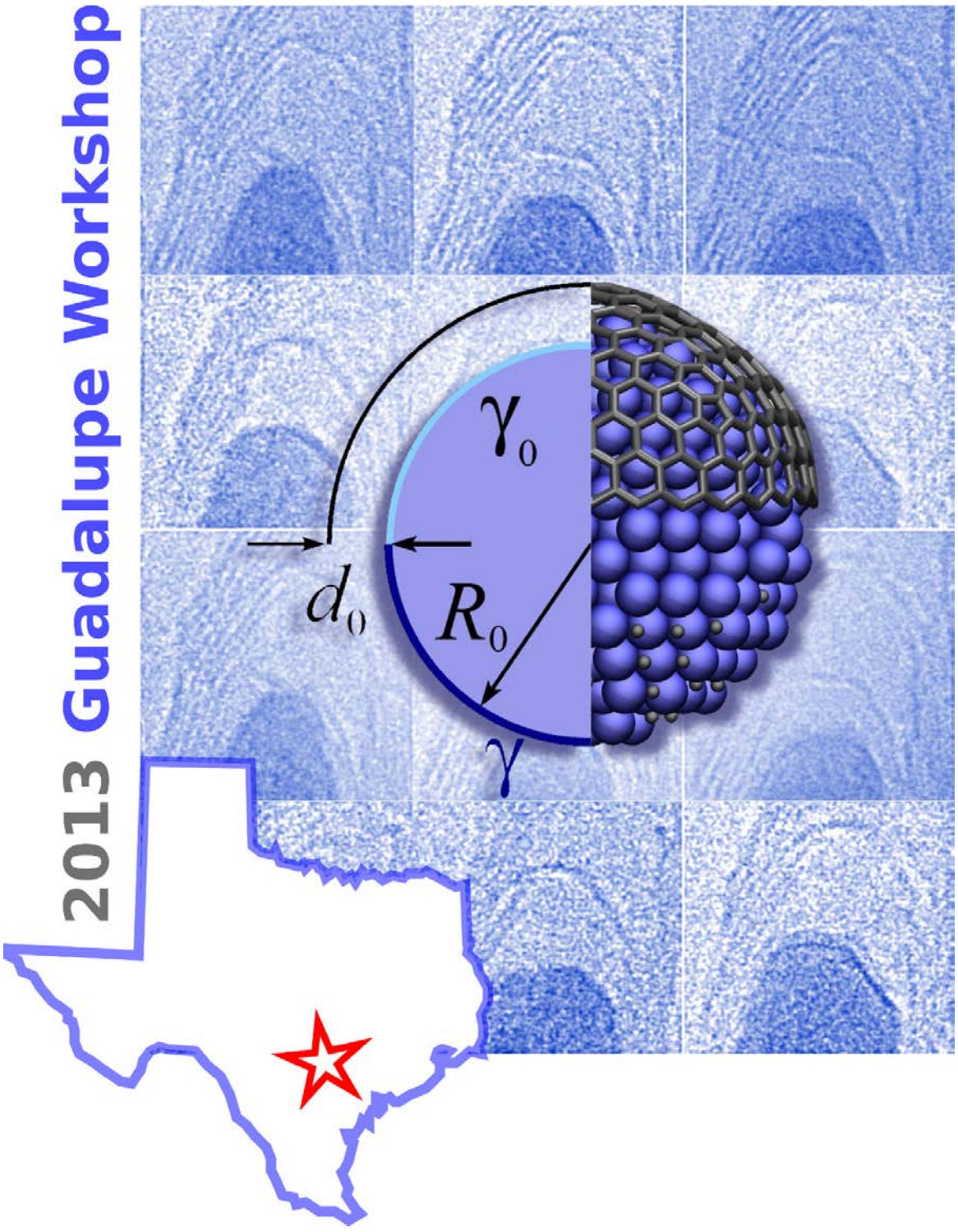

Report on the 6th Rice University, Air Force Research Laboratory, NASA, and Honda Research Institute Workshop on Nucleation and Growth of Single-wall Carbon Nanotubes
(Guadalupe Workshop VI)
April 12-16, 2013

Our Sponsors

Report on the 6th Rice University, Air Force Research Laboratory, NASA, and Honda Research Institute Workshop on Nucleation and Growth of Single-wall Carbon Nanotubes
(Guadalupe Workshop VI)
April 12-16, 2013

The Richard E. Smalley Institute for Nanoscale Science and Technology of Rice University through the Smalley-Curl nanoCarbon Center, the Air Force Research Laboratory (Materials and Manufacturing Directorate), NASA Johnson Space Center, and the Honda Corporation conducted the sixth highly successful workshop on growth mechanisms of single-wall carbon nanotubes (SWCNTs). International scientists and engineers, experts on various aspects of production and modeling of SWCNTs, met at the Flying L Ranch, near Bandera, Texas for three and one half days. Participants presented and discussed nucleation and growth techniques associated with arc and RF discharge vaporization, laser ablation, chemical vapor deposition (CVD), and surface growth techniques, continued growth and carpet growth, along with *in situ* measurements, and modeling. Insights were obtained from empirical and theoretical analyses given in twenty-seven presentations and twenty posters. The poster session included the opportunity of each presenter to give a 1.5-minute presentation as a preview of his/her poster.

The keynote talks that began the meeting focused on growth and characteristics of graphene. Dr. Phaedon Avouris, of IBM presented a keynote talk “Graphene: Applications in Electronics and Photonics,” and Professor Rod Ruoff, of the University of Texas at Austin presented a keynote talk on “Graphene-based and graphene-derived materials and a perspective on new carbon materials”.

Besides researchers, the workshop was attended by representatives of private companies involved in producing nanotubes. About 70 people attended the workshop. Attendees of the workshop may access all available presentations at the Workshop web site:
http://swcnt.nano.rice.edu/Default.aspx?id=2147484139
At this sixth workshop, there was increased interest in *in situ* measurements of SWCNT growth and catalyst behavior, computational modeling, and CVD growth of SWCNTs, particularly vertically aligned (carpet) growth. In addition a number of presentations included the possibility of growing carbon nanotubes on graphene surfaces. As in the previous workshops, each session had one or two rapporteurs who served to summarize presentations of their session. We report the significant results of the workshop in a summary of the presentations, given in Appendix A. Also, some of the findings and results of the Poster Session are given at the end of Appendix A.

In previous workshops a list of “Top 10 Questions” was developed with the objective of helping guide further research (Table 1). With continued research in modeling, *in situ* nanotube and catalyst character measurement, and parametric studies, several of the previous “Top” questions were addressed and answered at this Sixth Guadalupe Workshop. Many of the talks addressed and helped answer some of these questions, some explicitly identifying the questions and others implicitly. The previous top 10 questions are shown in Table 1, along with an additional question developed at this workshop. It is hoped that information synthesized during the workshop, such as improved catalysts and operating conditions, will help enable commercial production of single-wall carbon nanotubes and their applications on a large scale.

The final session included a discussion with a large amount of audience participation to summarize some of the top questions and how they were addressed by the speakers' research.

Although there will be no proceedings of the workshop, there is planned to be written a comprehensive paper that addresses the results of the meeting and how this and previous meetings have addressed top questions in the nucleation and growth of single-wall carbon nanotubes.

The organizing committee of the 2013 workshop, co-chaired by Dr. Wade Adams and Dr. Benji Maruyama, is listed in Appendix **A**. The Scientific Advisory Committee, co-chaired by Dr. Avetik Harutyunyan, Dr. David Geohegan, and Dr. Pavel Nikolaev, is listed in Appendix **B**. The agenda of the workshop is given in Appendix **D**, while the poster presenters are shown in Appendix **E**. The names of participants are given in Appendix **F**. Further information about the goals and the agenda can be found at the website:
http://swcnt.nano.rice.edu/Default.aspx?id=544&linkidentifier=id&itemid=544

A seventh workshop on a topic related to nucleation and growth of SWCNTs is planned for April 2015. It will be held again at the Flying L Ranch in the Hill Country of Texas. Researchers are encouraged to work on the questions listed in Table 1 and present their results in 2015. Information about the seventh workshop can be found at http://swcnt.nano.rice.edu/.

Table 1

Top Ten Questions in SWCNT Growth - Guadalupe Workshop 2011

1. Nucleation	**1. What determines the nucleation efficiency of nanoparticles, alone and in ensembles?**
2. Catalyst Efficiency	**2. What determines the catalytic efficiency of free and supported catalyst nanoparticles for nanotube growth?**
3. Chirality	**3. Is chirality determined during nucleation or growth (in high and low-T methods)?**
4. Structure	**4. What factors determine the diameter, chirality, number of walls, and defects in nanotubes during nucleation and growth?**
5. Chemistry	**5. What are the reactive species (including oxidants and promoters) and the chemical reaction pathways leading to the effective nucleation, growth, and termination of carbon nanotubes?**
6. Surface reactions at the catalyst	**6. What is the nature of the carbon species near the nanoparticle/nanotube interface (e.g. dimers dissolved within, or on the surface of) and the insertion reactions for carbon incorporation?**
7. Catalyst support	**7. How does the nature and geometry of the catalyst support alter the mechanisms of nanotube nucleation, growth and chirality selection ?**
8. Catalyst structure	**8. How do the phases and crystalline orientations of nanoscale catalyst particles affect nanotube diameters, nucleation and growth kinetics, and chirality in both high- and low-temperature synthesis methods?**
9. Termination	**9. What are the mechanisms for growth termination?**
10. Kinetics	**10. What are the rate-limiting steps in SWNT growth?**

11. An additional question from 2013: How are nanotubes nucleated in catalyst-free growth or with carbon as a catalyst? Does carbon have active sites for incorporation of additional carbon, and what about cloning?

Appendix A -Summary of Technical Results

Session 1- Computational and Modeling 1

Growth models for sp2-carbon: chiral-less graphene and chirality-driven nanotubes, Prof. Boris Yakobson, Rice University
Invoking the chemical potential this work developed effects on chirality and growth rates of SWCNTs for several catalysts. It also addressed how cooperative kinetic effects in carpet growth, with various rates of growth according to different chiralities, lead to rather flat overall growth.

Nucleation mechanisms of SWCNTs in plasma enhanced CVD, Dr. Erik Neyts, The University of Antwerp
Using hybrid molecular dynamics/Monte Carlo calculations the growth of both semiconducting and metallic SWNTs was simulated. The chirality was observed to change after initial cap nucleation. An applied electric field of suitable magnitude may enhance growth rate. Nucleation is governed by the competition between diffusion and migration, and is enhanced by low energy ion bombardment.

Insights into the synthesis of carbon nanotubes from computer simulation, Dr. Christophe Bichara, CINaM, Marseille University, France
Application of the tight binding model and Monte Carlo code to simulation of growth of SWCNTs led to understanding of the liquid/solid and chemical states of catalyst particles, and incorporating the proper chemical potential leads to nucleation and growth of SWNTs. Carbon is added via chains. The interfacial properties of the particles with sp^2 carbon walls show that they strongly depend on the amount of dissolved carbon. An attempt to grow defect-less nanotubes would allow investigation of chiral selectivity. Under growth conditions smaller particles are liquid or amorphous and nickel particle surface is not crystalline.

Nucleation and growth of single-walled carbon nanotubes on supported metal nanocatalysts, Prof. Perla Balbuena, Texas A&M University
Density functional theory computations are used to investigate the nucleation and growth of SWCNTs. These results indicate that after nucleation, near-armchair nanotubes are kinetically favored, thus chiral control should focus on controlling nucleation of chiral caps. There is a structural correlation between the catalyst particles and nanotubes. Nanotube growth evolution is driven by thermodynamic forces and influenced by kinetic energy barriers. Knowledge of these values may enable one to predict growth in new systems. Enhancing the template effect for nanotube growth character suggests need to minimize carbon dissolution since surface diffusion is sufficient for growth and nanoparticle supersaturation is not necessary to initiate nucleation. Horizontal growth of nanotubes is induced by nanotube/quartz surface interaction, which depends on structure and surface terminal groups.

Session 2- Computational Modeling 2

SWCNT Growth from Chiral and Achiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Local Growth Rates, Dr. Stephan Irle, Nagoya University
Quantum chemical calculations are used to simulate chirality controlled, catalyst free growth of SWCNTs from ethynyl (C_2H) radical addition to organic precursors. These are able to remove H and add to SWCNTs with little barrier. The growth rate is significantly affected by chiral angle. A maximum local growth rate exists for an optimum diameter/chirality combination for given C_2H/C_2H_2 ratios. Defect formation is affected by the intrinsic quality of the SWCNT edge.

A molecular dynamics simulation of SWNT growth by CVD method-Octopus and VLS modes, Dr. Shigeo Maruyama, The University of Tokyo
Molecular dynamics simulations are used to explore the possibility of controlling the growth process. A new classical potential for metal clusters was used. Two growth modes were detected in the simulations.

The preferred structure at low temperatures is the “Octopus” mode where several carbon chains wrap around the metal catalyst particle. The other mode is the VLS mode where carbon atoms are dissolved in the metal cluster and the growth rate is controlled by the feed rate of carbon to the cluster. In the octopus mode the cluster size determines the nanotube diameter; whereas in the VSL-like mode, chirality and nanotube stability are correlated. Surface chemical reactions limit the growth rate.

Session 3: In- Situ Measurements

In-situ Raman Spectroscopy Applied to SWNT Growth Kinetics, Dr. Benji Maruyama, Air Force Research Laboratory
A rapid technique for assessing the effects of multiple parameters on the growth of SWCNTs, called “Adaptive Rapid Experimentation and *In-situ* Spectroscopy system was described. This technique was applied to SWNT initial growth rate and to a comparison of iron and nickel as catalysts over a wide range of temperatures. It was found that, while for nickel the lifetime of the catalyst decayed as temperature increased, the iron catalyst underwent a discontinuous increase in catalyst lifetime. The was explained using the binary Fe-C and Ni-C phase diagrams, showing that the jump in lifetime around 1000^{o} C correlates well the Fe-C eutectic temperature modified for the nano-size of the catalyst. In contrast, no jump was seen for nickel, which is explained by the higher eutectic temperature in the Ni-C phase diagram.

The growth, termination and defect density of carbon nanotubes in Chemical vapor deposition from in situ imaging and Raman spectroscopy, Dr. Paul Finnie, National Research Council Canada
The lifecycle of SWCNT nucleation, growth, and termination in a CVD reactor are visualized using real time optical imaging and Raman spectroscopy of vertically aligned carbon nanotube forests. Simple imaging tracks the height of growth, while Raman determines distributions and defect densities. Many features of nanotube forests are activated by the growth temperature. For acetylene CVD on cobalt/alumina thin films we find that a single activation energy controls the defect density. The diameter distribution, while not clearly activated, follows a simple and commonly observed trend, with low temperatures producing smaller diameter tubes. Some insight into the temperature dependence of the grown material can be obtained from simple assumptions about the thermodynamics of growth. Interestingly, different CVD precursors imply a different scaling. One way to look at the grown distribution is as the consequence of a series of filters, each representing a different mechanism and each constraining the distribution in their own way.

Towards an understanding of catalytic graphene and CNT CVD, Dr. Stephan Hofmann, University of Cambridge
Systematic use of in-situ characterization techniques, including environmental scanning and transmission electron microscopy, high-pressure X ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), combined with process development for a range of industrial CVD reactors to reveal some of the key mechanisms of catalytic graphene and CNT CVD. In particular, highlighted and compared are the importance of kinetic aspects for nano-particulate CNT catalysts and poly-crystalline thin film/foil graphene templates.

Session 5: Electron Microscopy

Direct Observation of SWNT growth by environmental scanning transmission electron microscopy, Dr. Renu Sharma
In situ high-resolution transmission electron microscopy (HRTEM) combined with electron energy loss (EELS) and Raman spectroscopies are used to probe the first stages of growth of SWCNTs. An original approach based on pulsed gas introduction artificially increases the time resolution of the study. The critical chemical and physical changes occurring at the nanoparticle scale for different experimental growth conditions were measured.

Real time observations of the initial stages of single-walled nanotube carpet growth, Dr. Eric Stach, Brookhaven National Lab
Environmental transmission electron microscopy was used to observe fundamental characteristics in carbon nanotube growth, including detailed descriptions of the evolution of catalyst morphology during, as well as the initial stage of nanotube nucleation. Due to several improvements, experimental studying the nucleation and growth of CNTs in a plan-view geometry has improved significantly, allowing the opportunity to understand the initial self-organization of nanotube carpets. These experimental improvements include greater control over vacuum condition, improved delivery of reactant streams, increased control over thermal drift during imaging and significant improvements in the rate of image capture. These improvements increased understand the relationship between the initial state of the catalysts (size, density and proximity) and the resulting self-organization of the carpet array. These real time observations are placed in a broader context of understanding single-walled nanotube carpet growth.

Session 6: Nucleation and Chirality Control 1

Morphological Equilibrium of a Faceted Catalyst and Implications for the Growth Mechanism of Carbon Nanotubes, Dr. Avetik Harutyunyan, Honda Research Laboratory
The speaker synthesized data and analysis from many sources to develop a scenario of SWCNT nucleation and growth in an attempt to explain how chirality is determined and foresee a goal of obtaining chirality controlled growth. Thermodynamics of faceted nanocatalysts explains commonly accepted reconstruction of catalyst shape during nanotube growth by free energy changes of the facets due to carbon atom adsorption, which indeed helps to reveal some peculiarities of growth mechanism. Yet, carbon nanotube growth is strictly not an equilibrium process. Kinetic processes of catalyst facets (edges, steps/kinks) reconstruction during equilibration based on in situ electron microscopy observation of carbon nanotube growth below the catalyst roughening temperature are shown to determine growth. The kinetics of catalyst morphological evolution during equilibration not only unites various modes of growth mechanisms but also suggests the path for mastering chiral selective growth of single-walled carbon nanotubes via control of the terrace-step-terrace structure of the catalyst. Nucleation begins by the formation of a graphene embryo bounded between neighboring opposite step edges on the catalyst surface. The embryo develops into a dome when one of the steps propagates and crosses the edge of an adjacent facet. Further motion of the steps leads to elongation of the nascent nanotube.

Fundamental Studies towards (n,m) Controlled CVD Synthesis of SWCNTs, Dr. Esko Kauppinen, Helsinki University of Technology
Parallel studies on SWCNT growth from carbon monoxide (CO) using supported CVD methods, both at ambient CO pressure in the in-situ Raman microscope as well as at 7 mbar pressure inside the dedicated, Cs-corrected environmental TEM (ETEM). Narrow chiral distribution SWCNTs were produced when using supported bimetallic Fe-Cu catalysts at ambient pressure. Epitaxial formation of cobalt (Co) nanoparticles from CoxMg1-xO solid solution reduction (when deposited into MgO via impregnation) enables growth of SWCNTs in CO. These have a narrow diameter distribution, predominantly (6.5) tubes. ETEM studies at reduced pressure reveal that the Co nanoparticles remain in metallic state and their epitaxial contact with MgO support remains coherent during SWCNT root growth process.

Vapor-phase epitaxial growth of SWCNTs, Dr. Chongwu Zhou, the University of Southern California
A general strategy for producing carbon nanotubes was demonstrated. The SWCNTs have predefined chiralities using purified single- chirality nanotubes as seeds for subsequent metal catalyst free growth, resembling vapor-phase epitaxy commonly used for semiconductor films. Successfully synthesized were (7, 6), (6, 5) and (7, 7) nanotubes, as shown by Raman spectroscopy and unambiguously that the original chiralities of the nanotube seeds are preserved. Furthermore, electrical measurements on synthesized individual (7, 6) and (6, 5) nanotubes confirm their semiconducting nature. The vapor-phase epitaxy approach is found to be highly robust and should enable a wide range of fundamental studies and technological developments.

Session 7: Nucleation & Chirality Control 2

Selective Synthesis of (9, 8) Single Walled Carbon Nanotubes, Dr. Yuan Chen, Nanyang Technical University
Improved nanotube selective growth was obtained using a sulfate-promoted CoSO4/SiO2 catalyst. An amorphous catalyst Co-TUD-1 was developed to selectively grow large-diameter (9,8) single walled carbon nanotubes (SWCNTs) at 1.17 nm in CO chemical vapor deposition. The produced (9,8) nanotubes account for 51.7% of semiconducting tubes and 33.5% over all tube species. Sulfur doping was necessary to achieve the greatest selectivity for this and other types of Co/SiO_2 catalysts.

Direct synthesis of semiconducting single-walled carbon nanotubes by selective etching, Dr. Hui-Ming Cheng, Institute of Metal Research
Semiconducting SWCNTs were selected from mixtures of nanotubes produced in an oxygen-assisted floating catalyst CVD process. Nanotubes were selected according to their reactivity to oxygen, which depends on their metallicity, diameter, and chirality. Electron nano-beam diffraction of the nanotubes was used to determine reactivity. Metallic nanotubes were preferentially oxidized, particularly using NiO as an etchant. An all-SWCNT field effect transistor (FET) was fabricated with the aid of a patterned NiO mask, where the as-grown SWCNTs behave as source/drain electrodes and the remaining semiconducting SWCNTs that survive in the carbothermic reaction act as an active layer. The all-SWCNT FETs demonstrate a current on/off ratio of about 10^3.

Chirality Specific Growth of Single-Walled Carbon Nanotubes Using Alloyed Nanoparticles with Designed Structure as Catalysts, Dr. Yan Li, Peking University
A strategy to produce SWNTs with specific chirality was described. Catalyst nanoparticles containing alloys of tungsten with designed structure as templates were used to regulate the chirality of the grown SWNTs. This idea was enabled by introducing a new class of catalysts, a family of bimetallic alloy nanoparticles which have high melting points and consequently are able to maintain their solid structure during the chemical vapor deposition (CVD) process. By careful chirality assignment and quantification using Raman spectroscopy, UV-Vis-NIR absorption, and electron diffraction, it was found that the (12,6) and (14,4) SWNTs were synthesized at the abundances higher than 92% and 95%, respectively. Even for the zigzag (16,0) tubes, which are believed to be kinetically unfavorable, were still able to be produced at the content of ~82%. The structures of the catalyst nanoparticles were characterized with HRTEM, XRD, and EXAFS. Density functional theory (DFT) calculation demonstrates that the catalyst particles with well-defined structure facilitate the growth of SWNTs with specific chirality. This strategy paves a way for the ultimate chirality control in SWNT growth and thus may promote the development in SWNT applications.

Session 8: Chemical Effects on Growth

Controlling Defects and the Morphology of Nanotubes during Growth: The Role of Dopants, Dr. Mauricio Terrones, Pennsylvania State University
Sulfur, boron and nitrogen are used in the synthesis of carbon nanotubes and nanotube networks during chemical vapor deposition. These dopants are responsible for significant changes in the nanotube morphology and electronic properties. For example, sulfur induces the formation of pentagons and heptagons, whereas boron aids the growth of heptagonal carbon rings, and nitrogen promotes the formation of pentagonal cusps. It is possible to assemble/grow carbon nanotube networks with careful control of dopants. High resolution electron energy loss spectroscopy (HR-EELS) studies on these nanotubes indicate the locations of boron, sulfur and nitrogen within nanotubes. First principles theoretical calculations on nanotubes containing pentagon, hexagons and heptagons show the effect of these dopants on the band gaps. Results of recent experiments on doped graphene layers were presented.

Roles of sulfur and oxygen in floating catalyst CNT synthesis, Dr. Alan Windle, Cambridge University
Of the many parameters that affect carbon nanotube growth in a floating catalyst reactor used for spinning nanotube fibers attention is given to the influence of sulfur and oxygen. It is shown that sulfur is necessary for the spinning process by yielding longer and more numerous CNTs. If sulfur is available soon after the release of Fe from ferrocene, then growth of Fe particles in methane is retarded by

collision. With sulfur it is possible to make fibers in which all the SWNTs are armchair. The effect of oxygen is studied using various alcohols. The number of oxygen atoms in different alcohols does not affect the C/Fe/S ratios for optimum spinning, but the 'higher' n alcohols release OHs more easily and thus sooner after Fe becomes available. Butanol, gives better carbon yield and cleaner fibers
All alcohols leave a few % of synthesis product on the bundle surfaces. "Improvement " from ethanol to butanol is not continued to pentanol.

Session 9: Forest Growth I

Controlling Synthesis of Single-walled Carbon Nanotubes Forests, Dr. Kenji Hata, National Institute of Advanced Industrial Science and Technology (AIST)
Water-assisted CVD known as the "super-growth" technique is one method to grow SWNT forests in a short time. An investigation of experimental results and the literature is analyzed using the Ashby Y-y plot technique to understand what is possible and what cannot be done. Super-growth started from using ethylene as a carbon source and water as a growth enhancer, subsequent studies have shown that any combination of growth enhancers and carbon sources following a basic rule can provide highly efficient growth, and that many Fe compounds can be used as a catalyst. These features have provided an interesting opportunity to tailor the nanotube structure, such as degree of alignment, diameter, and crystallinity. Some specific combinations of carbon source and growth enhancers provide unique outputs such as very high growth yield, and wall number-control and also insight into regions parameter space not reachable.

Growth of High Density Vertically Aligned Carbon Nanotube Forests, Dr. John Robertson, University of Cambridge
Certain applications of carbon nanotubes such as interconnects in future integrated circuits or thermal interface materials require extremely high area densities of over 10^{13} cm^{-2}. In fact, the area density of most existing 'high density' vertically aligned CNT forests is only about $6x10^{11}$ cm^{-2}, and use only 5% of the cross sectional area. The density can only be increased by increasing the density of the original catalyst nanoparticles for the CVD process. Three different methods are shown to increase the catalyst and CNT density to $3x10^{13}$ cm^{-2}. The three processing methods that can be used to increase the catalyst density: (1) use a more diffusion resistant underlying support layer by plasma compaction to allow use of thinner catalyst layers and thus growth of smaller diameter SWNTs, (2) use a multi-cycle catalyst deposition process that increases the catalyst density cumulatively, and (3) use a short time carbon plasma to immobilize the catalyst particles before the growth step. The catalyst de-wetting process is described in detail.

Nucleation and growth of catalyst particles and carbon nanotubes on substrates and in the gas-phase, Dr. Suguru Noda, Waseda University
Some of the "top ten" questions posed in previous Guadalupe Workshops are addressed. Various sets of data are compared and analyzed, including both substrate growth and gas-phase growth of SWCNTs. The following were concluded:
2. High carbon feed increases nucleation efficiency of CNTs (possibly non-linearly) and growth rate linearly. It also increases the nucleation of additional walls and graphitic layers, resulting in MWCNTs, (onions, possibly), and catalyst death.
4. On substrates, CNT diameter is roughly determined by that of catalyst particles (from combinatorial catalyst screening). Number of walls and defects are largely enhanced by the degree of particle supersaturation, which becomes high at low temperatures and high carbon feed.
5. To enhance CNT nucleation, carbon feed needs be enhanced. C_2H_2 is effective for that purpose because of its high reactivity with catalyst metals. But just enhancing the carbon feed results in the carbonization of catalysts, and oxidative reagents are effective to suppress carbonization. Two step feeding would also be effective, in which nucleation is first enhanced by feeding C_2H_2 at high pressure and then carbonization is suppressed by reducing carbon feed.
9. Growth termination stems from:

(1) Catalyst coarsening, through Ostwald ripening, inherent for unstable small particles.
(2) Catalyst carbonization, when we hurry up growing SWCNTs by feeding excess carbon.
(3) Catalyst/CNT oxidation, when we add excessive oxidative additives to overcome carbonization.
10. SWCNTs grow through a series of processes, and any of them can be the rate-limiting step. Avoiding carbon diffusion through or carbon precipitation from catalyst particles is the key for sustainable growth.

Session 10: Forest Growth 2

Growth of carbon nanotube arrays for membrane applications: Lessons and challenges, Dr. Alexandr Noy, Lawrence Livermore National Laboratory
The author addresses the need for highly efficient membranes for water and air purification. Carbon nanotubes have the potential of forming them due to their high permeability and small diameter porosity. Limiting this goal is the lack of sufficiently high quality and high density and purity membranes. The authors conclude the following .Understanding the growth kinetics depends on source purification. Growth is terminated by catalyst Ostwald ripening and not by carbon poisoning or catalyst etching, but water inhibits catalyst ripening. Growth of high G/D ratio CNT arrays on large (4-in diameter) substrates requires careful tuning of growth parameters.

Investigation of Alumina Effect on Growing Vertically Aligned Carbon Nanotubes, Dr. Yoshikazu Homma, Tokyo University of Science
To determine how alumina functions to activate catalysts iron and cobalt, acetylene and ethanol are compared as sources of carbon in vertically aligned CNT growth as well as non-vertically aligned growth. Catalyst metals diffuse into alumina and precipitate nanoparticles on the surface, provided a minimum alumina thickness of about 20 nm is deposited. The length of grown nanotubes is determined according to the stability of catalyst particles against ripening. Short tubes are formed on SiO_2 in cases where the iron nanoparticles change rapidly; longer tubes (sub-millimeter) tubes form when these nanoparticles are stabilized. Metal atom diffusion on and in the alumina determines catalytic activity and lifetime of metal catalysts. The particular gas feeding growth affects this diffusion. Atoms diffuse rapidly on silica leading to rapid ripening; whereas alumina suppresses surface and sub-surface diffusion of Fe atoms and becomes saturated with Fe, leading to slow ripening.

Mechanical and chemical coupling in carbon nanotube population growth, Dr. John Hart, University of Michigan
Spatially resolved synchrotron X-ray scattering is used in conjunction with diameter-dependent growth models to estimate forces exerted by mechanically coupled CNTs within vertically aligned forest growth. TEM is used to study the *in situ* growth dynamics and diameter distributions. In addition, a chemical model of the coupling among growing nanotubes can explain the spatial variations of the height of nanotubes in micro-pillar array growth. The model quantitatively predicts these variations as function of pillar size and spacing. These studies support the concept that mechano-chemical feedback influences the growth of CNTs proximate to other CNTs and surfaces. It was noted that sparse nanoparticle densities led to very long nanotubes, whereas dense nanoparticles led to forest growth.

Session 11: Non-Equilibrium growth

Real-time optical diagnostics of single-wall carbon nanotube and graphene growth induced by pulsed chemical vapor deposition, Dr. David Geohegan, Oak Ridge National Laboratory
In situ laser reflection and Raman measurements are used to measure growth of nanotubes in a CVD reactor. Along with pulsed delivery of the feedstock gas used for chemical vapor deposition, the nucleation and growth kinetics of graphene and aligned single-wall carbon nanotube arrays on catalytic are characterized using a combination of real-time Raman spectroscopy, optical imaging, and optical reflectivity in conjunction. Pulsed CVD is used to provide digital delivery of feedstock with well-defined temporal arrival and duration, as well as partial pressure for flux-dependence studies. Graphene growth on Ni under otherwise typical conditions is studied to address fundamental synthesis questions including fast nucleation and growth kinetics and their dependence on partial pressure, and the fraction of growth

that occurs at temperature and upon cool down. For aligned arrays of single-wall carbon nanotubes (SWNTs) grown on Fe nanoparticles, the nucleation and growth kinetics, as well as the density and diameter distribution of the nanotubes in the array, are shown to be highly dependent upon the flux of feedstock gas. Growth of graphene on nickel surfaces is also measured using real time optical reflectivity, Raman, and videography techniques. These measurements show that most of the graphene grows isothermally, with higher acetylene partial pressure leading to larger fractions of isothermal graphene growth and shortened nucleation and growth periods. Growth kinetics seems to be autocatalytic, with an induction time noted before the appearance of graphene, then growth and termination, as explained in terms of a dissolution/precipitation model. Graphene is possibly a catalyst.

Investigations of the CVD growth and bonding of carbon allotropes to each other, Dr. Robert Hauge, Rice University

The energy to collapse nanotubes into a ribbon is shown to depend on diameter and its kinetics must overcome a potential energy barrier to form a low energy ribbon. Graphene/nanotube composites are discussed that have potential to overcome the problem of electrical contact between nanotubes and external sources. Growth of CNT and graphene is characterized by Raman spectroscopy, TEM and ohmic contact electrical measurements. It is suggested that such materials may be used for super capacitors, battery electrodes, and hydrogen storage.

• APPENDIX B – Organizing Committee

Smalley Institute for Nanoscale Science and Technology of Rice University, nanoCarbon Center
- **Dr. Wade Adams, co-chair**
- **Dr. Robert Hauge**
- **Mr. John Marsh**
- **Mr. Carlos Garcia**
- **Mrs. Addy Saenz (financial)**

AFRL/RX
- **Dr. Benji Maruyama, co-chair**
- **Dr. Pasha Nikolaev**
- **Mrs. Sandy Miller**

NASA Johnson Space Center
- **Dr. Carl Scott (retired)**
- **Dr. Edward Sosa**

ORNL
- **Dr. David Geohegan**

SUNGKYUNKWAN UNIVERSITY
- **Prof. Sivaram Arepalli**

HONDA RESEARCH INSTITUTE USA, INC.
- **Dr. Avetik Harutyunyan**
- **Dr. Rahul Rao**

UNIVERSITY OF MICHIGAN
- **Dr. John Hart**

Appendix C - International Scientific Advisory Committee

International Scientific Advisory Committee
Chair - Dr. Avetik Harutyunyan, Honda Research Institute USA, Columbus OH, USA
Co-Chair - Dr. Pasha Nikolaev, AFRL/RX, Wright-Patterson AFB, Ohio, USA
Co-Chair - Dr. David Geohegan, Oak Ridge National Laboratory, Tennessee, USA
Prof. Pulickel Ajayan, Rice University, Houston TX, USA
Prof. Sivaram Arepalli, Sungkyunkwan University, Suwon, South Korea
Dr. Christophe Bichara, CNRS and AIX Marseille University, Marseille, France
Prof. Kim Bolton, Chalmers University of Technology, Göteborg, Sweden
Prof. Hui Ming Cheng, Institute of Metal Research, Shenyang, China
Dr. John Hart, University of Michigan, MI USA
Dr. Robert Hauge, Rice University, Houston TX, USA
Prof. Yoshikazu Homma, Tokyo University of Science, Japan
Prof. Esko Kauppinen, Helsinki University of Technology, Finland
Prof. Young Hee Lee, Sungkyunkwan University, Korea
Prof. Shigeo Maruyama, University of Tokyo, Japan
Prof. John Robertson, University of Cambridge, UK
Dr. Benoit Simard, NRC Canada, Ottawa, Canada
Dr. Eric Stach, Brookhaven National Lab, Upton, NY, USA
Prof. Alan Windle, Cambridge University, UK
Prof. Boris Yakobson, Rice University, Houston, TX, USA

Appendix D – Agenda

Friday April 12, 2013

Transportation from Airport/Arrival/Check-in
Set up Posters
Dinner Period
Welcome
Session 0 Keynote Chair: Wade, Avetik
Keynote Talk 1 Phaedon Avouris
Keynote Talk 2 Rodney Ruoff

Day One Saturday, Apr. 14

Breakfast Period
General Remarks about Workshop: Wade Adams & Dave Geohegan

Speaker	***Title***
Session 1 Computational Modeling	*Chair: S. Maruyama Rapporteurs: S. Irle, Erik Neyts*
Boris Yakobson	*Growth models for sp2-carbon: chiralless graphene and chirality-driven nanotubes*
Feng Ding	*The Origin of SWCNT's Chirality and Strategies of Chirality-Selection in Growth*
Break	
Christophe Bichara	*Insights into the synthesis of carbon nanotubes from computer simulation*
Perla Balbuena	*Nucleation and growth of single-walled carbon nanotubes on supported metal nanocatalysts*
Session Summary	
Lunch	
Session 2 Computational Modeling	*Chair: C. Bichara Rapporteurs: P. Balbuena, F. Ding*
Stephan Irle	*SWCNT Growth from Chiral and Achiral Carbon Nanorings: Prediction of Chirality and Diameter Influence on Local Growth Rates*
Shigeo Maruyama	*A molecular dynamics simulation of SWNT growth by CVD method - Octopus and VLS modes*
Session Summary	
Break	
Session 3 In Situ Measurements	*Chair: G. Eres Rapporteurs: E. Stach, J. Hart*
Benji Maruyama	*In-situ Raman Spectroscopy Applied to SWNT Growth Kinetics*
Paul Finnie	*The growth, termination and defect density of carbon nanotubes in chemical vapor deposition from in situ imaging and Raman spectroscopy*
Stephan Hoffman	*Towards an understanding of catalytic graphene and CNT CVD*
Session Summary	
Session 4 Poster+Plus Session	*Chair: Wade Adams Rapporteurs: D. Geohegan, P. Nikolaev, C. Scott, R. Rao*
Dinner	

Poster Plus Session *Includes 90 sec. oral presentations*

Sunday 14 April

Breakfast Period
Free Time
Lunch
Session 5 Electron Microscopy Chair: R. Sharma Rapporteur: S. Hoffman, D. Zakharov

Kazu Suenaga	HR-TEM of Carbon Network, - Towards Individual C-C Bond Imaging
Eric Stach	Real time observations of the initial stages of single-walled nanotube carpet growth

Session Summary
Break
Session 6 Nucleation and Chirality Control 1 Chair: B. Yakobson
Rapporteurs: J. Robertson, P. Nikolaev

Avetik Harutyunyan	
Esko Kauppinen	Fundamental Studies towards (n,m) Controlled CVD Synthesis of SWCNTs
Chongwu Zhou	Chirality-Controlled Synthesis of Carbon Nanotubes using Vapour-Phase Epitaxy

Session Summary
Dinner
Session 7 Nucleation & Chirality Control 2 Chair: E. Kauppinen
Rapporteurs: Y. Homma

Yuan Chen	Selective Synthesis of (9,8) Single Walled Carbon Nanotubes
Hui-Ming Cheng	Direct synthesis of semiconducting single-walled carbon nanotubes by selective etching
Yan Li	Chirality Specific Growth of Single-Walled Carbon Nanotubes Using Alloyed Nanoparticles with Designed Structure as Catalysts

Session Summary

Monday April 15

Breakfast Period
Session 8: Chemical Effects on Growth Chair: J. Robertson
Rapporteurs: S. Noda, R. Sharma

Mauricio Terrones	Controlling Defects and the Morphology of Nanotubes during Growth: The Role of Dopants
Alan Windle	Roles of sulphur and oxygen in floating catalyst CNT synthesis.

Session Summary
Break with Snacks, Coffee/Tea, etc
Session 9 Forest Growth I Chair: P. Finnie
Rapporteurs: R. Hauge, M. Schultz

Kenji Hata	Controlling Synthesis of Single-walled Carbon Nanotubes Forests
John Robertson	Growth of High Density Vertically Aligned Carbon Nanotube Forests
Suguru Noda	Nucleation and growth of catalyst particles and carbon nanotubes on substrates and in the gas-phase

Session Summary

Lunch
Free Time horse riding, hiking, etc.
Dinner
Session 10 Forest Growth 2 Chair: V. Shanov Rapporteur: K. Hata , Cary Pint

Alexandr Noy	Growth of carbon nanotube arrays for membrane applications: Lessons and challenges
Yoshikazu Homma	Investigation of Alumina Effect on Growing Vertically Aligned Carbon Nanotubes

Break with Snacks, Coffee/Tea, etc

John Hart	Mechanical and chemical coupling in carbon nanotube population growth

Session Summary

Tuesday April 16

Breakfast
Session 11 Nonequilibrium Growth Chair: M. Terrones Rapporteur: R. Rao

David Geohegan	Real-time optical diagnostics of single-wall carbon nanotube and graphene growth induced by pulsed chemical vapor deposition
Robert Hauge	Investigations of the CVD growth and bonding of carbon allotropes to each other

Summary Session Chair: Pavel Nikolaev Rapporteur: David Geohegan
Meeting Summary and Action Items

Goodbye/Checkout
Transportation to Airport
Stragglers Lunch

Appendix E – Posters

Powerful characterization tool for predicting active catalyst supports in carbon nanotube carpet growth
Placidus B. Amama, Shawn A. Putnam, Andrew R. Barron, and Benji Maruyama

Understanding single-walled carbon nanotube growth through reactive molecular dynamics simulations
Jenni Beetge, Diego A. Gomez-Gualdron, and Perla B. Balbuena

Sub-parts-per-trillion gas detection with carbon nanotubes and graphene
Gugang Chen and Avetik R. Harutyunyan

The growth of vertically aligned forest of single-wall carbon nanotubes kept small diameter
Toshiyuki Ohashi Ryogo Kato Takumi Ochiai Hiroshi Kawarada and Toshio Tokune

Graphene as an Atomically Thin Interface for Vertically Aligned Carbon Nanotube Growth
Rahul Rao, Andrew Taris, Gugang Chen, Avetik R. Harutyunyan

Preferential Adsorption of Zigzag Single-Walled Carbon Nanotubes on the ST-cut Surface of Quartz

Automatic and Autonomous Growth of SWNTs with ARES
Daylond Hooper, Rahul Rao, Pavel Nikolaev, Benji Maruyama

The Path of Carbon: Refining the Carbon Nanotube Mechanism
Erick Jones Jr., Diego Gomez-Gualdron, and Perla B. Balbuena

Refried beans: chirality control in single-walled carbon nanotubes produced by pulsed laser vaporization
Pavel Nikolaev, Sivaram Arepalli and Benji Maruyama

Methane-assisted CVD yielding millimeter-tall single-wall carbon nanotubes of smaller diameters
Zhongming Chen, Dong Young Kim, Kei Hasegawa, and Suguru Noda

Growth of high-density carbon nanotube arrays on conductive underlayers at 400 °C
Nuri Na, Yeong-Gi So, Yuichi Ikuhara, and Suguru Noda

Nucleation mechanisms of SWCNTs in plasma enhanced CVD
E. C. Neyts

Reaction-mechanism analysis on the CNT Growth by eDIPS method using ^{13}C carbon source
Takayoshi Hirai Yuki Kuwahara Masaharu Kiyomiya Takeshi Saito

Ionically Tunable CNT Electrodes in Organic Photovoltaic and Light Emitting Devices
Alexander Cook Jonathan Yuen and Anvar Zakhidov,

Effect of the additional carbon source on the growth of double-walled carbon nanotubes by eDIPS method and their characterization by Raman spectroscopy
Yuki Kuwahara Keita Kobayashi Masaharu Kiyomiya Takayoshi Hirai Shigekazu Ohmori Bikau Shukla and Takeshi Saito

Appendix F - Attendees

Last	First	Address	City	State	Country	email
Adams	Wade	Rice University	Houston	TX	US	wadams@rice.edu
Artyukhov	Vasilii	Rice University	Houston	TX	US	artyukhov@rice.edu
Avouris	Phaedon	IBM - T.J. Watson Research Center	Yorktown Heights	NY	US	avouris@us.ibm.com
Balbuena	Perla	3122 TAMU	College Station	TX	US	balbuena@tamu.edu
Beetge	Jenni	Rice University	Houston	TX	US	beetgejenni@gmail.com
Bichara	Christophe	CINaM - CNRs and Aix-Marseille University	Marseille		FR	xtof@cinam.univ-mrs.fr
Buck	Will	Applied Nano	Houston	TX	US	wbuck@appliednano.com
Burgos	Juan C.	3122 TAMU	College Station	TX	US	burgos@tamu.edu
Chen	Zhongming	Department of Applied Chemistry	Tokyo		JP	z_chen@chemsys.t.u-tokyo.ac.jp
Cheng	Hui-Ming	Institute of Metal Research	Shenyang		CN	cheng@imr.ac.cn
Darmanyan	Sergey	6745 Banyon Drive	Plano	TX	US	sdarmanyan@gmail.com
Dyke	Christopher	Nanoridge	Houston	TX	US	cdyke@nanoridge.com
Eres	Gyula	Oak Ridge National Laboratory	Oak Ridge	TN	US	eresg@ornl.gov
Fan	Xiujun	Rice University	Houston	TX	US	xf3@Rice.edu
Finnie	Paul	National Research Council Canada	Ottawa	None	CA	Paul.Finnie@nrc-cnrc.gc.ca
Geohegan	David	Oak Ridge National Laboratory	Oak Ridge	TN	US	odg@ornl.gov
Gomez-Ballesteros	Leonardo	3122 TAMU	College Station	TX	US	leogomez_iq@hotmail.com
Hart	John	University of Michigan	Ann Arbor	MI	US	ajohnh@umich.edu
Harutyunyan	Avetik	Honda Research Institute USA	Columbus	OH	US	aharutyunyan@honda-ri.com
HATA	Kenji	National Institute of Advanced Industrial Science and Technology	Tsukuba, Ibaraki		JP	sgt-info-ml@aist.go.jp
Hauge	Robert	Rice University	Houston	TX	US	hauge@rice.edu
Hirai	Takayoshi	TASC - NT	Higashi		JP	hirai@tasc-nt.or.jp
Hofmann	Stephan	Department of Engineering	Cambridge		GB	sh315@cam.ac.uk
Holmes	William	University of Texas -Dallas		TX	US	holmes@utdallas.edu
Homma	Yoshikazu	Tokyo University of Science	Tokyo		JP	homma@rs.tus.ac.jp

Hooper	Daylond	UES Corp.	Dayton	OH	US	dhooper@ues.com
Irle	Stephan	Nagoya University	Nagoya		JP	sirle@chem.nagoya-u.ac.jp
Jaswal	Hari	Rice University	Houston	TX	US	hj11@rice.edu
Jones	Erick	3122 TAMU	College Station	TX	US	yamierick@tamu.edu
Kauppinen	Esko	Aalto University	Espoo		FI	esko.kauppinen@aalto.fi
Kim	Keun Su	National Research Council Canada	Ottawa		CA	KeunSu.Kim@nrc-cnrc.gc.ca
Kittrell	Carter	Rice University	Houston	TX	US	kittrell@rice.edu
Kuwahara	Yuki	Nanotube Research Center, AIST	Tsukuba		JP	yuki.asada@aist.go.jp
Lashmore	David	University of New Hampshire	Durham	NH	US	David.Lashmore@unh.edu
Lepro	Xavier	University of Texas -Dallas	Richardson	TX	US	xn.lepro@gmail.com
Li	Yan	College of Chemistry, Peking University	Beijing		CN	yanli@pku.edu.cn
Li	Jinghua	Duke University	Durham	NC	US	jl423@duke.edu
Marsh	John	Rice University	Houston	TX	US	jfm3@rice.edu
Maruyama	Benji	Air Force Research Laboratory	WPAFB	OH	US	Benji.Maruyama@wpafb.af.mil
Maruyama	Shigeo	University of Tokyo	Tokyo		JP	maruyama@photon.t.u-tokyo.ac.jp
Meshot	Eric	Lawrence Livermore National Lab	Livermore	CA	US	meshot1@llnl.gov
Moloney	Padraig	Lockheed Martin Co.	Boston	MA	US	padraig.moloney@lmco.com
Na	Nuri	University of Tokyo	Tokyo		JP	nanuri@chemsys.t.u-tokyo.ac.jp
Neyts	Erik	University of Antwerp	Antwerp		BE	erik.neyts@ua.ac.be
Nikolaev	Pavel	Air Force Research Laboratory / UES Inc.	Dayton	OH	US	pavel.nikolaev.ctr@wpafb.af.mil
Noda	Suguru	Department of Applied Chemistry, Waseda University	Tokyo		JP	noda@waseda.jp
Noy	Aleksandr	Lawrence Livermore National Lab	Livermore	CA	US	anoy@ucmerced.edu
Ohashi	Toshiyuki	Honda	Wako		JP	toshiyuki_ohashi@n.f.rd.honda.co.jp
Orbaek	Alvin	Rice University	Houston	TX	US	aok@rice.edu
Oviedo Robles	Juan Pablo	University of Texas -Dallas	Richardson	TX	US	suzanne.e.potts@utdallas.edu

Pint	Cary	Vanderbilt University	Nashville	TN	US	cary.l.pint@vanderbilt.edu
Rao	Rahul	Honda Resesarch Institute USA	Columbus	OH	US	rrao@honda-ri.com
Pierce	Neal	1381 Kinnear Rd., Suite 116	Columbus	OH	US	NPierce@oh.hra.com
Robertson	John	Cambridge University	Cambridge		GB	jr@eng.cam.ac.uk
Ruoff	Rodney	University of Texas - Austin	Austin	TX	US	r.ruoff@mail.utexas.edu
Samarakone	Nandasiri	RF Nano, Corp	Newport Beach	CA	US	nanda.samarakone@rfnano.com
Schulz	Mark	University of Cincinnati	Cincinnati	OH	US	mark.j.schulz@uc.edu
Scott	Carl	NASA Johnson Space Center (Retired)	New Braunfels	TX	US	cds789@netzero.com
Shanov	Vesselin	University of Cincinnati	Cincinnati	OH	US	vesselin.shanov@uc.edu
Sharma	Renu	National Institute of Standards and Technology	Gaithersburg	MD	US	renu.sharma@nist.gov
Stach	Eric	Brookhaven National Laboratory	Upton	NY	US	estach@bnl.gov
Terrones	Mauricio	The Pennsylvania State University	University Park	PA	US	mut11@psu.edu
Tokune	Toshio	Honda, Japan	Wako-shi, Tokyo		JP	toshio_tokune@n.f.rd.honda.co.jp
Weisman	R. Bruce	Applied NanoFluorescence	Houston	TX	US	rbw@appliednano.com
Windle	Alan	Cambridge University	Cambridge		GB	ahw1@cam.ac.uk
Xu	Yaqiong	Vanderbilt University	Nashville	TN	US	yaqiong.xu@vanderbilt.edu
Zakharov	Dmitri	Brookhaven National Laboratory	Upton	NY	US	dzakharov@bnl.gov
Zakhidov	Anvar	University of Texas - Dallas	McKinney	TX	US	zakhidov@utdallas.edu
Zhou	Chongwu	University of Southern California	Los Angeles	CA	US	chongwuz@usc.edu
Liu	Bilu	University of Southern California	Los Angeles	CA	US	biluliu3@gmail.com
Liu	Jia	University of Southern California	Los Angeles	CA	US	jialiu@usc.edu