NER: Carbon Nanotube Coated with Nanoparticles - An Enabling Structure for Nanomanufacturing and Nanodevices

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ABSTRACT: This IREE program entails a graduate student visiting the Hong Kong Polytechnic University (HKPU) to study the growth of CuO nanowires. These nanowires are useful for the synthesis of 3-D hybrid nanotube/nanowire/nanoparticle architectures proposed in the NER project. During the IREE visit, the growth of CuO nanowires by direct oxidation of surface mechanical attrition treated (SMAT) copper is investigated and compared to that of ordinary (non-SMAT) copper. The morphology, composition, and structure of the product CuO nanowires were analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and small area electron diffraction (SAED). The growth rate of the CuO nanowires from SMAT copper was two to four times greater than non-SMAT copper, whereas the diameters were roughly the same (~100 nm). The accomplishment of this international research experience goes beyond the scientific results produced during the trip. The opportunity helped to strengthen existing networks, forging new collaborations, and instilled further appreciation for cultural diversity.

INTRODUCTION

The nanoscale exploratory research (NER) grant was awarded to the University of Wisconsin-Milwaukee with Dr. Junhong Chen as the PI. Based on the initial success in the nanoparticle assembly onto carbon nanotubes (CNTs) by the PI [1], the NER project intends to explore three applications for nanoparticle-coated CNTs: (1) to manufacture ultra-thin nanoparticle line features; (2) to grow hierarchical 3-D hybrid nanoarchitectures; (3) to fabricate an ultrasensitive hydrogen sensor. To grow hierarchical 3-D hybrid nanoarchitectures, catalyst nanoparticles (e.g., Fe and Ni) produced using a mini-arc plasma source [2] are assembled onto CNTs first. The catalyst-coated CNTs are placed into a chemical vapor deposition furnace to further grow CNTs or nanowires (NWs) on the external surface/tips of CNTs. The newly grown nanocomponents can be further coated with nanoparticles of design. Very complicated 3-D hybrid architectures can be produced through the multi-step growth-coating-growth process.

The objective of this IREE supplement is to leverage the expertise of Dr. Jian Lu at the Hong Kong Polytechnic University (HKPU) to grow high-quality CuO NWs that can be incorporated into the 3-D hybrid nanoarchitectures. The proposed activities are meant to extend the scope of the current NER project and will significantly impact the project. Dr. Jian Lu's lab has invented a surface mechanical attrition treatment (SMAT) technique, which is a grain refinement technique where millimeter-size steel balls are acoustically driven to impact the copper surface randomly and in all directions to produce nanocrystalline material [3]. The very high strain rates produced in the random directions of impact results in the formation of nanometer sized twins followed by their dislocation and subsequent evolution into nanograins which saturate to an average diameter of ~10 nm [3]. It is believed that the oxidation of SMAT copper would increase the rate of oxide formation and CuO NW growth, and possibly reduce the oxidation temperature needed for CuO NW growth.

One graduate student, Benjamin Hansen, traveled to HKPU and visited Dr. Lu's lab for three months (May 21, 2008 through August 25, 2008). To coordinate the proposed IREE activities, the PI visited the HKPU in early June 2008 and had frequent teleconferences with Ben and Dr. Lu to discuss the project results and progress throughout the IREE period. Ben was believed to be the most qualified candidate for the IREE visit. He has worked with the PI as an NSF research experience for undergraduates (REU) student on the growth of CuO NWs from regular copper and copper-containing substrates. His creativity in experimental design and data analysis has proved him a well qualified researcher with very high chance of success. His REU research results have been published in *Journal of Nanomaterials* with him as the first author.

The proposed IREE program serves as a catalyst for the international collaboration between Dr. Lu and the PI in the area of nanostructure growth. The student is expected to continue to work on the project for a M.S. thesis. The IREE project is expected to provide a powerful platform to transmit the cutting-edge nanotechnology and the excitement of frontier research from the NER project to students and to augment the broader impacts of the NER project. The student who participates in the IREE program not only benefits from the scientific excitement of the project but also has the opportunity to appreciate the culture and business practice of Hong Kong. This program thus adds a cultural dimension to the student training and increases the competitiveness of the student in securing employment opportunities that require international expertise.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

The ability to manipulate and engineer the properties of materials through nanoscale engineering is one of the most exciting and technologically relevant topics of future nanotechnology. In particular, nanowires (NWs) are one-dimensional nanostructures that can efficiently transport electrical carriers and have fantastic mechanical and photonic properties. NWs are emerging as promising multifunctional materials that can be utilized as both wiring and device elements, providing an easy pathway to building a variety of hybrid nanoelectronic, nano-optoelectronic, and nanomechanical technologies [4]. Furthermore, we have been able to fabricate novel heterostructures through the decoration of pre-existing 1-D nanostructures such as carbon nanotubes or nanowires with nanoparticles; opening doors to a host of new device applications [1]. The ability to independently grow 1-D nanostructures for subsequent nanoparticle decoration using our system is an important step in the overall nanofabrication process. Therefore, the IREE trip was used to gain knowledge and expertise in the growth of cupric oxide (CuO) nanowires, a promising material for next-generation gas sensing applications.

The research program pursued included improved growth techniques of CuO NWs using SMAT copper. Previous research by *W.P. Tong et. al.* [5] has shown that nitriding of SMAT treated iron could be done at substantially lower process temperatures and durations. Nitriding is a chemical treatment carried out at elevated temperatures which enables diffusion of nitrogen into the surface of iron. The large number of grain boundaries formed in SMAT treated iron may act as fast atomic diffusion channels, thus expediting the nitriding process. In a similar manner it is believed that the oxidation of SMAT treated copper would decrease the oxidation temperature and growth time needed for high density nanowire growth. Furthermore, a decrease in growth temperature may also result in the growth of smaller nanowires.

During the trip, a series of experiments were carried out in which copper samples were SMAT treated, followed by the oxidation growth of CuO nanowires at various temperatures. The morphology of the NWs was then analyzed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and small area electron diffraction (SAED). The results were compared to NWs grown from non-SMAT treated copper with the same oxidation process parameters.

Figure 1 (a) and (b) are SEM images of the NW growth morphology of SMAT treated copper and non-SMAT treated copper, respectively. SMAT treated copper resulted in a much larger NW growth density, in addition to increased NW length (from ~5 μm to 10 μm). Further evidence of the increased NW length can be seen by comparing the TEM images of CuO nanowires of Figure 1 (c) and (d). The inset of Figure 1 (c) is an SAED of the NW which verifies both the high crystallinity of the NWs and the monoclinic structure corresponding to CuO.

This research greatly benefited from the collaboration with Dr. Jian Lu (co-inventor of SMAT) at HKPU. Direct interaction with Dr. Lu and his students, in addition to being allowed to access an SMAT machine, were instrumental in this research. Furthermore, all of the other necessary facilities, such as TEM, SEM, and furnaces were generously provided throughout the program which helped to expedite the research project further. The high-quality CuO NWs grown using the new technique can be incorporated into the 3-D hybrid nanoarchitectures proposed in the NER project. Several manuscripts are currently under preparation for journal publication.

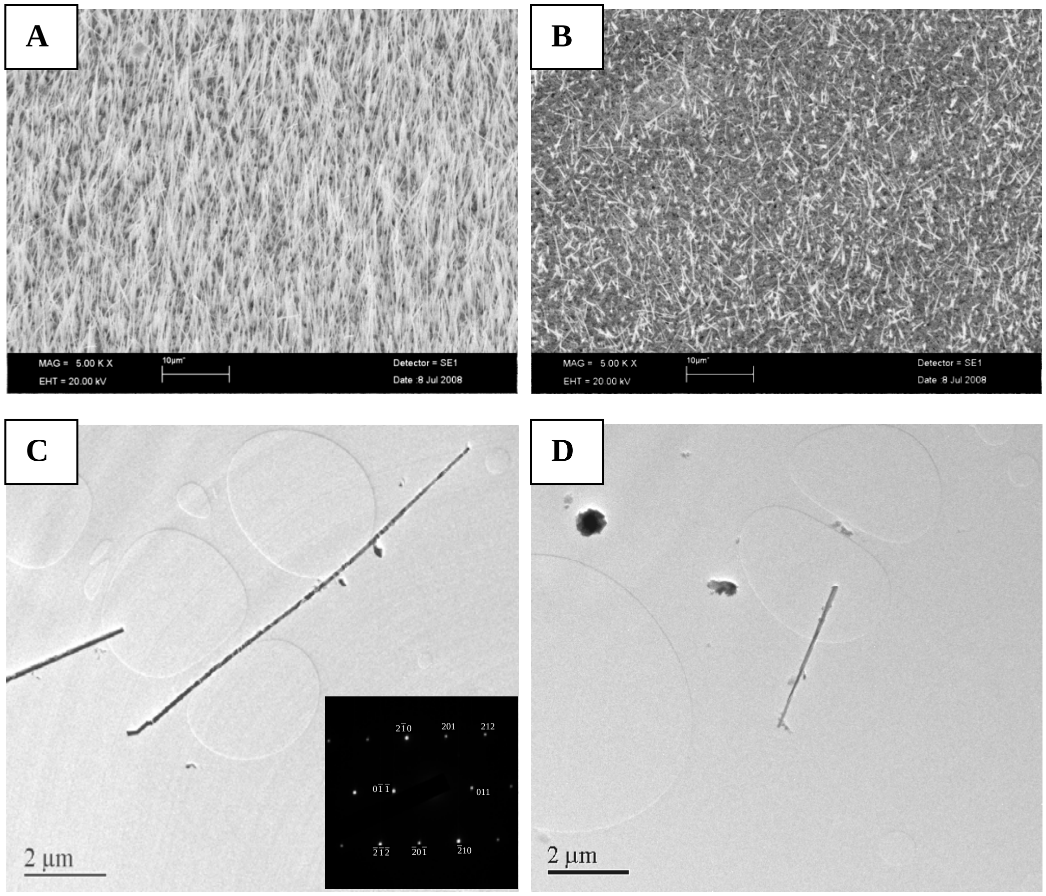

Figure 1. SEM images of NW growth morphology from SMAT Cu (a) and non-SMAT Cu (b). TEM images of NW grown off SMAT treated Cu (c) and non-SMAT treated Cu (d).

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

The ability to independently grow 1-D nanostructures for subsequent nanoparticle decoration is an important step in the overall nanofabrication process proposed in the original NER project. The IREE program helps to gain knowledge and expertise in the growth of CuO NWs. The high-quality CuO NWs grown using the new technique can be incorporated into the 3-D hybrid nanoarchitectures proposed in the NER project.

Hong Kong is often referred to as the place where east meets west and was therefore an excellent IREE trip location for maximizing diversity. The culturally rich experience exposed the research not only to Chinese culture, but also other western cultures. Formally a British colony, Hong Kong has many western influences and many students from all over the world study abroad in Hong Kong. Therefore, the IREE student had the unique opportunity to interact with students and professors from all over the world, including China, France, Germany and Switzerland, which fostered an even greater appreciation for cultural diversity.

The experience not only strengthened existing networks, but also created new networks. During the trip the researcher had a lot of interactions with graduate and post-doc researchers as well as professors. Some of the relationships forged during the trip will inevitably result in future collaborations which will increase productivity as well as international cooperation. In fact, the PI is continuing the collaboration to further refine the CuO NW growth technique and the characterization and application of the product NWs.

DISCUSSION AND SUMMARY

Through the IREE program, we demonstrated that CuO nanowires grown from SMAT treated Cu have larger growth density and are longer than those from the non-SMAT copper under the same growth conditions. The mechanism for improved growth rate may be related to the increase in grain boundaries formed from SMAT treated copper, which enhances the atomic diffusivities during oxide and nanowire growth.

The accomplishments of our international research experience goes beyond the scientific results produced during the trip. The opportunity helped to strengthen existing networks, forging new collaborations, and instilled further appreciation for cultural diversity. The research project is ongoing and will continue to result in co-publications from this international collaboration.

The IREE conference was instrumental in preparation for the IREE trip to Hong Kong. By interacting with past participants, the trip was streamlined and the transition was efficient. It was also useful for networking with other recipients traveling to the same destination. We recommend continuing with the IREE conference for the benefit of future recipients by maximizing the impact of the award.

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BRIEF BIOGRAPHIES OF RESEARCHERS

Benjamin Hansen received the B.S. degree in Mechanical Engineering and Physics from the University of Wisconsin-Milwaukee in 2007. He is working towards an M.S. in Mechanical Engineering at Boston University. As an undergraduate, he participated in the Fermilab Cooperative Education Program in the Cryogenics Department. As a senior, he participated in the NSF REU program at UWM supervised under Dr. Junhong Chen. He is a recipient of the 2008 NSF Graduate Research Fellowship. His research interests include the growth and fabrication of nanoscale materials for device applications.

Junhong Chen received the B.E. degree in Thermal Engineering from Tongji University, Shanghai, China, in 1995 and the M.S. and Ph.D. degrees in Mechanical Engineering from University of Minnesota, Minneapolis, MN, in 2000 and 2002, respectively. His graduate work focused on dc corona plasmas and corona-enhanced chemical reactions. From 2002 to 2003, he was a postdoctoral scholar in Chemical Engineering at California Institute of Technology, where he worked on arc plasma synthesis of nanoparticles. In August 2003, he became an Assistant Professor in the Department of Mechanical Engineering at the University of Wisconsin-Milwaukee. He was promoted to Associate Professor with tenure in June 2008. His current research interests include nanoparticle synthesis, assembly, and nanofabrication, carbon nanotubes and hybrid nanomaterials, nanostructure-based gas sensors and biosensors, energy conversion, conservation, and renewable energy, sustainable environment and pollution control, and corona discharges and plasma reacting flows.

Jian Lu was a senior research engineer and the head of the laboratory (from 1990) of residual stress and coating adhesion at CETIM (French Technical of Mechanical Industry) from 1986 to 1994. Since 1994 he has been Professor, Head of the Department of Mechanical Systems Engineering (1994-2004) and Director of the mechanical systems and concurrent engineering laboratory (CNRS-FRE2719) (20 faculty members) at the University of Technology of Troyes, France. His recent research interests are: residual stress, multiaxial fatigue, biomaterial, metal matrix composite, nanomaterial, plasma spraying coating and thin film. He has published about 300 papers in above fields. He is a member of Editorial board of the Journal of Strain Analysis for Engineering Design, International Journal of Mechanics and Materials in Design. He has also served as an associate technical editor of Experimental Mechanics (International Journal of Society for Experimental Mechanics, USA, 1998-2001) and a member of Editorial board of the ACTA MECHINICA Sinica (2001-2004). He was a consultant expert for different worldwide leading companies in the field of Energy (Framatome, Alstom, EDF), Aerospace (EADS, Airbus, SNECMA), Automobile (Renault, PSA, Bosch) for about 20 years. In 2005 he became Chair Professor and Head of the Department of Mechanical Engineering at The Hong Kong Polytechnic University.