**REU Site: SENSORS--Design to Implementation**

**IREE project summary October 2007- October 2008**

Keith J. Fahnestock,[1] Holly A. McIlwee,[1] Caroline L. Schauer[1], and Sabine Szunerits[2]
*[1]Drexel University, Department of Materials Science and Engineering, Philadelphia, PA, 19104, USA Email: cschauer@coe.drexel.edu [2]Institut d'Electronique, de Microélectronic et Nanotechnologie (IEMN), Institut de Recherche Interdisciplinaire (IRI), Villeneuve d'Asq, 59652, France*

*ABSTRACT: Under an international partnership between Dr. Caroline L. Schauer of Drexel University in Philadelphia, PA and Dr. Sabine Szunerits of the Institut d'Electronique, de Microélectronic et Nanotechnologie in Lille, France, and through a grant from the National Science Foundation, Keith Fahnestock and Holly McIlwee traveled to work in Lille for three months. The research goal was to investigate the selectivity of chitosan-gold nanoparticle thin film interfaces through the localized surface plasmon phenomenon. Upon completion of the program, a chitosan thin film interface had been tailored to the application, and it was found that chitosan has a chromium charge selectivity between trivalent and hexavalent chromium. As a result of this partnership, a paper with Drs. Schauer and Szunerits has been submitted to The Analyst and a poster was presented at the American Chemical Society's Fall 2008 national conference.*

## INTRODUCTION

Drs. Schauer and Wen (Drexel University) are PIs on a National Science Foundation (NSF)-Research Experiences for Undergraduate (REU) site award entitled "SENSORS: from design to implementation" (EEC 0552711). The REU program provides selected REU participants with a rare research opportunity: exposing them to the entire exploration process of creating a viable sensor and sensor network for various real-life applications. Hands-on research activities, a multi-disciplinary working environment, systematic research education, strong industrial connections, and comprehensive ethics activities have been designed to increase the participants' knowledge and interest in research and sensor technology from design to implementation, as well as to instill a strong desire to continue with research at the graduate level.

We requested a supplement from International Research and Education in Engineering (IREE) with the aims of (**1**) enabling an extended-stay visit of two current or former REU participants from the PI's, Dr. Caroline Schauer, laboratory to intensify an existing collaboration with a French engineering school (INPG, Grenoble) and to (**2**) enhance the education experience of an REU participant through a project-based collaborative

partnership between the home institution, Drexel University, and the host laboratory, Institut d'Electronique, de Microélectronic et Nanotechnologie (IEMN) of the Institut de Recherche Interdisciplinaire (IRI), France.

Dr. Sabine Szunerits is an expert in the field of Surface Plasmon Resonance (SPR) sensors. Dr. Szunerits' group is heavily involved in the fabrication of new interfaces for SPR and electrochemical sensing and has been recently awarded a three year research grant for the investigation of local SPR affects due to the presence of gold nanoparticles irreversibly linked to surfaces.

Keith Fahnestock was the first traveler on this grant and is currently a senior undergraduate student at Drexel University with an expected graduation date of June 2009. He was a prime candidate for this program, as he was highly interested in both Drs. Schauer and Szunerits' research, but was unsure of his future in engineering. The purpose of this program was to give REU participants an international research experience in the hope that it would inspire them to further themselves and continue their education. A recommendation from Keith's professor stated, "Keith needs something to spark his interest for research, to get him really excited about the field." From an educational standpoint, this has been a complete success. Keith traveled to and researched in Lille, France from March 2008 – June 2008. Upon coming back from France, he joined the SENSORS REU program at Drexel working on a new sensing system and had a changed perspective on research and intends to pursue a PhD under Dr. Schauer.

During Keith's second to last week in France, Dr. Schauer paid a site visit to begin writing up his findings. The remaining work was to be completed during Holly's visit. We have submitted a paper to *The Analyst* under the title "Selective detection of hexachromium by localized surface plasmon resonance measurements of gold nanoparticle-chitosan composite interfaces."[1]

Holly, working off her two papers[2, 3] she obtained as a 2007 REU student, joined the French lab in June 2008. However, she was only there two weeks before a family tragedy (resulting in the death of both of her parents) required her to return home for the rest of her planned time in France. Therefore, Mr. Mael Manesse completed the last of the experiments for the paper.

**Research Activities and Accomplishments of the International Cooperation**

A simple modification of the conventional SPR system has made it possible to utilize the surface plasmon phenomena in combination with normal standard laboratory equipment. We have recently shown that gold nanoparticles (Au NPs) entrapped within, and in between, a cross-linked thin chitosan film, cast onto a glass substrate form a platform for the sensing of heavy metal ions in solution.[3] Changes in the localized surface plasmon resonance (LSPR) properties[4] of the chitosan/Au NP composite film, visualized by transmission UV/Visible absorption spectroscopy, were used for detection and discrimination between $Fe^{3+}$ and $Cu^{2+}$.[2]

While $Cr^{3+}$ is an essential trace element for the proper functioning of living organisms, $Cr^{6+}$ compounds exert toxic effects on biological systems. The toxicity of $Cr^{6+}$ arises primarily from its highly oxidative nature and is enhanced by its high water solubility and mobility compared to trivalent chromium. The objective of our study was to selectively detect $Cr^{6+}$ and/or $Cr^{3+}$ by following the change in the LSPR characteristics of the

interface upon immersion in chromium ion-containing solutions. The effect of pH and the presence of foreign ions on the adsorption capacity of the composite interface were evaluated. While the use of LSPR active interfaces has been widely employed for biological sensing; the examples shown for chemical sensing, via surface-based LSPR, focus mainly on the investigation of the change in the refractive index of the external medium. [5-7]

To form an LSPR interface, there must be a plane of material that will propagate a plasmon wave. For the LSP phenomenon, gold nanoparticles are particularly active. In this study, it was necessary to first test the commercially available nanoparticle sizes from 5-20nm. **Figure 1** indicates that 10nm gold colloid produces the most significant plasmon peak and demonstrates the lack of an absorption characteristic in chitosan alone.

**Figure 1**: Various commercially available gold nanoparticles in chitosan matrix.[1]

Changes in the LSP properties of the chitosan/Au NP composite film, visualized by transmission UV/Vis absorption spectroscopy, can be used for detection and discrimination of heavy metals. The position of the maximum and the overall shape of the LSP absorption peak depend on both the refractive index and depth of the environment. The interaction of heavy metal ions with the chitosan matrix results in thickness and refractive index changes. Through trials of chromium adsorption at 400 ppm, the chitosan/gold nanoparticle interface showed selectivity for $Cr^{6+}$ vs. $Cr^{3+}$, as shown in **Figure 2**.

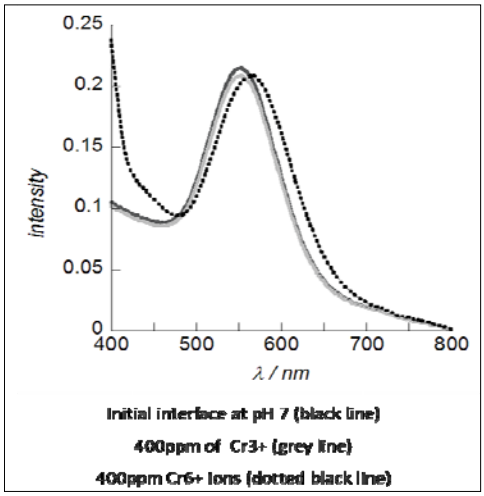


**Figure 2**: Effects of chromium species on the LSPR signal.[1]

To ensure real world applicability, the stability of this interface and the associated adsorption was tested. A pH range and variety of interfering materials were introduced. The interface proved to be stable in the range of pH 1.5-13, though the adsorption of metal ions was found to be best at pH 6.8, the $pK_a$ of chitosan. Adsorption of $Cr^{6+}$ was found to be unaffected by foreign salts, losing signal only under the extreme pH conditions of 1M NaOH or HCl.

This vein of research ties directly into the SENSORS program as initially funded by the NSF. The creation of a chitosan thin-film sensor, sensitive to a specific metal ion, has a definite set of real-world applications and allowed for hands-on experience in a multidisciplinary research group. In the host laboratory, an assortment of techniques was made available, such as ellipsometry, SPR, and UV-visible spectroscopy. Full training by an expert in the use of each technique was provided. In addition to training on pertinent

machines, seminars relating to group research were offered; notably, sessions in both nanowire synthesis and lithography were provided. To ensure that the research was progressing in a proper direction, biweekly meetings with Dr. Szunerits were held, which directly contributed to the success of the project.

At the close of the international experience, a paper has been submitted to The *Analyst*[1] and Keith presented a poster on this research at the national American Chemical Society's (ACS) conference fall 2008. The results from this three month session will also have implications in the future research of both the Natural Polymers and Photonics Group at Drexel under Dr. Schauer, and the IRI under Dr. Szunerits.

## BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

Originally, the SENSORS program was intended to provide selected participants with an opportunity to experience research firsthand at Drexel University. The entire program was designed to increase the participants' knowledge and interest in research and sensor technology, as well as instill a strong desire to continue with research at the graduate level. This supplement took that idea and expanded it to allow for select students to experience sensor design, but more importantly, to experience research from an international perspective. Through hands-on experience with the host laboratory, the participants learned how to design and carry out a research plan in close cooperation with fellow researchers and students. In addition, the participants were able to see a project progress from formation to completion, participate in the writing of a formal publication, and present a poster at the ACS national conference.

Such positive research experiences such as this greatly increase the likelihood of future interactions between the IEMN and Drexel University. While exploring IEMN, Keith was able to view and learn a host of techniques such as vapor deposition, nanowire production, lithography, microfluidics and SPR that are not currently available at Drexel University. While he was given opportunities unavailable at Drexel, there are definite areas where IEMN could benefit from utilizing Drexel's available instrumentations and specialties.

Being part of a multinational group has expanded Keith's cultural horizons as well. The Szunerits group of thirteen had representatives from Vietnam, China, Belgium, France, Italy, India, Brazil, Austria, Algeria, French Canada and the United States. Keith found that not only were they co-workers, but also they became friends outside of research. Several times per week, they gathered for home-cooked international cuisine, to practice their French and English, and at the heart of it, to enjoy their time in Lille. Keith had the opportunity to teach several of his coworkers English, and one in particular took full advantage of this. Phong Nhung Nguyen, from Vietnam, became a pupil of his when it came to the English language. They had weekly sessions where they would spend an hour going over English vocabulary lists, her pronunciation and general grammar. This exposure to such varied cultures gave him a perspective that he would never have had otherwise, from simple cultural lessons in French customs, to deeply held political and social beliefs that he had never encountered, each day was a learning experience.

## DISCUSSION AND SUMMARY

Through this grant with the NSF there have been a number of significant measurable milestones reached. We have submitted a paper exploring the interaction of chitosan thin films with various heavy metal ions. In addition to this, Keith, an undergraduate student, attended and presented a poster at the ACS national conference in Philadelphia, PA upon returning to the United States. In a more general sense, the research that was accomplished with the assistance of this grant into the selectivity of chitosan for hexavalent chromium has opened the option of customizable sensors, sensitive to a particular ion. It has also contributed to our general understanding of the interaction of chitosan thin-films with metal ions, and has expanded the possible applications for this technology.

When considering less quantifiable results of this program, foremost for Keith has been his personal growth and growth as an engineer. This experience exposed Keith to a wide variety of people, languages and cultures and it has given him a completely new perspective on his own environment. Before entering this program, Keith was unsure of his intended destination, whether it be industry, academia, or otherwise. Keith now has a goal in mind, and thanks to his experiences in Lille, he has confidence that it is the right decision to pursue a PhD.

## ACKNOWLEDGEMENTS

We would like to thank the Ms. Ester Bolding and NSF for financial support under Grant Number: EEC 0552711 and 0738548. The Agence Nationale de la Recherche (ANR), the Centre National de la Recherche Scientifique (CNRS) and the Institut National Polytechnique de Grenoble are gratefully acknowledged for financial support.

## REFERENCES

1. K. J. Fahnestock, M. Manesse, H. A. McIlwee, C. L. Schauer, R. Boukherroub and S. Szunerits, “Selective detection of hexachromium by localized surface plasmon resonance measurements of gold nanoparticles-chitosan composite interfaces” *The Analyst,* **2009***, in press.*
2. V. P. Praig, H. A. McIlwee, C. L. Schauer, R. Boukherroub and S. Szunerits, Localized Surface Plasmon Resonance of Gold Nanoparticle-modified Chitosan Films for Heavy-Metal Ions Sensing” *J. Nanosci. Nanotechnol.*, **2009**, 9, 350–357.
3. H. A. McIlwee, C. L. Schauer, V. G. Praig, R. Boukherroub, and S. Szunerits “Thin chitosan films as a platform for SPR sensing of ferric ions” *The Analyst* **2008**, 133, 673-677
4. M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers and R. G. Nuzzo, “Nanostructured Plasmonic Sensors” *Chem. Rev.*, **2008**, *108(2)*, 494.
5. E. M. Larsson, J. Alegret, M. Kall and D. S. Sutherland, “Sensing Characteristics of NIR Localized Surface Plasmon Resonances in Gold Nanorings for Application as Ultrasensitive Biosensors” *Nano Lett.*, **2007**, *7(5)*, 1256.
6. L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz and R. P. Van Duyne, “Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms” *Nano Lett.*, **2006**, *6(9)*, 2060.

7. C. L. Haynes and R. P. Van Duyne, “Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-dependent Nanoparticle Optics” *J. Phys. Chem. B*, **2001**, *105(24)*, 5599.

## BRIEF BIOGRAPHIES OF RESEARCHERS

**Keith Fahnestock** was a SENSORS participant summer 2008 and is expected to receive his BS in Materials Science and Engineering from Drexel University in June of 2009. His concentration is on polymeric materials. He plans to continue his education with Dr. Caroline Schauer at Drexel by pursuing a PhD investigating the synthesis and characterization of polymer thin film interfaces.

**Holly McIlwee** was a SENSORS participant summer 2007 and received her BS/MS in Materials Science and Engineering from Drexel University under the direction of Dr. Schauer June 2008. She received an NSF Graduate Research Fellowship 2009-2011 and will begin her PhD at Harvard University in the Department of Bioengineering fall 2009.

**Caroline Schauer** received a BS in Chemistry from Beloit College in Beloit, WI in 1991; MS and PhD in Chemistry from SUNY@ Stony Brook in 1994 and 1997, respectively. She was a postdoctoral researcher at SMCT at University Twente, the Netherlands, Chemistry Department at Tufts University and the Center for Bio/Molecular Science and Engineering at NRL. She joined Drexel University as an assistant professor in the Department of Materials Science and Engineering fall 2003. Her current work is focused on nanofibers for filtration and thin films of polysaccharides for metal ion detection. Dr. Schauer has over 26 peer-reviewed publications in such fields as thin films, biosensors, metal ion detection and nanofibers.

**Sabine Szunerits** received an M.SC. (1994) in Chemistry from University of Vienna, Austria and a PhD (1998) in Physical Chemistry from the Queen Mary and Westfield College, University of London, UK. She was a postdoctoral researcher in Ecole Normale Super CNRS, Paris, France and the Chemistry Department at Tufts University. Since 2002, she is a professor at the Grenoble-INP Laboratoire d’Electrochimie et de Physiochimie des Materiaux et des Interfaces (LEPMI) in France. Dr. Szunerits has over 72 peer-reviewed publications in such fields as SPR, biosensors, modified diamond surfaces, LSPR and electrochemistry.