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Optimization of Chemical Vapor Deposition Process for Reducing the Fiber Diameter and Number of Graphene Layers in Multi Walled Carbon Nanocoils

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Multi walled carbon nanocoils (MWCNCs) were synthesized by chemical vapor deposition (CVD) and the experimental parameters were optimized to reduce their fiber diameter. The conditions for the synthesis of the thinnest MWCNC in this experiment were as follows: reaction temperature, 700 °C; C_2H_2/N_2 pressure, 0.67 kPa; and C_2H_2/N_2 ratio, 0.01. A low C_2H_2 gas flow rate and a low partial gas pressure were important in reducing the fiber diameter. The reaction temperature affected both the MWCNC fiber diameter and purity, which depends on the content of MWCNCs and multi walled carbon nanotubes (MWCNTs). At high temperatures (≥750 °C), MWCNTs were predominant and their crystallinity increased, which was confirmed by the detection of the radial breathing mode and high intensity ratios of the G peak to the D peak in the Raman spectra. By contrast, MWCNCs were produced preferentially at low temperatures (approximately 700 °C). Transmission electron microscopy showed that the fiber diameter of the thinnest MWCNC was less than 5 nm at both the helix and tip and that the thinnest MWCNC had a triple walled structure. Under optimized conditions, the vacuum deposition of a thin film of Sn on a Si substrate and the mounting of Fe catalyst supported zeolite on a Sn/Si substrate effectively increased MWCNC purity. MWCNC purity was improved by up to 30%, which is the highest purity we have observed thus far.

1. Introduction

Following the discovery of multi walled carbon nanotubes (MWCNTs) in 1991,[1] helical carbon nanotubes or multi walled carbon nanocoils (MWCNCs) were successfully fabricated in 1994.[2] There are several types of helical carbon nanofibers, including carbon microcoils (CMCs),[3] carbon nanocoils (CNCs),[4] carbon nanotwists,[5] and MWCNCs. These structures are classified by their dimensions and fiber structure. As the CNC diameter decreases, the structure of the CNCs changes from amorphous layers to multi walled graphitic layers, which are similar to that observed in the chemical vapor deposition (CVD) synthesis of MWCNTs.[6] It has been postulated that MWCNCs are formed when heptagonal and pentagonal rings are inserted into CNTs.[7,8] Other growth mechanisms for MWCNCs have been reported elsewhere.[9] The conductivities of CNCs and CMCs are about 180 and 100 S/cm, respectively.[10,11] The Young's modulus of CNCs (0.1 TPa) is higher than that of CMCs (0.54 MPa) embedded in epoxy resin.[10,12] MWCNCs with a multi walled graphitic structure have a higher Young's modulus (0.7 TPa) than CNC and CMCs.[13] Pan et al. reported that MWCNCs have a higher electric field emission efficiency than MWCNTs because of their three-dimensional structure.[14]

These differences in the mechanical and electrical properties among CMCs, CNCs, and MWCNCs are a result of their size and crystallinity. Therefore, reducing the size of the carbon materials could enhance these properties. Consequently, it is very important to take into account the purity of MWCNCs during application, such as in electronic and composite materials.[13,15,16] Some researchers have reported the synthesis of very thin MWCNCs with a fiber diameter of 3 nm.[9] The synthesis of MWCNCs only a few layers or a single layer thick, and a mass production technique for the growth of high-purity MWCNCs are required before MWCNCs can find broad applications.

In our previous study, MWCNCs were grown from a Fe/Sn-supported mesoporous material, such as zeolite or MCM-41, by CVD at atmospheric pressure.[6,17] The average fiber and coil diameters of the MWCNCs were 15 ± 5 and 50 ± 20 nm, respectively, and there were 10–20 graphitic layers. In this study, we investigated the reduction in the fiber diameter and number of graphitic layers in MWCNCs by changing the CVD parameters, including pressure, temperature, and the ratio of the source gas (acetylene, C_2H_2) to the dilution gas (nitrogen, N_2). The effects of these changes on the MWCNC purity were studied. The growth mechanism for reducing the diameters of MWCNCs is discussed.

2. Experimental Procedure

2.1 Catalyst preparation

Fe_2O_3/zeolite was prepared by mixing Y-type zeolite (Tosoh HSZ-390HUA) in an iron acetate ethanol solution with an iron acetate mass fraction of 5%. The mixture was homogenized by sonication for 10 min. Then, the mixture was calcined at 100 °C for 20 h in a furnace. To produce the Fe/Sn catalyst on zeolite, Sn was evaporated onto the surface of Fe_2O_3/zeolite under vacuum.[17] The distance between the Sn wire ($\phi = 0.2$ mm, length 7 mm) and Fe_2O_3/zeolite was 8.5 cm. The Fe/Sn molar ratio was 33 in this experiment, which was calculated from the molar quantity of Fe nanoparticles supported on zeolite and the Sn thin film deposited on Fe_2O_3/zeolite.

To improve the purity of the MWCNCs (Sect. 3.4), a Sn wire ($\phi = 0.2$ mm, length = 5 mm) was vacuum deposited as a film on a Si substrate measuring 1×1 cm^2, and 10 μL of Fe_2O_3/zeolite solution was added dropwise to the surface of this film. The distance between the Sn wire and Fe_2O_3/zeolite was 15 cm.

