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Controlled synthesis of carbon nanocoils with selective coil diameters and structures by optimizing the thickness of catalyst film

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ABSTRACT

Carbon nanocoils (CNCs) with selective coil diameters and structures have been synthesized by chemical vapor deposition using Sn/Fe binary catalyst films. CNCs, carbon nanofibers and irregular carbon nanowires could be selectively obtained by changing the thickness of the catalyst film. It is found that the coil diameters of CNCs gradually decrease with a decrease in the thickness of the catalyst films within a certain range, indicating that the coil diameters of CNCs can be effectively controlled by adjusting the thickness of Sn/Fe catalyst films. The morphology of the CNCs tends to change from spring-like to plait-like, and the graphitization degree of the CNC increases when their diameters are reduced. Our results provide important guidelines for the controlled synthesis of CNCs with selective coil diameters and selective structures by optimizing the catalyst film thickness.

1. Introduction

Carbon nanocoils (CNCs), a new type of three-dimensional helical nano-material, exhibit outstanding optical, mechanical, and electrical properties [1–6] and have received considerable attention in recent years. Because of these outstanding properties, CNCs are an ideal candidate for a wide range of applications, including electromagnetic wave absorbers [7], micro-sensors [8], and field emission devices [9]. To date, it has been observed that the performance of CNCs is closely linked to their morphology and structure [10–12]. Deng et al. observed that the resonance frequency of a CNC is dependent on its morphology [13]. Ma et al. reported that the resistivity of CNCs decreases with the increase in the annealing temperature, owing to the improvement in the coils' crystallinity [14]. Pan et al. observed that the turn-on voltage of a CNC field emitter is decreased by decreasing the coil diameter of the CNC [15]. Therefore, developing a simple way to synthesize CNCs with controllable coil diameters and structures would be most desirable.

Due to its controllable and simple operation, chemical vapor deposition (CVD) has been widely employed to synthesize CNCs. To date, many metals and their alloys, such as Fe, Cu, Ni, Ti, Co, and Pd [16–19] have been used to grow CNCs, where Fe–Sn–O has proven to be an efficient catalyst and therefore attracted the attention of many researchers.

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Several methods have been used to prepare Fe–Sn–O catalysts, such as dropping, dipping, or spin-coating a solution of catalyst precursor on substrates; physical evaporation; and sputtering [20–22]. Sputtering is an effective method for obtaining a uniform catalyst film with controllable thickness. In recent years, much work has been done to control the morphology and structure of CNCs. Zheng et al. observed that the reaction temperature greatly affects carbon nanostructures [23]. Liu et al. controlled the morphologies of CNCs by changing the flow rate of acetylene [24]. Li et al. successfully synthesized CNCs with a controlled coil diameter, coil pitch and structure by adjusting the reaction temperature and the delivery of acetylene in a CVD system [25]. In addition, our previous study revealed that the distribution of coil diameters could be altered by increasing the deposition time [26]. It is noted that all of these studies have focused on controlling the morphology of CNCs by changing the reaction conditions in a CVD system or the methods for preparing catalyst particles. The thickness of the catalyst film is also a crucial factor for the growth of CNCs and may affect the size and the distribution of the formed catalyst particles. However, the effects of Sn/Fe catalyst film thickness on the growth and morphology of CNCs have not been adequately investigated.

In this study, we investigated the coil diameter and structure of CNCs growth by monitoring changes in the thickness of Sn/Fe catalyst films. CNCs with different coil diameters and structures could be selectively synthesized by optimizing the thickness of the catalyst film. The mechanism governing the growth of CNCs by Sn/Fe catalyst films was also investigated.

2. Experimental

Sn–Fe binary metals were used as the catalyst precursors for synthesizing CNCs. To prepare the Sn/Fe catalyst precursors, a tin film was first sputtered on a silicon substrate (size: $1 \times 1\ cm^2$) by a vacuum magnetron sputtering system (JCP-200, BTSC563). Then, an iron film was sputtered onto the tin film. The thickness ratio of Sn to Fe was maintained at 1:20, and the mole ratio of Sn to Fe was approximately 1:46. A series of Sn/Fe films with thicknesses ranging from 0.035/0.7 to 16/320 nm was prepared. The prepared Sn/Fe catalyst films were then calcined at 710 °C for 30 min in the air to oxidize the catalysts, which prevents Sn from vaporization during heating in Ar, because the melting point of Sn is 231.89 °C [20]. Finally, CNCs were synthesized in a thermal CVD system at 710 °C by introducing Ar and C_2H_2 at flow rates of 230 and 30 sccm, respectively.

The morphology and structure of the synthesized CNCs were analyzed by scanning electron microscopy (SEM; FEI, NOVA NanoSEM 450), transmission electron microscopy (TEM; FEI, Tecnai G2 F30 S-Twin), and Raman spectroscopy (Renishaw inVia plus, He-Ne laser, 632.8 nm). The Sn/Fe catalyst films were characterized by atomic force microscopy (AFM; Agilent PicoPlus II, Agilent, Santa Clara, CA) and SEM.

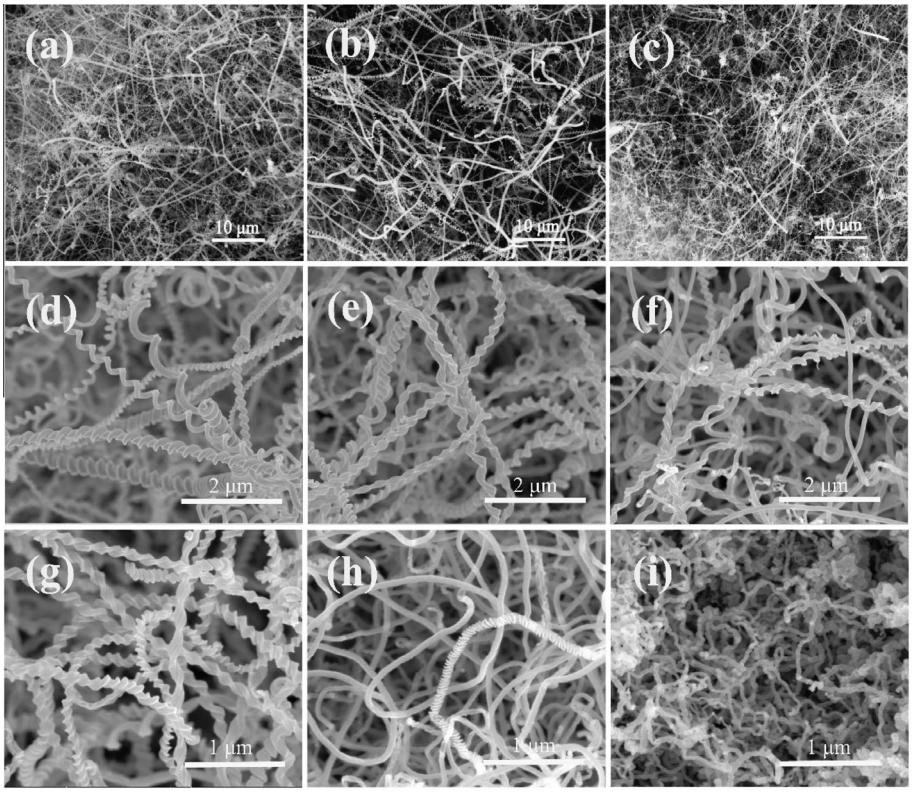

Fig. 1 – SEM images of carbon deposits synthesized using Sn/Fe catalyst films with different thicknesses of, (a) 16/320 nm, (b) 8/160 nm, (c) 4/80 nm, (d) 2/40 nm, (e) 1/20 nm, (f) 0.5/10 nm, (g) 0.35/7 nm, (h) 0.15/3 nm, and (i) 0.035/0.7 nm.