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INTRODUCTION

The Center for Nano-enabled Device and Energy Technologies (CNXT) was organized in late 2004 and announced in April of 2005. The Center will harness the diverse nanometer-scale science and engineering work at Carnegie Mellon University to bring focus and purpose to select societal problems. At its inception, eleven multidisciplinary and collaborative projects, involving 21 faculty members, were seeded with internal support. This support was made possible through the offices of the Dean of Engineering (Dr. P. K. Khosla), the Director of the Institute for Complex Engineered Systems (Dr. C. H. Amon), and the Dean of Science (Dr. R. D. McCullough).

The mission of the Center is to address critical contemporary problems whose solutions might be found in appropriate nano-enabled technologies. The current focus is on highly sensitive, compact and rugged nano-enabled sensor technologies; as well as on efficient and cost-effective energy technologies. In sensors, current projects range from implantable biosensors to environmental remediation nanotechnologies. Projects in the energy arena include solid-oxide fuel cell technologies and direct methanol fuel cell technologies, as well as polymer solar cell technologies. CNXT draws heavily on expertise from departments across the colleges of engineering and science. It pursues basic research in science and engineering activities at the nanometer-scale. The overarching goal of these activities is to enable the design of innovative systems. The unifying theme of the work is nanometer-scale materials that are synthesized, self-assembled, assisted to self-assemble, or structured by engineering know-how to create novel properties, processes, or principles. It is the new properties or principles that are taken advantage of in the design and engineering of innovative (i) unique structures, (ii) devices, (iii) arrays of devices, and (iv) ultimately systems.

This document contains summaries of ongoing projects that were seeded in the first year of the Center’s operation. Additional information about the Center or about any of its projects may be found at the Website cnxt.web.cmu.edu or obtained by contacting us at cmu-nano@cmu.edu. The information also may be obtained directly from the participating faculty (whose profiles and contact information are provided at the back of the booklet).

Elias Towe
Director
Efficient conversion of sunlight to hydrogen by photolysis — the splitting of water through direct photocatalysis — is expected to be a major enabling technology for the hydrogen economy, but improvements in catalyst design are required. In this seed work, we will carry out basic materials and systems research aimed at understanding, designing and producing novel nanocomposite catalysts that facilitate photolysis of water using solar energy. The composite catalysts we plan to study and improve upon incorporate internal electric fields that will be manipulated to control the spatial separation of both charge carriers and half-cell reactions by the phenomenon we call the dipolar field effect. The nanoscale nature of the components in these composite catalysts is essential for controlling the internal fields, charge carrier separation, and absorption; and it will increase the surface area of the catalysts. We propose that building composite photocatalysts around a ferroelectric base will not only minimize losses from recombination events, but it will then enable the incorporation of components to optimize absorption and catalytic properties; ultimately leading to improved solar hydrogen production. We propose that the solution to overcoming these issues is to combine inorganic materials that alone or together efficiently promote one or more of these processes. In other words, our hypothesis is that nanostructured catalysts comprised of the appropriate building blocks will be able to realize efficient solar photolysis.

Selected Highlights

Most efficient photocatalytic materials belong to the oxide families containing closed-shell transition metal cations such as titanium (+4) and niobium (+5). These materials exhibit photocatalysis using UV light, but their conversion efficiencies are too low to be useful. Furthermore, because they are transparent to visible light, they are inactive in the spectral region where the solar spectrum is most intense. There are six characteristics that the ideal solar photocatalyst should exhibit:

(i) Photogenerated charge-carrier separation to reduce recombination losses and increase surface resident times;
(ii) Spatial separation of electrochemical half-cell (redox) reactions to reduce back-reactions of intermediates;
(iii) Long-term chemical stability in the operating conditions;
(iv) Catalytic activation of the oxidation-reductions reactions to minimize overpotential losses;
(v) A band-edge match of the photocatalyst with the solution electrochemical potentials; and
(vi) An overlap of the absorption spectrum of the photocatalyst with the solar spectrum.

We focused our attention to three main areas related to the above-described issues:
(1) Determine the nature of the Dipolar Field Effect on photocatalysis for BaTiO₃ / TiO₂ composites. This aims to improve characteristics (i), (ii) and (iii).
(2) Develop methods to quantify the efficiency of powders and pellets based around ferroelectric composites, where the ferroelectric provides the DFE to be active in a photocatalytic portion of the composite. This also aims to improve characteristics (i)–(iii), but using a catalyst form that may be technologically more relevant, and in a quantitative manner that will build towards improving characteristic (iv).
(3) Use nanoengineered artificial structures to design photocatalysts that include a solar-active photocatalysts. This area aims at incorporating a material that exhibits characteristic (vi) into the composites that exhibit characteristics (i)-(iv).

In area (1), we used polycrystalline BaTiO$_3$ compacts that exhibit ferroelectricity. In the left panel of the figure given below (Fig. 1), we show an atomic force microscopy (AFM) image taken on one of our BaTiO$_3$ samples, which clearly exhibits contrast variations in the topography. This relief actually is related to the direction of the internal field (or polarization) in this ferroelectric $^4,5$. This is confirmed by the image in the middle panel of the figure, which is a scanning potential microscopy (SPM) image of the same region. In this image, the contrast is related to the potential (or field) at the surface of the ferroelectric. There is a one-to-one correspondence between the AFM topography and the SPM contrast, as expected. We deposited films, whose thickness was on the nanoscale, of TiO$_2$, a well-known photocatalyst $^1,5,6,8$, on the BaTiO$_3$ polycrystals [this has an element of area (3) in it as well]. We then carried out aqueous photocatalytic reactions that leave insoluble products on the surface at locations where the reduction reaction occurred $^4-6, 9$. The right hand panel of the figure is an AFM image of the surface topography after this photocatalytic reduction was carried out on the TiO$_2$-coated BaTiO$_3$. It is clear that the white regions, which are silver deposits that indicate photoreduction took place at this location, form patterns identical to those of the ferroelectric domains. This indicates that the field of the BaTiO$_3$ support influences the spatial location of the half-reaction.

![Figure 1](image1)

In area (2), we have built two different apparatuses to quantitatively determine photochemical activity. These experimental setups are given in the figure below (Fig. 2). The setup on the left is based around the use of a spectroscopic method, wherein the photocatalyst is suspended in a reactive dye. A UV-vis spectrometer is used to measure quantitatively the amount of the dye in the solution. A functioning photocatalyst will decompose the dye, decreasing the signal on the spectrometer, and the reaction process can be monitored quantitatively over time. The apparatus on the right has a photocell coupled directly to a gas chromatograph, allowing the photolysis reaction to be monitored for production of H$_2$ and O$_2$ from the photochemical dissociation of H$_2$O. Initial testing of both of these apparatuses has been run, and their sensitivity is currently being optimized for the reactions of interest.

![Figure 2](image2)
In area (3), we have carried out experiments to develop thin coatings of known UV-photocatalysts, as well as their solar-absorbing oxynitride counterparts. For example, Sr$_2$Nb$_2$O$_7$ is a well-known UV-active photocatalyst\(^7\). By substituting N(-3) for O(-2) anions, one can produce a related material, SrNbO$_2$N, which has a band gap of 1.9 eV; almost ideal for solar activity\(^11\). We have explored a variety of deposition conditions to understand the effects of temperature, pressure, substrate type, and gas type (O\(_2\), N\(_2\), and NH\(_3\)) on the growth of materials in this family\(^10\). Significantly, we were able to obtain both the photocatalytic material Sr$_2$Nb$_2$O$_7$ and a perovskite SrNbO$_{2+x}$N$_{1-x}$ as thin coatings, which can be incorporated into composite structures. The X-ray diffraction patterns given in the left panel illustrate that we can grow c-axis textured Sr$_2$Nb$_2$O$_7$ photocatalysts in O\(_2\). The figure below (Fig. 3) illustrates that by changing to N\(_2\) gas, the structure changes to the perovskite of the SrNbO$_{2+x}$N$_{1-x}$ phase. Furthermore, by depositing in NH\(_3\), we obtain similar films to those deposited in N\(_2\) in terms of diffraction results. We currently are determining the N contents in the films deposited in N\(_2\) and NH\(_3\).

References:
Synthesis, fabrication and testing of nanostructured catalyst morphologies for direct methanol fuel cells

**Project Summary**
An ideal anode catalyst for Direct Methanol Fuel Cells (DMFC) requires minimum loading of the precious material catalyst (Pt-Ru); highest specific surface area for triggering the required electrocatalytic reaction and efficient removal of generated CO2 molecules. The present proposal describes the fabrication and testing of nano-structured forms of Pt-Ru catalyst compositions in nano-scale powders and nanotubular configurations with variable dimensions which will validate the theoretical and modeling studies being conducted in a related project. The result of the tests will be compared with model predictions. The present approach attempts to exploit the heterogeneous catalysis concepts of fine particles, and catapult it into a higher domain by exploring the advantages of nano-scale microstructures of the catalyst. Thus, the generation of nano-tubes or nano-rods, 1–2nm in diameter of the catalyst will likely achieve the combined advantages of high specific surface area on the order of 500 m2/g by configuring the length and diameter of the tubes, the spacing between the tubes, and the porosity while also maximizing surface coverage. The ability to design controlled nano-tube architectures with precise spacing and nanotube dimensions correlate well with the steady-state and transient modeling results in the related sister project. The resultant architectures have been characterized for structure, composition, microstructure, and electrochemical performance by testing in standard three-electrode, half-cell configurations. Initial results show that the performances of these catalysts exceed the performance of the traditional catalysts. The optimum configurations of the tubular structures then will be tested in a full cell as well.

**Selected Highlights**
Direct methanol fuel cells have received considerable attention as power sources for several defense and automotive applications due to their lower weight and volume compared with indirect fuel cells. These advantages in weight and volume are due to the elimination of additional fuel reformation processes, resulting in simple design and operation, higher reliability, and reduced costs of operation and maintenance. Therefore, the capacity of providing continuous power with the use of a low-cost fuel such as methanol makes it an ideal candidate as a low-cost alternative power source for use in automotive applications in comparison to rechargeable batteries. One of the key issues arising in the development of high-performance direct methanol fuel cells is the improved catalytic activity of the anode. There have been significant efforts to synthesize anode catalysts possessing excellent catalytic activity for oxidizing methanol. To this extent, Pt-based alloys have been developed and mostly investigated as the anode catalysts. It is well known that the catalytic activity of platinum for methanol electro-oxidation can be increased by the addition of second elements such as Sn, Ru, Re, and Os. This is because the addition of these second elements enhances methanol oxidation due to the formation of metal-oxygen bonds, which is one of the important parameters and is the main rate-determining step in the oxidation of methanol. Among Pt-based binary bifunctional catalysts, Pt-Ru is known for its most promising catalytic activity. Equimolar catalysts corresponding to Pt:Ru = 1:1 supplied by Johnson Matthey (JM) are considered as the standard for comparing the catalytic performance of electrocatalysts. All of the catalytic activity of equimolar compositions of Pt:Ru=1:1 reported in the literature to date, however, have been inferior to the JM catalysts. Studies conducted in the current PITA grant, however, indicate that the addition of trace amounts of transition metals such as osmium has the potential of matching and even exceeding the catalytic activity of JM catalysts. Nanotubular forms of the Pt-Ru catalysts also could offer improved catalytic activity due to the enhancements in surface area that are likely with the generation of the nanotube configurations.
Limitations of current system and approaches:
The equimolar composition (Pt:Ru=1:1) has been considered as the promising electrocatalyst system to date, and the JM commercial catalyst corresponding to this composition has been accepted as the gold standard for evaluating and assessing the performance of electrocatalysts. There also are several approaches reported for synthesizing Pt-Ru catalysts. Most of these approaches involve the use of halide salts of Pt and Ru, which require a follow-up washing treatment to remove the undesired halide residues. As a result, these processes are cumbersome and can cause significant loss of the starting noble metal precursors, rendering them cost-intensive. Furthermore, the approaches are limited in terms of the surface area, morphology and electrocatalytic efficiency.

Objectives of the current work
The present study capitalizes on the results obtained in the ongoing work. In the current PITA grant, the addition of transition metal additives such as osmium (Os) and iridium (Ir) to the equimolar Pt-Ru composition have led to the sol-gel derived catalysts exhibiting catalytic activity matching that of the JM catalyst. These results suggest that the generation of high specific surface area catalysts corresponding to the new compositions likely will exhibit catalytic activity exceeding that of the JM catalyst. The present proposal therefore is aimed at developing novel sol-gel approaches using non-halogen-based precursors to synthesize improved compositions of Pt-Ru catalysts containing varying amounts of Os and Ir in addition to Ni and Co. These approaches will result in high surface areas on the order of 140-200 m\(^2\)/g of the new compositions that likely will exhibit electrocatalytic activity superior to that of the JM catalysts. We already have demonstrated the feasibility of the approach. The present work will focus on engineering and optimization of the sol-gel process and the compositional design to attain improved catalysts that will exhibit both surface areas and electrocatalytic performance that has never been seen or reported using hitherto known approaches for generating Pt-Ru catalysts.

Results to date
Novel non-halide-based sol-gel approaches have been developed to synthesize nanostructured forms of Pt-Ru and Pt-Ru-Os formulations that exhibit comparable and even superior performance to the standard Johnson Matthey (JM) catalysts. These catalysts have been generated using precise control of the heat treatment environment to eliminate the nonconducting carbonaceous species, thus generating catalysts with surface areas as high as 160 m\(^2\)/g. The addition of trace amounts of Os helps to further enhance the performance of the catalysts, rendering them superior to the standard JM catalysts. Fig. 1 shows the high-resolution TEM image of the 2–5 nm catalyst particle that is devoid of any defect. Fig. 2 shows the improved catalytic performance obtained. Preliminary results on nanotubular configurations of these catalysts on novel non-carbon supports that are much more stable to electrocatalytic oxidation and reduction environments of the DMFC are currently ongoing. These results will be reported shortly.
References

Nanostructured electrolytes for single-chamber planar fuel cells

**Project Summary**

Solid oxide fuel cells (SOFCs) that operate at intermediate (600 °C – 800 °C) and low temperatures (< 600 °C) are expected to form the basis of alternate power technologies in the future. Decreased operational temperatures allow for simpler cell geometries that overcome several of the downsides to the high-temperature SOFCs used for distributed power, including sealing and cost, as well as for novel devices such as single-chamber (SC-) SOFCs that can be used in portable power applications. SC-SOFCs are a new type of cell that use combined fuel-oxidant mixtures that are selectively reacted at the anode-cathode, respectively, and have been formed into operational batteries. Nevertheless, intermediate- and low-temperature SOFCs require improved electrochemical performance from the materials used in their components. SOFC materials often are complex and have a large number of interfaces and boundaries that are electrochemically active, but which are poorly understood. In this work, novel nanostructured components were developed, and advanced characterization methods were exploited for IT- and LT-SOFCs in order to gain a better understanding of the structure and properties of interfaces in SOFCs. This work is expected to serve as the basis of a larger scale future effort focusing on a systems development of these SOFC technologies. In this work, a student will develop nanostructured fuel cell components and characterize them structurally and electrochemically. Materials will be tested with the aid of external government participants who are experts in electrochemistry. Furthermore, orientation imaging microscopy will be used to investigate the nanoscale microscale features in industrially prepared SOFCs.

**Selected Highlights**

The work has focused on developing the advanced tools required to investigate the structures and stabilities of interfaces in solid oxide fuel cells (SOFCs). The first tool is a structural characterization technique, called orientation imaging microscopy, which nominally is capable of identifying and classifying a statistically relevant number of interfaces SOFC materials. The goal is to quantify the entire interfacial structure of the SOFC, and then correlate that structure with electrochemical performance. To date, we have succeeded in implementing this approach on SOFC cathodes. The second tool is layer-by-layer, thin-film deposition, which is capable of both producing a large number of specific interfaces and determining the preferred types of interfaces. The goal is to develop samples with a limited number of specific interfaces, allowing us to investigate their electrochemical properties, and to isolate the thermodynamically preferred interfaces. To date, we have determined that no single epitaxial relationship exists for the low-index surfaces of cathodic materials, but that nanostructured thin films can indeed be grown and characterized.

Because of the collaboration developed with researchers at NETL, we focused in this period on the interfaces in SOFC cathodes. The cathode is believed to be problematic with respect to long-term degradation of HT-SOFCs and to losses in IT-SOFCs. Cathodes are complex, three-phase materials that are composed of interpenetrating, contiguous phases that conduct ions, electrons, or gas molecules. The main reaction that occurs at the cathode is the reduction of a gaseous oxygen molecule (O₂), using electrons (e⁻) taken from the electron conductor, to oxide ions (O²⁻) in the ion conductor. The gas molecule is transported through the pore network, and the overall reaction occurs at the pore phase-ionic conductor-electronic conductor boundary. In current SOFCs, the electron conductor is (La,Sr)MnO₃ (LSM) and the oxide ion conductor is yttria-stabilized zirconia (YSZ), or (Zr,Y)O₂-x. The reaction can be written as:
SOFCs contain an enormous number of interfaces, whose features vary their length scale from nanoscopic to macroscopic. The atomistic electrochemical processes that govern the physical properties and performance, however, should be most sensitive to the nanoscale structural features at these interfaces. Still, very little is known about the nature of any of the real interfaces in SOFC cathodes.

With respect to the first goal, we have adapted the use of OIM to SOFC cathodes, and have generated the first orientation maps of these complex materials. The left image in the figure below (Fig. 1) is a raw (unprocessed) inverse pole figure map of the grains in a cross-sectional image of a commercially prepared SOFC. The upper-most region is the pure YSZ electrolyte. The middle region is the electrochemically active cathode. The lower region is pure LSM, the electronic contact with the external circuit. The colors represent the orientation of the grain that is normal to the image. From these maps, one can construct the distribution of the crystallographic traits of all interfaces. A back-scattered electron detector can be used to determine the phase of each grain. The back-scattered image is shown below in the right-hand image. The two different solid phases show up as distinct shades of grey, while the pores are black. We currently are working to merge these two techniques to directly map phase and grain boundaries, as well as internal surfaces. This will be carried out on several SOFCs, and correlated to electrochemical properties and processing history.

With respect to the second goal, thin film methods have been used to generate (1) LSM / YSZ heterostructures to determine the preferred interfaces and (2) LSM/YSZ superlattices to observe the properties and degradation of nanoscale features in cathodes. (1) In this work, we focused on the growth of either LSM on single-crystal surfaces of YSZ or YSZ on thin films of LSM. These limiting cases allow us to frame our expectations for the boundary distributions determined via OIM, but they will not be discussed here in detail. (2) Superlattices are films that have two or more distinct materials alternated in such a manner to produce a periodic structure, which can be observed with structural probes. A schematic is given in the lower portion of the figure below that follows (Fig. 2). Nanoscale superlattices allow us to both investigate the spatial extent of interfacial regions, by spacing interfaces in close proximity with one another; and to build in specific types, and compare their behavior. Because perfect interfaces were difficult to obtain in part (1)—textured polycrystalline films were observed in all cases—superlattices with precisely determined interfacial structures could not be obtained for the LSM-YSZ couple. This is illustrated by the large number of peaks observed in the X-ray diffraction scan (given in the upper portion of the figure) for a YSZ-LSM superlattice of ~ 4 nm period. In this image, it is impossible to say if there is a superperiod present. Nevertheless, the low-angle X-ray diffraction scan (given in the lower portion of the figure: blue is data and red is simulation) shows evidence of a superlattice period on the order of 4 nm. These films now are being tested for their electrochemical properties.
References

Nanoscale transport processes modeling for direct methanol fuel cells

Project Summary

Novel simulation tools for Direct Methanol Fuel Cell (DMFC), where the multiphase reaction rate is controlled by the transport of molecular species near the nanoscale structured catalyst surfaces, are constructed for the improvement of the overall DMFC performance. Although macroscale transport processes are well-documented, nanoscale transport and its influence on system design still are poorly understood. Our goal is to augment the emerging technology of nanomanufacturing and nanoenergy via accurate modeling of multiscale transport processes in DMFC, including chemical reactions, which will open a new paradigm in miniaturized energy sources for electronic devices and sensors. Our modeling work is complemented by the sister experimental work performed by Kumta and Yao and our coworkers at Korea Institute of Energy Research (KIER), where they fabricated and tested various configurations of nano-catalysts for next-generation DMFC. The nanotubes will provide a 104-fold increase in surface area as compared to a standard catalyst configuration. However, the improvement in reaction rate is much less drastic as the transport processes become the rate-limiting step. The motivation behind this project is to provide a better understanding of these complex nanoscale transport processes to control and improve the performance of DMFC via the development of reliable design tools by investigating complex multi-phenomena, multi-component, multiphase transport processes across the molecular, nano, micro, and macro scales.

Selected Highlights

During the past period of this research, we have verified the Monte Carlo (MC) molecular dynamics (MD) simulations and lattice Boltzmann methods (LBM) with various nanoscale systems. We examined the static and dynamic properties of nanoscale hard disk drive lubricant via MC/MD simulations. We also simulated 2D liquid bearing and air-bearing systems, which are critical parts for reliability of the hard disk drive system, via LBM. Recently, we applied our simulation technique to 3D simulation of the liquid-bearing system of the head disk interface in the hard disk drive in order to verify whether the LBM is capable of efficiently describing and simulating more complex geometries and physical phenomena. The DMFC system, which we plan to describe, is a progressive energy technology for small power systems (e.g., portable systems such as cell phones and laptops). In this system, it is extremely important to optimize the structure of the cell and the efficiency of the energy produced. Since the energy efficiency of the fuel cell is mainly dependent on the reaction at the anode of the system, we focus on the transport phenomena of the fuel to the catalyst, as well as the CO2 gas produced, which may hinder the amicable fuel flow and the reaction on the anode catalyst.

We are in the process of conducting the coarse-grained, non-Hamiltonian MC and MD simulations for the agglomeration of gaseous CO2 molecules on the catalyst surface, and the formation of clusters and nucleation of these molecules into bubbles. Our expertise, developed in the MC/MD simulation techniques using Langevin equation for the oligomeric molecule/solid surface interaction, will be used to examine the diffusion processes of small gas bubbles in a liquid medium near both solid surfaces and larger gas bubbles. These bubbles will migrate within the nanotube array and fill the empty zones, if any, due to the net surface tension force resulting from different interfacial curvatures. One of our goals is to examine the conditions that facilitate the release of larger CO2 gas bubbles from the catalyst surface, which promotes higher operational efficiency by facilitating more methanol to react on the
catalyst surface. LBM, based on recent collaborated work by Amon and Jhon, will be used for tracking the vapor-liquid interface, as well as to integrate the nanoscale transport at the catalyst surface with the mesoscale and macroscale transport at the device level.

As shown in Fig. 1, our proposed work will integrate the atomic/nanoscale transport at the catalyst surface, via MC/MD simulations, with the meso/macroscale transport at the device level, via LBM. It also will incorporate the complex physical phenomena and geometric structures, which will contribute to the nanomanufacturing research by blending the system level optimization with our proposed multiscale modeling based on the first principles. The novelty of our approach is the incorporation of hierarchical modeling of a multi-scale, multi-phenomena system, which will bring the advances of nanotechnology to practical engineering systems. This will enable the development of next-generation technologies for improving chemical reactions with specific contribution to DMFC. Our work will accelerate the application of nanotechnology to practical engineering design and manufacturing.

I have promoted U.S.-Korea collaboration in fuel cell research to enhance our modeling capabilities based on physical reality and industrial relevance. For this purpose, our graduate student visited the DMFC lab in KIER to learn experimental details and integrated design concept. Our modeling will be practically and precisely improved and validated by comparing it with the experimental data obtained at KIER.

References:
Development of contacts for polythiophene-based organic photovoltaics (OPVs)

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Project Summary

Since the discovery of conducting properties in polyacetylene in 1977, many other organic materials also have been found to have (semi)conducting properties. The versatile attributes of these materials make them particularly well-suited for applications such as electronic displays on flexible substrates and large-area photovoltaics. The latter application is particularly exciting in light of the need for economical and expansive methods for renewable energy production. The low cost of producing organic semiconductor materials, in combination with theoretical efficiencies that are approaching those of amorphous silicon PVs, make wide-scale production of renewable energy a realistic goal. However, a critical limitation of OPV device development is the ability to control the properties of the contacts.

In this project, we propose to focus on understanding, and ultimately optimizing, the properties of ohmic contacts for polythiophene-based OPVs. Polythiophenes are one of the most widely studied classes of (semi)conducting polymers. In this study, we are investigating interfaces between metal contacts and semiconducting, regioregular polythiophene for OPVs. Our approach emphasizes a consideration of the chemistry, the nanomorphology of the materials, and the energy level alignment at the contact-organic interfaces to improve the ohmic contacts. A variety of metal contacts will be deposited in Prof. Porter’s ultra-high-vacuum deposition system using both metal-on-organic and organic-on-metal configurations. To enhance ohmic behavior, chemical bonding at the interfaces will be enhanced via regiochemical positioning of selected side chains on the base polymer. We have considered particular chemistries for high-workfunction metals, such as Pt and Au.

Selected Highlights

During the first year of this project, we have focused on understanding the effect of polymer/device processing conditions on the properties of the materials/devices. The results are summarized below.

- Effect of solvent and concentration: Different solvents such as chloroform, toluene and trichlorobenzene were used to dissolve the polymer and allow it to be dispersed as a thin film on a substrate (e.g., silicon). We found that the solvents with high boiling points yielded better film structure and morphology. This result is attributed to the slower evaporation rate. We also found that a higher concentration of polymer in the solution is desirable.
- Effect of Doping: The introduction of iodine as a dopant resulted in increased current by $10^4$-$10^5$ orders of magnitude.
- Effect of time: The polymer films became more resistive when exposed to air for a number of days.
- Effect of molecular weight of polymer: Higher molecular weight $\Rightarrow$ better crystallinity.
- Effect of metal contact choice: The nature of contact (i.e., Ohmic/Schottky) depends on the metal used.
- Effect of deposition method: Chamber cast method slows down evaporation rate $\Rightarrow$ Uniform film, higher % crystallinity, higher currents, and better ohmic contacts. Our determined order of preference for the film deposition methods: chamber cast $>$ drop cast $\sim$ drop cast with slow spin $>$ spin cast.
In summary, we have found that processing conditions substantially affect the electrical characteristics, and have optimized the conditions as follows:

- **Deposition method:** We have developed a novel method (chamber casting) for depositing the polythiophene films. This method results in films with the best thickness uniformity, good crystallinity, high conductivity, and ohmic contacts.
- **Solvent:** Chloroform yielded films with the best crystallinity.
- **Polymer concentration:** 10mg/ml yielded the thickest films with high crystallinity.

In the future, we will be focusing on the following research activities:

- Fabrication of organic field effect transistors for contact resistance and mobility measurements (see Fig. 2).
- Barrier height measurement using photoemission techniques.
- Optimization of the chemistry and the contact characteristics.
- Device development: OLEDs and OPVs.

References:


Fabrication of polymer nanofibers for novel nanosensors

**Project Summary**

The objective of the project is to develop in parallel two methods of fabricating micro/nanofibers using proximal probes for nanosensor applications. In the first proposed method, a very small area of polymer thin film is locally melted by contacting with a hot probe tip. Upon subsequent withdrawal of the probe tip, a liquid polymer bridge is formed. The fiber dimensions are controlled by the imposed cooling rate and probe tip pulling speed. In the second proposed method, polymer solution is pumped through a micropipette. The tip is brought in contact with a substrate and subsequently retracted, thus forming a liquid polymer bridge. The fiber dimensions are controlled by the solvent evaporation rate and micropipette pulling speed. These techniques offer the capability of forming three-dimensional structures, which currently are not available with competing techniques such as electrospinning, self-assembly, etc.

**Selected Highlights**

With current nanofiber fabrication approaches, various forms of micro/nanofibers are demonstrated (Fig. 1).

Different forms of nanofibers are heavily dependent on which methods are applied between two different approaches, which are the solution-based and melting-based methods. By the solution-based approach, typically, suspended fibers, nano-cantilevers, and a net of many nanofibers can be fabricated, while self-standing fibers, fiber rings and nanofiber on micropipettes can be fabricated by the melting-based approach.

**Fig. 1** (a) Cross of fibers, (b) Fiber Net, (c) Pulled fiber on micropipette (250nm), (d) Fiber ring (200nm)
The recent research progress in the project has provided an advanced pathway for developing nano-enabled sensing devices, since the approaches are natively cost-effective and easy to integrate, as well as contributing robust mechanical properties and excellent sensitivity. For example, conductive polymer nanoscale cantilevers can be built on electrodes with the solution-based approach for chemical gas sensing. The variation of the external analyte concentration modifies the mechanical properties of nano-cantilever, such as the rigidity and the damping coefficient. These modified properties change its resonant frequency, which is measured with electrostatic actuation and detection.

As another optical nano-biosensor, transparent, high-aspect-ratio pulled nanofiber on the tip of a micropipette can be used to detect a specific protein in a single cell, such as cytochrome c. An antibody-coated nanofiber can penetrate and sample individual, live cells while minimally disturbing normal cellular processes. The intracellular components bound to the antibodies immobilized on the nanofiber can be monitored using evanescent fields caused by a laser beam delivered to the micropipette, which has its nanofiber at the tip. For this purpose, compared with current tools such as nanoprobe, the nanofiber is smaller and has a much less tapered shape, which causes less perturbation to the cell. Finally, the well-known gecko fibers or super-hydrophobic surface also can be potential applications of the future work of developing the multi-arrayed fiber-pulling approach.

Fig. 2 Nanosensors based on suspended nanofiber cantilever

Fig. 3 Immunoassay on the nanoprobe. Enzyme-linked immunoassorbent assay (ELISA) is performed on the nanoprobe in order to indirectly detect the cytochrome c bound to the mouse anti-cytochrome c immobilized on the nanoprobe. As a result of ELISA, enzymatic product (cleaved DDAO) could be amplified [1].

References:
Nanostructured resonance-based sensors, transducers and devices

Project Summary

We aim to create regular arrays of carbon nanostructures, but at extremely small dimensions; well below the conventional lithographic limits. Our approach is to make use of the self-assembling process of chemical and biological agents as well as mechanical systems. We’ve chosen polymers and proteins which self-assemble into uniform 2D or 3D surfaces and then use these uniform surfaces as building blocks for carbon nanostructure growth. These uniform carbon nanostructures potentially can be used in a wide range of applications such as field emission, supercapacitors, photonics, and data storage. Of primary interest is the use of the nanostructured films as field emitter arrays for Field Emission Display (FED) technology. The FED requires a highly uniform and well-ordered field emitter array for high, uniform brightness over the full display area. However, the high cost and poor quality of field emitter arrays have kept the FED in the research phase. Self-assembly processing can potentially solve the problems of uniformity and order at a lower cost than conventional lithography.

Selected Highlights

As a first step in the research, a system was built to measure the field emission properties of films. This semi-automated measurement system is able to scan both over a sample surface and perpendicular to the sample surface with a 30nm resolution. The system is supplemented by a program to analyze the collected field emission data using multiple conduction and field emission models. Multiple materials have been tested including: films of carbon nanotubes in a matrix of polystyrene; hydrogenated amorphous carbon films produced by Professor Gellman’s group in the Chemical Engineering Department; and highly conductive, nanostructured carbon films obtained by the use of self-assembled block copolymers from Prof. Kowalewski’s group in the Chemistry Department.

The block copolymer film is composed of two immiscible polymer chains—polyacrylonitrile (PAN) and poly-butyl acrylate (PBA). The polymer is deposited using the “zone casting” technique and, once deposited, the polymer film self-orders into alternating stripes of PAN and PBA. This film then is pyrolyzed in a furnace at a constant temperature between 500C and 1200C, causing the polymer to break down, leaving only graphitic carbon stripes at the original location of the PAN stripes. The resulting film has a stripe structure with a periodicity of approximately 35nm and a surface roughness of between 1nm to 10nm, See Fig 1. More information on this process can be found in Ref [1]. For an example field emission curve from the self-assembled block copolymer, see Fig. 2.

Work has also begun on determining the proper processing parameters for generating 2D lattices of polystyrene spheres, and ferritin—a protein cage containing a metal particle with a very narrow size distribution, which self-orders into a 2D hexagonal array (See Fig. 3L). These arrays then will be used as templates for carbon nanotube growth. Metal will be evaporated through the polystyrene sphere lattice to create a well-ordered array of catalyst for carbon nanotube growth using Plasma Assisted Chemical Vapor Deposition (PACVD). The metal particles within the ferritin similarly will be used as catalysts for carbon nanotube growth in PACVD.
Another possible biological material for study is the S-layer protein obtained from the surface of certain bacteria. This protein is capable of bonding to nanometer-sized metal particles, and then self-ordering into 2D hexagonal arrays—creating well-ordered lattices of the original metal particles (See Fig. 3R). This particle array then will be used as a catalyst for growing carbon nanostructures.

Figure 1. Phase AFM of (L) zone cast block co-polymer (R) pyrolyzed film. [1]

Figure 2. Field Emission curve from block co-polymer film pyrolyzed at 800C. Measurement taken at a probe-sample spacing of 15um.

Figure 3. TEM images of (L) metal nano-particles in Ferritin array [2] (R) Au particles in Deinococcus radiodurans S-layer protein array [3].

References:
Molecular brushes prepared from functionalized PDMS surface for biomimetic adhesives inspired by gecko foot-hairs

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**Project Summary**

The goal of this study is to prepare novel biomimetic adhesives inspired from gecko foot-hairs. Gecko foot-hairs consist of micro-, nano- and molecular-scale-compliant fiber/brush structures for adhering to almost any surface in any environment with around 10 N/cm² adhesion pressures by adapting to the macro-, micro-, nano-, molecular-scale roughness without leaving much dirt on their surface (Fig. 1). These unique and one of the most advanced adhesives in nature was synthetically mimicked and characterized in this study for developing novel adhesives, and improving our understanding of the gecko adhesion design and mechanism in more detail.

Molecular-brush, which can be grown from the crosslinked Polydimethylsiloxane (PDMS), is proposed for the first time in this study for synthetic gecko adhesive applications, and it will enable tunable adhesion properties of the gecko tape at the molecular level as a new design parameter. Dry adhesion of gecko setae is primarily governed by van der Waals forces. In order to increase van der Waals forces, nano-scale roughness was created by polymerizing n-butyl acrylate (n-BA) using atom transfer radical polymerization (ATRP) from the surface of the PDMS. The surface roughness was characterized by atomic force microscopy (AFM). The preload-adhesion test also was carried out to prove that the adhesive property of PDMS was improved after creation of nano-scale roughness. The nano-sized roughness which was generated by surface polymerization of n-BA increased the van der Waals forces between the substrate and the PDMS brushes by expanding contact-area on the surface.

![Figure 1. Schematic of synthetic gecko adhesives using micro/nano/molecular-brushes mimicking the gecko foot-hair brush structures](image-url)

Figure 1. Schematic of synthetic gecko adhesives using micro/nano/molecular-brushes mimicking the gecko foot-hair brush structures
Selected Highlights

The synthetic route for the Poly(n-butyl acrylate) (PBA) brushes grown from the PDMS surface is outlined in Scheme in Figure 2. Essentially, the curing process involves platinum catalyzed hydrosilation reaction between vinyl groups of the siloxane base oligomers and hydrosilyl groups of the cross-linking oligomers, forming Si–CH$_2$–CH$_2$–Si bonds. When a small amount of allyl 2-bromoisobutyrate was added during a curing process, the –C=C- double bond from allyl 2-bromoisobutyrate also reacted with Si–H moieties during the curing reaction, forming a PDMS network films with ATRP initiating groups incorporated. This facile way of incorporating ATRP initiators is very simple. The ATRP initiating groups should be present both inside of the PDMS network and on the surface. Then, ATRP has been used to directly graft PBA from the PDMS surface with controlled molecular weight and low polydispersity.

AFM was carried out to demonstrate the successful creation of the nano-scale roughness (Fig. 3). During the curing process, chemically inhomogeneous allyl 2-bromoisobutyrate was phase-separated from the base PDMS and curing agent to form the nano-sized bumps on the surface (Fig. 3a). These characteristic initiator site bumps were no longer discernable after the nBA brush was grown from the surface.

The dry-adhesiveness of the PDMS brushes was tested. For performing adhesion measurements, a custom force measurement system was set up using an automated stage and a fifty-gram load (Fig. 4a). To take a measurement, stage moves PDMS sample toward the glass piece at a preset approach velocity. When the applied force reaches the desired preload value, the stage stops and the sample remains in contact with the surface for a preset amount of time. Finally, the PDMS sample is moved away from the glass piece with a preset retraction velocity. The adhesion force is the maximum measured force while the sample is being pulled away from the surface (Fig. 4b).
Adhesion forces for raw PDMS and PDMS with different lengths of the PBA brushes were measured (Fig. 5). Clearly, the adhesion forces for PBA brushes were higher compared with raw PDMS, and increased with the increase of the length of PBA chains. One of the possible reasons for such behavior is the increase of the amount of energy dissipated by mechanical extension of PBA chains upon breaking the adhesive contact between the probe and brush surface. This hypothesis will be tested through nanoscale, AFM-based adhesion measurements (force curve mapping).

This CNXT grant has provided the opportunity to study the biomimetic adhesives which would open new horizons for many advanced engineering applications (Fig. 6). As target applications in this study, they will be used for wall-climbing miniature robots that enable inspection and repair on space shuttles, search-and-rescue in disasters, etc. In unstructured environments, wireless endoscopic micro-capsule imaging devices that can be stopped and steered inside the human body for inspecting and treating diseases in the human digestive system, reusable and self-cleaning adhesives as an ad-hoc Velcro for novel industrial (general adhesives, textile, tire, pharmacological, sports, entertainment and toy industries) and space applications.

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**Figure 4.** Close up view of the adhesion measurement set up (left). The lowest value shows the maximum adhesion whereas the highest value is the maximum applied preload.

**Figure 5.** Preload-adhesion plots for PDMS with different lengths of the PBA brushes.

**Figure 6.** Concept of miniature wall-climbing space robots that can inspect and repair space shuttles in orbit using gecko tape attachment with low power consumption.
References
Gold-magnetite core-shell nanoparticles for intracellular biosensing

Project Summary

The goal of this project is to develop new bifunctional iron oxide (magnetite)/gold composite nanoparticles that combine the advantages of each constituent material for biomedical applications. The nanoparticles have magnetite cores that enable magnetic sorting of cells and/or biomolecules. These cores are surrounded by gold shells that exhibit localized surface plasmon resonance. This is a particularly strong optical effect that enables optical detection of single nanoparticles whose size is otherwise too small to be detected in a light microscope. Furthermore, the gold shells provide ideal surfaces for attaching biomolecules that allow the nanoparticles to recognize and bind complementary molecules, such as cell surface marker proteins that identify cells according to their type. The expression of certain cell markers is known to be diagnostic for diseases such as leukemia or HIV-AIDS. The nanoparticles being developed are smaller and less polydisperse in size than existing particles currently described in the magnetic separations literature.

Two immediate applications are envisioned in which the combined magnetic and optical properties are advantageous: improving the reliability of magnetically sorting cells on the basis of surface marker expression level, and providing the ability to directly image single magnetic nanoparticles in a microfluidic magnetic field gradient device for biomolecular separations.

Selected Highlights

The hybrid magnetic/plasmonic nanoparticles as conceived during this project are sketched below. “Core-shell” particles with single magnetite nanoparticle cores and gold shells will be prepared that have diameters on the order of 20–30 nm. These are to be used for quantitative cell sorting based on surface marker expression level. The second class of particles is described as “double shell” particles. These larger particles (~ 100 nm), consisting of silica nanoparticle cores, surrounded by a magnetite shell and an outer gold shell, are intended for magnetic sorting of individual biomolecules. Numerical modeling completed during this project indicates that, although the magnetophoretic force on the larger double shell particles is significantly stronger than the force on a single core-shell nanoparticle, when a cell surface is decorated by multiple copies of magnetic nanoparticles, the magnetophoretic force on the cell is stronger in the case of small core-shell nanoparticles. This is due to particle packing constraints on the cell surface.

Fig. 1: Schematic illustrations of hybrid magnetic/plasmonic nanoparticles. Biofunctionalization of the nanoparticle surfaces allows them to recognize specific biological targets.
This CNXT grant has supported the first stages of developing the nanoparticle synthesis procedures. Methods have been developed to reliably produce < 15 nm magnetite core nanoparticles with highly uniform size distributions, and to modify their surfaces to transfer them from the organic solvent in which they are synthesized into water where they ultimately will be coated with the gold shells. Methods also have been developed to attach gold seed particles onto the magnetite cores or onto silica cores. This research team is currently finalizing the methods to convert the gold seed particles to a uniform gold shell.

The optical properties of core-shell nanoparticles have been tested. The UV-VIS absorbance spectrum of silica core particles decorated by a monolayer of bound gold seed particles was compared to that of a silica core nanoparticle with a completed gold shell. The completed shell nanoparticles provide stronger plasmon resonance absorbance. This is advantageous for single nanoparticle detection and biosensing applications. These experiments were completed with silica-core nanoparticles, but similar effects are expected for magnetite core nanoparticles.

The strong plasmon resonance discussed above also provides extremely strong resonant Rayleigh scattering. As shown below for 35 nm radius core-shell particles, this strong scattering makes it possible to detect single nanoparticles using darkfield optical microscopy. This is well below the diffraction limit, so non-plasmonic nanoparticles would not otherwise be detectable. This mechanism will make it possible to track single nanoparticles that have bound specific target biomolecules to be magnetically sorted.

This CNXT grant has provided the seed funding necessary to advance the project to the point where the focus can shift from synthesizing the nanoparticles to developing biomedical applications based on the nanoparticles. This will ultimately lead to novel technology to sort cells based not only on the type of surface markers they express, but also on the number of these markers that are expressed on each cell. The first milestone on the way to this goal is to test this quantitative sorting ability using latex particles with predetermined numbers of marker proteins attached to their surfaces, serving as well-controlled model cells. Following that, the technology will be ready for testing on cells with unknown marker expression levels. This technology will be highly generalizable. It is anticipated that biomedical researchers and diagnostics manufacturers will be able to modify these nanoparticles according to the particular cell type or disease of interest, and use them to track disease progression or differentiation processes.

References:
Integration of porous SiC membranes with silicon MEMS microfluidic structures

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Project Summary

Using wafer bonding and MEMS technology, the goal of this project is to integrate porous silicon carbide membranes with micro-fluidic channels fabricated in silicon wafers. The SiC membranes form a semipermeable filter through which proteins and other macromolecules can diffuse, and with the microfluidic channels these molecules will be carried in a buffer solution to a molecular monitoring instrument. This entire device thus forms an implantable biosensor for the detection of disease and/or of hazardous chemical or biological agents. The technology for fabricating the membranes already exists, and this seed project specifically will explore the integration of the membranes with conventional Si MEMS technology to enable the necessary formation of microfluidic flow channels needed for a complete sensor. Future work would focus on monitoring instrumentation for the macromolecules, to be coupled to the membrane and micro-fluidic package.

Selected Highlights

The freestanding SiC membranes are formed by photo-electrochemical etching, and contain pores of a typical diameter of 100 nm, as shown in Fig. 1. They are fabricated by photo-electrochemical etching at the University of Pittsburgh in the group of Profs. Jim Choyke and Robert Devaty, collaborators in this project. A typical thickness for the membranes is 100 μm, so they are very fragile. This group at the University of Pittsburgh recently has succeeded in fabricating the membranes surrounded by a solid “frame” of SiC surrounding them, so that they are much more robust. A primary application of the membranes is to serve as a barrier between a biological tissue and a receiving buffer solution. Proteins of other molecules of appropriate size will diffuse through the membrane and then be carried in a buffer solution to a detector, as illustrated in Fig. 2. Dr. Alan Rosenbloom of ICES, another collaborator on this project, has tested the membranes for their throughput. It has been found that SiC offers an excellent alternative to the conventional polymer membranes used for microdialysis, since the former are known to degrade on the time scale of hours. The hardness and chemical inertness of SiC will prevent any degradation, and, in addition, SiC is known to be relatively biocompatible so that fouling of the membranes due to attack by antibodies will be minimized. The testing of the membranes in Dr. Rosenbloom’s laboratory currently is carried out utilizing cm-size test rigs that are handmade with the membranes epoxied to glass slides, which then are bonded to PDMS. Although these devices are suitable for testing purposes, they are entirely inappropriate for eventual implantable biosensors due to their large size, handmade construction, and lack of effective coupling to a miniature monitoring system. Thus, this CNXT grant enabled the first steps towards fabrication of a viable implantable sensor—the integration of the SiC membranes with a Si wafer.

Two approaches for integrating SiC to Si were explored: First, wafer bonding using chemically treated surfaces. Both SiC and Si were cleaned by RCA-cleaning. This is known to produce a hydrophobic surface on Si (weakly ionized Si-H bond formation) and a hydrophilic surface on SiC. Subsequent boiling of the Si in NH₄OH:H₂O:H₂O₂ solution forms polarized Si-OH bonds and makes that surface hydrophilic. Wafer bonding was attempted between the Si and SiC (and also between Si and Si for test purposes) by pressing the wafers between two ceramic pieces and annealing to 300°C for varying amounts of time. In all cases, however, little or no bonding was observed. Subsequent AFM images revealed contamination of the surfaces. In addition, optical inspection of the Si surface revealed a loss of its mirror-like
revealed contamination of the surfaces. In addition, optical inspection of the Si surface revealed a loss of its mirror-like finish which, by optical microscopy, was found to be due to surface roughening as revealed by triangular pits covering the surface. Thus, an intimate bond between the Si and SiC was not possible to obtain. Further experiments under cleaner conditions were contemplated but, instead, an alternate approach was tried as described below.

In the second method, CYTOP CTL-809M, an amorphous teflon-like fluorocarbon, was used as a bonding element between Si and SiC. CYTOP is resistant to most standard Si wet chemical processing, and produces good bonds irrespective of the surfaces used, (i.e., Si-Si, Si-Glass, etc.). Good mechanical stability and biochemical compatibility also makes it ideal for our application. A thin layer of CYTOP on a Si wafer was obtained by spin-coating and subsequent curing. SiC pieces were placed on the wafer and heated to 160°C with applied pressure to get good bonding between the Si and SiC. Figure 3 shows a photograph of the SiC pieces bonded to the Si. The SiC could not be removed by Scotch tape, and neither could it be separated from the Si using a razor blade. Thus, an excellent bond was obtained. With the success of the bonding, a process flow for bonding a SiC membrane to a patterned Si wafer is illustrated in Fig. 4. Holes in the Si are formed to enable access to the volume contained below the SiC membrane, and it is through this volume that the buffer solution will flow. Work is continuing towards completing the fabrication of this bonded SiC/Si structure.

Figure 1: Plan-view scanning electron micrograph of SiC wafer prepared by electro-chemical etching, and contains an array of pores with size on the order of 100 nm. The pores extend straight through the membrane as revealed by cross-section images (not shown).

Figure 2: Schematic illustration of biosensor employing a membrane. The membrane separates the tissue from the protein sensor, with proteins and other molecules diffusing through the membrane and being carried by a flowing buffer solution to the sensor.

Figure 3: Photograph of a piece of a SiC wafer bonded to the lower Si wafer. An upper Si wafer is also present, broken off to reveal the SiC wafer. This upper wafer is used simply as a protection piece for the SiC.

Figure 4: Process flow for bonded a SiC membrane in a rigid “frame” geometry to a Si wafer contains holes that access the volume beneath the SiC membrane.

References:
Programmable inorganic-organic nanodevices for In Situ treatment and sensing of environmental pollutants

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Project Summary

We propose to develop a novel, targeted delivery system that provides efficient source-zone remediation of groundwater contamination by chlorinated organic pollutants. The system is based on copolymer amphiphiles adsorbed onto reactive nanoparticles. The nanoparticles have zero valent iron cores ("nanoiron") that reduce chlorinated organic compounds to nontoxic products in situ. Optimizing the targeted delivery system requires attention to several colloidal, polymer synthesis, and engineering issues. This research will deliver an optimized, environmentally responsive, copolymer-based delivery system that stabilizes nanoiron suspensions in water; enables their transport through saturated soils that are impassable to unmodified nanoiron; and anchors them at the TCE/water interface, in order to provide efficient source-zone remediation. The functional requirements placed on the targeted delivery system are achieved by specifying the composition and architecture of the copolymer.

Selected Highlights

Chlorinated solvents present in the subsurface as dense nonaqueous phase liquids (DNAPL) are a consistent long-term source of groundwater contaminants that degrade environmental quality. Treatment poses significant technical challenges and lifecycle treatment costs are estimated to exceed $2 billion for ~3000 DNAPL-contaminated DoD sites. The goal of this interdisciplinary project is to design and evaluate Programmable Inorganic-Organic Nanodevices (PIONs) that can be delivered to subsurface DNAPL, and rapidly degrade it to nontoxic products. The nanodevice is a highly reactive Fe$_0$/Fe$_3$O$_4$ nanoparticle (~30nm diameter) that is modified with designer polymer assemblies that enables them to resist attachment to aquifer minerals and grains (Fig. 1a) and to preferentially locate at the DNAPL-water interface (Fig. 1b). Their nanosize allows them to be effectively transported in water saturated porous media, to reach DNAPL trapped in small hard to reach pores, and makes them highly reactive due to their high surface-volume ratio. The approach is inspired by targeted drug delivery in that the particles are injected non-specifically into a flow field and migrate passively until reaching the target (DNAPL-water interface), where the hydrophobic block swells and causes them to remain at the target.

![Figure 1. Conceptual model of nanoiron transport showing filtration, straining, and DNAPL targeting.](image)
The polymer assemblies are synthesized by atom transfer radical polymerization (ATRP), where the degree of polymerization and type and location of the polymer blocks is highly controllable and can provide the desired characteristics e.g., affinity for the DNAPL-water interface. The ability to synthesize polymers with highly controllable properties makes the targeting approach highly flexible. We have demonstrated the ability of these polymer coatings to enhance the mobility of reactive nanoiron through porous media, and to locate itself at the DNAPL/water interface. This approach could be used to accurately place subsurface barriers; deliver iron oxides for magnetic labeling as a sensitizer for remote sensing/imaging of subsurface DNAPL; or to deliver biosensors to specific targets. The general theme of providing nanodevices the ability to target specific regions of a system (the natural environment or otherwise) using passive thermodynamic affinity targeting will find broad utility as new nanodevices become available.

The ability of the polymer modifiers to enhance the mobility of reactive Fe\textsuperscript{0} iron particles through water-saturated porous media under varying geochemical conditions (e.g., ionic strength) was determined in sand columns. The effectiveness of the triblock copolymer was compared to a commercially available polymer-modified nanoiron (MRNIP). Breakthrough curves, generated from the bench-scale transport experiments, clearly show the effect of ionic strength on the ability of the particles to transport in water-saturated porous media. Figure 3 (a-b) shows the comparison of the effect of modification in transport for increasing sodium concentrations. Triblock copolymer-modified RNIP resists the effect of high salt condition even at molar concentrations, however the mobility of the commercial product (MRNIP) decreases significantly at an ionic strength of 100mM. This shows the importance of polymer modification, which provides electrosteric interactions rather than just electrostatic repulsions that can be screened by increases in the ionic strength.

Figure 2: Adsorbed block copolymers contain an polyacrylic acid anchoring block with n degree of polymerization (black circles on Figure 1a/b) that has high affinity for iron oxide surfaces, a hydrophobic block with m degree of polymerization (gray circles on Figure 1a/b) that has an affinity for DNAPL, and a polyelectrolyte block with p degree of polymerization (open circles on Figure 1a/b) that has an affinity for water.

Figure 3: Breakthrough curves at increasing ionic strength for (a) triblock copolymer modified RNIP and (b) a commercially available polymer-modified nanoiron.
The triblock copolymers developed in this research make the particles amphiphilic (i.e. they have both hydrophobic and hydrophilic character). This allows the particles to disperse in water and be mobile, but also provides them with an affinity for the DNAPL/water interface. The ability of the polymer-modified Fe\textsuperscript{0} particles to target the DNAPL/water interface was demonstrated using emulsification experiments. Emulsification of trichloroethylene (TCE), a DNAPL, was achieved using RNIP modified with one of the triblock copolymers synthesized; p(MAA)\textsubscript{42}-p(MMA)\textsubscript{26}-p(StS)\textsubscript{466} polyelectrolyte. Extremely stable (more than three weeks) oil-in-water emulsions were formed which can be characterized as Winsor Type I (bottom water-continuous emulsion phase with excess water top phase) emulsion. Figure 4 presents the physical evidence of emulsification showing the reaction vessel along with the micrographs for DNAPL.

The emulsions droplets formed using TCE ranged in size from 10-500 μm (the micrograph shown in Figure 4 does not show the smaller droplets clearly). Emulsification was attempted using unmodified RNIP, and there was no stable emulsion droplet formed in the experiments. This demonstrates the ability of the triblock copolymer to impart the desired amphiphilicity to RNIP, allowing it to preferentially localize and produce a NAPL-water interface.

References:

Figure 4: Emulsified TCE droplets by polyelectrolyte modified RNIP.
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In 2001, McCullough’s conducting polymers formed the basis of a Carnegie Mellon spinout company, Plextronics, Inc. Plextronics’ technology was named Frost and Sullivan’s 2005 Emerging Technology of the Year in Printed Electronics. A company founder, McCullough is the Chief Scientific Officer of Plextronics, Inc.

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