A Core-shell Nanostructure of Carbon

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Core-shell structured carbon nanospheres with 300–500 nm in diameter have been synthesized at 600 °C by reducing ethyl ether with metallic magnesium.

In 1991, the carbon nanotubes were observed and stimulated intense interest in the structures accessible to carbon.[1] In recent years, considerable efforts have been made to fabricate different carbon nanostructures and explore their applications.[2–9] Jiang and co-workers developed a catalytic-assembly benzene-thermal route to multiwall carbon nanotubes using reduction of hexachorobenzene by metallic potassium in the presence of Co/Ni catalyst at 350 °C.[10] Lately, Liu et al. has successfully synthesized bamboo-shaped carbon nanotubes on a large scale through an ethanol thermal reduction process, in which ethanol was used as the carbon source and metallic magnesium was used as the reductant.[11] In 1997, A. Krishnan and his co-workers have successfully synthesized graphitic cones by the pyrolysis of hydrocarbon in a carbon arc.[12] The hollow carbon cones have been synthesized by reduction of butyl alcohol with metallic magnesium at 500 °C.[13] Hu and his co-workers have synthesized hollow carbon spheres by a self-assembly approach using hexachorobenzene and Na.[14] In the previous work, hollow carbon spheres had been synthesized by the medial-reduction route using metallic magnesium powder, and the inorganic salts Na_2CO_3 and CCl_4 as reactants in benzene solvent.[15] To the best of our knowledge, there has been no report about the synthesis of the core-shell structured carbon yet.

Here we used a chemical approach to synthesize core-shell structured carbon nanospheres. Such a process involved ethyl ether as carbon source and magnesium as reducing agent. The redox reaction could be expressed as:

$$C_2H_5OC_2H_5 + Mg = 4C + MgO + 5H_2$$

In a typical experiment, 0.997 g of metallic magnesium powder (99%) and 15 mL of ethyl ether were put into a 20-mL stainless steel autoclave. After being sealed, the autoclave was maintained at 600 °C for 12 h and then cooled to room temperature naturally. The product was collected and washed with pure ethanol, dilute hydrochloric acid and distilled water several times. After that, the product was dried in vacuum at 60 °C for 6 h.

The phase of as-obtained products and the reaction were determined by XRD on a Philips X'Pert PROSUPER X-ray powder diffractometer (Cu Kα radiation $\lambda = 1.541874$ Å). Figure 1a shows the XRD pattern of the product before washing. All the reflection peaks can be indexed to the face-centered cubic MgO (JCPDS Card File, No. 78-0430) and amorphous carbon. Figure 1b is the XRD pattern of the products after being washed by dilute HCl aq solution and distilled water, which can be indexed to amorphous carbon. The results confirm the redox reaction.

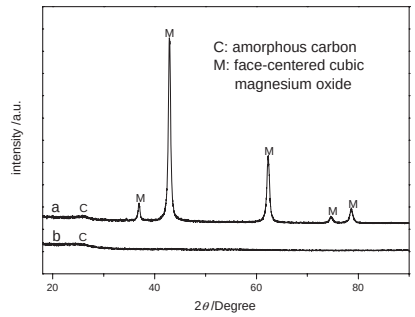

Figure 1. XRD patterns of the products with different treatments: (a) not washed: (b) washed with dilute HCl aq solution and distilled water.

The products were observed on a Hitachi 800 transmission electron microscopy (TEM) performed at 200 kV. From the TEM images in Figure 2, it can be seen that the sample consists of the core-shell structured nanospheres with 300–500 nm in diameter. There is a clear shell-like space between core and shell, which is essential to distinguish core and shell of the same component. The thickness of the shell is about 20 nm and the core is 200–400 nm in diameter. The gap between core and shell is about 30 nm. The electron diffraction (ED) pattern can be attributed to amorphous carbon, which confirms the XRD result.

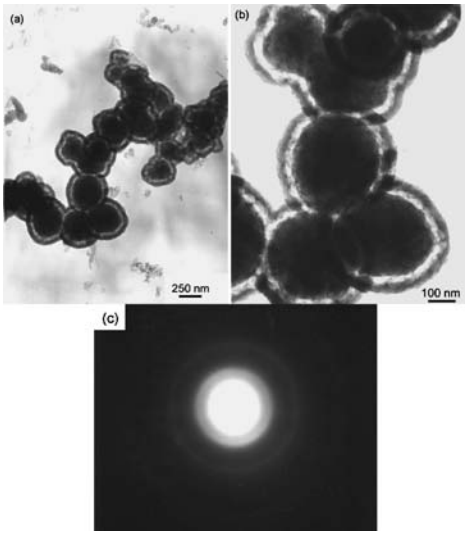

Figure 2. (a) and (b) TEM images of the washed sample by HCl. (c) The electron diffraction pattern, which was taken from one sphere in Figure 2b.

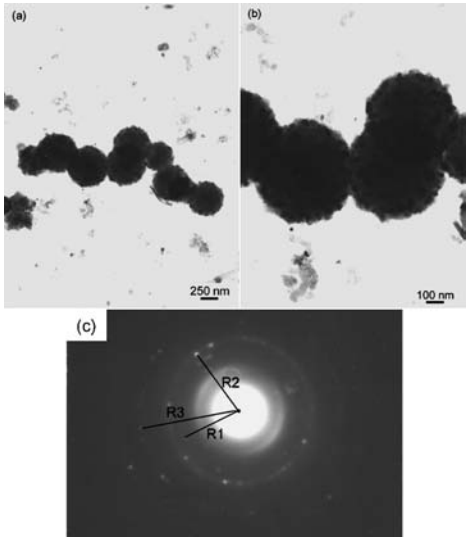

Figure 3. (a) and (b) TEM micrograph of the products without washing. (c) The electron diffraction pattern, which was taken from one of the spheres in Figure 3b.

To investigate the growth process of the core-shell structured carbon nanospheres, the products with various treatments have been studied. The XRD pattern of Figure 1a proves that the products includes MgO and C before being washed by dilute HCl aq solution, meanwhile, it can be seen from the TEM images in Figure 3 that the nanospheres are solid and include many darker and smaller particulates. And two sets of electron diffraction pattern are identified in Figure 3c. One is attributed to amorphous carbon. The other matches well to the diffraction pattern of the face-centered cubic MgO: R1 to 111, R2 to 200, and R3 to 220. These prove that the nanospheres include MgO. After being washed with dilute HCl aqueous solution, MgO is removed, which can be confirmed by XRD pattern of Figure 1b. And the core-shell structured carbon nanospheres can be seen in TEM images of Figure 2. So, we suggest that the enclosure-diffusion process could be used to explain the formation of the core-shell structure (in Figure 4): The reaction of this experiment is highly exothermic ($\Delta H^\circ = -349.6\,\mathrm{KJ{\cdot}mol^{-1}}$). In this synthetic system, metallic magnesium may form droplets owing to reaction heat generated from the exothermic reaction, and these metallic magnesium droplets may act as template in the formation process of core-shell structured carbon nanospheres. Firstly, upon increasing the reaction temperature to 600 °C, the ethyl ether began to vaporize. Strongly exothermic reaction took place on the surface of metallic magnesium powder, raising the local temperature near the surface and hence causing the magnesium to vaporize (bp 1100 °C). This magnesium vapor could form many small droplets in the autoclave. Secondly, the ethyl ether was adsorbed on the surface of the magnesium droplets and reacted with the exterior Mg to produce MgO and carbon. The produced MgO and carbon enclosed the unreacted interior metallic magnesium. Thirdly, based on the diffusion, the enclosed magnesium moved to the surface and adsorbed ethyl ether and reacted with it again. Consequently, the nanospheres were formed with the structure: the mixture of magnesium oxide and carbon in the core, the magnesium oxide in the interlayer and the carbon on the edge. The magnesium oxide was removed by washing the products with the dilute HCl aqueous solution. So the core-shell structured carbon nanospheres were left.

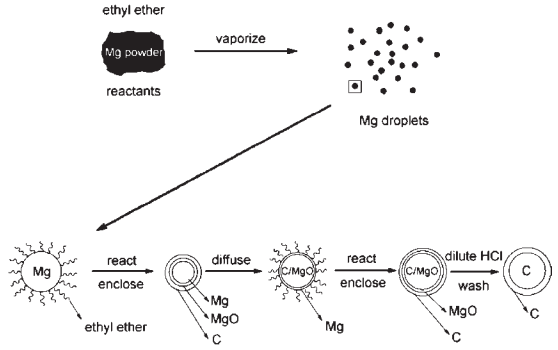

Figure 4. Schematic growth model for core-shell structure carbon nanospheres.

In summary, the core-shell structured carbon nanospheres 300–500 nm in diameter have been successfully prepared by an ethyl ether thermal reduction process with magnesium as reductant. The model of the core-shell structured carbon nanospheres growth can be summarized to enclosure- diffusion process. It provides a new pathway to interpret the core-shell structured carbon growth. It is also a promising approach to design and fabricate semiconductor, noble metal and transition metal/carbon core-shell nanostructure.

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