

Interdisciplinary Research Group (IRG) – 1: IRG – Materials for Energy

Project – 1: Multilayered, Transparent Electrodes

UTEP Faculty: Dr. Ramana Chintalapalle, Mechanical Engineering

This project work will explore multilayer stacks (≤ 100 nm) of dielectric(D)/metal(M)/dielectric(D) films with controlled interfacial structure and chemistry. Specifically, efforts will be focused on utilizing WO_3 , HfO_2 and MoO_3 for D-layers while M-interlayers will be either Ag or Al. TCOs transport photo-generated current from the active layer(s) of a device to an external load play a key role in optoelectronics (EO) and LEDs in addition to photovoltaics. Tin-doped indium oxide (ITO) is the current standard TCO for all practical applications in EO, PV and LED technologies. However, there has been much recent interest in finding indium-free TCOs and even better performing alternative candidates to substitute ITO. The driving factors, which are mainly associated with In metal, are: 1) scarcity, (2) rapid price increase, (3) unintended interfacial phenomena and (4) global politics. In addition, the poor mechanical flexibility and inevitable high deposition temperatures limit potential application of ITO in flexible and/or organic-based PV, EO and LED technologies. A large number of materials, such as metal nanowires, doped oxides, and graphene, have been extensively studied in recent years. However, none of them were found to adequately replace ITO. Recently, the concept of D/M/D multilayers has emerged as a highly promising strategy for efficient TCO design that overcomes many of the problems associated with ITO. However, the fundamental science, especially the underlying mechanism of component layers' interfacial microstructure and charge injection mechanisms are not well understood at this time. In this context, **the project will** investigate the fundamental science and engineering aspects of TCOs based on D/M/D multilayer films. The technical merit of the project is to use an asymmetric configuration, where the top and bottom D-layers are materials with different refractive index (such as WO_3 and HfO_2), which is expected to significantly improve the electronic behavior to meet the ideal requirements of TCOs. Therefore, experiments will be performed to understand the effect of various morphologies on the DMD-TCOs performance. D/M/D as well as other transparent oxide materials will be deposited using standard physical vapor deposition methods, such as sputtering, electron-beam deposition, and pulsed-laser deposition, under variable conditions of temperature, oxygen reactive pressure and D/M-layer thickness. The samples will be characterized by studying their crystal structure, surface/interface structure and morphology, chemical composition, and optical and electrical measurements. The structural and chemical characterization of the samples will be performed employing X-ray diffraction (XRD), X-ray reflectivity, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) measurements. The electrical properties of D/M/D samples will be measured employing the van der Pauw method while the optical properties will be probed employing spectrophotometry and spectroscopic ellipsometry (SE).

Project – 1: Uranium-Based Compounds for Energy Applications

UTEP Faculty: Dr. Skye Fortier, Chemistry

The use of unconventional uranium ceramics may give access to new photovoltaic materials or devices. Indeed, uranium oxide based, thin-film solar cells have been patented, demonstrating proof of concept. The problem with these materials is that they are difficult to make owing to their high melting point (e.g. UO_2 , m.p. 3,138 K) which complicates growing well-defined films or crystalline solids. Moreover, computational modeling of the local bonding interactions in the ceramics between uranium and the interstitial atom can be complicated due to $5f$ -electron relativistic effects, hindering critical understanding of the underlying chemistry.

In an effort to advance the use of uranium materials in energy applications, particularly in light harvesting devices, we propose to take a multi-prong approach. Specifically: a) new methods

for the deposition of UO_2 ceramic films and single crystals will be explored; b) the physical properties of these materials in devices will be investigated.

While the role of uranium ceramics has been the focus of study for several decades, owing to their importance in the nuclear fuel cycle, very little work has been performed in applying their unique properties to conducting materials. UO_2 is a semiconducting ceramic with an electronic bandgap of 1.3 eV, lying in-between Si (1.14 eV) and GaAs (1.39 eV), with a high dielectric constant of 22 at 300 K. Moreover, at room temperature, the intrinsic electrical conductivity of UO_2 is comparable to that of crystalline Si. The semiconducting behavior can be explained by unique 5f-electron-hopping using a Hubbard exciton model. UO_2 also has potential utility as a thermoelectric material as it exhibits a high Seebeck coefficient of 750 $\mu\text{V}/\text{K}$ (320 K, 0.01 $\text{W}/\text{cm}\cdot\text{K}$). The lack of study in this area is less likely a result of radioactivity (U is a weak α -emitter) and more a consequence of high-temperature synthesis of the refractory uranium ceramics.

The deposition of metal oxides via sol-gel methods is a well-established technique. The Fortier laboratory is working to extend this method to uranium as a low-temperature route to UO_2 thin film formation. To achieve this, the ditox ligand (ditox = $^-\text{OCH}^+\text{Bu}_2$) was chosen as it is both bulky and anticipated to provide high solubility in a wide range of solvents, thus conferring kinetic stability to the complex and ease of handling and processing.

Project – 3: Multifunctional Materials for Energy Harvesting Applications **UTEP Faculty: Dr. Ramana Chintalapalle, Mechanical Engineering**

Multifunctional materials, which can combine multiple properties and phenomena in the solid state, find numerous technological applications. The perovskite (ABO_3) structured BaTiO_3 , which is a classical ferroelectric (FE), and BTO-based solid solutions are an important class of materials that are useful for many of the current and emerging technological applications. BaTiO_3 and BTO-based materials are of great practical interest due to their excellent properties such as relatively high stability, high dielectric constant ($\epsilon' \sim 1700$), low dielectric loss ($\tan \delta \sim 0.01$), and moderately high piezoelectric coefficient ($d_{33} \sim 150$ pC/N). We propose to use non-magnetic (NM) Ce and Sn ions for incorporation into Ca-doped BTO to tune the structure, chemistry and physical properties. To produce the electronic structure changes, suitable ions must be doped at the Ti(B)-site that induce significant changes in the electronic structure (to facilitate charge carrier generation) while still maintaining the ferroelectric signature (to facilitate the charge transport) of BTO. From fundamental scientific perspective, doping at B-site by suitable metal ion(s) can induce changes in the octahedral ordering and local bonding, and thus facilitates the E_g -reduction. The substitution of Ti^{4+} by slightly larger Sn^{4+} and/or Ce is expected to induce such changes leading to unit cell expansion and property modification. The central theme and fundamental scientific aspects of the proposed research are to gain an insightful understanding of the structure-property-processing relationship, which can help in substantially advancing our fundamental understanding while elucidating the role of dopants on the properties.

Interdisciplinary Research Group (IRG) – 2: IRG - Biomaterials

Project – 4: Development of Biomimetic Scaffolds for 3D Tissue Engineering **UTEP Faculty: 1. Dr. Katja Michael (Chemistry), 2. Dr. Chunqiang Li (Physics);** **3. Drs. Thomas Boland & Binata Joddar (Metallurgical, Materials and Biomedical Engineering)**

Utilization of biomaterials requires a deeper understanding of the fundamental insights into processes, physical and chemical phenomena, and bio-related processes. This IRG will investigate the processing-structure-property relationships in biomaterials and fundamental insights into bioconversion processes. The team will generate new tools and understanding in the fields of materials science, photochemistry, and bioengineering. Results from this work are

expected to impact several current tissue engineering strategies. The photoreactive peptides proposed will be suitable to form a novel class of biomimetic hydrogels, in which precise microtunnels can be introduced by laser technology. The resulting scaffolds can provide an environment conducive for the infiltration of cells and the formation of a vasculature, two requirements that have been difficult to meet in the past due to the lack of appropriate scaffolds. The biomaterials envisioned here may help fundamentally understand and target this long-standing problem by enabling the growth of thick, dense tissue *in vitro*, and therefore they have the potential to transform the field of tissue engineering.

In order to grow tissue in culture, an appropriate environment for the cells to survive and proliferate must be provided. Many breakthroughs in scaffold design and vascularization have been reported, but a dense 3D tissue that mimics natural tissue and that is suitable for implantation is still elusive. Most progress has centered around 3D printing techniques. For example, pioneering work done by J. Lewis at Harvard's Wyss Institute uses fugitive ink as a precursor for tunnels, which leads to thick vascularized model tissues on a perfused chip. However, the tunnels have significantly wider diameters (1000 μm) than physiological capillaries, with much larger spaces between them (2000 μm) than required for normal tissue (~ 200 μm). Such a tissue is quite different from natural tissue and would not be viable when implanted into a host. While much progress has been made in growing cells on 2D surfaces or in thin gels, thick 3D tissue growth in culture that mimics tissues *in vivo* has not yet been accomplished. This limitation is due to a gap in knowledge about how to achieve vascularization in culture, necessary for the delivery of nutrients and O_2 deep into the tissue. Collagen-derived gels are amongst the most promising materials that provide support for cell growth in culture. When collagen gels are implanted into a host, neo-vascularization occurs at a rate of 0.1mm/week. However, this is too slow for the survival of any cells embedded in the gel. In order to overcome these problems, a scaffold that supports vascularization for 3D tissue growth, with capillaries no further than 200 μm apart from each other, is essential. Currently, there has been no perfect matrix material available that is rigid enough to support a stable tunnel architecture in which vascularization can occur, and soft/porous and cell-friendly enough for 3D tissue growth. *We hypothesize that a collagen-like scaffold that is filled with precise bio-inspired tunnels will allow endothelial cells to form a vasculature, and will support thick 3D tissue growth in vitro.* In the design of such a scaffold we have considered the following important factors: a) cross-linking capabilities of a collagen-derived peptide to create sufficient stiffness that supports tunnels; b) built-in functions that allow for break-down of the material at specific locations with light; c) the capability to convert a stiff scaffold into a soft one that provides an environment that allows cells to migrate into the gel and grow. To address these points we propose to incorporate photoreactive N-acyl-7-nitroindoline moieties into synthetic collagen-peptides as well as into the cross-linkers. Once a scaffold (**Fig. 9**) has been generated, endothelial cells can grow into a vasculature by forming a monolayer along the tunnel walls. The ideal hydrogel stiffness required for the infiltration by cells and their growth into a tissue is not known, therefore, a hydrogel whose mechanical properties can be modulated would be highly desirable. Our gel has the capability to be softened by broad illumination with indigo-colored light, which will cause cleavage of the remaining photoreactive groups throughout the gel, creating a soft, fully oxygenated matrix, conducive for thick 3D-tissue growth of up to 1cm^3 .

To meet the project goals an interdisciplinary team with expertise in synthetic chemistry, photochemistry, photonics, computation, and bioengineering is required. The team will train undergraduate and graduate students beyond their major discipline in all aspects of the project in a true interdisciplinary and collaborative manner, so that students gain foundational knowledge in the most important aspects of each discipline pertaining to this project. **Katja Michael** and her students will be responsible for synthesizing collagen-like peptides with photoreactive N-acyl-nitroindoline units, the cell adhesion sequence RGD, and photoreactive crosslinkers, and will propose and test new synthetic methods to improve existing synthetic pathways. Her laboratory has state of the art synthetic chemistry equipment (glassware, rotary evaporators, a peptide

synthesizer, a Rayonet photoreactor, an FPLC system, a lyophilizer, ovens, a UV-VIS spectrophotometer, refrigerators, and a -50°C freezer). In addition, she has access to the departmental NMR and MS facility. **Chunqiang Li** and his students are responsible for generating the tree-like micropatterns using a spatial light modulator, and carving out precise tunnels (15-40 μm in diameter, 200 μm apart) by using the laser of his in-house developed two-photon microscope. **Boland** will train students in measuring the hydrogels' creating vascularized scaffolds. He and his students will apply the appropriate cell stains and verify microscopically that a monolayer of endothelial cells is indeed populating all tunnel surfaces throughout the scaffold. Afterwards he will illuminate the gel broadly with indigo light (420 nm) to accomplish softening of the gel by photolysis without harming the endothelial cells, and verify the reduced gel stiffness.

In a perfusion bioreactor, **Joddar** and her students will grow stem cell tissue in the vascularized scaffold and determine the cell density of the tissue microscopically. In order to further verify that the stem cell tissue is not only viable but functional, she will differentiate the tissue into osteoblasts. Her laboratory is equipped with a Sartorius bioreactor, a cell culture room with CO₂ incubators, a bench centrifuge, a biological hood, an inverted fluorescent Olympus microscope for fluorescent imaging of samples, water baths, refrigerators, a -85°C and -140°C freezer for sample storage, glassware for dialysis, a freeze-drier, a confocal microscopy system with one Nikon TiU inverted microscope and a Nikon AZ100 MultiZoom microscope with C1si scan head and detector, four laser lines, spectral detector and automated incubators, and a UV/visible-lamp within chamber (UVitron).

Project – 5: Photothermal Nanomaterials for High-Efficiency Biomass Conversion **UTEP Faculty: Dr. Xiujun (James) Li, Chemistry**

To address the low-efficiency problem of biomass conversion, this team will systematically study fundamentals of the localized heat of photothermal effects of a variety of nanomaterials for efficient biomass conversion. The central hypothesis is that localized heat generated from the nanomaterial-medicated photothermal effect on the catalyst surface can significantly increase the catalytic efficiency. The team members will work synergistically on various aspects, which include nanomaterial and nanocomposite synthesis, characterization, photothermal effects, biomass conversion efficiency and catalytic synthesis, *modeling*, kinetics and mechanisms.

Conversion of plant-based biomass into valuable biofuels and fine chemicals has gained increasing significance due to the growing demand for renewable energy and materials. Through the biomass conversion of cellulose and related carbohydrates, many value-added chemicals can be produced. 5-(Hydroxymethyl)furfural (**HMF**) is one of such examples. HMF upon oxidation yields 2, 5-furandicarboxylic acid (**FDCA**), which is one of the most important bio-renewable alternatives to terephthalic acid and starting chemicals for the manufacturing of petroleum-based polymers such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT) plastics. However, current methods for the oxidation of HMF into FDCA are of low efficiency and dependent on lengthy reaction time, high pressures, and toxic catalysts.^{63,64-65} Exploration of new methods for efficient biomass conversion becomes vital to the production of valuable materials from biomass resources.

Although photothermal effect is extensively studied for cancer photothermal therapy due to its unique noninvasive characteristics, it is rarely studied for biomass conversion. One of the key attributes of photothermal effect is its ability to cleave strong chemical bonds rapidly from **localized heat** generated from the surface plasmon resonance of nanoparticles. Further, when utilized in catalysis, this localized heat can aid in more rapid conversion of reactants than the heat supplied externally to the reaction medium, thus dramatically improving the catalytic efficiency of biomass conversion. Our preliminary studies show a photothermal method (at 60 °C, in a bulk solution) can lead to 400% enhancement in the time required for >99% conversion of HMF, compared with the same HMF oxidation process at 60 °C by conventional heating of bulk

solutions, while more than **70-fold enhancement** was observed when compared with the room temperature method. Different gold nanoparticles, nanorods and nanoshells were observed to have catalytic effects in biomass conversion. Because those nanomaterials also have good photothermal effects, this **dual effect (localized heat and their catalytic effect)** can significantly increase the biomass conversion efficiency. The majority of the existing reports on photothermal effects focus on gold nanoparticles. Some the photothermal effects of other nanomaterials such as the porous gold nanosponge (**PGN**) and nanocomposites were never reported. Systematic studies of photothermal effects of different nanomaterials are expected to provide fundamental scientific clues to dramatically improve the biomass conversion.

James Li's group focuses not only microfluidic lab-on-a-chip, but also nanomaterials. **James Li** developed the first photothermal immunoassay using a common thermometer as the signal reader, based on a conversion strategy from iron oxide-to-Prussian blue nanoparticles. Therefore, the **James Li** group will study photothermal effects of various nanomaterials via UV-VIS spectroscopy. They will optimize the wavelengths for best photothermal effects of those nanomaterials. Probing the localized temperature is vital to gain insight into the mechanisms of biomass reactions and quantitative roles of photothermal effects in enhanced biomass conversion. In addition, we will use Surface-Enhanced Raman Scattering (SERS) to measure the localized temperature of nanomaterial surface.

The photothermal catalytic performance of materials on multiple biomass-derived materials will be investigated, such as the oxidation of HMF to **FDCA, carbazoles, and lignin disassembly**. The **James Li** group will focus on FDCA generation. The catalytic performance at room temperature, higher temperatures by conventional heating and by the photothermal method will be systematically studied and compared, which will gain insight into the contribution of localized heat to the enhanced catalytic efficiency. **Li** will first use a low-cost NIR laser (e.g. 808 nm, ~2.0 W) as the light source to study the effect of photothermal nanomaterials for efficient biomass conversion, and then will test the efficiency using a regular NIR light bulb (850 nm, 250 W, 5000 life hours, ~\$5) aiming to explore the feasibility of mass biomass conversion. Based on collected data, **Li's** group will explore whether those photothermal biomass conversion undergoes the same pathway as conventional biomass conversion methods by identifying and quantifying their reaction products using HPLC. The team with expertise in nanomaterials, physical chemistry, photochemistry, modeling, and engineering will perform the work to ensure the project success.
