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A novel route to hollow and solid carbon spheres

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Carbon spheres (CSs) have been a subject of considerable attention from both scientific and practical points of view due to their potential applications as reinforcement materials for rubber, supports for catalysts and lubricating materials [1], and anodes in second lithium ion batteries [2]. Various approaches including self-assembly template process [3], pyrolysis [4], reduction [5] and hydrothermal method [6] have been carried out to prepare hollow or/and solid CSs with different yields and sizes.

As there is an emerging need for the production of carbon spheres in large quantities under mild experimental conditions for cost-effective production, here we report a easy and low cost approach to obtain CSs in large quantities with diameters in the range of 30–580 nm by pyrolyzing the mixture of C_2Cl_4/$Fe(C_5H_5)_2$ in a stainless-steel autoclave using a glass-tube as inner reactor wall at 550 °C, and their thermal stability in dynamic N_2 atmosphere was investigated.

In a typical procedure, C_2Cl_4 (5 ml, 97%) and $Fe(C_5H_5)_2$ (5 mmol) were loaded into a glass-tube of 20 ml capacity, then the latter was put into a 65 ml stainless-steel autoclave. After the autoclave was sealed and put into an electronic furnace at 150 °C, the temperature of the furnace was increased to 550 °C in 40 min and maintained at 550 °C under cal. approximately 8 MPa for 16 h. Then it was allowed to cool down to room temperature naturally. The dark solid materials obtained in the glass-tube were divided into two parts: Sample 1 was collected without washing; Sample 2 was heated in dilute HCl solution (0.5 M) at 60 °C for 10 h and washed with distilled water and absolute ethanol for several times, after it was dried in a vacuum at 60 °C for 4 h then it was collected for characterization. The yield of carbon materials was ~84% based on raw materials, and the proportion of CSs was ~90%. These products were analyzed by X-ray powder diffraction (XRD) (Philips X'pert diffractometer with $CuK\alpha_1$ radiation ($\lambda = 1.5418$ Å), Raman spectrum (SPEX 1403), field emission scanning electron microscopy (FSEM, JEOL JSM-6300F), transmission electron microscopy (TEM, HITACHI 800) and thermogravimetric analysis (TGA, Shimadzu TAG-50H, heating rate: 10 °C/min; N_2 floating rate: 20 ml/min).

Fig. 1(a) and (b) show typical XRD patterns of Sample 1 and 2, respectively, the sharp diffraction peaks with high peak intensity presented in Fig. 1(a) could be indexed as $FeCl_2 \cdot 4H_2O$ (JCPDS no. 1-218), while the broad peaks with low peak intensity could be indexed as "graphite"; Fig. 1(b) includes two broad diffraction peaks with low peak intensity centered at about $2\theta = 23.5°$ and 43.0°, which may be indexed as 002 and 100 diffraction peaks of turbostratic, polyaromatic carbon. The broadening of the "graphite" peaks actually indicates the existence of highly disordered structures in the product. The Raman spectrum (Fig. 2) of Sample 2 shows two broad peaks centered at about 1349 and 1580 cm^{-1}, which are associated with the

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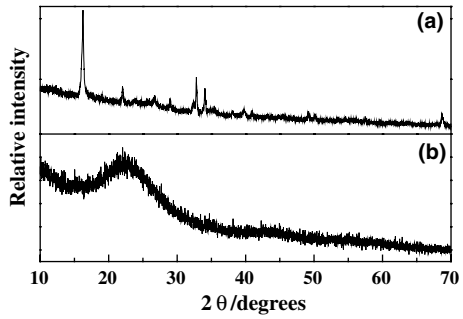

Fig. 1. Typical XRD patterns of (a) Sample 1, (b) Sample 2.

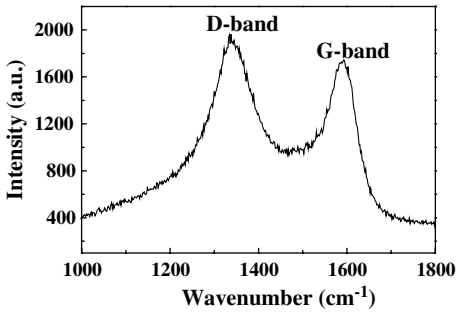

Fig. 2. Typical Raman spectrum of Sample 2.

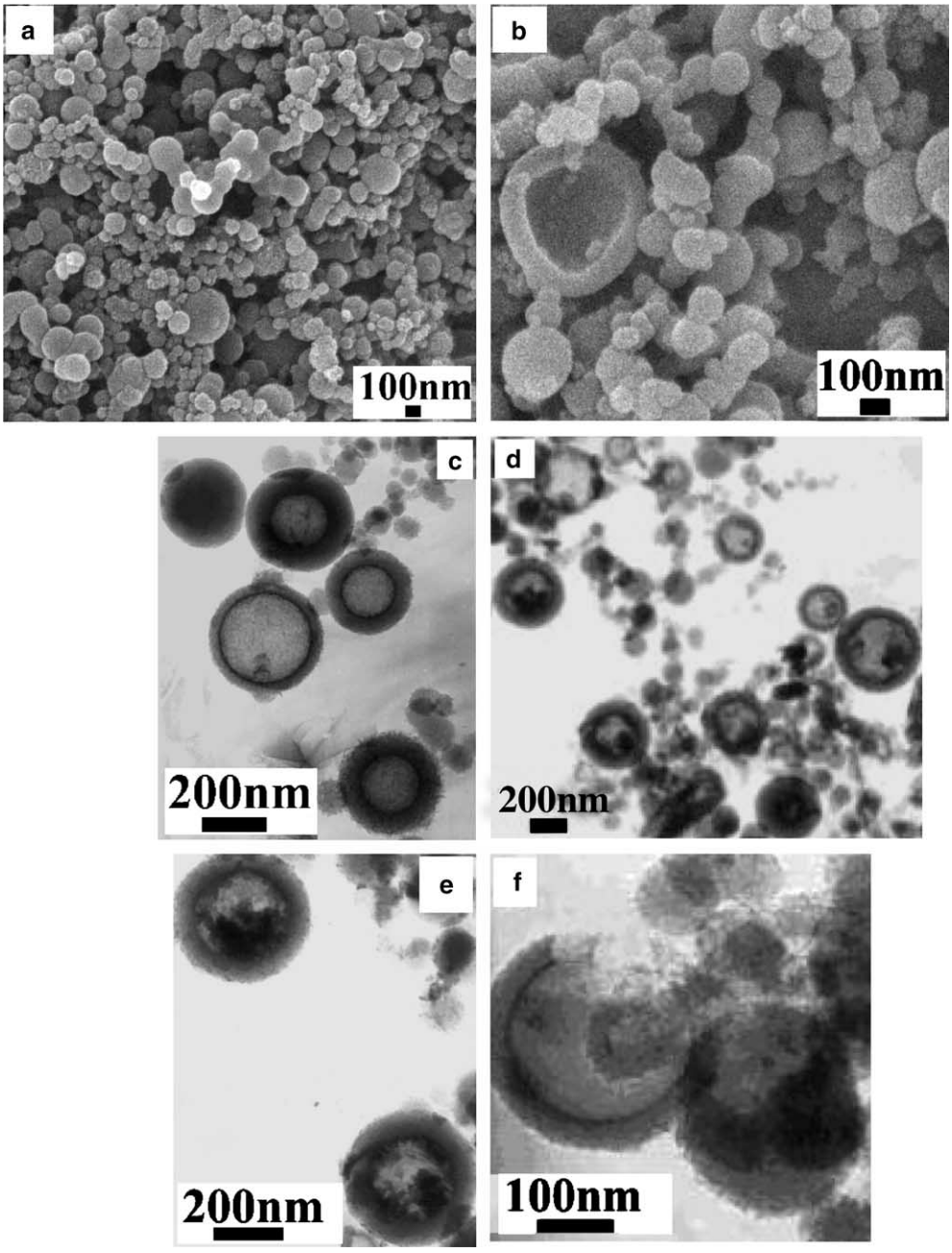

Fig. 3. Typical FSEM and TEM images of: (a–c) Sample 2, (d–e) Sample 1, (f) Sample 2 after an annealing process at 950 °C in dynamic N_2 for 4 h.

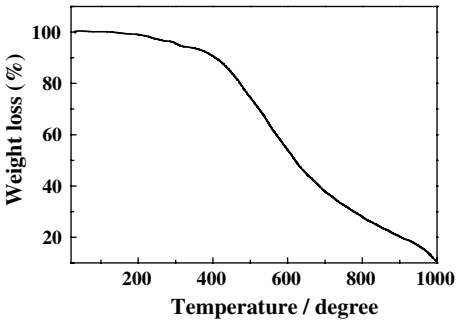

Fig. 4. TGA curve of Sample 2 in dynamic N_2 atmosphere.

vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite and the vibrations in all sp^2 bonded carbon atoms in a 2-dimensional hexagonal lattice, respectively [6,7]. The intensity ratio of D to G band (I_D/I_G) is calculated to be 1.15, further reflecting the relative disorder and low graphitic crystallinity of the CSs.

Fig. 3(a)–(c) show typical FSEM and TEM images of Sample 2, it can be seen that large quantities of carbon spheres with a proportion of not less than 90% and with diameters in the range of 30–580 nm were obtained. These CSs include hollow spheres (external diameter: 110–580 nm; shell thickness: 20–100 nm) and solid spheres (diameter: 30–200 nm). Fig. 3(d) and (e) show typical TEM images of Sample 1, it is worth noting that some particles are co-existing with the CSs. According to the fact that these particles could give a green color solution in water and to the result of XRD pattern analyses, it is concluded that these particles are $FeCl_2 \cdot 4H_2O$ which is formed by the reactions between Fe nanoparticles, HCl (resulting from the reaction between $Fe(C_5H_5)_2$ and C_2Cl_4) and H_2O (introduced by the unpurified C_2Cl_4). However, their roles played in the final formation of the CSs still needs research. A typical TEM image of Sample 2 after 950 °C annealing shown in Fig. 3(f) reveals that only few hollow spheres were broken while the other CSs still kept their original spherical shape, demonstrating their relative thermal stability.

Fig. 4 shows a typical TGA curve of Sample 2, in which a gradual decrease in the weight loss curve from a onset decomposition temperature of ~330 °C can be clearly seen, which suggests that these CSs have a relatively high thermal resistance in N_2 atmosphere in accordance with the result of TEM analysis (Fig. 3(f)).

In summary, a novel co-pyrolysis method was successfully developed to prepare high yield and proportion of CSs with diameters in the range of 30–580 nm by pyrolyzing $C_2Cl_4/Fe(C_5H_5)_2$ mixture at 550 °C, and their thermal stability was investigated. The as-obtained CSs might have potential use as a lubricant additive or reinforcing material.

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