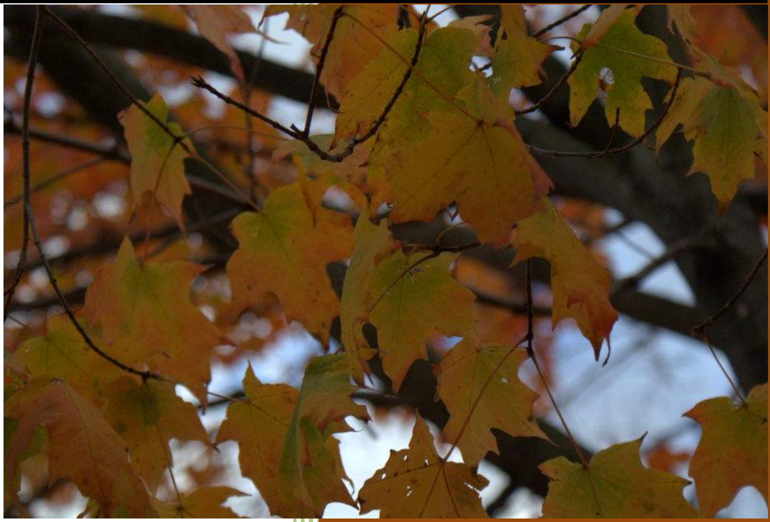
AMEBA

2015

Advanced Materials for Energy and Bioengineering Applications



UNIVERSITY OF VERMONT
DAVIS CENTER
SILVER MAPLE BALLROOM
DEC 7TH 2015

Schedule and abstracts available for download at www.uvm.edu/~mrsuvm

MRS UVM Chapter

OMEGA OPTICAL Light You Need

The UNIVERSITY of VERMONT

Advanced Materials for Energy and Bioengineering Applications (AMEBA) Symposium Program
Dec 7th, 2015
Grand Maple Ballroom, Davis Center, University of Vermont

7:00 AM - 8:30 AM	**Continental Breakfast**
	Morning Session I **Session Chair: Matthew White (Univ. of Vermont)**
8:30 AM - 9:00 AM	**Tsukasa Yoshida** (Yamagata University, Yonezawa, Japan) *Electrochemical Self-Assembly of ZnO / Rhodamine B Nano-Turing Pattern*
9:00 AM - 9:30 AM	**Sheetal Chanda** (Omega Optical, Brattleboro, VT) *Photovoltaic R&D at Omega Optical – current status*
9:30 AM - 10:00 AM	**Jing Wan** (University of Vermont, Materials Science) *Transient phases during crystallization of solution-processed organic thin films*
10:00 AM - 10:20 AM	**Dominik Farka (**Johannes Kepler University, Linz, Austria) *Bioconjugation of hydrogen-bonded organic semiconductors with functional proteins*
10:20 AM - 10:40 AM	**Coffee Break**
	Morning Session II **Session Chair: Madalina Furis (Univ of Vermont)**
10:40 AM - 11:00 AM	**Sun He (**Yamagata University, Yonezawa, Japan) *Synthesis and solar cell application of structure controlled nanocrystals*

11:00AM - 11:20 AM **Selina Yao** (University of Vermont, Mech. Eng)
Measurement Methods for Solubility and Diffusivity of Supercritical Gases in Polymer and its Limitations

11:20 AM - 11:50 PM **Joe Berry** (National Renewable Energy Laboratory)
Efforts at the National Renewable Energy Lab to realize the promise of metal-halide perovskite solar cells

11:50 PM - 1:00 PM **Lunch at the Davis Center**

Afternoon Session I
Session Chair: Severin Schneebeli (Univ of Vermont)

1:00 PM - 1:30 PM **Eric Głowacki** (Johannes Kepler University, Linz, Austria)
Biocompatible hydrogen-bonded supramolecular conductors for bioelectronic interfaces

1:30 PM - 2:00 PM **Fred Sansoz (**University of Vermont, Mech. Eng& Mat. Sci)
Role of Intrinsic Defects in Plasticity of Nanotwinned Metals

2:00 PM - 2:30 PM **Talia Gershon** (IBM TJ Watson Research Center)
Optical characterization of $Ag_2ZnSnSe_4$ *thin film absorbers for photovoltaics*

2:30 PM - 2:50 PM **Coffee Break**

Afternoon Session II
Session Chair: Randall Headrick (Univ. of Vermont)

2:50 PM - 3:20 PM **Adam Whalley** (University of Vermont, Chemistry & Mat. Sci)
Controlling the Properties of PAHs through Ring-Size Manipulation

3:20 PM - 3:50 PM **Severin Schneebeli** (University of Vermont, Chem. & Mat. Sci)
Bioinspired Functional Nanomaterials built with Chirality-Assisted Synthesis

3:50 PM - 4:10 PM **Stefanie Schlager** (Johannes Kepler University, Linz, Austria)
Bio-electrocatalytic CO_2 Reduction using Enzymes and Microorganisms

4:10 PM - 4:40 PM **Rachael Oldinski** (University of Vermont, BioEng & Mat. Sci)
Title to be announced

4:40 PM - 4:50 PM **Coffee Break**

4:50 PM - 6:00 PM **Poster Session and Reception**

Morning Session I
8:30 AM – 9:00 AM

Electrochemical Self-Assembly of ZnO / Rhodamine B Nano-Turing Pattern

TSUKASA YOSHIDA[1], Matthew White[2], Shu Uno[1] and Lina Sun[1]
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Beautiful shapes and patterns of the animal skins such as that of zebra are occuring from a surprisingly simple mechanism. Alan Turing developed a mathematical model, reaction-diffusion system, to predict spontaneous formation of patterns reflecting the changes of concentrations for two competing production of chemicals. Such patterns are called "Turing Patterns" and the RD system is now proven to be the principle for the evolution of graphical patterns that we see on skins of animals, fish, etc...

We have discovered electrochemical process to evolve unique Turing patterns in nano-scale for cathodic electrodeposition of hybrid thin films of zinc oxide and rhodamine B. Little addition of rhodamine B into the bath for electrodeposition of ZnO employing reduction of O results in a variety of Turing pattens comprising of crystalline ZnO and solid rhodamine B. Rhodamine B is electrochemically reduced to form complex with Zn and that is oxidized with O bubbles, releasing ZnO and regenerating rhodamine B. Due to such a catalytic cycle, rhodamine B fulfills the function as an "activator" for formation of ZnO. While precipitated rhodamine B is highly insoluble and diffuses slowly, ZnO can repeat dissolution / recrystallization cycle and diffuses about a decade faster than rhodamine B, so that it prevents the growth of rhodamine B. Thus, ZnO fulfills its function as the "inhibitor" for formation of rhodamine B. This way, the conditions for Turing pattern formation by the RD model is satisfied. The structure of the hybrid materials is nicely compared to that obtained by mathematical simulation of modified RD model. Also obtained was the total 3D image of the ZnO / rhodamine B labyrinthine structure by FIB-SEM observation technique that nicely supports the film growth reflecting the "standing wave" of ZnO / rhodamine B concentrations at the frontier of the electrochemical precipitation.

In the talk will be presented the special properties of rhodamine B and will be discussed the reasons for this phenomenon. We also envision the use of such self-assembled hybrid nanostructures in hybrid solar cells to realize endless regeneration of solar panels from "one-pot".

Morning Session I
9:00 AM – 9:30 AM

Photovoltaic R&D at Omega Optical – current status

SHEETAL CHANDA, **John Barton, Sarah Locknar, Gary Carver**

Omega Optical, Inc.
21 Omega Drive
Brattleboro, Vermont

Omega Optical is interested in leveraging its extensive thin films expertise into the photovoltaic arena. This presentation will summarize our earlier work with organic photovoltaics, and proposed work with perovskites. We are focused on contributing to an understanding of the lifetime of perovskite photovoltaic cells.

Morning Session I
9:30 AM – 10:00 AM

Transient phases during crystallization of solution-processed organic thin films

JING WAN,[1] Yang Li,[1] Jeffrey G. Ulbrandt,[1] Detlef-M. Smilgies,[2] Jonathan Hollin,[3] Adam C. Whalley,[3] Randall L. Headrick[1]

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[3] Department of Chemistry, University of Vermont, Burlington VT 05405, USA

The electronic properties of organic semiconductor thin film are greatly influenced by the crystalline packing of molecules within each layer, which may depend on the processing methods and conditions. The crystallization mechanisms turn out to be both subtle and varied, with different behavior for different materials. Here we report an in-situ study of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C_8-BTBT) organic semiconductor thin film deposition from solution, which exhibits multiple transient phases during crystallization. Films were prepared with controllable grain size and morphology via hollow pen writing. Under very high writing speed (25 mm/s) the films have an isotropic morphology, although the mobilities can be fairly high, up to 3.0 cm^2/V·s. To understand the crystallization in this highly non-equilibrium regime, we employ in-situ microbeam grazing incidence wide-angle X-ray scattering combined with optical video microscopy during deposition at different substrate temperatures. A sequence of crystallization was observed, in which a layered smectic liquid-crystalline (LC) phase of C_8-BTBT precedes inter-layer ordering. For films deposited above 80ºC, a transition from LC phase to a transient crystalline state that we denote as Cr1 occurs after a temperature-dependent incubation time, which is consistent with classical nucleation theory. After an additional short time (<1s), Cr1 transforms to the final stable structure Cr2. The sequential formation of LC→Cr1→Cr2 phases follows Ostwald's rule of stages. Based on these results, we demonstrate a method to produce extremely large crystalline grain size and high carrier mobility during high-speed processing by controlling the nucleation rate during the transformation between LC and solid phases.

Morning Session I
10:00 AM – 10:20 AM

Bioconjugation of hydrogen-bonded organic semiconductors with functional proteins

E. D. Głowacki,[a] R. R. Tangorra,[b] H. Coskun,[a] D. FARKA,[a] A. Operamolla,[bc] Y. Kanbur,[a] F. Milano,[d] L. Giotta,[d] G. M. Farinol[ab] and N. S. Sariciftci[a]

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[d] Istituto per i Processi Chimico Fisici, Consiglio Nazionale delle Ricerche, Via Orabona, 4, 70126 Bari, Italy

We demonstrate the direct bioconjugation of hydrogen-bonded organic semiconductors with two different complex functional proteins in an aqueous environment. The representative semiconductors are vacuum evaporated epindolidione and quinacridone

These molecules in thin films react spontaneously with N-hydroxysuccinimide functionalized linkers. Using covalent attachment for Rhodobacter sphaeroides reaction centre (RC) and the biotin-streptavidin lock-and-key system, the proteins were bound to the semiconductors, conserving their biofunctionality.

Surface-functionalization by linkers was investigated by Attenuated Total Reflection, Fourier Transform Infrared Spectroscopy ATR-FTIR, water contact angle measurements, and atomic force microscopy. Presence and integrity of the RC was investigated by charge recombination assay, in the case of biotinylation a quantum-dot labelled streptavidin was used.

As key results, our work shows that upon bioconjugation, the semiconductors preserve their favourable electrical properties even under water making hydrogen-bonded semiconductors promising platforms for bioelectronics devices.

Morning Session II
10:40 AM – 11:00 AM

Synthesis and solar cell application of structure controlled ZnO nanocrystals

SUN HE
Yamagata University

Nanoparticles of oxide semiconductors play crucial roles in mesoscopic solar cells such as dye-sensitized solar cells (DSSCs), quantum dot solar cells and perovskite solar cells. Not only the absolute size of the particles but also their shape and preferentially exposed crystal facets are expected to cause drastic changes in their performance, because it serves as the interface for carrier extraction and also for recombination. Also expected is the influence to the chemical stability of the light absorber (dye, Q-dot, perovskite) to be deposited onto the oxide surface.

While titanium dioxide is widely used, zinc oxide (ZnO) is an attractive alternative due to its high electron mobility and flexibility in its structure control. We have succeeded in synthesis of size and structure controlled ZnO nanoparticles by rapid hydrothermal crystallization employing microwave radiation and structure directing agents (SDAs). Here, the synthetic methods, structural characterizations and their properties in DSSC applications are reported.

Microwave radiation for 30 min to aqueous solutions containing $Zn(CH_3COO)_2$ and SDAs such as triethanolamine (TEOA) and 1,2,4,5-benzenetetracarboxylic acid (BTCA) with controlled pH by addition of KOH resulted in formation of differently shaped highly crystallizad ZnO. ZnO with hexagonal bi-pyramidal (HBP) shape and with nanosheet (NS) shape in about 50 to 100 nm size were obtained by use of TEOA and BTCA, respectively. Combination of the observation techniques of scanning electron microscope (SEM) transmission electron microscope (TEM), selected area electron diffraction (SAED) revealed that the axis of the HBP ZnO corresponds to the *c*-axis of ZnO,while the triangular sides in 6-fold symmetry correspond to the (102), making it the predominantly (84%) facet to be exposed. On the other hand, the predominantly exposed facet of the NS ZnO was identified as that of the (100) and it accounted as much as 76% of the total surface area.

Dye adsorption capability of these ZnO nanoparticles was checked by employing D149 and also for commercial polycrystalline ZnO (TAYCA MZ-500) for comparison. The surface area occupied by a single D149 molecule at saturation was determined as 0.68, 0.62 and 1.2 nm^2 for MZ-500, HBP and NS, respectively, indicating the superior dye stability on the (102) surface. DSSC devices employing these sensitized ZnO photoelectrodes exhibited differences in current and voltage; J_{sc} ($mA\ cm^{-2}$) = 12.0 (HBP) > 11.2 (MZ) > 8.04 (NS), V_{oc} (mV) = 615 (NS) > 580 (MZ) > 565 (HBP). Densely adsorbed D149 on the (102) surface appears to be the most efficient for electron injection. On the other hand, either the elevated band position and/or suppressed recombination may be the reasons for the high voltage of the NS.

Morning Session II
11:00 AM – 11:20 AM

Measurement Methods for Solubility and Diffusivity of Supercritical Gases in Polymer and its Limitations

SELINA XIANGXIAO YAO & PATRICK C. LEE
Mechanical Engineering
University of Vermont

Investigation of solubility and diffusivity of gas in polymer system is one of key aspects for creating lightweight porous structures for biomedical and energy applications such as tissue scaffold, and battery separators. The foam morphologies such as cell population density, expansion ratio, porosity, etc. depend on solubility and diffusivity of gas in a polymer structure. Therefore, it is critical to understand and measure solubility and diffusivity of a gas (i.e., CO2, N2) in a polymer

In this presentation, I will categorize different methods of measuring solubility and diffusivity with emphasis on major theories, experiments, models and equations. In addition, the limitations of each method and application area for each method will be briefly described. Some forward-looking discussions on the future of gas in polymer structure and applications would also be discussed.

Morning Session II
11:20 AM – 11:50 AM

Efforts at the National Renewable Energy Lab to realize the promise of metal-halide perovskite solar cells

JOSEPH J. BERRY
National Renewable Energy Laboratory
Hybrid Perovskite Solar Cell Team Lead

Photovoltaic devices based on hybrid organic-inorganic perovskite absorbers have reached outstanding performance over the past few years, surpassing power conversion efficiency of over 20%. In the scientific community these technologic advances supply a tremendous driving force to understand the fundamental physical and chemical properties of this material class. In particular, the underlying mechanisms with respect to charge separation and collection remain unresolved, and the understanding of electronic coupling to adjacent charge extraction and transport layers is in its infancy. The transition from the potential promise for photovoltaic (PV) applications requires that these basic physical properties be understood so to address the outstanding questions regarding stability and ultimately scalability for PV. In this talk efforts at NREL on perovskite solar cell to characterize basic aspects of PV relevant interfaces and associated component materials properties in the context of advancing metal-halide based devices will be discussed. Specifically, interfacial charge transport studies will be presented for MA and FA based metal halide perovskite PVs. The implications of these results on the direction of future efforts in this area will also be touched upon.

Afternoon Session I
1:00 PM – 1:30 PM

Biocompatible hydrogen-bonded supramolecular conductors for bioelectronic interfaces

ERIC DANIEL GŁOWACKI
Linz Institute for Organic Solar Cells (LIOS)
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Here I review recent work from our group on using natural-origin materials in semiconductor-based devices for interfacing with biology. Many natural materials offer both excellent semiconducting properties, and importantly, electronic as well as ionic conductivity. Biochemical systems are ionic, and not electronic, thus any attempts of active bioelectronics devices must involve ionic/electronic transducing elements. In particular, progress in the use of nanocrystalline and microcrystalline organic hydrogen-bonded pigments will be discussed. These materials have been ubiquitous throughout history and are widely produced today industrially as colorants in everyday products as various as cosmetics and printing inks, and have numerous properties that make them intrinsically biocompatible. The bioconjugation chemistry of these materials and subsequent deployment in electronic devices requiring reliable and specific bio-sensing will be covered. Next the aqueous electrochemistry of such Hydrogen-bonded nano- and microstructures will be covered. Finally, I will show results on photoeffects at semiconductor/cell interfaces measured using patch clamp electrochemistry.

Afternoon Session I
1:30 PM – 2:00 PM

Role of Intrinsic Defects in Plasticity of Nanotwinned Metals

FREDERIC SANSOZ
Mechanical Engineering & Materials Science
University of Vermont

This talk will present our recent progress in understanding the fundamental mechanisms of plasticity and fracture in face-centered cubic metals and alloys strengthened by coherent twin boundaries (CTBs) using atomistic simulations and nanoscale experiments. The ability of CTBs in strengthening and maintaining ductility has been well documented; yet most understanding of the origin of this mechanical behavior relies on a perfect interface assumption. This presentation will focus on the important role played by intrinsic kink-like twin boundary defects in controlling strength and plasticity in nanotwinned Cu and Ag-Cu alloys. First, using simple bicrystal models, it is found that kink-like twin boundary steps have a profound impact on screw dislocation - CTB interactions, resulting in significant strengthening behavior. Second, massively-parallel molecular dynamics simulations will be used to describe new defect-dependent plastic deformation processes in columnar-grained and nanocrystalline microstructures containing inherently defective CTBs with kink-like steps. New Monte Carlo simulations will also be presented to discuss the influence of atom segregation on deformation mechanisms and twin size effects in nanotwinned Ag-Cu alloys.

Afternoon Session I
2:00 PM – 2:30 PM

Optical characterization of $Ag_2ZnSnSe_4$ thin film absorbers for photovoltaics

T. GERSHON,[1] **Y.S. Lee,**[1] **R. Haight,**[1] **K. Sardashti,**[2] **E. Chagarov,**[2] **A.C. Kummel**[2]
[1] IBM TJ Watson Research Center, 1101 Kitchawan Rd, Yorktown Heights, NY
[2] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, USA

$Cu_2ZnSn(S,Se)_4$ (CZTSSe) has attracted great interest in recent years as an earth-abundant photovoltaic absorber. While efficiencies have improved steadily, the limiting performance parameter remains a deficit in the open-circuit voltage (Voc). This Voc deficit has been correlated with excessive band-tailing stemming from electrostatic potential fluctuations of the valence and conduction bands and/or band gap inhomogeneity in the material. A number of studies have identified widespread disorder on the Cu-Zn sublattice as a key parameter contributing to the band tailing and hence Voc loss. The covalent radii of Cu and Zn differ by only 5%, which may be why site exchange occurs so readily. Therefore, substituting either Cu or Zn with an element possessing a larger covalent radius (e.g. Ag) is expected to reduce the probability of site-exchange and hence improve the optoelectronic quality of the semiconductor. This contribution will present optoelectronic characterization of $Ag_2ZnSnSe_4$ (AZTSe) thin films grown by co-evaporation and annealing. We will compare the bulk defect structures of CZTSe, AZTSe, and CIGSe (via photoluminescence characterization at ~6K) and show that the replacement of Cu with Ag significantly suppresses the formation of charged sub-Eg states. This in turn suppresses the harmful band tailing associated with the Voc deficit. We will show that AZTSe is optoelectronically more similar to CIGSe than to CZTSe. Additionally, we will discuss important considerations for device preparation based on AZTSe thin films.

Afternoon Session II
2:50 PM – 3:20 PM

Controlling the Properties of PAHs through Ring-Size Manipulation

ADAM WHALLEY
Chemistry & Materials Science
University of Vermont

The incorporation of 8-membered rings into polycyclic aromatic hydrocarbons can have a profound effect on both their structural and electronic properties. In this presentation, we will describe the single-step preparation of a cyclic tetramer of acenaphthylene through the Lewis acid catalyzed Aldol cyclization of 1-acenaphthenone. This previously unexplored material differs from the better-known cyclic trimer, decacyclene, due to the presence of a central 8-membered ring. This ring not only forces the molecule to distort significantly from planarity but it is also responsible for its unique electronic properties including a decrease in both the reduction potential (by ~0.4 eV) and optical gap (by ~0.73 eV) when compared to the more planar decacyclene. The compound crystallizes into a unique packing structure with significant π-stacking observed between adjacent molecules. Furthermore, due to its boat-like shape, the cyclic tetramer is able to form shape-complementary interactions between its concave surface and the convex outer surface of buckminsterfullerene to generate co-crystalline supramolecular assemblies that resemble bulk-heterojunctions.

Afternoon Session II
3:20 PM – 3:50 PM

Bioinspired Functional Nanomaterials built with Chirality-Assisted Synthesis

SEVERIN T. SCHNEEBELI
Chemistry & Materials Science
University of Vermont

This short lecture will introduce chirality-assisted synthesis (CAS), a new approach to precisely control the shapes of nanoscale objects. Invented recently at the University of Vermont (see: Liu, X.; Weinert, Z. J.; Sharafi, M.; Liao, C.; Li, J.; Schneebeli, S. T. *Angew. Chem. Int. Ed.* **2015**, *54*, 12772) CAS provides access to a variety of polymeric nanostructures with well-defined shapes, including C-shaped strips, freeform spirals, cubes, etc. The shape of molecules defines the placement of chemical substituents in three-dimensions and with it, to a large extend, the properties of the resulting materials. Thus, we anticipate that with CAS, we will be able to build unprecedented, folded polymeric structures, which will retain their shapes in a large range of solvents and temperatures. We are currently investigating such bioinspired entities as selective catalysis (e.g. to replicate synthetic polymers or site-selectively functionalize proteins) and as the starting point to build exceptionally strong and flexible materials for defense applications. Given the central role molecular shape plays, however, in creating advanced, functional materials, it is not unlikely that other potential applications of CAS created structures could start to emerge via collaborations started at the MRS Workshop on Advanced Materials.

Afternoon Session II
3:50 PM – 4:10 PM

Bio-electrocatalytic CO_2 Reduction using Enzymes and Microorganisms

STEFANIE SCHLAGER
Johannes Kepler University
Linz Institute for Organic Solar Cells (LIOS)

In this work the electrochemical reduction of CO_2 using biological and biochemical catalysts such as bacteria and dehydrogenase enzymes is shown. The enzymatic reduction reactions of CO_2 using dehydrogenase enzymes is well known from natural processes and has been investigated by several groups. Ruschig et al. presented in 1976 the reduction of CO_2 to formate using formate dehydrogenase and NADH as electron and proton donor.[1] In works of Aresta et al. the reduction of CO_2 to carbon monoxide and methanol using dehydrogenase enzymes is discussed.[2,3] CO_2 is reduced to acids, aldehydes and finally alcohols in a three step reaction with each catalyzed by a different dehydrogenase and using the coenzyme Nicotinamideadenin dinucleotide (NADH) as sacrificial electron and hydrogen donor. We show the immobilization of these enzymes in an alginate matrix on a carbon felt electrode suitable for a reproducible CO_2 reduction without any sacrificial mediator such as NADH needed.[4] Reductions using dehydrogenase enzymes provide highly selective product generation. In another approach the application of microorganisms on such carbon felt electrodes gives the opportunity for a further selective CO_2 reduction.[5,6] Immobilized mixed cultures metabolize CO_2 to methane in an electrochemical system with CO_2 as only carbon-source and without any H_2 added artificially. Electrochemical measurements are shown and were performed for characterization and product generation in two compartment cells, using carbon felt electrodes modified with enzymes or microorganisms respectively as working electrode. Cyclic voltammograms are recorded for investigating electrochemical redox behaviour. Product generation is obtained by long-term electrolysis in potentiostatic mode. Results from analysis of liquid and gaseous products in ion chromatography, gas chromatography and liquid gas chromatography are depicted. The authors acknowledge for the funding the European Union and the county of Upper Austria for funding the Regio 13 project "REG-STORE", the Austrian Science Foundation FWF within the Wittgenstein Prize (Z222-N19) and FFG within CO2TRANSFER project (5148105).

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Afternoon Session II
4:10 PM – 4:40 PM

Title TBA
Rachael Oldinski
Bioengineering & Materials Science
University of Vermont

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POSTER SESSION

Visible Light Crosslinked Alginate Sub-Microspheres for Targeted Immunotherapy

SPENCER L. FENN, Tianxin Miao, Dimitry N. Krementsov, Rachael A. Oldinski
Bioengineering and Materials Science, University of Vermont

Poster Number: P001

Alginate microspheres have been investigated for drug delivery extracellularly, however, less attention has been focused on intracellular delivery mechanisms. Our goal is to design a drug delivery vehicle to internally deliver therapeutics to immune cells. In a previous study we demonstrated the ability to use alginate-based microspheres to intracellularly deliver bioactive therapeutics. While our preliminary experiments indicate that macrophages indeed readily take up microspheres in a mono-culture, it is unclear whether there would be any selectivity when other cell types are present. To address this, we investigated the selective uptake of alginate-based sub-microspheres (ASMs) in mixed cell cultures. Methacrylated alginate (Alg-MA) was synthesized by reacting sodium alginate (Protanal, FMC Biopolymer) with methacrylic anhydride in dimethyl sulfoxide. Aqueous solutions of Alg-MA were mixed with photoinitiators for visible green light activation (eosin Y, triethanolamine and 1-vinyl-2-pyrrolidinone). A 2% (w/v) Alg-MA solution was formed into microspheres using a water/oil emulsion and subsequent exposure to green light (530 nm) for 10 min. ASMs were labeled with Alexa Fluor® 647 Cadaverine. Dynamic light scattering quantified hydrodynamic diameters. Mixed cultures of primary murine splenocytes (a mixture of B cells (CD19+), T cells (CD3+), macrophages (CD11b+, CD3-, CD19-), DCs (CD11c+, CD3-, CD19-), and other cells (negative for all 4 markers)), were isolated from spleens of naïve C57BL/6 mice. Spleens were homogenized to a single cell suspension. Red blood cells were removed by hypotonic lysis, and the remaining leukocytes were washed, counted, and cultured in non-tissue culture treated 24 well plates at 500,000 cells per well overnight in DMEM-F12 with 10% FBS with the indicated concentrations of ASMs. Cells were then resuspended and analyzed by flow cytometry on a BD LSRII cytometer. Average diameters for the ASMs were between 300-450 nm. We measured uptake of ASMs by each cell type, and found that macrophages and dendritic cells (DCs) indeed take up our ASMs more efficiently compared to other cell types. At 100 µg/mL all cells became positive due to a high concentration and aggregate formation; however, uptake (or just stickiness/dye leaching, etc.) is likely non-specific. At 1 - 10 µg/mL internalization is more evident in the immune cells. B cells take the ASMs quite readily; however, at lower concentrations the macrophages and DCs are more efficient at internalizing the sub-microspheres, 10-15% of the macrophage and DC population internalized ASMs compared to 4% of B-cells at 1 µg/mL. In summary, size-selectivity of immune cells increased internalization of ASMs compared to other cell types in mixed culture at concentrations of 1 - 10 µg/mL. Future experiments will investigate enteric coatings comprising cell targeting moieties for optimizing immune cell internalization.

Exploration of Excitonic States in Alloyed Organo-Metallic Semiconducting Thin Films

LANE W. MANNING, Naveen Rawat, Randall Headrick, Rory Waterman, Madalina Furis, Arthur Woll

Poster Number: P002

Small organic molecules have come to the forefront in past decade when discussing new trends in fabricating and understanding the physics of organic electronic devices, in particular due to the record high electronic mobilities and exciton diffusion lengths reported for these systems. These molecules belong to an intermediate regime where excitons are neither fully localized on individual molecules like the Frenkel excitons of most molecular crystals nor fully delocalized like the Wannier excitons of inorganic semiconductors. Among these molecules are the ubiquitous aromatic systems, specifically the phthalocyanines (Pc), which represent viable test systems for investigating excitons in this intermediate regime due to their cost-effectiveness, broad visible absorption bands and chemical stability even after air exposure. Here we propose a radical new way of looking at excitonic behavior in organic crystalline semiconducting thin films, using substituted phthalocyanines derivatives as a case study. We focus on mixtures (alloys) of metal and metal-free Pc with octabutoxy side-chains (OBPc), fabricating films using a solution-processing, hollow pen-writing technique that produce millimeter sized grains with long range macroscopic order. The solutions used in thin film depositions contained Co, Ni, Mn, or CuOBPc molecules mixed in ratios with the metal-free Pcs (H_2OBPc) ranging from 1:1 to 1000:1. Excitons are investigated using temperature dependent absorption/transmission/linear dichroism and time and polarization- resolved photoluminescence (TRPL) spectroscopy. All optical characterization and grazing-incidence X-Ray scattering indicate a uniform mixing of the species is achieved in films without loss of the long range order previously observed in individual species. The spectroscopy experiments produced two important results that offer great insight into the fundamental quantum mechanics of delocalized excitons in small molecule semiconductors. First, they indicate that the delocalization of bandgap excitons extends over approximately 10s of lattice sites (~ 45 Å) and second, the presence of the metal-Pc molecule inside the metal-free Pc film introduces a radiative transition that may involve localized electronic states of both species. Low temperature, high magnetic field Magnetic Circular Dichroism (MCD) reveal some of these systems also exhibit enhanced magnetic exchange interactions mediated by the same delocalized exciton states. These studies also indicate that solution-processing deposition techniques in tandem with chemical synthesis design of small molecule soluble derivatives is a viable avenue for exploring organic analogues of alloyed systems such as SiGe or polar semiconductors such as GaAs where the role of conduction electrons is played by the delocalized π-electrons and the anion/cationroles are played by n-type/p-type derivatives within the same molecular family.

Transient phases during crystallization of solution-processed organic thin films

JING WAN,[1] Yang Li,[1] Jeffrey G. Ulbrandt,[1] Detlef-M. Smilgies,[2] Jonathan Hollin,[3] Adam C. Whalley,[3] Randall L. Headrick[1]

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Poster Number: **P003**

The electronic properties of organic semiconductor thin film are greatly influenced by the crystalline packing of molecules within each layer, which may depend on the processing methods and conditions. The crystallization mechanisms turn out to be both subtle and varied, with different behavior for different materials. Here we report an in-situ study of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C_8-BTBT) organic semiconductor thin film deposition from solution, which exhibits multiple transient phases during crystallization. Films were prepared with controllable grain size and morphology via hollow pen writing. Under very high writing speed (25 mm/s) the films have an isotropic morphology, although the mobilities can be fairly high, up to 3.0 $cm^2/V \cdot s$. To understand the crystallization in this highly non-equilibrium regime, we employ in-situ microbeam grazing incidence wide-angle X-ray scattering combined with optical video microscopy during deposition at different substrate temperatures. A sequence of crystallization was observed, in which a layered smectic liquid-crystalline (LC) phase of C_8-BTBT precedes inter-layer ordering. For films deposited above 80ºC, a transition from LC phase to a transient crystalline state that we denote as Cr1 occurs after a temperature-dependent incubation time, which is consistent with classical nucleation theory. After an additional short time (<1s), Cr1 transforms to the final stable structure Cr2. The sequential formation of LC→Cr1→Cr2 phases follows Ostwald's rule of stages. Based on these results, we demonstrate a method to produce extremely large crystalline grain size and high carrier mobility during high-speed processing by controlling the nucleation rate during the transformation between LC and solid phases.

Exploration of exciton delocalization in organic crystalline thin films

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Poster Number: P004

The electronic properties of organic semiconductors play a crucial role in designing new materials for specific applications. Our group recently found evidence for a rotation of molecular planes in phthalocyanines that is responsible for the disappearance of a delocalized exciton in these systems for $T > 150K$.[1] In this study, we attempt to tune the exciton delocalization of small organic molecules using two different methods: (1) strain effects, (2) alloying different molecules in the same family. The exciton behavior will be monitored using polarization resolved photolumniscence (PL) spectroscopy. Specifically, organic crystalline thin films of octabutoxy phthalocyanine (H_2OBPc), octyloxy phthalocyanines (H_2POC_8) and H-bonded semiconductors such as the quinacridone and indigo derivatives are deposited on flexible substrates (i.e. Kapton or polyimide and polyethylene napthalate also known as PEN) using an in-house developed pen-writing method[2] that results in crystalline films with macroscopic long range ordering and improved electronic properties. The 0.4% H_2OBPc deposited on Kapton of 75mm thickness indicates redshift and polarization change upon bending without cracking the film.

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A Novel Multi-Material 3D Printing Technology for Functionally Complex Prototypes

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Poster Number: **P005**

Rapid prototyping technology has advanced exponentially since the 1980's, specially, the development of small scale, homemade, additive manufacturing printers (3D printers). An synergistic online community evolved in the last 5 years and lines of open source rapid prototyping machines and accompanying software, such as the MakerBot, RepRap, PrintrBot, Slicer, and Repetier, have progressively appeared. Most of these machines and software present many limitations, such as mono-extruding and lack of accompanying software. The current study being presented is the alteration of a RepRap MultiColor's extruder assembly for the integration of a layer multiplying die. Previous works in simultaneous extrusion of polymers involves static and dynamic mixing of polymers for color mixing applications, whereas this study focuses on the implementation of a proof of concept layer multiplier mechanism that will allow the non-mixing extrusion of 2 materials. With this advanced capability in 3D printing, the potential application areas are limitless; for example, a functionally complex part which requires both highly conductive and dielectric layers (e.g., ultra-high density capacitor) can be printed with this new technology in a continuous manner. Another example is to manufacture a prototype with different degrees of stiffness and modulus within a part. So far no studies have been performed to address the feasibility of 3D printing using multi-material nano-layered filaments to create functionally tunable prototypes. By continuously controlling the ratios of layers A and B (potentially more materials can be introduced in the future) in the filaments, multi-phase nanostructures of functionally tunable materials can be created.

Measuring adhesion between modified asphalt binders and aggregate minerals using particle probe scanning force microscope

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Poster number: P006

Adhesion between asphalt binders and aggregates is important to the performance of asphalt mixtures. Polymeric modifiers are added to improve the performance of different binders. Thus, it is essential to quantitatively characterize the adhesion between the modified binders and aggregates. In this study, a scanning force microscope (SFM) with particle-modified probes was used to measure the adhesion between the controlled binder PG 64-22 and three modifications using styrene-butadiene rubber, polyphosphoric acid, and styrene butadiene styrene, respectively. Unit surface energy was used to distinguish the adhesion between corresponding modified binder and aggregates. Results showed that the alumina-binder adhesion increased as the weight percentage of the modifier increased. However, the adhesion between silica/calcium carbonate modified probes and binders was irregular. The surface morphology of modified binders has shown consistent variation in microscopic structures due to added modifiers.

In Situ Real Time Optical Spectroscopy Monitoring of TIPS-pentacene Thin Film Growth and Polymorphic Transformations during Hollow Pen Writing

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Poster Number: P007

The nucleation mechanisms during solution deposition of organic semiconductor thin films determine the grain morphology and may even influence the final crystalline polymorph. Here, in-situ optical spectromicroscopy in reflection mode is used to study the growth mechanisms and thermal stability of 6,13- bis(trisopropylsilylethynyl)-pentacene (TIPS-pentacene) thin films. The results show that the films form in a supersaturated state before transforming to a solid film. Molecular aggregates are observed by optical spectroscopy in this supersaturated region corresponding to subcritical nuclei in the crystallization process. During deposition on a heated substrate, a progressive blue shift of optical absorption peaks of the solid film is observed at higher deposition temperatures due to a continuous thermally driven change of the crystalline packing. As crystalline films are cooled to ambient temperature they becomes strained although cracking of thicker films is observed, which allows the strain to partially relax. Below a critical thickness of 30 nm, cracking is not observed and grazing incidence X-ray diffraction measurements confirm that the films are constrained to the lattice constants corresponding to the temperature at which they were deposited. Optical spectroscopy results show that the room temperature polymorph can even be strain-stabilized during annealing for temperatures up to at least 135˚C.

In Situ Visualization and Shear Stress Measurement Apparatus for Polymer Gas Mixtures

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Poster Number: P008

Many applications in bioengineering utilize materials with porous structures such as foamed polymers used in tissue engineering scaffolds. A more complete understanding of the manufacturing conditions used to produce these structures is needed for better control over final properties of foamed polymers, such as pore size, density, porosity, etc. The objective of our study was to develop a novel system to both observe and measure the local shear stress of gas saturated polymers under typical processing conditions (i.e., high pressures and temperatures). To accomplish this, the system would apply a uniform simple shear flow to a polymer sample saturated with an inert gas such as CO2 and N2 under high temperature and pressure. As the sample undergoes shear, the chamber would be quickly depressurized to create thermodynamic instabilities in the material to induce foaming. . Simultaneously, a capacitive shear stress transducer would be used to directly measure the local resultant shear stress on the surface of the sample. The chamber geometry would allow for the visualization of the foaming process and would be captured using a camera with high spacial and temporal resolution. The proposed system would provide new insights into the formation of foam structures in polymeric materials.

In-Situ Investigation of Nanocluster Deposition and Sintering using Synchrotron X-Ray Scattering

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Poster Number: P009

Nanocluster thin films are one of the simplest deposition systems, offering a way to observe fundamental surface and bulk processes with particles larger than individual atoms, but small enough to interact significantly with each other through mechanisms such as stress and surface mobility. A key mechanism affecting the properties is the ability of the nanoclusters to sinter upon contact with each other. In-Situ X-ray Reflectivity and Grazing Incidence Small Angle X-Ray Scattering (GISAXS) were used to monitor thin-films grown from Tungsten Disilicide (WSi2) and Copper (Cu) nanoclusters. The nanoclusters ranged in size from 2nm to 9nm diameter and were made by high-pressure magnetron sputtering via inert-gas condensation. X-Ray Reflectivity measurements of the film at various stages of growth reveal that the resulting films exhibit very low density, approaching 15% of bulk density. This is consistent with a simple off-lattice ballistic deposition model where particles stick at the point of first contact without further restructuring. We observe a small change of the shape of GISAXS spectra when the films are several particle layers thick, which we interpret as modest sintering at the contact points between particles. WSi2 Nanoclusters of a larger diameter (5-9 nm) show little to no sintering, while smaller diameter Nanoclusters (2.6 nm) show a modest effect. Copper Nanoclusters with a similar diameter (5 nm) to the larger WSi2 Nanoclusters showed a greater degree of sintering than WSi2.