

Final Report

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Project Title

Field-Flow Fractionation of Carbon Nanotubes and Related Materials

Principal Investigator/Project Director

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Award period with approved budget amount

U. S. Department of Energy EPSCoR Program, \$225,000, 8/15/00 - 8/14/04

Participating National Laboratory

N/A

Project goal and objective

The principal aim of this project was to investigate the chemistry and particle-size distribution of nanoparticles. A particular emphasis was to develop Field-Flow Fractionation (FFF) as a routine tool for the analysis of carbon nanotubes and related nanoparticles. We hoped to use FFF to monitor reactions of nanoparticles, much as a chemist uses gas or liquid chromatography to monitor reactions of soluble species.

6. Description of accomplishments and their significance to the field.

Abstract

During the grant period, we carried out FFF studies of carbonaceous soot, single-walled and multi-walled carbon nanotubes, carbon nano-onions and polyoxometallates. FFF alone does not provide enough information to fully characterize samples, so our suite of characterization techniques grew to include light scattering (especially Photon Correlation Spectroscopy), scanning and transmission electron microscopy, thermogravimetric analysis and spectroscopic methods. We developed convenient techniques to deposit and examine minute FFF fractions by electron microscopy.

In collaboration with Arthur Cammers (University of Kentucky), we used Flow Field-Flow Fractionation (Fl-FFF) to monitor the solution-phase growth of keplerates, a class of polyoxometallate (POM) nanoparticles. We monitored the evolution of Mo-POM nanostructures over the course of weeks by using flow field-flow fractionation and corroborated the nanoparticle structures by using transmission electron microscopy (TEM). Total molybdenum in the solution and precipitate phases was monitored by using inductively coupled plasma analyses, and total Mo-POM concentration by following the UV-visible spectra of the solution phase. We observe crystallization-driven formation of $\{\text{Mo}_{132}\}$ keplerate and solution phase-driven evolution of structurally related nanoscopic species (3-60 nm).

FFF analyses of other classes of materials were less successful. Attempts to analyze platelets of layered materials, including exfoliated graphite (graphene) and TaS₂ and MoS₂, were disappointing. We were not able to optimize flow conditions for the layered materials. The metal sulfides react with the aqueous carrier liquid and settle out of suspension quickly because of their high density.

Methodology

1. Field-Flow Fractionation

Field-flow fractionation (FFF) is a chromatography-like separation and sizing technique based on elution through a thin, empty channel. The main difference between FFF and chromatography is that FFF separation is (ideally) induced only by physical interactions with an external field rather than physicochemical interactions with a stationary phase. FFF is based on the application of a field perpendicular to the fluid flow down the axis of a thin channel (100 - 500 μm). This externally applied field drives unlike particles to different average positions across the thin channel, where they are caught up at different flow velocities and are thus eluted at different times. The most common fields are cross-flow of a carrier liquid and centrifugation, giving rise to flow FFF (FIFFF) and sedimentation FFF (SedFFF) subtechniques.

For a small particle, typically less than 1 μm , elution time depends on the diffusivity of a particle and its interaction with the field. Separations in this mode, termed normal mode, result in smaller particles eluting ahead of larger particles. Larger particles tend to stay near the channel wall and move through the channel with lower flow velocities. An alternative mode, termed steric or hyperlayer mode, is designed for sizing particles larger than 1 μm . A reversal of the elution order is achieved because the larger particles necessarily protrude into regions of higher flow velocity. Utilizing these two modes, it is possible to probe a mass range spanning 15 orders of magnitude, from molecules of 1000 Dalton molecular weight up to particles 100 μm in diameter. FFF is uniquely capable of separating materials over such wide size range. At the time we undertook this project, FFF had not been applied to carbon nanoparticles..

2. Other methods of analysis

It became clear that FFF alone does not provide enough information to fully characterize samples, so our suite of characterization techniques grew to include light scattering (especially Photon Correlation Spectroscopy), scanning and transmission electron microscopy, thermogravimetric analysis and spectroscopic methods. We developed convenient techniques to deposit very small samples, including FFF fractions, for examination by electron microscopy.

Results

1. Soot particles

A flow-field-flow fractionation (FIFFF) study of carbonaceous soot formed in an ethylene co-flow laminar diffusion flame, supplied by Prof. Kozo Saito's group at the

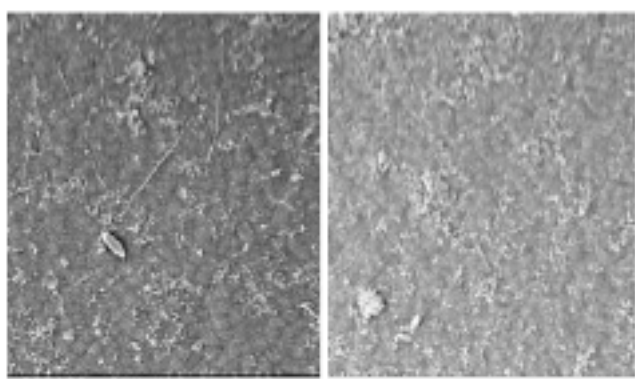
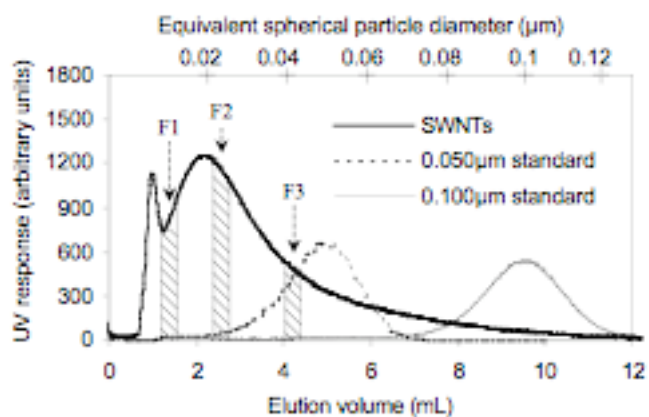
University of Kentucky, revealed changes in the primary soot particle size and extent of aggregation depending on the sampling height. Soot collected at 8.5 cm and 11.5 cm show maximum primary particle diameters of 40 nm and 32 nm, respectively, by SEM. These primary particles are linked into a distribution of aggregates with mean diameters of 142.5 nm and 97.1 nm, respectively. Photon Correlation Spectroscopy measurements complement the FIFFF measurements, showing mean particle diameters of about 178 nm and 155 nm, respectively, for the two samples. We later examined even smaller soot particles from lower flame heights. An article on this work was submitted to *Combustion Science and Technology*, but unfortunately was not accepted for publication and no students are available to clean up the details.

2. Carbon nanotubes

We separated both single-walled and multi-walled carbon nanotubes by using FIFFF. {Chen, 2005 #701} Initial fractionation of treated or shortened single-walled nanotubes led to elution of a broad nanotube peak under a variety of conditions, including FL-70, SDS and Triton X-100 carrier solutions; regenerated cellulose and polycarbonate membranes; various channel and cross flows. Nanotube recovery (total nanotubes that eluted from the channel, measured spectrophotometrically) ranged from 22% to 98%. SEM examination of fractions collected, lyophilized, re-suspended in a minimum of water and electro-deposited on copper substrates indicated that that nanotubes that eluted early were generally smaller and thinner than nanotubes eluted later. That is, single-walled nanotubes elute in normal rather than steric mode. Recovery is higher and separation is better with slower channel and flow rates.

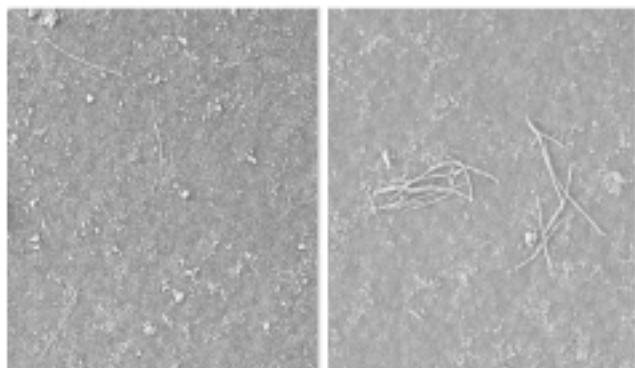
Electro-deposition on copper substrates produced samples that were so heavily contaminated with surfactant and other impurities that it was not possible to discern features of the nanotubes themselves. We devised a simple filtration method to prepare FIFFF fractions for SEM. A small volume (~0.3 mL) of a FFF fraction was suction-filtered through a ~2-mm square of an alumina filter membrane (Whatman Anodisc 13, pore size 0.020 μm) was attached to the tape, followed by washing with a few drops of Milli-Q water to remove the surfactant. After filtration, the membrane was dried at room temperature, cut from the tape, and placed onto the copper plate of the SEM specimen holder. The sample was finally coated with Au prior to SEM measurement.

Oxidatively shortened single-walled carbon nanotubes were characterized by using FIFFF in normal mode. Narrow size fractions were collected from FIFFF separations. The carbon nanotubes in each fraction were further characterized by using scanning and transmission electron microscopy. FIFFF separates carbon nanotubes principally on the basis of length, leading to fractions with relatively uniform lengths.



Before FFF

Fraction 1



Fraction 2

Fraction 3

3 μm

Figure 3. (Top) FIFFF fractograms of SWNTs and standards. (Bottom) SEM images of SWNTs before and after FIFFF separation. The SEM images were measured at a magnification of 10 K.

Multi-walled carbon nanotubes proved more of a challenge. As-supplied MWNT grown by vapor-phase decomposition of toluene on an iron catalyst at the Center for Applied Energy Research suspend very poorly in water. However, vigorous oxidation with $\text{H}_2\text{SO}_4/\text{KMnO}_4$ leads to shortened MWNTs that can be suspended in SDS and analyzed by FIFFF. These oxidized multi-walled carbon nanotubes were characterized by using FIFFF in steric mode (i.e., long tubes elute before short tubes). Narrow size fractions were collected from FIFFF separations. The carbon nanotubes in each fraction were further characterized by using scanning and transmission electron microscopy. FIFFF separates carbon nanotubes principally on the basis of length, leading to fractions with relatively uniform lengths.

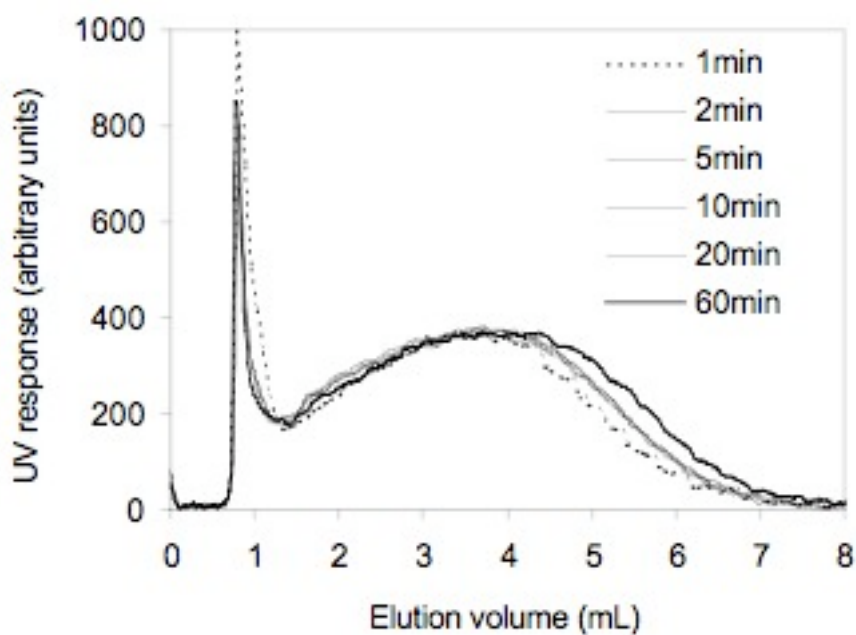
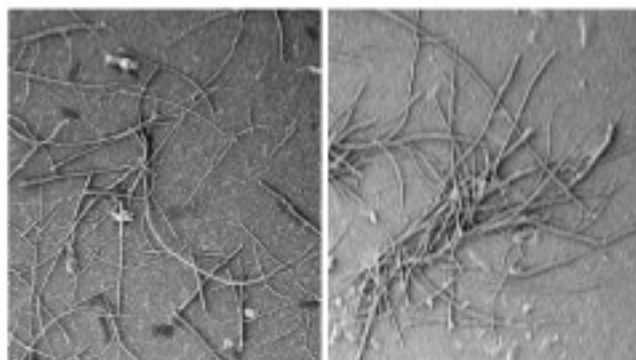
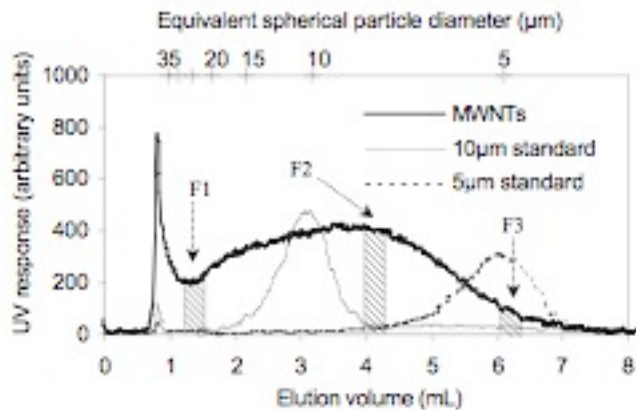
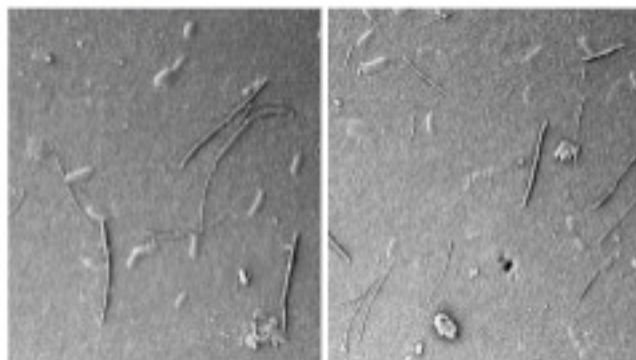


Figure 1. FIFFF fractograms of MWNTs with various sonication times.



Before FFF

Fraction 1



Fraction 2

Fraction 3

10 μm



Figure 5. (Top) FIFFF fractograms of MWNTs and standards. (Bottom) SEM images of MWNTs before and after FIFFF separation. The SEM images were measured at a magnification of 3 K.

In collaboration with scientists at Los Alamos National Laboratory we analyzed solubilized carbon nanotubes by using capillary electrophoresis (CE). Raman spectra confirmed that carbon nanotubes eluted in several fractions. AFM analysis showed

carbon nanotubes in several fractions, but microscopy was complicated by the presence of high salt and surfactant concentrations.¹

3. Carbon Nano-Onions

Carbon nano-onions resemble nearly spherical fullerenes nested like Russian dolls. These materials are under-investigated compared to fullerenes and nanotubes. We investigated nano-onions prepared by striking an arc between carbon electrodes under water. Scanning and transmission electron microscopy, FIFFF and photon correlation spectroscopy indicate that the primary nano-onion particles have a diameter distribution in the range of tens of nanometers, peaking at about 30 nm. The primary particles are bound into grape-like clusters with diameters up to about 300 nm. The clusters do not fall apart upon ultrasonication, but chemical treatment with oxidants such as sodium hypochlorite breaks them up into individual nano-onions. Hydrogen peroxide appears to remove amorphous carbon from the nano-onion surfaces with a slight decrease in their size, as shown by transmission electron microscopy. We began to study the Raman and ¹³C NMR spectra of the onions. We found that, like carbon nanotubes, the surfaces of nano-onions are derivatized by electrophilic reagents such as formaldehyde/hydrobromic acid.⁴

4. Biological effects

The increasing use of nanotechnology in consumer products and medical applications underlies the importance of understanding its potential toxic effects to people and the environment. Although both fullerene and carbon nanotubes had been demonstrated to accumulate to cytotoxic levels within organs of various animal models and cell types and carbon nanomaterials had been exploited for cancer therapies, the molecular and cellular mechanisms for cytotoxicity of this class of nanomaterials had not been investigated at the time of our investigation. To address this question, we supplied Fanqing Frank Chen of Lawrence Berkeley National Laboratory with carbon nano-onions and MWCNTs for biological testing. Exposing cells to carbon nano-onions and MWCNTs at cytotoxic doses induces cell cycle arrest and increases apoptosis/necrosis. Multiple cellular pathways are perturbed after exposure to these nanomaterials at these doses, with material-specific toxigenomic profiles observed. More adverse effects are observed upon exposure to MWCNTs as compared to MWCNOs.{Ding, 2005 #699}

5. Lamellar Materials

Attempts to size-sort lamellar materials, in particular exfoliated metal disulfides and graphite (i.e., graphene), by FIFFF were largely unsuccessful. TaS₂ and MoS₂ react with n-butyllithium to give the intercalation compounds Li_xMS₂. Hydrolysis produces nano-sized plates of exfoliated MS₂. Unfortunately, the exfoliated material does not form stable suspensions in aqueous surfactants. The particles hydrolyze too quickly, and also tend to settle out of suspension because of their high density. We also produced graphite nanoparticles (graphene) by using KC₈·(NH₃)_x exfoliation, but were unable to find suitable conditions for FIFFF analysis.

6. Polyoxometallates

Further afield, we found that FFF provides a way to monitor nanoparticle growth in suspensions of polyoxomolybdates. In particular, the reduction of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ in $\text{NH}_4\text{CH}_3\text{CO}_2/\text{CH}_3\text{CO}_2\text{H}$ buffer produces nanoparticles of the keplerite polyoxomolybdate $\{\text{Mo}_{132}\}$ (i.e., $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{CO}_2)_{30}(\text{H}_2\text{O})_{72}] \cdot \text{ca.} \cdot 300\text{H}_2\text{O} \cdot \text{ca.} \cdot 10\text{CH}_3\text{CO}_2\text{NH}_4$). We were able to fully monitor the evolution of a $\{\text{Mo}_{132}\}$ suspension by using flow field-flow fractionation (FIFFF) to monitor the particle-size distribution *in situ*, atomic force and high-resolution transmission electron microscopy (AFM, SEM and HRTEM) to confirm particle sizes, inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the Mo content of the FIFFF-separated fractions, and UV/visible spectroscopy to confirm the identity of the species in suspension. We observe the formation of 3- to 75-nm polyoxomolybdate particles in suspension and the dynamic growth of $\{\text{Mo}_{132}\}$ crystals.⁵

7. A list of papers or patents (already published, in press, submitted) in which DOE support is acknowledged.

Publications (* = based in part on EPSCoR results)

1. *Stephen K. Doorn, Robert E. Fields, III, Hui Hu, Mark A. Hamon, Robert C. Haddon, John P. Selegue, and Vahid Majidi, "High resolution capillary electrophoresis of carbon nanotubes," *J. Am. Chem. Soc.* **124** (12), 3169-3174 (2002).
2. *David Bom, Rodney Andrews, David Jacques, John Anthony, Bailin Chen, Mark S. Meier, and John P. Selegue, "Thermogravimetric Analysis of the Oxidation of Multiwalled Carbon Nanotubes: Evidence for the Role of Defect Sites in Carbon Nanotube Chemistry," *Nano Letters* **2** (6), 615-619 (2002).
3. Bailin Chen and John P. Selegue, "Separation and Characterization of Single-Walled and Multiwalled Carbon Nanotubes by Using Flow Field-Flow Fractionation," *Anal. Chem.* **74** (18), 4774-4780 (2002).
4. Bailin Chen, John P. Selegue, Lavanya Wijeratne, David Bom, and Mark S. Meier, "Characterization of carbon nano-onions by using flow field-flow fractionation," *Proceedings of Carbon '02, An International Conference on Carbon* [ISBN 7-900362-03-7], 22.27.75 (2002).
5. Bailin Chen, Huijian Jiang, Yan Zhu, Arthur Cammers, and John P. Selegue, "Monitoring the Growth of Polyoxomolybdate Nanoparticles in Suspension by Flow Field-Flow Fractionation," *J. Am. Chem. Soc.* **127** (12), 4166-4167 (2005).
6. *John D. Craddock and John P. Selegue, "Boron-doped and oxide-coated carbon nano-onions," *Prepr. Symp. - Am. Chem. Soc., Div. Fuel Chem.* **53**, 489-490 (2008).
7. *Lianghao Ding, Jackie Stilwell, Tingting Zhang, Omeed Elboudwarej, Huijian Jiang, John P. Selegue, Patrick A. Cooke, Joe W. Gray, and Fanqing Frank Chen, "Molecular Characterization of the Cytotoxic Mechanism of Multiwall Carbon Nanotubes and Nano-Onions on Human Skin Fibroblast," *Nano Letters* **5** (12), 2448-2464 (2005).

M.S. thesis based in part on EPSCoR results

8. *Aaron S. Tomasek, "1. Field-Flow Fractionation Analysis of Fuel Soot and Carbon Nanotubes. 2. Reactions of Dibromomethano[60]fullerene," 1998-2000,

Ph.D. Dissertation based in part on EPSCoR results

9. Yan Zhu, Transmission Electron Microscopy And Flow Field-Flow Fractionation: Exploration Of The Nanoscopic Components In Partially Reduced Polyoxomolybdates By Kinetic Precipitation With De Novo Organic Molecules," Directed by Prof. Arthur Cammers

Presentations (* = based in part on EPSCoR results)

10. *J. P. Selegue, "From Carbon Ligands to Carbon Particles: Field-Flow Fractionation of Carbon Nanotubes and Soot," (Invited Lecture), July 16–20, 2000, US-German-French Workshop on Carbon-Rich Organometallic Compounds, Erlangen, Germany,
11. John P. Selegue, Bailin Chen, Lavanya Wijeratne, Mark S. Meier, Zhongwen Wang, Robert C. Haddon, Hui Hu, and Rodney Andrews, "Field-flow fractionation of single- and multi-walled carbon nanotubes," 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001, IEC-114 (2001).
12. *R. Andrews, J. E. Anthony, R. G. Bergosh, R. C. Haddon, H. Hu, C. Landis, M. S. Meier, F. McKenzie, G. J. Palmer, T. Rantell and J. P. Selegue "Modified Nanotubes in Composite Materials," August 26–30, 2001, 222nd American Chemical Society National Meeting, Chicago, IL.
13. *J. P. Selegue, J. E. Anthony, G. J. Palmer, R. Andrews, D. Jacques, and F. E. Huggins, "Mössbauer Analysis of the Iron Catalyst Residue in Multi-walled Carbon Nanotubes", in *Materials Research Society Fall Meeting* (Boston, MA, 2001), Poster W9.18.
14. J. P. Selegue, B. Chen, M. S. Meier, Z. Wang, R. Andrews, D. Jacques, R. C. Haddon, M. A. Hamon and H. Hu "Field-Flow Fractionation of Single-Walled and Multi-Walled Carbon Nanotubes," (Poster), November 27, 2001, Materials Research Society Fall Meeting, Boston, MA.
15. *R. Andrews, D. Jacques, J. E. Anthony, R. G. Bergosh, M. Ho, C. Landis, F. McKenzie, M. S. Meier, G. J. Palmer, J. P. Selegue, E. Grulke and M. Kannadaguli "Chemical Functionalization of Carbon Nanotubes," November 29, 2001, Materials Research Society Fall Meeting, Boston, MA.
16. B. Chen and J. P. Selegue, "Separation and Characterization of Carbon Nanotubes and 'Buckyonions' by Using Flow Field-Flow Fractionation," July 2–5, 2002, Tenth International Symposium on Field-Flow Fractionation, University of Amsterdam, Amsterdam, Netherlands.
17. John P. Selegue, Bailin Chen, and Lavanya Wijeratne, "Sizing and fractionation of carbon nano-onions by using flow field-flow fractionation," 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002, INOR-338 (2002).
18. *Stephen K. Doorn, Robert E. Fields, Hui Hu, Mark A. Hamon, Robert C. Haddon, John P. Selegue, Vahid Majidi, Michael O'Connell, Erik Haroz, Kevin D. Ausman, and Richard E. Smalley, "Geometry-based separations of carbon nanotubes using capillary electrophoresis," 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002, COLL-054 (2002).
19. J. P. Selegue, B. Chen and H. Jiang, "Field-Flow Fractionation of Carbon Nanotubes and Related Materials," (Poster), June 2–4, 2003, DoE EPSCoR Conference 2003, Albuquerque, NM.
20. B. Chen, J. P. Selegue, L. Wijeratne, D. Bom and M. S. Meier, "Characterization of Carbon Nano-Onions by Using Flow Field-Flow Fractionation," September 15–20, 2002, Carbon '02, An International Conference on Carbon, Beijing, China.

21. A. Cammers-Goodwin and J. P. Selegue, "Monitoring the Solution-Phase Growth of Polyoxomolybdates: a Combined Field-Flow Fractionation–Transmission Electron Microscopy Study," Y. Zhu, B. Chen, H. Jiang, October 7–10, 2003, 11th International Symposium on Field-Flow Fractionation, Cleveland, OH.
22. B. Chen, H. Jiang and J. P. Selegue, "Characterization of Raw, Cleaned and Functionalized Carbon Nano-Onions," October 7–10, 2003, 11th International Symposium on Field-Flow Fractionation, Cleveland, OH.
23. B. Chen, H. Jiang and J. P. Selegue, "Separation and Characterization of Carbon Nanotubes and Nano-Onions by Using Flow Field-Flow Fractionation," (Invited Contribution), October 20, 2003, FACSS 2003, Fort Lauderdale, FL.
24. John Selegue, Bailin Chen, Yan Zhu, Huijian Jiang, and Arthur Cammers-Goodwin, "Monitoring the solution-phase growth of polyoxomolybdates," 55th Southeast Regional Meeting of the American Chemical Society, Atlanta, GA, United States, November 16-19, 2003, 474 (2003).
25. A. Cammers, Y. Zhu, J. P. Selegue, B. Chen and H. Jiang "TEM and Kinetic Precipitation of Solution Phase Polyoxomolybdate: A Window to Solution Phase Nanostructure," (Poster), May 14–15, 2004, 2nd Annual Ohio Valley Organic Chemistry Symposium Student Union, Wright State University, Dayton, OH.
26. J. P. Selegue, A. Cammers, B. Chen, Y. Zhu, H. Jiang, "Monitoring the solution-phase growth of polyoxomolybdates" Pacifichem 2005 (poster, symposium on "Polyoxometalate Chemistry for Molecular Design and Nano-engineering"), December 19, 2005, Honolulu, HI.
27. *John D. Craddock, John P. Selegue, "Mechanochemical reactions of carbon nano-onions" (poster), 7th Annual Ohio Inorganic Weekend, November 17, 2006, Athens, OH.
28. *John P. Selegue, "Organometallic and Materials Chemistry" (poster), Graduate Student Recruiting Weekend, February 20, 2007, University of Kentucky, Lexington, KY.
29. *John P. Selegue, "Organometallic and Materials Chemistry" (poster), Thirty-Third Annual Naff Symposium on Chemistry and Molecular Biology, April 13, 2007, University of Kentucky, Lexington, KY
30. *John D. Craddock, John P. Selegue, "Boron-Doped and Metal Oxide-Coated Carbon Nano-Onions" (poster), 8th Annual Ohio Inorganic Weekend, November 9, 2007, Oxford, OH.
31. *John P. Selegue, Nathan Tice, Sean Parkin, Minh Truong, John Anthony, John D. Craddock, Mark Meier, Rodney Andrews, "Organometallic and Materials Chemistry" (poster), 8th Annual Ohio Inorganic Weekend, November 9, 2007, Oxford, OH.
32. *John P. Selegue and John D. Craddock, "Boron-doped and oxide-coated carbon nano-onions," Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008, FUEL-231 (2008).
33. *Rituraj Borgohain, John P. Selegue, " Functionalization and Characterization of Electric Arc-Prepared Carbon Nano-Onions," Kentucky Academy of Sciences, November 1, 2008, Lexington, KY (won second prize for graduate student presentation)

34. *Mahendra Sreeramoju, John P. Selegue, "Preparation, Functionalization and Characterization of Nanodiamond-Derived Multi-Layered Fullerenes (Carbon Nano-Onions)," Kentucky Academy of Sciences, Lexington, KY, November 1, 2008

8. A total list of people who worked on the project –number of graduate and undergraduate students, postdocs, visitors, technicians, etc, during the total funding period. Please indicate for each person whether they received full or partial support under this award. In case of partial support indicate percentage of support.

Postdocs

Bailin Chen: full support March 2001–May 2004

Huijian Jiang – full support June 2002–December 2003

David Bom: no DoE support

Graduate students

Lavanya Wijeratne: full support January–August 2002

Yan Zhu: supported by Arthur Cammers (collaborator)

John D. Craddock: no DoE support (arrived at end of project period)

Aaron S. Tomasek: no DoE support (left near beginning of project period)

Minh Truong: full support May–August 2003

Chad Snyder: full support May–August 2003

David Eaton: partial support (10% supplement to University fellowship), January–May 2001

9. An updated list of other support (current and pending, federal and non-federal.) For each, indicate the overlap, if any, and/or distinctiveness with the DOE-supported project. This could be brief – one or two sentences.

No current support

10. Cost status: Show approved budget for the full budget period and actual costs incurred. For cost- sharing, breakout by DOE share, recipient share and total costs. Financials Statements should be reported to DOE Chicago Operations as requested.

Submitted by University of Kentucky Research Foundation