

First Society for Applied Spectroscopy (SAS) Student Poster Contest in Clemson University

April 17th, 2015

Sponsored by:

SAS and VWR



Announcement of New Luminescence Laboratory in Clemson

Luiz G. Jacobsohn

Assistant Professor

Department of Materials Science and Engineering, Clemson University

luiz@clemson.edu

A new luminescence laboratory will be available for collaboration with faculty and researchers of the Clemson community this summer. A custom-designed Lexsyg Research spectrometer has been acquired and will be installed soon. The following techniques will be available:

- **Radioluminescence** - RL: under the excitation of 50 kV X-rays (1 mA), with sample at temperatures from room temperature up to 700 °C and emission being detected from about 280 to 950 nm (detection quantum efficiency > 20%)
- **Thermoluminescence** - TL: spectroscopy with the same detection spectral range as above, from room temperature up to 700 °C. It will also be possible to obtain “standard” glow curves using a bi-alkali cathode photomultiplier tube (PMT) for integrating light emission in the 300-650 nm range. The PMT can be combined with a filter wheel to narrow the detection range
- **Optically Stimulated Luminescence** - OSL: with stimulation at 458 and 525 nm from room temperature up to 700 °C

It is noted that the X-ray source is coupled with an ionization chamber for precise dose determination. Materials in the form of powders, nanopowders, crystals, ceramics, glasses, thin films, etc. can be measured.

In addition to the above, a fluorescence lifetime spectrometer will also be acquired to allow for photoluminescence measurements in the time domain.

In summary, luminescence measurements in the spectral, temporal and thermal domains will be possible, benefiting numerous research areas including the investigation of scintillators and materials for ionizing radiation detection, optical dosimeters, phosphors, dyes, and luminescent materials in general.

“Some things though they are not in their nature fire nor any species of fire, yet seem to produce light”, Aristotle.

Poster #001

Polydiacetylene Sensor Substrates: Cellulose and Cellulose Acetate

Sarah C. Hill and Dr. William Pennington*

Department of Chemistry

Abstract:

Polydiacetylenes (PDAs) are conjugated polymers with interesting optical properties, useful for a variety of sensing applications; such as temperature, mechanical impact, and detection of biological entities. The visible signals exhibited by PDA sensors make them preferential to electrochemical sensors for many applications, particularly within food safety and medical industries. The PDA 10,12-pentacosadiynoic acid (PCDA) has been incorporated into cellulose acetate to create a polymer-blend, which serves as a colorimetric strain and temperature sensitive film. PCDA monomers and liposomes decorated with tryptophan or tyrosine exhibit a colorimetric response in the presence of *E. coli*. Thermochromic and bacteria-sensitive PCDA-coated cotton substrates will also be discussed.

Poster #002

Influence of Spacer Length and Rigidity on Properties of Phosphonium Polymers and on their Supramolecular Assembly with a Conjugated Polyelectrolyte

Xiaoyan Yang and Rhett Smith*

Department of Chemistry

Abstract:

A series of seven cationic polymers have been prepared wherein the length of spacer between chargebearing sites has been varied. Thermal stability of the polymers was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The length of spacer has obvious effect on thermal stability as well as on the extent of crystallinity as revealed by X-ray powder diffraction. The cationic polymers were tested for their ability to form supramolecularly-assembled films with an anionic polythiophene derivative by a layer-by-layer (LbL) deposition process. Film growth was followed by spectroscopic techniques and surface morphologies were examined by atomic force microscopy (AFM). Interesting dependence of film morphology and composition were observed depending on whether an even- or odd-number of methylene spacers were present between charge-bearing sites.

Poster #003

Immobilization of Polydiacetylene Sensors onto Cellulose

Sara Garbowski, Salley Reamer and William Pennington*

Department of Chemistry

Abstract:

Polydiacetylenes (PDAs) are a class of conjugated polymers with unique optical properties. PDAs exhibit a chromatic response to a variety of chemical, biological and environmental stimuli. In order to develop cheap and effective sensors for food safety applications, we have coated cellulose-based media (cotton fibers and paper) with 10,12-pentacosadiynoic acid (PCDA) and derivatives. The characterization, properties, and potential applications of these PCDA-coated untreated native cellulose and base-treated mercerized cellulose sensors will be reported and discussed.

Poster #004

Translucent SrAl₂O₄:Eu²⁺Dy³⁺ ceramics produced in open atmosphere by laser sintering

David Sampaio, Ronaldo da Silva, John Ballato*

Department of Materials Science and Engineering (MSE, Clemson University)

Abstract:

The co-doped Strontium aluminate has gained attention because its persistent luminescence property that can last for many hours. The material glows in the dark after previous excitation by solar light or even common lamps. But in order to achieve this property, the reduction of the europium ion from his usual valence 3+ to 2+ is necessary. Frequently this is achieved using special conditions, for example a controlled atmosphere of N₂/H₂ (95%:5%). In the current work Sr_(0.97)Al₂O₄:Eu_{0.02}²⁺Dy_{0.01}³⁺ powders were synthesized by Pechini's method and sintered, in an open atmosphere, using the laser sintering method in which a CO₂ laser ($\lambda = 10.6 \mu\text{m}$) is used as the main heat source. The pallets were pressed uniaxially and sintered using a power density of 3,1 W/mm². The process results in extremely high heating and cooling rates, estimated in 2000 °C/min. The structural and microstructure characteristic of the samples were analyzed using XRD and SEM. Optical spectroscopy was used to characterize the emission and excitation spectra and transmittance measurements were performed. The samples presented the SrAl₂O₄ monoclinic phase and a homogenous microstructure. They also presented a translucence of 45 % between 450 nm and 800nm. The photoluminescence showed that even with the sintering process carried out in an open atmosphere, the europium was successfully reduced to 2+ and the material presented the persistent luminescence characteristic.

Poster #005

Further Assessment of PPCPs in Feed Grade Chicken Feather Meal Including Potential Sources

Zhixin Chen, Chen Liu, Joseph Thrasher*

Department of Chemistry

Abstract:

The poultry and rendering industries have played important roles in people's diet and environmentally sustainable development. However, the public worries that the pharmaceutical and personal care products (PPCPs) might be used in the poultry industry, which should be prohibited, and the banned PPCPs would be transferred to rendered by-products, like chicken feather meal, and then be consumed and accumulate in the bodies of chickens or other animals, and finally re-entering into the bodies of humans. A recent article published by Dr. D. C. Love and co-workers of Johns Hopkins Center for a Livable Future revealed these authors' concerns based on results showing twenty-four PPCPs that were detected above the reporting limits in a total of twelve feather meal samples (five feed grade and seven fertilizer grade) bought in the United States and China.

Since this publication may have flaws in terms of representing most of the chicken feather meal samples in United States, and insufficient evidence existed to support the source of the contamination found in the feather meal samples, we thought that additional studies were warranted. We collected or received samples of fresh chicken feather meal from three rendering plants from different geographical regions of the country, as well as samples of raw chicken feathers. To analyze our samples, we followed EPA method 1694 and adjusted our HPLC-MS/MS (high-performance liquid chromatography tandem mass spectrometer) conditions to test the performance of low-concentration (ppb level) drug detection of sixteen analytes: acetaminophen, erythromycin, norgestimate, sulfachloropyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfamethizole, sulfamethoxazole, thiabendazole, enrofloxacin, norfloxacin, 1,7-dimethylxanthine, caffeine, ofloxacin, and diphenhydramine. The results showed that our mass

spectrometer, which contains a quadrupole ion-trap analyzer, has lower sensitivity and thus a higher detection limit for the aforementioned sixteen analytes than a triple quadrupole analyzer, which is the standard instrument recommended by the EPA method and AXYS Analytical Services Ltd. In order to continue the project, we sent our samples to AXYS Analytical Services Ltd., the same firm that the Johns Hopkins Center for a Livable Future used. Our results show that chicken feather meal is not as contaminated as claimed in the aforementioned publication, and the contamination may come from the raw chicken feathers and accumulated in dissolved air filtration (DAF) system. The poultry industry should take care of the source of diphenhydramine, anhydrochlortetracycline (ATCT), and sulfadimethoxine, of which showed high concentrations in our samples.

Poster #006

Mixed Ionic / Electronic Conductivity of Electrolyte-Modified Carbon/Zirconia

Composites

Jamie A. Shetzline and Stephen E. Creager*

Department of Chemistry

Abstract:

A recently developed method for independently obtaining electronic and ionic contributions to electrical conductivity was used to study conductivity in thin-film samples of carbon/zirconia nanocomposite materials for which molecular and polymer electrolytes were covalently grafted onto the carbon/zirconia particle surfaces. The method relies upon careful control of the nature of the contact between the sample and the currentcarrying electrodes. Electronic conductivities are derived from currents obtained when using electronically-conductive glassy carbon electrodes to contact the sample, whereas ionic conductivities are derived from currents obtained when using ionically-conductive Nafion electrodes to contact the sample. Carbon / zirconia samples were prepared from zirconia sol precursors combined with RF carbon aerogels and also with carbon black to produce carbon containing integrated zirconia. Solution-phase treatment with molecular electrolytes containing organo-phosphonate groups resulted in electrolyte attachment via zirconia-phosphonate binding. Thin-film samples of the resulting electrolytes were prepared and their mixed electronic and ionic conductivity studied as functions of temperature and relative humidity.

Poster #007

An investigation into the effect of metal ion in PA and TEM8 binding

Zhe Jia, Christine Ackroyd, Kenneth Christensen, Brian Dominy*

Department of Chemistry

Abstract:

Anthrax toxin is transported into human cells after its protective antigen (PA) binds to its receptor. The receptor, tumor endothelial marker 8 (TEM8), has been identified as a potential anticancer target for its involvement in angiogenesis. This project investigates the role of the metal ion in TEM8/PA binding mechanism to provide information relevant to anticancer therapy. Homology to a closely related x-ray crystal structure, canonical conformational ensembles of TEM8/PA complexes involving different metals were generated through molecular dynamics simulations. Binding thermodynamics were assessed using Molecular Mechanics/Generalized Born Surface Area (MM/GBSA) method. In addition, the dissociation constant between TEM8 and PA in the presence of different divalent metal ions was determined via fluorescence resonance energy transfer (FRET). Both computational and experimental results indicate the metal ion in TEM8 contributes significantly to the binding affinity. Simulation shows the existence of Mg^{2+} , Zn^{2+} or Ca^{2+} in TEM8 corresponds to a sequentially reduced affinity between TEM8 and PA. Further, computational analyses suggest the differences in TEM8/PA affinity consistent with the behavior of closely related integrins known to adopt two conformations linked to changes in activity. The conformation of TEM8 shifted from “open” (high affinity) to partially “closed” (low affinity) in the presence of Ca^{2+} .

Poster #008

Riboswitches as targets for antibiotics

Soheila Rezaei Adariani, Feng Ding, Hugo Sanabria*

Department of Physics and Astronomy

Abstract:

Nowadays antibiotic-resistant infections are one of most serious health threats. In the United States alone, each year, 2 million people suffered an infection with antibiotic resistant strain of bacteria and over 23,000 people died as a direct result of resistant bacteria according to the 2013 CDC report. Recently it was proposed to target riboswitches as an innovative approach avoiding the antibiotic resistance generated by changes in the rRNA target; therefore, bringing solutions to this imminent threat. Riboswitches are messenger RNA's that regulate gene function in response to second messengers. In essence, riboswitches control gene expression. Our long-term goal is to select and design innovative antibacterial drugs that target riboswitches. However, in order to get to that goal, the structure information in all conformational states is needed. Riboswitches are intrinsically dynamic, as they require conformational changes (allosteric modulation) upon target binding to be able to stop gene expression. However, riboswitches represent a significant challenge to classical methods in structural biology. Therefore, we take advantage of Förster Resonance Energy Transfer (FRET) and a novel approach using FRET-restrained Positioning and Screening (FPS) to determine structural models of riboswitches. First, we performed Discrete Molecular Dynamic (DMD) simulations of the TPP-riboswitch; we observed that the TPP-riboswitch is in equilibrium between two conformational states. Both conformations are potential targets for binding new small-molecules. Based on our simulations, we designed a FRET-riboswitch with site specific labeling using Alexa 488 as the donor and Cy5 as the acceptor fluorophores. In this work we present single-molecule FRET studies of the TPP-riboswitch at various conditions and compare simulations and experiments. The next step is to measure a network of FRET-riboswitches to derive structural models using FPS which in turn will be used to screen *in silico* for binding of FDA approved small molecules.

Poster #009

Utilizing Advanced Fluorescent Techniques for Subcellular Analysis in *T. brucei*

Sheng Lin, Kenneth A. Christensen*, Meredith T. Morris, and James C. Morris

Department of Chemistry

Abstract:

Trypanosoma brucei is a parasitic protozoa and the causative agent of Human African Trypanosomiasis (HAT), also known as sleeping sickness. Subcellular measurements were performed in *T. brucei* glycosomes, the organelle responsible for glycolysis and essential for cell survival. For quantitative pH measurements, a fluorescein-tagged peroxisomal targeting sequence (F-PTS1, acetyl-CKGGAL) was designed. When added to cells, these fluorescent peptides are targeted to glycosomal structures and can be visualized after 30-60 min. Using fluorescein's ratiometric response to pH, we were able to observe the pH conditions inside glycosomes in response to starvation conditions. In the absence of glucose or proline metabolites, the glycosome exhibits an acidification from pH 7.4 ± 0.2 to 6.8 ± 0.2 .

The glucose concentration within glycosomes was also investigated using FRET protein constructs. The protein-based biosensor (FlipGlu), consisting of CFP and YFP FRET pairs bound by a periplasmic binding protein (PBP), was constitutively expressed in glycosomes of *T. brucei*. PBP is able to bind to glucose and change conformation, resulting in a measurable change in FRET. Using this platform, we were able to accurately quantify the glucose concentration in glycosomes of live *T. brucei* - $\sim 225 \mu\text{M}$ under normal growth conditions, but can drop to under $\sim 50 \mu\text{M}$ during starvation. These experiments represent a proof-of-principle for quantitative pH and glucose monitoring platform. This approach greatly simplifies resource and time requirements while allowing measurements to be performed with high throughput on live cells with subcellular and time resolution.

Poster #010

X-ray luminescent and fluorescent spectral rulers for non-invasive strain measurement through tissue

Melissa M. Rogalski, Nakul Ravikumar, Hunter Pelham, Joshua Lake, John D. DesJardins, and Jeffrey N. Anker*

Department of Chemistry

Abstract:

We describe novel luminescent spectral rulers to non-invasively evaluate mechanical strain on implanted orthopedic device surfaces to monitor fracture healing and aid in detection of hardware fatigue (e.g. load sharing, implant loosening, and non-union). The strain sensors measure the relative motion between two patterned substrates: (1) an “encoder” patterned with alternating luminescent lines, and (2) a transparent “analyzer mask” patterned with opaque lines that overlay and mask a portion of the encoder below. Moving the encoder with respect to the analyzer generates a color change that is detected by spectrometer and analyzed in MATLAB. We have fabricated a bromocresol purple patterned encoder that overlays an X-ray scintillator film ($\text{Gd}_2\text{O}_2\text{S}:\text{Eu}$). The dye absorbs a portion of the $\text{Gd}_2\text{O}_2\text{S}:\text{Eu}$ luminescence spectrum in a position-dependent manner. Our x-ray scintillator sensors reproducibly detect small displacements (~10 microns-1 mm) through 6 mm thick chicken breast tissue. Additionally, we have fabricated sensors that do not require ionizing radiation; a 633 nm laser is used to excite fluorescent dyes or nanoparticles on the encoder. These spectral rulers provide a non-invasive method for strain analysis through tissue.

Poster #011

Modification of polyethylene terephthalate capillary-channeled polymer (C-CP) fiber stationary phase for affinity separations

Liuwei Jiang and R. Kenneth Marcus*

Department of Chemistry

Abstract:

Capillary-channeled polymer (C-CP) fibers have been under investigation and development as stationary phase for high performance liquid chromatography (HPLC) separations for over ten years. They are unique due to the eight capillary channels extending the whole length of the C-CP fiber. This unique shape offers them ~3x greater surface area than that of circular cross-section fibers with the same nominal diameter. When packed into a column, C-CP fibers self-align, yielding a monolith like structure of 1-5 μm open, parallel channels. As a result, C-CP fiber stationary phases exhibit excellent fluid transport properties. A traditionally sized HPLC column packed with C-CP fibers can be operated at high linear velocity ($> 100 \text{ mm s}^{-1}$) with low backpressure ($< 2000 \text{ psi}$). In this study, a polyethylene terephthalate (PET) C-CP fiber packed microbore HPLC column was sequentially functionalized. The coupling strategy of solid phase peptide synthesis (SPPS) was employed for the attachment of ligands. The common biotin-streptavidin affinity pair was used as a demonstration of the basic methodology, wherein biotin was the immobilized ligand. The subsequent streptavidin binding homogeneity and binding capacity were studied by breakthrough curve experiments and frontal analysis. The biotin functionalized PET C-CP fiber column was shown to be able to affinity capture streptavidin from an enhanced green fluorescence protein (EGFP)-spiked *E. coli* cell lysate with high selectivity and efficiency. The SPPS coupling method used here yields PET C-CP fiber stationary phases with great potential for further functionalization by a variety of affinity ligands and used for affinity chromatography applications.

Poster #012

Fiber structures from hydrothermal treatment of cellulose nanocrystals

Yimei Wen and George Chumanov*

Department of Chemistry

Abstract:

Cellulose is the most abundant and inexpensive material available for chemical synthesis. Hydrothermal treatment of cellulose nanocrystalline can resemble the nature carbonization process of carbon species. We carefully carry the hydrothermal treatment of cellulose nanocrystalline and analysis the product. Fiber structures resemble nanotube were observed under Atomic Force Microscopy. Raman Spectroscopy and Transmission Electron Microscopy results show more information about the fibers, which may further prove our assumption to use cellulose nanocrystalline to synthesis nanotube in mild hydrothermal treatment conditions.

Poster #013

Magnetically Modulated Optical Nanoprobes (MagMOONs) for De-gelation Detection through Tissue

Khanh Van Thi Nguyen and Jeffrey Anker*

Department of Chemistry

Abstract:

We describe a method to detect through tissue the chemically-induced changes in viscosity and de-gelation process of alginate gels using magnetically modulated optical nanoprobes (MagMOONs). The MagMOONs are fluorescent magnetic microspheres coated with a thin layer of opaque metal on one hemisphere. The metal layer prevents excitation and emission light from passing through one side of the MagMOONs, which creates orientation-dependent fluorescence intensity. The magnetic particles also align in an external magnetic field and give blinking signals when they rotate to follow an external modulated magnetic field. The blinking signals from these MagMOONs are distinguished from background autofluorescence and can be tracked on a single particle level in the absence of tissue, or for an ensemble average of particles blinking through tissue. This approach can potentially be employed in drug delivery systems based on enzyme-catalyzed breakdown of gel components.

Poster #014

Temperature controlled fluorescence resonance energy transfer (FRET) on poly-propargyl acrylate nanoparticles modified with oxadiazole and naphthalimide derivatives

Oleksandr Klep and Dr. Stephen Foulger*

Department of Material Science and Engineering

Abstract:

An effective strategy to control fluorescence resonance energy transfer (FRET) using temperature was developed. The ability of poloxamer to change size is used to control the distance between two dyes thus to change the extent of FRET between them. By using solid core poly-propargylacrylate nanoparticles we achieve greater stability and reproducibility of results if compared to systems that consist of only non-bonded poloxamer, and, since these particles are fully organic, they have the potential to be used in medical applications. Oxadiazole and naphthalimide dyes were chosen as a working pair of dyes due to their great spectral overlap and high quantum yield of oxadiazole dye. Because both dyes are highly hydrophobic, they have very low emission from an aqueous environment leaving greater potential for improvement. Tunability to a specific temperature region can be achieved by using different compositions of poloxamer copolymer, which allows greater sensitivity in desired region

Poster #015

One-Pot Synthesis and Application of Highly Concentrated, Monodisperse Silver Nanoparticles with an Ultra-Thin Silica Shell.

Daniel Willett and George Chumanov*

Department of Chemistry

Abstract:

Ultra-thin silica shells (UTSS) are an effective way to improve the stability and compatibility of nanoparticles without significantly attenuating their intrinsic optical properties. This is of particular importance to plasmonic particles used in sensing or surface related studies such as localized surface plasmon resonance (LSPR) or surface enhanced Raman spectroscopy (SERS). For silver nanoparticles an UTSS can both hinder oxidation of the Ag in both air and water as well as establish a scaffold for functionalization through well-established silane chemistry.

UTSS on metallic nanoparticles such as gold or silver generally involve first using a silane coupling agent to render the surface vitreophilic followed by precipitation of silica by the Stober method or addition of sodium silicate species. Here we present a method to obtain silver nanoparticles with a silica shell of a thickness between 1-20 nm on silver nanoparticles ranging in size from 20-300 nm. It is obtained during the growth of the nanoparticles themselves by addition of a silica source to the well-established method of silver nanoparticle synthesis by hydrogen reduction of silver(I) oxide in water that both catalyzes the reaction as well as generates the shell. This allows for fairly monodisperse spherical silver nanoparticles to be obtained in concentrations of approximately 4.8×10^{12} AgNP per litre (for 100 nm AgNP with 1 nm silica shell). This silica shell greatly improves the particle stability allowing for further concentration of the particles in water up to solutions containing 50% Ag by weight. In addition we demonstrated the ability of these particles to be easily integrated into substrates for both SERS and LSPR applications.

Poster #016

Uranyl Speciation in Aqueous Acetate Employing Liquid Sampling-Atmospheric Pressure Glow Discharge (LS-APGD) Mass Spectrometry

Lynn X. Zhang and R. Kenneth Marcus*

Department of Chemistry

Abstract:

Research on uranium detection is of sustained interest, particularly in nuclear technology, safeguards and forensics. A variety of techniques have been utilized to examine uranium, both chemically and physically. Alpha spectrometry, gamma spectrometry and mass spectrometry are the most common techniques used for uranium analysis. Detection of solution based uranium samples using mass spectrometry (MS) is centered on either the aqueous chemistry dominated by the uranyl dication, UO_2^{2+} (e.g., electrospray ionization- MS) or atomization of the sample (e.g., inductively coupled plasma MS). An increased interest in this field pertains to obtaining molecular information from native samples, the poor ability of handling samples with high salt, acid, or base content limits the use of ESI on complicated native samples.

Marcus and co-workers have developed a liquid sampling-atmospheric pressure glow discharge (LS-APGD) as a low power, small footprint, and cost efficient ionization source for mass spectrometry. The glow discharge is sustained between the surface of an electrolytic solution, introduced through a 0.28 mm (i.d.) capillary housed inside a 1 mm (i.d.) metal capillary, and a stainless steel counter electrode mounted at a 90° angle while helium sheath gas flows between the two capillaries. The source is interfaced to a mass spectrometer to analyze uranyl compounds. This technique has been utilized in a Round-Robin Test (RRT) organized by the Helmholtz-Zentrum Dresden-Rossendorf laboratory. This inter-laboratory RRT involved researchers from more than 30 institutes using different spectroscopic methods to obtain comprehensive molecular information of the actinide complex system U(VI)/acetate in aqueous solution. Using the LS-APGD was able to generate uranyl ions with various ligands attached, and their solvent additives along

with the uranium atomic ion. The relationship between the abundance of such ions and pH has also been studied. The intensity of UO_2Ac^+ , $\text{UO}_2\text{Ac}_2\text{H}^+$, UO^{2+} with its solvent additives ions are affected by the pH of the sample, the trends are corresponding with the ion concentration in the solution.

Poster #001-015 are competing for prizes.

*-- Advisors from Clemson University