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Research Article

Preferential Gas Phase Reactions of Carbon Nanotubes (CNTs)

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Abstract

Gas phase reactions including metal catalysts at elevated temperatures and pressures can be used for both growth and purification of carbon nanotubes. Chemical vapor deposition (CVD) is used at optimized conditions to grow multiwall carbon nanotubes (MWCNTs) utilizing iron seed catalysts. Carbon dioxide (CO_2) extractions are performed at the optimum extraction conditions to enhance metal catalyst removal efficiency. The analytical studies included Thermogravimetric analysis to evaluate metal catalyst removal, Raman spectroscopy and fluorescence spectroscopy to assess the properties of the treated carbon nanotubes as well as Transmission electron microscopy to evaluate metal size and size distribution of metal impurities before and after purification. A significant result is that using carbon dioxide leads to better extraction efficiency at higher temperatures and intermediate pressures. A single extraction at 65°C and 325 atm shows 16.7 wt % of final ash content compared with 20 wt % for multiple extractions at 45°C and 325 atm.

Keywords: Single wall carbon nanotubes, Metal catalyst impurities, Carbon dioxide

Introduction

Carbon nanotubes (CNTs) have been the focus of recent research due to their unique electronic and mechanical properties. Their properties have been mainly utilized for incremental improvements in various applications such as solar cells, electronic components, as well as in composite polymer materials. When CNTs were deposited on conductive films in solar cell applications instead of conductive glass substrates, they were made transparent while remaining highly conductive as they show high transparency in a wide spectral range from the UV-visual to the near IR range. CNTs films can be coated by various techniques such as spraying or spin coating on glass substrates [1]. However, the integration of CNTs in any application mandates their synthesis method for yield, alignment and purity. Purification of CNTs from inherent metal impurities is important for making effective conductive films [2]. Lagemaat, et al. [3] reported purification of single wall carbon nanotubes (SWCNTs) using an acid reflux method and films of low sheet resistance and high transmittance. However, most purification processes that use strong acids or oxidative environments to remove the impurities result in oxidizing the carbon nanotube sidewalls and thereby affecting their electronic properties. Blackburn et al. showed the substantial reduction of florescence intensity due to protonation of carbon nanotubes [4].

Wang, et al. [5] reported the highly selective purification one pot technique, where the carbon nanotubes are dissolved in an aqueous mixture of hydrogen peroxide and hydrogen chloride. However, that method causes defects to the carbon nanotube structure. Magnetic purification of carbon nanotubes has been studied by Wiltshire, et al. [6], where scalability of that method can be a setback. Chiang, et al. [7] used a wet gas method by oxidizing and annealing in a gas environment. Raman spectroscopy of the treated sample in their study shows defects to the structure of the nanotubes. Wang, et al. [8] reported high metal extraction efficiency from carbon nanotubes using electrochemical pretreatment step with ethylene diaminetetraacetic acid (EDTA) electrolyte. However, that method can be limited by accessibility of metals in the carbon nanotubes for oxidation.

Transport in nanopores is critical for reactions synthesis in nanomaterials. Inefficiencies of wet methods are attributed to high surface tension of liquids solvents. Conducting reactions in carbon dioxide (CO_2) enables control of viscosity, diffusivity and surface tension. In this paper, supercritical carbon dioxide (Sc-CO_2) is used to purify different types of SWCNTs from their inherent metal catalyst impurities at different

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temperatures and pressures. Multiple extractions are performed for optimum extraction condition, to enhance metal removal efficiency. Synthesis of vertically aligned multi wall carbon nanotubes (MWCNTs) on SiO_2 wafers using iron seed catalyst was carried out by Chemical Vapor Deposition (CVD) using water vapors. The carbon nanotubes samples are analyzed by TGA, Raman spectroscopy and fluorescence to assess metal catalyst removal and properties of the carbon nanotubes. Transmission electron microscopy is used to evaluate metal catalyst size and distribution before and after purification.

Materials and Experimental

Materials. Tri-n-butyl phosphate (TBP-99% purity from Sigma-Aldrich), and hexafluoroacetylacetone (HFA – 95% purity from Sigma-Aldrich) were used as received. Hipco single wall carbon nanotubes (SWCNTs) were used as received. CO_2 was used as received. Reactor was purchased from Pressure Company. 1 nm Fe/10 nm Al_2O_3/20 SiO_2 wafer substrates were acquired from CVD Materials Corporation.

Experimental. Hipco carbon nanotubes were processed to remove metal catalyst impurities used in their synthesis by sc-CO_2 extraction at temperatures ranging from 35 to 65°C and pressures between 250 and 400 atm. TBP was used as an oxidizing agent and HFA was used as a chelating agent at a ratio of 2:1 vol %. Chemical vapor deposition was carried out using First Nano 2000. The ratio of hydrocarbon gases is controlled using a specified growth recipe.

Reagent and solubility limitation was probed by using TBP with an acid complex, 70% HNO_3 (1:1 vol %) and 5 % ethanol as a co-solvent for Hipco carbon nanotubes in Sc-CO_2 extraction at 60°C and at 200 atm.

The effect of acid treatment on carbon nanotube properties was shown by using the one pot method with a sample of Hipco carbon nanotubes. The carbon nanotubes are dissolved in an aqueous mixture of hydrogen peroxide and hydrogen chloride at 40-70°C for 4-8 h.

Sc-CO_2 extraction. Syringe pump was used to pressurize CO_2 to the micro reactor. Approximately 22 mg of Hipco carbon nanotubes and a small stir bar were wrapped in filter paper and inserted into the reactor. The oxidizing and chelating agents were loaded according to the raw carbon nanotube metal content into the reactor.

The reactor was loaded with CO_2 to the desired pressure and allowed to reach equilibrium. CO_2 was again loaded until the desired pressure was reached. The reactor was held at the extraction conditions for 1 h and 30 min followed by dynamic extraction for 15 min to flush out the used reagents. The sc-CO_2 was then slowly vented and bubbled through water, yielding purple droplets in the water solution [8-10]. The carbon nanotubes were recovered from the reactor and bath sonicated in ethanol for 30 min. The suspension was then filtered through a 0.1 µm PTFE membrane and washed with hexane.

Characterization. Thermogravimetric (TGA) analysis was conducted in air up to 800°C at a ramp rate of 10°C/min. Inductively Coupled Plasma Spectroscopy (ICP) analysis was performed on homogenized collected effluent. Raman spectra were recorded on the solid carbon nanotubes using a Raman with excitation from a 785 nm diode laser. For fluorescence measurements, carbon nanotubes were dispersed in 1 wt % SDBS surfactant. The suspension was homogenized with 10,000 rpm for 1 hour followed by tip sonication for 10 min. Toluene was added to the suspension and then mixed with vortex at 1,500 rpm for 30 seconds. Finally, the suspension was allowed to settle for 2 hours. The suspension was characterized using a Fluorescence spectrometer.

Results and Discussion

Effect of pressure and temperature in Sc-CO_2 extraction. For the raw Hipco carbon nanotubes, initial metal content ranged from 25 to 30 %. TGA of purified Hipco carbon nanotubes showed final ash content ranging from 21.6 to 43.5 %. This increase in ash content was attributed to residual amounts of reagents in samples. This is supported by the results obtained for the final ash content of Hipco carbon nanotubes treated with TBP, which was found to be higher than that of TBP or Hipco carbon nanotubes alone. Analysis using TGA results was performed to determine the actual amount of metal oxide left in each treated sample. TBP weight is determined as the difference of sample weights during the TGA ramp program at 110°C and 307°C, the sample temperature after the boiling of water and TBP, respectively.

The percentage of TBP left in the tested carbon nanotube sample was 11.87 %. Based on this result, the final metal oxide content without TBP is calculated for each purified carbon nanotube sample. The results show that the best overall removal efficiency was found at an intermediate temperature 45°C and an intermediate pressure of 325 atm, see Figure 1. The removal of metals presents in Hipco carbon nanotubes such as Fe, Mg, Mo and Ni followed different reaction conditions. ICP showed optimum iron removal from Hipco carbon nanotubes of around 40 ppm at the highest temperature of 55°C and highest pressure 400 atm, see Table 1

Effect of multiple extractions and higher temperatures. Multiple extractions with fresh chelating agent and oxidant were

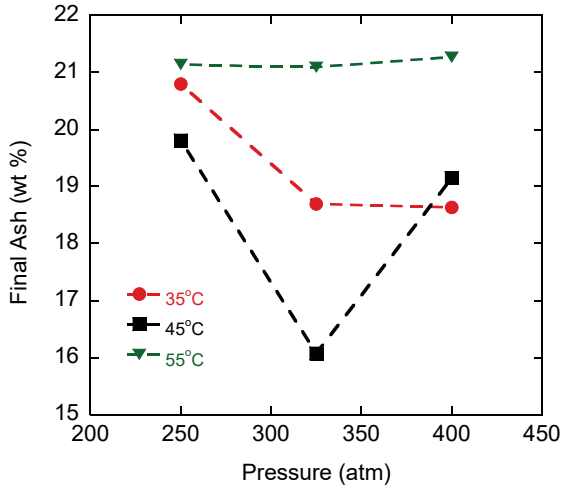

Figure 1: Final metal oxide content of treated Hipco carbon nanotubes. Sc-CO_2 extraction was performed at temperature from 35 to 55°C and pressures from 250 to 400 atm. A single extraction at 45°C and 325 atm shows 16 % of final ash content.

Table 1: Metal ions removed from Hipco SWCNTs. ICP analysis was performed on effluent from the different sc-CO_2 extraction conditions. The detection level is 0.004, 0.003, 0.012 and 0.026 ppm (mg of metal/ kg of solvent) for Mo, Ni, Fe and Mg, respectively. BDL stands for below detection level.

SWCNTs	T (°C), P (atm)	Mo (ppm)	Ni (ppm)	Fe (ppm)	Mg (ppm)
Hipco	35, 325	0.22	0.26	36.13	3.53
	45, 325	0.07	0.31	37.49	1.77
	55, 325	0.24	0.06	39.35	1.21
	45, 250	0.18	0.27	38.51	0.54
	45, 400	0.11	0.19	40.43	BDL

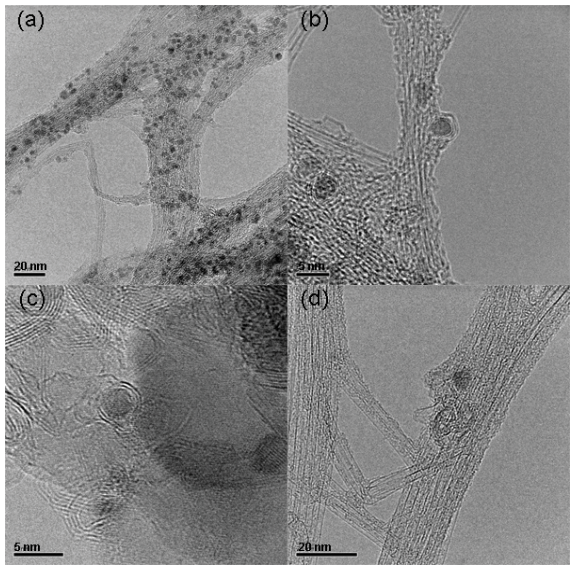

Figure 2: TEM images of raw Hipco (a,c) treated Hipco (b,d) carbon nanotubes. The carbon nanotubes have density of metal impurities in the 3-5 nm range.

performed at optimum conditions for Hipco carbon nanotubes. Hipco carbon nanotubes did not show better metal removal efficiency at any of the conditions tested. This confirms that efficiency limitation was not due to lack of reagents. Hence, a single extraction step was sufficient under these conditions.

The extraction at 55 °C and 325 atm showed a similar final ash content of 20 % with a single extraction. Extraction was repeated 4 times at 55 °C and 325 atm but did not show further reduction in metal content. Further, the efficiency was performed at 65°C and 325 with a single extraction and showed final ash content of 16.7 %. Extraction was repeated at that condition but did not show removal efficiency improvement. These results show the best extraction conditions are at the higher temperature of 65°C and the intermediate pressures of 325 atm. This is primarily due to optimum oxidation and chelating conditions for removal of magnesium.

Hipco carbon nanotubes have higher density of metal impurities in the 3-5 nm range, see Figure 2.

The high metal content in the carbon nanotubes allows high initial oxidization and removal of metals, which makes more inaccessible metal sites available for oxidization. Hipco low metal size content prevents solvent penetration and further oxidization of additional metals sites.

The solubility of the reagents in sc-CO_2 was found to have no

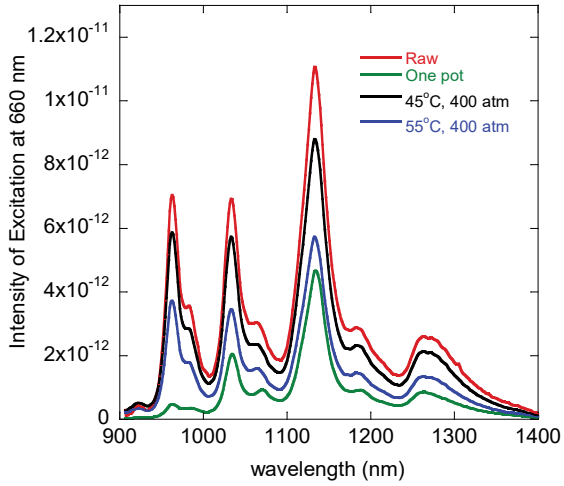

Figure 3: Fluorescence of raw and treated Hipco carbon nanotubes. Sc-CO_2 extractions at 45 to 55°C and 400 atm show comparable intensity to the raw sample. One pot method shows least intensity.

effect on further removal. Adding 5 % of ethanol as a co-solvent did not enhance extraction efficiency. Moreover, the processing condition of the carbon nanotubes had no effect on removal; two Hipco carbon nanotubes sample were processed with and without crushing and both samples showed the same final ash content. Finally, combining sc-CO_2 extraction with acid treatment did not enhance oxidation and metal removal. This shows that the CO_2 method was sufficient in a single extraction step when performed at optimum conditions.

Carbon nanotube integrity assessment. Raman spectra were performed on the solid carbon nanotubes. The Raman spectra for the Hipco nanotubes show the characteristic peaks at 1594 and 1295 cm^{-1}. The low D/G ratio is indicative of high quality carbon nanotubes with few defects. The Raman spectra of treated Hipco carbon nanotubes correspond to those of other carbon nanotubes. These results show that there was no sidewall damage caused to the nanotubes during the sc-CO_2 extraction process. The one pot method showed final ash content of 12 %. However, Raman spectra shows lower D/G ratio, indicative of nanotube defects. Fluorescence is a sensitive analysis technique to probe any oxidative environment on the carbon nanotubes. The peaks of fluorescence of treated Hipco carbon nanotubes correspond to those of other carbon nanotubes. The spectra showed no decrease in intensity after purification, see Figure 3. Fluorescence of one pot treated carbon nanotubes show the least intensity compared with other treated samples.

Conclusion

Metal impurities were effectively removed at intermediate pressures and higher temperatures for Hipco carbon nanotubes using Sc-CO_2 extraction. This was due to enhanced oxidation and chelation conditions of the metal catalyst in each carbon nanotube material. The effective extraction was due to Sc-CO_2 low surface tension and high diffusivity. The carbon nanotubes were purified from their impurities without sidewall damage or decreased fluorescence intensity. Growth of MWCNTs shows effect of gas phase reaction conditions on metal catalyst growth (the subject of a forthcoming manuscript).

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