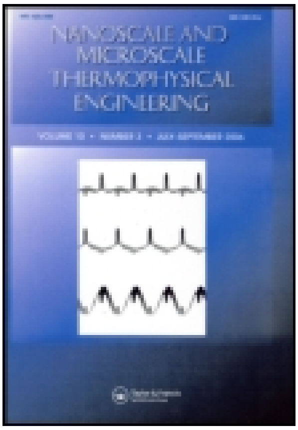

Nanoscale and Microscale Thermophysical Engineering
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/umte20

Report on Carbon Nano Material Workshop: Challenges and Opportunities

S. Acharya [a], J. Alvarado [b], D. Banerjee [b], W. E. Billups [c], G. Chen [d], B. A. Cola [e], W. Cross [f], E. Duke [g], S. Graham Jr. [e], H. He [h], H. Hong [f], S. Jin [i], S. Karna [j], C. Li [k], C. H. Li [l], J. Li [m], G. P. Peterson [e], J. A. Puszynski [n], J. Routbort [o], J. Shan [p], D. Shin [q], A. Smirnova [r], P. Smith [j], X. Wang [s], A. Waynick [t], R. White [u], X. Yan [v] & W. Yu [o]

[a] U.S. National Science Foundation, Thermal Transport Process, Arlington, Virginia, USA

[b] Department of Mechanical Engineering, Texas A&M University, College Station, Texas, USA

[c] Department of Chemistry, Rice University, Houston, Texas, USA

[d] Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

[e] George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA

[f] Department of Material and Metallurgical Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakotau

[g] South Dakota NASA EPSCoR, South Dakota School of Mines and Technology, Rapid City, South Dakota

[h] Department of Chemistry, Rutgers University, Newark, New Jersey, USA

[i] Department of Mechanical & Aerospace Engineering, University of California, San Diego, California, USA

[j] US Army Research Laboratory, Aberdeen Proving Ground, Maryland

[k] Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina, USA

[l] Department of Mechanical Engineering, Villanova University, Villanova, Pennsylvania, USA

[m] Center for Nanotechnology, NASA Ames Research Laboratory, Moffett Field, California, USA

[n] Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota

[o] Energy Systems Division, Argonne National Laboratory, Argonne, Illinois, USA

[p] Department of Mechanical & Aerospace Engineering, Rutgers University, Piscataway, New Jersey, USA

[q] Department of Mechanical & Aerospace Engineering, University of Texas at Arlington, Arlington, Texas, USA

[r] Department of Chemistry, South Dakota School of Mines and Technology, Rapid City, South Dakota

[s] Department of Mechanical Engineering, Iowa State University, Ames, Iowa, USA

[t] R&D Division, NCH Corporation, Irving, Texas, USA

[u] Office of Research, South Dakota School of Mines and Technology, Rapid City, South Dakota

[v] Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, South Dakota

Version of record first published: 22 Jan 2013.

Nanoscale and Microscale Thermophysical Engineering, 17: 10–24, 2013

ISSN: 1556-7265 print / 1556-7273 online
DOI: 10.1080/15567265.2012.745912

REPORT ON CARBON NANO MATERIAL WORKSHOP: CHALLENGES AND OPPORTUNITIES

S. Acharya[1], J. Alvarado[2], D. Banerjee[2], W. E. Billups[3], G. Chen[4], B. A. Cola[5], W. Cross[6], E. Duke[7], S. Graham Jr.[5], H. He[8], H. Hong[6], S. Jin[9], S. Karna[10], C. Li[11], C. H. Li[12], J. Li[13], G. P. Peterson[5], J. A. Puszynski[14], J. Routbort[15], J. Shan[16], D. Shin[17], A. Smirnova[18], P. Smith[10], X. Wang[19], A. Waynick[20], R. White[21], X. Yan[22], and W. Yu[15]

[1]*U.S. National Science Foundation, Thermal Transport Process, Arlington, Virginia*
[2]*Department of Mechanical Engineering, Texas A&M University, College Station, Texas*
[3]*Department of Chemistry, Rice University, Houston, Texas*
[4]*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts*
[5]*George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia*
[6]*Department of Material and Metallurgical Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakotau*
[7]*South Dakota NASA EPSCoR, South Dakota School of Mines and Technology, Rapid City, South Dakota*
[8]*Department of Chemistry, Rutgers University, Newark, New Jersey*
[9]*Department of Mechanical & Aerospace Engineering, University of California, San Diego, California*
[10]*US Army Research Laboratory, Aberdeen Proving Ground, Maryland*
[11]*Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina*
[12]*Department of Mechanical Engineering, Villanova University, Villanova, Pennsylvania*
[13]*Center for Nanotechnology, NASA Ames Research Laboratory, Moffett Field, California*
[14]*Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota*
[15]*Energy Systems Division, Argonne National Laboratory, Argonne, Illinois*
[16]*Department of Mechanical & Aerospace Engineering, Rutgers University, Piscataway, New Jersey*

Manuscript received 25 July 2012; accepted 30 October 2012.

This workshop was financially supported by the South Dakota School of Mines and Technology, the Georgia Institute of Technology, the U.S. Army Research Laboratory, the South Dakota NASA Experimental Program to Stimulate Competitive Research (EPSCoR), and the National Science Foundation.

Address correspondence to H. Hong, Department of Material and Metallurgical Engineering, South Dakota School of Mines and Technology, 501 Saint Joseph Street, Rapid City, SD 57701. E-mail: Haiping.Hong@sdsmt.edu

[17]*Department of Mechanical & Aerospace Engineering, University of Texas at Arlington, Arlington, Texas*
[18]*Department of Chemistry, South Dakota School of Mines and Technology, Rapid City, South Dakota*
[19]*Department of Mechanical Engineering, Iowa State University, Ames, Iowa*
[20]*R&D Division, NCH Corporation, Irving, Texas*
[21]*Office of Research, South Dakota School of Mines and Technology, Rapid City, South Dakota*
[22]*Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, South Dakota*

The objective of this workshop was to focus on new directions in carbon nanomaterial research, with a particular focus on new frontiers in nanotube alignment and applications of nanofluids. The first Carbon Nano Material Workshop was held at the Radisson Hotel, Rapid City, South Dakota, from October 30 to November 1, 2011, and was organized by Dr. G. P. "Bud" Peterson, Georgia Institute of Technology, and Dr. Haiping Hong, South Dakota School of Mines and Technology. More than 70 people from various government agencies, national labs, universities, and industries attended the workshop. The workshop agenda follows. The workshop included keynote plenary sessions and invited and contributed sessions, as well as a dedicated poster session of selected presentations assembled from an open call for papers.

KEY WORDS: carbon nanomaterial, thermal property, nanofluids, carbon nanotube, graphene

OPENING RECEPTION AND PRESENTATION

Dr. Robert A. Wharton, president of the South Dakota School of Mines and Technology, opened the workshop and welcomed participants. Dr. G. P. "Bud" Peterson [1, 2], president of the Georgia Institute of Technology, added his welcome and provided a program overview and logistical announcements. Pauline Smith, technical coordinator of the Army Research Lab (ARL), briefly talked about the research interests of ARL. Dr. Sumanta Achaya, program manager of Thermal Transport Processes, National Science Foundation (NSF), gave a presentation on "Research Priorities in Thermal Transport at NSF." Finally, Dr. Edward Duke, director of South Dakota National Aeronautics and Space Administration (NASA) Experimental Program to Stimulate Competitive Research (EPSCoR), outlined NASA-related opportunities at the South Dakota School of Mines. Following the keynote plenary session, chaired by Dr. Ronald J. White, vice president of research, South Dakota School of Mines and Technology, the South Dakota School of Mines and Technology hosted a welcome reception.

Keynote Plenary Session

The first keynote plenary speaker was Dr. Sungho Jin [3] from the University of California, San Diego, who gave a presentation titled "Nanostructures and Applications Based on Carbon Nanotubes." Professor Jin stated that in order to implement successful engineering applications of carbon nanotubes and related nanostructures, an ability to control their basic configurations is essential. Geometry manipulations and appropriate placements of these structures were discussed. Various processing techniques for controlling the nanotube geometry and microstructure, such as diameter, length, alignment, spacing, periodicity, 90° bend or zig-zag bending, single- or multi-branching, opening, cutting, shortening, and bonding, were also discussed. In addition, geometry modifications such as the removal of catalyst metal particles, tip opening and filling of nanotubes for nanocomposite formation, and coating of nanotubes with Pt catalyst nanoparticles were discussed. The implications of such geometry controls for physical, electronic, chemical, and mechanical properties were discussed in relation to potential technical applications such as field emission devices, sensors, atomic force microscopy (AFM) probes, electrodes, electronic circuit nano interconnections, and nanocomposites.

Dr. Gang Chen [4] from the Massachusetts Institute of Technology gave a plenary presentation titled "Peculiar Transport in Graphite Suspensions." The presentation summarized experimental work from his group on studying thermal and electrical transport properties of graphite suspensions. It has recently been demonstrated that such suspensions, when going through repeated phase changes, show reversible switching behavior in their thermal and electrical conductivities. Thermal percolation in such suspensions has also been observed. He also discussed the implications of these results on the understanding of heat transfer in nanofluids.

Dr. Shashi Karna [5] from the U.S. Army Research Laboratory gave a plenary presentation on "Growth, Characterization, and Electron Transport Studies of Carbon Nanostructures." He asserted that carbon nanostructures, especially nanotubes and graphene, have been extensively studied in the past decade due to their attractive mechanical, thermal, optical, and electrical properties. Though these materials are of general interest for applications in a wide range of technologies—ranging from ultra-lightweight, high-strength structures to flexible displays—they are especially important for numerous Army technologies such as wearable electronics, sensors, micro-autonomous systems, power storage, and multifunctional structures. In order to establish potential applications of carbon nanostructures in Army technologies, the Army Research Laboratory has been engaged in extensive in-house research in the scaled-up growth and relevant structure–property relationship characterizations.

Session 1: Carbon Nanotubes I

In Session 1, five speakers talked about their research on carbon nanotubes.

Dr. Jan A. Puszynski [6] from the South Dakota School of Mines and Technology spoke on "Application of Carbon Nanotubes in Energetic Systems." The presentation focused on the utilization of carbon nanotubes in several energetic systems, including bottom-up formation of pyrophoric substrates and synthesis of metallic and intermetallic foams and dense articles using combustion synthesis techniques. Many different nanosize metal nanoparticles are pyrophoric when exposed to air. Pyrophoric materials based on iron are highly desirable because iron oxide is readily available and easy to reduce to iron. In addition, the environmentally benign nature of the oxidation product of iron oxide is a benefit. It has been previously shown that iron nanoparticles can be generated by the reduction of iron-based precursors in a hydrogen atmosphere at elevated temperatures (300–550°C). Such iron nanoparticles generate combustion temperatures greater than 900°C when exposed to ambient air. A new bottom-up fabrication method for the formation of porous self-supporting substrates based on multiwalled carbon nanotubes (MWNTs) with encapsulated pyrophoric iron nanoparticles was presented. The second application of carbon nanotubes discussed in this presentation was related to the formation of metallic and intermetallic foams and dense articles reinforced with carbon nanotubes. The formation of foams has been done using one-step solution combustion synthesis and the densification of in situ synthesized nickel aluminides was conducted using combined self-propagating high-temperature synthesis and the application of uniaxial force.

Dr. W. E. Billups [7] from Rice University gave a talk on "Carbon Nanomaterials." Reductive alkylation of single-walled carbon nanotubes (SWNTs) using lithium and alkyl halides in liquid ammonia yields sidewall functionalized nanotubes that are soluble in common organic solvents. AFM and high-resolution tunneling electron microscopy of dodecylated SWNTs prepared from raw HiPco nanotubes and n-dodecyl iodide showed that extensive debundling had occurred. Analysis of the by-product hydrocarbons by mass spectrometry indicated that alkyl radicals are intermediates in the alkylation step. The debundling can be explained in terms of extensive intercalation of lithium into the bundled SWNTs. Electron transfer from lithium to the SWNTs was investigated by in situ monitoring of the Raman spectrum as lithium was added incrementally to a dispersion of the SWNTs in liquid ammonia. The electron/lithium uptake saturation level was determined to be $\sim C_2/Li$. This was higher than previous SWNT doping results and similar to C_2F, which was the limit found previously for direct fluorination of SWNTs.

Reduction of the graphenic edges of annealed nanodiamond by sodium in liquid ammonia leads to a nanodiamond salt that reacts with either alkyl or aryl halides to yield radical anions that dissociate spontaneously into free radicals and halide. The resulting free radicals add readily to the aromatic rings of the annealed nanodiamond. Nanodiamonds functionalized by phenyl radicals were sulfonated in oleum and the resulting sulfonic acid was converted to the sodium salt by treatment with sodium hydroxide. The salt exhibited high solubility in water (248 mg/L). Annealed nanodiamond functionalized by carboxylic acid groups could be prepared when 5-bromovaleric acid was used as the source of free radicals. The solubility of this material in water was determined to be 160 mg/L.

A facile route to water-soluble graphene that uses graphite as the starting material was described. The method relies on the addition of phenyl radicals with subsequent sulfonation of the phenyl groups. Atomic force microscopy, high-resolution transmission electron microscopy, and scanning tunneling microscopy images showed that a high degree of exfoliation occurred during the sulfonation step. The sheet resistance of the bulk films of the water-soluble graphene prepared by vacuum filtration using an anodic membrane was found to be 212 Ω/sq relative to the starting graphite, which gave 960 Ω/sq.

Dr. Jing Li [8] from NASA Ames Research Laboratory spoke on "Carbon Nanotube–Based Nanotechnology for NASA Mission Needs and Societal Applications." She discussed NASA needs in nanotechnology. In addition, she presented the results of carbon nanotube for sensor applications. Her work led to NASA's recent testing of the Nano ChemSensor, the first nanotechnology-based electronic device to fly in space. The test showed that the sensor could monitor trace gases inside a spaceship. This technology could lead to smaller, more capable environmental monitors and smoke detectors in future crew habitats. The Nano ChemSensor uses carbon nanotube–based nanostructures to sense different chemicals. The intention of developing this chemical sensor using nanostructures is to improve the sensitivity and miniaturize the sensor size, as well as to attempt to decrease the power consumption compared to commercially available chemical sensors. The applications of these sensors are for environmental monitoring, leak detection, and homeland security and defense applications like warfare agent detection and at airports for trace detection of explosives.

Dr. Baratunde A. Cola [9] from the Georgia Institute of Technology presented "Carbon Nanotube Forests as Thermal Interface Materials: Challenges and Opportunities."

Increasingly, high-performance electronic devices, circuits, and systems require improved heat transfer characteristics. Such improvements are also vital for enabling increased efficiency of solar and thermal energy harvesting. His presentation covered an application of carbon nanotube (CNT) forests designed to achieve reduced thermal contact resistance in electronic packages and energy systems. Fundamentals of thermal contact resistance were also reviewed briefly. The performance of various CNT forest thermal interfacial materials (TIMs) that produce thermal resistances near or below the range of resistances achieved by the best commercial materials used today were also discussed. Important characteristics and current performance bottlenecks for integrating a CNT forest TIMs with real devices were highlighted throughout his talk. A discussion of new research directions for improved integration and performance of CNT forest TIMs concluded the presentation.

Dr. Jerry Shan [10] from Rutgers University spoke on "Suspensions of Highly Anisotropic Particles with Field-Induced Microstructure: Fundamentals and Potential Applications." He stated that one- and two-dimensional nanoparticles such as nanotubes and flakes are highly polarizable particles that can be readily manipulated with external electric fields. As a result, electromagnetic forcing of anisotropic nanoparticles in liquid suspension offers a simple and highly controllable experimental system for exploring the nanoscale physics, as well as the macroscopic thermophysical consequences of field-induced particle alignment and assembly. He introduced the basic electromechanics of anisotropic particles under external fields and described his experimental work on (1) the hydrodynamic resistance of individual SWNTs forced to rotate in a quiescent fluid, (2) the equilibrium orientation of SWNTs under the competing effects of shear flow and an external field, and (3) determining the poorly known electrical properties of one-dimensional nanoparticles. He also discussed his work on the effective viscosity, thermal conductivity, and speed of sound in suspensions of anisotropic particles under external fields. Such suspensions with a field-induced microstructure have the potential to be novel smart fluids having highly unusual, actively controllable thermophysical properties.

Session 2: Nanofluids

In the second session, six speakers talked about their research on nanofluids.

Dr. Jules Routbor [11] from the Argonne National Laboratory gave a presentation on "Thermal Properties of Ceramic-Based Nanofluids." His presentation included the results of investigations into the viscosity, thermal conductivity, heat transfer, and pumping power of suspensions of various ceramic nanoparticles in fluids. The particles included graphite, alumina, and silicon carbide. The cooling efficiency of nanofluids depends on many variables, including particle size, shape, concentration of the base fluid, and temperature. The highest thermal conductivity enhancement of 40% was found for a solution of 1.75 vol% graphitic nanoparticles in a mixture of 50% ethylene glycol-50% water, far in excess of that predicted by the effective medium theory. A suspension of 4.0 vol% SiC (90 nm) in a 50–50 mixture of ethylene glycol–water showed a 14% increase in the heat transfer coefficient in the laminar region and a 5% increase in the turbulent region (at 70°C), correcting for the $\approx$6% (measured at 30°C) pumping power increase required to pump the nanofluid. The calculated pumping power based on the pressure drop of a single-phase fluid and experimental values of pumping power agreed within a few percent. Recent results on the friction and wear of steel on steel using a lubricant of poly-alpha-olefin containing BN and MoS_2 nanoparticles were also discussed.

Dr. Wenhua Yu [12], also from the Argonne National Laboratory, presented "Convective Heat Transfer of Nanofluids in Turbulent Flow." He talked about the progress made on the turbulent flow convective heat transfer of nanofluids that has long been of interest to the nanofluid research community and that has recently become a main focus of nanofluid research. Specifically, three essential aspects of the turbulent flow convective heat transfer of nanofluids relevant to their applications were comparatively reviewed in detail based on both theoretical analyses and experimental data, including (1) selection—the comparison criteria of the thermophysical property-related heat transfer performance of nanofluids and their base fluids; (2) design—the predictions of the heat transfer coefficients of nanofluids based on homogeneous fluid models by using nanofluid thermophysical properties; and (3) effectiveness—the enhancements of the heat transfer coefficients of nanofluids over their base fluids.

Dr. Calvin Hong Li [13] from Villanova University spoke on "Advances in Biofuel, Medicine, and Energy Efficiency with NanoEngineered Materials." He discussed that in recent years, nanoengineered materials have been one of the most important and exciting forefront research topics in energy, medical applications, and security. Ongoing and anticipated breakthroughs in the near future will result in technological advances in a wide range of applications. He emphasized the nanoengineered materials that facilitate timely utilizations in biofuel combustion energy density improvement, multifold benefits to drug delivery systems, and an ultra-high heat flux and efficiency thermal management system. Some of the latest experimental and theoretical studies were presented and discussed with broad coverage and insight into the areas.

Dr. William M. Cross [14] from the South Dakota School of Mines and Technology presented "Nanoparticle Inks for Energy Harvesting Applications." He defined *energy harvesting* as a process of collecting energy from available natural sources and storing it for later use. To utilize the features of direct write technology for some energy harvesting applications, metallic nanoparticulate inks with low sintering temperature and high post-sintering conductivity are necessary. The conductivity of the printed pattern mainly depends on the mass loading of nanoparticles in an ink and the energetics between the capping agent and the metal surface of a nanoparticle. Understanding metal-capping agent interactions will help fabricate high-efficiency, low-cost, and robust devices for energy harvesting applications. In this study, short-chain single and mixed carboxylic acid–encapsulated silver nanoparticulate inks were prepared. Carboxylic acid–capped silver nanoparticles were prepared with diameters between 4 and 7 nm and subsequently dissolved in toluene. As the capping agent chain length increased, the concentration of the silver nanoparticles that could be suspended in the inks increased. As a result, inks with a wide range of concentrations (3–66 wt%) could be prepared. The stability of the as-prepared inks was studied by performing a mass drying test and most of the inks were observed to be stable for at least one month. The viscosity (0.8–10 cP) and surface tension (16–26 dyn/cm) of these inks were measured and found to be appropriate for many direct write systems. As a result, it may be possible to print various electronic circuits using different direct write systems that can be sintered at low temperatures for device fabrication.

Dr. Debjyoti Banerjee [15], from Texas A&M University, spoke about "Nanomaterials for Thermal Energy Storage." In the experimental, numerical, and analytical studies performed by his research group he observed anomalous enhancement in the specific heat capacity when nanoparticles were mixed with various materials (i.e., neat solvent or solid matrix). However, nanoparticle additives can cause Newtonian solvents to demonstrate non-Newtonian behavior (e.g., shear thinning or shear thickening). The enhancement of the thermophysical properties on addition of nanoparticles is of significant importance in reducing the operational cost of thermal energy storage (TES) devices and systems. TES can be utilized for levelizing peaks in cyclical energy demands (or duties) as well as in renewable energy applications where the energy source may be intermittent—such as in solar thermal, geothermal, and nuclear energy applications. These nanomaterials can be integrated into Stirling cycle (or Rankine cycle) powered systems to enhance system thermal efficiencies by increasing the operating temperature. This can also be achieved by enhancing the operating temperature as well as heat capacity of the thermal energy storage devices. In addition, the effect of nanocoatings in enhancing phase change phenomena (boiling, condensation) was discussed.

Dr. Donghyun Shin [16], from the University of Texas at Arlington, presented the work "Molten Salt Nanomaterials for Thermal Energy Storage." The study involved development of novel nanomaterials for enhanced TES and heat transfer fluids (HTF). He investigated nanoscale transport phenomena involving base materials doped with nanoparticles. Using dispersed nanoparticles in conventional thermal energy storage materials (e.g., molten salts), effective specific heat capacity and effective thermal conductivity were enhanced by significant margins. He developed novel nanomaterial synthesis protocols. Using these methods, he observed that nanoparticles or groups of nanoparticles induced special micro/nanostructural changes in the samples, which were potentially responsible for the enhancement of the thermophysical properties of the thermal energy storage materials. He is currently exploring the applicability of the nanomaterials for thermal energy storage in renewable energy systems, especially for concentrated solar power systems and geothermal systems.

Session 3: Carbon Nanotubes II

In the third session, five researchers shared their work on carbon nanotubes.

Andy Waynick [17] from NCH Inc. was sick, his colleague, Dr. Adrian Denvir talked about "Development and Evaluation of the World's First Lubricating Grease Thickened by Carbon Nanotubes" in his absence. It is well known that carbon nanotubes have been shown to be capable of performing as thickeners for lubricating grease compositions. Single-walled carbon nanotubes are about twice as efficient as multiwalled carbon nanotubes as grease thickeners. Unlike all prior art references [18] to carbon nanotubes as components in lubricant compositions, stable grease structures using carbon nanotubes do not require dispersants. In fact, dispersants generally have an adverse effect on grease structure. This technology is now covered by a U.S. patent. The additive-free greases obtained by using carbon nanotubes as the sole thickeners [19] are characterized by high dropping point, relatively low oil bleed, and good shear stability. They tend to show some level of structural incompatibility with greases thickened by commonly used conventional thickeners, although the level of this incompatibility varies depending on the conventional thickener. Nonetheless, stable greases that use mixtures of conventional thickeners and carbon nanotubes are possible. Details concerning these characteristics of carbon nanotube lubricating greases were provided.

Dr. Chen Li [20] from the University of South Carolina gave a presentation about "Super-Nucleating Interfaces Made from Functionalized Carbon Nanotubes." Novel nanoengineered interfaces made from functionalized CNTs have been developed to promote nucleate boiling and thin-film evaporation. To improve the local liquid supply, the novel interfaces were coated on the surfaces of sintered biporous structures, which consisted of multiple layers of copper meshes and a microchannel array. Superhydrophilic functional groups were attached on pure CNTs in a nitric acid thermal bath. A mixture made of nitric acid (HNO_3), Nafion, and isopropanol was used to achieve great CNT dispersion. Thermal and mechanical bonds were also strengthened by heating Nafion at approximately 130°C for 5 min. The highly ordered hydrophilic–hydrophobic network, which is created by intrinsically hydrophobic CNTs and superhydrophilic functional groups, can create nearly perfect nanoscale or submicrometer cavities for nucleating. Through the use of the novel nanoengineered interfaces, the heat transfer coefficient in nucleate boiling and thin-film evaporation has been found to be substantially enhanced. A stable heat transfer coefficient (HTC) at 240 $kW/(m^2 \cdot k)$ has been obtained on a 500-nm-thick CNT coating. Compared to microchannels, the critical heat flux (CHF) was increased up to 300%. The novel nanoengineered interfaces are desirable to a wide range of emerging and traditional applications such as energy, bioengineering, thermal management, etc.

Dr. Jorge L. Alvarado [21] from Texas A&M University presented "Adsorption of Methanol in an Activated Carbon and Carbon Nanotube Matrix." Adsorption of hydrocarbon gases in carbon materials has been a subject of intense research interest for several decades. Recently, much attention has been given to the adsorption of methanol in activated carbon for a host of applications, including solar-based refrigeration. However, little is known regarding how effectively methanol can be adsorbed in other carbon-based structures, including CNTs. A recent research study conducted by Texas A&M University revealed [22] that using a matrix of carbon nanotubes and activated carbon (AC) resulted in enhanced adsorption of methanol. The adsorption study consisted of annealing and chemically treating CNTs in order to enhance adsorption levels at different temperatures. Experimental results indicated that methanol adsorption increased with temperature when AC and pristine CNT were used independently; however, annealed 10- to 20-nm and 40- to 60-nm CNTs showed invariant levels of adsorption with respect to temperature due in part to an increase in the graphitization of the material as confirmed by Raman spectra. CNT size was also found to affect the level of adsorption. For annealed CNTs, adsorption was found to vary linearly with carbon nanotube diameter. Acid treatment and ultrasonication detrimentally affected the ability of CNTs to adsorb methanol compared to AC samples by as much as 60%. Several mixtures of CNTs and AC were prepared and tested to explore their effects on adsorption. It was observed that using a mixture of 85% AC with 15% CNTs resulted in adsorption enhancements as high as 50%. Analysis of the experimental data suggested that annealed CNTs in AC increased adsorption levels due to the fast diffusion transport of methanol taking place within hydrophobic carbon nanotubes. The data also suggested that CNTs form a well-distributed percolation network that allows methanol to have greater access to porous cavities within AC. A detailed description of the chemical and thermal processes used to treat CNTs was also presented.

Dr. Alevtina Smirnova [23] from the South Dakota School of Mines and Technology talked about "Carbon Aerogel Materials as Fuel Cell Catalytic Substrates." She said that there is great potential for fuel cells as power generating devices that are capable of efficiently converting the chemical energy of the fuel into electricity. Polymer electrolyte fuel cells (PEMFCs) utilize the ability of the catalysts to initiate and maintain the oxygen reduction reaction on the cathode and the fuel oxidation reaction on the anode. In order to increase the efficiency of the PEMFC catalysts, high-surface-area mesoporous carbons, carbon blacks, carbon nanotubes, and carbon aerogels have been used. Among various types of carbons, carbon aerogels (CAs) combine a large number of attractive properties such as high porosity, high surface area, controllable nanoscale pore structure, narrow pore size distribution, high electrical conductivity (25–100 S/cm), low cost, and remarkable mechanical and thermal properties derived from a three-dimensional interconnected nanonetwork structure. The exceptional properties of CAs for PEMFC applications were also demonstrated.

Dr. Haiping Hong [24], also from the South Dakota School of Mines and Technology, gave a presentation about "Carbon Nano Material Applications: Grease, Fluid and Reinforce Membrane, and Nanofluids." He said that carbon nanomaterials, especially SWNTs, have attracted a great deal of interest due to their superior electrical conductivities, thermal conductivities, mechanical properties, etc. For example, the thermal conductivity of SWNTs at room temperature is about 7,000 times greater than that of water and about 20,000 times greater than that of engine or pump oil. Consequently, fluids containing suspended solid carbon nanotubes are expected to display significantly enhanced thermal conductivities relative to conventional heat transfer fluids. In addition, SWNTs are believed to be ideal mechanical reinforcements for lightweight systems. They have been known to have an elastic modulus of up to 1 Tpa and a tensile strength close to 60 Gpa. These values are 5 and 10 times greater than those for steel, respectively, at just one sixth the weight. He presented some interesting research progress in the applications of grease, fluid, and reinforced membranes.

Session 4: Graphenes

In the fourth session, five speakers talked about their research on graphenes.

Dr. Xinwei Wang [25] from Iowa State University talked about "Graphene–SiC Interface: Extremely Localized Thermal Probing and Thermal Resistance." He noted that very limited internal phonon coupling and transfer within graphene in the out-of-plane direction significantly affects the graphene–substrate interfacial phonon coupling and scattering and leads unique interfacial thermal transport phenomena. By simultaneous characterization of graphene and SiC Raman peaks, Dr. Wang's group was able to distinguish the temperature of a graphene layer and its adjacent 4H-SiC substrate for the first time. The thermal probing resolution reached nanometers on the graphene side ($\sim$1.12 nm) and approximately a few micrometers in SiC next to the interface. A very high interfacial thermal resistance was observed by using the Raman frequency method under surface Joule heating. This value was much higher than the molecular dynamics prediction. The analysis by Dr. Wang's group showed that the measured anomalous thermal contact resistance stemmed from the thermal expansion mismatch between graphene and SiC under Joule heating. This thermal expansion mismatch led to interfacial delamination/separation and significantly enhanced local phonon scattering. An independent laser heating experiment was conducted under the same condition and a higher interfacial thermal resistance was obtained. Furthermore, the peak width method of Raman thermometry was employed to evaluate the interfacial thermal resistance.

Dr. Samuel Graham, Jr. [26] from the Georgia Institute of Technology presented "Direct Synthesis of Large Area Graphene Films from Solid Source Precursors." The synthesis of graphene through chemical vapor deposition (CVD) on copper substrates has proven a viable method to create large-area films not obtainable through epitaxial growth or exfoliation from graphite. Typical methods for CVD on copper involve the annealing of metal foil substrates in a reducing environment followed by exposure to a mixture of methane, hydrogen, and argon at temperatures between 900 and 1000°C. Graphene was then formed through the cracking of the hydrocarbon sources that facilitates the dissolution of carbon atoms in copper that later form graphene upon cooling. Though gas sources have proven to be reliable in producing monolayer to few-layer graphene, recent methods have shown that it is possible to utilize polymer materials as a solid carbon source in order to grow graphene on copper substrates. The use of polymer layers allowed for the potential to pattern the graphene growth in specific areas as well as tune the properties of graphene through in situ p- or n-doping.

He also presented a new method of creating graphene films from a solid polymer source consisting of polymethylmethacrylate (PMMA). The combination of PMMA and copper foil was used to process uniform graphene films on copper substrates over areas exceeding 4 cm $\times$ 4 cm in area. Data based on Raman spectroscopy show that the films possessed excellent 2D and G peak intensities and low defect peaks. Integration of these films onto Si and transparent substrates to create field effect transistors and transparent conductive electrodes was discussed. It was found that the development of composite graphene–carbon nanotube films enabled transparent electrodes with sheet resistances below 100 ohms/sq at a transmissivity of 80%. Methods to scale and improve this technology were described.

Dr. Huixin He [27] from Rutgers University talked about "Rapid Production of Highly Conductive and Amphiphilic Graphene Sheets." Due to its excellent electronic, thermal, and mechanical properties and its large surface area and low mass, graphene holds great potential for a range of applications. Except for ultra-high-speed electronics, most of the proposed applications require large quantities of high-quality, low-cost graphene (preferably solution-processable) for practical industrial-scale applications. Examples include energy and hydrogen storage devices, inexpensive flexible macroelectronics, mechanically reinforced conductive coatings including films for electromagnetic interference shielding in aerospace applications, and nanofluids with high photothermal efficiency. Though extensive efforts have focused on enabling cost-effective mass production of solution-processable graphene sheets, the dominant approaches rely on Hummer's or modified Hummer's methods. These methods involve tedious and time-consuming procedures. In brief, one must first oxidize graphite powder, exfoliate the oxidized product to form nonconductive graphene oxide (GO) suspensions, and finally reduce it to recover some fraction of its electrical conductivity. An unprecedented quick and scalable approach was reported to directly produce highly conductive graphene sheets with controlled sizes from a few nanometers to tens of micrometers. The resulting graphene sheets were of higher quality than those formed through GO approaches. They were thermally stable, highly conductive, and had higher photothermal efficiency without the requirement of a reduction process. Even in the absence of polymeric or surfactant stabilizers, high concentrations of graphene dispersions with clean and well-separated graphene sheets can be obtained in both aqueous and organic solvents. This greener, rapid, and scalable approach produces high-quality amphiphilic graphene sheets, enabling a broad spectrum of applications by low-cost solution processing techniques.

Finally, Dr. Xingzhong Yan [28] from South Dakota State University talked about "Graphene for Reversible Hydrazine Fiber Optic Sensors." He noted that hydrazine and its derivatives are important hypergolic fuels on the Space Shuttle for auxiliary power and orbital maneuvering systems used by NASA. In addition, hydrazine has a multitude of uses in other fields, such as agricultural chemicals, drugs, metal and glass plating, fuel cells, solder flux, explosives, photographic developers, and as a corrosion inhibitor in water-cooled nuclear power plants. Despite its usefulness, hydrazine is flammable and explosive at high concentration and is highly toxic to humans and the environment, even with an extremely low exposure. Thus, it is critical to control its release and monitor the failure of the storage of hydrazine. Several instrumental methods for hydrazine detection have been investigated in previous studies. These techniques [29] include chemiresistor, colorimetry, electrochemistry, and fiber optics. Fiber optic sensors have numerous advantages compared to conventional sensors, including immunity to electromagnetic interference, compact and small size, remote sensing, the ability to be embedded into other textile structures, high sensitivity, and the ability to be multiplexed. These characteristics have attracted much attention in the area of gas sensing. The developed class of fiber optical sensor was based on the technique of modified cladding. This contribution reports a novel development of a reversible fiber optic sensor using graphene. It was proven that graphene oxide can be worked as a sensing material for hydrazine gas detection at 1,310 nm. Due to the linear relationship between optical output power drop percentage and hydrazine gas concentration, this sensor has the feasibility of detecting both the presence and concentration of hydrazine gas. Sensors with the capability to detect a concentration at the parts per million level were demonstrated.

Group Discussions: Carbon Nano Materials: Challenges and Opportunities

After sessions 1 and 2 as well as 3 and 4, there were group discussions about the challenges and opportunities of carbon nanomaterials. Attendees were divided into three groups: carbon nanotubes, nanofluids, and graphene.

Nanofluids *Nanofluids* are defined as fluids containing a suspension of nanometer-sized particles with enhanced thermal properties compared to base fluids.

For heat transfer applications that require large heat removal, high thermal conductivity enhancement with minimal viscosity increase is important. The amount of thermal conductivity enhancement depends on specific application.

The general consensus was that the participants would not be able to make significant breakthroughs in this interesting and challenging field without proper understanding of the fundamental scientific nature of nanofluids. At this point, surface chemistry and material play a critical role. Specific heat capacity enhancement observed in certain classes of nanofluids holds promise for thermal energy storage applications.

- Challenges:
  - Stability is important because inorganic nanoparticles such as metal oxides (Fe_2O_3, Al_2O_3) and carbon nanotubes are hydrophobic.
  - Heat transfer enhancement is too low for practical applications. The associated increase in viscosity could be a challenge for practical implementation of nanofluids in thermal management.
  - Specific heat capacity enhancement is a recent and novel development that requires further exploration for different classes of nanofluids (e.g., aqeous, nonaqeous, organic/ inorganic, ceramic/ metallic, etc.).
  - Nanoparticle coatings can potentially deliver similar metrics for thermal management without the associated disadvantage of viscosity enhancement. This topic requires further exploration by comparing both methods; that is, comparing the

performance of nanoparticle additives in heat transfer fluids with the efficacy of nanoparticle coatings/nanostructured surfaces involving the same coolants for thermal management and thermal storage applications.
  - No theory fits all experimental observations.
  - Funding sources are limited and often are application specific.
- Opportunities:
  - Particle stability could be improved by functionalization, chemical treatment, and the use of surfactants.
  - Further understanding of the surface chemistry of nanoparticles such as particle size, shape, pH, viscosity, zeta potential, etc., is necessary.
  - Further understanding of particle alignment, aggregation, solvent effect, etc., is also necessary.
  - An understanding of the effect on the interface for nanofluids by experimentation including Raman spectroscopy and theoretical methods, including molecular dynamics (MD).
  - Opportunity for enhancement of mass specific heat capacity (C_p).
  - Thermal storage applications, potentially for concentrated solar power, geothermal energy harvesting, etc.
  - Opportunities in thermal applications under static conditions.
  - Particle–liquid interface effects on C_p: inherent phase change phenomena that are potentially induced on the nanoparticle–solvent interface.
  - Synthesis of novel nanoparticles with appropriate multifunctional groups.
  - Aligned carbon nanotube by external magnetic field in the fluids could be applied in polymer composites to enhance their physical properties.
  - Using existing theories, models, and methods to predict (simulate) the thermal conductivity values with alignment under a magnetic field.
  - What kind of physical parameters of carbon nanotubes would make them useable in a flowing system, such as L/D ratio, functionalization, or coatings?

Carbon Nanotubes Carbon nanotubes are defined as allotropes of carbon with a cylindrical nanostructure, including SWNTs, MWNTs, and DWNTs. They have novel properties that make them useful in a variety of applications in nanotechnology, electronics, optics, and fields of nanomaterials science.

Our primary focus was on thermal science and potential applications of carbon nanotubes.

- Challenges:
  - There is need for tunable grease with different viscosities. The question is how to modify the viscosity.
  - It is possible to align nanotubes on the substrate. The challenge is how to use them in nanofluids and polymer composites.
  - How to make highly conductive thermal interface materials, due to the interface (contact) between nanotube and metal such as Ag, Cu, In, etc.
- Opportunities:
  - The stipulation in regards to the price for carbon nanotubes (single-walled) and potential decreases to less than \$1/g will make some nanotube products such as nanogrease commercially competitive.
  - During the meeting, participants learned that it is possible to obtain a 99% metallic nanotube, which is very encouraging as thermal interfacial material.

- In addition, it is possible to obtain a 99% purified semiconducting nanotube and this discovery could revolutionize how solar power is harvested.
- It is well known that prime nanotubes can be aligned by an AC electrical field. It could be interesting to explore whether functional nanotubes could be aligned by an AC electrical field or a magnetic field.

Graphenes *Graphenes* are defined as an allotrope of carbon with atoms densely packed in a honeycomb crystal lattice. The unique properties of graphene make it attractive for a wide range of potential electronic devices.

The primary focus was on thermal science and application of graphene.

- Challenges:
  - Graphene has a number of extremely useful properties, including very fast electron mobility and high mechanical strength, but many of the extreme values that have been reported apply only to isolated graphene. Graphene's properties under the complex conditions that are present in real technological devices should be studied.
  - How to make highly conductive thermal interface material, due to the interface (contact) between nanotube and metal such as Ag, Cu, In, etc.
- Opportunities:
  - Dynamic thermal transport behavior of graphene in fluid. First, graphene is flat, very thin, and has very high interfacial area with the base liquid (at least twice that for CNTs). Second, graphene is soft compared to CNTs. Therefore, graphene can fold/unfold when it is immersed in liquid and features fast oscillating behavior. Such oscillation can induce relative movement between liquid molecules and the graphene surface, leading to potentially enhanced conduction/reduced interfacial thermal resistance. The viscosity might be quite high. Further research could involve studying the thermal transport behavior and interfacial thermal conduction for liquid dispersed with graphene.
  - Functional graphene could enhance the solubility, suppress the heat buildup, and/or decrease the viscosity of the fluids.
  - Graphene-based ultrafast and ultrasensitive acoustic sensors. Graphene is very thin and has very little mass. This means that it could be used as an ultra-performance membrane covering a pre-prepared hole to form a novel microphone. Such a microphone will have the capability to pick up very weak ultrasonic signals. At present, ultrasonic sensors require a high signal to measure and have low sensitivity. Therefore, graphene-based ultrasonic or subsonic sensors can be used as a "third ear" for soldiers to hear the subsonic and ultrasonic signals induced by machines and explosions in very far distance. This will provide critical information and help soldiers to significantly reduce casualty in wars.
  - A significantly simplified technique to grow large-scale graphene with good quality control is possible. In addition, it is feasible to obtain soluble large-scale graphene in solution. These techniques can be used to fabricate various sensors for optical and chemical sensing with complicated feature structures.
  - Graphene oxide is soluble in water and organic solvents. According to the layered structure and oscillating behavior, fluids based on this material should have high thermal properties. In addition, graphene oxide can be dissolved in a polymer solution. It is also possible to reduce graphene oxide to prime graphene. Therefore, polymer graphene composites are very attractive due to their high thermal, electrical, and mechanical properties.

- Graphene has good electronic mobility and conductivity. Together with CNTs or other inorganic materials, they may replace indium tin oxide as the electrode.
- Graphene-based electrically and thermally conductive inks. The main challenge in formulating conductive inks is that the use of additives to improve printability and processability can interfere with the electrical characteristics and thus the key functionality of the printed object.

CONCLUSION

The group echoed what Dr. Peterson pointed out in the opening remarks: "It is not the end. It is just the beginning." To meet the new challenges and opportunities of carbon nanomaterial with a focus on nanofluids, carbon nanotubes, and graphene, efforts are being made to form a Carbon Nano Material Alliance, led by Dr. Peterson. Important research challenges, opportunities, and directions were summarized, and priority areas where future research should be focused in carbon nanomaterial fields were identified. During the workshop, the primary focuses were on thermal and electrical applications. Carbon nanomaterials have other applications, such as for catalysis and in batteries.

The positive impact of the workshop will attract an interdisciplinary audience and help the broader scientific community to better understand important issues related to carbon nanomaterials and applications as well as their potential benefits to society.

We are seeking seed grants from various agencies to initiate an internal collaboration. The next carbon nanomaterial workshop should be available within next one to two years.

REFERENCES

1. M. Horton, H. Hong, C. Li, B. Shi, G.P. Peterson, and S. Jin, Magnetic Alignment of Ni-Coated Single Wall Carbon Nanotubes in Heat Transfer Nanofluids, *Journal of Applied Physics*, Vol. 107, p 104320, 2010.
2. H. Hong, X. Luan, M. Horton, C. Li, and G.P. Peterson, Alignment of Carbon Nanotubes Comprising Magnetically Sensitive Metal Oxides in Heat Transfer Nanofluids, *Thermochimica Acta*, Vol. 525, pp. 87–92, 2011.
3. S. Jin, Nanostructures and Applications Based on Carbon Nanotubes, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
4. G. Chen, Peculiar Transport in Graphite Suspensions, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
5. S. Karna, Growth, Characterization, and Electron Transport Studies of Carbon Nanostructures, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
6. J.A. Puszynski, Application of Carbon Nanotubes in Energetic Systems, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
7. W.E. Billups, Carbon Nanomaterials, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
8. J. Li, Carbon Nanotube–Based Nanotechnology for NASA Mission Needs and Societal Applications, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
9. B.A. Cola, Carbon Nanotube Forests as Thermal Interface Materials: Challenges and Opportunities, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.

10. J. Shan, Suspensions of Highly Anisotropic Particles with Field-Induced Microstructure: Fundamentals and Potential Applications, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
11. J. Routbor, Thermal Properties of Ceramic-Based Nanofluids, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
12. W. Yu, Convective Heat Transfer of Nanofluids in Turbulent Flow, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
13. C.H. Li, Advances in Biofuel, Medicine, and Energy Efficiency with NanoEngineered Materials, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
14. W.M. Cross, Nanoparticle Inks for Energy Harvesting Applications, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
15. D. Banerjee, Nanomaterials for Thermal Energy Storage, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
16. D. Shin, Molten Salt Nanomaterials for Thermal Energy Storage, presented at Carbon Nano Materials And Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
17. A. Waynick, Development and Evaluation of the World's First Lubricating Grease Thickened by Carbon Nanotubes, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
18. H. Hong, D. Thomas, A. Waynick, W. Yu, P. Smith, and W. Roy, Carbon nanotube grease with enhanced thermal and electrical conductivities, *Journal of Nanoparticle Research*, Vol. 12, pp. 529–525, 2010.
19. H. Hong and J.A. Waynick, US Patent 7,871,533, Carbon nanoparticle-containing nanofluid.
20. C. Li, Super-Nucleating Interfaces Made from Functionalized Carbon Nanotubes, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
21. J.L. Alvarado, Adsorption of Methanol in an Activated Carbon and Carbon Nanotube Matrix, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
22. S. Sambath, *Study of the adsorption of methanol in an activated carbon and carbon nanotube matrix for use in a solar based refrigeration cycle*, Master Thesis, Texas A&M University, December 2010.
23. A. Smirnova, Carbon Aerogel Materials as Fuel Cell Catalytic Substrates, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
24. H. Hong, Carbon Nano Material Applications: Grease, Fluid and Reinforce Membrane, and Nanofluids, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
25. X. Wang, Graphene–SiC Interface: Extremely Localized Thermal Probing and Thermal Resistance, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
26. S. Graham, Direct Synthesis of Large Area Graphene Films from Solid Source Precursors, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
27. H. He, Rapid Production of Highly Conductive and Amphiphilic Graphene Sheets, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
28. X. Yan, Graphene for Reversible Hydrazine Fiber Optic Sensors, presented at Carbon Nano Materials and Applications Workshop, Rapid City, SD, October 31–November 1, 2011.
29. A. Andrawis, B. Ranjitkar, X.Z. Yan, and Y.L. Peng, *Reversible low-loss fiber optic hydrazine sensor*, Proceedings of SPIE: Advance Environmental, Chemical, and Biological Sensing Technologies VII. 7673, DOI: 10.1117/12.861426, 2010.