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Purpose of the Workshop

The workshop will be focused on new developments in the understanding of SWCNT nucleation and growth mechanisms. The workshop will bring together world experts to present experiments, theory, and modeling efforts focused on all aspects of SWCNT nucleation growth and production. Substantial progress has been made in the two years since the last workshop, especially in the growth of SWCNT vertically aligned arrays and in directed growth. It is important that these new developments be understood and disseminated to the nanotube growth community. Sufficient understanding of the growth mechanisms should enable better production methods of SWCNT for particular applications. Likewise, there is increased interest in producing SWCNTs of a single chirality. It is hoped that researchers and developers will benefit from this open scientific exchange and publication of a workshop proceedings resulting in commercial methods to produce SWCNTs of specific chirality and characteristics.

Workshop Background

The great potential of single-wall carbon nanotubes (SWCNTs) is limited by our inability to produce large quantities and ones of a particular type. The development of a reliable source of large quantities of SWCNTs depends on better production methods. However, the nucleation and growth mechanisms of single-wall carbon nanotubes have not been well understood. This has limited the development of production methods to produce large quantities of SWCNTs, including the laser ablation/oven technique, the arc vaporization process, and chemical reaction methods such as the high-pressure carbon monoxide disproportionation (HiPco) and chemical vapor deposition (CVD). This workshop will address the scientific issues and knowledge of nucleation and growth mechanisms that could lead to improved production methods and the ability to selectively produce SWCNTs of particular types, with high purity. The workshop will bring together the world's experts in the field of nanotube synthesis and processing to present their latest understanding, based on experiments, theory, and modeling. The third workshop identified several key areas for recommended expansion of activity. Although no one has complete understanding of the mechanisms, progress has been made which show promise of being able to translate this into better production methods. This workshop will be organized around fundamental issues and areas of new interest, and yet will still allow for entirely new thinking. It is hoped that through this continuing scientific exchange and publication of a fourth workshop proceedings, knowledge will be synthesized to give funding agencies, researchers, and developers the insight necessary to develop efficient and commercially viable SWCNT production methods and programs.
International Scientific Advisory Committee

Chairman: Dr. Benji Maruyama, Air Force Research Laboratory, WPAFB, OH, USA
Co-Chairman: Dr. Avetik Harutyunyan, Honda Research Institute USA Inc., Columbus, OH, USA

Prof. Pulickel Ajayan, Rice University, Houston, TX, USA
Dr. Sivaram Arepalli, Sungkyunkwan University, South Korea
Prof. Kim Bolton, University of Borås, Sweden
Prof. Hui Ming Cheng, Institute of Metal Research, Shenyang, China
Dr. David Geohegan, Oak Ridge National Laboratory, Oak Ridge, TN, USA
Dr. Robert Hauge, Rice University, Houston, TX, USA
Prof. Young Hee Lee, Jeonbuk National University, Korea
Prof. Yoshikazu Homma, Tokyo University of Science, Japan
Prof. Stephan Irle, Nagoya University, Japan
Prof. Esko Kauppinen, Helsinki University of Technology, Finland
Prof. Jie Liu, Duke University, Durham, NC, USA
Dr. Annick Loiseau, ONERA, Chatillon, France
Prof. Shigeo Maruyama, The University of Tokyo, Tokyo, Japan
Dr. Pasha Nikolaev, Sungkyunkwan University, South Korea
Prof. Daniel Resasco, University of Oklahoma, Norman, OK, USA
Prof. John Robertson, University of Cambridge, Cambridge, United Kingdom
Dr. Benoit Simard, NRC Canada, Ottawa, Canada
Prof. David Tomanek, Michigan State University, East Lansing, MI, USA
Prof. Alan Windle, Cambridge University, Cambridge, United Kingdom

Organizing Committee

Air Force Research Laboratory
  • Dr. Benji Maruyama
  • Ms. Sandy Miller, Assistant

Rice University, Smalley Institute for Nanoscale Science and Technology
  • Dr. Wade Adams
  • Mr. Carlos Garcia, Financial Administrator
  • Dr. Robert Hauge
  • Mr. John Marsh

Honda Research Institute USA
  • Dr. Avetik Harutyunyan

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NASA Johnson Space Center
  • Dr. Carl D. Scott
  • Dr. Edward Sosa

Sungkyunkwan University
  • Dr. Sivaram Arepalli
  • Dr. Pasha Nikolaev
Flying L Guest Ranch

Since 1947, The Flying L Guest Ranch, Bandera, Texas has been a favorite destination for guests from all over the world. Bandera is the Cowboy Capital of the World is nestled in the heart of Texas Hill Country. The Flying L is best noted for its incredible staff. They pride themselves on our high level of true Texas hospitality. The Flying L Ranch transports you back in time to when Hollywood legends like John Wayne and Erol Flynn made this spot their hideaway. It’s easy to imagine the Duke striding across the rough-hewn floorboards of the saloon or galloping across the broad expanse of countryside.

After stowing your gear, hightail it out for some real Texas fun on the 772-acre Ranch. There are horseback rides, hayrides, an 18-hole golf course and driving range, outdoor pool, lightened tennis courts, petting corral, playground, and General Store. After sundown, get along to the Branding Iron Saloon and enjoy the great western entertainment, or just gaze at the big, starry skies above.

**Activities No Charge:**

- Water Park & Swimming Pool
- Putt-Putt Mini Golf
- Tennis
- Shuffleboard
- Basketball
- Volleyball
- Ping-Pong
- Horseshoes
- Hiking
- Fishing

**Activities with a Fee:**

- Golf
  - 18-hole - $35 each, Greens & Cart
  - 9-hole - $17 each, Greens & Cart
- Horseback Rides $49 one-hour trail

**Spa Services**

Complete your stay at the Flying L Guest Ranch with a relaxing, stress-busting massage or enjoy the therapeutic and relaxing effects of our unique facial treatments. For scheduling, please call the front desk at 800-292-5134.
Area Attractions

Downtown Boerne – Surrounded by the beautiful Texas Hill County, is a wonderful combination of Old World charm and Texas hospitality. The tastefully restored Hauptstrasssa (Main Street) offers a feast of antique, gift and art galleries, restaurants, coffee shops, turn-of-the-century European architecture, and picturesque gardens and greenbelts.

Cave without a Name – Less than 12 miles from Boerne, in the heart of the scenic, rolling hills of the Texas Hill Country. Cave without a Name is a natural, living cavern filled with spectacular formations of stalactites, stalagmites, delicate soda straws, cave drapery, magnificent flowstones, rim stone dams, and more. Enjoy a tour of the six major rooms in comfort; 66° year-round, easy walkways, brilliant lighting.

Six Flags Fiesta Texas – A 200-acre park featuring awesome rides, great shows, and incredible attractions, plus White Bay Water Park, located in San Antonio.

Hill Country Wine Tour – Offers enchanting tours of wineries in the Texas Hill Country. For reservations call 830-997-8687.

Sea World of Texas – Is the Aquatic theme park with animals, roller coasters, and fabulous shows.

Lyndon B. Johnson Ranch – Lyndon B. Johnson National Historical Park tells the story of our 36th President beginning with his ancestors until his final resting place on his beloved LBJ Ranch.

Fredericksburg – Located in the very heart of the beautiful Texas Hill Country, is a blend of German heritage and Texan hospitality for over 150 years. Fredericksburg is home to the Mintz Pacific Naval War Museum.

Historical Luckenbach – These days Luckenbach Texas is, to paraphrase John Steinbeck, a state of mind – A Texas state of mind, where you can kick back, relax and get away from the hustle and bustle of everyday life—like a step back in time. This tiny hill country hamlet where “Everybody’s Somebody” was established as a Trading Post in 1849 making it one of the oldest settlements in Gillespie County.

San Antonio – One of the largest cities in Texas and home of the Alamo and the River Walk (world renowned entertainment destination).
Friday, 8 April 2011

Dinner  
**Texas Range & Surf Buffet:**  
Tomato Basil Soup; Cowboy Salad Bar with Iced Field Greens w/assorted Dressings and all the Fixin’s, Pasta Salad and Carrot Salad; Carved Sage Roasted Breast of Turkey w/Serrano Cranberry Relish, Lemon-Pepper Seasoned Baked Haddock w/Mushroom Sauce; Down Home Cheesy Mashed Potatoes, Whole Carrots; Focaccia Bread w/Dipping Sauce; Assorted Liquor Cakes and Bread Pudding; Coffee (Regular & Decaf), Iced Tea, & Pear Cactus Lemonade

Saturday, 9 April 2011

Breakfast  
Sliced Seasonal Fruit, Array of Cold Cereals & Fresh Milk, Assorted Berried Yogurts, Scrambled Eggs, Bacon and Sausage, Hash browns, Biscuits & Gravy, Pancakes & Syrup, Breakfast Breads & Muffins, Omelet Station: Ham, Cheese, Peppers, Mushrooms, Olives, Tomatoes, etc., Assorted Juices & Coffee (Regular and Decaf)

Lunch  
**Mini Ranger Crossing Buffet:**  
Iced Texas Greens w/assorted Dressings, Pasta Salad and Carrot Salad; Hill Country Chicken Salad, Peppered Oven Roast Turkey, Honey Cured Ham, Big Eye Swiss and American; Basket of Breads; Green Leaf Lettuce, Sliced Tomatoes, Kosher Dill, Dark Mustard & Mayonnaise; Russet Potato Chips; Assorted Cookies; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade

Dinner  
**Chisholm Trail Cookout:**  
Outlaw Slaw & Texas Tater Salad; Bubba’s Pit Smoked Beef Brisket, Texas BBQ Yard Bird w/Flying L’s own label BBQ Sauce; Sweet Field Corn on the Cob; Jalapeno Cheddar Cornbread; Homemade Bacon Borracho Pinto Beans; Medina Apple Cobbler & Fredericksburg Peach Cobbler; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade

Sunday, 10 April 2011

Breakfast  
Sliced Seasonal Fruit, Array of Cold Cereals & Fresh Milk, Assorted Berried Yogurts, Scrambled Eggs, Bacon and Sausage, Hash browns, Biscuits & Gravy, Pancakes & Syrup, Breakfast Breads & Muffins, Omelet Station: Ham, Cheese, Peppers, Mushrooms, Olives, Tomatoes, etc., Assorted Juices & Coffee (Regular and Decaf)

Lunch  
Hamburgers & Grilled Chicken; Cheese, Lettuce, Onions, Pickles and Potato Salad; Cake or Cookies; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade
Dinner  Mexican Fiesta Buffet:
Tortilla Soup, Pecos Pass Salad Bar with Iced Field Greens w/assorted Dressings and all the Fixin’s; Fire Seared Chicken Fajitas w/Roasted Onions & Peppers, Warm Flour Tortillas; Taco Station w/Grated Cheese, Shredded Lettuce, Diced Tomatoes, Guacamole, Sour Cream and Poncho Villas, Three Onion Pico de Gallio; Flying L’s Own Green Chili / Sour Cream Enchiladas; Cilantro Spanish Rice & Mama Rosa’s Refried Frijoles; Cinnamon Churros & Empanadas; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade

Monday, 11 April 2011

Breakfast  Sliced Seasonal Fruit, Array of Cold Cereals & Fresh Milk, Assorted Berried Yogurts, Scrambled Eggs, Bacon and Sausage, Hash browns, Biscuits & Gravy, Pancakes & Syrup, Breakfast Breads & Muffins, Omelet Station: Ham, Cheese, Peppers, Mushrooms, Olives, Tomatoes, etc., Assorted Juices & Coffee (Regular and Decaf)

Lunch  Little Italy Buffet:
Caesar Salad w/Italian & Caesar Dressing; Meatballs, Lasagna; Cream Basil Sauce, Alfredo Sauce, Marinara Sauce; Pasta Action Station w/Penne, Linguini and Cheese Tortellini; Italian Sausage, Ham, Chicken; Assortment of Fresh Produce; Focaccia Bread w/Basil Herb Dipping Sauce; Italian Cream Cake; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade

Dinner  Down Home Buffet:
Mushroom & Brie Bisque; Cowboy Salad Bar: Iced Field Greens w/assorted Dressings, Pasta Salad, and Carrot Salad; Carved Bourbon & Molasses Pit Ham and Country Meatloaf; Garlic Mashed Potatoes, Candied Yams, Green Beans, and Baked Beans; Focaccia Bread w/Garlic Dipping Sauce; Chocolate Mousse and Banana Pudding; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade

Tuesday, 12 April 2011

Breakfast  Sliced Seasonal Fruit, Array of Cold Cereals & Fresh Milk, Assorted Berried Yogurts, Scrambled Eggs, Bacon and Sausage, Hash browns, Biscuits & Gravy, Pancakes & Syrup, Breakfast Breads & Muffins, Omelet Station: Ham, Cheese, Peppers, Mushrooms, Olives, Tomatoes, etc., Assorted Juices & Coffee (Regular and Decaf)

Lunch  Ranger Crossing Buffet
Chopped BBQ Beef & Chopped BBQ Chicken on a Corn Dusted Roll, Potato Salad, Cole Slaw, Pinto Beans; Apple Cobbler; Coffee (Regular & Decaf), Texas Iced Tea, and Pear Cactus Lemonade
AGENDA

Friday, 8 April 2011

2:00pm – 7:30pm  Transportation from Airport, Arrival, & Check-in
4:00pm – 6:00pm  Registration – Main Building-Lobby
4:00pm – 6:00pm  Poster Set-up – Roy Rogers Room
6:00pm – 7:30pm  Dinner – Main Dining Room
7:30pm – 7:45pm  Welcome – Roy Rogers Room
                    Dr. Benji Maruyama, Air Force Research Laboratory
7:45pm – 8:45pm  Session 0 – Keynote
                    Session Chair:  Dr. Avetik Harutyuyan, Honda Research Institute USA, Inc.
7:45pm – 8:45pm  From the Lab to the Fab:  A Journey through CMOS Qualification,
                    Dr. Brent Segal, Director & Chief Technologies, Lockheed Martin Nanosystems
8:45pm – 10:00pm Networking Reception with Open Bar

Saturday, 9 April 2011

7:00am – 9:00am  Breakfast – Main Dining Room
9:00am – 9:15am  General Remarks
                    Dr. Carl Scott, NASA
9:15am – 3:20pm  Session 1 – Computational and Modeling 1
                    Co-Chairs:  Dr. Fei Wei, Tsinghua University &
                                Prof. Eric Stach, Purdue University
                    Rapporteur:  Prof. Esko Kauppinen, Helsinki University of Technology
9:15am – 9:55am  Nucleation and Growth of Carbon Nanotubes as Heterogeneous
                    Catalysis Process, Dr. John Robertson, Cambridge University, UK
9:55am – 10:35am Modeling and Growth of Carbon Nanotubes, Mr. Anders Börjesson,
                    University of Borås, Sweden
10:35am – 10:55am Break with Refreshments
10:55am – 11:35am Growth and Healing Mechanisms of SWNT from Tight Binding Computer
                    Simulations, Dr. Chrisophe Bichara, CIaM, Marseille University, France
11:35am – 12:15pm In-situ Diagnostic-based Modeling of Carbon Nanotube Growth,
                    Dr. Alex Puretzky, Oakridge National Laboratory, USA
12:15pm – 1:15pm  Lunch – Main Dining Room
AGENDA
(Continued)

Session 1 – Computational and Modeling 1 (Continued)

1:30pm – 2:10pm  QM/MD Simulations of SWCNT Nucleation and Growth with and without Metal Catalysts: Implications for Experiment, Prof. Stephan Irle, Nagoya University, Japan

2:10pm – 2:50pm  Theory of Chiral Growth: Nanotubes to Graphene, Graphene to Nanotubes, Prof. Boris Yakobson, Rice University, USA

2:50pm – 3:20pm  Session Summary

3:20pm – 3:35pm  Break with Refreshments

3:35pm – 5:55pm  Session 2: Graphene and Metamaterials
Co-Chairs: Prof. Boris Yakobson, Rice University & Dr. Anvar Zakhidov, University of Texas at Dallas
Rapporteur: Prof. Perla Balbuena, Texas A&M University

3:35pm – 4:15pm  Graphene Growth Mechanism, Dr. Young Hee Lee, Sungkyunkwan University, South Korea

4:15pm – 4:55pm  Controlled Continuous Spinning of Fibres of Single Wall Carbon Nanotubes, Dr. Krzysztof Koziol, University of Cambridge, UK

4:55pm – 5:35pm  Fundamentals Issues on CVD Growth on CNTs, Dr. David Lashmore, Nanocomp Technologies, USA

5:35pm – 5:55pm  Session Summary

6:00pm – 7:45pm  Dinner – Wagon Ride to Creek Side

8:00pm – 11:00pm  Poster-Plus Reception with Open Bar

8:00pm – 11:00pm  Session 3: Poster-Plus Session – Roy Rogers Room
Co-Chairs: Dr. Wade Adams, Rice University & Dr. Avetik Harutyuyan, Honda Research Institute USA, Inc.
Rapporteurs: Dr. Christophe Bichara, Marseille University & Dr. Pavel Nikoleav, Sungkyunkwan University

Sunday, 10 April 2011

7:00am – 9:00am  Breakfast – Main Dining Room

7:00am – 12:00pm  Free Time

12:00pm – 13:00pm  Lunch – Main Dining Room
<table>
<thead>
<tr>
<th>Time</th>
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| 1:15pm – 4:45pm | Session 4 – Carpet Growth Synthesis | Co-Chairs: Dr. Chris Kingston, National Research Council & Dr. Takeshi Saito, National Institute of Advanced Industrial Science and Technology (AIST)  
Rapporteur: Dr. Albert Nasibulin, Aalto University, Finland |
| 1:15pm – 1:55pm | SWNT Amplification: Concepts and Results | Prof. Andrew Barron, Rice University, USA |
| 1:55pm – 2:35pm | Atom-Resolved Imaging and Chirality Control of Carbon Nanotubes | Dr. Hongwei Zhu, Tsinghua University, China |
| 2:35pm – 2:55pm | Break with Refreshments | |
| 2:55pm – 3:35pm | Growth Mechanism of Well Aligned Single-Walled Carbon Nanotubes on Quartz Substrate | Dr. Jie Liu, Duke University, USA |
| 3:35pm – 4:15pm | Growth Mechanism of Single-Walled Carbon Nanotubes from Non-metal Catalyst | Dr. Chang Liu, Chinese Academy of Sciences, China |
| 4:15pm – 4:45pm | Session Summary | |
| 5:45pm – 6:45pm | Dinner – Main Dining Room | |
| 7:00pm – 10:20pm | Session 5: Synthesis | Co-Chairs: Dr. Robert Hauge, Rice University & Dr. Suguru Noda, The University of Tokyo  
Rapporteur: Dr. John Robertson, Cambridge University |
| 7:00pm – 7:40pm | Toward Controllable Growth of Carbon Nanotubes | Dr. Avetik Harutyuyan, Honda Research Institute USA, Inc., USA |
| 7:40pm – 8:20pm | Selective Nucleation of Specific Chiralities of Carbon Nanotubes on Bimetallic Catalysts | Prof. Mohan Sankaran, Case Western Reserve University, USA |
| 8:20pm – 8:40pm | Break with Refreshments | |
| 8:40pm – 9:20pm | Oriented CVD Growth of Carbon Nanotubes with Performed Near Mono-Dispersed Fe3O4 and Fe2Al04 Nanoparticles | Dr. Robert Hauge, Rice University, USA |
| 9:20pm – 10:00pm | Grow Single-walled Carbon Nanotubes from Carbon Nanomaterials | Prof. Jin Zhang, Peking University, China |
| 10:00pm – 10:20pm | Session Summary | |
Monday, 11 April 2011

7:00am – 9:00am  Breakfast – Main Dining Room

9:00am – 1:00pm  Session 6 – In-Situ Measurements and Combinatorial
Co-Chairs:  Prof. Stefan Irle, Nagoya University
Rapporteur:  Dr. Jie Liu, Duke University

9:00am – 9:40am  Complementary In-situ Probes for Graphene and CNT CVD,
Dr. Stephan Hofmann, Cambridge University, UK

9:40am – 10:20am  Studying the Catalytic Growth of Single-Walled Carbon Nanotubes with
In-situ Raman Measurements, Prof. Vincent Jourdain, University of
Montpellier, France

10:20am – 11:00am  Effects of Water on Rapid Growth of Single-Walled Carbon Nanotubes,
Prof. Suguru Noda, The University of Tokyo

11:00am – 11:20am  Break with Refreshments

11:20am – 12:00pm  Understanding Chiral-Selective Growth of Carbon Nanotubes:  In-Situ
Raman Studies of Individual Single Walled Carbon Nanotube Growth,
Dr. Benji Maruyama, Air Force Research Laboratory, USA

12:00pm – 12:40pm  In-situ Studies of Nanotube Nucleation, Growth, and Growth
Termination, Prof. Eric Stach, Purdue University, USA

12:40pm – 1:00pm  Session Summary

1:00pm – 2:00pm  Lunch – Main Dining Room

2:00pm – 6:00pm  Free Time

6:00pm – 7:00pm  Dinner – Main Dining Room

7:15pm – 10:40  Session 7 – Synthesis/Floating Catalyst
Co-Chairs:  Dr. Stephan Hofmann, University of Cambridge &
Dr. Alex Puretzky, Oak Ridge National Laboratory
Rapporteur:  Dr. Kim Bolton, University of Borås, Sweden

7:15pm – 7:55pm  Efficient and Controlled Synthesis of SWCNTs by Enhanced Direct
Injection Pyrolytic Synthesis (eDIPS) Method and their Applications,
Takeshi Saito, National Institute of Advanced Industrial Science &
Technology (AIST), Japan

7:55pm – 8:35pm  Highly Efficient Laser Synthesis of SWCNT from Renewable Carbon, and
Continued Process Development for Large Scale Synthesis of SWCNT by
RF Induction Thermal Plasma, Dr. Prof. Chris Kingston, National Research
Council, Canada

8:35pm – 8:55pm  Break with Refreshments
8:55pm – 9:35pm  High Speed Growth of Chirality Consistent Long, Semiconducting Carbon Nanotubes, Dr. Wei Fei, Tsinghua University, China

9:35pm – 10:15pm  Aerosol Synthesis and Formation Mechanism of Single-Walled Carbon Nanotubes, Dr. Albert Nasibulin, Aalto University, Finland

10:15pm – 10:40pm  Session Summary

Tuesday, 12 April 2011

7:30am – 8:15am  Breakfast – Main Dining Room

8:30am – 10:00am  Summary Session - Meeting Summary and Action Items
Co-Chair: Benji Maruyama, Air Force Research Laboratory
Rapporteur: David Geohegan, Oak Ridge National Laboratory

10:00am  Checkout

10:30am – 2:00pm  Transportation to Airport

11:30am – 12:30pm  Stragglers Lunch – Main Dining Room
Friday, 8 April 2011
7:45pm – 8:45pm

Session 0 Keynote

**Chair:**
Dr. Avetik Harutyuyan,
Honda Research Institute USA, Incorporated
With the discovery of the carbon nanotube now 20 years old, the technology promise has been stated and restated. The limitations and difficulties of moving a new material to production will be discussed along with the description of a partnership pathway that led to carbon nanotubes being integrated with CMOS in a hybrid approach with great success.
Saturday, 9 April 2011
9:15am – 3:20pm

Session 1 – Computational and Modeling 1

Co-Chairs:
Dr. Fei Wei, Tsinghua University and
Prof. Eric Stach, Purdue University

Rapporteur:
Prof. Esko Kauppinen, Helsinki University of Technology
Nucleation and Growth of Carbon Nanotubes as Heterogeneous Catalysis Process

John Robertson and J. Wang,
Engineering Department
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The catalytic growth of carbon nanotubes on transition metal nano-particles from hydrocarbons is analysed in terms of general heterogeneous catalysis. This leads to a volcano plot of catalyst efficiency vs. metal d orbital energy. In this plot, noble metals are inefficient because they poorly dissociate the feedstock, early transition metals are inefficient as they do not release the nanotube and their surface sites become carbon blocked, whilst the optimum catalyst dissociates the feedstock readily while releasing the nanotube.

The model is extended to cap nucleation and helps explain that armchair nanotube growth is favored on flat catalyst surfaces. Based on the chirality selection at nucleation model [1], the interface energy of various carbon caps is calculated on both flat (111) surfaces of Ni, Co and Fe, and also on 54 atom fcc-based clusters of Ni, Co, and Fe. It is found that the flat surface generally has the lower interface energies, and as such, these surfaces favor armchair nanotubes over chiral nanotubes. This explains why it is useful to encourage the catalyst to display a (111) like faceting by control of the ambient atmosphere with weakly bound species.

References

NOTES
We present studies that address different stages of carbon nanotube growth, spanning from the properties affecting the initiation to the parameters affecting the termination of the growth. It is shown that the catalyst particles adapt their shape to the shape of the carbon nanotubes to which they are attached and that this is the case for both pure metal particles and metal-carbides. It is also discussed that the rate of the Ostwald ripening of catalyst particles may depend on the diameters and chiralities of the carbon nanotubes to which they are attached. This may lead to a difference in time scale of the Ostwald ripening of catalyst particles on different nanotubes and thus, a separation in the number of nanotubes of each type being attached to a cluster. The impact of these results on carbon nanotube growth and continued growth is discussed.

NOTES
Selectively growing single wall carbon nanotubes is quite a challenging task and a number of papers recently reported significant steps forward in this direction. An atomic scale understanding of the nanotube – catalyst particle interface and of the way carbon atoms get incorporated in the tube, under the conditions of the experiments is then highly desirable.

Using a carefully parameterized order N tight binding model [1], we could identify the temperature and carbon chemical potential conditions for the nucleation of a tube cap on nickel particles. We could show that the nucleation takes place after the outer Ni layer(s) are saturated with carbon [2, 3]. We also discussed the role of Ni in the healing of defected carbon structures [4].

Recent technical improvements of the algorithm of our tight Grand Canonical Monte Carlo code made it significantly faster and make it now possible to address the tube growth and the defect healing mechanisms, by varying the growth parameters. We will summarize these results and discuss the possible practical implications of our findings.

Starting configuration of a GCMC calculation A tube cap with 84 C atoms de C (grey) is located on a 85 Ni atoms cluster…

After incorporating 138 additional C atoms (in black). Growth conditions (temperature, carbon chemical potential and number of relaxation steps between two successful carbon incorporations) are essential to obtain an acceptable tube structure and possibly keep the cap chirality.

References
Understanding the growth mechanisms of carbon nanotubes requires a combination of in situ diagnostics of the growth process and theoretical modeling. In this talk first we’ll overview our growth kinetic model, that was developed based on in situ time resolved reflectivity measurements and direct optical imaging of vertically aligned carbon nanotube (VANTAs) growth under continuous flow conditions. In the second part of the talk we’ll explore the non-equilibrium effects on growth kinetics and product distributions resulting from pulsed feedstock gas introduction. In the pulsed-CVD approach, short acetylene gas pulses (~200 ms FWHM) of variable flux were injected into a low-pressure, high-velocity flow of Ar/H₂ to limit the pulse broadening due to diffusion. New effects in fast growth kinetics of VANTAs revealed by pulsed growth will be discussed.

QM/MD Simulations of SWCNT Nucleation and Growth with and without Metal Catalysts: Implications for Experiment

Prof. Stephan Irle, Alister J. Page, Ying Wang, HuJun Qian, K. R. S. Chandrakumar, Yasuhiro Ohta, Yoshiko Okamoto, and Keiji Morokuma

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2 Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, 606-8103, Japan
3 Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, USA

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Over the past 5 years we have used quantum chemical molecular dynamics simulations (QM/MD) based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) method to simulate time-resolved elementary atomic-scale processes of single-walled carbon nanotube (SWCNT) nucleation and growth. A wide variety of catalyst nanoparticles (NPs) and sizes were employed (“traditional catalysts” iron [1] and nickel [2] NPs as well as their carbides [3], and “non-traditional catalysts” SiO2 [4], Si, and SiC NPs). In nonequilibrium MD simulations we supplied pure carbon (C atoms and C2 molecules) as well as hydrocarbons (acetylene, ethanol) and made the following observations:

1) Cap nucleation in the absence of hydrogen proceeds by network formation from short linear carbon chains, forming Y-junctions and subsequently pentagons followed by pentagon/hexagon/heptagon growth via ring condensation [1]. The adhesion of carbon to the NPs is important: strong covalent binding like that occurring in non-traditional catalysts will interfere with this mechanism and slow down nucleation and growth [4], while weaker binding such in the case of nickel will promote this mechanism and enhance nucleation and growth [2].

2) The presence of hydrogen will interfere with the nucleation process, and PAH growth may be promoted depending on the H:C ratio of the system.

3) Nanometer-scale transition metal carbides are rather unstable and immediately precipitate carbon to their surface, after which the nucleation mechanism described under 1) ensues [3].

4) Growth of short caps or tube fragments by addition of carbon fragments does not follow orderly screw-dislocation models but occurs in random positions of the tube-catalyst interface. Pentagons/hexagons/heptagons receive high probabilities of formation, and only gradual healing during annealing will result in the final hexagonal carbon network [5].

We propose [6] that short, chirality-specific fragments prepared by conventional organic synthesis such as [n]-cycloparaphenylenes etc. may serve as template to achieve chirality-specific growth, if growth conditions are carefully chosen. The required conditions include slow growth and a minimum number of hydrogen.

References
Chiral symmetry of carbon nanotubes defines most of their basic properties. There are also good reasons to believe that the chiral symmetry (angle $\chi$) determines the speed $K(\chi) \sim \chi$ of growth itself, whenever it is limited by the carbon accretion at the open edge [1]. On the other hand, the chiral type of SWNT is decided at the initial stage of its nucleation, which should be in turn statistically controlled by the energy of the emerging carbon cluster. Energy of its edge in contact with catalyst is similar to graphene edge. It depends on the cut-direction, can be precisely computed, and is shown to vary with the chemical conditions [2] in a particular form of a “chemical phase shift”, $E_{\text{edge}} \sim \cos (\chi + C)$. This suggests the ways to be able, in principle, to grow SWNT with certain chiral preference (while also points to limitations in such tunability). In particular, it may lead to sentient catalyst design for specifically growing armchair tubes, building material for the armchair quantum wire (AQW): if nearly all constituents are truly armchair metallic, the resistivity will be mostly reduced to the intertube junctions in a cable setting. As a fundamental quantity, edge energy is also practical, being definitive for the shapes of nanoribbons, islands, and interfaces in patterning the 2D-electronics [3] or growth of graphene grains [4-5].

References
Saturday, 9 April 2011  
3:35pm – 5:55pm  

Session 2 – Graphene and Metamaterials  

Co-Chairs:  
Dr. Boris Yakobson, Rice University and  
Dr. Anvar Zakhidov, University of Texas at Dallas  

Rapporteur:  
Dr. Perla Balbuena, Texas A&M University
Large area graphene has been synthesized on various metal surfaces such as Ni, Co, and Cu using chemical vapor deposition method, where carbon solubility plays an important role in controlling the number of graphene layers. Although it is still premature to discuss the growth mechanism of graphene, we will present our preliminary data for graphene growth mechanism with several parameters: different gas compositions, temperature, role of the roughness, metal grain boundary, and impurity particles.
The control of the structure of carbon nanotubes (CNT) remains a central issue in rapidly developing science and technology. Of the various structural parameters of nanotubes, namely, diameters, number of walls, length, and chirality, it is the control of chirality which presents significant challenges as well as opportunities.

Synthesis of carbon nanotubes by chemical vapour deposition (CVD) process and its direct assembly into macroscopic entities such as fibres and films is attractive and desirable for a wide range of applications. CVD involves the decomposition of gaseous or volatile carbon compounds in the presence of transition metal catalyst nanoparticles (either formed in situ or prior to the reaction), which nucleate CNT growth under reaction temperatures ranging from 600 °C to over 1000 °C. However controlled nucleation and growth of nanotubes at high temperatures in the floating catalyst has been a massive challenge.

We have been studying the effect of heteroatoms on the growth stability of carbon nanotubes. The reaction parameters have a profound effect on the morphology of the synthesised nanotubes. Furthermore low symmetry catalyst, which is capable of surface reconstruction to form close packed surface layers, which are able to template the graphene layers of the nanotube may open up strategies for a molecular control.

**NOTES**
Nanocomp Corporation is a high volume low-cost commercial manufacturer of CNT yarns and sheets and for some applications has attained high manufacturing and technical readiness levels. Most properties of CNT macrostructures such as large sheets, yarns, as well as their derivative products such as EMI shielding, ESD shielding, thermal transport, electrical cables, and composites depend among other things on the CNT length so understanding the growth mechanism is very important. In this presentation mechanisms of growth rates will be discussed in detail. Among the issues considered include: (1) catalyst formation mechanisms, (2) mass transport of carbon from the gas phase to the growth sites, (3) the dependence of CNT length on temperature, and (4) growth limiting mechanisms. It is suggested that for the very short times, about 10 seconds, required for high temperature CVD growth that CNT length is affected by fuel starvation resulting from poor control over catalyst size distribution.
Saturday, 9 April 2011
8:00pm – 11:00pm

Session 3 – Poster Plus Session
(Alphabetically by Author’s Last Name)

Co-Chairs:
Dr. Wade Adams, Rice University and
Dr. Avetik Harutyuyan, Honda Research Institute USA, Inc.

Rapporteur:
Dr. Christophe Bichara, Marseille University and
Dr. Pavel Nikolaev, Sungkyunkwan University
Encapsulation of Catalyst Nanoparticles during Growth of Single-walled Carbon Nanotubes

Juan C. Burgos and Perla B. Balbuena
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Catalytic chemical vapor deposition (CVD) is recognized as the most selective techniques for nucleation of single-walled carbon nanotubes (SWCNTs) over other carbon structures. It is generally accepted that the metallic nanocatalyst particle plays a fundamental role controlling important structural variables such as diameter and helicity of these tubular structures. However, specific process variables (pressure and temperature), size and shape of the catalyst, catalyst/substrate interactions, and the presence of other inert species (water, nitrogen, or reaction intermediates) may lead to the synthesis of a wide variety of carbon structures that eventually can provoke surface poisoning and encapsulation of the catalyst particle.

We report an analysis derived from reactive classical molecular dynamics simulations\textsuperscript{1-3} that provides new insights about reaction mechanisms and helps identifying some critical variables that define SWCNT growth vs. encapsulation. In regions of phase space where growth is favorable, we characterize the quality and type of structures formed (from single and double-wall tubes to amorphous carbon). Among the main findings this study reveals that high temperatures, low metal-carbon adhesion, and small catalyst particles favor SWCNT growth over graphitic encapsulation. Furthermore, the strength of the substrate/metal catalyst interaction determines specific effects on the catalyst shape and structure of its exposed facets which also define growth vs. encapsulation regimes. Finally, we present preliminary results of the effect of inert substances during the reaction and their influence on the nanotube quality and catalyst poisoning.

References

NOTES
Healing Mechanisms during the Growth of Carbon Nanotubes

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Despite considerable progress in synthesis processes, the detailed microscopic mechanisms involved in the growth of carbon nanostructures are still lacking. In situ experimental atomic scale investigations are very difficult, whereas computer simulations allow such investigations. Nevertheless, whether the employed method is empirical or semiempirical, all final configurations are plagued by a high concentration of atomic-scale defects. These include, but are not limited to; heptagon-pentagon topological defects, adatoms, and atomic vacancies. In the present work, we investigate the healing processes of defective carbon nanotubes at atomic scale. We have developed a tight-binding (TB) model for nickel and carbon that uses Monte Carlo simulations in the grand canonical ensemble to study the formation of carbon structures (graphene and nanotubes) from a metallic substrate[1, 2]. In particular, we have recently discussed the key role played by metallic atoms in the reconstruction of a defected graphene sheet by annealing defects[3]. We use our TB model to study the evolution at finite temperatures of defected nanotubes. Different lengths and diameters of nanotubes have been investigated at various temperatures ranging from 500 to 3000 K. We have also investigated the role played by the metal catalyst and a vapor of carbon atoms in the healing process. The building up of the tube chirality is analyzed and discussed through electron diffraction patterns. The approach proposed here could help identify individual healing mechanisms during growth that produces perfect tube structures and those favoring a definite chirality[4].

References

NOTES
Vertically aligned carbon nanotube forests show varying morphologies on both macro- and micro-scales. These morphologies result from the interplay of the mechanisms of growth and the nature of nanotube interactions. Conversely, it should be possible to learn about these mechanisms and interactions by investigating morphologies. We observe nanotube forest morphologies both ex situ, post growth, and in situ, dynamically, during atmospheric pressure thermal chemical vapor deposition from patterned metal/alumina seed particles using acetylene as the carbon source and assisted by water vapor. In situ observations allow the separate characterization of nucleation, growth and termination phases, and the exploration of the connections between forest morphology, growth parameters, and growth dynamics. We observe both gradual deceleration and sudden termination phases over a wide range of parameters. Forests systematically show different gross morphologies, ranging from uniform to cracked, delaminated, and periodically rippled. The rippling instability in particular gives rise to optical iridescence, which can even be tracked in situ. The local and global morphology is discussed in terms of the balance of forces within the forests including cohesion, adhesion, and stiffness. We propose a simplified model which predicts sudden termination arising from an imbalance in such forces. We show how growth rate differences drive many morphological effects, and show the underlying origins of some of these growth rate differences.

NOTES
Pulsed growth of carbon nanotubes and graphene combined with in situ optical diagnostics allows one to explore effectively the growth kinetics of these nanomaterials, as well as grow them incrementally, which is important for controlling the length in the case of carbon nanotubes and the number of layers in the case of graphene. In this poster we’ll present our latest results on pulsed growth of vertically aligned carbon nanotubes (VANTAs). In this study we explored both the temperature and the feedstock gas pulsing, using fast laser heating and pulsed valve gas introduction, respectively. By doing this we were able to grow VANTAs incrementally in wide range of the partial feedstock gas concentrations. New interesting results obtained using this approach will be discussed.


NOTES
Can the Substrate Assist the Nanoparticle Template Effect on the SWCNT Growth?

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An important connection exists between chirality of single-walled carbon nanotubes (SWCNTs) and their optical and electrical properties. Such properties are outstanding in comparison to those of other materials, but lack of chirality control during SWCNT synthesis is an obstacle for the widespread application of SWCNTs. First-principles density functional theory (DFT) calculations show that an unsupported catalyst would undergo an inverse template effect with the nanotube structure, while classical MD calculations suggest that certain catalyst/substrate strengths may induce some degree of control of the catalyst structure during SWCNT growth. Accordingly, we present preliminary studies of the behavior of iron and cobalt nanoparticles on realistic substrates such as cristobalite to characterize the supported catalyst at the reaction conditions. Classical MD simulations allow studying the nanoparticle structure, facet orientation, and atomic mobility at the reaction temperatures. Such calculations suggest that the extent of the template effect of the substrate depends on the nature of the metal catalyst. Force field parameters for MD simulations are derived from DFT calculations studying the interaction of iron, cobalt, carbon and hybrid structures with the substrate of interest. DFT calculations give additional insights on catalyst-substrate interactions such as electronic changes in the metal, variations on the metal/substrate interactions upon carbon adsorption, as well as the competition of carbon/metal, carbon/substrate and metal/substrate relevant to the growth mechanism of vertical and horizontal SWCNTs. Finally, we study the effect of varying the metal/substrate interaction on the appearance of carbon species (e.g. C, C₂, and C₃) during SWCNT growth, and its potential influence on the formation of specific chiralities.

Reference

NOTES
Alkyne-Assisted Carbon Nanotube Synthesis Reveals Pathways to Clean and Efficient Production

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While carbon nanotube (CNT) synthesis by thermal chemical vapor deposition (CVD) can be achieved using myriad combinations of carbon-containing precursors and nanoparticle catalysts, there is relatively little mechanistic understanding of how the precursor is incorporated into a growing CNT. Identification of efficient CNT growth pathways is essential for cost-effective scaling of CNT synthesis for commercial applications and for understanding of the potential environmental impacts of CNT manufacturing. Using a custom-built cold-wall apparatus, where a Fe/Al2O3 catalyst-coated silicon substrate is locally heated, we test gas species by direct injection without preheating. This technique enables precise quantification of the performance of various hydrocarbon feedstocks, in relation to the growth rate and yield of CNTs. We identify that thermal decomposition of C2H4/H2 creates a mixture of species including various alkanes, alkenes, and alkynes, as well as polycyclic aromatic hydrocarbons (PAHs). These analyses, in concert with real-time measurements of growth kinetics via the forest height, reveal a positive correlation between growth rate and the relative abundance of specific molecules. By directly delivering select species with the normal growth gases C2H4/H2 in the absence of preheating, we identify that alkynes, including acetylene, methyl acetylene, and vinyl acetylene, selectively enhance forest growth (rate and ultimate height) and are thereby a family of efficient precursors for CNT manufacturing. We also show molecules that have previously been proposed as key precursors to CNT formation, such as methane and benzene, exhibit low conversion efficiencies in our system. Further, ethylene is required for enhanced CNT growth in our system, suggesting that the alkyne and ethylene may react in concert at the metal catalyst. This suggests a distinct CNT formation mechanism where the chemical precursors may be intact during C–C bond formation, such as in polymerization reactions, challenging the widely accepted hypothesis that precursors completely dissociate into C (or C2) units before “precipitating” from the metal. While unprecedented in the CNT literature, this mechanism has close analogues in the homogeneous metal catalysis literature, where new C–C bonds form via cyclic intermediates (e.g., between an alkene and an alkyne). Armed with these mechanistic insights, we form high-purity CNTs rapidly with a 15-fold improvement in yield, a 50% reduction in energetic costs, and order of magnitude reduction in unwanted byproduct formation (e.g., toxic and smog-forming chemicals and greenhouse gases).

NOTES
While many studies have made great progress in explaining the various processes involved in the growth of vertically aligned carbon nanotube (CNT) forests, there remains a void in understanding how the dynamics of catalyst nanoparticle formation influence the nucleation of small-diameter CNTs. In order to manufacture forests with uniform attributes (e.g., diameter, alignment density) we must decipher the origin of temporal and spatial variations in the size and shape of the catalyst and CNTs.

We combine in situ small-angle X-ray scattering (SAXS) and ex situ scattering and absorption studies with complementary ex situ TEM and AFM analyses to elucidate the early and late stages of collective CNT growth. A cold-wall chemical vapor deposition (CVD) apparatus is mounted directly in the G1 beamline at the Cornell High Energy Synchrotron Source (CHESS), enabling real-time grazing incidence (GISAXS) and transmission (SAXS,) scattering measurements of the thin-film catalyst during annealing, as well as CNTs during nucleation and growth. This non-destructive technique allows sampling of statistically significant populations of nanostructures (10^10) without subjecting the material to damaging electron beams or requiring low pressures, such as in TEM and XPS.

Starting with a thin film of Fe and Al2O3 on Si, we observe rapid dewetting of the Fe film and agglomeration followed by slow coarsening. During rapid heating (~100 °C sec⁻¹), we observe that the film agglomerates at different temperatures depending on the gas chemistry; 550 °C in H2/He and 400 °C in C2H4/H2/He. The particle scattering signature becomes stable in H2/He after the initial transient until C2H4 is introduced, and an average of 15 sec elapses before the CNT signature appears. Conversely, the presence of C2H4 during annealing induces nearly simultaneous particle formation and CNT nucleation. By fitting the particle scattering pattern with a model that describes the particles as a normally distributed population of truncated spheres, we quantify the evolution of particle size and spacing during annealing. Similar modeling of the CNTs as hollow cylinders shows that the mean diameter and variance decrease rapidly, as larger diameters overwhelm the population after the initial appearance of the CNT signature. Quantification of CNT alignment reveals that the forest self-organizes within seconds, showing a transition from tangled to vertically aligned CNTs, which represents the well known “crust” at the top of a CNT forest. We corroborate this initial transient with an increase in CNT density, as measured by ex situ X-ray absorption. After the initial density increase, a slow decay in density proceeds eventually toward abrupt self-termination of growth. Further, we investigate the effects of adding oxidizing agents (i.e., H2O, C2H5OH) to the gas atmosphere on the dynamics of particle formation and CNT growth, as well as the effects of varying both catalyst and support layer thicknesses.

Our findings reveal low-temperature limits for particle formation and CNT nucleation under particular process conditions, and show that significant CNT diameter changes can occur quickly during nucleation and self-organization of CNT forests. Knowledge of these intrinsically rapid processes is vital to improved precision in control of CNT structure (chirality, number of walls), and to synthesis of high-density arrays of long, straight CNTs.

NOTES
Half-Centimeter-Tall Single-Walled Carbon Nanotubes
Growing Taller at Lower Temperatures More Slowly

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We recently reported simple condition for rapid growth of millimeter-tall single-walled carbon nanotubes (SWCNTs) using C$_2$H$_2$/Ar without additives such as H$_2$O and H$_2$. The essence for such growth was to keep moderate C$_2$H$_2$ pressure so as not to kill the catalysts. But a difficult problem, i.e. growth termination due to catalyst coarsening, became evident. This time, we systematically studied SWCNT growth at a range of temperatures and C$_2$H$_2$ pressures. Lower temperature led to lower "moderate" C$_2$H$_2$ pressure and lower growth rate, but even lower coarsening rate. And 4.5-millimeter-tall single-walled carbon nanotubes were grown in 4.5 h at 700 ºC.

NOTES
Aerosol-assisted Floating Catalyst Chemical Vapor Deposition Method for Single-Walled Carbon Nanotube Growth

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As an alternative to template based super growth, the floating catalyst method has its advantages for bulk production for single-walled carbon nanotube (SWCNT) growth. We studied the properties and production yield of SWCNTs synthesized in an aerosol assisted CVD (AACVD) reactor at atmospheric pressure using ethanol-ferrocene precursor. Optimization is based on measurement of yield, Raman spectra, studying topography by SEM and TEM and the feedback of these results to input parameters: flow rate, temperature, precursor feed rate, concentration of catalyst in the carbon source and the geometry of the CVD furnace. In the poster we will analyze the role of these parameters on the reaction kinetics and eventually on the produced nanotubes. The growth and properties of SWCNTs produced with AACVD will be compared to that of the more complicated water-assisted, aluminum-supported iron catalyst template method.

NOTES
In this contribution, we demonstrate the use of NH3 to control the production of largediameter single-walled carbon nanotubes (SWCNTs) with a narrow distribution of chiral structure. SWCNTs were synthesized in a gas-phase floating catalyst CVD reactor where iron nanoparticles derived from ferrocene vapor decomposition act as catalyst in a 400 cm3/min flow of carbon monoxide (CO) and 2 cm3/min of carbon dioxide (CO2) at 880 °C. As an etching agent, small amounts of NH3 were introduced into the reaction to amend the nanotube structure. Chirality distribution analysis of the SWCNT products was performed using electron diffraction technique which allows direct \((n, m)\) measurements on individual SWCNTs. It is found that chiralities of carbon nanotubes produced in presence of 500 ppm NH3 at 880 °C are narrowly distributed around the major semiconducting \((13,12)\) nanotube with over 90% of SWCNTs having large chiral angles in the range 20°-30°, and nearly 50% in the range 27°-29°. The developed synthesis process enables chiral-selective growth at high temperature for structurally stable carbon nanotubes with large diameters.

**NOTES**
Flexible High-Performance Carbon Nanotube Integrated Circuits

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Carbon nanotube thin-film transistors are expected to enable the fabrication of high-performance, flexible and transparent devices using relatively simple techniques. However, as-grown nanotube networks usually contain both metallic and semiconducting nanotubes, which leads to a trade-off between charge-carrier mobility (which increases with greater metallic tube content) and on/off ratio (which decreases). Many approaches to separating metallic nanotubes from semiconducting nanotubes have been investigated, but most lead to contamination and shortening of the nanotubes, thus reducing performance. Here, we report the fabrication of high-performance thin-film transistors and integrated circuits on flexible and transparent substrates using floating-catalyst chemical vapour deposition followed by a simple gas-phase filtration and transfer process¹. The resulting nanotube network has a well-controlled density and a unique morphology, consisting of long (about 10 µm) nanotubes connected by low resistance Y-shaped junctions. The transistors simultaneously demonstrate a mobility of 35 cm² V⁻¹ s⁻¹ and an on/off ratio of 6 x 10⁶. We also demonstrate flexible integrated circuits including a 21-stage ring oscillator and master–slave delay flip-flops that are capable of sequential logic. Our fabrication procedure should prove to be scalable, for example, by using high-throughput printing techniques.

Reference

NOTES
Targeting at mass production of sub-millimeter-long carbon nanotubes (CNTs), we applied the rapid growth method of vertically aligned SWCNTs on substrates to fluidized-bed chemical vapor deposition (FB-CVD) using ceramic beads as catalyst supports. This time, we applied various catalyst preparation methods to enrich the variety of CNTs. Sputter-deposited catalysts yielded over 0.5-mm-long, over 95wt%-pure single-walled CNTs at a yield over 65% and solution-based catalysts yielded 0.2-mm-long multi-walled CNTs, both in a batch operation. Catalysts by FB-CVD yielded over 0.4-mm-long, about 99wt%-pure few-walled CNTs at a yield over 70% in semi-continuous operation. Mass-production of various submillimeter-long CNTs is now underway.

NOTES
High Quality Single Walled Nanotubes for Superacid Processing from Aerosol Assisted Chemical Vapor Deposition

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Synthesis of specialty CNTs aims at the fabrication of high quality and defect-free nanotubes for devices, thin films and single molecule applications. Conversely, mass production is needed for bulk applications, in which high yield is sought-out, often to the detriment of quality. In this work, we explore the production of high quality and bulk quantity of SWNTs of sufficiently high quality to permit processing by dissolution in acid solvents. We used aerosol assisted CVD (AACVD) and produced high purity SWNTs as shown by Raman and TGA analysis. The ensuing material was tested for solubility in chlorosulfonic and sulfuric acid, in order to assess its suitability neat CNT fiber spinning and film casting. The results show how defect density is a critical parameter for acid dissolution. High defect CNT do not dissolve in superacids. This work is promising for the development of a scale-lab reactor able to produce bulk quantity defect-free SWNTs suitable for spinning processes.

NOTES
Multifunctional Free-Standing Single-Walled Carbon Nanotube Films

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The unique properties of single-walled carbon nanotube (SWNT) films, such as high porosity and specific surface area, low density, high ratio of optical transmittance to sheet resistance, high thermal conductivity and chemical sensitivity, and tunable metallic and semiconducting properties, open up a new avenue for a wide range of applications. Free-standing films offer a unique form factor for novel applications. We report here a simple and rapid method to prepare multifunctional free-standing SWNT films with thicknesses from a sub-monolayer to a few micrometres having outstanding properties for a broad range of exceptionally performing devices. We have fabricated state-of-the-art key components for nanoparticle filtration with a figure of merit of 147 Pa⁻¹, transparent and conductive electrodes with a sheet resistance of 84 Ω/□ and a transmittance of 90%, electrochemical sensors with extremely low detection limits below 100 nM, and polymer-free saturable absorbers for ultrafast femtosecond lasers. Furthermore, the films performed as the main components in gas flowmeters, gas heaters and thermoacoustic loudspeakers.

Reference
Nasibulin et al. ASC NANO. Publication date (Web): March 1, 2011. DOI: 10.1021/nn200338r

NOTES
An approach to obtaining the optimum single walled carbon nanotube (SWNT) nucleation and growth conditions for a particular catalyst system has been investigated. Using a Co-Fe (50:50) mixed metal catalyst system; SWNTs were grown at 900 °C with a feedstock of CH₄:H₂ in a 50:50 ratio. The number of SWNTs grown per unit area was found by AFM to be much lower than the number of catalyst particles. After quantification by SEM the samples were subjected to secondary growth, using a range of CH₄:H₂ ratios. It was found that for the Co-Fe (50:50) catalyst the highest nucleation / growth occurred with a CH₄:H₂ ratio of 40:60. The optimum condition resulted in > 10x increase in SWNT nucleation and hence catalyst activation as compared to off-optimum conditions.
The ability of non-metal “catalysts”, notably SiO$_2$, to assist the nucleation and growth of single-walled carbon nanotubes (SWNTs) via chemical vapor decomposition (CVD) has recently been established experimentally (see [1] and references therein). A number of different proposals regarding the mechanism of SWNT nucleation and growth on SiO$_2$ have since been put forth [1-3]. Most recently, QM/MD simulations [3] and experiments [4] have indicated that SWNT nucleation on SiO$_2$ proceeds via a vapor-solid-solid (VSS) mechanism. In addition, these QM/MD simulations indicate that SWNT nucleation on SiO$_2$ features an intermediate SiO$_2$-core/SiC-shell structure in the solid phase. The presence of such an amorphous SiC phase leads to the possibility of catalyst-independent SWNT nucleation mechanisms for Si-based “catalysts”. While such catalyst-independence is established for transition metal catalysts (in the form of the VLS mechanism), it has not yet been established in the context of Si-based “catalysts”. In this work we will review our recent QM/MD simulations of SWNT nucleation on SiO$_2$, SiC and Si nanoparticles. In particular, we will demonstrate that, in each case, SWNT nucleation occurs via a VSS mechanism in which the nanoparticle remains in the solid phase. In particular, it is apparent that SWNT nucleation from both SiO$_2$ and Si “catalysts” occur via an amorphous SiC intermediate structure that is analogous to nanoparticle SiC itself.

References
Vertically aligned carbon nanotube (VACNT) carpets were grown by thermal chemical vapor deposition (CVD). The effect of substrate orientation, carrier gas, carbon precursor, buffer layer, and catalyst composition on carpet height and morphology, tube density, and tube quality was investigated using ex-situ Raman spectroscopy and electron microscopy. Our results show that changes in VACNT carpets are related to changes in catalyst morphology brought about by termination mechanisms, such as Ostwald ripening and sub-surface diffusion [1]. The understanding of parameters that influence the growth of VACNTs coupled with insight on growth termination mechanisms will guide future efforts on the rational design of catalysts for controlled carpet growth.

Reference
In-Situ Raman Spectroscopy Study of Catalyst Lifetimes in Single-Walled Carbon Nanotubes Grown from Iron and Nickel

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We have developed a unique system that incorporates a chemical vapor deposition (CVD) chamber for single-walled carbon nanotube (SWNT) growth with a micro-Raman spectrometer. Growth occurs when catalyst nanoparticles deposited on thermally isolated silicon islands are irradiated with the micro-Raman excitation laser (532 nm), which also serves as a localized heat source. Automated control of substrate temperature, position, feed gas composition, and chamber pressure enable rapid real-time exploration of SWNT growth parameter space. In this study we use thin (2-3 nm) films of nickel and iron which form nanoparticles upon exposure to the Raman laser under typical CVD conditions. Raman spectra in the D and G band region are acquired continuously during SWNT growth, and the temporal evolution of the G band is plotted in the form of growth curves. The in-situ Raman growth curves are fitted by a self-exhausting exponential equation, from which we obtain the reaction time constants (or catalyst lifetimes) for SWNT growth. We compare the catalyst lifetimes of iron and nickel catalysts, and will discuss the origins of these differences.

NOTES
In this work, we present our progress towards growing single-walled carbon nanotubes with narrow property distributions suitable for use in optoelectronic devices. The performance of optoelectronic devices based on carbon nanotubes is often limited by the heterogeneity of the starting nanotube material. Better control over the average diameter and the diameter distribution is of particular interest. While significant progress has been made in this area for smaller diameter nanotubes, much less work has been done to improve the properties of large diameter nanotubes. We employ low pressure chemical vapor deposition to grow large diameter, vertically-aligned single-walled carbon nanotubes from solution-synthesized iron oxide nanoparticles in order to control the diameter and diameter distribution of the resulting nanotubes. The availability of a greater variety of narrow diameter distribution nanotubes will expand the performance envelope and improve the flexibility of using carbon nanotubes in optoelectronic devices.

NOTES
QM/MD Simulations of CNT Nucleation on Iron Nanoparticles Using Acetylene Feedstock

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The growth of carbon nanotubes by catalytic chemical vapor deposition (CVD) is of great interest for many applications, although the growth mechanism is still unclear. Since iron is known to be highly effective for the CNT growth in the CCVD process, and C_2H_2 is an excellent carbon source for high CNT yield, we performed quantum chemical molecular dynamics (QM/MD) simulations to investigate the self-assembly process of carbon nanotubes from acetylene molecules on Fe_{38} and Fe_{55} particles.

We found that one of the H atoms of C_2H_2 transfers to the iron particle or other C_2H_2 units, prior to oligomerization of C_2H_n units to longer chains. It thus appears that oligomerization is initiated by the C_2H radical. In our simulations we use a relatively high concentration of acetylene on the nanoparticles. In this situation, oligomerization proceeds at a faster rate than hydrogen abstraction, and the developing carbon structures C_yH_x remain hydrogenated. Compared to simulations with carbon-only source (C_2 or atomic carbon), the presence of hydrogen atoms prohibits ring-condensation and prevents fast sp^2 carbon network growth. Nevertheless, after about 100 ps, network growth does set in, but involves structures different from those observed in the carbon-only simulations. For instance, we find that hexagons are similarly likely candidates for first carbon ring structures as pentagons, different from the carbon-only simulations where pentagon formation from Y-junctions initiates ring network generation [1]. In order to incorporate the effect of the slower H abstraction, we removed two H atoms randomly from the cluster on the metal particle when a C_2H_2 was added. In ~500 ps combined Monte-Carlo Molecular Dynamics simulations, we found that at a low H:C ratio, a pentagon-rich cap-like structure is formed (structure a). If the H:C ratio is higher, ‘standing wall’ structures were more likely formed (structure b). It seems possible that such several graphene-like sheets on a particle (structure c) may coalesce to form the open tube, similar to the mechanism proposed by Eres et al. [2].

NOTES

References
We will report results from the CVD growth of CNTs with the preformed monodispersed nanoparticle catalysts: iron oxide and iron-aluminum oxide. Comparisons between CNTs grown by iron oxide and iron-aluminum oxide nanoparticles with regard to the diameters, the number of walls, as well as the quality will be given.

NOTES
Sunday, 10 April 2011
1:15pm – 4:45pm

Session 4 – Carpet Growth Synthesis

Co-Chairs:
Dr. Chris Kingston, National Research Council and
Dr. Takeshi Saito, National Institute of Advanced
Industrial Science and Technology (AIST)

Rapporteur:
Dr. Albert Nasibulin, Aalto University
Understanding the relationship of the identity of a metal catalyst to the activation/growth of carbon nanotubes as well as the control over the diameter/chirality of the nanotubes is an important step in being able to optimize and control tube growth. We have concentrated in understanding the amplification process, first demonstrated in the Barron Group, with regard to the parameter that will allow for the successful synthesis of large quantities of specific nanotubes. Single walled carbon nanotubes (SWNTs) seeds grown using nanoparticles on spin-on-glass were subjected to a range of methane:hydrogen ratios at 900 °C. Resulting in a maximum amplification with CH4:H2 ratio of 80:20. Amplification is further enhanced at 800 °C, compared with etching at 1000 °C. Amplification of SWNTs is in equilibrium with etching; higher carbon feedstock pressure and decreased temperature increase the rate of amplification, the converse increases etching.

NOTES
Atomic configurations of individual carbon nanotubes have been obtained by high-resolution transmission electron microscopy with atomic sensitivity. A structural reconstruction is carried out by Fourier-filtered analysis of Moiré patterns, and it is now possible to acquire the carbon honeycomb lattice images through the entire periphery of individual nanotubes. This visualization technique provides supplementary access in nanoscale characterizations by combining with other techniques. Based on this, a strategy to control the chirality of single-walled carbon nanotubes by chemical vapor deposition is presented. Atomic-resolution imaging of nucleation points makes it possible to explore the structural correlation between the catalysts and the corresponding nanotubes. It is found that the angle of step edge on (111) plane of the catalytic particle with respect to nanotube growth direction is the key factor in determining the tube chirality. The result shows the potential in promoting some experimental advances in synthesis of nanotubes with the desired structure. Similar studies could be extended and used to obtain a more detailed understanding of the role of crystal structure in other catalyst systems.
Growth Mechanism of Well Aligned Single-Walled Carbon Nanotubes on Quartz Substrate

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Even though the devices made from individual nanotubes have shown outstanding performances such as high mobility, high current, high thermal conductivity, good chemical and mechanical stability, the high hope for the next generation of carbon nanotube based electronics is hampered by several major problems. Among them are the lack of reliable methods to control the alignment and position of nanotubes as well as and perhaps most problematically, the simultaneous growth of nanotubes with different chiralities, yielding random mixtures of metallic and semiconducting nanotubes. Even though the post-growth separation of metallic from semiconducting SWNTs have made good progress, the alignment and assembly of the separated nanotubes into devices are still challenging and not suitable for large scale fabrication. Consequently, a method that can directly produce well aligned arrays of pure semiconducting nanotubes is thought to be the ideal choice for large scale fabrication of nanotubes FETs. In this talk, we show that such a method is not a dream. We developed a chemical vapor deposition (CVD) approach, which allows selective growth of high-density arrays of well-aligned SWNTs with almost exclusively semiconducting SWNTs. Analysis of the samples shows that at least over 95% of nanotubes are semiconducting. This method demonstrates great promise to solve two of the most difficult problems which limit application of carbon nanotubes in nanoelectronics – the coexistence of metallic and semiconducting nanotubes in samples produced by most, if not all, growth methods and the simultaneous control of the alignment of the nanotubes.

NOTES
Metal, especially transition metal are usually used as the catalyst for growing CNTs. We have recently found that non-metal catalyst, such as SiO$_x$ can also catalyze the growth of SWNTs effectively [1]. Due to the much slower growth velocity of SWNTs from SiO$_x$ nanoparticles, a direct length-controlled growth of SWNTs was achieved [2]. However, how the SiO$_x$ catalyst functions is still unclear. A proper understanding on the growth mechanism of these non-metal catalysts will facilitate the optimization of the catalytic growth systems and facilitate the structural control of SWNTs. We investigated the nucleation and growth mechanism of SWNTs from SiO$_x$ by comparing the functions of Si and SiO$_x$ nanoparticles in both chemical vapor deposition (CVD) and \textit{in situ} transmission electron microscopy (TEM) growth processes. The results of experiments and calculations indicate that SiO$_x$ nanoparticle catalyze the growth of CNTs via a vapor-solid-solid (VSS) mechanism, and the function of oxygen in SiO$_x$ is to provide an enhanced hydrocarbon adsorption compared to pure Si. We propose that both particle size and composition of the catalyst are important for the growth of CNTs [3].

References
[1] BL Liu, WC Ren, LB Gao, SS Li, SF Pei, C Liu, CB Jiang, HM Cheng, \textit{JACS} 2009, 131: 2082

NOTES
Sunday, 10 April 2011
7:00pm – 10:20pm

Session 5 – Synthesis

Co-Chairs:
Dr. Robert Hauge, Rice University and
Dr. Suguru Noda, The University of Tokyo

Rapporteur:
Dr. John Robertson, Cambridge University
The thermodynamics of various nucleation mechanisms of carbon nanotubes on metal clusters and their implications for the controllable growth are analyzed. Despite the variety of the nucleation models, all suggested mechanisms include a common step such as formation of carbon nanoclusters on the metal surface. On the other hand, there are conceptual differences between these mechanisms about the emerging paths of the carbon atoms on the metal surface and the state of metal. These analyses helped to reveal the favorable terms for the controllable growth of carbon nanotubes and can be extended on recent results [1] on preferential growth of SWCNTs with metallic conductivity. We show that the preferential growth of metallic tube chiralities can be understood in the terms of its epitaxial relationship [2] with the corresponding facet structure of the catalyst particle. More specifically, (111) facet structure of iron catalyst can be liable for nucleation of metallic nanotube.

References
Typical growth methods for carbon nanotubes rely on nanoscale metal particles to catalyze dissociation of the carbon feedstock and support nanotube nucleation and growth. Recent theoretical [1,2] and experimental [3,4] efforts have shown that the structure of the metal catalysts helps determine the chirality of as-grown nanotubes. In this talk, I will present our efforts to understand how the catalyst structure influences nanotube chirality and our approach to enriching the as-grown chirality distribution by engineering compositionally- and structurally-controlled bimetallic catalysts [4].

References
Oriented CVD Growth of Carbon Nanotubes with Preformed Near Mono-Dispersed Fe3O4 and Fe2AlO4 Nanoparticles

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Carbon nanotubes, single wall and few wall, have been grown as carpets with oriented CVD. The production and characterization of near monodispersed catalyst particles of different sizes will be given. A comparison of growth with iron only and iron-aluminum oxide particles has been investigated for different sized particles. Observations regarding the growth-lifetime of catalyst particles, correlations between the diameters of particles and nanotubes, number of walls and the in situ functionalization of nanotubes during and after growth will be given.

Comparison of carpet height from two different catalysts

![Graph showing comparison of carpet height from two different catalysts](image)

NOTES
How to grow single-walled carbon nanotubes (SWNTs) with controlled diameter, chirality, and metallic/semiconducting property, is still in its infancy. There are many research groups focused on this topic. We will discuss herein the growth of SWNTs from carbon nanomaterials, such as tetramantanes molecules, opened C_{60}, carbon nanohore, and open end SWNTs. We suggest this CVD growth process will follow the vapor-solid (VS) or vapor-solid-solid (VSS) mechanism. In which the carbon nanomaterials were not melted, they might be possible to control the structure of carbon nanotubes in principle.
Monday, 11 April 2011
9:00am – 1:00pm

Session 6 – In-Situ Measurements and Combinatorial

Co-Chairs:
Prof. Stefan Irle, Nagoya University and

Rapporteur:
Dr. Jie Liu, Duke University
The understanding of the role of transition metal templates in the chemical vapour deposition (CVD) of graphene and carbon nanotubes remains incomplete and more direct experimental data is required to serve as basis for detailed growth modelling. We present a combination of high-pressure X-ray photoelectron spectroscopy (XPS), environmental transmission electron microscopy (ETEM), and in-situ X-ray diffraction (XRD) experiments comparing the behaviour of thick (>100 nm), poly-crystalline and nano-particulate catalysts during hydrocarbon exposure at temperatures ranging from 300-900°C, and during cooling to room temperature. We further compare graphene precipitation based on a solid C source to growth via CVD. Our complementary approach of integral and point probing allows detailed insights into transient states and size- and solubility-dependent mechanisms and shows that the often suggested simplistic surface adsorption vs precipitation picture is inadequate.
We investigated the CCVD growth of SWNT using in situ Raman measurements for different growth conditions and catalyst-precursor couples [1]. During SWNT growth, Raman and HRTEM evidence the by-formation of disordered carbon nanostructures around catalyst nanoparticles. Their proportion depends on the kinetic equilibrium between the supply of carbon atoms from the gas phase and their surface mobility. Radial Breathing Modes were also exploited to monitor the distribution of SWNT diameter. Most noticeably, the growth of small diameter nanotubes is promoted in a narrow domain of growth parameters. Two-steps growth experiments were performed to identify the processes responsible for this [2].

References

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Effects of Water on Rapid Growth of Single-Walled Carbon Nanotubes

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Millimeter-tall vertically aligned single-walled carbon nanotubes (SWCNTs) were grown in 10-15 min by chemical vapor deposition from C$_2$H$_2$/Ar with or without water addition. The key for millimeter-scale growth of SWCNTs is to limit the C$_2$H$_2$ supply to below a certain concentration to retain an active catalyst. Water prolongs the catalyst lifetime under excess C$_2$H$_2$ supply whereas it deactivates small catalyst particles and degrades the quality of SWCNTs at the same time. We also observed a gradual increase in the diameter of SWCNTs with growth because of the coarsening of catalyst particles and found that water had no effect on this phenomenon. The growth of millimeter-tall SWCNTs from a simple C$_2$H$_2$/Ar gas without water addition reveals the mysterious role of water and will open a practical route for the large-scale production of SWCNTs.

NOTES
In-situ Raman scattering has been used to obtain growth kinetics of individual single-walled carbon nanotubes (SWNTs) using a custom designed cold-wall chemical vapor deposition (CVD) chamber coupled to a Raman spectrometer. Raman spectra are collected during SWNT growth and plots of the G band area versus time are fitted to self-exhausting exponential curves, from which we obtain SWNT growth rates and catalyst lifetimes (time constant). Chiral index assignments are made for several individual SWNTs via analysis of the radial breathing modes. The growth rate of the SWNTs is shown to be proportional to the chiral angle. In addition we find a positive correlation between SWNT length (obtained from SEM analysis) and the growth rate. This confirms the model put forth by Ding et al. [1] which links SWNT growth rate to the chiral angle. A growth model based on our results illuminates an as-yet unexplained distribution in the chiral yield of typical CVD-grown nanotubes as being driven by chiral-selective growth kinetics.

Reference

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In order for carbon nanotubes to find widespread application, we must have a deeper understanding of the mechanisms by which they nucleate, growth and cease growth, in an effort to fully control the resulting structures. Here we will describe how we can exploit the unique capabilities of in-situ environmental cell transmission electron microscopy to observe multiple aspects of these processes. With this approach we can directly visualize how the catalysts that mediate nanotube growth respond to various changes in the growth environment, and correlate these changes with the resulting nanotube structures.

In the first part of the presentation, we will investigate how dynamic changes in the catalyst morphology are correlated with the termination of growth in vertically aligned SWNT arrays. In particular, we have investigate how the processes of catalyst coarsening, Ostwald ripening and diffusion into the catalyst support can lead to growth termination, and we will describe how changes in the growth feedstock – in particular the incorporation of controlled amounts of water vapor – can alter the catalyst evolution.

In the second portion of the presentation, we will describe how altering other aspects of the growth feedstock – in this case the carrier gas, in combination with the water vapor content – can not only affect catalyst morphological evolution, but can also significantly bias the chiral distribution of the resulting nanotubes. We will correlate the changes in growth ambient with a faceting / defacting transition, as well as a resulting change in the rate of Ostwald ripening.
Monday, 11 April 2011
7:15pm – 10:40pm

Session 7 – Synthesis/Floating Catalyst

Co-Chairs:
Dr. Stephan Hofmann, Cambridge University and Dr. Alex Puretzky, Oak Ridge National Laboratory

Rapporteur:
Dr. Kim Bolton, University of Borås, Sweden
Efficient and Controlled Synthesis of SWCNTs by Enhanced Direct Injection Pyrolytic Synthesis (eDIPS) Method and their Applications

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The controllability of the tube diameter would be the first step to the chirality-controlled synthesis of SWCNTs. Recently we have paved the new way for diameter-controlled synthesis of SWCNTs by the original floating catalyst CVD designated as the enhanced direct injection pyrolytic synthesis (eDIPS) method [1]. Our results of TEM observation and optical absorption spectroscopy suggested that the mean diameter of SWCNTs synthesized by eDIPS method was selectively tuned at any point within the range of ca. 1.0 nm to 2.0 nm [2]. Furthermore the photoluminescence mapping showed the dominant chirality of (7,5) in the narrower SWCNTs synthesized by this method [3]. By analyses of the exhaust gas, the sp$^2$ C$_2$ species, C$_2$H$_3$/C$_2$H$_4$, has been found as a key precursor for the efficient growth of SWCNTs by CVD from hydrocarbons [4, 5]. Additionally we will present our recent progress of application researches using eDIPS SWCNTs, such as structural [6] and property separations for electronic devices.

References

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We have successfully synthesized very high purity SWCNT from BioChar, a biologically renewable carbon source produced as a co-product of the fast pyrolysis of cellulosic biomass for BioOil production, using our laser vaporization process. Extensive characterization indicates that the Bio-SWCNT is composed predominantly of nanotubes with relatively little amorphous or impurity carbon content. Full details of the synthesis and characterization of this exceptional quality SWCNT material will be presented.

We have also developed a large-scale process for the synthesis of SWCNT based on RF induction thermal plasma technology that is capable of producing SWCNT at a rate of a few kilograms per day. Here we present the results of ongoing hardware and process development aimed at optimizing SWCNT purity, process yield, and system efficiency.
The gas flow-directed growth method used here is effective to obtain semiconducting SWNTs/DWNT/TWNTs of uniform structure and as long as 400mm. Adding 0.43% water was effective in increasing the growth rate of centimeters long CNTs to 80-90 μm/s. This was five times faster than without the addition of water. The chiral index of the long CNTs are consistent within centimeter long distance. The chiral angle distributions of the centimeter long CNTs are apparently between 20° and 30°, indicating the extremely high selectivity of CNTs with definite structure. The mechanism of CNTs fast growth with addition of water is discussed. This method also implies an effective method to selectively grow semiconducting CNTs. Concentric shells with controlled electronic properties also bring the opportunity to construct co-axial devices. The long range homogenous CNTs structure could be a platform to make high-density, reproducible nanodevices as well as integrated logic circuits that can be assembled on a single nanotube.

**NOTES**
Here, we report the investigation of the formation mechanism of single-walled carbon nanotubes (CNTs) by two different aerosol (catalyst floating) CVD methods based on physical evaporation-condensation production and chemical synthesis of catalyst particles. In order to investigate the processes occurring in the reactor we have carried out in situ sampling from different locations in the reactor. The growth rate constant can be described by an Arrhenius dependence with an activation energy attributed to the carbon diffusion in solid iron particles. On the basis of parametric investigations and in situ sampling experiments the mechanisms of CNT formation are proposed.

NOTES
Tuesday, 12 April 2011
8:30am – 10:00am

Summary Session – Meeting Summary and Action Items

Co-Chair:
Dr. Benji Maruyama, Air Force Research Laboratory

Rapporteur:
Dr. David Geohegan, Oak Ridge National Laboratory