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The Preparation of Hollow Carbon Spheres by Thermal Decomposition of Poly(tetrafluoroethylene)

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Hollow carbon spheres with in diameter ranging from 50 to 150 nm have been successfully synthesized by the decomposition of poly(tetrafluoroethylene) ($[CF_2CF_2]_n$, PTFE) at 550 °C using NaN_3 as a defluorination reagent. The formation mechanism of hollow carbon spheres is also proposed. The present study provides a promising route to decompose other plastics that are difficult to degrade in the environment.

The discovery of carbon nanotubes by Iijima in 1991[1] has stimulated intense interest in carbon structures. Carbon nanotubes and other carbon structures have a wide range of applications in the fields of conductive and high-strength composites, semiconductor devices, field emission displays, and gas storage media.[2,3] Previously, carbon spheres had been synthesized by various methods. For example, hollow carbon spheres of several micrometers in diameter have been formed from C_{60} fullerene powder after shock compression up to 57 GPa.[4] Wang and Yin produced graphitic carbon solid spheres via a mixed-valent oxidecatalytic carbonization (MVOCC) process at 900–1050 °C.[5]

Polytetrafluoroethylene ($[CF_2CF_2]_n$, PTFE) is one of the most widely used plastic materials due to its exceptional properties such as stability against heating, chemical inertness, low surface tension, weathering, and excellent tribological performance. However, waste PTFE materials may become persistent solid pollutants that are difficult to degrade in the environment.

The decomposition of PTFE has been the focus of recent studies. By reducing sodium azide, hollow carbon spheres can be produced in this process. To the best of our knowledge, such a reaction has not yet studied in the literature. The reaction used in our approach can be formulated as follows:

$$[CF_2CF_2]_n + 4nNaN_3 \rightarrow 2nC(\text{hollow spheres}) + 4nNaF + 6nN_2. \quad (1)$$

In a typical experiment, 1 g of PTFE and 2.60 g of NaN_3 (the molar ratio NaN_3/PTFE is 4.0) powders were placed into in a stainless steel autoclave of 12 mL capacity. The autoclave was sealed and maintained at 550 °C for 10 h and then allowed to cool to room temperature naturally. A dark precipitate was collected and washed with distilled water and absolute ethanol, successively. After that, the obtained sample was dried in a vacuum at 65 °C for 5 h.

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of nanocrystalline hollow carbon spheres was examined from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. Raman spectra were recorded with a Spex 1403 Raman spectrometer at ambient temperature. Field emission scanning electron microscopy (FESEM) was performed on a JEOL JSM-6700F scanning electron microanalyzer.

X-ray diffraction powder patterns were taken following the reaction. Figure 1a shows the XRD pattern of the products, which were not washed. Two sharp reflection peaks can be indexed to cubic NaF with the lattice parameter $a = 4.60$ Å (JCPDS 73-1922). Figure 1b is a typical XRD pattern of the as-prepared products washed with distilled water and absolute ethanol. No obvious diffraction peak could be detected, which indicates that low crystalline or amorphous carbon is produced.

Representative TEM micrographs of the products are shown in Figs. 2a and 2b. Based on large numbers of TEM observations, the proportion of hollow carbon spheres in the samples is estimated to be about 50%. The external diameter of the hol-

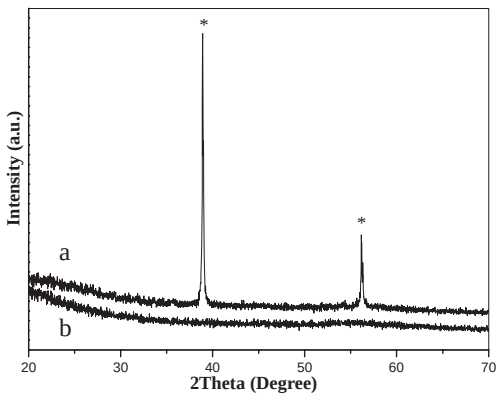

Fig. 1. XRD patterns of the products: (a) not washed, (* Face-centered cubic NaF); (b) washed with distilled water and absolute ethanol.

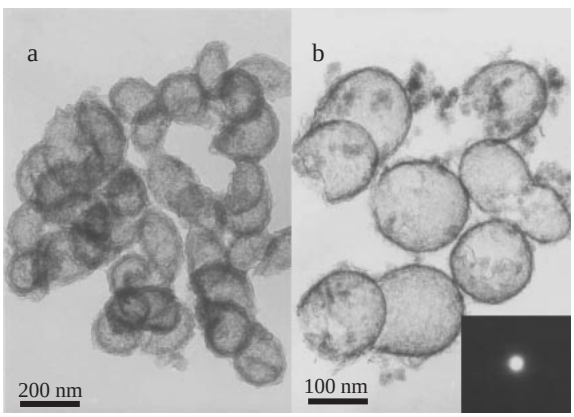

Fig. 2. TEM images and ED pattern of as-prepared products: (a) typical area; (b) magnified hollow carbon spheres, (inset) ED pattern of the hollow carbon spheres.

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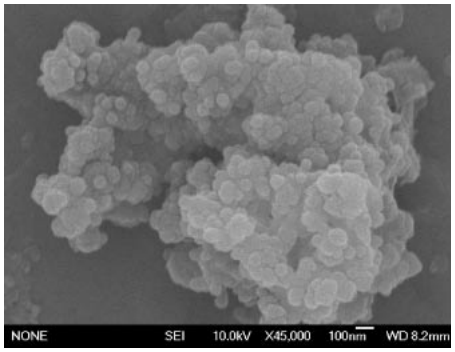

Fig. 3. FESEM micrograph of the products.

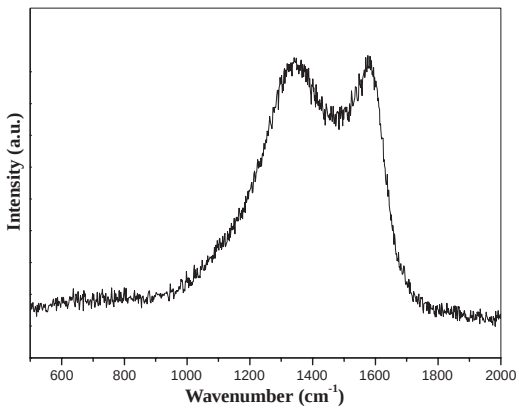

Fig. 4. Raman shifts of amorphous hollow carbon spheres.

low carbon spheres is 50–150 nm and the thickness of the wall is about 10 nm. The diameter and wall thickness are similar to that of the hollow carbon spheres reported in the literatures.[6]

From the contents of Fig. 1, the XRD pattern of the product, there are no diffraction peaks that can be observed in the ED (inset of Fig. 2b) of one typical hollow carbon sphere. Field-emission scanning electron microscope (FESEM) micrograph of the hollow carbon spheres of the product is shown in Fig. 3. Large scaled hollow carbon spheres are found within the diameter range from 50 to 150 nm, in good agreement with the TEM results.

The product was used directly to record the Raman spectrum (Fig. 4) at room temperature using a con-focal laser Raman micro-spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. Two broadened bands at around 1587 and 1346 cm^{-1} were recorded, which correspond to the typical Raman peaks of graphitized carbon nanospheres. The peak at 1346 cm^{-1} could be assigned to the vibrations of carbon atoms with dangling bonds in planar terminations of disordered graphite. The peak at 1587 cm^{-1} (G-band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms.

The formation mechanism of hollow carbon spheres is proposed. The possible process is schematically illustrated in Fig. 5. In this reaction system, the thermal decomposition of NaN_3 is known to proceed according to the previous report.[7] The resultant metallic sodium may form droplets owing to the heat generated from the exothermic reactions, and these metallic Na droplets may also act as templates in the formation process of hollow carbon spheres. Also upon increasing the reaction temperature to 500 °C, PTFE began to decompose to monomers[8] (Step 1). On the surface of the Na droplet, the produced monomer C_2F_4 is reduced into NaF and amorphous carbon clusters. Similar to the synthesis of other hollow spheres using emulsion droplets as templates,[9] the produced carbon shell could stabilize the sodium droplets, thus preserving the spherical shape (Step 2). As the reaction continues, the amount of sodium becomes depleted and the shell gradually thickens, finally resulting in hollow carbon spheres (Step 3).

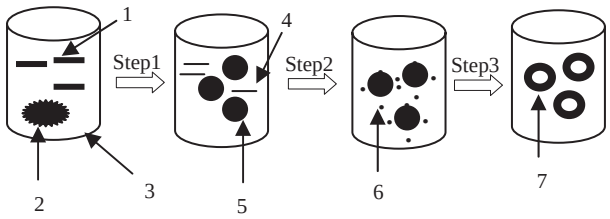

Fig. 5. Scheme of synthesis process of hollow carbon spheres (1-PTFE; 2-NaN_3; 3-autoclave; 4-monomer; 5-Na droplet; 6-carbon cluster; 7-carbon hollow sphere).

In summary, hollow carbon spheres have been synthesized by the decomposition of PTFE at 550 °C using NaN_3 as a defluorination reagent. The formation mechanism of hollow carbon spheres is also proposed. The significance of the present study embodies the two aspects: One is a route to decompose plastics, and the other one is a way to prepare hollow carbon spheres in nano-scale.

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