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Synthesis of carbon nanostructures with unique morphologies via a reduction-catalysis reaction route

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Abstract

Large-scale carbon nanostructures with unique morphologies were successfully synthesized by a reduction-catalysis reaction route. The as-synthesized products, characterized by XRD, SEM and TEM, revealed that hollow carbon nanospheres with diameters in the range of 100–200 nm can be formed at 500 °C while the tetrapod-like carbon nanotubes with bamboo structure can be synthesized with the typical diameters of about 100 nm and length of over 1 μm. Two strong and wide Raman peaks at 1600 cm^{-1} (G-band) and at 1347 cm^{-1} (D-band) are observed at room temperature and their mechanism of formation is discussed. These unique carbon nanostructures offer potential applications, such as nanoscale transistors, amplifiers, switches and ballistic rectifiers and so on.
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1. Introduction

In recent years, carbon nanostructures have been extensively studied because of their various potential applications, such as catalyst support materials for fuel cells [1], electrode materials for supercapacitors [2], and gas storage media [3]. Since carbon nanotubes were discovered in 1991 [4], a large number of novel carbon nanostructures have been fabricated using various methods [5–7] including helix-shaped graphitic nanotubes [8], graphitic nanocones [9], nanohorns [10], microtrees [11], nanopipettes [12], etc. Recently, metal-catalyzed chemical methods have been used to synthesize carbon nanomaterials. For example, Campbell et al. [13] prepared small-diameter carbon nanotubes by a catalytic method using a decomposition of ethylene over a Ni–Fe thin film as a catalyst. More recently, Qian and co-workers [14] synthesized CNTs by a thermal reduction of ethanol using magnesium. Yacaman and co-workers [15] also reported the synthesis of carbon onions by gold nanoparticles and electron irradiation.

Among these carbon nanostructures, carbon spheres (CSs) have attracted considerable attention recently in the view of scientific and practical points owing to their potential applications as reinforcement materials for rubber, supports for catalysts and lubricating materials [16], and anodes in secondary lithium ion batteries [17]. Therefore, many fabrication methods including self-assembly template process [18], reduction [19] and hydrothermal method

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[20] have been proposed to prepare hollow or/and solid CSs with different yields and sizes. Nanospheres with a hollow interior, particularly when filled with some functional secondary materials, can be exploited as useful materials for catalysis [21], development of artificial cells [22], delivery of drugs and dyes [23], and protection of biologically active agents [24]. To the best of our knowledge, however, there are only a few reports on the synthesis of hollow CSs via a chemical method. Hence, there is urgent need for the practical route of synthesizing hollow CSs on a large scale. In the present work, we report the large-scale synthesis of hollow CSs via the reduction reaction of methanol with magnesium at 500 °C.

2. Experimental

All the chemicals were purchased from Beijing Chemical Reagents Co. and used without further purification. Hollow carbon nanospheres were synthesized as follows: magnesium powder (0.45 g, 99%) and methanol (15 mL, analytical grade) were mixed under ultrasonication for 30 min, and put into a stainless steel autoclave of 40 mL. The autoclave was sealed and maintained at 500 °C for 12 h and then cooled to room temperature naturally. The obtained products were treated with 50 mL of 5 M HCl aqueous solution at 65 °C for 2 h and then left in the HCl aqueous solution for 2 days at room temperature. After the samples were washed with methanol and distilled water at least three times, they were dried in a vacuum oven at 50 °C for 10 h.

The as-prepared products were characterized with transmission electron microscopy (TEM, JEOL 2010) using an accelerating voltage of 200 kV and scanning electron microscopy (SEM, JEOL JSM-6700F). X-ray diffraction (XRD) patterns were taken with a Rigaku X-ray diffractometer (model-2028, Cu Kα radiation, 20 kV). The Raman spectra were recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm.

3. Results and discussion

The chemical reaction to synthesize the carbon nanostructures is similar to that used to prepare carbon nanotubes by Qian and co-workers [14], which can be formulated as follows:

$$CH_3OH + Mg \rightarrow C + MgO + 2H_2 \quad (1)$$

In this route, methanol acts as the carbon source, while Mg is used as both the reductant for the reaction and catalyst for the formation of hollow CSs.

The XRD patterns of the HCl aqueous solution-treated and untreated products obtained at 500 °C are illustrated in Fig. 1. The broad diffraction peak at $2\theta = 26.3^\circ$ can be assigned to graphitic carbon [0 0 2]. The peaks in the range of $2\theta = 35–80^\circ$ for the untreated sample (Fig. 1a) can be indexed as a face-centered cubic structure of MgO with lattice

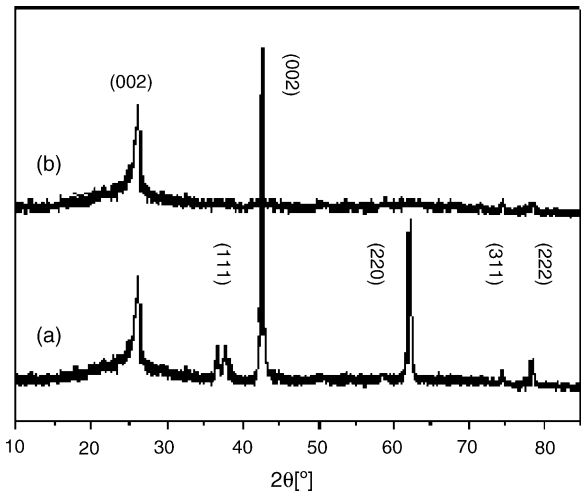

Fig. 1. X-ray diffraction patterns of the products synthesized at 500 °C: (a) before and (b) after HCl aqueous solution treatment.

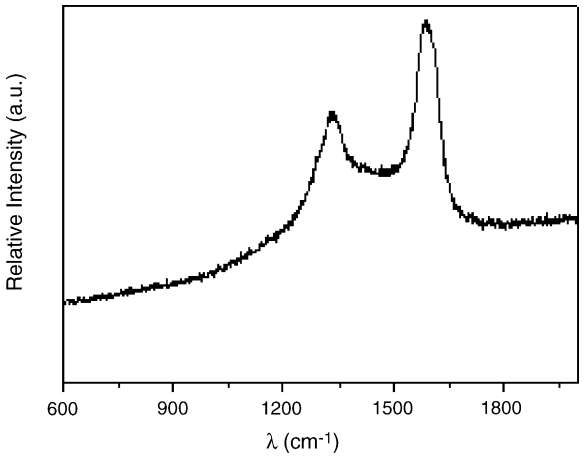

Fig. 2. Raman spectrum of the products synthesized at 500 °C.

parameter of 0.435 nm, which is not close with the reported value of 0.4212 nm (JCPDS 78-0430) [25] maybe due to the amorphous carbon in the XRD patterns. From the X-ray pattern (Fig. 1a), the hexagonal Mg could also be found, whose main peak is located at $2\theta = 36.6^{\circ}$ near the (1 1 1) of MgO [26]. As predicted, the peaks of MgO and Mg was not observed after the sample was treated with HCl aqueous solution (Fig. 1b), verifying that the MgO and Mg were completely dissolved with the HCl aqueous solutions.

The Raman spectrum (Fig. 2) of the product prepared at 500 °C shows mainly two Raman bands at 1600 cm^{-1} (G-band) corresponding to an E_{2g} mode of graphite and relating to the vibration of sp^2-bonded carbon atoms in a two-dimensional graphite layer, which shifts towards a higher wavelength because of the less orderly arrangement of the carbon atoms, and at 1347 cm^{-1} (D-band) associated with vibration of carbon atoms with dangling bonds at the plane termination of disordered graphite or glass carbon [27]. According to the relationship $La = 4.4(ID/IG)^{-1}$ (in nm) [28], the small microcrystalline planner size is 3.0 nm for the hollow CSs obtained.

The morphologies of the hollow CSs are characterized using SEM and TEM. The low magnification of SEM image of the products synthesized at 500 °C is shown in Fig. 3a, which exhibits that CSs with diameters of 100–200 nm were formed. In addition, most of the CSs were found to be connected via the surfaces of other spheres. The yield of CSs was estimated to be about 80% from the SEM observation. And the other 20% of the product is amorphous carbon which is similar to the results reported by Qian and co-workers [14]. TEM image, shown in Fig. 3b, reveals that the diameters of the most CSs are in the range of 100–200 nm, and that the nanospheres have hollow cores with diameter of about 60–100 nm. TEM images also show that some hollow carbon nanospheres were grown from the surfaces of the other nanospheres, which can be explained via the catalytic growth mechanism. The electron diffraction of these hollow CSs indicates that they are of amorphous materials, which was also confirmed in the TEM images (Fig. 3b).

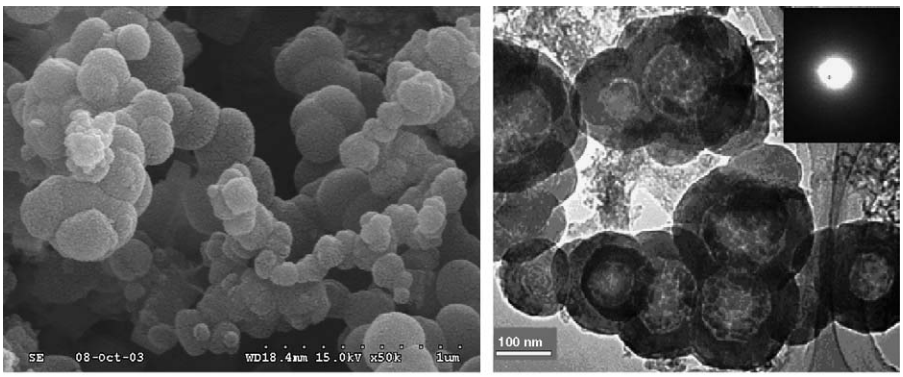

Fig. 3. (a) and (b) SEM and TEM images of hollow CSs synthesized at 500 °C.

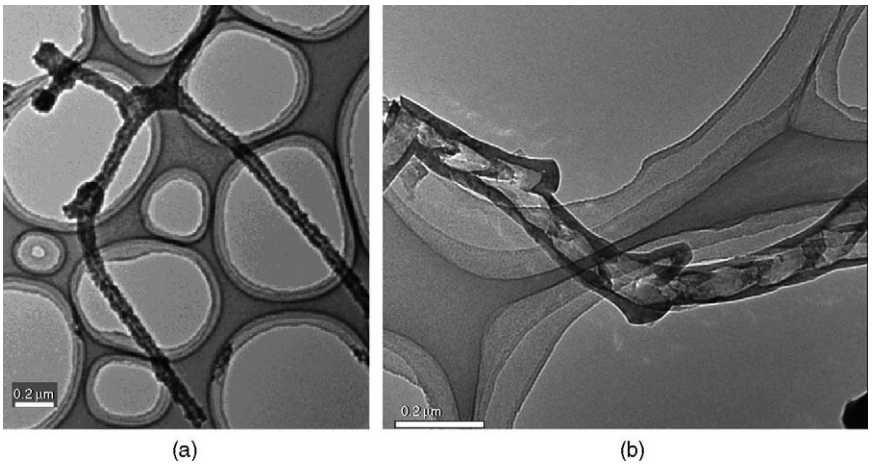

Fig. 4. (a) and (b) TEM images of a typical tetrapod-like carbon nanotubes synthesized at 850 °C.

It is well known that reaction temperature plays a crucial role in influencing the morphologies of carbon nanomaterials during synthesis process. So we have also investigated how the morphology will change by reacting magnesium and methanol at a different temperature, 850 °C, while keeping all the other reaction conditions the same. It was found that tetrapod-like carbon nanotubes were formed, as shown in Fig. 4a. The outer and inner diameters of the carbon nanotubes are about 90 and 60 nm, respectively. The curvatures of the carbon nanotube are similar to the bamboo structure (as shown in Fig. 4b), whose structure is similar to those obtained by Qian and co-workers [14].

As described above, different morphologies can be obtained depending on the reaction temperature: hollow carbon nanospheres at 500 °C, and tetrapod-like carbon nanotubes at 850 °C. Their possible formation mechanism is discussed hereafter. It is well known that the temperature dependence of the growth rate of carbon nanomaterials can be related to the combination of several factors, including carbon concentration, diffusion rate of carbons, and the rate of carbon self-assembly [29]. It is generally agreed that the diffusion rate of carbon is the rate-determining step in the growth of carbon nanomaterials [30]. In this paper, we propose a metal reduction-catalysis mechanism [31] to account for different morphologies obtained in our work. Fig. 5 illustrates the schematic model to form hollow carbon nanospheres. During the reaction process, carbon can be formed after the MeOH is reduced with magnesium, and the carbon layer is coated on the magnesium particles (Fig. 5b). Due to the low energy associated with a lower reaction temperature, the produced carbon diffuses slowly in the reactor and the magnesium particle is then covered with carbon layer by layer. With the reaction proceeding, the magnesium core is progressively converted into the magnesia (MgO), and more and more carbon shells is formed as shown in Fig. 5c.

Similarly, the formation mechanism of the tetrapod-like carbon nanotubes can be illustrated using the schematic diagram of the possible growth model as shown in Fig. 6. When the reaction temperature increases to 850 °C, carbon, which was formed from the reduction of methanol by magnesium, is adsorbed on the catalytic metal particles. Then it diffused through surface and bulk to form the graphitic sheets as a cap on the metal particles. As the cap lifts off the catalyst, a closed tip with hollow interior is produced. The driving force of carbon to move away from the catalytic particle can be the stress accumulated under the graphitic cap. The size of the catalytic particle limits the diameter of

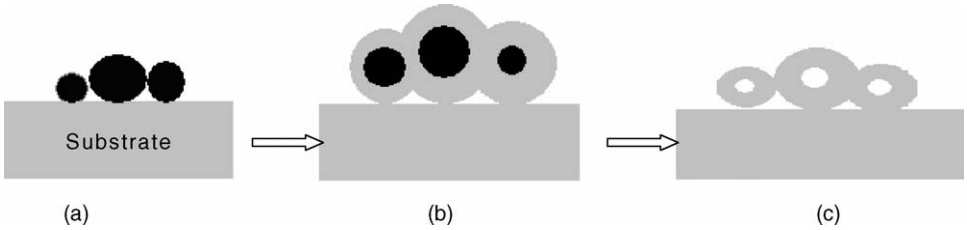

Fig. 5. Schematic representation of the possible growth model of hollow CSs: (a) different size magnesium clusters; (b) graphitic shells formed by reduction reaction; (c) hollow carbon nanospheres formed after treatment with HCl.

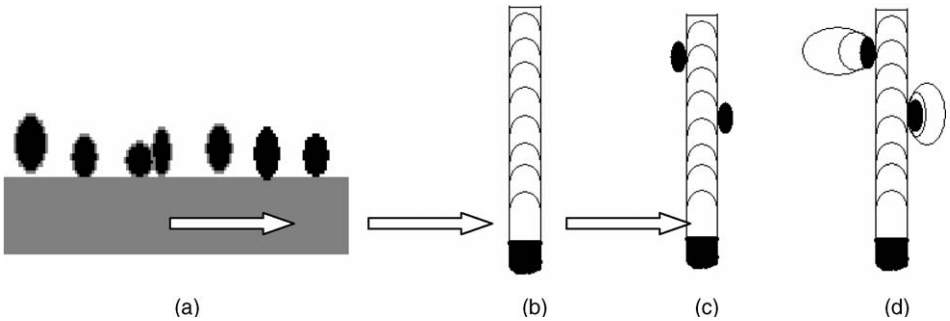

Fig. 6. Schematic representation of the possible growth model of the tetrapod-like carbon nanotubes: (a) magnesium particles on the substrate; (b) bamboo-structure carbon nanotube; (c) attachment of magnesium particles on the sidewall of nanotubes; (d) growth of the tetrapod-like carbon nanotubes.

the growing tube. The carbon accumulated at the inside surface of the catalytic particles, probably mainly via bulk diffusion, can form the compartment graphitic sheets. They grow by joining with the graphitic sheets of wall, and eventually move away from the catalytic particles due to the stress. While the wall grows upward, the next compartment layers are produced on the catalytic particle and will be combined again with the wall. The periodic connection of the compartment layers with the wall yields the bamboo-like shape (shown in Fig. 6b). Fortunately, TEM images (not shown) show that the metal can been found in the tips of carbon nanotubes, also testifying that the metal-catalytic growth mechanism can be applied to account for the formation of carbon nanotubes. During the process of the reaction, the catalytic metal can stick to the outer surface of carbon nanotubes (Fig. 6c). Then carbon in the bulk was also covered on the magnesium surface to form the tetrapod-like carbon nanotubes (Fig. 6d).

4. Conclusion

We synthesized carbon nanostructure with unique morphology via a reduction-catalysis reaction route. We obtained hollow carbon nanospheres with 100–200 nm diameter and tetrapod-like carbon nanotubes with diameters of about 100 nm and lengths of over 1 μm using methanol via the metal reduction route at 500 and 850 °C, respectively. The results of SEM, TEM, XRD and Raman measurements provide evidences for the formation of hollow CSs and tetrapod-like carbon nanotubes depending on the reaction temperature. The reduction-catalysis growth mechanism is proposed to account for the formation of the hollow carbon nanospheres and tetrapod-like carbon nanotubes. These nanostructures may offer interesting device applications, such as nanoscale transistors, amplifiers, switches, ballistic rectifiers, etc.

Acknowledgments

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