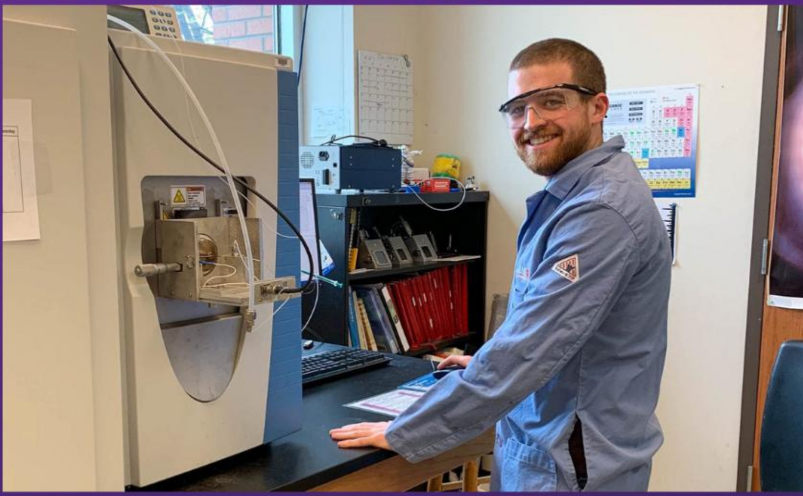
CLEMSON
CHEMISTRY



5th Annual

Department of Chemistry

Research Symposium

1889

MARCH 13, 2021
9-12 PM

Dear Faculty, Staff, Students, and Honored Guests,

Welcome to the 2021 Chemistry Research Symposium, which highlights research performed at Clemson by our students and at other institutions by our honored guests. All of these students have worked very hard to highlight the variety and importance of research being done in chemistry. Interact with the poster authors and experience the enthusiasm and dedication they have for their work. Enthusiasm is contagious, and we hope that you will be inspired by your conversations with them to want to know more. Science isn't hard work for the curious, but it does provide education and training for a wide variety of careers and vocations, and chemistry, as the central science, provides a jumping-off point to a world full of opportunities.

We hope you enjoy your time with us!

Bill Pennington
Chair

Keynote Lecture

Applied to Fundamental Research in Forensic Chemistry

Dr. Suzanne Bell
Professor and Chair emeritus
Department of Forensic and Investigative Sciences
West Virginia University

Forensic chemistry is applied analytical chemistry seasoned with dashes of organic, physical, and biochemistry. Forensic research is historically problem-driven and applied. Several factors are driving the evolution towards fundamental research. This change is partly due to the recognized need for a more in-depth knowledge base to support forensic methodology and practices. Academic acceptance and the advent of Ph.D. programs at research-intensive universities are also drivers. This presentation will describe recent developments in forensic science research and education to illustrate how forensic chemistry research is advancing and expanding. Collaborative research programs involving undergraduates through doctoral students from different departments will be highlighted. The common theme is applying advanced mass spectrometry to the characterization of biological and chemical evidence ranging from novel psychoactive substances to firearms discharge residue.

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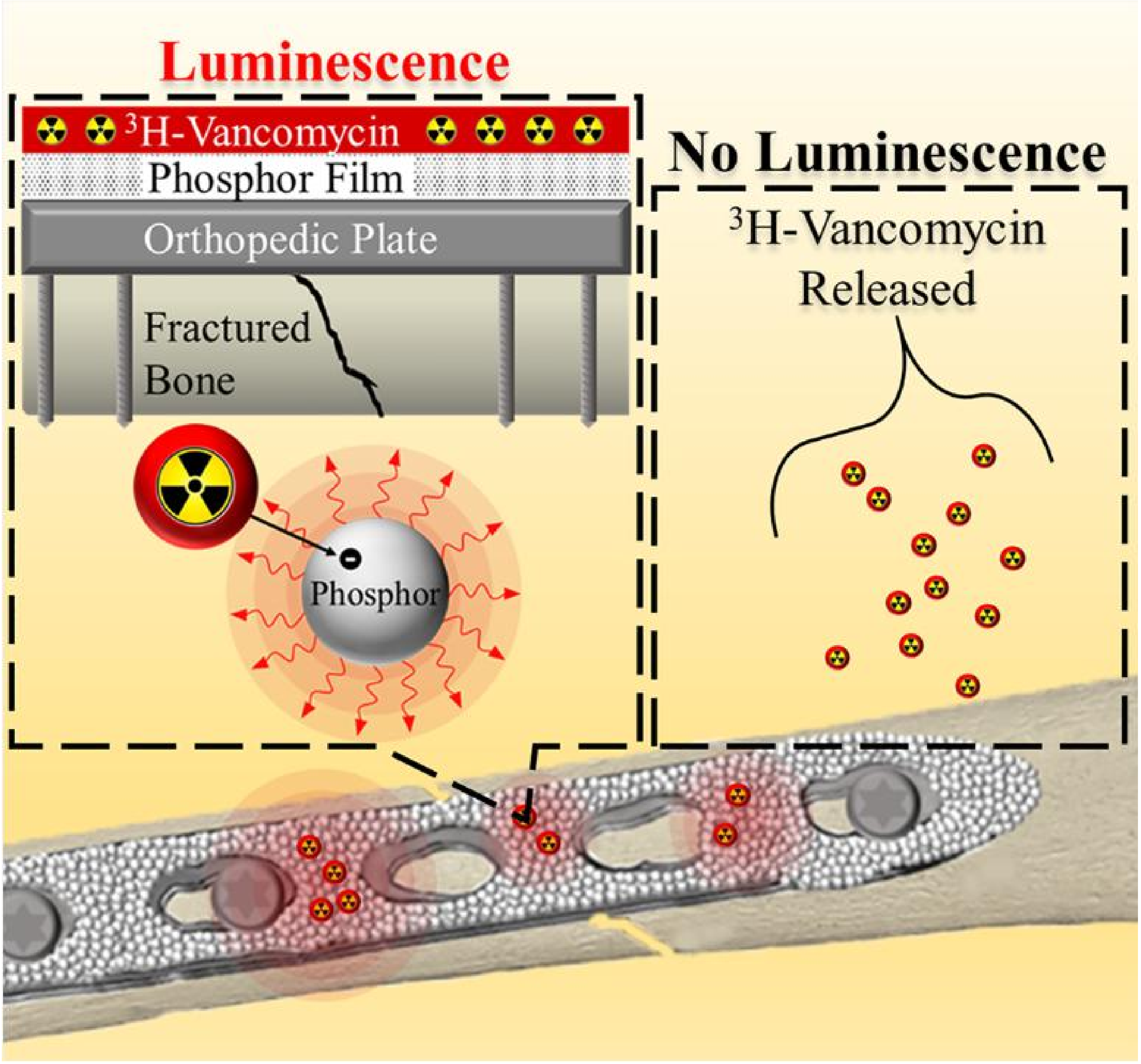
Organized by research group


Luminescence
³H-Vancomycin
Phosphor Film
Orthopedic Plate
Fractured Bone
Phosphor
No Luminescence
³H-Vancomycin Released

Imaging Radiolabeled Drug Release from Orthopedic Implant Surface using Radioluminescent Phosphors

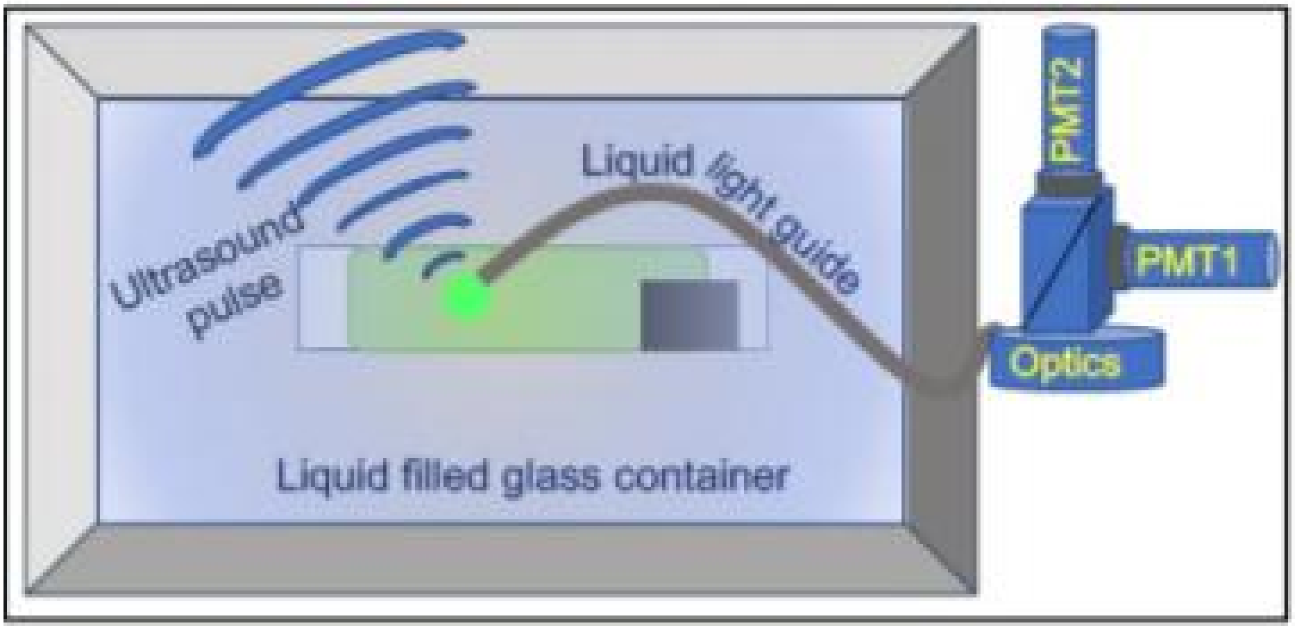
Gretchen B. Schober [1], Jeffrey N. Anker [1,2]
1. Department of Chemistry and Center for Optical Materials Science Engineering Technology (COMSET)
2. Department of Bioengineering, Clemson University

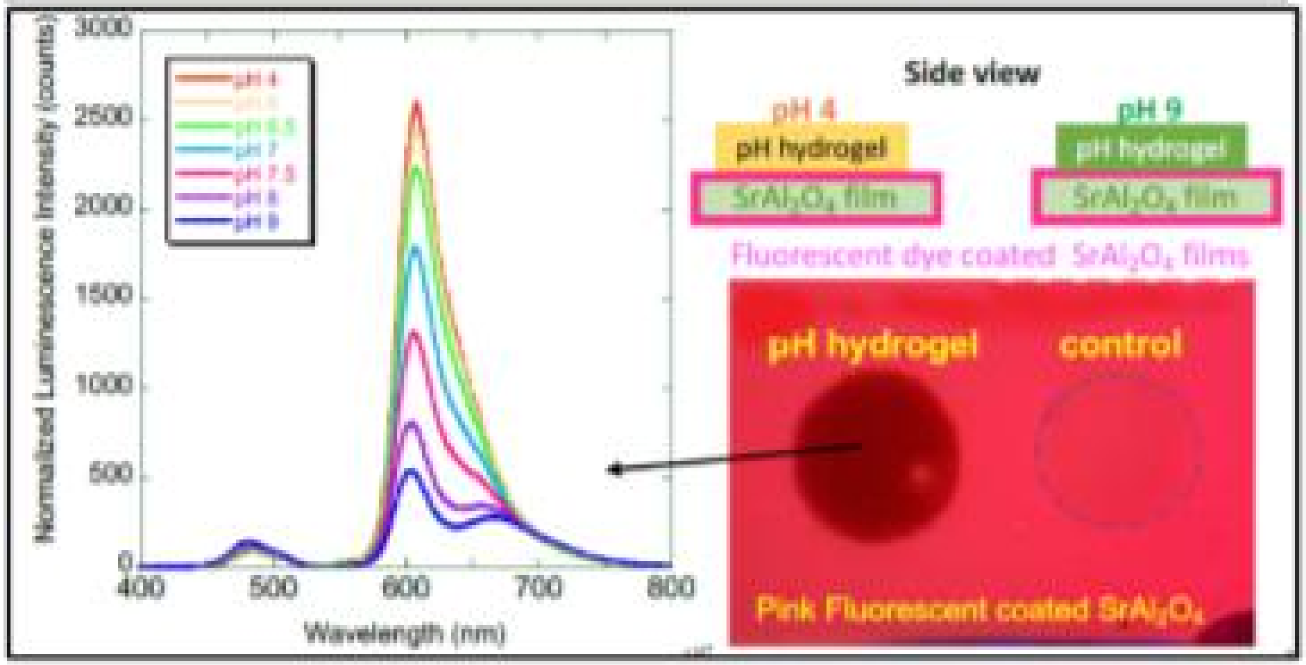
We developed a coating and imaging technique to monitor radiolabeled pharmaceutical release from the surface of biomedical implants. Radioactive decay from radiolabeled drug will excite radioluminescent phosphor particles, and generate luminescence, when in close proximity. By coating an implant surface with a film of radioluminescent phosphor particles, changes in luminescence intensity indicates the presence, or absence, of radiolabeled drug. The luminescence is captured and quantified using a CCD camera and custom MATLAB image processing scripts. Herein this technique is applied in detecting tritium labeled vancomycin (3H-vancomycin) concentration on the surface of an orthopedic implant using radioluminescent film of Gd2O2Eu3+. Orthopedic implants are susceptible to colonization by bacterial biofilms, which often require aggressive, and invasive treatment for eradication.[1] As a result, there has been a surge of research developing infection specific imaging techniques[2], and non-conventional antibiotic administration techniques, for prevention and treatment of infection.[3] Smart implants that can control antibiotic release and/or measure antibiotic accumulation are promising methods to study infection treatments and develop controls. To be effective, drug release needs to be maintained within a therapeutic dosage window at the site of infection. However, assessing local drug release/accumulation is challenging for in vivo applications. Our method permits surface specific monitoring of drug release at the biomedical implant surface through tissue and provides a promising avenue for development of effective drug release motifs.

Rapid and on-site detection of COVID-19 using buoyant and magnetic microbeads.

Chuanlei Wang, Meenakshi Ranasinghe, Jeffrey N. Anker
Undergraduate students: Hanna Campbell, Kiersten Barnett, William Pons
Clemson University

COVID-19 is the current outbreak of coronavirus disease 2019, caused by a severe acute respiratory syndrome-coronavirus-2 (SARS-Cov-2) virus. According to statistics, on 26th February 2021, there are above one hundred million positive cases and two million deaths worldwide. The most common diagnostic tests of COVID-19 are molecular (RT-qPCR) and antibody tests. However, these methods have drawbacks. RT-qPCR takes one to two days to get results and requires complex instruments and technical knowledge to perform. The antibody test is suitable to identify past infections, not current infections of COVID-19. Therefore, we need a rapid, on-site test to address these limitations. We are developing a rapid screening test to detect and quantify SARS-CoV-2 in a patient's saliva using buoyant and magnetic microbeads. The microbeads are functionalized with antibodies that can specifically bind to the SARS-CoV-2 nucleocapsid protein present in saliva to form buoyant-and-magnetic (BAM) complexes. The BAM complex consists of a buoyant microbead and a magnetic microbead bound to a single viral protein through antibodies. These BAM complexes are typically in quantities that are visible to the naked eye. However, small quantities up to a single BAM complex can be detected using video capture and MATLAB analysis to track the particles' motion. This "single-particle analysis" improves the sensitivity and decreases the cost and number of microbeads required by detecting small numbers of complexes. Currently, we are working on a water-soluble delivery system consisting of a jello-based capsule to release the microbeads into saliva. We also designed and 3D-printed stands to allow us to conduct multiple tests in parallel. These advances will make the test user-friendly and minimize reagent handling. We are also working on concentrating virus content in saliva samples to improve the specificity of the test. Once optimized, this test should be able to deliver on-site results within 15 minutes without complex equipment, thereby providing a robust and quickly executable point of care test for COVID-19.


Ultrasound pulse
Liquid light guide
PMT2
PMT1
Optics
Liquid filled glass container

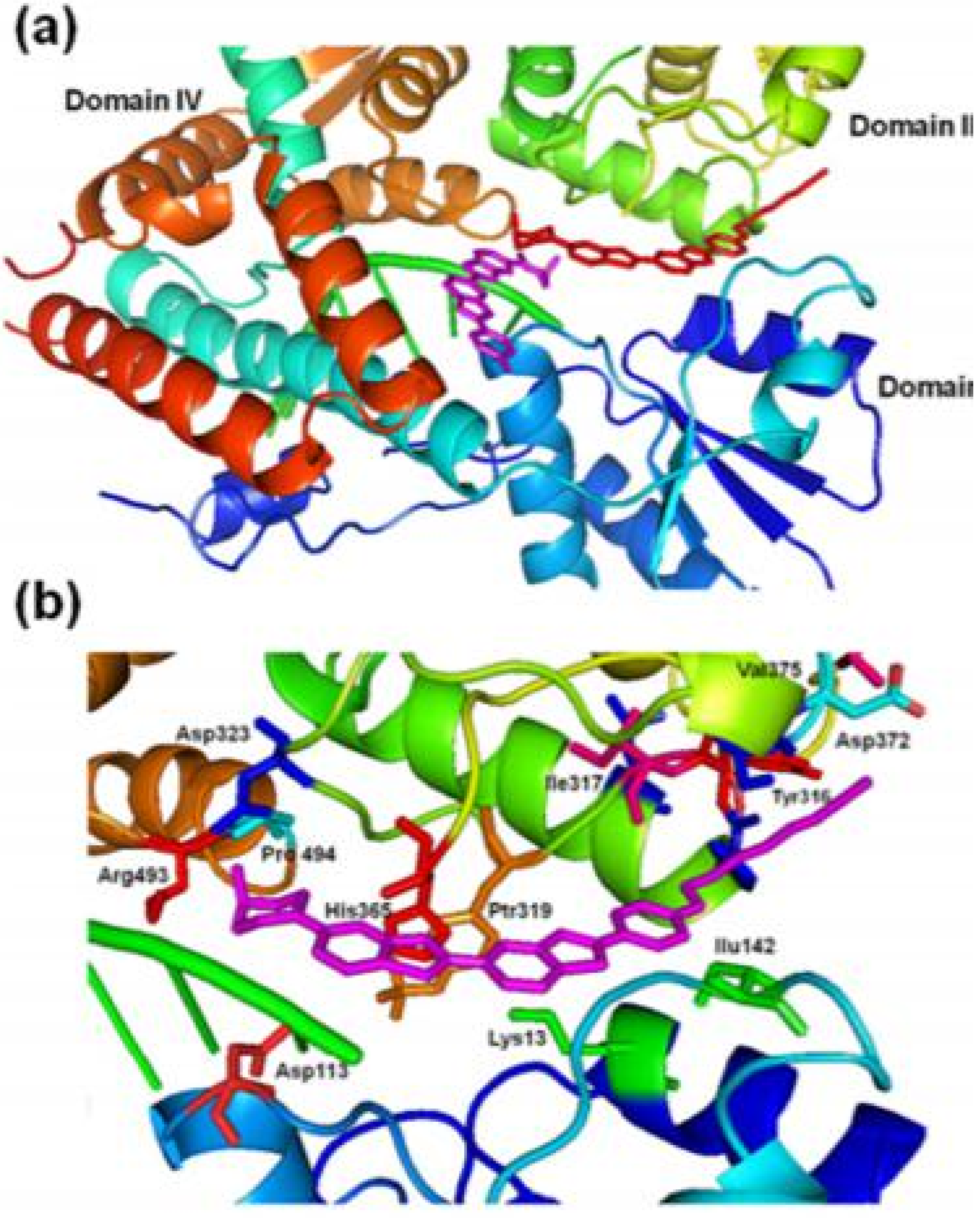

3000
2500
2000
1500
1000
500
0
Normalized Luminescence Intensity (counts)
400
500
600
700
800
Wavelength (nm)
pH 4
pH 6
pH 6.5
pH 7
pH 7.5
pH 8
pH 9
Side view
pH 4
pH hydrogel
SrAl$_2$O$_4$ film
pH 9
pH hydrogel
SrAl$_2$O$_4$ film
Fluorescent dye coated SrAl$_2$O$_4$ films
pH hydrogel
control
Pink Fluorescent coated SrAl$_2$O$_4$

Ultrasound Luminescence Chemical Imaging: A tool for detection of implant infection via monitoring of pH changes at implant surface

Sriparna Bhattacharya,[1] Gretchen Schober,[2] Unaiza Uzair,[2] Morgan Reel,[2] Herbert Behlow,[1] Vigjna Abbaraju,[2] Apparao M. Rao[1], Jeffrey N. Anker[2,3]

1. Department of Physics and Astronomy, Clemson Nanomaterials Institute, Clemson University. 2. Department of Chemistry, Clemson University. 3. Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University.

Orthopedic implants and other medical devices are often susceptible to bacterial infection that forms biofilms on the surface of the implant and are highly resistant to antibiotics and host's immune system[1]. Early detection of the infection and elucidating the local biochemical environment would help in developing therapeutic strategies for successful treatment of infection. Therefore, it is imperative to develop methods for in vivo monitoring of changes in the chemical environment such as pH and oxygen concentration of tissues in the proximity of the implanted medical devices that could act as early indicators of implant related infection. We developed a chemical imaging technique to probe the biochemical environment on the implant surface using focused ultrasound pulses to generate luminescence in mechanoluminescent film (SrAl2O4:Eu,Dy microparticles in PDMS) that can be imaged through tissue. UV excitation causes mechanoluminescent films to emit green phosphorescence afterglow and when an ultrasound beam is incident on this film it will luminescence more brightly. Turning the ultrasound ON and OFF modulates the luminescence at focal spot. This method was applied to image changes in the luminescence spectra of the ultrasound luminescent film (mechanoluminescent film coated with Fluorescent dye) modulated by the pH sensitive dye (bromothymol blue) coating[2] in different pH environments through a light scattering media. The measurements were acquired using raster scanner where the emitted light is collected using liquid light guide followed by detection using photo multiplier tube(PMT), and finally the intensity profile was processed using MATLAB. High resolution images were obtained that are limited by the ultrasound focal spot size. Hence, this technique can be promising for detection and monitoring of implant infection.


(a)
Domain IV
Domain I
Domai
(b)
Val375
Asp323
Asp372
Ile317
Tyr316
Pro 494
Arg493
His365
Ptr319
Ilu142
Lys13
Asp113

The modification of Bisbenzimidazoles for the Selective inhibition of bacterial DNA topoisomerase I

Adam Gaynor, Andrea Conner, Geoffrey Chesser, Dev P. Arya
Clemson University

The emergence and resilience of antibiotic resistance in bacteria has once again led to an alarming problem. Antibiotics that were once effective for treatment of otherwise deadly bacterial infections have become ineffective. Now, daunting challenges for health professionals and drug developers alike lie ahead. Ideally, antibiotics that are active for novel targets or work through alternate mechanisms are developed to maximize their duration as effective therapeutics. Intuition might have us believe that the DNA of bacteria would be a reasonable target as the transcription of DNA is essential for the persistence of any bacterium. Despite this, targeting a specific coding sequence of DNA with a small molecule would be difficult. However, targeting an enzyme that interacts with DNA could be a much more practical approach. DNA topoisomerase I is an enzyme which is responsible for unraveling supercoiled DNA, a critical function as supercoiled DNA cannot be transcribed. Therefore, DNA topoisomerase I is a practical choice as a novel antibacterial target. It's been shown in literature that Hoechst 33258 interacts strongly with the minor groove of B-DNA and the benzimidazole scaffold is seen in medicine across many facets and is therefore considered a privileged structure. Despite this, the bioactivity of Hoechst 33258 based bisbenzimidazoles has been sparsely studied for its therapeutic value. Hoechst 33258 analogs, previously reported, have been shown to interact with both DNA topoisomerase I and the minor groove of B-DNA. Therefore, the development of various Hoechst 33258 analogs seems to clear a path for successful lead optimization. The primary modifications already reported involve the variation of the linker length and composition on the bisbenzimidazoles, along with the inclusion of a carboxylic acid group on the end of the linker. We also aim to modify the methylpiperazine moiety by replacing it with morpholine.

Cyclic beta-Peptoid-Based Analogs of Enterobactin for Iron Recognition and Bacterial Uptake

Brandon G. Wackerle, Mikeclinton N. Agejo, Dr. Julia L. Brumaghim, and Dr. Modi Wetzler
Clemson University

Siderophores are small organic molecules excreted by bacteria to facilitate iron uptake from the environment. Two of the prototypical ones are enterobactin and bacillibactin, which differ by the presence of additional chirality and glycine spacer in bacillibactin compared to enterobactin. Both of these siderophores are exquisite in their high affinity and selectivity for iron, but require a synthetically challenging trilactone backbone with limited options for further functionalization. In contrast, peptoids (poly-N-substituted glycines) are completely facile to cyclize and can incorporate a wide range of side chains. Peptoids are also intriguing because they lack the chirality associated with peptides, and the chirality of the siderophore-metal complex is known to affect the availability of iron to the bacteria. We are investigating the impact of spacer length and chirality on iron recognition by these siderophore analogs using potentiometric titrations and uptake of the resulting complexes by bacteria

Development of Highly-Covalent, Radiolytically Stable Ligands for Trivalent Separations

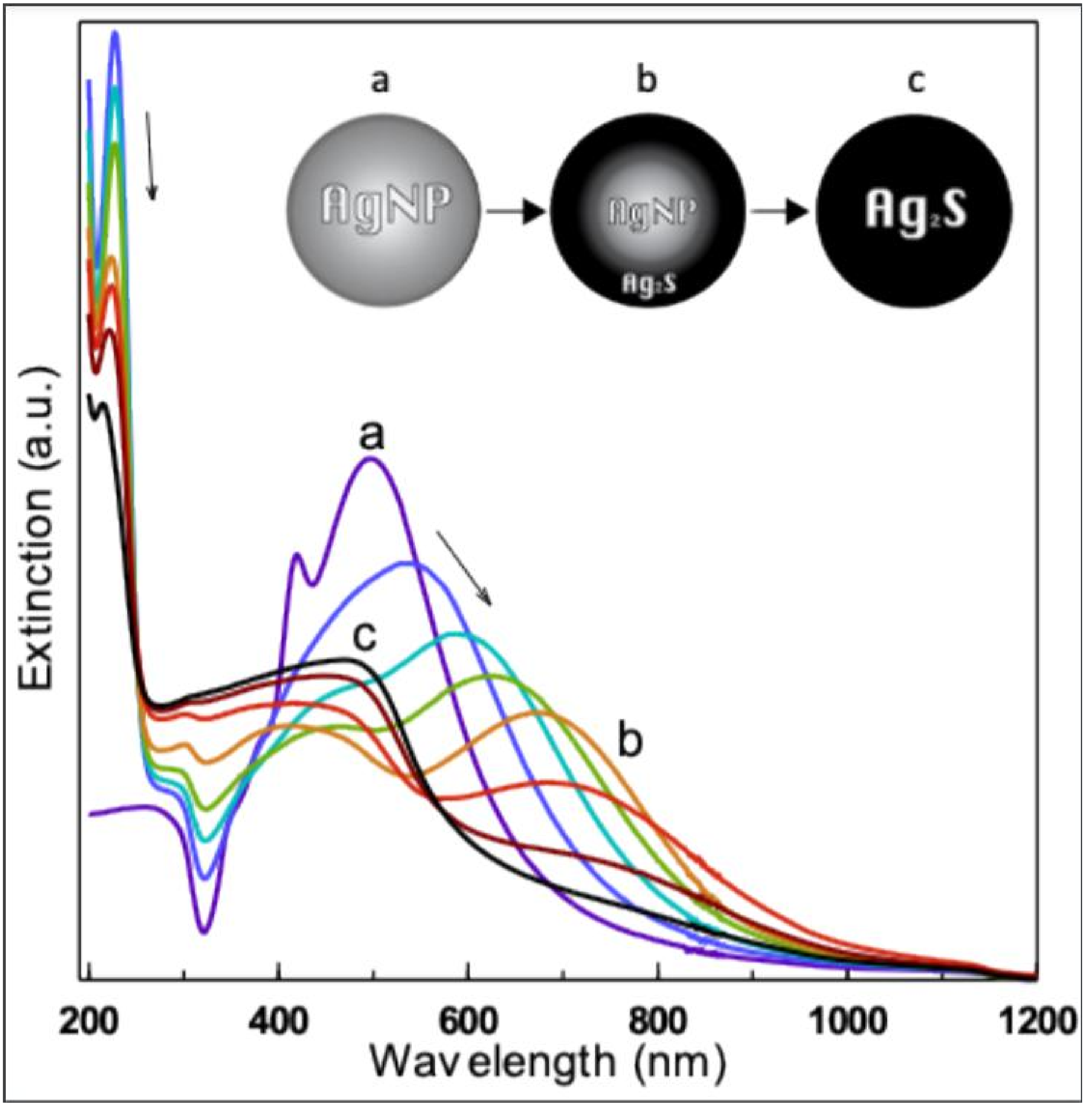
Rhianna Wolsleger, Dr. Julia L. Brumaghim
Clemson University

Nuclear energy is responsible for approximately 20% of the electricity generation in the United States per year and more than 50% of the electricity generated in South Carolina.1,2 The United States does not recycle spent nuclear fuel, but instead utilizes a once-through fuel cycle, sending the waste to long-term storage.3 Were the U.S. to recycle its nuclear fuel, the first step would be one of several separation processes, such as PUREX (Plutonium URanium EXtraction), to recover the useable U-235 and Pu-239 nuclear fuel, followed by a second step such as ALSEP (Actinide Lanthanide SEParation) or a similar process that removes trivalent minor actinides (MA), primarily Am(III) and Cm(III), from the remaining waste to facilitate long-term storage. The ALSEP process uses an organic solvent and acidic aqueous extraction process to separate actinides (An) and lanthanides (Ln) in the nuclear waste. A polyaminocarboxylate ligand such as diethylenetriaminepentaacetate (DTPA) is added to extract the MA into the aqueous phase, leaving the Ln in the organic layer.4 Although these MA and Ln are of similar size, the An(III) ions are slightly more covalent than the Ln(III) ions, so the slightly more covalent nitrogens of DTPA retain the An(III) in the aqueous solution preferentially to the Ln(III).5 Because nitrogen is only a marginally covalent ligand, and because DTPA is an oxtadentate ligand, it has very poor kinetics for complexation and decomplexation.6 A ligand incorporating a much more covalent donor atom, such as sulfur, would significantly improve Ln(III) and An(III) separations, and including fewer carboxylates would provide faster complexation and decomplexation kinetics.Imidazole thiones are good candidates for An coordination as the highly covalent sulfur is resistant to oxidation into disulfides and to protonation at low pH. The imidazole can be substituted at both nitrogens, enabling incorporation of carboxylate arms to enthalpically drive coordination of the Ln(III)/An(III) ions. Successful synthesis of two novel chelating imidazole thiones has been accomplished using a single electron transfer (SET) reaction.7 Synthesis of these compounds has expanded the scope of the reported SET reaction and raised questions about the mechanism by which this reaction proceeds. Electron paramagnetic resonance studies may lead to revision of the existing mechanism. The radiolytic stability of the chelating imidazole thiones, and the stability of their complexes with Ln(III) at low pH will be quantified to test their viability for Ln(III)/An(III) separations complexants. Determination of coordination stoichiometry by mass spectrometry will demonstrate how many of these ligands are required for metal binding, and potentiometric titrations will be done to determine formation constants. Development of imidazole thiones provides an opportunity to tune the identity of the carboxylate-containing substituents, serving to develop a better understanding of the sterics, kinetics, and electronics of these ligands. It is possible to create a new class of ligands with potential application in the separation of Ln(III)/An(III) which will improve upon existing separation methods in the ALSEP process.

Metal Silicate Complex

Dimuthu Edirisinghe, Tatiana A. Estrada-Mendoza, George Chumanov
Clemson University

Metal nanoparticles exhibit interesting and important properties that are different from the bulk state. Such as large surface to volume ratio as well as size-dependent properties. The excitation of plasmon resonances, the collective oscillation of the conductive electrons, in silver nanoparticles (AgNPs), represents the most efficient mechanism, by which light interacts with matter.1,2 Based on the method developed in our laboratory, AgNPs are synthesized by the reduction of a saturated solution of silver oxide with hydrogen gas in the presence of silicate in water.3 The formed nanoparticles are chemically cleaned without extra stabilizing agents and are stable for long time. The stability of AgNPs is important when they are used to synthesize hybrid nanoparticles.4 It was observed that there is a correlation between the amount of silicate available in solution and the size and amount of particles that are synthesized over the same period of reaction time. Larger concentrations of silicates yield higher concentrations of smaller nanoparticles while smaller silicate concentrations yield lower concentrations of larger nanoparticles for the same amount of silver and reaction time.4 The role of silicate was described as stabilizing and catalytic agent.4 However, questions still remain related to the interaction of silver ions (Ag+) and silicate (SiO32-) in the solution. Further elucidating the role of silicate and its initial interactions with Ag+ will help to develop this matrix as a general approach to the synthesis of other metal nanoparticles and nanostructures. It was proposed that silicate can make a complex with Ag+ ions, making a stable intermediate 'nanoreactor' that concentrates the Ag+ and makes them available for further reaction. Ag + reacts with SiO32- to result into Ag2SiO3 which is significantly less soluble in water compared to NaSiO3. The low solubility facilitates the condensation of silver silicate into NPs that function as nanoreactors. The formation of silver-silicate nanoreactors was monitored by UV-visible spectroscopy. The titration of silicate into the Ag+ solution revealed the formation of the silver silicate complex. The ability to monitor the metal silicate complex provides a foundation for the controlled synthesis of metal nanoparticles and other nanostructures.


a
b
c
AgNP
AgNP
Ag2S
Ag2S
a
c
b
Extinction (a.u.)
200
400
600
800
1000
1200
Wavelength (nm)

Optical studies of hybrid silver/silver sulfide nanoparticles

Tatiana Estrada Mendoza, George Chumanov
Clemson University

Noble metal nanoparticles (NP) exhibit plasmon resonances which are the collective oscillations of free electrons within the NP boundaries. The restoring force that is caused by the nuclei attraction to the free electrons makes the oscillations coherent1,2. Plasmon resonances in silver nanoparticles (Ag NPs) consists of light absorbing and light scattering components. The scattering component dominates in NPs larger than 60nm. The spectral position of the plasmon resonance of these particles can be tuned across visible and Near-IR spectral range. This is possible by changing the size of the nanoparticle3. This tunability is advantageous for designing materials that will absorb in the solar spectrum. In our laboratory, AgNPs are synthesized in a silicate matrix that aids in size control and results in a stabilizing thin silicate shell.4 The stability of our NPs allows for the modification of Ag NPs to hybrid silver/silver sulfide (Ag/Ag2S) NPs by exposing the suspension of NPs to sulfide ions (S2-). S2- have high affinity for soft metal cations, such as silver (Ag+) resulting in the formation of a silver sulfide (Ag2S) layer around the Ag NP forming hybrid NPs. The reaction starts as S2- enter the Ag NP suspension. The silicate shell controls the reaction kinetics. For 2-3 nm thick silicate shell, it takes up to two days for the system to reach equilibrium at which the reaction rate approaches zero. The sulfidation reaction was monitored using UV-Visible, extinction, absorption and scattering spectroscopy. The hybrid particles at different stages of sulfidation were characterized by XRD, AFM and EM. The extinction of fully converted NPs (Ag NPs to Ag2S NPs) was three times higher than that of Ag2S NPs that were synthesized using an alternative method. A surprising and important finding relates to the fact that even with a thin silver sulfide layer, the plasmon resonance changed from being scattering dominant to absorption dominant.

CVD Graphene-based membrane with polymeric support for water desalination

Mansour Saberi [a], Stephan Creager [a]
[a] Department of Chemistry, Clemson University, Clemson South Carolina, USA

To meet humanity's increasing and unavoidable need for water, we must convert saline water into fresh water through desalination. Nevertheless, Reverse Osmosis (RO) is ubiquitous because of the slightly fast transport of water molecules through a membrane while obstructing all ions; desalination through RO faces several challenges. For example, high operation cost due to high pressure during the process or its degradable polymeric active layer in contact with Chlorine-containing compounds. Polymeric membranes are also susceptible to various foulants, such as biofouling, which become more problematic in the absence of chlorine treatments. In terms of general functionality, water transport through membranes could still be improved by increasing membrane permeability.

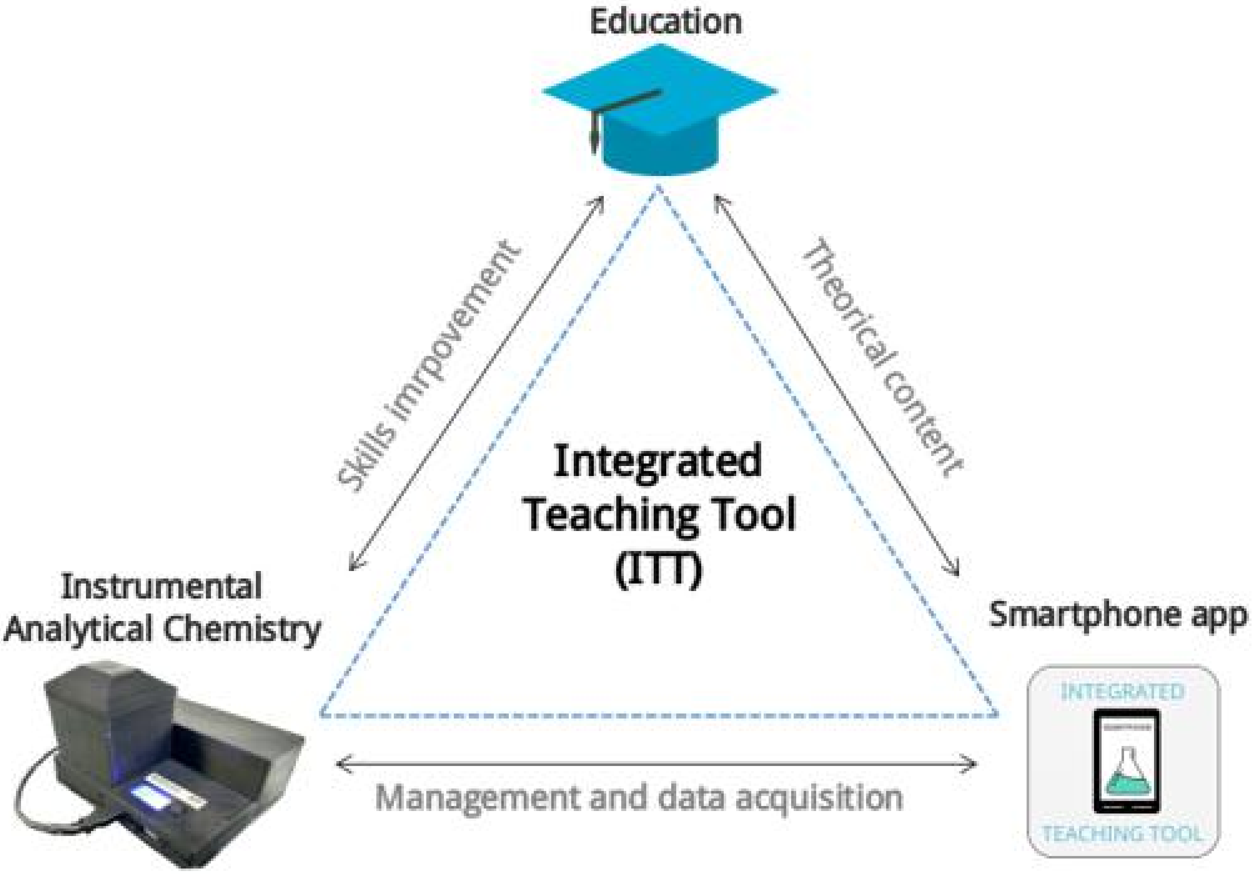
One of the most famous and recently studied candidates for use in RO or NF membranes is Graphene, which has excellent chemical, and mechanical stability. It is the most prominent thinnest possible membrane, with its one atom thickness acting as the membrane. As a further benefit, Graphene manifests more excellent resistance to chlorine than current polyamide membranes. This research focused on developing graphene membranes with higher flux and better ion/molecule selectivity than the RO/NF membranes currently available on the market.

In this study, the process of transferring Chemical Vapor Deposition (CVD) Graphene onto a hydrogel and the performance of the graphene-based membrane will be discussed. The method of transferring the membrane to the substrate is challenging: CVD graphene is fragile and can easily be torn if it is directly transferred to the support structure. A hydrogel substrate—polyvinyl alcohol (PVA)—has been synthesized and cross-linked to allow transference without damage. The degree of crosslinking, the thickness of the casting can affect a PVA membrane's permeability.

Using plasma through the Graphene can create sub-nanometer pores that make the Graphene more selective. Consequently, the plasma method results with the different conditions used to apply nanometer pores on the graphene surface will be discussed.

Experimental work combined with membrane characterization methods (FESEM, AFM, and LEXT) and membrane performance studies using a RO system to examine the Graphene as RO/NF membrane will be presented.

This research will provide insights into developing CVD graphene-based membranes with high water permeability and excellent size selectivity, membranes that will be highly attractive for water purification and desalination because of their high energy-efficiency.



Schematic representation of Integrated Teaching Tool and their three fundamental aspects: i) Low cost analytical instrumentation ii) Android APPS e Iii) Quickly access study guides.

Integrated Instrumental Analysis Teaching Platform with Smartphone-Operated Fluorometer

Lucas B. Ayres, Fernando S. Lopes, Ivano G.R. Gutz, Carlos D. Garcia
Clemson University

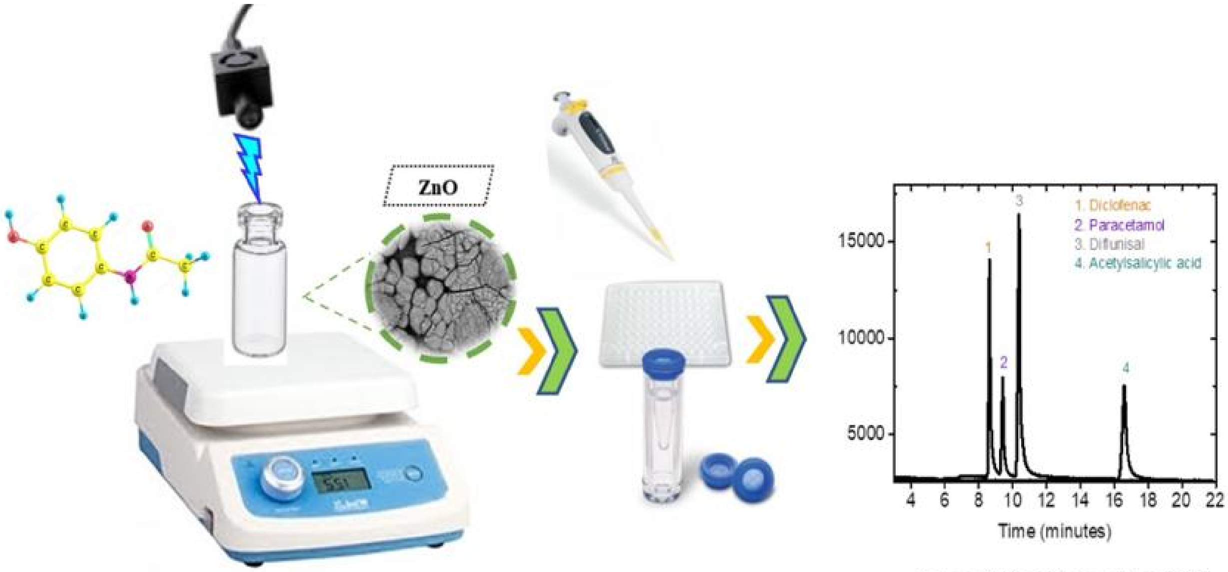
It is fairly known that laboratories teaching sections contribute to students̀ knowledge consolidation in any area of education. However, this strategy is tough to implement in low-income settings when high-cost instrumentation is needed. The majority of commercial instruments are expensive, require a computer for their management, as well as specialist for the maintenance. Alternatively, strategies based on open source technologies (e.g. Arduino microcontrollers and 3D printers) offer significant advantages towards the development of low-cost chemistry instruments such as photometers1, potentiostats2 and pHmeters3. The present work aims to describe an Integrated Teaching Tool (ITT) based on these technologies, to facilitate the learning process in analytical chemistry. The ITT has three fundamental aspects: i) low cost chemistry instrumentation; ii) Android Applications (apps), iii) easily access of theoretical and technical content about the sensor. The chemistry instrument developed for the ITT is a wireless portable fluorometer, produced by 3D printing. The instrument is managed via BLUETOOTH by the ITT app, it has a Teensy 3.1 as microcontroller, a high power UV-LED, a secondary filter and an auxiliary electronic circuit. As for the educational purpose, theoretical content about the fluorescence method as well as technical information about the instrument (e.g. Emission curve of the LED and secondary filter absorption spectrum) are provided as a module in the app. The described ITT platform proved to be appropriate for the remote management of the fluorometer as an example of low cost analytical instrumentation and presents great promise for the development of new applications.

Micelle Encapsulation of Ferromagnetic Nanoparticles of Iron Carbide@Iron Oxide in Chitosan as Possible Theragnostic Agent

Perla Y. Sauceda-Oloño[1], Hector Cardenas-Sanchez[2], Anya I. Argüelles-Pesqueira[2], Cindy Gutierrez-Valenzuela[2], Mario E. Alvarez-Ramos[3], Armando Lucero-Acuña[2,3] and Paul Zavala-Rivera[2,3]

1 Department of Chemistry, Clemson University, Clemson, SC, 29634
2 Posgrado en Nanotecnología, Departamento de Física, Universidad de Sonora, Hermosillo 83000, Mexico.
3 Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo 83000, Mexico.

In this work, the synthesis and characterization of core/shell nanoparticles of iron carbide@iron oxide ($Fe_3C/\gamma\text{-}Fe_2O_3$) encapsulated into micelles of sodium dodecylsulfate and oleic acid and stabilized with chitosan was developed. The materials were sonosynthesized at low intensities using standard ultrasonic baths with iron pentacarbonyl ($Fe(CO)_5$) as iron source and oleic acid as hydrophobic stabilizer, obtaining nanoparticles with a hydrodynamic diameter of 19.71 nm and polydispersive index (PDI) of 0.13. The iron carbide@iron oxide nanoparticles (ICIONPs) in oleic acid were used as the organic phase during the self assemble of nanoemulsion with sodium dodecylsulfate in water to obtain the metastable micelles. The final step involved the stabilization of the micelles using low molecular weight chitosan solution at 2% in acetic acid by ultrasonication bath. The nanosystem showed a hydrodynamic diameter of 185.30 nm, a PDI of 0.15 with a superficial charge ζ of 36.70 mV. Due to the several properties previously measured of the ICIONPs, it is believed that can be used as a possible theragnostic agent.



Quantification using CE

Monitoring the Advanced Oxidation of Paracetamol using ZnO films via Capillary Electrophoresis

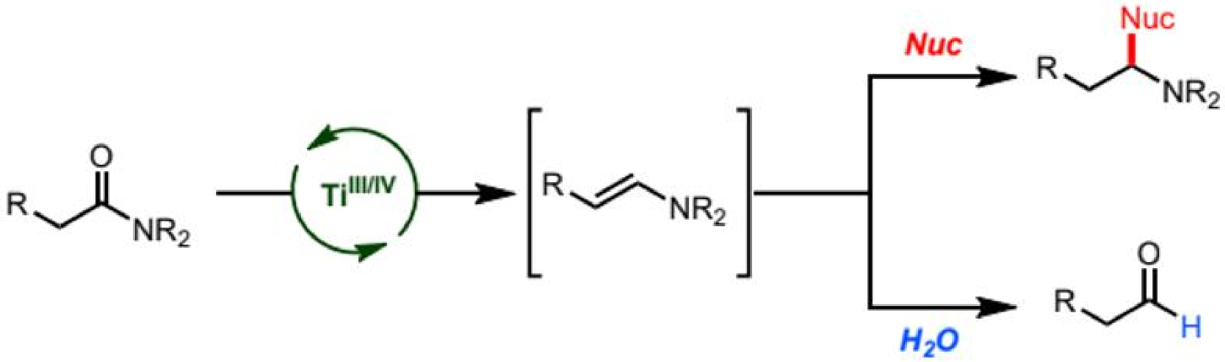
Luz A. Hernández-Carabalí, Rakesh Sachdeva, Jose B. Rojas-Trigos, Ernesto Marín, and Carlos D. Garcia
Clemson University

With the goal of investigating the effect on ZnO on the photo-chemical degradation of pharmaceuticals (using paracetamol as a model compound), a thin film of ZnO was grown -by means of ultrasonic spray pyrolysis- on glass substrates. The morphology, crystalline structure and elemental composition of the obtained thin films were determined by scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy techniques. UV-Vis spectroscopy was used to determine the corresponding optical bandgap. To evaluate the catalytic activity of zinc oxide films towards the degradation of selected pharmaceutical compounds, capillary electrophoresis was used. The structure of the by-products generated during the photocatalytic reactions, was determined by gas chromatography coupled with the mass spectroscopy. According to our results, the film allowed coupling relatively mild conditions (0.35% H2O2 and UV light 365 nm / 6 W·cm-2) and still reach a degradation efficiency of 88.1%. Under the selected experimental conditions, the approach was also applicable to other compounds with similar properties (diclofenac, paracetamol, diflunisal and acetylsalicylic acid).

Use of universal 3D-Printed smartphone spectrophotometer to develop a time-based analysis for hypochlorite

Ezequiel Vidal, Anabela S. Lorenzetti, Carlos D. Garcia, Claudia E. Domini
Clemson University

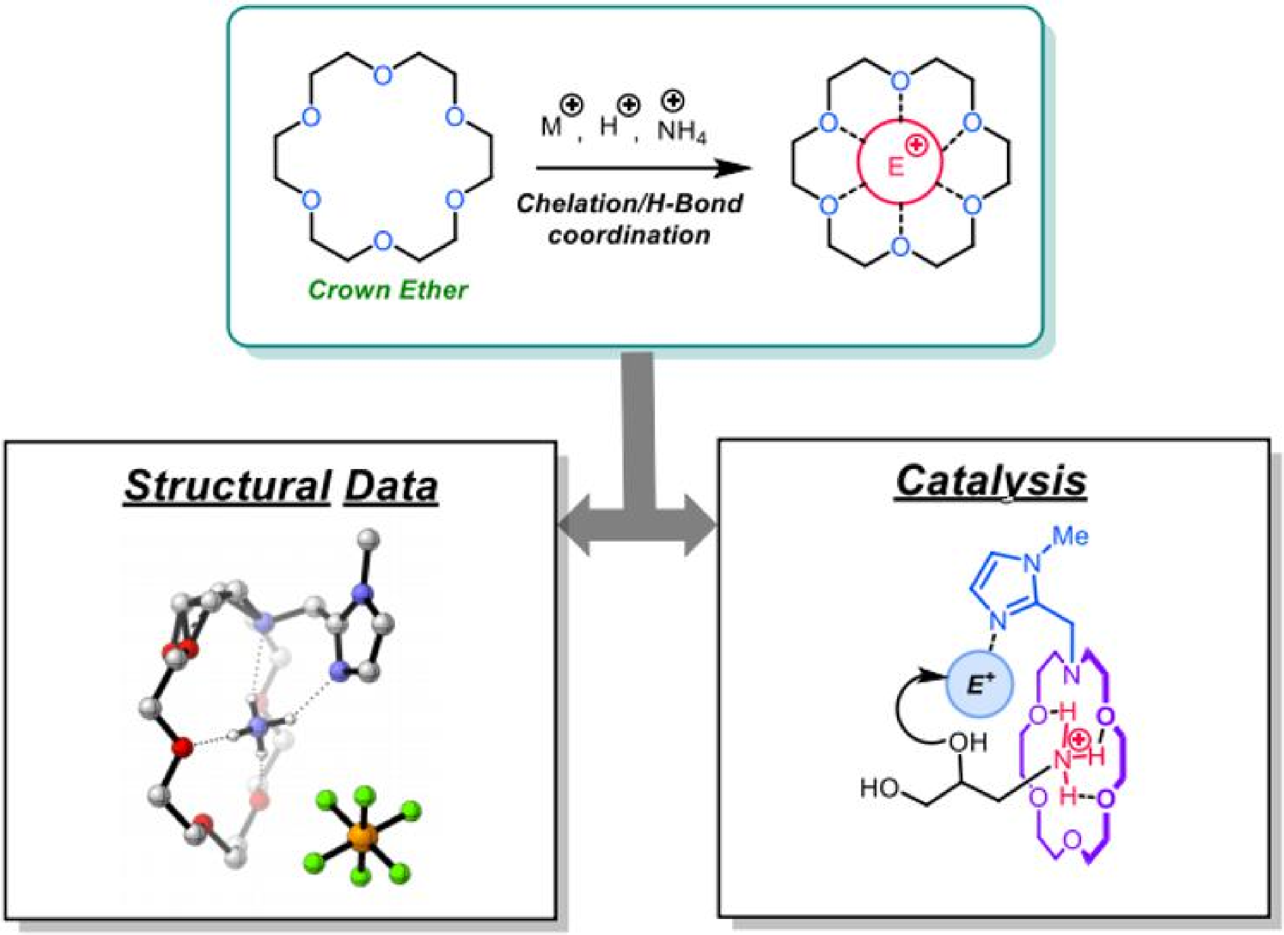
A fully-functional smartphone-based spectrophotometer was designed and built using 3D printing. The major advantage of this approach is its capacity to be interfaced with a variety of smartphones, allowing the use of the smartphone's camera and display, and regardless of the relative position of the camera. The analytical performance of the device was analyzed using a model dye (crystal violet), leading to a proportional response for concentrations in the 0.06–15.0 mg L−1 range, with a variability of 1.0% (intra-day) and 2.6% (inter-day). To demonstrate the functionality of the device, the degradation process of the dye by sodium hypochlorite was studied. The results obtained were applied to develop a paper-based test for NaClO in sanitation solutions, in which the time required to bleach the dye was used to estimate the concentration of the solution. This device represents a simple and inexpensive tool for everyday laboratory use and could address important analytical challenges in low-income communities and features a versatile arrangement, that is compatible with a wide variety of smartphones and software platforms.


O
R
NR2
Ti^III/IV
R
NR2
Nuc
Nuc
R
NR2
H2O
O
R
H

Chemical Catalytic Diversification of Amides

Giovani Gutierrez, Jason Wilt, Byoungmoo Kim*
Department of Chemistry, Clemson University

Due to the ubiquitous presence of amides in peptides and bio-active compounds, our interest is to design a catalyst system that is capable of functionalizing amide motifs in a chemo- and site-selective manner. We have recently explored the potential of titanium and hydrosilane reagents for reductive functionalization of amides to furnish the corresponding enamine derivatives. Based on our preliminary results, we envision the enamine intermediate will provide us a versatile platform to explore a sequential enantioselective functionalization, which will generate a library of chiral scaffolds. Furthermore, we are interested in the development of new catalytic methods which will allow us to convert to amides to other carbonyl derivatives via heteroatom exchange process.


Crown Ether
M⊕, H⊕, NH4⊕
Chelation/H-Bond coordination
E⊕
Structural Data
Catalysis
Me
N
N
E+
OH
HO
O-H
N-H
H
H
O
O
O
O

Non-covalent interactions in crown ethers - A guide for rational catalyst design

Austin Seilkop, Amaechi Odoh, and Byoungmoo Kim*
Department of Chemistry, Clemson University

Non-covalent interactions play many crucial roles in biological processes ranging from nucleobases aggregation, enzyme-substrate interactions, and metabolic pathways. Over the years, efforts have been channeled towards harnessing the potential of non-covalent interactions in the design of synthetic materials that can exhibit desirable properties for molecular recognition application in both pharmaceutical and research settings. One class of molecules that show great potential for non-covalent interactions are crown ethers because they contain several oxygen heteroatoms which are potential strong hydrogen-bond acceptors and good metal ion chelators. Our group is exploiting this coordinating and hydrogen-bond accepting capability of the crown ethers in the design of catalyst libraries that could be useful for both asymmetric and site-selective transformations. By combining crystal structure data and solution studies, we have recently demonstrated that aza-crown ether macrocycles can be decorated with a variety of small organic motifs to create a catalyst library that exhibit defined geometrical orientations and specific binding interactions with both metal ions and ammonium salts.

HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF COBALT TYPE ATACAMITE FAMILY MEMBERS: AN APPROACH TO THEIR GEOMETRICALLY FTRUSTRATED SYSTEM.

Mahsa Foroughian, Colin D. McMillen, Joseph W. Kolis,
Department of Chemistry, Hunter Chemistry Laboratory, Clemson University, Clemson SC, 29634

The growth of high-quality artificial crystals plays an essential role in developing technologies since crystals are necessary for science and technologies such as lasers, semiconductors, and transistors. A wide variety of synthetic techniques are available to chemists for materials discovery. Typically, each new composition's preparation is ultimately achieved by utilizing a unique set of optimized reaction conditions. One method for materials synthesis is the hydrothermal method, which is a way to synthesize high-quality single-crystals of new solid-state compounds.

The synthesis and structural characterization of materials with open-shell transition metals in geometrically frustrated lattices can lead to complex magnetic behavior. The presence of empty d-orbitals in the oxyanion bridging units can also significantly affect the value and sign of the coupling constant. This study investigates the hydrothermal synthesis of cobalt chloride hydroxide (Co2Cl(OH)3) family members known as Atacamite family structural types. These are excellent candidates for research on the effect of frustration in quantum magnets due to Kagome lattices' presence, which are a network of corner-sharing triangles formed from the metal octahedral. Almost all examples of these materials are Cu2+ based. The Co2+ ions in these compounds provide a promising framework to explore exotic ground states such as quantum spin liquid.

These compounds were synthesized hydrothermally in Teflon-lined autoclaves at the low-temperature condition and crystallized in Tuttle-seal autoclave with silver reaction ampoules at mid-temperature conditions. Herein, the synthesis and structural characterization of these compounds will be discussed.

Hydrothermal Synthesis of Rare Earth Ruthenium Pyrochlores and Perovskites

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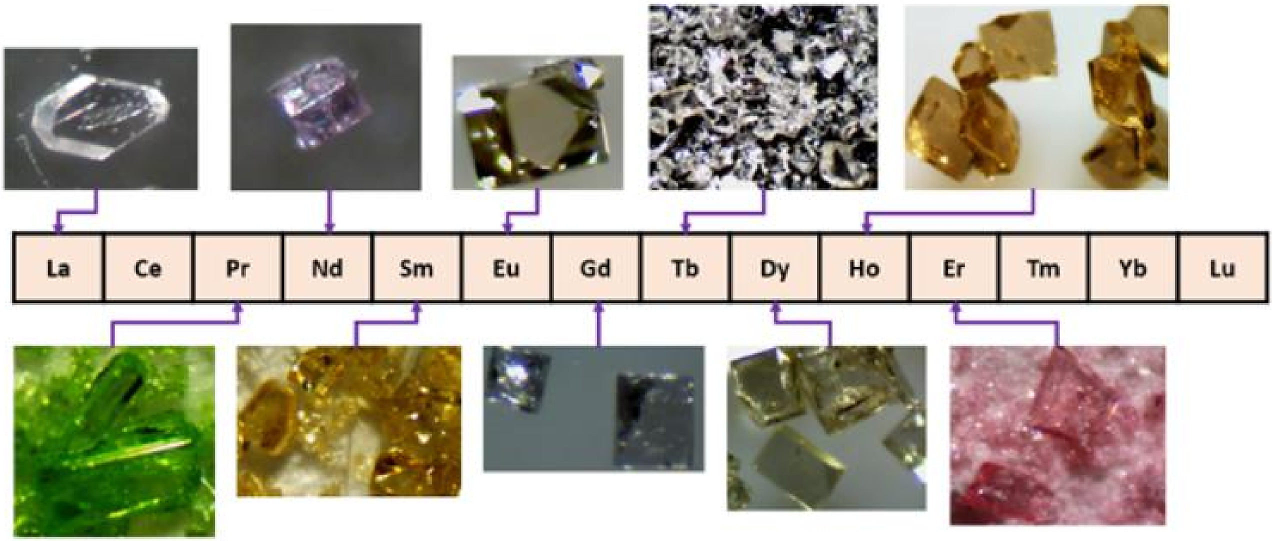
Clemson University

Rare earth ruthenates are highly desired in the solid-state field due to their potential magnetic and electronic properties. For second-row elements, such as ruthenium, the orbital overlap and spin-orbit coupling are comparable in energy, so they have the potential to have very interesting magnetic and spectroscopic properties. Ruthenium can exist in multiple oxidation states so its reaction chemistry can be very extensive. The reactants to be used include rare earth oxides which are very refractory, so many crystal growing methods are not suitable because they cannot easily melt or solubilize the reactants. Instead, we will employ hydrothermal synthesis, which emulates natural mineral-forming conditions, to generate crystalline materials via aqueous solutions at relatively low temperatures (500-700°C) and pressures (1-2 kbar) to access high-quality single crystals from these highly refractory materials. The focus will be on two structural types of the rare earth ruthenates, namely pyrochlores (A2B2O7) and perovskites (ABO3). We were able to synthesize single crystals of rare earth ruthenium pyrochlores and perovskites with no detectable site disorder or lattice defects, which has been shown to be a significant problem in these metal oxides. These compounds include LnRuO3 (Ln= La, Pr, Nd, Sm) and Ln2Ru2O7 (Ln= La, Pr, Nd, Sm-Gd). These compounds were characterized by single-crystal and powder x-ray diffraction which showed interesting structural features such as tilted octahedra, minimal site disorders, and long-range ruthenate chains and layers. Understanding the synthesis and resulting structures enables the measurement of their magnetic and electronic properties and will enable us to obtain neutron scattering data with our collaborators at Oak Ridge National Laboratory.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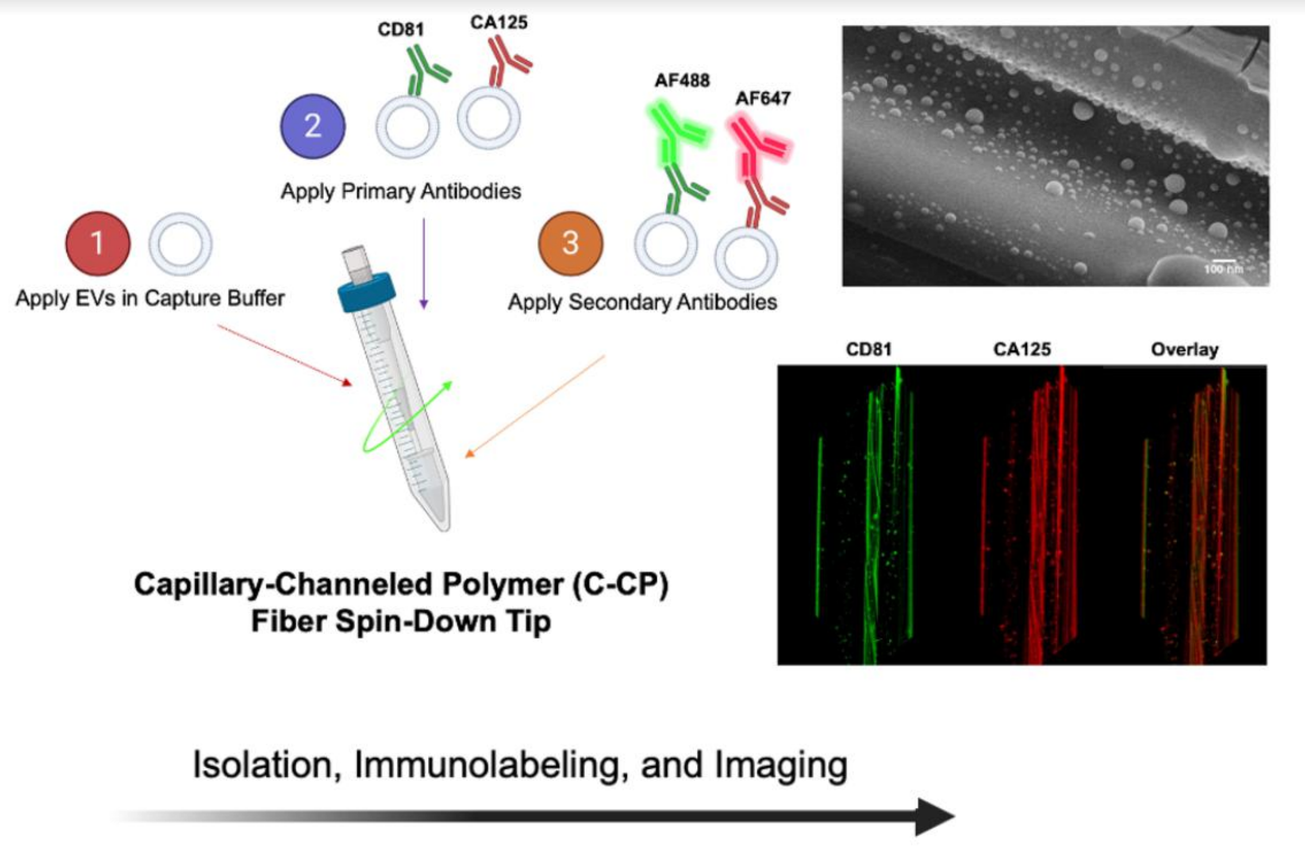
Improved Synthesis of Lanthanide Stannate Pyrochlores (Ln2Sn2O7) and Orthoscandate Perovskites (LnScO3) via Hydrothermal Methods

Matthew S. Powell, C. McMillen, K. Ross, J. Kolis
Clemson University

The lanthanides have garnered increased attention due to their range of electronic spin states and spectroscopic properties that have been theorized to allow for quantum spin liquids and potential high-mobility electron gas substrates. Quantum materials such as those require highly ordered crystalline lattices without defects that could otherwise impact performance. The slower, more controlled growth using hydrothermal fluids allows for high-quality crystals with minimal crystalline defects such as those typically seen in conventional solid state and melt growth techniques. Hydrothermal methods also allow access to crystals containing refractory materials, those with melting points in excess of 2,000℃ and include oxides such as SnO2 and Ln2O3, at temperatures less than a third of what would be required using highly specialized melt-based techniques. Recently, great improvements have been made to the bulk growth of lanthanide stannate pyrochlores (Ln2Sn2O7) for potential use in optical and quantum devices. Single crystals ranging in size from 0.5 to 2 mm of Ln = Ce, Er, and Yb have been grown and selected as quantum materials with ongoing magnetic and neutron diffraction studies to assess the unique spin behavior. Additionally, lanthanide orthoscandate perovskites (LnScO3) crystals ranging from 0.5 to 1 mm have also been successfully synthesized without evidence of lanthanide deficiencies within the lattice as seen in crystals pulled from melts. These potential substrates will serve as the basis for continuing hydrothermal work with Ln perovskites to fine tune the electronic properties of these materials..



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Apply EVs in Capture Buffer
2
CD81
CA125
Apply Primary Antibodies
3
AF488
AF647
Apply Secondary Antibodies
100 nm
CD81
CA125
Overlay
Capillary-Channeled Polymer (C-CP) Fiber Spin-Down Tip
Isolation, Immunolabeling, and Imaging

A Capillary-Channeled Polymer (C-CP) Fiber Spin-Down Tip Approach for the Isolation, Imaging, and Characterization of Extracellular Vesicles from Healthy and Diseased Sources

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There is a high demand for methods to efficiently isolate high concentrations of EVs and virus particles from complex biofluid patient samples for disease detection. Nevertheless, many EV-based approaches are limited by time-consuming isolation methods (> 1 hour), producing low quality and quantity recoveries. With this challenge, much interest lies in the development of novel methods to recover high concentrations of EVs and virus particles with minimal contaminating species (i.e., lipoproteins, protein aggregates). Proposed here is a capillary-channeled polymer (C-CP) fiber spin-down tip approach for the hydrophobicity-based isolation of EVs and virus particles. The polyester (PET) C-CP fiber micropipette tips have been previously employed in the isolation of EVs from complex biological matrices (cell culture media, urine, saliva, plasma, and serum) using a hydrophobic interaction chromatography (HIC) solvent system in a tabletop centrifuge. The C-CP tip workflow preserves the morphology and functionality of EVs, as confirmed by SEM, TEM, NTA, and confocal microscopy upon immunolabeling the fiber-captured vesicles with antibodies to tetraspanin proteins (CD81, CD63). The C-CP tip method allows for highly concentrated EV recoveries (>1E11 particles from 100 μL of serum) to be obtained in less than 10 minutes, with the ability for imaging and immune characterization to be performed directly on the fiber surface. Based on the similarities in size, membrane structure, and cargo type, the HIC-based C-CP tip method was extended to the isolation of SARS-COV-2 virus particles from relevant biofluid matrices (saliva, nasopharyngeal mucus). The proposed C-CP tip method offers a cost-effective (<$10) method to isolate EVs and virus particles from relevant biofluid matrices, potentially enabling clinical assays, fundamental analyses, and large-scale processing of EVs and viruses for therapeutic applications, including drug delivery and gene therapy.

Employing Polypropylene Capillary-Channeled Polymer Fiber Column as the Second Dimension in a Comprehensive Two-dimensional System for Analysis of Complex Macromolecule Mixtures: Proteins and Polymers

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Two-dimensional liquid chromatography (2D-LC) offers a level of tunability (selectivity) in separation that is not achieved in one-dimensional liquid chromatography. The two-dimensional separation is popular for proteins and polymers due to the improved peak capacity and resolution. Fast runs in the second dimension (2D) are a fundamental requirement of comprehensive 2D-LC due to the need for fast re-equilibration and shortened cycling times. The 2D separation is the limiting factor in the total analysis time, relying on both the 2D column kinetics and hydrodynamics, so efforts to shorten the analysis without affecting the resolution have been a major focus.

Polypropylene (PP) capillary-channeled polymer (C-CP) fibers have been studied as a stationary phase in 2D of 2D-LC. C-CP fibers allow for high flow rates and low back-pressure due to their monolithic structure. The self-alignment of the fibers into a multiple, parallel-channeled column, minimizes twisting and crimping, creating the monolithic structure of the column. Large through pores and channels, while having limited intraphase porosity, enable them to perform macromolecule separations at high flow velocities (50-100 mm s-1) and low back pressure while maintaining high mass transport efficiencies (no van Deemter C-terms).

The research presented here demonstrate the use C-CP fibers in the 2D of comprehensive 2D-LC the separation of both proteins (RP x RP) and polymers (SEC x RP). The studies presented here leverage the developments of C-CP fiber stationary phases directed at high throughput and rapid separations as 2D materials in comprehensive 2D-LC. The ability to operate C-CP fiber columns at extremely high throughput without sacrifice in protein resolution is first step towards 2D implementation. What must be realized are fast elution gradients and rapid re-equilibration to minimize cycling times (modulation periods). Thus, different flow rates and gradient programs have been tested to assess the potential benefits of C-CP fiber, and directly comparing them to commercial columns. Here, high shear rates and shorter column residence times allow elution in shorter gradient windows. Very importantly, at the shortest possible gradient recycling time on this instrument, 30s, there is no significant degradation in peak capacity. Finally, a comparison of separation efficiency, recovery and reproducibility between seven commercial RP columns and the PP fiber column is presented for a standard, eleven protein mixture and a model polymer mixture solution, using optimal operating conditions for each column type.

Evaluation of Exosome Loading Characteristics in their Purification by HIC Method on a Polyester, C-CP Fiber Phase

Sisi Huang, Lei Wang, Terri F. Bruce and R. Kenneth Marcus

Exosomes are membrane-secreted vesicles, with sizes ranging from 30 - to - 150 nm, which play a key role in intercellular communication. There is intense interest in developing methods to isolate and quantify exosomes towards clinical diagnostics and fundamental studies of intercellular processes. Current methods for exosomes isolation and quantification are time consuming and have operational high costs; few combine isolation and quantification into a singular operation unit. This report describes the use of hydrophobic interaction chromatography (HIC) process on a polyester capillary-channeled polymer fiber (C-CP) chromatography column, employing a step-gradient for exosome elution, including use of glycerol as a solvent modifier. The entire procedure is completed in 8 minutes, while maintaining the structural integrity and biological activity of the isolated exosomes. Electron microscopy was used to verify the size and structural fidelity of single exosomes. Absorbance response curves for a commercial exosome sample were used for exosome quantification in the chromatographic separations. In order to determine the dynamic loading capacity for exosomes, different volumes of D. discoideum cell culture milieu supernatant was loaded at different column lengths (5 - 30 cm) and loading flow rates (0.2 - 0.5 mL min-1). A loading capacity of 5.4E12 exosomes derived from D. discoideum milieu was obtained on a 0.8 x 300 mm column, while yielding recoveries of over 80%. It is believed that this isolation and purification strategy holds many advantages towards the use of exosomes across a wide breadth of medicine and biotechnology.

Isolation, Quantification, and Evaluation of Extracellular Vesicles via a Hydrophobic Interaction Chromatography Method on Polyester Capillary-Channeled Polymer Fiber Phase

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Extracellular vesicles (EVs), which include exosomes and microvesicles, are micro-sized vesicles that deliver biological information from the cell of origin to target cells. Recently, the isolation, quantification, and classification of extracellular vesicles in clinical settings have become of increased interest due to the upsurge in evidence showing tumor cells secrete more extracellular vesicles than normal cells. Current techniques for extracellular vesicle isolation and quantification are time-consuming, expensive, and rarely combine the two methods into one. The aim of this study was to develop an efficient, rapid, and low-cost isolation and quantification method for extracellular vesicles in urine samples based on hydrophobic interaction chromatography (HIC) on capillary-channeled polymer (C-CP) fiber columns. Additionally, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the isolated extracellular vesicles were obtained, providing further evidence to the efficiency of the combined method described.

Metal Analysis in Cell Culture Media via Liquid Sampling – Atmospheric Pressure Glow Discharge Compact Mass Spectrometry

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Described herein is the preliminary evaluation of the liquid sampling – atmospheric pressure glow discharge (LS-APGD) ionization source paired with an Advion ExpressionL compact mass spectrometer (CMS) directed at the analysis of trace metals in cell culture media. A two-step design of experiment (DoE) parameterization approach was used to identify the optimal plasma operating conditions of the LS-APGD when coupled to the CMS. A comparison of the analytical performance pre- and post-DoE was performed, with the post-DoE conditions delivering improved performance for all target metrics. The analytical performance of metals relevant to cell culture media analysis (Cu, Co, and Zn) was evaluated, and limits of detection (LODs) of less than 1 μg mL-1 were obtained, readily meeting the targets for this specific application. Response curves of the test metals in the native cell culture media were generated, but only Cu was quantitatively recovered due to high spectral backgrounds. An on-line separation step was employed to remove organic components from the matrix to decrease spectral matrix effects in an effort to improve spike recoveries and overall analytical performance. The separation was effective at retaining organics from the matrix before introduction to the microplasma, resulting in metal recoveries >70%. Metals were present at concentrations below the LOD of the LS-APGD in the basal media formulation, but the concentrations calculated for the feed media formulation were in acceptable agreement (<27% difference) with ICP-OES. Overall, the methodology presents a practical approach to this specific target application of simplified metals determinations that can be affected in biotherapeutic production environments.

Roles of Collisional Dissociation Modalities on Spectral Composition and Isotope Ratio Measurement Performance of the Liquid Sampling – Atmospheric Pressure Glow Discharge / Orbitrap Mass Spectrometer Coupling

Tyler J. Williams, Edward D. Hoegg, Jacob R. Bills, R. Kenneth Marcus

Coupling of the liquid sampling – atmospheric pressure glow discharge (LS-APGD) ionization source with Orbitrap mass spectrometers has demonstrated tremendous success in regards to isotope ratio (IR) measurements. Isotope ratios from a wide variety of analytes have been measured, with a primary focus on the 235U/238U measurement, yielding IR measurement accuracy and precision that meets international targets. Orbitrap mass spectrometers are not commonly associated with either elemental analysis or isotope ratio measurements. Understanding sources of IR errors and imprecision which arise from both the LS-APGD ionization source and the Orbitrap system itself can assist with enhancing measurement figures of merit. Because a variety of solvent-related species are generated in the LS-APGD, the preponderance of those species in the orbitrap analyzer affects the recoveries and IR qualities for target analytes. In this work, the effects of the collisional dissociation of solvent-related species are investigated as a source of variability in IR measurements. Additionally, the quadrupole band-pass filter used in the ThermoScientific Q Exactive Focus is investigated for its transmission properties along with the effects of the transmission window on IR accuracy and precision. With these considerations, updated IR measurements are presented for a few analytes, with measurement precision never exceeding 0.71% RSD, and going down to a level of 0.05% for diverse species. It is expected that these considerations will inform how IR measurements should be taken on this platform, with lessons that may be applicable to other instruments.

The Simultaneous Analysis of Inorganic and Organic Arsenic Species Utilizing the Liquid Sampling - Atmospheric Pressure Glow Discharge Ionization Source (LS-APGD)

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The LS-APGD has been previously described as an ionization source capable of combined atomic and molecular analytes. Thus far, limited work has been done to couple the LS-APGD to an HPLC for online speciation analysis. The analysis of arsenic species and speciation qualities often employs ICP- MS, which dissociates all arsenic species to elemental arsenic and necessitates HPLC for speciation information. There is much interest in the determination of arsenic speciation since arsenic toxicity is very dependent on the speciation, with inorganic arsenic being the most toxic. Anion exchange chromatography was utilized for the separation of arsenic species in this study. One problem with ICP is the lack of structural information obtained by ICP-MS due to excessive heat breaking all bonds. This work focuses on the coupling of a Thermo Scientific TSQ Quantum Access MAX with a Thermo Finnigan Surveyor, utilizing the LS-APGD as the ionization source. The LS-APGD has previously been coupled to the TSQ Quantum Access MAX for direct analysis of atomic species with a 2% nitric acid solution and molecular species with a 70/30 MeOH/H2O. This work utilized the LS-APGD coupling for the simultaneous detection of inorganic and organic arsenic species in 2% nitric acid, while still obtaining structural information of each species that is lacking by HPLC-ICP-MS. This HPLC-MS system was able to obtain detection limits of 27 to 31 ng mL-1 when operating in SIM mode and 9-11 ng mL-1 when operating in SRM mode for the three arsenic species (tens of pg absolute). A commercially available bladderwrack sample was tested using the HPLC-MS system which comprised of 0.63 µg mL-1 total arsenic, with the majority (0.53 µg mL-1) of arsenite (inorganic As(III)) and the remainder (0.10 µg mL-1) of dimethyl arsenic acid suggesting that the majority of the total arsenic concentration is the most toxic form of arsenic. This was validated by ICP-OES of the bladderwrack which gave 0.67 µg mL-1 of total arsenic. There was a good correlation between the HPLC-LS-APGD-MS method and the ICP-OES method (~5% difference)

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There is considerable interest in obtaining a deeper understanding of the relationship between nanoscale structure and charge transport properties of conjugated polymer nanoparticles (CPNs). Time-of-flight, voltage–current studies and recently, femtosecond pump-push spectroscopy have provided some understanding of the early steps of charge separation and charge-transport in CPNs, however the information is an average over large areas and many charge carriers. As such, questions remain regarding how local heterogeneity and the associated nanoscale energy landscape dictate the time and length scales of carrier motion, as well as the relationship between structure and carrier motion in conjugated polymers. In this research work, we took advantage of a unique super resolution imaging technique to track single charge carriers in CPNs and further developed a novel method to map the nanoscale energy landscape for single charge carrier transport in CPNs based on simultaneous, correlated super-resolution charge carrier tracking and single-particle fluorescence spectroscopy.

Improved Super resolution Imaging Using Telegraph Noise in Organic Semiconductor Nanoparticles

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Small semiconductor structures often exhibit "telegraph noise". If the number of charge carriers is small, then spontaneous changes in the number of carriers can lead to abrupt switching between two or more discrete levels, leading to burst noise or popcorn noise in transistors. We have observed similar behavior in the fluorescence of organic semiconductor nanoparticles, where typical carrier populations are often less than ~10 carriers per nanoparticle. Spontaneous changes in the number of charges results in abrupt switching between 2 or more fluorescence intensity levels, because the charges act as highly efficient fluorescence quenchers. The equilibrium number of charges is determined by competition between a photo driven ionization process and spontaneous recombination. Doping with redox-active molecules also affects the balance. Nanoparticles of the conjugated polymer PFBT doped with the fullerene derivative PCBM, rapidly establish a fluctuating steady-state population of tens of hole polaron charge carriers, sufficient to nearly completely suppress nanoparticle fluorescence. However, fluctuations in the number of charges lead to occasional bursts of fluorescence. This spontaneous photo switching phenomenon can be exploited for super resolution imaging. The repeated, spontaneous generation of short, intense bursts of fluorescence photons results in a localization precision of ~0.6 nm, about 4 times better than typical resolution obtained by localization of dye molecules.

Crystal Engineering: Investigating Organic Transformations via Halogen and Chalcogen Bonding

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b Department of Chemistry & Chemistry Research Center, Laboratories for Advanced Materials
United States Air Force Academy, Colorado Springs, CO 80840

Due to an anisotropic distribution of electrostatic potential, which is maximized for heavier atoms, halogen and chalcogen bonding can be powerful influences in the packing of crystalline materials. In an effort to utilize these interactions to probe organic transformations, diiodotetrafluoro- and trifluorotriiodobenzenes were added to the aerobic oxidation of methyl hydrazines. These oxidations revealed the oxidation products sym-hexahydro-1,4-dimethyltetrazine (from methylhydrazine) or tetramethylammonium iodide (from 1,1-dimethylhydrazine). Additionally, oxidation of the biologically relevant organic substrate phenothiazine in a variety of solvents allowed the isolation of this radical cation, in both solvated and unsolvated forms, and for the first time to be studied by single-crystal X-ray diffraction, it's dimer, 10-(3-phenothiazinylidene)phenothiazinium. A wide variety of chalcogen and halogen bonding interactions stabilize these species.

Effects of Ionic Clusters on Dynamics of Sulfonated Polystyrene Blends: Computational Insight

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Gary Grest
Sandia National Laboratories, Albuquerque, NM

Blends of ionizable polymers have an immense potential to enhance a broad range of technologies from clean energy to water purification and biotechnology, where their structure and dynamics determine their function. Cast from common solvents, blends of ionic and non-nonionic polymers could be formed. Their phase structure and stability however are unknown. In contrast to blends of non-charged polymers, these materials are constrained by ionic clusters, affecting their time and temperature evolution. Here we follow the formation of ionic-non-ionic interfaces in blends of short 20-mers of polystyrene (PS) and polystyrene sulfonates (SPS) using molecular dynamics simulations with the overarching goal of resolving the effects of ionic clusters on their phase behavior and dynamics. Blends of 1:1 made by merging dilute implicit solvent solutions and compressing the systems to melt densities were followed for times up to 1000 ns. The static and dynamic structure factors were extracted and correlated with the distribution of ionic clusters. We find that for these low Mw and low sulfonation the polymers are fully miscible. Even though small clusters are formed and slow the motion of the molecules, both the PS and SPS chains remain dynamic.

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Effects of Solvent Polarity on Segmental Dynamics in Slightly Sulfonated Polystyrene Ionomers: Quasi Elastic Neutron Scattering Study

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Incorporating ionic groups into a polymer changes dynamics in a significant way. These ionic groups serve as cross links and form clusters which unlocks different pathways. Here, the effects of solvent dielectrics on segmental dynamics of slightly sulfonated (3mol%) polystyrene (PSS) networks formed in non-polar environment were studied by quasi elastic neutron scattering (QENS) technique. Solvent dielectrics were tuned by addition of ethanol to 10%(w/w) PSS in cyclohexane. QENS experiment was carried out for q range 0.3 Å-1 to 1.3 Å-1 which captures the dynamics of 21 Å–5 Å in length scale. QENS scattering patterns were analyzed by Kohlrausch-Williams-Watts (KWW) to extract characteristic relaxation times. We find that PSS dynamics in cyclohexane is constrained at larger dimensions. Addition of small amount of ethanol (5% v/v) release the constrains. Surprisingly however, further addition of ethanol decreases segmental motion. This reduction could be attributed to overall plasticization of the polymer in presence of ethanol.

Solvent Dielectrics as a Key to Unlocking-Locking Ionic Clusters in Ionomers

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A small number of ionic groups on a polymer back bone strongly affect structure and dynamics of macromolecules. Understanding the effects of these ionic groups on properties of polymers is imperative to designing polymers for targeted applications. Here the structure and dynamics of slightly sulfonated polystyrene (PSS) as observed by molecular dynamics simulations (MD) and neutron spin echo studies are presented. Dynamic behavior is probed from bond dimensions to that of an assembly of chain in solutions on a time scale of 1-100ns. Measurements were carried out in toluene, hydrophobic solvent, and dielectrics were increased by addition of ethanol. We find that with increasing dielectrics cluster size decreases and concurrently the dynamics increase.

Electrically Conducting Double-Helical Metal–Organic Framework Featuring Butterfly-Shaped π-Extended Tetrathiafulvalene Ligand

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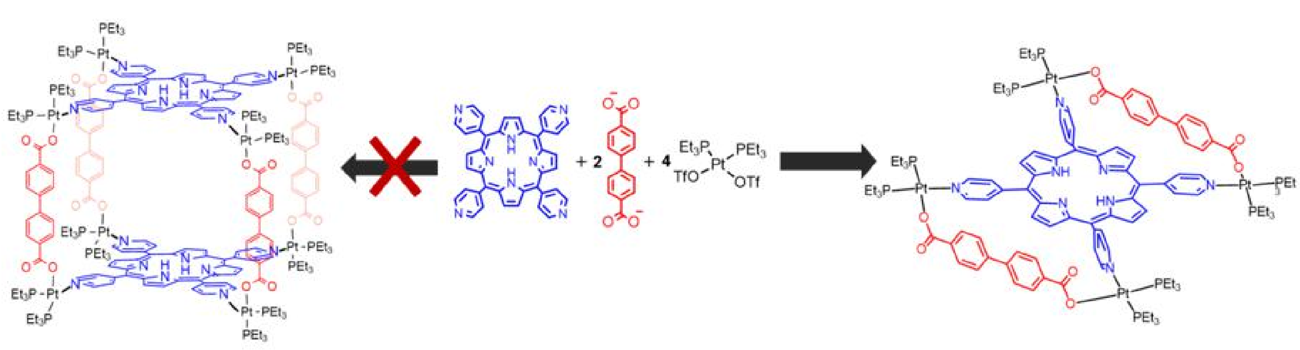
In order to diversify metal–organic framework (MOF) structures beyond traditional Euclidean geometries and to create new charge delocalization pathways beneficial for electrical conductivity, we prepared a novel double-helical MOF (dhMOF) by introducing a new butterfly-shaped electron-rich π-extended tetrathiafulvalene bearing four benzoate groups (ExTTFTB). The dhMOF formed ovoid cavities suitable for guest encapsulation and exhibited π–π-interaction between the ExTTFTB ligands of neighboring strands. Iodine vapor diffusion led to oxidation of half of the ExTTFTB ligands in each double helix to ExTTFTB•+ radical cations, which presumptively formed intermolecular ExTTFTB/ExTTFTB•+ π-donor/acceptor charge-transfer chains with neutral ExTTFTB ligands of an adjacent strand, creating new delocalization pathways along the helix seams. As a result, the electrical conductivity of dhMOF increased from 10−8 S/m up to 10−4 S/m range after iodine doping. Thus, by introducing a new electroactive ligand with a unique shape and unveiling a new charge transport pathway beneficial for electrical conductivity, this work holds promise for the synthesis of new ExTTF-based MOFs with unique structures, properties, and functions.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PEt3
TfO
Pt
OTf

Heteroleptic coordination-driven self-assembly of planartricomponent supramolecular coordination complexes

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The use of cis-capped Pt (II) has shown to promote the heteroleptic coordination of carboxylate and pyridyl ligands, although recent studies claimed the possibility of self-assemble thermodynamic stable metal organic cages when (Et 3 P) 2 Pt(II) is reacted with tetrapyridylporphyrin (TPyP) and dicarboxilate ligands, careful crystallographic and NMR (1 H, COSY, ROESY) spectroscopic studies in our laboratory unequivocally demonstrated that in reality, these three components actually self-assembled into 2D panels via preferential intramolecular bridging of two adjacent Pt-coordinated pyridyl terminals by linear dicarboxylate ligands instead of forming the proposed 3D cages. Furthermore, computational studies showed that this behavior was directed by the restricted dihedral angle of the pyridyl group in the porphyrin which determines the orientation of the complementary carboxylate ligand.

Stronger than Cement: Simultaneous Utilization of Anthropogenic Waste Products and Reduction of Environmentally Deleterious Cementitious Materials

Moira K. Lauer
Advisor: Prof. Rhett C. Smith
Clemson University

Modern societal infrastructure relies heavily on Portland cement—a seemingly cheap solution to a widespread necessity but with a high environmental price. Portland cement is comprised of hydrated calcium and magnesium oxides mixed with a small amount of gypsum (~2–3%) and it is estimated that its production accounts for 8% of anthropogenic CO2 production as the transformation from mined calcium and magnesium carbonates to their respective oxides necessarily produces stoichiometric quantities of CO2 and requires temperatures in excess of 1400 °C. It is additionally estimated that the production of Portland cement is responsible for 30% of global materials utilization. Currently, new formulations are being explored to reduce CO2 production but still require massive amounts of resources while producing a completely non-recyclable material with a limited operational lifetime. An alternative proposed by our group involves the synthesis of composite materials at comparatively low temperatures (~180 °C) utilizing low-value waste products already generated by energy and agriculture sectors. This is accomplished through the facile modification of various biopolymers or raw biomass and their subsequent reaction with thermally-generated radical sulfur catenates thereby forming a crosslinked composite material. Materials prepared in this fashion by our group have been found to have strength properties on par or better than Portland cement while also retaining those strength characteristics over several reprocessing cycles. The work towards this end focusing on waste sulfur produced by energy sectors and biomass produced by agriculture will be discussed including material synthesis, characterization, and mechanical properties.

Designing New Functional Materials for Microelectronic Applications

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The advancement of information technology has expanded the need for high-density data storage devices that operate with a low electric current. Spin-based electronics, where data transmission is via electron spin rather than the charge, are at the forefront of information science with potential applications in data processing and quantum computing.1,2 This is because the extra degrees of freedom of the electron spin increases the number of permutations of the energy states.3 Quantum magnets such as magnetic skyrmions and quantum spin liquids are actively researched as the future of microelectronic technology,1,2 however, the design of these quantum materials is challenging because of the difficulty to control both the crystal structure, atomic arrangement, and electronic states of the frontier orbitals in a single system.

Magnetic skyrmions - topologically distinct spin textures - are induced by asymmetric exchange interaction between magnetic spins facilitated by spin-orbit coupling.2 In quantum spin liquids, there is an absence of magnetic ordering, and this results from strong magnetic exchange between neighboring spins interacting antiferromagnetically in a geometrically frustrated lattice.1 In this symposium, we will be discussing our chemical design strategies for designing these two sets of materials. We utilized low temperature chemistry such as hydrothermal and flux-growth methods to synthesize functional materials. Structural characterization was performed using single crystal, powder, and high-resolution synchrotron X-ray diffraction. The magnetic structure and magnetic properties of our materials were investigated by performing neutron diffraction, magnetization, and heat capacity measurements. Density functional theory calculations were also performed to gain better insights into chemical bonding and exchange interaction in these compounds. The results and knowledge gained from this work will be discussed.4

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Assessment of The Physicochemical and Bacteriological Properties in Polyethene Packaged Sachet Water Generally Known As “Pure Water” Produced And Sold In Sagamu Local Government Area Of Ogun State, South West, Nigeria

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This present study was undertaken to study the assessment of the physicochemical and bacteriological properties in polyethene packaged sachet water generally known as “pure water” produced and sold in Sagamu local government area of Ogun state, South West, Nigeria. In this research, polyethene packaged sachet water from various producers, sources and distributors were analysed for its physicochemical and microbiological characteristics. Samples were collected randomly from six (6) different locations/towns in Sagamu Local Government. The samples were analysed for its physicochemical and bacteriological parameters. The results of the analyses were compared with the permissible limit set by WHO, EPA, Canada, and NIS. It was found that most of the parameters were in the expected range of the permissible limits set by WHO, EPA, Canada, and NIS. However, the pH 4.73 – 6.10 of the sachet water samples tends to be acidic below the expected range 6.5 – 10.5. The Total Heterotrophic Bacteria count and Enteric Bacteria count tends to be a little lower below the permissible limits. Total Enteric Bacteria 300 – 480cfu/100ml with permissible limits of Bacteria 280 – 380cfu/100ml. It was recommended that water producing industries should site their raw water site in a safe location free from contamination, the government should involve the participation of equipped private and government hospitals with good laboratory to monitor and report accordingly the situation of all water packaging industries in their vicinity, the government should also involve the participation of genuine and reputable individuals to produce and provide paid pipe borne waters to people in their community and regulatory bodies such as SON and NAFDAC should take responsibility by continually re-assessing the production and packaging quality of drinking water in every community.

Key Words: Sachet Polyethene Water, Sagamu, Drinking Water, Enteric Bacteria Count, Total Heterotrophic Bacteria Count, Bacteriological, Heterotrophic plate count

Cloning of Candidate Stress Response Genes from Paspalum vaginatum

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Abiotic stress, such as high salinity, has a negative effect on the ability of crops to grow and take in water. It is estimated that at least 20% of the world's cultivated land is impaired by salinity, with more and more viable land lost each year due to changing environments. Plants that grow in tropical and coastal regions, such as seashore paspalum (Paspalum vaginatum), are very salt tolerant. The purpose of this study is to clone seashore paspalum candidate genes potentially involved in plant salt stress response and study their function in transgenic plants so that they can be used in crop species for enhanced salt tolerance. We have chosen five genes that exhibited high differential expression between normal and stressful conditions, with the m.11 being successfully cloned. PCR, gel electrophoresis, bacterial transformation, colony and RACE PCR were some of the techniques used during the experiment. After sequencing and a BLAST search, the m.11 gene has been related to the WRKY genes family, known to be involved in abiotic stress response. If transgenic plants overexpressing m.11 begin to demonstrate increased tolerance to salt, then it is clear that the m.11 gene is indeed involved in plant response to abiotic stress. Introducing a gene that increases plant resilience would allow a more diverse set of growth environments for crop production
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Gene Specific Predictability of Protein Levels in mRNA Levels in Humans

Ben Usry

The extent to which transcriptomic abundance can be predictive of protein abundance remains debated. The central dogma of molecular biology would presume a strong correlation between transcript and protein levels, but various regulatory mechanisms within the cell often make these predictions more complex. We propose a robust multi-model, gene-specific method of predictability that sorts genes into one of three categories based on the relationship between their transcript and protein abundance. In order to sort genes, we used the mean fraction squared error (MFSE) between observed protein levels and predicted protein levels as a way to pick which model is best for a given gene. For the majority of genes, protein levels remain relatively constant across tissues despite changes in mRNA levels. For other genes, these protein levels vary with mRNA levels in a relatively linear manner as presumed by the central dogma. Finally, some genes have protein levels that vary uniquely for that gene, primarily due to expression in only a small number of tissues. We hypothesize that by sorting genes into the model that best describes this measured relationship, we will be able to reveal novel insights into the biological origins of protein predictability while also studying the regulatory dysfunction present in cancer cell lines.


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