**From Academic Soot Research to Commercial Synthesis of Single-walled Carbon Nanotubes**

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Single-walled carbon nanotubes (SWCNT) are expected to be used in an increasing number of industrial products and to help meet societal needs. Their potential applications include selective gas sensors pertinent for counter-terrorism [1-3], the reinforcement of a new generation of high-strength, high-stiffness polymers allowing for new concepts in the aerospace industry [4-6], drug delivery [7-8] and electronics [9-12]. While first products are in the process to reach market maturity, large-scale production could be limited by increasing concerns over quality of currently available SWCNT [13]. Expansion of the commercial use of these products requires cost-efficient, reliable, reproducible and environmentally friendly production technology for SWCNT. Combustion synthesis is a promising route to fulfill these needs. The exothermic character of the process and easy control of all operating parameters such as fuel-to-oxygen ratio, catalyst concentration and fresh gas velocity contribute to its scalability.

## *Academic Research: A Base for Commercial Success*

The ongoing work at Nano-C, a technology company based in Westwood, MA, on cost-efficient synthesis of high quality single-walled carbon nanotubes, was made possible by a long-term academic research effort. Fuel-rich combustion of hydrocarbons has been studied with an increasing range of interest for several decades [14,15] by many investigators including the authors of the present study. Much of the work was motivated by health concerns associated with the release of species such as polycyclic aromatic hydrocarbons (PAH) and soot particles from combustion processes in transportation, incineration or power generation. Well-defined laboratory systems such as well-mixed or plug-flow reactors have been studied. Chemical processes involved in the practical combustion of hydrocarbons, including the formation and depletion of PAH and soot, have been assessed by a large range of experimental techniques such as on-line mass spectrometry, optical methods and probe sampling followed by chemical or optical analysis [14,15]. The internal structure of growing soot particles has been investigated in some detail using transmission electron microscopy (TEM) [16]. More recently, increasingly complex kinetic models targeting a quantitative description of combustion processes including PAH and soot formation have been developed and demonstrate encouraging predictive capabilities [17,18].

Combustion research at MIT began to focus increasingly on the synthesis of carbonaceous materials following the identification of fullerene ions in flames by means of on-line mass spectrometry [19] and the macroscopic synthesis of closed-shell fullerenes in electric arc systems [20]. Premixed low-pressure combustion of aromatic hydrocarbons was identified as powerful tool for the synthesis of fullerenes [21-23] and carbon shells including carbon nanotubes were observed in condensed materials [24-25]. Higher concentrations of larger fullerenes up to $C_{116}$ have been observed in combustion synthesis than with other methods [26]. High-pressure liquid chromatography (HPLC) was used for the unambiguous detection of fullerenes accessible by solvent extraction [26,27] while TEM was used for the detailed analysis of condensed materials [16,24,25] and allowed also for the visualization of individual fullerenes [28].

Selective synthesis of SWCNT in premixed low-pressure hydrocarbon flames has been achieved by addition of a catalyst precursor with the fresh gas mixture [29-32]. Different from the identification of some carbon nanotube structures under sooting conditions in earlier studies [24,25,33], large abundances of SWCNT contaminated with only small quantities of other carbonaceous materials have been observed [29-32]. Further development of this technology including the demonstration of its scalability is focus of the study described here.

### *The Founding of Nano-C*

Nano-C was founded in 2001 by Prof. Jack B. Howard, responsible for the corresponding research activities at MIT, motivated by the performance and scalability of the combustion synthesis of fullerenic materials and their commercial potential. Nano-C holds patents for the pertinent technology developed at MIT [34-37] and applied for world-wide patent protection of significantly improved second-generation fullerene combustion synthesis allowing for further, approximately 10-fold, increase in cost efficiency [38]. Nano-C has contributed significantly to the emergence of an industrial fullerene market. Nano-C has synthesized and commercialized high-purity fullerene derivatives such as phenyl-$C_{61}$-butyric-acid-methyl-ester (PCBM), currently used in conducting polymers such as organic solar cells. A license from Nano-C to a fullerene-producing subsidiary of a group of major Japanese corporations for the non-exclusive use of the combustion method in the form in which it was initially developed at MIT is contributing to a fullerene market in Asia [39]. Current activities at Nano-C are focused on ***a)*** Technology for the large-scale production of fullerenes and fullerene derivatives and ***b)*** Synthesis and characterization of SWCNT. Nano-C's combustion technology with the control of operating conditions allows targeted synthesis of spheroidal molecules (fullerenes, e.g., $C_{60}$, $C_{70}$, …, $C_{84}$, …), nanostructured particles (fullerene black) and SWCNT.

### *Synthesis of SWCNT*

Combustion synthesis of SWCNT was initially not part of Nano-C's activities but was developed at MIT after the founding of Nano-C in the context of the Ph.D. thesis of M. J. Height [29-32,37]. Initial funding of the company from private investors and early income from licensing were used for the improvement of combustion synthesis of fullerenes. Later, NSF SBIR support was obtained to enable activities in the field of flame synthesis of SWCNT. Successful performance and completion of Phase I generated considerable interest of private investors which, combined with the ongoing NSF Phase II project, has allowed synthesis of SWCNT to become a major thrust of Nano-C's current activities.

### *Nano-C's Benefits in Interacting with MIT*

Success of the work is significantly facilitated by previously established collaborative research activities between the researchers involved at Nano-C and MIT. Nano-C has been largely benefited from expertise and equipment available at MIT, particularly in the Department and Center Materials Science and Engineering. Raman spectroscopy has been a major tool for the identification of SWCNT and the determination of the diameter distribution of analyzed samples whereas high resolution electron microscopy (HRTEM) has allowed for the more detailed investigation of structural features. Visualization of larger sample areas has been achieved by means of scanning electron microscopy (SEM). Thermogravimetric analysis (TGA) has been conducted for a semi-quantitative assessment of impurities, particularly metal or metal oxide and amorphous carbon. During the Phase I of the SBIR project, Prof. Vander Sande acted as consultant, conducted the electron microscopic work and facilitated access to other instrumentation such as Raman spectroscopy at MIT.

In order to handle the increased volume and depth of the work, in the Phase II of this SBIR project materials characterization was subcontracted to Prof. Vander Sande's laboratory at MIT. This arrangement, instead of the previous consulting agreement, allows for the use of additional human resources such as a postdoctoral researcher and undergraduate as well as visiting students, and eases sample characterization with additional techniques. For instance, scanning transmission electron microscopy (STEM) will be used on samples of particular interest in order to establish structural and compositional maps of specimens. Insight into the formation mechanism of SWCNT will be gained in addition to information about the most efficient purification strategies. Other, complementary, techniques such as Atomic Force Microscopy (AFM), will be explored for the visualization and further characterization of SWCNT.

### *MIT's Benefits in Interacting with Nano-C*

SBIR funding subcontracted to MIT allows participation of an academic laboratory in research at the forefront of technology development in industry. Involvement of undergraduate, graduate and postdoctoral researchers contributes to an efficient training of workforce by providing an industry-relevant experience. A project duration of at least two and up to four years (including Phase IIB options) is sufficiently long to conduct research meeting highest academic standards while satisfying all expectations of the industrial partner. In addition to the joint work on characterization of SWCNT, the SBIR activities at Nano-C have facilitated two projects in the Department of Chemical Engineering at MIT. A postdoctoral researcher (John Wen) has received a Canadian NSERC PDF fellowship for the development of a kinetic model describing catalytic formation of carbon nanotubes in flames. His model will be validated by means of data generated at Nano-C. A student (Joanna Yu), in the PhD in Chemical Engineering Practice program, organized in collaboration with the Sloan School of Management at MIT, has investigated in her "Integrative Perspective Paper" correlations between Nano-C's technological innovations and the evolution of the SWCNT market. This analysis has been highly valuable for the further refinement of Nano-C's business strategy.

### *The Current Status of the Work*

Significant progress has been made in the optimization of nanotube synthesis in premixed flames. Consistent with its low sooting tendancy [14], methane has been found to be the most suitable of the fuels used to date to achieve maximized yields of SWCNT with little or no contamination with other carbonaceous materials. Since methane is the main (>95%) component of natural gas [40] and the other hydrocarbon components would be expected to be useful in SWCNT synthesis based on experiments with other hydrocarbons [29-31,41], use of natural gas is envisioned for future scale-up and is expected to be straight forward.

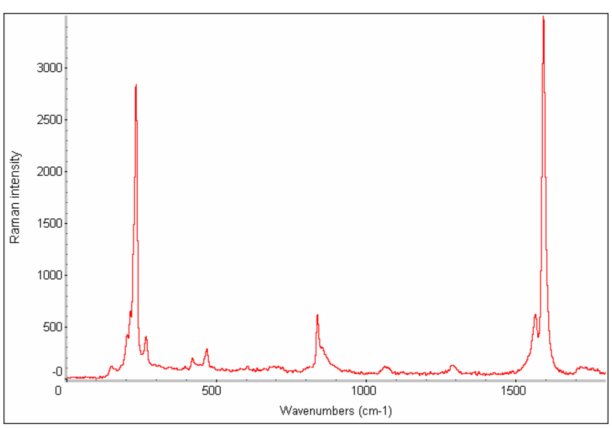


**Fig. 1** Raman spectrum of as-produced combustion-generated material. 785 nm.

Operation at pressures significantly higher than previously used 50 torr [29-31], has been found to be suitable for the synthesis of reproducible batches of high-quality SWCNT and allows for increased throughputs with an unchanged burner configuration. Nanotube material was characterized by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The Raman spectrum of as-produced combustion-generated material is shown in Fig. 1. Details on the characterization of SWCNT by means of Raman spectroscopy are reported in [42] and references therein. While the G-band occurring in the 1500-1605 $cm^{-1}$ range corresponds to tangential vibrations and allows assessing the abundance of conducting nanotubes vs. that of semi-conducting SWCNT, the radial breathing mode (RBM) reflects the diameter of the detected SWCNT. Combustion-generated material (Fig. 1) shows a narrow diameter distribution, a wave number of 220 $cm^{-1}$ corresponds to a tube diameter of approximately 1.1 nm. The weakness of the peak near 1350 $cm^{-1}$ (D-band) indicates an only low level of impurities or other symmetry-breaking defects.

Scanning electron microscopy (SEM) has been conducted using a JEOL 6320 instrument. Figures 2a and b show two different locations of a randomly selected sample of as-produced material.

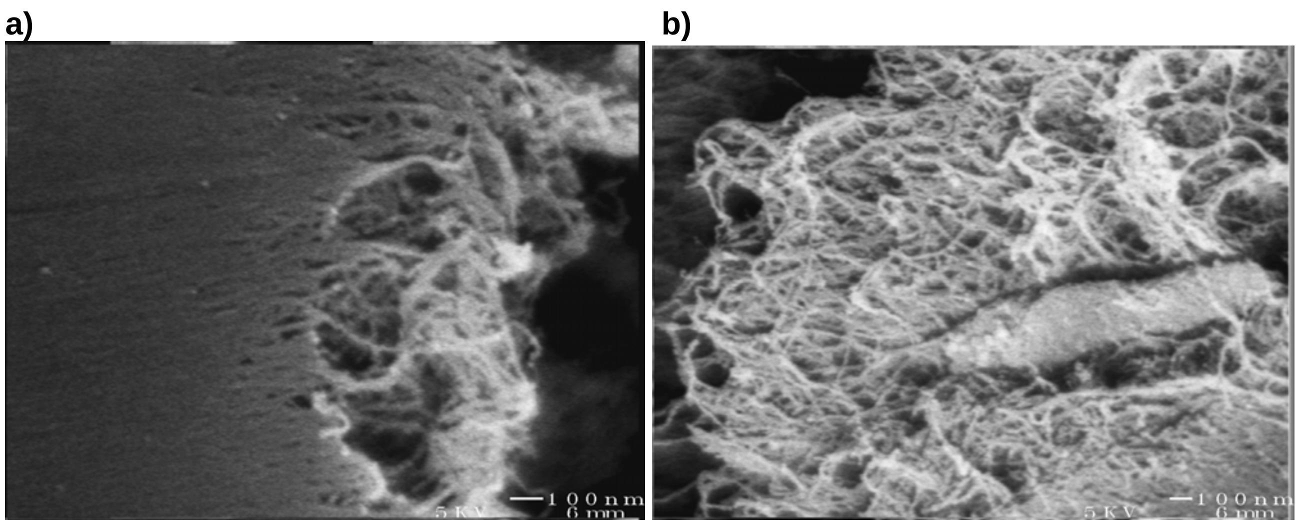


**Fig. 2** Scanning electron microscopy (SEM) of as-produced material.

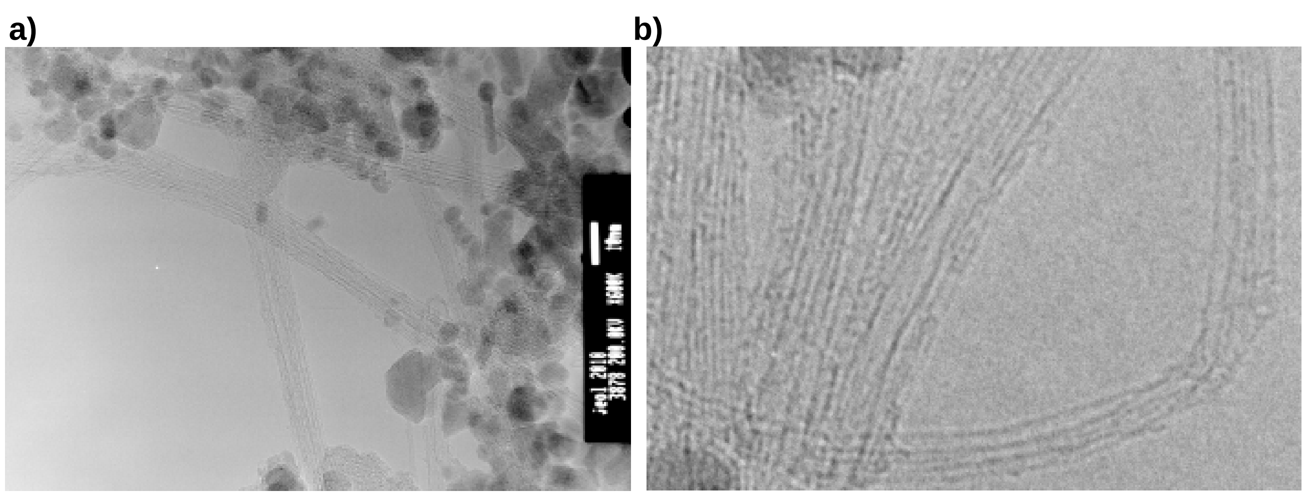


**Fig. 3** Transmission electron microscopy (TEM) of as-produced material.

As confirmed by transmission electron microscopy (TEM), the observed strands correspond to rafts of individual SWCNT (Fig. 3). Different degrees of ordering, partially aligned in Fig. 2a and rather randomly oriented in Fig. 2b can be observed. Bright spots, observed in both images of Fig. 2, are thought to be remaining catalyst particles or their reaction products. Transmission electron microscopy (TEM) images of as-produced material, taken with a JEOL 2010 instrument, are given in Fig. 3 and b. Fig. 3 b represents a magnified partial view which shows unambiguously the presence of rafts of individual SWCNT.

Purification of as-produced nanotube material has been conducted by acid treatment allowing for removal of remaining catalyst particles and their reaction products [43-45]. In the present work, reflux with 6 N HCl as well as 3 N $HNO_3$ has been investigated. SEM images of material after 24 h treatment with 6 N HCl is shown in Fig. 4. Sheets of entangled rafts of

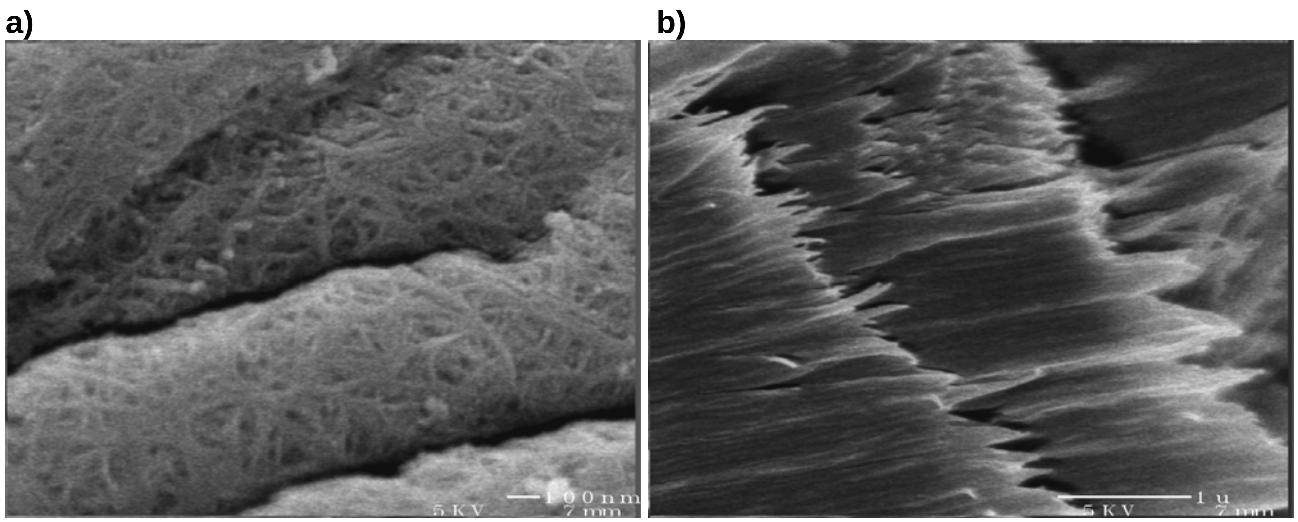


**Fig. 4** Scanning electron microscopy (SEM) of material after 24 h reflux with 6 N HCl.

carbon nanotubes (Fig. 4a) as well as regions of increased alignment can be observed. While some metal particles normally remain, the use of HCl, a non-oxidative acid, allows minimizing the effect of purification on the characteristics of individual nanotubes.

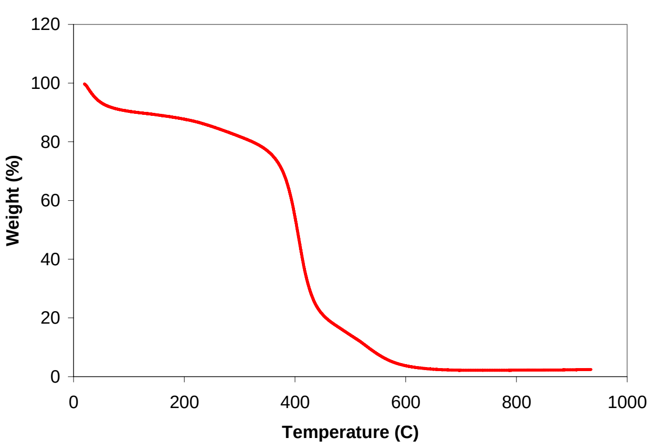


**Fig. 5** Thermogravimetric analysis (TGA) of combustion-generated SWCNT material after 24 h reflux in 3 N $HNO_3$.

Reflux of as-produced materials with 3 N $HNO_3$ during 24 h let to nearly quantitative removal of metal particles. After filtration and drying, a free-standing mat of tangled SWCNT rafts (“bucky paper” [45]) was obtained. Thermogravimetric analysis (TGA) under air between room temperature and approximately 900 °C at 5 K/min showed a remaining mass of only ≈ 2%, (Fig. 5) which is thought to correspond to oxidized metal particles whereas carbonaceous material (mostly SWCNT) are converted to CO and $CO_2$.

### *Conclusions and Future Work*

Flame synthesis was found to be suitable for the reproducible synthesis of high-quality SWCNT. Experience gained previously with the similar fullerene-production process will allow scale-up of SWCNT production rates in answer to the expected increasing demand. Optimization of the combustion process will continue, e.g., a range of catalyst precursors will be investigated. Detailed characterization of SWCNT material will emphasize the assessment of sample homogeneity.


### *Acknowledgments*

This work has been supported by the National Science Foundation SBIR program under grants DMI-0419100 and DMI-0522093. Dr. P. Mendes Jardim and Mr. M. Frongillo are gratefully acknowledged for conducting electron microscopy and Mr. T. McClure for assistance with Raman spectroscopy. Dr. M. J. Height, formerly MIT and now at HeiQ Materials Ltd., Zürich (Switzerland) is thanked for many valuable discussions. We are grateful to the MIT Center for Materials Science and Engineering supported by the National Science Foundation under award #DMR-0213282.


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