

Preparation of carbon nanospheres by non-catalytic chemical vapor deposition and their formation mechanism

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Abstract: Carbon spheres with different sizes were prepared by non-catalytic chemical vapor deposition from gas mixtures of CH₄ and H₂. The influence of the deposition temperature, pressure, and gas ratio on the formation and growth mechanism of the spheres was investigated. The carbon spheres obtained were characterized by XRD, SEM and TEM. Results indicated that carbon nanospheres (50-100 nm) could be obtained at 1150°C and 5 kPa from a gas mixture with a CH₄/H₂ volume ratio of 0.25. The deposition temperature had no obvious effect on the sphere size and structure. The sphere size increased with the deposition pressure and the gas ratio. A model was proposed to elucidate their formation and growth.

Key Words: Carbon spheres; CVD; Natural gas; Hydrogen; Nucleation Mechanism.

1 Introduction

Carbon materials have a variety of structures and properties owing to the chemical nature of carbon atoms with various hybridizations (sp, sp², and sp³) depending on precursors and reaction conditions [1]. Until now, various routes have been used to produce a wide range of carbon materials, such as fullerenes [2], carbon nanotubes [3,4], pyrolytic carbon [5], and carbon spheres [6-10].

Since carbon spheres have potential applications as adsorbents [11], catalyst carriers [12], and anodes in secondary lithium ion batteries [13, 14], their synthetic routes are receiving much attentions in recent years. Typical approaches such as self-assembly template processes [15], pyrolyses [16], reductions [17], and hydrothermal methods [18], have been used to prepare hollow or solid carbon spheres with different sizes and yields. Chemical vapor deposition (CVD), is most popular in terms of economy and versatility and can be divided into three types: catalytic [19], non-catalytic [20], and template methods [21]. To obtain pure carbon spheres from catalytic or template CVD, removal of the catalyst or template from the resultant products is an essential step, which is cost ineffective and complicated. Consequently, research into high yield, one-step, and low cost synthetic routes has been attracted much interest. At present, non-catalytic CVD appears to be the best choice considering all factors of operation and costs. Some researchers [22-24] have synthesized carbon spheres by CVD from liquid hydrocarbons such as styrene, toluene and hexane. But carbon sphere fabrication by the natural gas/hydrogen mixture with the

non-catalytic method has not been reported in former studies to our knowledge.

This paper reports preparation of carbon spheres with CVD from a natural gas/hydrogen mixture in the absence of a catalyst. The influences of deposition temperature, pressure and the natural gas/hydrogen ratio on the formation of carbon spheres were investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) to characterize the sphere morphology, size and structure. Based on the these results, a model is proposed for the formation mechanism of carbon spheres.

2 Experimental

2.1 Preparation of carbon spheres

Preparation of carbon spheres was performed in a typical CVD furnace (Fig. 1). At ambient temperature, air in the CVD furnace was evacuated and flushed with highly pure nitrogen for 10 minutes. Temperature was measured using a Pt thermocouple, pressure was controlled by an electromagnetic valve connected to an absolute pressure transformer and the flow rate of reactant gas was adjusted by a mass flow controller. When deposition temperature was reached, natural gas and hydrogen (purity>99.999%) were continuously introduced into the reaction chamber for 2 h and the reaction products were collected after the chamber was cooled to room temperature. The natural gas was consisted of methane (98%), propane (0.3%), butane (0.4%), nitrogen (1%), and other hydrocarbons (0.3%). Details of process parameters are listed in Table 1.

Received date: 28 Jul 2016; Revised date: 3rd October 2016

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DOI: 10.1016/S1872-5805(16)60025-2

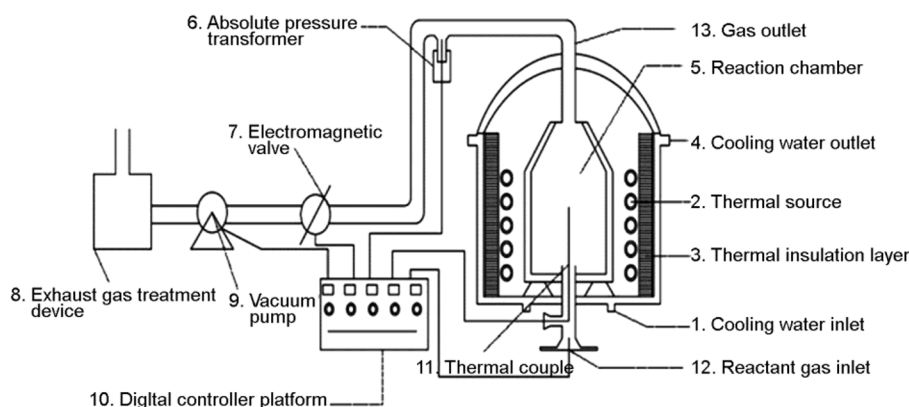


Fig. 1 A schematic illustration of experimental setup of chemical vapor deposition.

Table 1 Experimental conditions for different runs

Series No.	Temperature (°C)	Pressure (kPa)	Flow rate of natural gas (sccm)	Flow rate of hydrogen(sccm)
T1	1070	5	500	500
T2	1100	5	500	500
T3	1150	5	500	500
T4	1200	5	500	500
P1	1150	3	500	500
P2	1150	10	500	500
P3	1150	15	500	500
R1	1150	5	500	0
R2	1150	5	500	1000
R3	1150	5	500	2000

2.2 Characterization

The XRD pattern of the resultant products was measured with a Siemens D5000 X-ray diffractometer ($\text{Cu } K\alpha=0.15418 \text{ \AA}$) and the morphology and microstructure were studied by SEM (LEO-5000, 15 kV) and TEM (H7100, 100 kV). Samples for TEM were dispersed into ethanol with ultrasonication for 0.5 h, transferred to a Cu grid, and air-dried.

3 Results

3.1 Influence of deposition temperature

The influence of deposition temperature on growth and morphology of carbon spheres was studied over a deposition temperature range of 1050-1200 °C. This range was selected because soot was obtained below 1050 °C and conglomeration of carbon spheres increased above 1200 °C under the other conditions employed here. A SEM image of carbon spheres deposited at 1070 °C showed the diameters of carbon spheres to be 1-2 μm and the spheres were not perfectly spherical, but somewhat elliptical or egg-shaped (Fig. 2a, white arrows). When the deposition temperature was increased to 1100 °C,

carbon spheres with diameters of 500 nm-1 μm were obtained and the spheres were observed to be brittle, showing many broken carbon spheres, and hollow ones (Fig. 2b, white arrows). With further increase in the deposition temperature, monodispersed carbon spheres were difficult to observe and conglomeration of carbon spheres became apparent (Fig. 2c, 2d). There was discernable difference in the conglomeration of carbon spheres deposited at 1150 °C and 1200 °C, with small spheres linked to large ones observed at 1150 °C, a phenomenon confirmed in TEM micrographs of these spheres (Fig. 3). In contrast, at 1200 °C, more carbon spheres of uniform size were linked into clusters, and the sphere surfaces were much rough.

XRD patterns of carbon spheres obtained under T1, T2, T3, and T4 conditions showed only two broaden peaks at 25.4°- 25.8° and 42.7°- 43.8°, which were characteristic of typical graphite (002) and (100) planes (Fig. 4). However, the interlayer spacing d_{002} value of carbon spheres obtained ranged from 0.344 37 nm to 0.350 51 nm with increasing the deposition temperature from T1 to T2. They all were much higher than the d_{002} value (0.335 41 nm) of graphitic crystal, even higher than the d_{002} value (0.344 0 nm) of turbostratic

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