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A novel method for preparation of hollow and solid carbon spheres

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Abstract. **Hollow and solid carbon spheres were prepared by the reaction of ferrocene and ammonium carbonate in a sealed quartz tube at 500°C. The morphology and microstructure of the product were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. The carbon spheres are amorphous and their diameters range from 0·8–2·8 μm. The shell thickness of the hollow carbon spheres is not uniform and ranges from 100–180 nm. It is suggested that ammonium carbonate is crucial for the formation of carbon spheres and its amount also influences the morphology of the product. The method may be suitable for large scale preparation of carbon spheres.**

Keywords. **Hollow carbon spheres; solid carbon spheres; ferrocene.**

1. Introduction

Carbon spheres, including hollow carbon spheres (HCSs) and solid carbon spheres (SCSs), exhibit excellent properties such as outstanding biocompatibility (Bokros 1977), high chemical inertness, high specific surface area, thermal insulation, low effective density and high compressive strength (Li *et al* 2006), which make them appropriate materials to be used in lithium-ion batteries (Lee *et al* 2003), fuel cells (Wen *et al* 2007), drug delivery, active material encapsulation (Zhong *et al* 2000), damping materials and composites (Zhang *et al* 1993) etc. For these potential applications, extensive efforts have recently been devoted to the exploration of various synthesis approaches for carbon spheres with emphasis on CVD, template assisted and solvothermal methods. Generally, the CVD method, which is popular in preparation of a diverse range of carbon nanostructures, can also be used to prepare SCSs by pyrolysis of hydrocarbons (Wang *et al* 2007). On the other hand, the template assisted method is usually employed to synthesize HCSs (Wang *et al* 2006). In brief, the templates are first coated either by pyrolytic carbon or polymers on their surfaces to obtain core-shell structures. Then the templates are subsequently removed by wet chemical etching in an appropriate solvent or calcination at elevated temperature in an inert atmosphere to create HCSs. For the solvothermal method, both HCSs and SCSs can be prepared under high pressure and at a moderate temperature for several hours in an autoclave using different reactants and solvents (Wu *et al* 2006; Yi *et al* 2007).

However, low yield and complex process are still the main factors that hinder the applications of carbon spheres. Therefore, there is an emerging need for the cost-effective production of carbon spheres in large quantities under mild experimental conditions. In this paper, we report an efficient and low cost method to prepare HCSs and SCSs by the reaction of ferrocene and ammonium carbonate in a sealed quartz tube at 500°C. The formation mechanism is also discussed.

2. Experimental

In a typical experiment, 100 mg ferrocene and 150 mg ammonium carbonate (a mixture of NH_4HCO_3 and NH_2COONH_4) were put into a quartz tube (about 30 ml in volume) which was then sealed after pumping. Next the tube was heated in an air furnace to 500°C at a ramp rate of 25°C/min. After being held for 30 min, the furnace was cooled down naturally. The as-prepared product was thoroughly washed with HCl solution and deionized water for several times in sequence, and finally dried in an oven at 100°C for 12 h. The product was characterized by Shimadzu XRD-6000 X-ray diffractometry (XRD) with CuKα radiation (λ = 1·5418 Å). The morphologies of the product were recorded by Hitachi S-4700 field emission scanning electron microscopy (SEM) and Phillips Tecnai F30 transmission electron microscopy (TEM). The Raman measurement was carried out with a Jobin-Yvon LabRam Raman microscope at an excitation laser wavelength of 632·8 nm.

3. Results and discussion

Figure 1a is the typical XRD pattern of the as-prepared product before washing and all the sharp diffraction peaks

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could be well indexed as Fe_3O_4 (JCPDS 19-0629). The broad peak around $2\theta = 26°$ with low peak intensity becomes evident when the Fe_3O_4 was removed by the acid washing process, as shown in figure 1b. The broad peak indicates that the product is amorphous, probably due to the low synthesis temperature.

Figure 2 is the Raman spectrum of the product after washing recorded at room temperature. The prominent peaks at 1341 and 1586 cm^{-1} correspond to the carbon D-band and G-band vibration modes, respectively. The G-peak originates from the vibrations of sp_2-bonded carbon atoms in a two-dimensional graphite plane, while the D-peak is related to double-resonance Raman process in disordered carbon (Antunes *et al* 2006). The high intensity ratio of D to G band suggests that the graphitization of the product is poor, which is consistent with the XRD pattern (figure 1b).

Figure 3a shows a SEM image of the carbon spheres without dispersion and centrifugal treatment. It is clearly demonstrated that the majority of the products exhibited perfect spherical morphology. The spheres vary from 0·8–2·8 μm in diameter with very smooth surfaces. Figure 3b presents the morphology of some broken and shrivelled HCSs, suggesting that some spheres have hollow structures. From the fractured spheres, it could be assessed that the wall thickness is not uniform and ranges from 100–180 nm.

Figure 4a shows a TEM image of a shrivelled HCS with a crack. The hollow structure could be indicated by the pale interior and dark edge. The diameter of the sphere is about 2·8 μm and the thickness of the shell is uniform and about 170 nm. Additionally, the dark spheres of 1 μm in diameter could also be found, which should be SCSs, as shown in figure 4c. Figures 4b and d provide the high resolution TEM (HRTEM) images of the fine structure near the surface of the HCS and SCS. It is shown that both of them have amorphous structures, which is consistent with the XRD and Raman results.

In order to investigate the formation mechanism, additional experiments were further carried out. It was found that only the carbon of irregular shapes could be synthe-

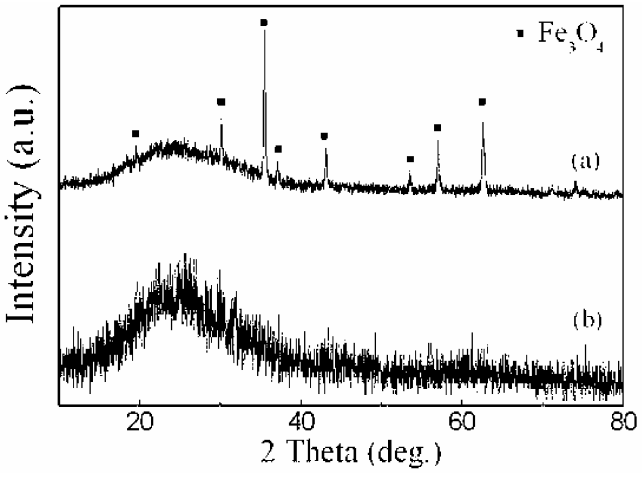

Figure 1. XRD patterns of (a) the as-prepared product in the quartz tube and (b) the product after acid washing.

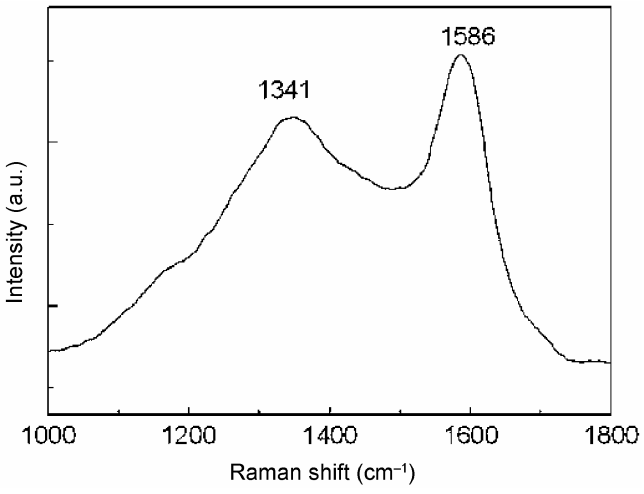

Figure 2. Raman spectrum of the product after acid washing.

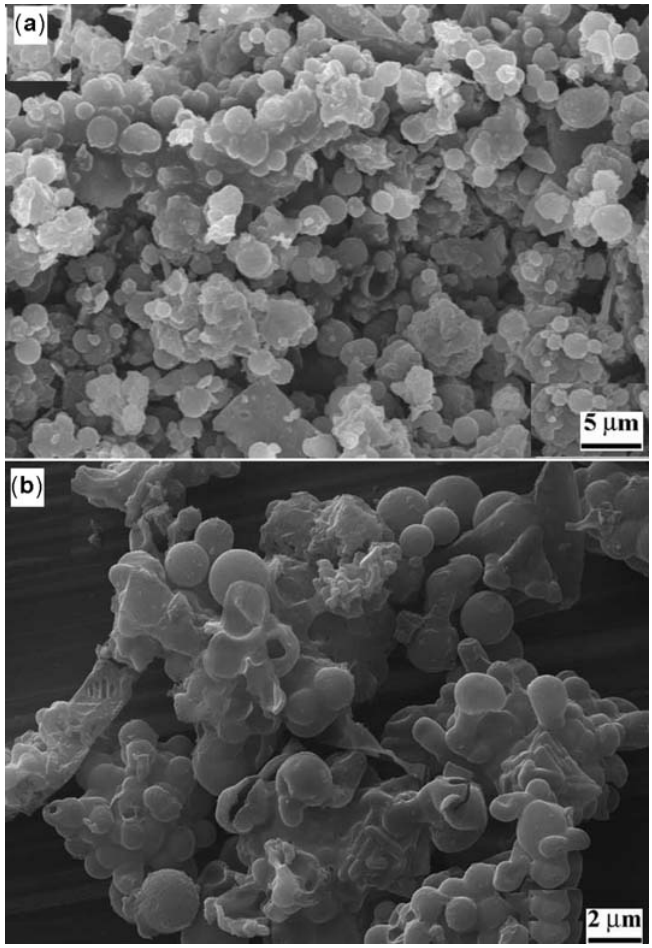

Figure 3. SEM images of (**a**) the large scale of carbon spheres and (**b**) the broken hollow carbon spheres.

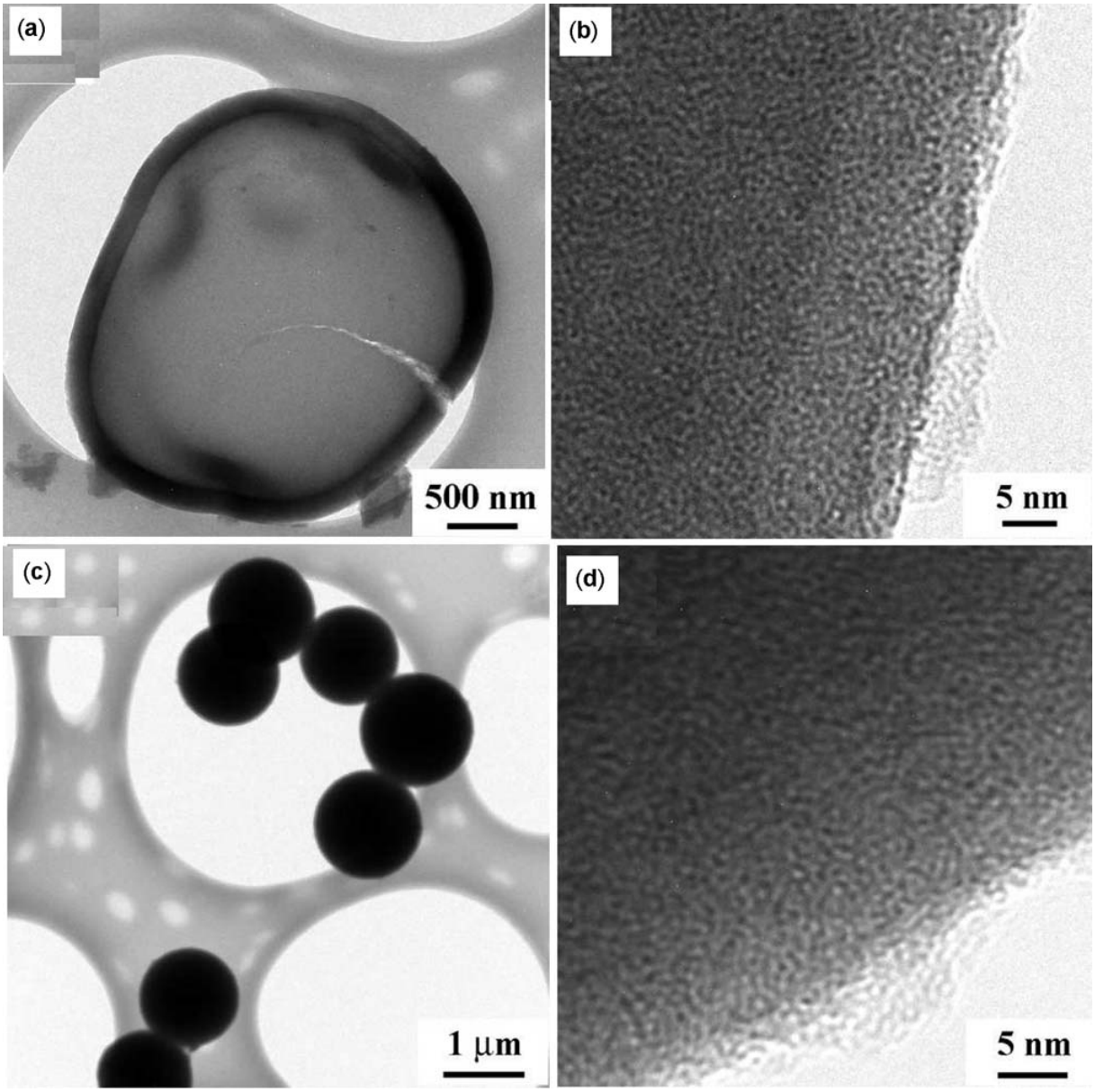

Figure 4. TEM images of (**a**) one shrivelled HCS, (**c**) some SCSs and HRTEM images of (**b**) HCS and (**d**) SCSs.

sized when ferrocene was used as the only reactant, indicating that ammonium carbonate may play a crucial role in the formation of carbon spheres. The process could be represented as follows: the unstable ammonium carbonate would first decompose into NH_3, H_2O and CO_2 at low temperature. Next, carbon and iron could be produced by the decomposition of ferrocene at about 400°C (Hou *et al* 2002). Then the iron would soon be oxidized by CO_2 and H_2O to form Fe_3O_4 (Kaushik and Fruehan 2006), which is detected in the as-prepared product by XRD in figure 1a. And the Fe_3O_4 crystals grew larger by consuming the newly generated ions or molecules near the crystal nucleus. At the same time, some carbon feed stock, composed of basic structural units (BSUs), might cover on the sphere-like Fe_3O_4 particles to form carbon encapsulated Fe_3O_4 and the HCSs could be obtained after acid washing by removal of Fe_3O_4 particles. On the other hand, some carbon feed stock would form SCSs to maintain a low surface energy. And the solid/gas interface usually results in a random texture of the sphere due to the random arrangement of the BSUs (Inagaki 1997), leading to the formation of amorphous HCSs and SCSs. Thus, both HCSs and SCSs could be synthesized simultaneously in the process.

However, when 300 mg ammonium carbonate was used instead with other synthesis parameters unchanged, carbon encapsulated six-armed Fe_3O_4 would be obtained (supplementary material, figure 5), suggesting that the amount of ammonium carbonate also plays a crucial role on the

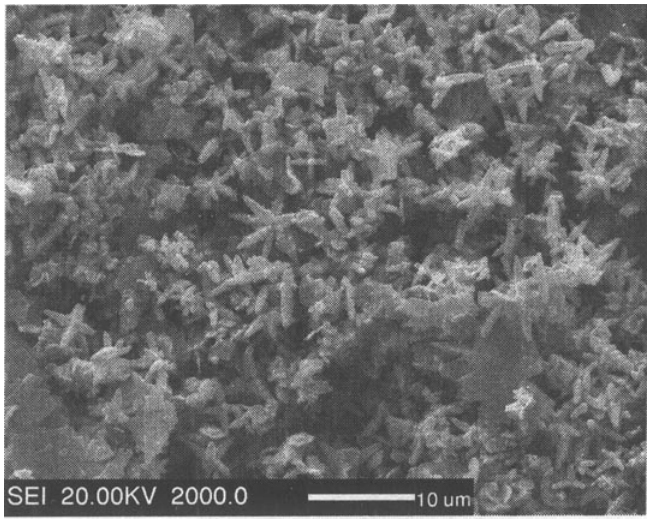

Figure 5. Carbon encapsulated six-armed Fe_3O_4 synthesized by the reaction of 100 mg ferrocene and 400 mg ammonium carbonate at 500°C.

morphology of the product. Therefore, further investigation is needed to better understand the exact effects of ammonium carbonate on the formation of carbon spheres.

4. Conclusions

In conclusion, this paper reports a novel method for the synthesis of hollow and solid carbon spheres by the direct reaction of ferrocene and ammonium carbonate in a sealed quartz tube at 500°C. Ammonium carbonate is crucial for the formation of carbon spheres. The method is efficient and the reactants are inexpensive. Considering that the gas pressure in the reactor is relatively low compared with the solvothermal method, the method may be suitable for large scale preparation in future.

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