University of North Carolina Institute for Advanced Materials, Nanoscience & Technology: Research Focus Areas

The Institute for Advanced Materials, Nanoscience and Technology (IAM) is a relatively new research endeavor at UNC whose goals are to promote interdisciplinary research in the areas of physical and health related materials science. We draw faculty and students from four core departments (chemistry, physics and astronomy, math, and computer science), and build bridges between these departments and other units on campus including the School of Medicine, School of Pharmacy, Environmental Sciences and Engineering, and the Renaissance Computing Institute (RENCI). This past year we opened our shared instrumentation facility – Chapel Hill Analytical and Nanofabrication Laboratory (CHANL) – and we expect a period of rapid growth given the opening of our new 2200 ft^2 cleanroom and the imminent arrival of major nanofabrication and surface analysis tools in the Spring 2007 semester. CHANL will serve researchers not only at UNC, but across the Research Triangle area, and will provide a state of the art collection of instrumentation and training not possible in individual PI laboratories.

Materials science at UNC was recognized in the latest Chronicle of Higher Education rankings as second in material science and engineering programs across the country. In addition, the chemistry department at UNC has a longstanding position of leadership in research and training in the chemical sciences. The chemistry faculty includes 6 members of the National Academy of Sciences, one member of the National Academy of Engineering, a past President of the American Chemical Society, a Priestley Medal recipient, and numerous winners of other national awards in Chemistry. The chemistry graduate program is consistently ranked in the top 15, with certain areas such as analytical and polymer chemistry ranked at or near number one. The soft condensed matter group, housed in Physics, Chemistry and Applied Mathematics, has achieved a variety of distinctions, including major interdisciplinary funding from NASA, NSF, DOE and most recently NIH. The Computer Science program is routinely ranked at the top in visualization and graphics, and their faculty work closely with medical scientists in imaging and real-time visualization of experimental data. The Applied Mathematics program, while only 10 years old, has major funding for interdisciplinary research collaborations and training. This group provides computational modeling and simulation tools across the physical and biomedical sciences, with ongoing funded research projects.

Nanophotonics (Rene Lopez)

One of the greatest challenges presented in nanoscale science is understanding and controlling electromagnetic wave propagation within nanostructured solids. The nanoscale optical properties of many materials have yet to be discovered; however, the potential impact of nano-optics on modern nanotechnology, photonics and optical communications can not be overestimated. Technologies such as nanolithography, high density optical data storage, photochemistry on a nano and molecular scale, materials imaging and surface modification with subwavelength lateral resolution, local linear and nonlinear spectroscopy of biological and solid-state structures, and inclusive quantum computing can all benefit from a greater understanding of these nanophotonic effects.

In principle, wave control via photonic design is capable of outperforming all geometric optics approaches for sensor, telecommunication and even solar energy harvesting applications in certain wavelength ranges. In contrast to geometric optics, which treats all wavelengths of light equally, photonic methods can be targeted to enhance select wavelength ranges. With the advanced nanofabrication capabilities of CHANL, the Lopez group will pursue development opportunities in the following areas:

- Photonic light trapping for solar cell applications
- Photonic crystal waveguides/cavities/couplers for filtering and sensing based in chromogenic metal transition oxides (WO_3, V_2O_5, IrO_2)
- Subwavelength control of electromagnetic fields via plasmonic nano-devices
- Bio-inspired photonic designs for optimization of photonic crystal devices
- Novel magneto-optic photonic switching structures based on coherent enhanced faraday effects
- Optical initialization and readout of photonic/spin networks of doped TiO_2 for spin-based quantum computing.

Organic Spintronics (Wei You)

Conventional electronic devices are charge-based: they ignore the spin properties of the charge carriers (electrons). The emerging field of spintronics (spin transport electronics), in which the spin degree of freedom (up or down) of the electrons is used in addition to, or instead of, the charge degree of freedom, is full of opportunities, since spin can be manipulated at a faster speed and lower energy cost than charges. Numerous materials for spin-based multifunctional devices have been proposed for or implemented in memory devices, spin valves, spin-transistors, and spin-light emitting diodes. Until quite recently however, nearly all activities in spintronics have been focused on studying inorganic magnetic heterostructures. Organic molecular materials possess a variety of properties that make them well-suited for spintronics applications. First, spintronics requires a long spin diffusion length in order to manipulate spins, and the weak spin-orbit and hyperfine interactions in organic molecules, are expected to increase the spin diffusion length as compared to conventional metals and semiconductors. A second but equally important feature is the tunability of the electronic structure of organic molecules through chemical structure modification. It has been shown theoretically and experimentally that for an organic spin valve with magnetic contacts, large magnetic resistance effects can be produced in both tunneling and conducting regimes.

We plan to further explore the potential of organic materials for spintronics applications by tuning the properties of these active materials through synthetic chemistry and by fabricating these devices on the molecular scale. Individual organic molecules, while only a few nanometers in dimension, have been shown to be fully functional, and in some cases they show vastly improved electrical function over bulk systems. Molecular-scale spin-based devices, such as organic spin valves, are attractive for meeting the increasing demand for miniaturization and high performance information processing. We are trying to combine conjugated organic molecules with magnetic nanoparticles to fabricate spin valves through a layer-by-layer approach. This effort is important academically (how to manipulate spin in nanoparticles and organic molecules) and has numerous applications such as memory devices. In order to investigate these mechanisms, we are exploring molecular spin valve construction through rational design and synthesis of novel conjugated molecules, and will investigate the spin transporting properties using scanning tunneling microscopy.

<u>Organic/Inorganic Hybrid Solar Cells (Wei You)</u>

To reduce the greenhouse effect associated with burning fossil fuels and to sustain healthy growth of the world economy, it is imperative to search for alternative, renewable energy sources, such as solar energy. There has been a tremendous amount of effort to construct (PV) cells with high energy conversion efficiency and low production cost. Compared with mainstream photovoltaic (PV) cells which are typically built with expensive crystalline silicon, PV cells using organic semiconductors have unique advantages: (1) high optical absorption coefficients; (2) adjustable band gaps to harvest a larger fraction of the solar spectrum; (3) compatibility with flexible substrates and low cost high throughput printing techniques. However, until now, the highest efficiency of organic PV cells has only reached ~ 5%.

By approaching this problem from multiple angles we hope to achieve a comprehensive solution to push PV cell energy conversion efficiency towards 20%. We are applying the following strategies: (1) synthesizing novel small bandgap materials to harvest more photons (2) building well ordered materials and device structures to capture more excitons and to efficiently separate them into mobile charges; (3) engineering the interface between dissimilar materials to further improve charge separation and subsequent charge transport; (4) controlling the intermolecular assembly processes to enhance charge mobilities.

<u>Electron Transfer in Molecular Assemblies (Tom Meyer)</u>

Current activities in the Meyer research group include extensions of long standing research efforts in the *photophysical and photochemical properties of molecular excited states and molecular assemblies in sol-gels and thin organic films and on the surfaces of nanoscale oxides*. Of interest in these studies is creating the fundamental understanding for potential device applications in information storage and energy conversion.

The photophysical properties of these excited states are investigated by transient laser spectroscopies including absorption, emission, IR, resonance Raman- and, in collaboration with the Papanikolas group, by ultrafast methods. The studies are largely based on robust metal complexes such as $[Ru(bpy)_3]^{2+}$ (bpy is 2,2'-bipyridine) in composites including organic electron and energy transfer carriers.

In rigid media, such as poly(methyl methacrylate) (PMMA) and SiO_2 sol-gels, excited state properties are significantly modified due to the rigidity of the environment. Rapid inter-site energy transfer occurs by percolation in highly loaded films. In current experiments intrafilm electron and energy transfer are being investigated systematically with added electron and energy transfer carriers in order to establish the "rules" for long range electron and energy transfer. In a second generation of experiments redox traps will be introduced to create a basis for introducing local electric fields and systematic non-linear effects which are erasable in optical write-read cycles.

Experiments have also been initiated on the photophysical properties of derivatized, high surface area, optically absorbing nanoparticle films of TiO_2, ZrO_2, and SnO_2. The surface structures are formed by utilizing chemically stable phosphonate or carboxylate links to metal complex light absorbers, molecular assemblies, and organic electron or energy transfer carriers. On these surfaces excitation is followed by rapid cross-surface energy and electron transfer controlled by the composition and nature of the electron or energy transfer carriers. As in the film studies described above, introduction of redox traps is being investigated as a means for introducing local electric fields and transiently stored redox equivalents.

NanoSciences Research (Rich Superfine, Sean Washburn, Otto Zhou, Jianping Lu, Mike Falvo)

With the NanoSciences Research Group we develop the science and technology for studying molecular devices, materials and circuits. We have a range of electron and scanned probe microscopies and synthesis capabilities to create nanomaterials, to place them inside single molecule devices and to test their mechanical and electrical properties. Ongoing research includes electromechanical devices based on individual single wall carbon nanotubes, hybrid DNA-metal/semiconductor nanorod self assembling circuits and nanocolloid magnetic elastomers for actuating materials. We have a strong interest in biophysics, including developing new instrumentation for measuring forces at the single molecule, cellular and tissue level. Our NIH funded center for Computer Integrated Systems for Microscopy and Manipulation (CISMM) is a collaboration between Physics and Computer Science to combine instrumentation systems with advanced user interfaces, image analysis and visualization. Our biophysics interests, in collaboration with a wide assortment of researchers across the country, include the rheology of biofluids and engineered tissue scaffold, the forces of cell division and cell mechanoresponse, magnetic particle drug delivery, fibrin gel (blood clotting) properties and the biophysics of how the lung clears infections (see the Virtual Lung description below).

Our work is enabled by instrument development for biophysics most recently involving magnetic force systems. The instrumentation we have invented applies large, fast forces to magnetic beads within the biosystem. We have been developing a single specimen sample for several years, and are most recently developing a system to be used in a 96 well format for high throughput screening. We believe this new technology will have a significant impact in drug discovery and delivery for cancer, blood clotting and mucus clearance pathologies.

Drug Delivery with Monodisperse Nanoparticles (Joe DeSimone)

Nanoparticles, nanoscopic “vessels” and polymer-drug conjugates can be the most effective drug delivery vehicles – if they are engineered to be biocompatible, site-specific, have optimal capability to carry relevant cargo, and can demonstrate controlled release of that cargo. Nanofabrication of organic particles to develop an effective platform delivery system for use in nanomedicine can be accomplished using a technique, called **PRINT** (**P**article **R**eplication **i**n **N**on-wetting **T**emplates). **PRINT** is based on molds of new fluoropolymers which are liquids at room temperature and can be photo-chemically cross-linked into elastomeric solids. These polymers enable both improved high resolution imprint lithography, an emerging technique from the microelectronics industry, and the fabrication of organic particles. **PRINT** allows for the precise control over particle **size** (20 nm to >100 micron), particle **shape** (spheres, cylinders, discs/platelets, toroidal), particle **composition** (organic/inorganic, solid/porous, textured/untextured), particle **cargo** (hydrophilic or hydrophobic therapeutic molecules, biologicals, peptides, proteins, oligonucleotides, siRNA, imaging agents such as MR contrast agents, positron emitters, fluorophores, etc.), particle **modulus** (rigid, flexible, deformable) and particle **surface properties** (avidin/biotin complexes, targeting peptides, antibodies, aptamers, cationic/anion charges, stealth PEG chains for steric stabilization).

PRINT is delicate and versatile enough to be compatible with a wide variety of important biomaterials targeted for advanced understandings and therapies in disease prevention, detection, diagnosis and treatment. To date, we have fabricated monodisperse particles from a wide range of particle matrix materials including biocompatible poly(ethylene glycol) (PEG) and bioabsorbable poly(D-lactic acid). The compatibility of **PRINT** with fragile biological cargos has been demonstrated by incorporating proteins, DNA, and anti-cancer agents such as doxorubicin into PEG nanoparticles using the **PRINT** technique. For certain applications, the release of cargos from the matrix materials is desired, and the carriers should be able to be designed so that they can release their cargo via several different mechanisms. Specifically, the triggered release mechanisms that we propose to explore include i) biological and chemical degradation of the matrix, ii) endosomal release via the proton sponge effect, and iii) the externally-induced, inductive heating of the carriers using magnetic fields. In various delivery technologies, it has been demonstrated that the judicious attachment of various chemical moieties onto the surface of drug carriers can also have a significant effect on the bio-distribution and ultimate efficacy of the delivery vectors, especially as it relates to receptor-mediated cellular uptake. Methods to conjugate specific targeting ligands such as antibodies, cell-targeting peptides, aptamers, and a variety of vitamins are being developed. Because of the versatility and power of the **PRINT** technology all of the attributes mentioned above can be independently designed to create truly engineered drug therapies. For the first time, it should be possible to simultaneously design key therapeutic parameters such as bioavailability, biodistribution, and target-specific cell penetration into a single therapy.

Micro and Nanofluidics (Mike Ramsey)

We are interested in utilizing micro- and nanofabrication strategies to create devices that enhance our abilities to gather chemical and biochemical information. Our motivations for fabricating devices include high-throughput biochemical experimentation, development of new types of chemical sensors, and understanding of fluid transport mechanisms in nanoscale-confined spaces. The devices that we develop have application to drug discovery, health care, environmental monitoring, and basic research.

Our efforts in developing microfluidic devices are primarily focused on technology for high throughput interrogation of the biochemical heterogeneity of single cells. The biochemical characteristics being probed include cell signaling pathways, protein expression related to cancerous disease states and comprehensive protein expression. Approaches to these problems primarily involve engineering of conventional laboratory measurement strategies onto microfabricated fluidic platforms. The motivations for such development include the small volumetric scales that can be manipulated (nanoliters to attoliters, thus approaching the volume of a single cell) and the speed advantages accruing from mass transport across small length scales and automation by monolithic integration.

More fundamental in nature is the study of molecular transport through molecular scale conduits, what we refer to as nanofluidics. There are a number of experimental challenges in this area of research, including fabrication of fluid conduits at molecular length scales and reduction to practice of experiments to observe transport at the single molecule level. We are studying both fluid and polymer transport through individual nanoscale conduits or pores that are top-down fabricated in hard materials such as glass, quartz, silicon, and silicon nitride. Focused ion beam milling strategies are being augmented to produce features below 10 nm in insulating materials. Further, electron beam milling techniques are being investigated to push top-down fabrication capabilities to the 1 nm length scale. We are also attempting to reduce lateral dimensions of channels and pores further utilizing bottom-up strategies and by interfacing molecular assemblies to features formed in hard materials. While this work is fundamental, we are also investigating their potential applications, which include the separation and analysis of biopolymers, new types of chemical sensors, and technology for rapid, low cost sequencing of single DNA molecules. In the latter application, we are interfacing nanowire electrodes with nanochannels in an attempt to interrogate individual nucleotides comprising a single oligonucleotide using electron tunneling. Computational simulations have suggested that the four different nucleotides in DNA can be differentiated by such measurements. Our developments in nanofabrication will obviously have other potential applications in fields such as nanoelectronics, e.g., nanoimprint lithography molds.

Virtual Lung Project (Greg Forest, Michael Rubinstein, Rich Superfine, Tim Elston, Russ Taylor, Sorin Mitran)

The Virtual Lung Project has spawned a wide spectrum of nanotechnology applications. In this collaboration between faculty and students from Applied Mathematics, Chemistry, Computer Science, Pharmacology, Physics & Astronomy, and the Cystic Fibrosis Center, we are adapting and designing instrumentation from nano-scale microscopy toward understanding the physical and chemical properties of pulmonary cells, tissues, liquids, and cilia, and toward understanding how biological components in an organ interact to perform vital functions in "normal" versus "diseased" states.

The classical view of the airway surface liquid (ASL) is that it consists of two layers – the mucus and the periciliary layer (PCL). The mucus layer is propelled by cilia and rides on top of the PCL, which is assumed to be a low viscosity dilute liquid that does not hinder cilia beating and acts as a lubricating layer for mucus motion. This simple classical model of ASL has a major problem, however. It does not explain what stabilizes the mucus layer and prevents it (and the pathogens it contains) from penetrating the PCL and adhering to the cell surface. We propose a different model of the ASL in which the PCL consists of a dense brush of mucins attached to cilia and microvilli. This brush stabilizes the mucus layer and prevents its penetration into the PCL, while providing lubrication and elastic coupling between beating cilia, as well as protecting cells from particles and bacteria contained in the mucus. The predictions of our polyelectrolyte brush model, such as mucus concentration dependence on PCL thickness and of mucus transport velocity, are in good agreement with fluorescence probe and confocal data. This systems level approach toward pulmonary function and dysfunction, built up from nanoscale components and experiments, has implications for many health technologies: new methods of drug discovery, approval, and delivery; new methods for probing the physical and chemical properties of biological material; and the theoretical and computational foundations for interpreting data.