NSF/NSEC Center for High-rate Nanomanufacturing

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The Center for High-rate Nanomanufacturing (CHN) is developing tools and processes to enable high-rate/high-volume bottom-up, precise, parallel assembly of nanoelements such as carbon nanotubes, nanoparticles, and polymer nanostructures. The Center's nanotemplates and processes have already demonstrated fast, massive directed assembly of nanoscale elements. Development of these processes and nanotemplate tools requires a fundamental understanding of the interfacial behaviors and forces necessary to assemble, detach, and transfer nanoelements at high rates and over large areas. These efforts will result in (i) Understanding the fundamentals of synthesis and control at the nanoscale to enable high-rate/high-volume bottom-up, precise directed assembly of nanoelements (ii) Translation of the nanoscale science into practical applications in energy, bio/medical, electronics and materials (iii) Development of responsible manufacturing by understanding and managing potential risks of nanotechnology and (iv) Educating the current and emerging nanomanufacturing workforce. CHN is uniquely positioned to enable the commercialization of nanotechnology. Our processes and tools continue to bridge the gap between nanoscale science and development of commercial products in application areas from bio/med, energy, electronics and materials. In doing so CHN has built strong partnerships with numerous local and national companies (over 26 companies on our IAB). CHN has and continues to presents the technology and societal impacts of nanomanufacturing to a wide range of audiences.

CHN efforts are broadly classified into four thrust areas *(i) Synthesize nanoelements and create versatile nanotemplates (ii) Employ nanotemplates to enable high-rate/high-volume manufacturing (iii) Proof of Concept Test Beds, Emerging Applications, and Manufacturing Readiness and (iv) Concurrently assess the environmental, economic, regulatory, and ethical impacts of nanomanufacturing*

THRUST 1. Nanoelements and Nanotemplates: Most low cost, high-rate nanomanufacturing processes will require bottom-up methodologies whereby molecules, polymers and other nanoelements assemble in predictable ways to form precise superstructures. In order to develop a suite of low cost, high rate nanomanufacturing processes, uniform, robust nanoelements must be engineered at the molecular level and the intermolecular forces between them must be fully understood. The spontaneous assembly is driven by intermolecular interactions (e.g., van der Waals forces, H-bonding, $\pi-\pi$ stacking, electrostatic interactions, etc.) and interactions with the substrate, all of which are critically dependent upon nanoelement structure. Consider, for example, that thin film organic photovoltaics (OPVs) are considered an important alternative energy technology that is amenable to high rate, low cost, roll-to-roll manufacturing. However, the organic semiconductors that comprise the bulk heterojunctions are only stable to oxidation over relatively short durations (2-3 years). Until more robust devices are made, most consumers will reject this technology. Likewise, efficiencies of OPVs are well below those of Si based photovoltaics, in large part because methods to engineer precise thin film architectures containing well defined donor and acceptor nanoscale features are lacking. At CHN, the design and synthesis of well defined, robust nanoelements is aggressively pursued in concert with the development of new assembly strategies and nanomanufacturing processes.

THRUST 2. High-rate Directed Assembly and Transfer: CHN has developed a suite of templates and assembly processes to achieve high-rate nanomanufacturing. These assembly processes utilize electric fields and/or chemical functionalization, capillary force and convection. The template includes either nanowires or nanotrenches structures or patterns. For a variety of applications, a second transfer step may be required and the CHN is investigating transfer processes. We have also demonstrated a directed assembly approach without the use of a transfer process (template-free directed assembly). The assembly is carried out via electrostatic or chemical means directly on the prefabricated existing device structures, i.e. the device itself serves as a platform and final location for the assembly. Using this approach, there is no need for a transfer process to transfer the assembled structure to another substrate. Below we describe how each of these types of nanotemplates can be used to assemble a wide variety of nanoelements ranging from nanoparticle to nanotubes, followed by application of these templates to site-specific directed assembly of polymers.

THRUST 3: Proof of Concept Test Beds, Emerging Applications, Manufacturing Readiness: The two CHN testbeds were chosen to verify manufacturing processes, provide easy to measure output, and to validate process functionality. These testbeds along with the other applications also demonstrate the breadth of product types and materials that can be manufactured using the Center's nanomanufacturing approaches. We are demonstrating the efficacy of the directed assembly process and nanotemplates by developing two products; a nonvolatile nanotube memory device and a biosensor.

THRUST 4. Environmental, Economic, Regulatory and Ethical Impacts of Nanomanufacturing: Complementing the work in Thrusts 1, 2 and 3, the research in Thrust 4 concurrently addresses issues that relate to improving the pathway towards high-rate manufacturing. The rapid rate of development to commercialization requires a thorough understanding of the production costs, environmental and occupational health risks, and broader societal impacts associated with various nanomanufacturing processes.

Research Highlights: A few of the significant accomplishments are briefed below.

Self-assembly of Pentacene Derivatives into One Dimensional Nanostructures: CHN developed self-assembled nanostructures from functionalized pentacenes to make p-type organic semiconducting nanostructures. Different nanoarchitectures like nanobelts and nanohelices are fabricated by optimizing π–π stacking (non-covalent) interactions between the pentacene backbones by selecting proper solvent systems. Morphological, optical and electrical characterizations reveal anisotropic properties making these nanostructures ideal candidates for novel optoelectronic devices. We demonstrated a chemoselective oxidation of the sulfide function on 6,13-bis(decylthio)pentacene, 1, to produce an exceptionally long-lived, robust monosulfoxide derivative

***Synthesis and Characterization of Photooxidatively Resistant Phenethylthio Substituted Pentacene Derivatives**:* We demonstrate for the first time that steric and electronic substituent effects can be synergistically combined using a single substituent, the phenethylthio group, to produce the longest lived pentacene derivatives known. Pentacene derivatives bearing 6,13-bis(phenethylthio) susbtituents (e.g., compounds 2-3) are dramatically longer-lived than any other known pentacene derivatives. Accordingly, they represent prime candidates for thin-film electronic device applications using low cost manufacturing techniques.

Damascene templates for directed assembly: Designed and fabricated a damascene template that offers the advantage of having the same charge on all the nanowires by having all these wires and structures connect to a conductive film underneath. The template has a flat smooth surface with embedded wires to facilitate the transfer process and enable the reuse of the template for hundreds of times. We have achieved directed assembly nanoparticles and SWNTs on damascene template by electrophoresis that were then transferred onto flexible substrates.

Novel Electrophoretic Assembly of Nanoparticles on Insulating Surfaces: Developed an electric field enhanced fluidic assembly technique to assemble nanoparticles on insulating surfaces. Previous methods are very slow processes, and have low throughput results for assembly on insulating surfaces. This technique enables high-rate nanoelement assembly on any insulator material and increases the speed of the directed assembly process by 100 times.

Room temperature, Bottom-up Nanomanufacturing of 3-D Nanostructures Using Nanoparticles: Metallic nanoparticles are precisely assembled and fused into nano pillars and rods using a controlled dynamic electric field. The assembly process is high-rate and conducted at room temperature and pressure making it highly desirable for large scale manufacturing of nanoelectronics, sensors and optical devices. The process does not require any chemical reactions.

Light-Induced Transfer of Nanoelements: Assembly of fluorescein onto TiO2(110) was achieved by irradiating the surface in air through a photomask containing equally spaced lines and was then immediately spun-coated with an ethanolic fluorescein solution. Fluorescence microscopy confirmed successful patterning.

Nanoparticle Chemical Sensor based on Surface Enhanced Raman Spectroscopy: We have developed a non-vacuum based directed assembly process for large array of dense nanometer-sized gaps for SERS based chemical sensors. The assembly is versatile that by optimizing nanoparticle shape/size and gap spacing independently on would be able to get <10nm gaps. We were able to create long-range periodic plasmonic structures, which exhibited SERS enhancement factors of 10^7.

***Chemical Sensor for the Detection of H_2S in Extreme Environments*:** We have designed fabricated and tested a micro-scale robust single wall carbon nanotube (SWNT) based chemical sensor arrays for detection of H_2S in harsh environments. These sensors are conductance based and they exhibit very high sensitivity down to ppms. Modification of these sensors can enable multiple species detection. This device can serve as a platform for measurement of corrosive species, pH, temp, etc in harsh environments.

Process Economics, Scale-up and Life Cycle Assessment: Examination of the full life cycle of nano-enabled products will provide insight on potential releases of nanomaterials. Targeted lifecyles areas are shown where development of methods is important for understanding potential releases of nanomaterials. First steps involve establishment of life cycle inventories in each stage.

Broader Impact

The Center for High-rate Nanomanufacturing is leveraging current and future efforts in nanoscience and technology to bridge the gap between scientific research and the creation of commercial products by established and emerging industries, such as electronics, bio/medical, energy, and materials.

***Education and Outreach**:* As previously developed courses modules and UML's Graduate Certificate in Nanotechnology have become institutionalized, CHN's education and outreach efforts have been focused on a range of other successful programs and a few new efforts. With the assistance of an REU Site Award, 32 undergraduate researchers, including 12 women, and seven members of underrepresented groups, participated in CHN's 2010 Summer REU program and its unique cross-university professional development program. An additional 10 undergraduates (~50% women) were employed as undergraduate researchers during the summer and academic year. CHN sponsored another K-12 teacher conference (with an attendance of 43) in spring 2010 and advised two K-12 teachers in the summer 2010 RET program. K-12 outreach continued with (a) *Project SMART* (UNH), a summer experience for high-school students; (b) *Nanotech will Travel* (UML) which served middle school extended day programs, (c) expanding participation in *Building Bridges* (NEU), and (d) a fourth successful *Region IV Middle Science and Engineering Fair* (UML). The partnership with Museum of Science, Boston, continued to produce new benefits. More advanced Sharing Science workshops were offered, allowing CHN graduate students to presented nanotechnology activities at the Museum for NOVA's Making Stuff and 2010 *NanoDays* events as well as at CHN's booth at the *USA Science and Engineering Festival* in October 2010. Collaboration between CHN and the MOS has produced additional live presentations, cablecasts, Podcasts, YouTube video, and *The Nano Brothers Juggling Show* designed to educate the general public about nanomanufacturing; the audience for these programs was over 3,500,000 million people. Evaluations of the *The Nano Brothers Juggling Show* confirmed that the show was teaching diverse audiences about nanotechnology. The partnership has also provided interaction between CHN and the NISE Network as well as continued training of REU participants. Professional development was available through the *New England Nanomanufacturing Summit, Destination Nano,* and short courses. Finally, CHN's nanotechnology game, *Geckoman!* (NEU) was uploaded to a public website. Through these programs and other short events, CHN researchers have continued to present the technology, benefits, and societal impact of nanomanufacturing to a wide range of audiences.

***Industrial Partnership and Outreach**:* CHN is continuing to engage industry through Ideation Workshops in addition to other events, such as the "Industry Day Showcase" to help translate CHN's research to commercial products. Three "Pre-Ideation Workshops" for CHN researchers were held from April to September 2010 to ensure a productive interaction with companies that will increase the possibilities of a positive outcome in the CHN/Industry Ideation workshop. The attendees were invited faculty, researchers, post-doctoral researchers and senior graduate students from the three campuses in the Center for High-Rate Nanomanufacturing. Following these pre-ideation workshops two "Ideation workshops" that included participants from industry were held on September and October 2010. The goal of this effort was to translate nanotechnology research concepts into products through collaborative research projects with small and big companies. Fifty-two companies, located in the New England area, whose research objectives are closely related to CHN were identified and invited to attend the workshop. Representatives from twenty companies participated in each Ideation workshop. As a result of the Ideation workshop, 14 technologies were identified which have potential market capabilities.

[1] For further information about this project link to www.nano.neu.edu