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A Simple Method to Synthesize Multi-branched Carbon Fibers Using Cupric Chloride Aqueous Solution as Catalyst Precursor

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Carbon fibers with multi-branched structures were synthesized by chemical vapor deposition method using cupric chloride as catalyst precursor and acetylene as carbon source at different reaction temperatures. Effects of water vapor and reaction temperature on the growth mode of carbon fibers were investigated. Experimental results demonstrate that initial reaction conditions and temperature are key factors for the formation of different carbon materials. Carbon fibers with typical multi-branched structures can be obtained at 450 °C when cupric chloride solution was used as catalyst precursor. X-ray diffraction, field emission scanning electron microscopy, and transmission electron microscopy are used to characterize carbon materials, and the growth mechanisms of multi-branched carbon fibers were discussed.

KEY WORDS: Amorphous materials; Carbon materials; Electron microscopy; Microstructure

1. Introduction

Carbon materials, including carbon nanofibers[1] and carbon nanotubes[2], possess unique physical and chemical properties, such as high electrical conductivity[3,4], high surface area[3,5,6], superb catalyst support[5−8], and excellent hydrogen adsorption[9,10], which have laid a solid foundation for future broad applications. Generally, these carbon materials can be obtained by chemical vapor deposition (CVD) method. During this synthesis process, hydrocarbon gas (i.e., acetylene, ethylene, and methane) and transition metal particles (i.e., Fe, Co, Ni, and their alloys) are used as carbon source and catalyst, respectively. Unlike ordinary carbon nanofibers or nanotubes, carbon materials with specific morphologies[11−13] (i.e., multi-branched carbon fibers and carbon nanocoils) have more advantages for their unique properties.

Different methods have been explored to synthesize carbon materials with specific morphologies. For instance, Zhao et al.[14] employed carbon fibers as substrates to fabricate aligned multi-walled carbon nanotubes by floating catalyst CVD method. Guo[15] reported that macroscopic multi-branched carbon trees could be obtained through the aggregation of iron-encapsulated carbon micro-spheres. Shi et al.[16] utilized an improved floating catalytic method to synthesize branched carbon fibers on the aggregated cores of Fe−SiO_2 composites. Although great efforts have been made on controlling the morphology of carbon structures, a number of problems need to be solved, especially obtaining catalyst particles with defined morphology and dimension.

Catalyst powder is usually used as catalyst precursor for the CVD growth of carbon structures[11−13,17], and the introduction of water vapor can be used to affect the growth process. For example, Hata et al.[17] found that water can stimulate the activity of catalyst particles and elongate their lifetime; Lee et al.[18] reported the effects of water on the yield of carbon nanotubes; and Amama et al.[19] demonstrated the interactions between water and catalyst particles. All the studies above indicate that water can play a critically important role in the growth of carbon materials.

In this study, we synthesized carbon fibers with multi-branched structures using cupric chloride aqueous solution as a catalyst precursor at 450 °C. Effects of water vapor (H_2O) and reaction temperature on the growth of carbon fibers were investigated, and the growth mechanism of multi-branched carbon fibers was discussed.

2. Experimental

2.1. Synthesis of carbon fibers

A catalytic CVD method was employed to synthesize carbon fibers in a quartz tube (8 cm in diameter and 100 cm in length). At

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first, cupric chloride ($CuCl_2 \cdot 2H_2O$, ≥99.999%) or its aqueous solution (3 mol/L) as a catalyst precursor was put into a ceramic boat, which was placed at the center of the reaction tube. Then the ambient pressure inside the tube was maintained in a low vacuum environment of 0.133 Pa (10 mTorr) before the carbon source acetylene was introduced at 200 °C. Reaction temperature was set as 300, 350, 400 or 450 °C for 20 min. The conditions of catalyst precursor were investigated at 200 °C in a vacuum environment and at 300 °C after the introduction of acetylene for 10 min. To further verify effects of water, carbon fibers were fabricated with the introduction of water vapor at 450 °C.

2.2. Characterization of carbon materials

The morphology and structures of as-synthesized carbon materials and catalyst precursors were examined by field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL) and transmission electron microscopy (TEM, JEM-2100, JEOL). Crystal structure of carbon materials was characterized by X-ray powder diffraction patterns (XRD, D-max-γA, Rigaku) with Cu$K\alpha$ irradiation ($\lambda = 0.154178$ nm).

3. Results and Discussion

During a CVD process, catalyst plays a critical role in the decomposition of hydrocarbon gas and the formation of carbon materials. The growth mode and morphology of carbon fibers correlate with physical and chemical characteristics of catalyst particles. The state of catalyst particles can also be altered by changing reaction atmosphere and reaction temperatures, and subsequently different kinds of carbon materials can be obtained[20,21].

3.1. Effects of catalyst precursor and reaction temperature

Reaction temperature is one of the most important parameters in a CVD process[20]. A higher temperature can provide more energy for the catalyst to decompose hydrocarbon gas, such as acetylene. In this study, cupric chloride was grinded prior to the CVD synthesis to enhance its catalysis activity. Fig. 1(a−d) displays FESEM images of carbon products using cupric chloride powder as a catalyst precursor at different reaction temperatures: 300, 350, 400, and 450 °C, respectively. Cupric chloride exhibits low catalytic activity at 300 °C since only small carbon pieces formed on the surface of catalyst particles (Fig. 1(a)). While the reaction temperature was increased to 350, 400 and 450 °C, carbon fibers were obtained (Fig. 1(b−d)). With the increase in reaction temperature, the morphology of carbon structures was changed from mixture of carbon pieces and fibers (Fig. 1(b)) to fibers (Fig. 1(d)). It is obvious that large catalyst particles produce pieces and small catalyst particles lead to fibers. This suggests that the conditions of catalysts can directly affect the growth of carbon structures.

On the other hand, cupric chloride aqueous solution (3.0 mol/L) was used as catalyst precursor to synthesize carbon fibers, the aim of which is to alter initial reaction conditions for changing the growth mode of carbon materials[22]. As shown in Fig. 2, similar to powder catalysts, no carbon materials with typical fiber morphology were obtained at the reaction temperature of 300 °C. When the reaction temperature was increased to 350 and 400 °C, carbon fibers and multi-branched carbon fibers were obtained, respectively. At the reaction temperature of 450 °C, the proportion of branched carbon fibers was circa 35%. Most of the fibers had three or four branches formed on the surface of

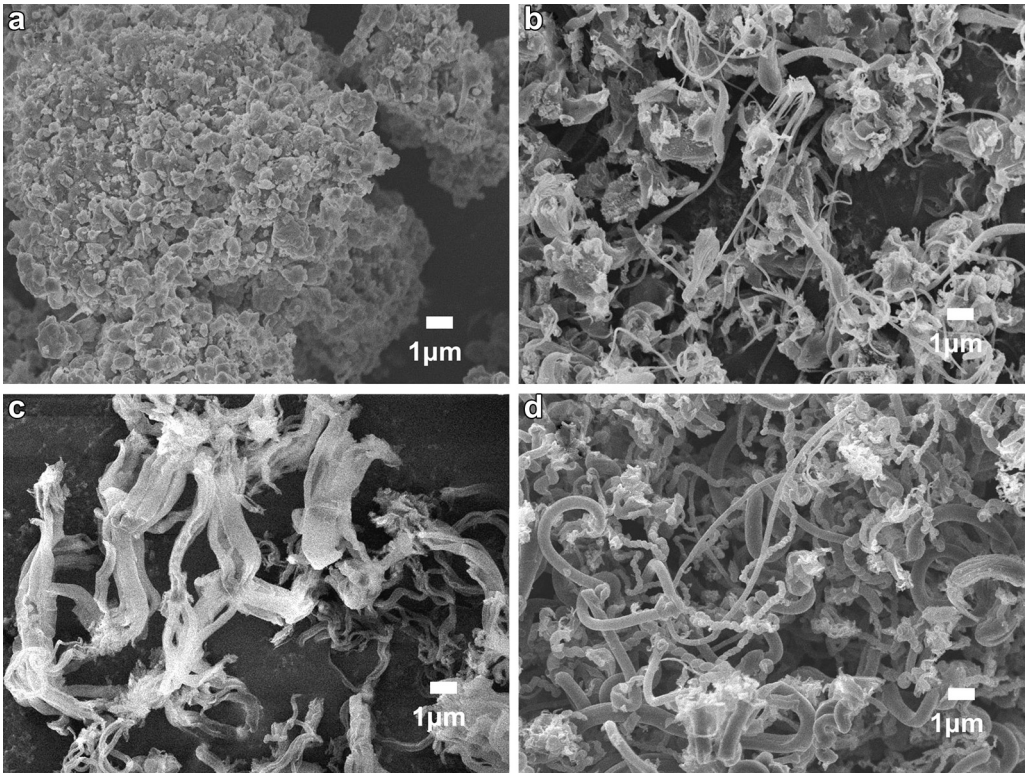

Fig. 1 FESEM images of as-prepared carbon materials using cupric chloride powder as catalyst precursor at different reaction temperatures: (a) 300 °C; (b) 350 °C; (c) 400 °C; (d) 450 °C.

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