Nanoscale Science and Engineering Center for Directed Assembly of Nanostructures

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The NSF *Nanoscale Science and Engineering Center for Directed Assembly of Nanostructures* (www.nano.rpi.edu) was founded in September 2001 at Rensselaer Polytechnic Institute (RPI), in collaboration with the University of Illinois at Urbana-Champaign (UIUC), and Los Alamos National Laboratory (LANL). Our Nanoscale Science and Engineering Center (NSEC) addresses the fundamental scientific issues underlying the design and synthesis of nanostructured materials, assemblies, and devices with dramatically improved capabilities for many industrial and biomedical applications. Directed assembly is the fundamental gateway to the eventual success of nanotechnology. Therefore, our NSEC strives to discover and develop the means to assemble nanoscale building blocks with unique properties into functional structures under well-controlled, intentionally directed conditions. We combine theory and computational design with experimentation to focus on discovery of novel pathways to assemble functional multiscale nanostructures with junctions and interfaces among structurally, dimensionally, and compositionally different building blocks. Our NSEC integrates research, education, and technology dissemination to serve as a leading national and international resource for fundamental knowledge and applications in nanoscale science and technology.

The NSEC *research program* consists of three coordinated interdisciplinary and inter-institutional thrusts. *Thrust 1: Nanoparticle Gels and Polymer Nanocomposites* focuses on the synthesis, phase behavior, structure, and assembly of organic and inorganic nanoparticles with homogeneous or heterogeneous surfaces by means of chemical and/or physical control. Its goal is to guide the organization of nanoscale building blocks to create 3D hierarchical materials with novel properties. *Thrust 2: Nanostructured Biomolecule Composite Architectures* is focused on incorporation of biological macromolecules into nanocomposite materials to enable specific applications, including directed assembly based on biorecognition and biocatalysis, which impact tissue engineering, biosensing, self-cleaning and self-repair capabilities, and the design of novel functional nanostructures. Its goal is to enable the efficient and selective interaction of biomolecules with synthetic nanoscale building blocks to create useful assemblies. The goals of *Thrust 3: Serving Society through Education and Outreach* are to serve society by: (i) raising public science literacy through informal and formal education, and reaching a diverse audience to broaden the technical reach of our NSEC through programs that are carefully designed to integrate nanotechnology research with education, and (ii) enhancing the responsible, safe, and efficient transfer of nanotechnology developments to industry, the primary route through which society can benefit from the fruits of our NSEC research. Hence, our continuing vision encompasses research, education, and outreach through interactions with students of all ages and researchers in universities, national laboratories, and industry.

Thrust 1 has created a unified and integrated experimental and theoretical understanding of the structure, assembly and viscoelasticity of nanoparticle-polymer systems, from nanoparticle gels to polymer nanocomposites, thereby conceptually bridging the fields of colloid and polymer science. We have synthesized organic and inorganic nanoscale building blocks with controlled size, composition, shape and surface functionality, studied the fundamental viscoelasticity, phase behavior and structure of both model and technologically relevant nanoparticle suspensions and mixtures, created 3D hierarchical structures via direct-write assembly of nanoparticle inks, and synthesized, assembled, characterized and modeled the behavior of diverse polymer nanocomposites.

Specific research accomplishments include the following: (1) Established an integrated experimental and theoretical understanding of the structure, elasticity, nonlinear rheological response, and kinetic arrest process of nanoparticle gels created by either polymer-mediated entropic depletion attraction or enthalpic driving forces; (2) Experimentally developed, and theoretically analyzed, a new class of biphasic nanoparticle inks based on tunable mixtures of attractive and repulsive particles for direct-write assembly of complex 3D architectures; (3) Developed a new theoretical approach, integrated with complementary scattering and mechanical experiments, to fundamentally understand and establish design rules for how competing enthalpy and entropy effects determine the multiscale structure, phase behavior, and viscoelasticity of polymer nanocomposites composed of bare fillers; and (4) Synergistically employed novel synthesis, physical characterization, statistical mechanical theory, and computer simulation to establish the role of competing attractive and repulsive forces on isotropic and anisotropic nanoparticle assembly, mechanical properties, and dynamics of a broad class of polymer nanocomposites based on tailored grafted-chain filler particles of controlled architecture.

Thrust 2 has made major advances to the nanoscale science and engineering knowledge base in multiple areas, with two fundamental research programs of greatest accomplishment: (1) Discovery of the effect of nanoscale size and curvature on biomolecule stability and function; and (2) Mechanistic understanding of multiscale phase behavior leading to functional biomolecule composite nanostructure assemblies. With respect to the former, we have discovered the unique behavior of proteins on highly curved surfaces, on which the arc of curvature is on the same scale as that of proteins. This unexpected result has been studied mechanistically and the influence of surface curvature on protein structure, stability, and (in the case of enzymes) catalytic function has been elucidated for the first time, both experimentally and computationally. As a result, we have identified a controllable nanoscale surface property that can control protein function that adds to more well-understood surface chemical properties. Stabilized proteins have been used to increase the efficiency of enzyme-nanomaterial-polymer composites that are being used commercially as antifouling and antimicrobial surfaces that are safe and efficient. With respect to the latter, molecular to nanoscale, and ultimately micro- to macroscale phase behavior has been elucidated both experimentally and computationally toward the goal of designing functional biomaterial systems.

Another very significant advance has been made in elucidating the ‘rules’ of interaction and self-assembly using electrostatic effects in water, which has considerable implications for problems in viable alternative energy areas (e.g., self-assembled systems for photovoltaics, photocatalysis, biofuels) and for problems in human health and disease (e.g., gene and drug delivery, cystic fibrosis, antimicrobials, viral fusion). An example of the impact on human health is in the design of cell-penetrating peptides that have the unique ability to disrupt cellular membranes for use as antimicrobial agents. Extensive molecular dynamics simulations of relevant peptides (e.g., HIV Tat) were performed to understand the physicochemical action of the peptides in their ability to disrupt the phospholipid bilayer structure, as well as controlling water structure leading to a gain in our understanding of pore formation in soft materials. Similar mechanisms may be involved in many other biological systems, like formation of pores by antimicrobial peptides, and voltage gating by movement of Arg-rich α-helices in ion channels. In addition, investigations of DNAzyme-catalyzed assembly and disassembly of nanoparticle-biomolecule conjugates have led to the creation of novel colorimetric environmental sensors with precise selectivity, high sensitivity, and wide dynamic range.

Thrust 3 and our other extensive education and outreach activities have enabled a number of innovative projects with high impact to serve society. Among these our NSEC has: (1) spawned the exciting Molecularium® Project, which was created and released to worldwide audiences the entertaining and educational ("stealth education") science-literacy shows "*Riding Snowflakes*", a 23-minute digital-dome show, and "*Molecules to the MAX!*", a 42-minute Imax show in both 2D and 3D formats; (2) developed high school curricula that have led to two ongoing courses in local high schools and nanotechnology modules in three others; (3) involved more than 60 undergraduates in summer research, a majority of whom are women or under-represented minorities; (4) spun out three start-up companies – *ANDalyze, Inc.*(formerly *DzymeTech, Inc.)*; *Solidus Biosciences, Inc.*; and *The Paper Battery Company, Inc.*, all stemming from our NSEC research; and (5) transferred several technologies based on NSEC research to our industry partners ABB Corporation, Albany International, and Chisso Corporation, including several licensed patents, that have been followed up by related commercialization activities.

There have thus been a significant number of major accomplishments in our NSEC program during the ten-year period 2001-2011. From a global perspective, our research efforts have fundamentally changed the way we look at polymer nanocomposites and gels, taking them from essentially separate scientific research disciplines to areas that inform one another to a conceptually integrated whole – nanocomposites – that spans the nanoparticle concentration range in polymers from dilute to concentrated. Our NSEC's research efforts have also fundamentally changed the way we look at biomolecule-nanostructure assemblies and composites, not only in terms of our ability to now construct new functional hybrid materials with practical applications in several energy, environmental, and health related areas, but also to see clearly the path forward to creating a wide range of heretofore unrealized opportunities for new materials, new devices, and new systems in the future.

Based upon our NSEC's research progress and successes over the past ten years on polymer nanocomposites and nanostructured biomolecule composites, we can see clearly how these two broad areas can now come together to create a new larger world of hierarchical hybrid material systems. These new material systems, and their manufacture, will be designed using a variety of nanoscale building blocks with surfaces intentionally modified through physical, chemical, or biological means interfaced with either synthetic or natural polymers, or combinations thereof, to expand the capabilities of material systems well beyond those available today. As such, we will be able to take full advantage of the significant public investment in our NSEC research programs to help solve major problems to benefit society. In addition, through the creation of our Molecularium® Project and its still developing efforts, we have opened up a new and expanding, entertaining and educational window for the general worldwide public into the nanoscale world of atoms and molecules, a world that is critical to public understanding of the science behind our major global problems and ultimately their solutions. Outstanding progress has thus been made in research, education, and outreach and we will continue to increase our NSF–NSEC's positive impact on both science and society as we move forward in the coming years.