Center for Templated Synthesis and Assembly at the Nanoscale

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The University of Wisconsin (UW) Nanoscale Science and Engineering Center (NSEC) is comprised of a diverse group of established, world-renowned senior faculty and promising junior faculty from over ten departments. The tightly interwoven multidisciplinary program addresses the directed assembly of complex materials and building blocks at the nanoscale with an exquisite level of detail, including the development of a unique program to explore and understand their societal and environmental implications. The UW infrastructure and breadth of expertise fosters a successful and vibrant NSEC. The research mission of the NSEC is organized into four interdisciplinary thrusts that explore the concept of directed assembly at the nanoscale from different angles:

Thrust 1: *Directed Self-Assembly and Registration of Nanoscale Chemical Architectures* addresses the question of assembling nano-structured objects into functional nanoscale systems. It explores the self-assembly of block copolymers on nanopatterned substrates, the convergent assembly of pre-fabricated nanoscale elements on nanoscale patterns, and the use of electric fields to direct the assembly of nanowires and nanorods in novel types of electronic and bio-electronic devices. The group relies on superb nano-patterning facilities and considerable expertise in the synthesis, manipulation and characterization of nanoscale building blocks, ranging from flexible copolymers to rigid nanowires. Recently we have integrated self-assembling block copolymer into the lithographic process towards the extension of current manufacturing practices to dimensions of 10 nm and less. Retaining the essential attributes of lithography, perfection and registration, we have demonstrated that we can pattern nearly the entire set of essential features required for integrated circuits and meet strict manufacturing criteria with respect to control over feature dimensions, reduced line edge roughness, and scalability. Through both experiment and theory this approach has been extended to create well-defined and predictable three-dimensional nanostructures. To impart greater functionality into the precisely assembled block copolymer domains, we have also synthesized functionalized spherical and cylindrical nanoparticles and intercalated them into lamellar and cylindrical block copolymer morphologies and are currently focusing on understanding how the chemical groups exposed on the nanoparticles control their subsequent intercalation into the block copolymer structures. We have successfully demonstrated the use of electric fields to manipulate individual nanowires across electrode gaps with simultaneous electrical detection, as a way of achieving completely automated assembly of nanowire-based devices.

Thrust 2: *Templated Chemical Synthesis of Sequence Specific Heteropolymeric Nanostructures* explores guided processes of chemical synthesis and assembly on the nanoscale. The group seeks to establish novel thermodynamically-controlled, template-directed synthetic strategies that bring an unprecedented level of control to the synthesis of amide heteropolymers with discrete sequences, shapes and assembly propensity. The group also explores the self-assembly of synthetic, highly stable but unnatural β-peptide sequences into unique nanostructures which are carefully characterized and examined in the context of several applications, including their use for antimicrobial materials and liquid-crystal based biosensors. Two recent accomplishments serve to illustrate the opportunity defined by these novel organic nanostructures. First, at a fundamental level, β-peptide-based nanostructures are providing a new tool box with which to understand the unwritten rules of self-assembly of nano-objects with patterned chemical functionality. Recent results reported in *Journal of the American Chemical Society* demonstrate that subtle variations in chemical patterns presented on the surfaces of β-peptide nanorods can have dramatic effects on their self-assembly. In particular, sequence control was used to manipulate the spatial distribution of charge over the surface of the nanorods, thus unmasking its key role in the expression of long range order, including liquid crystallinity. A second accomplishment is the discovery that β-peptide oligomers that form discrete, globally amphiphilic helices selectively associate with fungal membranes and display antifungal activity. The biological activity of these nanostructures was shown to be strongly influenced by the patterning of chemical functionality on their surfaces. Finally, the folding behavior and stability of individual helices has also been confirmed by using computational methods. In addition to studies in bulk solution, the thrust has initiated an effort aimed at studying the self-assembly of β-peptides at surfaces: these studies have revealed that β-peptides do form organized monolayers at interfaces. This result opens up the possibility of fundamental studies of single-molecule mechanical and electrical properties of individual β-peptides. Other areas of activity in the thrust include the development of synthetic strategies leading to amide heteropolymers.

Thrust 3: *Driven Nano-Fluidic Self Assembly of Colloids and Macromolecules* relies on concerted experimental and theoretical approaches to explore the use of non-equilibrium processes, such as the use of flow and other fields, for nanoscale assembly and manipulation of nanoparticles and macromolecules, including DNA, under severe confinement. Recently the group has developed new quantitative understandings of nanoconfined polymers, and this work was translated into a working integrated system for genomic analysis. The heart of the system centers on the use of nanoslits (rectangular channels bearing a high aspect ratio) demonstrated to significantly elongate long DNA chains under suitable buffer conditions. This robust single molecule display was enabled for "single molecule barcoding" by new labeling and imaging approaches, producing the first working nanoscale system for whole genome analysis.

Thrust 4: *Social, Legal and Environmental Impacts of Engineered Nanomaterials* is a one-of-a kind partnership among social scientists, legal scholars, toxicologists, and environmental scientists and engineers that is developing an integrated, multidisciplinary understanding of nanoscale science and engineering as it moves out of the laboratory and into society. Building on a successful citizens' consensus conference in 2005 and innovative Nano Cafés in 2006, Thrust 4 is continuing dialogue with policymakers and the public about nanotechnology's implications for social and environmental policy. Thrust 4 social scientists are identifying key risk assessment data gaps and legal issues that challenge nanotechnology risk assessors and policymakers. In this light, toxicologists and engineers in have initiated research on the effects of surface functionalization on the toxicology and environmental fate of engineered nanomaterials. Access to the unique synthetic and characterization capabilities present in Thrusts 1-3 allows investigation of a range of surface chemistries substantially broader than that available to most researchers. The toxicology studies focus on characterizing the developmental toxicity of functionalized nanoparticles using embryonic zebrafish as a model vertebrate organism; correlating uptake, bioavailability, and toxicity with nanoparticle characteristics; determining the influence of nanoparticle exposure on gene expression; and developing methods to classify nanoparticles by toxicity. We employ biomimetic catalytic systems to understand the influence of environmental redox processes on the stability functionalized nanoparticles. The toxicology of nanoparticles altered under simulated environmental conditions is characterized using the zebrafish assay. Determining transformation potential is critical for assessing the entire lifecycle of products incorporating engineered nanomaterials and will provide information on the biocompatibility of the materials. Engineered nanoparticles that induce toxic responses in developing zebrafish embryos are evaluated for their potential for transported in porous media (soils, aquifer materials). This integrated approach drawing on public dialogue, engagement of policymakers, and timely scientific information represents a new paradigm for evaluating and understanding the societal impact and public risks of nanotechnologies.

Thrust 1 examines situations and processes in which the self-assembly of mesoscopic materials and the resulting nanostructures can achieve a state of thermodynamic equilibrium. Thrust 2 considers synthetic routes that are also governed by thermodynamic equilibrium and nanoscale templates, but this time at the level of individual atoms and chemical reactivity. Thrust 3 is concerned with nanoscale self-assembly far from equilibrium, driven by the influence of external fields and severe confinement. Thrust 4 considers social influences on and implications of the development, design, reception, and uptake of self-assembling nanotechnological systems. Each group integrates the five essential elements required for forefront research in nanoscale science and engineering: synthesis, theory, structural characterization, property evaluation, and applications. An aggressive Seed program operates in a manner to foster innovation and promote growth and evolution into new, unexplored areas of opportunity. The established Thrusts and Seed projects share a common view, namely the precise synthesis of nanoscale elements, their assembly into nanostructured systems through the use of templates, self-organization and confinement, and the creation of materials, devices, and processes with hitherto unattainable functions.

NSEC education and outreach activities are designed to educate teachers, students, and the general public about nanoscience. Programs for teachers include Research Experience for Teachers, professional development workshops offered through the Wisconsin Summer Science Academies program, and an online nanotechnology course for high school and middle school teachers. NSEC supports programs directed toward K-12 students including projects that help build diversity within the scientific community. The SciEncounters program partners with the local Boys and Girls clubs to excite teenagers and middle school students about science and engineering. The NSEC is a partner with the ILAB program to develop instruments for blind and visually impaired high school and college students to work independently in the laboratory. For undergraduates NSEC hosts an annual Research Experience for Undergraduates program in nanotechnology. NSEC programs for the general public include the SPICE (Students Participating in Chemical Education) program that presents nanoscience and technology demonstrations shows at local public outings. An additional partnership with the UW's Business School assesses the commercial potential and possible pathways to commercialization of technologies under development in the NSEC.

The NSEC activities include the establishment of a Graduate Fellowship Program to recruit the most talented young scientists and engineers to the interdisciplinary field of nanoscale science and engineering and to foster a community of diversity. We have also established links to international laboratories on three continents that support living expenses of our students while they participate in substantive collaborative co-supervised research projects.

The shared experimental facilities of the UW NSEC serve internal and external users in academia and in industry and include the only open-access extreme ultra violet lithography tools in the nation and a new soft materials synthesis and characterization facility.

For further information about this project link to **www.nsec.wisc.edu** or email **nealey@engr.wisc.edu**