J Mater Sci (2006) 41:5242–5245
DOI 10.1007/s10853-006-0250-1

Study on the controlled growth of carbon nanospheres from de-oiled asphalt

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Received: 12 January 2006 / Accepted: 24 February 2006 / Published online: 8 June 2006

Abstract Carbon nanospheres were synthesized from de-oiled asphalt (DOA) by chemical vapor deposition (CVD). The morphology and microstructure of the products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM), and the influences of different parameters were disscussed. The results showed that carbon nanospheres could be synthesized from DOA, which were spherical with uniform size and amorphous structure. Such controlled growth of carbon nanospheres of DOA has never been reported; our work would offer reliable experimental data for the transformation of DOA into high-added value carbon materials.

Introduction

De-oiled asphalt (DOA) is a kind of by product in petroleum industry from heavy oil which has been deoiled deeply to get rid of saturates and aromatics as much as possible. DOA is a hard, crisp solid or powder at room temperature, with similar black or brown appearance with coal. The density is about 1.11 g/cm^3, and its molecular weight ranges from several thousands to tens of thousands. The content of carbon is beyond 80% and the ash content is very low. DOA has no fixed melting point and its softening point is above 120 °C, which makes it a kind of ropy semifluid at high temperatures [1, 2]. The mechanical properties of DOA are not very good, so it has been rarely used as bulky materials directly. In the past, most of DOA was used in some low-added value conditions, such as coking materials, binding materials, blast furnace fuel and correlative materials etc.

On the other hand, carbon spheres and onion-like fullerenes are going to play an important role as nanocarbon materials, conductive materials or high-strength composite materials in the fields of nanomaterial science [3, 4], nanoelectronics [5], nanobiology etc.. The study on the relationship between their structures and physical or chemical properties has not only significant theoretical values in the domain of condensed state physics, but also important instructive meanings to their broad application prospects.

In consideration of some excellent characteristics of DOA, such as high carbon content, low ash content and the predominace in source and price, if it is used as carbon source to synthesize carbon spheres, onion-like fullerenes and correlative materials, the products would be competitive. In this paper, DOA was used as carbon source to synthesize carbon spheres by CVD, some factors (atmosphere, reaction rate, temperature etc.) were investigated which possibly affected the structure of products, and reliable experimental data were offered for the transformation from DOA into high-added value carbon materials.

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Experimental

Materials and equipment

De-oiled asphalt (DOA): supplied by China University of Petroleum-Beijing. Table1 shows some analytical data of DOA.

The reactor is a CVD equipment [6]. A temperature controller was used to control the reaction temperature in a electronic resistance furnace; the inner diameter of the quartz tube is 35 mm and the valid heat length is 720 mm; the flow rate was controlled by a flowmeter.

Synthesis of carbon nanospheres

DOA was grounded to 200 meshes, weighed and put into a porcelain boat, which was located in the quartz tube at the entrance of the furnace. Ar was flowed to purge the air in the tube. After that, the quartz tube was heated to the designed temperature and kept at this temperature for 30 min under the protection of Ar (the purpose of this step was to make the entrance of the furnace reach a temperature balance, about 180–200 °C). Then the quartz tube was slowly moved so as to keep the front of the boat in the fixed temperature zone of about 180–200 °C to assure that DOA could be evaporated slowly. The reaction rate was controlled through the moving speed of the quartz tube (the deposition time used here was 10 or 30 min). After the reaction was finished, the furnace was cooled down naturally to room temperature in the atmosphere of Ar, the powder deposited on the wall of the quartz tube was collected and characterized.

Characterization

The morphology and structure of products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and high-resolution transmission electron microscopy (HRTEM).

Results and discussion

Influence of reaction temperatures

Among the factors of atmosphere, reaction rate and temperature, temperature has the least influence on the morphology and structure of final products. The temperature range used in this work was 600–1000 °C. These temperatures were not high enough for the graphitization of the products, resulting in the final products in amorphous states. Figure 1 is an XRD pattern of a product prepared at 1000 °C, 30 ml/min Ar flow, and 30 min reaction time. It can been seen that the two peaks at 2θ = 25.4 and 43.6° are all ascribed to the characteristic peaks of amorphous carbon, corresponding to C(002) and (100), respectively. There are no peaks of other materials in this XRD pattern, probably suggesting the high purity of the product. The results above show that DOA was evaporated at the entrance of the furnace, i.e. 180–200 °C temperature zone, producing a large amount of carbon clusters. These clusters decomposed and reacted in the reaction zone (1000 °C), finally formed carbon spheres in the deposition zone.

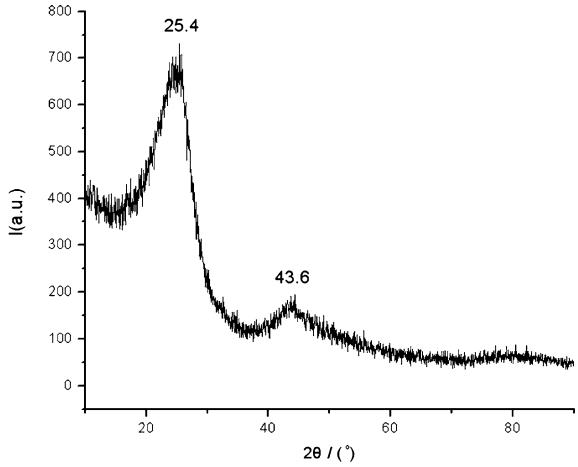

Fig. 1 XRD pattern of the product 1000 °C, 30 ml/min Ar flow, and 30 min reaction time

Influence of reaction rate

During the synthesis process, many factors, such as atmosphere, reaction rate and temperature, had influence on the quality and quantity of the final products, especially the size of the carbon spheres. High-purity, size-controllable and uniform carbon spheres were synthesized by controlling the reaction rate. Sample 1 and Sample 2 were prepared at reaction time of 10 and 30 min, respectively, with the other reaction conditions being kept the same: reaction temperature 1000 °C, Ar flow 30 ml/min. Figure 2a, b are SEM images of Sample 1 and Sample 2, respectively. These images show that the products were all

Table 1 The analytical data of DOA

Elemental analysis (wt. %)				H/C (mol.mol^{-1})	Softening point (°C)	Carbon residue (wt. %)
C	H	N	S			
88.11	9.05	1.35	0.42	1.23	199	41.12

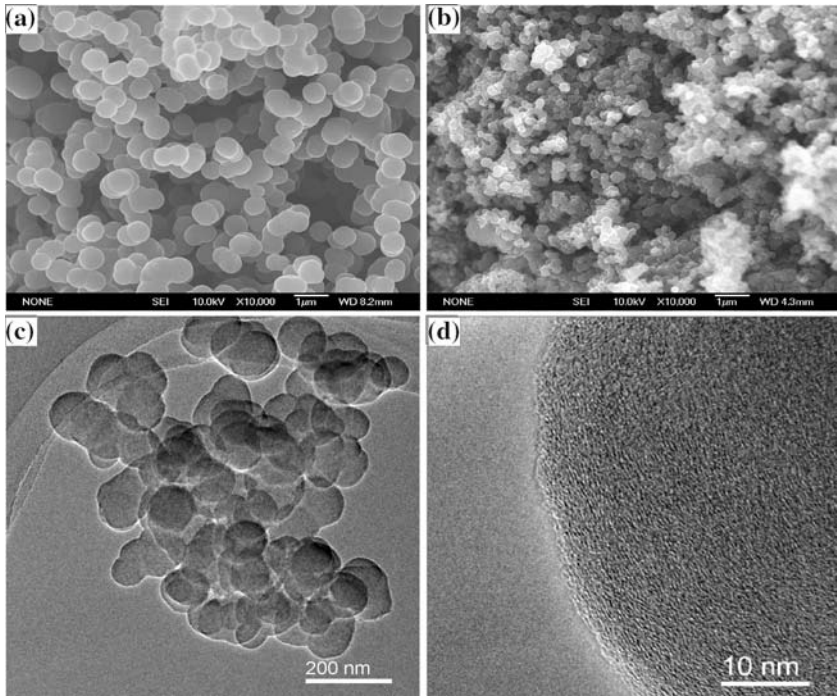

Fig. 2 SEM and HRTEM images of carbon nanospheres (a) SEM image of Sample 1(b) SEM image of Sample 2(c) TEM image of Sample 2(d) HRTEM image of Sample 2

regular spherical particles with uniform size. No other products, such as carbon fibers and graphite pieces could be observed, suggesting the high purity of the product. On the other hand, different samples show totally different size distributions (the size of the particles in Fig.2a is obviously larger than that in Fig.2b), changing from microscale to nanoscale, correspondent to the reaction rate. Figure 2c is a TEM image of Sample 2, which shows the product is composed of spherical particles with the average diameter of about 150 nm, in accordance with SEM results above. Figure 2d is a HRTEM image of a part of one carbon sphere in Sample 2, showing clearly that the carbon sphere was in amorphous state, as conformed the results of XRD analysis.

Ugarte presented the formation mechanism of quasi-spherical carbon particles induced by electron bombardment [7], Zhang et al. also reported a similar transformation of nanotubes into onion-like fullerenes under high temperature and high pressure [8], and Satoshi T et al. found the phenomenon that diamond nanoparticles could transform into carbon onions by only heat treatment [9]. All these works imply that carbon spheres could transform into onion-like fullerenes by proper treatment, for example heat treatment and a like. The high purity, uniform size distribution in nanometer scale and amorphous microstructure of the carbon spheres synthesized in this work applied a good prerequisite for the transformation. The graphitization of such amorphous structure by heat treatment can lower the surface energy, form curved and closed graphite layers and finally give onion-like fullerenes.

Influence of atmosphere

Besides reaction rate, atmosphere also played very important role in the synthesis of carbon spheres by CVD. Sample 3 was prepared under the following conditions: reaction temperature 1000 °C, reaction time 30 min, atmosphere of mixture gas of 30 ml/min Ar and 30 ml/min H_2. Figure 3a is the SEM image of Sample 3, in which many carbon fibers can be seen clearly but no carbon spheres could be observed. These carbon fibers grew in curved shape with the length of several micrometers and the diameter of about 50 nm. These fibers are hollow structure and the inner diameter is about 30 nm (Fig.3c). There are some mussy, discontinuous graphite stripes, suggesting the existence of microstructure defects. These products are very different from the carbon nanospheres synthesized in Ar atmosphere (Fig.3b).

Conclusion

(1) High-purity carbon nanospheres could be exclusively synthesized by CVD method with DOA as carbon source, thus offering reliable experimental data for the transformation of DOA into high-added value carbon materials.
(2) Among the reaction conditions (atmosphere, reaction rate, temperature etc.) affecting the structures of products, atmosphere and reaction rate played more important role than temperature in the used range.

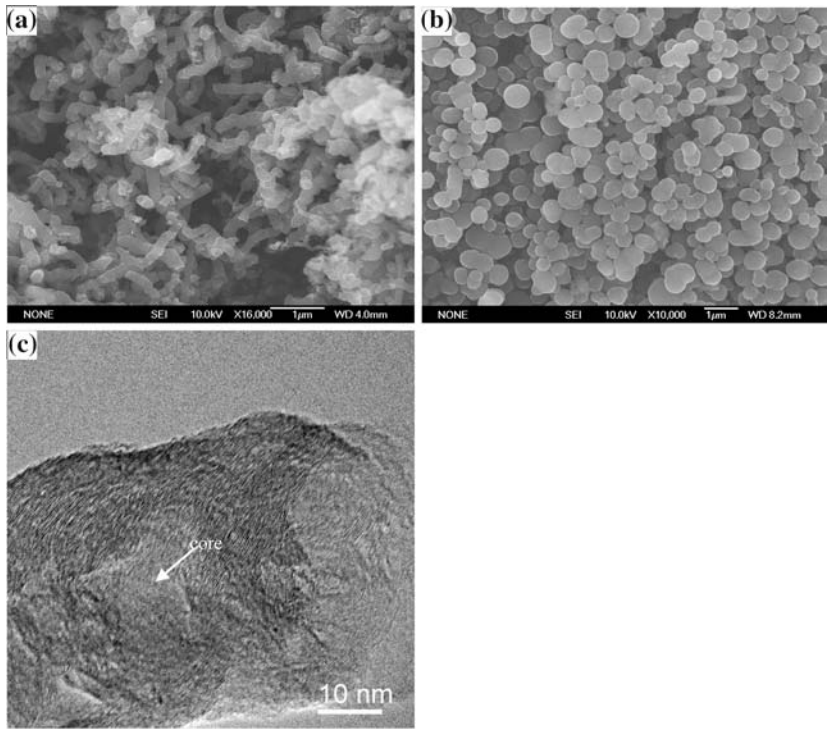

Fig. 3 SEM and HRTEM images of carbon fibers (a) SEM image of Sample 3 (b) SEM image of Sample 1 (c) HRTEM image of Sample 3

(3) In experiments, the formation process is as follows: DOA was evaporated at the entrance of the furnace, i.e. 180–200 °C temperature zone, producing a large amount of carbon clusters. They broke down and reacted in the reaction zone (1000 °C), finally formed carbon spheres in the deposition zone.
(4) The final products were in nanoscale size and in amorphous state, allowing the further transformation into onion-like fullerenes by graphitization treatment.

Acknowledgements This work was supported by National Basic Research Program of China (Grant No. 2004CB217808), National Natural Science Foundation of China (90306014, 50025103), Joint Project of NSFC and JSPS (50311140138), Natural Science Fund of Shanxi Province (20031021, 20031049).

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