R&D NOTE

Postsynthesis Microwave Treatment to Give High-Purity Multiwalled Carbon Nanotubes

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DOI 10.1002/aic.11641

Keywords: microwave-assisted acid digestion, purification, carbon nanotube, MWNT, fluidized-bed chemical vapor deposition

Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with extraordinary electrical, mechanical, and chemical properties, making them valuable in applications as diverse as advanced materials,[1] field emission devices,[2] biosensors,[3] and molecular electronic devices.[4] A single-walled nanotube (SWNT) is formed by a single graphene sheet rolled into a tube,[5] whereas a multiwalled nanotube (MWNT) is formed of a number such structures nested coaxially.[6]

To date, the major barrier to the widespread use of CNTs has been the lack of a truly large-scale manufacturing process. Fluidized-bed chemical vapor deposition (CVD) has been investigated as a promising technique for the economically viable, large-scale synthesis of CNTs,[7–15] which we have defined previously as being of the order of 10,000 tonnes per plant per year.[16] However, the products of fluidized-bed CVD are typically a mixture of CNTs, catalyst supports, metal catalysts, and reaction by-products, e.g., amorphous carbon. In particular, catalyst supports and metal catalysts typically occupy as much as 85 wt % of the as-synthesized materials.[17–21] Hence, purification is required to obtain high-purity CNTs for end use applications.

Separating the CNTs from impurities for the products synthesized over supported catalysts has been problematic to date. The general approaches either use hydrofluoric acid[18,22–24] or take several hours to dissolve the catalyst supports and metal catalysts using multistep digestion and filtration processes.[19,25] Both approaches pose challenges for designing a large-scale CNT process and require long residence times[17] and high costs.

A review of the literature shows that the purification efficiency of the catalyst-supported CNT products is far from satisfactory. To clarify this issue, we define the purification efficiency in terms of the removal weight loss of impurity per unit time. Okubo et al.[19] reported the purification of zeolite-supported CNT products by refluxing for 3 h in sodium hydroxide (NaOH) followed by 2 h in hydrochloric acid (HCl). This process increased the CNT purity from 1.6 wt % in the as-synthesized samples to 62.8 wt % in the purified samples, at a purification efficiency of 12.2 wt % per hour. Ramesh et al.[20] separated silica-supported CNT products using a combination of oxidation in air for 1 h at 450°C, immersion in NaOH for 3 h, immersion in HCl for 2 h followed by oxidation in air for 1 h again at 450°C. This increased CNT purity from 5 wt % to 92 wt %, at a purification efficiency of 12.4 wt % per hour. In addition, Huang et al.[21] reported the use of vacuum annealing at 2150°C for 5 h on the CNT products synthesized in a fluidized-bed by CVD on nanosized Fe-Mo-Al_2O_3 catalysts, increasing CNT purity from 89.0 wt % to 99.9 wt %, at a purification efficiency of 2.2 wt % per hour. Igarashi et al.[18] reported the effective removal of zeolite supported metal catalysts using a multistep purification of 1.5-h oxygen oxidation at 340°C, 1-h acid reflux in HF, and 1-h oxygen oxidation at 350°C. This process increased CNT purity from 15.4 to 99 wt %, at a purification efficiency of 23.9 wt % per hour. More recently, we reported that the use of microwave-assisted acid digestion on low quality fluidized-bed CNT products, increasing CNT purity from 2.6 wt % in the as-synthesized bed material to 67.9 wt % for samples treated in H_2SO_4 for 30 min.[17] This process has a purification efficiency of 130.6 wt % per hour. However, no research reporting high CNT purity and high purification efficiency have been published to date for the purification of the CNT products synthesized on micron-sized catalyst supports to date.

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To this end, we report a microwave-assisted acid digestion technique to purify alumina-supported CNT products synthesized by fluidized-bed CVD, giving very high purity CNT products at a high purification efficiency. Purification in H_2SO_4 at 230°C for 30 min in a microwave increases the CNT purity from 23.2 wt % in the as-synthesized bed material to 98.1 wt % in the purified sample. This process has a purification efficiency of 149.8 wt % per hour, which is highest obtained for the catalyst-supported CVD products reported in the literature to date. Furthermore, the purification method has two advantages: (i) high purity CNT products are produced from comparatively low quality feedstocks in less than 30 min and (ii) CNTs remain intact during purification process, as inferred from TGA, Raman, FTIR, and TEM measurements.

Experimental

CNT synthesis was performed over 5 wt % iron impregnated alumina (Fe/Al_2O_3) in the presence of ethylene, hydrogen, and nitrogen (C_2H_4:H_2:N_2) in the ratio of 25:25:50 at 600°C in a fluidized bed for 90 min. The fluidized bed reactor used had a 52 mm inside diameter and was 1000 mm in length. The calcined Al_2O_3 powders were sieved to a diameter of 125–150 μm prior to use. The catalysts were prepared by wet impregnation.[26] This entails dissolving iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] (analytical grade, Sigma-Aldrich) in absolute ethanol (analytical grade, Biolab Ltd.) and then mixing with calcined Al_2O_3 powders. This mixture was dried under vacuum at 0.5 bar overnight and then calcined in a muffle furnace at 800°C for 8 h. About 100 g of the calcined catalysts were loaded into the fluidized-bed and reduced at 600°C for 1 h before synthesis. At these conditions, the as-synthesized bed materials were typically a mixture of MWNTs, Fe catalyst, and Al_2O_3 supports.

CNT purification was carried out using a microwave digester (Milestone Microwave Labstation, ETHOS SEL). 100 mg of as-synthesized bed material was weighed and added to 20 mL of 4.8 mol/L sulfuric acid (H_2SO_4) in a sealed, Teflon lined, microwave pressure vessel. The as-synthesized bed materials were then heated at 230°C for 30 min. The CNT/acid mixture was removed from the microwave, filtered through a 0.5 μm hydrophilic PTFE membrane, after which distilled water was used to wash the sample until the filtrate reached neutral pH. The filtrate (i.e., the wet CNT products) was then dried in air at room temperature, obtaining the purified CNT products. This method was reported in our earlier study.[17]

The as-synthesized bed materials and purified CNT products were examined using thermogravimetric analysis (TA SDT Q600), Raman spectroscopy (Renishaw Raman using an Ar^+ ion laser at 514.5 nm wavelength), Fourier transform infrared spectroscopy (Bruker IFS66v FTIR spectrometer), and Transmission electron microscopy (Philips CM120 operated at 120 kV).

Results and Discussion

Thermogravimetric analysis (TGA) was used to quantitatively identify the efficiency of purification process. Figure 1 shows the weight loss and differential weight loss profiles for as-synthesized bed material and purified sample treated in H_2SO_4 at 230°C for 30 min. The total weight loss for the as-synthesized bed material was 23.2 wt %, in which only one weight loss region between 500°C and 700°C was observed in the corresponding differential profile. This region most likely corresponds to the oxidation of MWNTs.[13,27] However, the flat profiles from 50°C to 500°C and from 700°C to 1000°C show that the sample contains very little material that volatilizes in these temperature ranges. The residue obtained from the TGA experiment was a mixture of white and brown powders, most likely alumina and iron oxides, respectively. It can be inferred from the TGA results that the majority of the sample are metal catalysts and alumina supports.

The total weight loss for the purified sample treated in H_2SO_4 at 230°C for 30 min was 98.1 wt %, indicating that the quantity of CNTs increased by 74.9 wt % following puri-

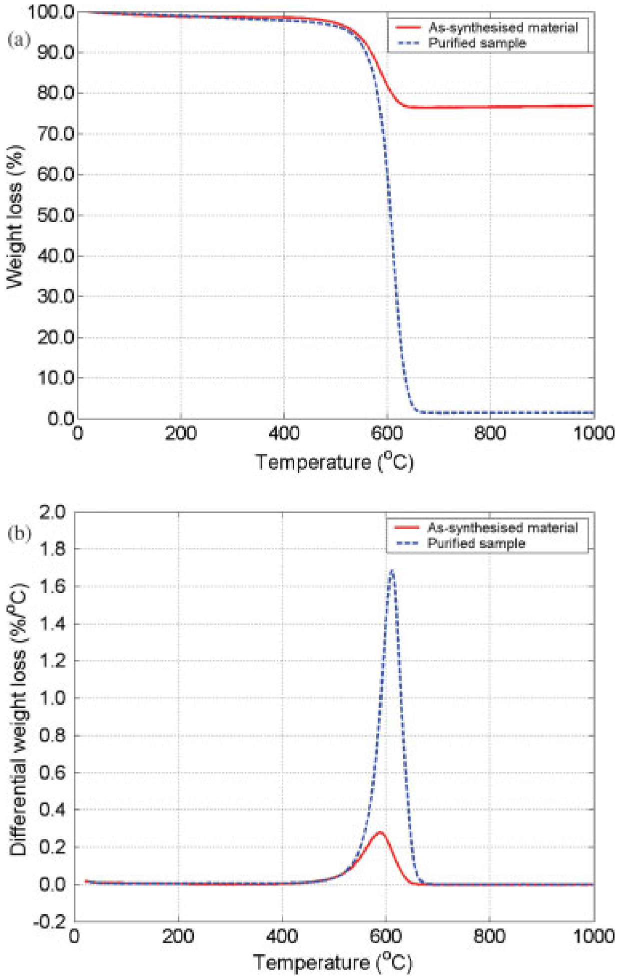

Figure 1. Thermogravimetric analysis (TGA) of as-synthesized bed material and purified sample treated in sulfuric acid at 230°C for 30 min, (a) weight loss profiles and (b) differential weight loss profiles.

The samples were heated in air between 25 and 1000°C at a ramp rate of 5°C/min. The air flow rate was 100 ml/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

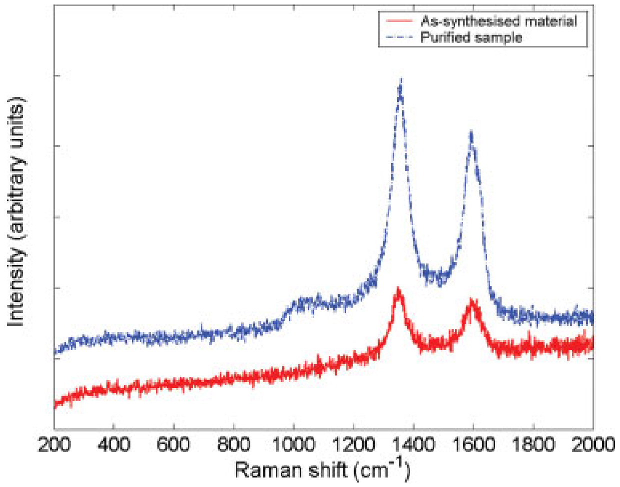

Figure 2. Raman spectra of as-synthesized bed material and purified sample treated in sulfuric acid at 230°C for 30 min.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fication. The differential weight loss profile for the purified sample shows the same weight loss region as that for as-synthesized bed material, suggesting that MWNTs remain intact during purification. To our knowledge, a CNT purity of 98.1 wt % purified from 23.2 wt % for the as-synthesized material within 30 min is the highest purification efficiency reported in the literature for catalyst-supported CNT products.

Raman spectroscopy was used to characterize the crystallinity of the CNT products. Figure 2 shows the Raman spectra of as-synthesized bed material and purified sample treated in H_2SO_4 at 230°C for 30 min. Two peaks are clearly visible in the spectra of both samples: (i) disordered carbon band (D-band) at approximately 1350 cm^{-1} and (ii) graphitized band (G-band) at approximately 1590 cm^{-1}. The D-band typically corresponds to defects in the walls of the CNTs, whereas the G-band is a characteristic of CNTs (a form of sp^2-bonded crystalline carbon).[20,28–30] The D-band and G-band peaks observed in the spectra of both samples suggest the presence of CNTs with wall defects. Furthermore, it is calculated that the ratio of D-band to G-band intensity (I_D/I_G) for as-synthesized bed material and purified sample are 1.3 and 1.6, respectively. Little difference in I_D/I_G suggests that the CNTs remain intact in the microwave-assisted purification, confirming the TGA results. However, it can be observed that the I_D/I_G ratio for the purified sample is slightly higher than that for the as-synthesized bed material, indicating that the purification process slightly increases the number and/or size of the wall defects in the CNTs.

It has been reported that acid treatment attaches acidic groups to the surface of CNTs during purification.[31,32] To investigate this, FTIR spectroscopy was used to examine whether acidic group attachment occurs during microwave-assisted acid digestion. Figure 3 shows the FTIR spectra of the as-synthesized bed material and the purified sample treated in H_2SO_4 at 230°C for 30 min. Little difference in the spectra between as-synthesized bed material and purified sample is observed, indicating that few acidic groups were attached during the digestion. A review of the literature shows that the commonly attached functional groups by H_2SO_4 treatment are carboxylic groups (—COOH) which causes —COO$^-$ and —C=O stretching vibrations at 1585 cm^{-1} and 1725 cm^{-1}, respectively, in the FTIR spectra.[31,32] However, no obvious peaks are observed at these wavelengths in the spectrum of purified sample, confirming that the microwave-assisted purification process causes no functional group attachment to CNTs.

Figure 4 shows the TEM images of as-synthesized bed material and purified sample treated in H_2SO_4 at 230°C for 30 min. CNTs interspersed with some solid particles are clearly visible in the TEM image of as-synthesized bed material (Figure 4a). These particles are most likely Fe catalysts, activating the growth of CNTs during the CVD process. It can be also observed that the CNT tips are covered with the metal catalysts. However, the quantity of Fe catalysts is substantially decreased in the purified sample treated with H_2SO_4 at 230°C for 30 min (Figure 4b). In particular, the CNTs are open-ended after purification, showing that the purification process is able to remove the metal catalysts from the CNT tips.

Conclusions

Microwave-assisted acid digestion in H_2SO_4 at 230°C for 30 min was used to purify alumina-supported CNT products synthesized by fluidized-bed CVD. The conclusions of the study are as follows:

Purification in H_2SO_4 at 230°C for 30 min in a microwave is effective at removing alumina supports and metal catalysts from CNTs synthesized by fluidized-bed CVD. CNT purity is increased from 23.2 wt % in the as-synthesized bed material to 98.1 wt % in the purified sample.

TGA, Raman, FTIR, and TEM results show that CNTs remain intact during the microwave-assisted acid digestion. Furthermore, FTIR spectra indicate that no acidic group

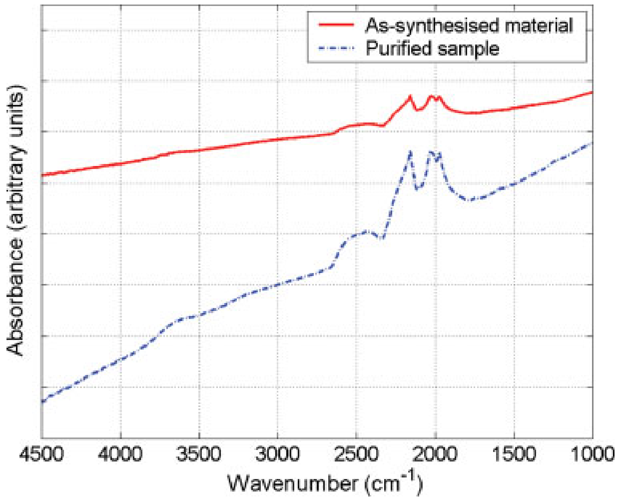

Figure 3. FTIR spectra of as-synthesized bed material and purified sample treated in sulfuric acid at 230°C for 30 min.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

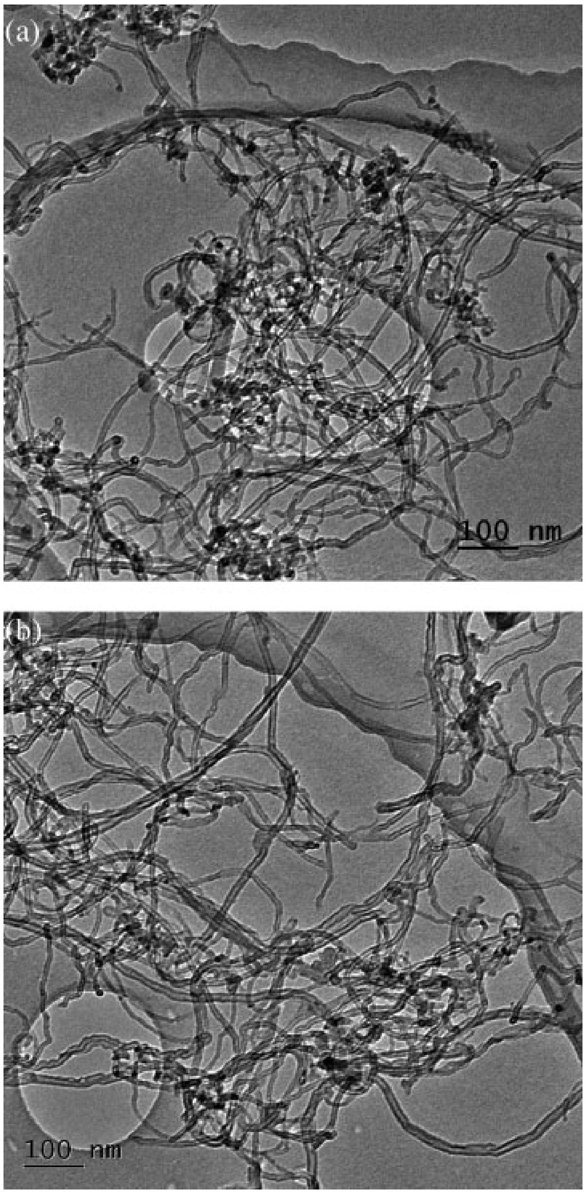

Figure 4. TEM images of (a) as-synthesized bed material and (b) purified sample treated in sulfuric acid at 230°C for 30 min.

attachment to CNTs occurs during purification. However, it can be observed from Raman spectra that the purification process slightly increases the wall defects of the CNTs. In addition, TEM results show that the purification process is able to remove the metal catalysts from the CNT tips.

Microwave-assisted acid digestion is able to achieve a high purity for the fluidized-bed products from comparatively low quality feedstocks in less than 30 min.

Acknowledgments

JL, OD, KM, and CS are grateful to the University of Sydney for Postgraduate Research support. The authors are grateful to E. Carter in School of Chemistry for assistance with the Raman and FTIR spectrometers, and A. Lukman and J. Shi in the School of Chemical and Biomolecular Engineering for assistance with the operation of the microwave digester.

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Manuscript received Apr. 16, 2008, and revision received July 10, 2008.