^2-bonded carbon atoms in a 2-D hexagonal lattice. The peak at 1343 cm^{-1} is attributed to a disorder Raman D mode of graphite.[12,13]

The morphology of the as-prepared sample was investigated

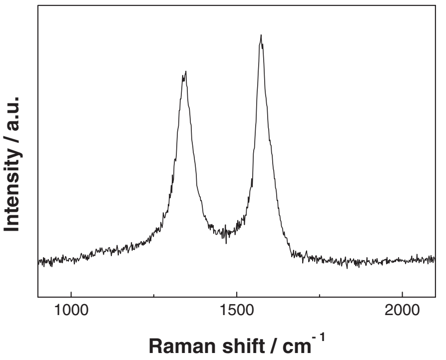

Figure 2. Room-temperature Raman spectra of the as-prepared sample.

by TEM. Figures 3A and 3B show the TEM images of the samples. It can be seen that the sample consists of hollow spheres with average diameter of about 250 nm and the thickness of the shell of about 10 nm. The strong contrast between the dark edge and pale center in Figure 3B is also the proof of the hollow nature.[14] The inset of Figure 3A shows the transmission electron-diffraction pattern of the selected area of the sample, in which two diffraction rings corresponding to graphite (101) and (110) can be observed. The absence of the (002) reflection may be due to the fact that the local (001) graphite plane is nearly perpendicular to the electron beam.[10]

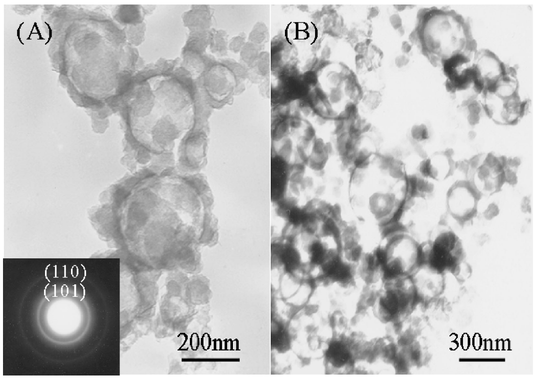

Figure 3. TEM images (A, B) and selected area electron-diffraction pattern (inset of Figure 3A) of the sample.

In our experiments, with the temperature increasing (up to 300 °C), NaN_3 decomposed generating N_2 and molten Na (melting point: 98 °C) following the overall equation $2NaN_3 \rightarrow 3N_2 + 2Na$. At a desired temperature, hexachlorobutadiene (C_4Cl_6) can be reduced continuously by Na to free C_4 chains, which disperse in the molten Na. The newly formed free C_4 chains are so active that they can directly react with each other to produce hexagonal lattice of sp^2-bonded carbon, which exists as graphite sheets. The graphite sheets cover the NaCl particles and form carbon spheres, in which some C_4Cl_6 and N_2 may be encapsulated. In the newly formed carbon spheres, C_4Cl_6 reacts with Na continuously. While the Na is consumed, the hollow carbon spheres can be formed.

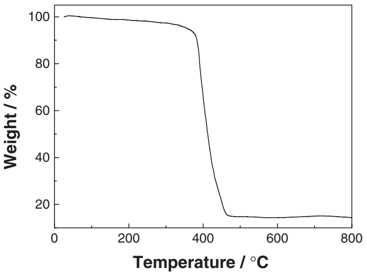

Figure 4. TGA curve for the as-prepared sample.

To investigate the thermal stability of the as-prepared sample, the thermogravimetric analysis (TGA) was carried out in air at atmospheric pressure. Figure 4 shows the TGA curve of the carbon hollow sphere sample. It indicates that a pronounced weight-loss step occurred around 400 °C, which can be attributed to the oxidation of carbon hollow spheres. This is about 250 °C lower than that of natural graphite particles, which is stable in air up to 650 °C.[15] The lower thermal stability of carbon hollow spheres may be due to the nanometer hollow structure of the sample, which makes the ratio of the surface to volume remarkably large. In addition, the van der Waals interactions for the graphite layers may be reduced by the increased spacing between the sp^2 carbon layers for the carbon hollow spheres, which also favors the oxidation. Therefore, the thermal stability of the as-prepared sample decreases greatly.

In summary, carbon hollow spheres with an average size of about 250 nm in diameter have been synthesized by a reaction of hexachlorobutadiene (C_4Cl_6) with NaN_3 at 400 °C. The thermal stability of the carbon hollow spheres sample decreases greatly, which may be due to the nanometer hollow structure.

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