# Improvement of carbon nanocoil purity achieved by supplying catalyst molecules from the vapor phase in chemical vapor deposition

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We investigated how changes in the method of supplying Sn and Fe carbon nanocoil (CNC) catalysts affected the results of chemical vapor deposition. The Sn/Fe catalysts were supplied using the following four materials: a thin Sn film, a drop-coated solution of $Fe_2O_3$, tetramethyltin (TMT) vapor, and ferrocene vapor. The CNC purity was evaluated using scanning electron microscopy. The CNC purity in the overall carbon deposit was also evaluated by analyzing the cross-section of the deposit. The CNC purity averaged over the overall carbon deposit was increased 1.5-fold by the TMT supply. We obtained a maximum CNC purity of 72% using a combination of TMT and ferrocene vapors, with Sn/Fe deposition on the substrate. Energy-dispersive x-ray spectroscopy analysis of the catalyst nanoparticles in the tips of the CNCs and carbon nanofibers (CNFs) revealed that there was a large difference in the Sn/Fe molar ratios for the angular- and round-type CNFs.

## I. INTRODUCTION

Carbon nanocoils (CNCs) are carbon nanofibers (CNFs) with a helical shape; typical fiber and coil diameters in CNCs are 120–400 nm and 400–1000 nm, respectively.[1–3] There are two types of CNCs: the first type, called CNCs, have an inner diameter; the second type does not have an inner diameter, and these are called carbon nanotwists (CNTws).[4] It is expected that CNCs will find applications as magnetic absorbing materials,[5] catalyst supports for fuel cells,[6] active materials for supercapacitors,[7] and nanosprings.[8]

We have studied the synthesis of CNCs using Sn/Fe catalysts.[9] Our laboratory has developed an automatic chemical vapor deposition (CVD) system with a consecutive substrate transfer mechanism; this system can be used to produce 2–3 g of helical CNFs on a catalyst-supported graphite substrate within an hour, using $C_2H_2$ feedstock. However, the problem of low CNC purity remains. The major problem in CNC synthesis is that although CNCs can be grown with high purity on the surface of the carbon deposit, a middle layer in which the CNC purity is very low exists inside the carbon deposit.[9–11] Binary alloy catalysts are crucial for the formation of the helical structure. It has been found that Fe is crucial in the formation of carbon tubules, and that neither CNCs nor carbon fibers can be grown using only $In_2O_3$ or $SnO_2$.[10] Various experimental methods have been proposed for the production of high-purity CNCs. Chang et al. coated a thin Sn film on a 304 SUS substrate from a $(C_2H_3O_2)_2Sn$ catalyst precursor to synthesize CNCs with a purity of 80%.[12] Bi et al. used a Co–P catalyst that was formed on a graphite substrate to synthesize CNCs with a purity of 76% from a $C_2H_2/C_4H_4S$ feedstock.[13] Qi et al. synthesized CNCs with a purity of 93% at a low temperature of 450 °C from a $C_2H_2$ feedstock.[14] Li et al. used $Fe_2(SO_4)_3/SnCl_2$ as a catalyst precursor to synthesize CNCs with a purity of 90%.[15] The CNC purity in these reports was evaluated by observing the surface of the carbon deposit. The variations in the CNC purity inside carbon deposits are not yet understood completely.

In this study, we performed experiments in which different catalyst metal vapors were supplied successively in a CVD reactor. The supply of catalysts during the synthesis of CNCs has been reported in only a few previous studies.[16,17] The synthesized CNCs were analyzed using scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS). X-ray photoelectron

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