PREM

12TH ANNUAL MEETING

Partnership for Research and Education in Materials (PREM)

University of Puerto Rico at Humacao

November 20TH, 2015

Wyndham Garden at Palmas del Mar

AGENDA

9:15 AM **Registration** and **Breakfast**

10:00 AM **Working Groups**

Room A: IRG 1, "Multifunctional Nanodevices from Optoelectronic Materials"

Room B: IRG 2, "Nanoscale Interactions of Macromolecules at Soft and Hard Interfaces"

Room C: "PREM Education and Outreach Group"

12:30 PM **Working Lunch**

1:45 PM **Group Photo**

2:00 PM **Welcome Messages**

Idalia **Ramos**, Program Director
Efraín Vázquez, UPR Humacao Chancellor
Arjun **Yodh**, PREM Co-PI and Director of PENN MRSEC

2:10 PM **Presentation of Participants** and **Organization of the New PREM**

Idalia **Ramos**, Program Director
Andrew **McGhie**, Associate Director PENN MRSEC

2:20 PM **IRG's** and **Education Group Reports**

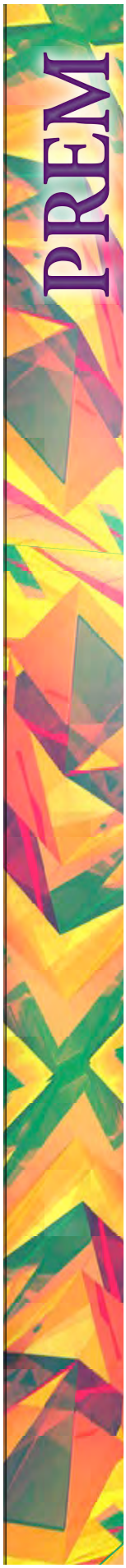
2:20 PM **IRG 1:** Idalia **Ramos** and Nicholas **Pinto**
2:40 PM **IRG 2:** Rolando **Oyola** and José **Sotero**
3:00 PM **Education:** Gilda **Jiménez** and Melissa **López**

3:20 PM **Coffee Break** and **Poster Setup**

3:30 PM **Student Poster Presentations**

5:00 PM **Advisory Committee meets to write report**

5:30 PM **Closing**



Poster Presentations

P1: Characteristics of P_3HT Modified with Lithium Aluminum Hydride

Authors: Manuel Mangual, Ezio **Fasoli**, and Josee **Vedrine**

Affiliation: *University of Puerto Rico at Humacao*

Our research is focus on the study of P_3HT organic polymer, and its modification to understand its absorption characteristics and potential use for improving their stability. Such modification gives the polymer more flexibility, which leads to reducing the oxidation, and improving the lifetime. To realize this research, we used poly (3-hexylthiophene), P_3HT polymeric films modified with lithium aluminum hydride (LAH) with the aim to partially reduce the double bonds in thiophene ring. The modification of the LAH improves the electrical properties of the polymer and also the chemical stability. The chemical modification was conducted as a technique to functionalize P_3HT with LAH, and the procedure was done inside a nitrogen atmosphere in order to prevent the oxidation and contamination of the polymer. We prepare two samples, one of P_3HT only, and one of P_3HT with the modification of the LAH. When having both of the samples we study the absorption of the polymer by ultra violet-visible spectroscopy (UV-VIS) and X-Ray Diffraction (XRD) techniques. The UV-VIS spectroscopy analysis showed that P_3HT sample without LAH modification had a higher absorption than P_3HT modified with LAH. The P_3HT exhibited the three inherent peaks at 520 nm, 550 nm, and 620 nm, while, the P_3HT-LAH showed presented peaks with a broadening of the shoulder at ~ 620 nm. On the XRD analysis revealed peaks at 5º (2ϑ) for both the P_3HT and the P_3HT-LAH. The peak of the P_3HT was more pronounced than the peak of the P_3HT-LAH, which confirms the degree of crystallinity for the P_3HT polymer and the P_3HT-LAH. After LAH modification, there's increase flexibility in the polymer chain reducing the overall crystallinity of the polymer.

P2: Cellulose Nanocrystal Model for Molecular Dynamics Simulations

Authors: Jordan Caraballo and José **Sotero**

Affiliation: *University of Puerto Rico at Humacao*

Cellulose is considered to be the most abundant polymer on Earth. Cellulose nanomaterials are renewable, sustainable and biodegradable materials derived primarily from abundant softwood pulp. The long range goal of this work is to study the interaction forces between the cellulose nanocrystals for different packing patterns, the interface between nanocrystals and other materials such as polymers, and the interaction between PABA functionalized crystals and selected proteins. These combinations offer novel alternatives for applications to fiber mats filters.

We constructed a cellulose nanocrystal model for classical molecular dynamics simulations to set the basis for those simulations. A cellulose polymer editor and a cellulose nanocrystal builder was added to Wolffia's Graphical User Interface (GUI). *Wolffia* is an open source program developed by our Computational Group at UPRH, which lets the user set-up, run, monitor, and visualize molecular dynamics simulations. Force fields were implemented and adapted to CHARMM from literature. Surface wetting properties play an important role in the packing interaction between cellulose nanocrystals in mats and between nanocrystals and other molecules. Surface tension of a water droplet on (100), (010) and (110) surfaces were measured by simulating the dynamics of a water droplet close to the three surfaces. Contact angles were computed and plotted as a function of time. At the end of a 10 ns period contact angles were 44, 67 and 65 degrees respectively.

P3: Determination of Ligand Density in Affinity Membranes for the Purification of Plasminogen Activators

Authors: Christian Ortiz[1] , Héctor Torres[2], Junellie Cruz[1], Zurisadai Rivera[1], Mayveliz Ríos[1], Verónica Forbes[2], Vibha **Bansal**[2] and Ezio **Fasoli**[1]

Affiliations: *[1]University of Puerto Rico at Humacao , [2]University of Puerto Rico at Cayey*

Separation and purification of therapeutic proteins from complex mixtures such as cell culture broth is a challenging task due to the high operating costs of chromatography systems. Development of an effective affinity membrane-based isolation process is viable alternative and is being pursued in this project. Regenerated cellulose (RC) membranes were purchased from a commercial supplier and chemically modified with epichlorohydrin leading to the introduction of a 5-atoms long spacer arm (linker) on the membranes. The spacer arm end group was further reacted with para-amino benzamidine (PABA), an affinity ligand selective for our target protein, plasminogen activators (Pas). PAs are serine proteases used in the treatment of thrombovascular disorders. The optimization of the chemical modification process of the RC membrane required treating the membranes with different concentrations of the spacer arm and ligand for different time periods. Confirmation of chemical modification was performed by FTIR, while an estimation of ligand density on membrane surface was performed using modification of the Glyoxal method. The membranes were then used successfully to capture the PAs from cell culture broth. To develop a better understanding of this separation method, membranes are being now synthesized by electrospinning to obtain different pore sizes. The effect of pore size on the protein binding capacity will then be studied.

P4: Direct Measurement of the Tryptophan-Mediated Photocleavage Kinetics of a Protein Disulfide Bond

Authors: Rachel M. Abaskharon and Feng **Gai**

Affiliation: *University of Pennsylvania*

The effect of UV radiation on protein structure and function has been an area of active research for over a century. Although UV light has been shown necessary for vitamin D generation in the cell as well as a useful tool in the treatment of various skin ailments, it can also lead to suppression of enzymatic activity as well as various diseases such as skin cancer and cataract formation. Much of this photodamage is due to aromatic amino acid absorption of UV light leading to disulfide bond cleavage and thus a structural change in the involved protein. This reduction is the result of the disulfide bond either interacting with the solvated electrons generated by the excited tryptophan residues or quenching the tryptophan triplet state. While a number of studies have been dedicated to gaining an equilibrium picture of this phenomenon, few have been able to look at the kinetics of such a reaction in a protein system. In this study, we use the $Z_{34}C$ peptide as a model system to directly measure the breakage of the terminal disulfide bond after irradiation of the nearby tryptophan residues with 266 nm light.

P5: Dynamics of a Three Molecule Array with an Area Restriction

Authors: Josean Velázquez and Pablo **Negrón**

Affiliation: *University of Puerto Rico at Humacao*

We study the problem of cavity formation in finite molecular arrays using a molecular dynamics model. We consider the theoretical scenario of three particles subjected to the constraint of fixed area for the molecular array. The corresponding static problem have been studied by Negrón-Marrero and López-Serrano (2015) where it is shown that there exists a critical area such that if the area of the array is smaller than this critical value, the stable configuration of the array corresponds to an equilateral triangle. However, if the area of the triangle is bigger than the critical area, the stable configuration of the array is not a symmetric one, thus signaling the initiation of cavitation. In this project we study the corresponding dynamical problem which mathematically is given by a dynamical system over certain manifold determined by the area constraint. For this dynamical system we study numerically its dynamical equilibrium and conditions for the existence of closed orbits.

P6: Effect of Motor Rotational Velocity on the Alignment of Cellulose Acetate Fibers

Authors: Jorge L. Berríos and Víctor **Pantojas**

Affiliation: *University of Puerto Rico at Cayey*

Cellulose constitutes the most abundant renewable polymer resource available today and has been used for centuries in the form of fibers or derivatives for a wide range of products. In the form of fiber mats, cellulose has been modified with ligands to be used as an affinity membrane for the separation of biological active proteins. The binding capacity of the membrane is expected to depend on the surface ligand density, length of the ligand spacer arm, available surface area and the size of the membrane pores. In this work, the size of the pores, formed by the spaces between fibers, will be controlled with the alignment of the fibers produced by electrospinning, a novel process used for the forming of polymer fibers with micro/nano diameters, in which the viscosity of the solution is the main factor that control the fiber diameter. This method is based on the action generated from the electrostatic forces under a polymeric solution jet (in this case, cellulose acetate) generating its deformation until submicron scale diameters and solidification over the metallic collector. Fibers alignment is obtained by depositing on a rotating drum which is computer-controlled. The rotation of the drum will be adjusted at different velocities and the degree of alignment will be characterized by scanning electron microscopy (SEM). Once the expected alignment is obtained, the sample will be manipulated so that consecutive depositions can produce regular-shaped pores with a narrow size distribution.

P7: Electrical Characterization of Reduced Carbon Spheres/PEO

Authors: César Nieves[1], Joshua Robles[2], Nicholas **Pinto**[1] and Idalia **Ramos**[1]

Affiliations: *[1]University of Puerto Rico at Humacao, [2]University of South Florida*

Carbon spheres (CS) were synthesized by hydrothermal method using a 0.8 M aqueous sucrose solution as the carbon source. The starting solution was heated in a stainless steel autoclave at 200 ^{o}C for 4h to produce carbon spheres with regular shapes having diameters in the range of 1-15 µm. The CS was reduced using thermal annealing reduction at 800^{o}C in N_2 for 1h. The obtained reduced CS (r-CS) was studied using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The r-CS has been organized by direct compression to provide efficient ion and electron transport using PEO, Poly(ethylene oxide) powder to keep the spheres in an order structure. The high capacity to conduct a current making them useful in supercapacitors, catalyst supports and absorbents. Conductivity measurements on these ordered 1:1 r-CS/PEO will be presented.

P8: Electrical Response of Monolayer MoS_2 to Vapors of Aliphatic Alcohols

Authors: Pablo I. Sepúlveda[1], Idalia **Ramos**[1], Carl H. Naylor[2], A.T. Charlie **Johnson**[2] and Nicholas J. **Pinto**[1]

Affiliations: [1]*University of Puerto Rico at Humacao,* [2]*University of Pennsylvania*

Monolayer MoS_2 crystals were used to sense vapors of Methanol, Ethanol and 1-Propanol. Due to the large surface area, these sensors are expected to show rapid response and recovery times. The current through the sensor was monitored as a function of time with a constant applied voltage. This current decreased in the presence of the sensing gas and recovered upon its removal. Our results show that the response time gets longer as the size of the alcohol increases, but the recovery time stays approximately the same (~20 s) regardless of the size of the alcohol. The sensitivity was also seen to decrease as the size of the alcohol increased. These observations could be associated with the slower diffusion of the larger alcohol molecules into the MoS_2 crystal. The sensors are also fairly robust since the same sensor was used in all of the measurements after annealing in air at 70° C for 10 minutes. Additional sensing measurements as a function of gas concentration will also be presented. This work was supported by NSF under grants DMR-PREM-1523463 and DMR-RUI-1360772.

P9: Extraction and Characterization of Cellulose Nanocrystals from Puerto Rico's Bamboo

Authors: Nicole Ramos[1], Mariana León[2], Nelson Granda[2], Wilfredo Otaño[2], and Josee **Vedrine**[1]

Affiliations: *[1]University of Puerto Rico at Humacao, [2]University of Puerto Rico at Cayey*

In our research work, we extracted and characterizeed cellulose materials to produce nanocrystals from Puerto Rico's Bamboo. The extraction process of cellulose microfibers and cellulose nanocrystals is incorporate as components in potential device applications. The organic material that we used for the extraction of cellulose nanocrystal is derived from one type of Bamboo found in Puerto Rico known as *Bambusa vulgaris Schrad. ex Wendl*. *Bambusa vulgaris Schrad. ex Wendl* is known as a common type of bamboo that can easily grow in areas with an annual rainfall between 500 to 3800 millimeters of rain. The process that we used to obtain these nanocrystal is summarized in four steps- alkaline, bleaching, hydrolysis and mechanical process. The alkaline treatment is based on the addition of NaOH to remove the cellulosic and non-cellulosic components inside the *B. vulgaris*. In addition we apply a bleaching treatment to make a color change in the cellulose. Also we apply a hydrolysis treatment to the bamboo fibers to extract cellulose nanocrystals (CNC). The hydrolysis treatment is based on the application of a sulfuric acid solution to remove the phenolic compounds and chromophoric molecules in lignin. The final step we realized was the recollection and characterization of these nanoparticles. Some of the analyses that we made to characterize these nanoparticles were XRD, SEM and AFM. CNC particles were measured with average physical dimensions of 1.437 µm (in length) and 0.334 µm (in diameter). We will also analyze the porosity, and surface roughness of bamboo CNCs for incorporation into biomaterial and photovoltaic applications.

P10: Flexible Organic Thin Film Device: Conductance Model using COMSOL Multiphysics

Authors: Carolyn Carradero and Josee **Vedrine**

Affiliation: *University of Puerto Rico at Humacao.*

In this research work, we developed a virtual model to analyze the electrical conductivity of multilayered thin films placed above a graphene conducting and flexible polyethylene terephthalate (PET) substrate. The organic layers of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as a hole conducting layer, poly(3-hexylthiophene-2,5-diyl) (P_3HT), as a p-type, phenyl-C61-butyric acid methyl ester (PCBM) and as n-type, with aluminum as a top conductor. COMSOL Multiphysics was the software we used to develop the virtual model to analyze potential variations and conductivity through the thin-film layers. COMSOL Multiphysics software allows simulation and modeling of physical phenomena represented by differential equations such as heat transfer, fluid flow, electromagnetism, and structural mechanics. In this work, using the AC/DC, electric currents module we defined the geometry of the model and properties for each of the six layers: PET/graphene/PEDOT:PSS/ P_3HT/PCBM/aluminum. We analyzed the model with varying thicknesses of graphene and active layers (P_3HT/PCBM). This simulation allowed us to analyze the electrical conductivity, and visualize the model with varying voltage potential, or bias across the plates, useful for applications in solar cell devices.

P11: Generation of Tin Oxide Nanoparticles for Biomedical Applications

Authors: Delaine Zayas-Bazán and Wilfredo Otaño

Affiliation: *University of Puerto Rico at Cayey*

Tin Oxide (SnO_2) nanoparticles have been a topic of investigation for various decades due to their multiple applications in technological and biomedical devices. In the field of biomedical devices, much investigation has been conducted proving its capability as gas sensor. SnO_2 films have an oxidative or reductive capability that generates a response in the electric conductivity when it is presented with certain gases. This response is augmented when the size of the nanoparticles is reduced. The aim of this project is to generate SnO_2 films that can accurately serve this purpose in detecting volatile organic gases. The samples were produced by sputtering tin on oxidized silicon (Si) wafers. Various parameters are known to affect the size of the nanoparticles and they were explored in this project. The substrate temperatures ranged from 23 °C to 260°C. The deposition time was also varied ranging from one second to 120 seconds. All of the samples were deposited at a constant pressure of 10 mTorr. The samples where then oxidized at 600 °C for twenty-four hours. The samples where characterized by both Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Fifteen SnO_2 films were obtained and characterized. Thickness profile measurements were performed on two films deposited without heating the substrate to profile the deposition arrival rate. The films were deposited for 60 and 120 seconds and the results were 134.3 nm ±8.08 and 202.3 nm ±3.21, respectively. These results suggest that the width of the film is related to the deposition time. The longer the deposition time, the larger amount of tin that will be deposited on the substrate. Therefore, longer deposition times result in increased diameter of the nanoparticles when the substrate is heated. SEM and AFM results show a relation between the morphology of the nanoparticles and the temperature of deposition. The particles that were deposited with substrate temperatures above the Sn melting point (232 °C) showed a more spherical morphology than the samples deposited at lower temperatures. All of these results provide us with the tools to optimize the procedure of obtaining SnO_2 films. Future studies should address this optimization and include further characterization. The ability of these films to act as gas sensors of volatile organic compounds must also be addressed.

P12: Mutant Ferritins for Improved Nanoparticle Encapsulation

Authors: Katie Pulsipher, Ivan J. **Dmochowski**, Jose Villegas and Jeffery G. Saven

Affiliation: *University of Pennsylvania*

As nanomaterials become more common in consumer products and medicine, increased understanding of their effect on biological molecules such as proteins is needed. We have made a stable protein–nanoparticle conjugate using thermophilic ferritin (tF) and 5 nm gold nanoparticles (AuNPs). tF self-assembles around the NP over 48 h under mild conditions (room temperature, gentle agitation). Upon self-assembling around an NP, tF maintains its native secondary structure, stoichiometry, ferroxidase activity, and thermal stability. The NP shows increased salt stability. To speed up conjugate formation, we have made three tF mutants, with the goal of decreasing intersubunit electrostatic repulsion. The mutants have been characterized by circular dichroism spectroscopy, transmission electron microscopy, native gel electrophoresis, size exclusion chromatography, and dynamic light scattering. The resulting mutant tF–AuNP conjugates have potential application in NP separations, templated NP reactions, or targeted delivery.

P13: Schottky Diode Based on WS_2 Crossed with PEDOT/PSSA

Authors: Deliris N. Ortiz[1], Nicholas J. **Pinto**[1], Carl H. Naylor[2] and A.T. Charlie **Johnson**[2]

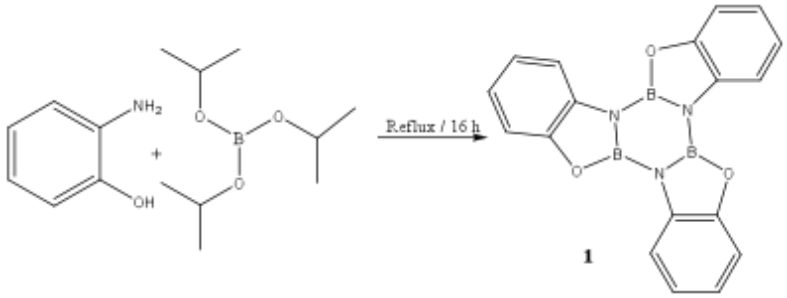
Affiliations: *[1]University of Puerto Rico at Humacao, [2]University of Pennsylvania*

An easy technique to fabricate a Schottky diode with WS_2 and PEDOT-PSSA under ambient conditions is presented. WS_2 is an air stable transition metal dichalcogenide semiconductor. When connected as a field effect transistor, WS_2 exhibited n-type behavior with a charge mobility of ~7 cm^2/V-s on SiO_2. PEDOT/PSSA is a conducting polymer that can be electro-spun to form fibers with a conductivity of ~ 1 S/cm. In this work we fabricated a Schottky diode by crossing a CVD grown monolayer WS_2 crystal with a single electro-spun PEDOT/PSSA fiber. The resulting diode characteristics were analyzed assuming the standard thermionic emission model of a Schottky junction. Analysis of the results includes the ideality parameter of 4.75, diode rectification ratio ~10, and a turn on voltage of 1.4 V. Efforts to investigate if these parameters are tunable with a back gate will also be presented. This work was supported by NSF-DMR-1523463 and NSF-DMR-RUI-1360772. ATJ acknowledges support from EFRI 2DARE EFMA-1542879.

P14: Synthesis and Characterization of Borazine Compounds

Authors: Jonathan Ramos, Melvin de Jesús, Viatcheslav Stepanenko and Margarita **Ortiz**

Affiliation: *University of Puerto Rico at Humacao*



Borazines are compounds with six-membered ring structure of alternating boron and nitrogen atoms. The multi-functionality and thermal stability properties of these compounds made them useful as semiconducting materials. The borazine derived from o-aminophenol (see figure 1) was prepared by the reaction with BH_3-DMS and BH_3-THF by our previous methodology. Then, due to the explosive danger of these reagents, we have been exploring new methods for the synthesis of borazines using $NaBH_4/BF_3$, trimethylborate and triisopropylborate under a variety of conditions. The desired crude borazine (figure 1) was obtained in high yield, although with some impurities. After attempted purification, the compound was characterized by IR, NMR and UV spectroscopic methods. We will continue improving these methods to obtain a practical synthesis of this and other borazines in a pure form. Using novel chemistry and environmentally benign boron compounds, these borazine will offer possible applications and inventions of advanced functional materials.

P15: The Photophysical Properties of a Borazine Derivative

Authors: Lilliana Ortiz, Margarita **Ortiz** and Rolando **Oyola**

Affiliation: *University of Puerto Rico at Humacao*

Borazine derivatives (BD) are multifunctional and thermally stable materials with high electron and moderate hole mobilities for applications in electroluminescent devices. They had been used as gasoline additives, polymerization catalyst and as neutron detectors. The borazine used is derived from 2-aminophenol. This work is focused on the determination of the photophysical properties of a borazine derivative with formula $C_{57}H_{56}B_6N_8O_8$. To fulfill this objective, we will use spectroscopic techniques, including UV-Vis, and fluorescence. UV-Vis spectroscopy will be used to determine absorption cross sections of the BD in different solvents. Fluorescence spectroscopy will be used to measure the intrinsic fluorescence quantum yield $\left(\Phi_F^{BD}\right)$ in different solvents. These measurements are useful for obtaining a complete scope of the properties of this compound in different microenvironments. More importantly, these measurements can help us to predict the potential uses of the BD for possible optoelectronic applications.

P16: The Study of the Oligomerization Process of IAPP in Presence of Gold Nanoparticles

Authors: Ambar S. Delgado and Rolando **Oyola**

Affiliation: *University of Puerto Rico at Humacao*

The analysis of the oligomerization process of the Islet amyloid polypeptide (IAPP) will be executed performing fluorescence emission studies with Thioflavin (ThT) as a probe, buffer solution (pH=7.5) and with different concentrations of 13 nm gold nanoparticles. To perform this study we synthetized the gold nanoparticles. The main objective of using different concentrations of gold nanoparticles is to observe the possible interactions or affinities of the peptide of interest with the surface of the nanoparticles, also to identify if the said interactions have effects on the kinetics, the size, and the oligomerization process of the polypeptide. Dynamic light scattering will also be performed to analyze the variety of sizes of the formed oligomers if they form at all. For following studies, we plan on determining the effect of nanoparticle concentration and its sizes in the oligomerization process of the polypeptide IAPP.

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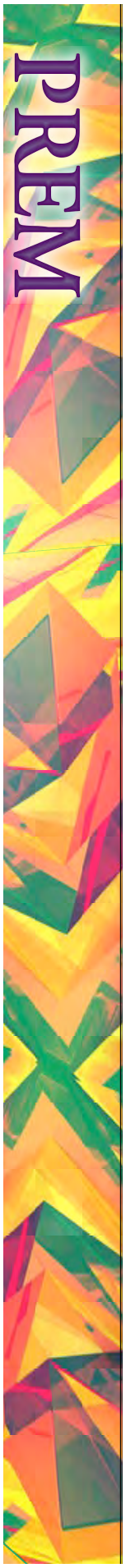

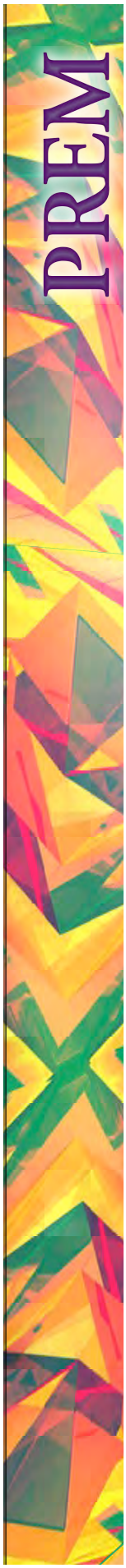

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PARTNERSHIP FOR RESEARCH AND EDUCATION IN MATERIALS (PREM)

NSF-DMR-1523463

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