Optimization and control of charge transport in nanostructured organic/inorganic composites

Organic/inorganic composites represent an exciting new class of electronic materials. They exhibit novel properties that can be tailored to specific applications through design and control of specific structural and electronic functionality in the constituents. Critical to the performance of these composites are the properties of the organic/inorganic interface. Tradeoffs between interfacial microstructure, and transport across the interface are common in organic/inorganic composites and the absence of a fundamental understanding of the role of interfacial microstructure on charge transport is limiting the performance of these materials.

Intellectual Merit: The goal of this project is to develop systematic surface modification strategies to improve charge transport between organics and inorganics. The proposed approach to solving this problem focuses on the first layer of organic molecules, strategies for creating beneficial layers, and for characterizing and optimizing the interaction of the layer with the inorganic surface and the organic constituent. Much of the research will be directed at developing surface molecular layers on an important class of inorganic electrodes, semiconducting oxides, with special emphasis on ZnO/polymer blends. These specific, well investigated, systems have intentionally been chosen to focus on the basic materials science of the interface, and how it changes as interfacial molecular layers are changed, without introducing too many other variables. The overall focus of this work, however, will be on developing design rules that can be then be applied to the broader class of oxide interfaces and organic constituents, simplifying future development of organic/inorganic composites. A broad set of advanced optical, structural and electronic characterization techniques will be applied to these systems to both develop an understanding of the properties of the specific functionalized surfaces under study, and to define a systematic approach to uncovering the interfacial electronic properties of organic/inorganic hybrids. The project includes a close collaboration with groups at the National Renewable Energy Laboratory and at the Los Alamos National Laboratory. The former bring strong expertise in semiconducting oxides and organic photovoltaics while the latter will assist in theoretical interpretation and modeling of results.

Broader Impacts: Organic/inorganic composites have the potential for creating electronic materials with entirely new functionality in energy efficiency, biological, medical, and environmental applications. This project will accelerate the development of these materials by providing fundamental understanding of one of the key issues limiting performance. The proposed project directly integrates research with education. Students and faculty will work with an existing outreach program at the Colorado School of Mines (CSM) aimed at Denver middle schools with large populations of under-represented groups. Modules which explore connections between microstructure and materials properties will be introduced into the middle schools. Assistance and guidance in developing the modules will be provided by colleagues at the IBM research division, and approaches developed during the project will be included in a summer middle school science recertification program taught by one of the Co-PIs.

The project will also include unique opportunities for graduate and undergraduate training in a highly interdisciplinary field. The students will work on a daily basis in an integrated team with their advisors, collaborators at the National Renewable Energy Laboratory (NREL) which is located in close proximity to CSM, and with scientists at Los Alamos. Involvement of undergraduate students in research, a focus on communication skills, and developing skills for work in a team environment are all integral parts of the proposed program.

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Introduction

Organic/inorganic composites represent a new and important class of electronic materials. Composites exhibit novel properties that can be tailored to specific applications. This is accomplished through design and control of specific structural and electronic functionality in the inorganic constituent (e.g. the size or composition of a quantum dot), the organic constituent (e.g. polymer ordering or chain length) or both. As examples, hybrid films composed of C60 derivatives dispersed in a polymer matrix hold the record for the highest efficiency polymeric photovoltaic (PV) devices.[1] Blends of organics with semiconductor quantum dots have also shown promise for improved efficiency and spectral control of organic light emitting diodes.[2] Considerable recent attention has also been devoted to bio-inorganic systems. Hydrogenase enzymes, for example, which are produced by microbial systems, are being actively studied as Pt replacement catalysts on carbon filaments in fuel cells.[3,4] A number of approaches to bio-conjugation of highly luminescent colloidal semiconductor quantum dots have been developed and are being explored as optical sensors for cell imaging and tracking,[5] DNA detection,[6,7] and fluoro-assays.[8]

Critical to the performance of these composites are the structural and electronic properties of the organic/inorganic interface. This is illustrated by our recent work on polymer/ZnO nanorod composite solar cells.[9,10] Optically generated excitons in semiconducting polymers are much more tightly bound than in their inorganic equivalents (e.g. silicon). To collect carriers the exciton must dissociate before it recombines and this typically happens at an interface. For the C60/polymer blend solar cells mentioned above, excitons created in the polymer diffuse to a C60 molecule and dissociate, with the electrons transferring to the C60.[11]

We have been exploring the use of ZnO nanofibers (Fig. 1a) as an alternative electron acceptor to C60 because collection of electrons, once the excitons dissociate, can occur directly through the higher mobility nanorods rather than requiring hopping from one C60 molecule to the next. For devices to work, however, the polymer must intercalate into the nanorod array. As can be seen in Fig. 1b, intercalation is seriously hindered by the hydrophilic nature of the ZnO surfaces, particularly the hexagonal growth surface. In spite of the unfavorable morphology, PV devices can made from composite films like those in Fig. 1b, but with efficiencies below the C60 blends. To address this problem, the ZnO nanorod surfaces were treated with phenyltrichlorosilane (PTS) to improve wetting by the polymer (Fig. 1c). Devices made from these films however, show poorer PV characteristics then untreated films with significantly reduced short circuit currents. While the interfacial layer improved wetting, it inhibited charge transfer.
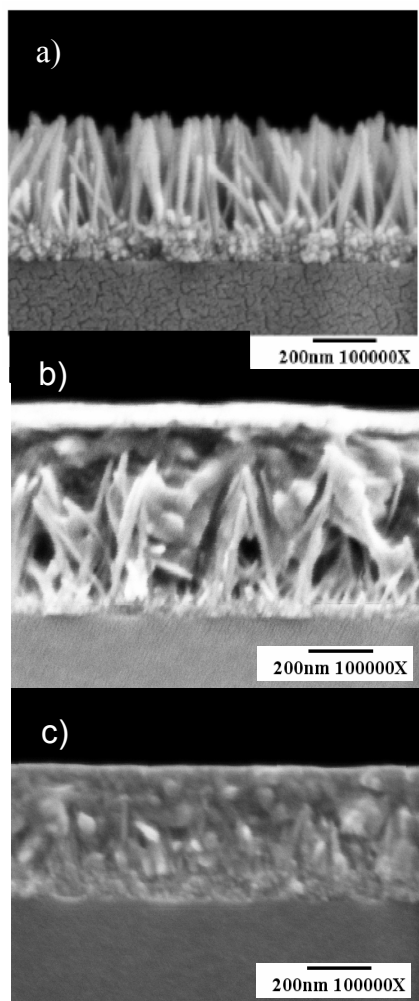

Figure 1 a) ZnO nanofiber network grown hydrothermally from a zinc nitrate solution. b) Nanofiber network intercalated with the polymer poly(3-hexylthiophene) (P3HT). c) Intercalation after surface treatment with phenyltrichlorosilane.

Tradeoffs between interfacial microstructure, and transport properties of the types described above are common in organic/inorganic composites. Much of the research, however, directed at controlling the organic/inorganic interface has investigated functionalization of the surface to address structural and stability issues, e.g. wetting, chemical stabilization, and dispersability with the hope that the charge transfer properties are not hindered. Issues that can arise in this approach include misalignment of molecular energy levels and energy bands at the interface, creation of interfacial charge transfer energy barriers, inefficient coupling of the conducting orbitals in the organic and inorganic, and low mobility (or insulating) interfacial layers.

Here we propose to develop systematic surface modification strategies to improve charge transport between organics and inorganics. We will focus on developing surface molecular layers in an important class of inorganic electrodes, semiconducting oxides. Initial work will explore terminations in ZnO, which, beyond its role in the organic solar cell, is a prototype material for other organic/inorganic applications. Nanostructured ZnO such as the quantum wires in Fig. 1 and quantum dots will also be used. The involved organics will be two common semiconducting polymers, poly(3-hexylthiophene) (P3HT) and poly(p-phenylene vinylene) (PPV). We have intentionally chosen this specific set of organic/inorganic interfaces to allow us to focus on the basic materials science of the interface, and how it changes as interfacial molecular layers are changed, without introducing too many other variables. The overall focus of this work, however, will be on developing design rules that can be then be applied to the broader class of oxide interfaces and organic constituents, simplifying future development of organic/inorganic composites. In the present case, once promising functionalizations have been developed in the ZnO systems, they will be tested on other oxide surfaces. As part of the project, a broad set of advanced optical, structural, analytical and electronic characterization techniques will be "married" with molecular modeling to both clarify the properties of specific functionalized surfaces under study, and to develop a systematic approach to uncovering the interfacial electronic properties of organic/inorganic interfaces.

Beyond the fundamental materials science goals of the project, success will accelerate the development of a novel new class of electronic materials. Organic/inorganic composites have the potential for low cost solution manufacturing, development of flexible electronics, and for creation of novel materials with entirely new functionality in energy efficiency, biological, environmental, and medical applications. Our proposal directly integrates research with education. We will develop novel teaching modules which introduce the basic connection between microstructural properties and macroscopic performance of materials. The students in the project will integrate the modules into an existing outreach program at the Colorado School of Mines (CSM) aimed at Denver middle schools with large populations of under-represented groups. Assistance and guidance in developing the modules will be provided by colleagues at the IBM research division, and approaches developed during the project will be included in a summer middle school science recertification program taught by one of the Co-PIs.

The project will also include unique opportunities for graduate and undergraduate research in an interdisciplinary field experiencing rapid growth. The students and faculty at CSM will work in an integrated team with collaborators at the National Renewable Energy Laboratory (NREL) which is located in close proximity to CSM, and at Los Alamos National Labs where theoretical modeling will be done. Involvement of undergraduate students in the project is considered a critical part of the educational experience of both graduate students, who will get the first experience in supervising, and undergrads alike. We also note that the PIs have a strong commitment to diversity. Both are involved in mentoring of women in science and have a history of recruiting under represented groups into their projects.

Research Plan

Zinc Oxide:

    <u>Background on Semiconducting Oxides</u>: The best known members of this group are the transparent conducting oxides (TCOs) which have sufficiently large bandgaps that they are transparent in the visible. From the standpoint of this project, working with semiconducting metal oxides has several advantages. They share similar surface chemistries making it more likely that a surface functionalization developed for one material will work with others. At the same time, electronic properties such as bandgap, work function, mobility, doping and carrier concentration can be tuned across fairly broad ranges. These oxides have also already shown considerable promise in organic/inorganic composites. In addition, a great deal is known about the properties and synthesis of semiconducting oxides (and TCOs in particular) since they are in heavy use as coatings for low emissivity windows and for transparent contacts in flat panel displays and solar cells.

    Historically, some of the most commonly used semiconducting oxides have been binary metal oxides such as TiO_2, SnO_2, ZnO, In_2O_3. Even within this small group of materials it is possible to choose from a range of work functions and bandgaps as shown in Fig. 2.[12,13,14] A word of caution is important here. Doping leads to variability in the bandgap. In addition, work function values are particularly sensitive to surface condition leading to large variation in reported values. As discussed below, we will exploit the sensitivity to dipole layers formed on the surface to tune oxide surface potentials.
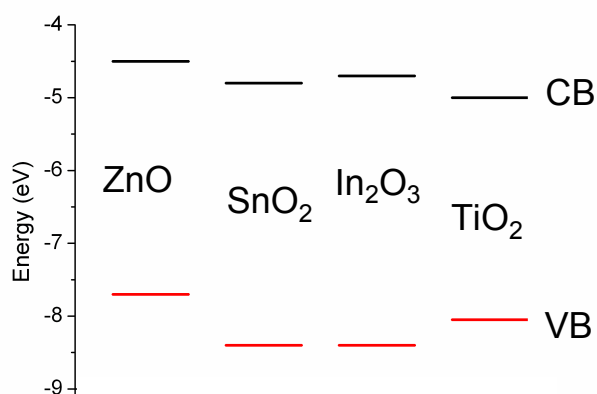
Figure 2 Band edges relative to vacuum for various binary transition metal oxides adapted from workfunction and band gap measurements in Refs. 12-14.

    Recent work directed at obtaining semiconducting oxides suitable for specialized applications has given rise to an expansion in the available metal oxides. Binary Cd and Ga containing TCOs have been explored along with ternary line compounds and alloys of most of the binary TCOs mentioned above. Cd_2SnO_4 for example, can be produced with nearly twice the mobility (>$50cm^2$/V-S) of conventional TCOs such as SnO_2.[15] Minami has investigated the properties of binary-binary and ternary TCO alloys and demonstrated work function and bandgap variations of over 1.0eV.[12] There has also been considerable interest in the catalytic behavior of metal oxides. Kudo et. al.[16] and Woodhouse et al.[17] have explored a broad range of metal oxides for photocatalytic water splitting as a way of producing hydrogen from sunlight. The later study used a combinatorial approach to screen many compositions and found materials with bandgaps below 1.5eV. This demonstrated ability to engineer oxides with specific electronic properties is one of the reasons they have found uses in a diverse range of applications. It also makes them good candidate materials for development of novel organic hybrids.

    Semiconducting oxides have also been materials of interest in organic/inorganic devices. An important example of an organic/transition metal oxide system is the dye sensitized solar cell.[18] In these devices an organic ruthenium bipyridal sensitizer (dye) coats a porous TiO_2 anatase network. The dye is anchored to the TiO_2 through carboxylated bipyridyl ligands. When the dye is optically excited, it rapidly injects an electron through the ligands into the TiO_2 conduction band. Dye

sensitization of TiO_2 has been studied extensively, good methods for dye attachment have been developed and a fairly complete picture of the structural and electronic requirements of the sensitizer-TiO_2 interface has emerged making this system an interesting source of ideas for surface treatments to be used in the present study as discussed below. TCOs, specifically indium tin oxide (ITO), are also the typical anode in organic light emitting diodes. Hole injection into the organic depends on alignment of the TCO Fermi level and of the HOMO energy level of the organic with larger work functions desirable for increased injection efficiency.

Our research will start with ZnO, and then move to other oxides as surface functionalization processes are developed and their effect on electronic properties tested. ZnO has several advantages over other oxides including the ability to control its conductivity from a nearly insulating material to essentially that of a metal. Undoped ZnO is typically oxygen deficient, a situation that leads to n-type conductivity. It can be doped to levels as high as $10^{21}/cm^3$ while maintaining optical transparency.[19] Reports of p-type conductivity in co-doped ZnO have been made.[20] There have also been recent studies of Mg doped ZnO which showed the gap can be increased from 3.2 to 3.4eV by the introduction of 5% Mg.[21] Work function has also been reported to have a strong dependence on doping.[12] These give additional parameters to tune in testing the effects on interface energetics of the surface treatments discussed below. We can also fabricate ZnO quantum dots and nanowires using low temperature solution synthesis techniques.[22] The wires in Fig. 1, for example, were grown hydrothermally on a ZnO seeded ITO substrate from a solution of zinc nitrate at pH 12 and 70°C. The synthesis process allows considerable control of nanorod geometry including fiber length, diameter and spacing.[10] Nanorods of other oxides can be prepared by similar methods on suitable substrates.

Zinc Oxide Surface Properties: Our focus will be the interface between organic electronic materials and metal oxides. Much is already known about metal oxide surfaces.[23] In the case of ZnO, the very different electronegativities of zinc and oxygen lead to antibonding orbitals that are localized near the cations, and bonding orbitals tend to be concentrated on the anion sites. Cation sites behave as Lewis acids, interacting readily with electron donors (such as water and ammonia) through electrostatic mechanisms (ion-dipole) and orbital overlap. The anion sites are basic, and so tend to form bonds with acceptors (such as hydrogen ions). The wurtzite structure of ZnO leads to polar and non-polar surfaces. The polar faces form perpendicular to the c-axis. A cleaved crystal separates into opposite sides having a zinc termination (0001) and an oxygen termination ($000\bar{1}$). So, it is the (0001) surface that shows the highest reactivity, not only toward water but also toward carboxylic acids.[24] By contrast, the O-terminated face has a greater tendency to form steps. The non-polar faces ($10\bar{1}0$) and ($11\bar{2}0$) have equal numbers of Zn and O atoms. But, the Zn ions relax away from the surface by a small amount. The different surface orientations also lead to different work functions (Φ), in the order $\Phi_{000\bar{1}} > \Phi_{10\bar{1}0} > \Phi_{0001}$.[25] This influences charge transfer at locally different sites.

Surface defects are common, with a trend toward oxygen vacancies. This tends to create an accumulation layer that is fairly shallow. It also leads to a situation under which the surface can be stabilized through water dissociation and its resulting hydroxylation.[26] Finally, as with most metal oxides, the surface properties of ZnO in air are influenced by adsorbed OH^- and H^+ and the resulting Bronsted acid-base chemistry.[27]

Charge Transfer at the Oxide/Organic Interface:

Motivation and approach: The polymer/ZnO heterojunction solar cell described in the introduction is an important prototype of the organic/inorganic composite and two examples from this system motivate our discussion. In the introduction we discussed treatment of ZnO nanorods with phenyltrichlorosilane to improve wetting of the metal oxide by the P3HT polymer. While the

treatment improved polymer intercalation (Fig. 1c), conversion efficiency performance was actually hurt.[10] This is a clear indication that the chemical modifier did not work as planned. A similar result was reached with surface chemical functionalization of another organic solar cell based on embedded ZnO nanoparticles.[28] In that case, the ZnO was treated with n-propylamine.

In the first of these two examples it was expected that the trichlorosilane end of the phenyltrichlorosilane would engage in a dehydration reaction resulting in a covalently-bonded polysiloxane network on the surface. This surface modification chemistry is commonly used to functionalize glass and oxidized silicon surfaces.[29] However, there are well-know problems with this approach. Trichlorosilanes are very reactive, particularly with water. There is a tendency for solution-phase polymerization to occur. Layers are still formed on the desired surface, but they frequently consist of globular, nonuniform films. More serious in the case of ZnO is the likelihood that the necessary surface hydroxyl groups were not present.[30] So, although the nanorods were coated with a layer that improved wetting by the polymer phase, the charge transfer characteristics of the surface modification were very poor.

In the second example, where n-propylamine was used, the surface chemistry was entirely different. It is likely that the molecules were adsorbed with the amine-terminated end facing the metal oxide through acid-base style bonding. However, the short alkane chain would not have promoted true self-assembly, as would be the case if longer chains had been used. On the other hand, longer chains would certainly have reduced the charge transfer properties of the system while the shorter chains might not be expected to inhibit transport. In fact, monolayers of aliphatic materials are now being explored as a replacement for inorganic oxides as an insulator in organic electronic devices.[31] Ultimately, it's not clear why the n-propylamine seemed to inhibit transport. This is a perfect example of an organic/inorganic composite electronic material system that suffers from lack of fundamental insight.

Motivated by the above examples, our approach to solving this problem focuses on the first layer of organic molecules, and strategies for characterizing the interaction of that layer with the metal oxide surface and organic and optimizing it. This can be viewed as chemical functionalization of the oxide. Through suitable manipulation of this first layer, it should be possible to achieve the best possible performance of the inorganic/organic boundary in an electronic device.

No matter what the particular application is, the chemical modification of metal oxides with organic monolayers always involves the same issues.[32]

- The molecules of the layer must be bonded to the oxide to enable efficient transfer of charge across the interface.
- The monolayer should be well ordered and uniform.
- The electronic properties of the monolayer should promote intra-molecular charge transfer, rather than barrier behavior.
- There should be favorable physical and electronic communication between the outer groups of the monolayer and the adjacent organic medium.

We will follow a plan designed to optimize these characteristics in the polymer/ZnO system. In the process, we will be assembling a valuable body of experience that can be applied to other interfaces between organic materials and nanostructured metal oxides.

Surface Modification Strategies: One of the most reliable ways to attach organic molecules to a metal oxide surface is through electrostatic bonding using carboxylate chemistry.[33] This method can be applied to ZnO.[34] To improve the attachment of the surface modification layer beyond that which can be achieved by simple electrostatic bonding, covalent bond chemistry is required. However, trichlorosilanes should be avoided. In addition, something needs to be done to the ZnO to ensure that polysiloxane networks really can form – and only at the surface, not in the bulk of the processing solution.

To achieve these goals we will do several things. We will use triethoxysilanes rather than trichlorosilanes. The former materials are much less reactive, and are not prone to coagulate by premature solution-phase polymerization. To enhance the surface reactivity, we will use a surface catalyst (n-butylamine). In our prior investigations, we have demonstrated that this combination of strategies leads to much more reliable processing and much higher quality monolayers (in the case of octadecyltriethoxysilane and other systems based on smaller molecules).[35] We expect this approach to significantly improve the coverage and uniformity of the surface modification. That is, by using phenyltriethoxysilane, together with the n-butylamine catalyst, we expect to avoid some of the more obvious problems of the simple treatment of ZnO with phenyltrichlorosilane. In addition, we need to properly prepare the ZnO surface. Unlike TiO$_2$, which is naturally hydroxylated, ZnO is not readily covered with OH groups. These are an essential feature of the dehydration reaction that leads to a two-dimensional siloxane network. To accomplish this, we will expose ZnO to above bandgap UV radiation to create surface oxygen vacancies. This has been shown to promote adsorption of atmospheric OH.[36] We'll use high energy photons from eximer laser flashlamps (~7eV), in close proximity to the ZnO, and then transfer the material to a controlled humidity atmosphere, prior to its introduction into the siloxane chemistry solution. With these methods we expect to achieve high-quality siloxane-based monolayers, not only of phenylsiloxane, but others as well.

Other surface attachment strategies will also be investigated, including phosphonic acid groups.[37] We would expect Zn-O-P to have good chemical stability, since P-OH groups react readily with hydroxylated Zn sites. So, the series of surface bonding tests for chemical modification of ZnO should involve a family of molecules such as: benzoic acid, phenyltriethoxysilane, and phenylphosphonic acid.[38] More exotic approaches will also be investigated. These involve two-step methods to alter the chemical nature of the ZnO to enable use of molecular layers that would not normally assemble on a metal oxide. For example, it's possible to deposit dimethyl zinc on the oxide, and then use thiols as the second layer.[39] So, as a member of our aromatic surface bonding series, we would use benzene thiol.

In a simplified view, many surface treatment molecules can thought of as composed of two parts, the oxide attachment group, and a terminating group with interacts with the organic component.[40] The later controls wetting and dispersion while both influence charge transport. To the degree that these things can be separated, looking at molecular species with the same surface attachment mechanism but different terminating groups will allow us to separate the effect of both groups on electronic and structural properties. It is probably easiest to use carboxylic acids for this study, so, we need to examine different organic acids, chosen for their favorable wetting, charge transfer, and interface energetics.
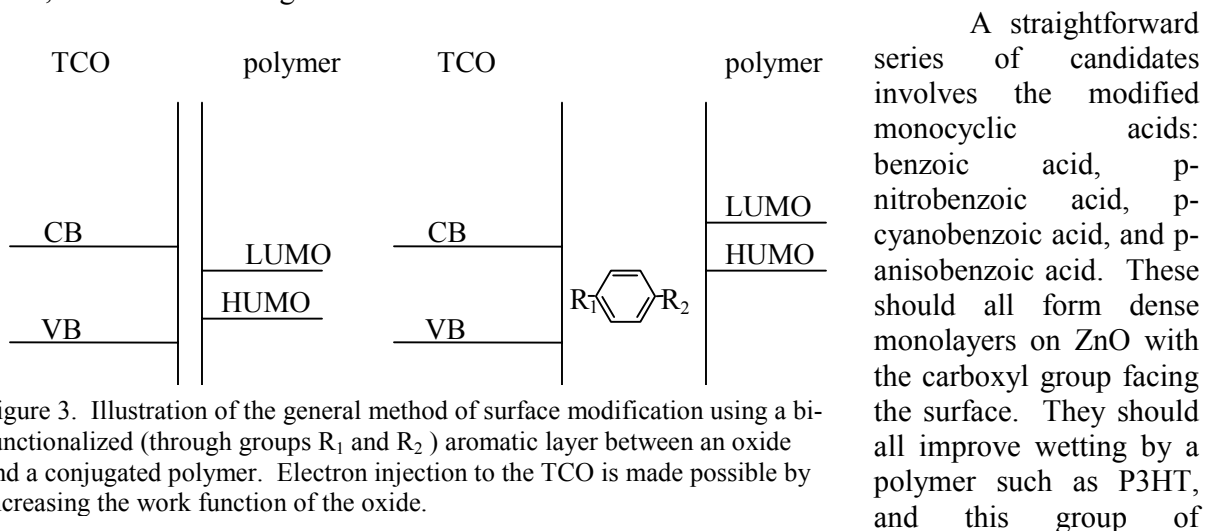
A straightforward series of candidates involves the modified monocyclic acids: benzoic acid, p-nitrobenzoic acid, p-cyanobenzoic acid, and p-anisobenzoic acid. These should all form dense monolayers on ZnO with the carboxyl group facing the surface. They should all improve wetting by a polymer such as P3HT, and this group of

Figure 3. Illustration of the general method of surface modification using a bi-functionalized (through groups R$_1$ and R$_2$) aromatic layer between an oxide and a conjugated polymer. Electron injection to the TCO is made possible by increasing the work function of the oxide.

molecules presents a range of dipole moments. The latter property should shift the effective work function of the oxide relative to the organic, influencing band alignment across the interface, and allowing energetics to be tuned for improved charge transfer efficiency as illustrated in Fig. 3. Systematic shifts of this type have previously been observed when molecular dipole layers are inserted at the metal organic interface in organic Schottky diodes.[41] The molecules we will use are all small, so, they should not contribute to barrier behavior, particularly since the orbitals in the benzene ring are delocalized pi states.

To move closer in molecular structure to poly(3-hexyltiophene) (P3HT), we can use 3-thiophene acetic acid,[42] a material that should promote intimate pi-orbital overlap with P3HT. An even closer analog can be achieved through a two-step surface modification approach. We should be able to cover the surface of ZnO with aminoacetic acid (glycene), followed by nesting of 3-hexylthiophene into the amino functionalized surface. A similar strategy has already been successfully applied to form monolayers of P3HT.[43] In that study the investigators formed an amino alkylsiloxane on silicon oxide. We will be interested in equivalent comparisons, using our optimized surface anchoring methods and shorter carbon chains.

Characterization

Approach: If the surface modification strategies described above are to be successful, a way of systematically investigating the structure, quality, chemical attachment configuration, molecular orientation distribution, surface energetics, and charge transfer characteristics of each process must be developed. This will help to identify the optimal strategy, which will certainly involve a mixture of our best ideas. However, this level of detailed study will only be applied to the most promising combinations. Our proposed program will treat each candidate in stages. The first experiments will use planar substrates, large area coverage, and basic interfacial studies to screen processes. These will begin with wetting experiments which will be correlated with atomic force microscopy (AFM) studies to identify processes that lead to expected chemical modification of the surface (e.g. hydrophbicity). Charge transfer energetics of promising systems will then be studied using the Kelvin probe method, electrochemical measurements and x-ray photoemission (XPS). At the second screening step, systems will be investigated with more sophisticated optical techniques such as photoluminescence (PL) quenching and transient absorption. We will also expand from planar substrates to nanostructured materials, wires and quantum dots, which are needed to create large interfacial areas suitable for the optical studies. Our objective in this stage will be to understand the interfacial electronic state alignment and surface chemical properties of the modified oxide. Finally, in the most detailed phase of our exploration, we will study the structure, bonding, and conformation of the best adsorbate/oxide combinations (using linear and nonlinear optical vibrational spectroscopies and optical reflection polarimetry), correlate this with charge transport, as well as perform quantum chemical modeling to determine the connection between microstructure, electronic and chemical properties, and performance. This overall strategy is a critically needed, systematic approach that will support intelligent engineering decisions involving organic/inorganic electronic materials development. More description of key techniques is given below.

Metal Oxide Samples: Initial work will begin with single crystals which can be purchased in various orientations.[44] The single crystal portion of our plan is important, since the surface characteristics of different orientations of ZnO are not the same. While single crystals will simplify analysis and interpretation of results, we will also work with thin film samples which are more consistent with the nanostructured configurations used in real devices. Oxide films at CSM will be prepared in a magnetron sputtering system recently purchased for oxide depositions by the Center for Solar and Electronic Materials. We will fabricate nanorod and nanoparticle oxide samples through existing solution synthesis techniques.[22, 45] An ongoing collaboration with David Ginley's group at NREL will be an integral part of the proposed project and particularly beneficial for preparation of

oxides. The NREL team is internationally recognized for their work on the properties and synthesis of oxides.[46] Through the collaboration, semiconducting oxide films prepared by alternative techniques such as laser ablation will be available for the work. In addition, the NREL group's deep understanding of oxide properties, film and nanoparticle synthesis techniques, of methods for characterizing oxides, and their work with organic solar cells, will be invaluable to the project. A letter of support from Dr. Ginley is attached as part of the supplementary information in this proposal

Planar Substrate Studies: The surface energies and wetting characteristics of the treated metal oxide will be determined through careful contact angle experiments involving both water and hexadecane. These are relative measures of the ability to form an effective nanoparticle composite, with, for example, a polymer, and also indicate the quality of the modified surface.[47]

It will be important to understand the physical topography of the modified surface. This will help to verify that true monolayer adsorption has taken place, and will also help us to understand the system's compatibility with the organic charge generation material. These are key properties in attempts to optimize organic/inorganic charge transfer.[48] We will use atomic force microscopy (AFM) to provide this information. Without this insight, we will not know if the modified surfaces are uniform.

Kelvin probe measurements of contact potential difference will provide quick screening of the effect of treatments on work function.[49] This will be followed by electrochemical methods which are one of the most direct methods of investigating charge transfer and energy state alignment. Ionic solutions, both aqueous and non-aqueous, make intimate and easily established contact with an electrode. The metal oxide surface can be biased with respect to a standard electrode using a three-electrode configuration. By controlling the bias, V_b, in the absence of a reduction-oxidation (redox) species in the solution, the space charge in the oxide, hence its capacitance C, can be altered. According to standard space charge theory (the Mott-Schottky model) the capacitance should follow $C^{-2} = (2/(\varepsilon\, e\, N_D\, A^2))(\, V_b - V_0 - kT/e)$, where ε is the dielectric constant of the oxide, e is the electron charge, A is the sample area, and V_0 is the *flat band* potential, measured with respect to the reference.[50] That is the condition where the space charge has been eliminated. By determining V_0 we establish the relative shift of the energy states between the oxide and an adjacent medium in the unbiased situation. This depends not only on work functions and ionization potentials, but also on the dipolar nature of the interface. The slope of C^{-2} versus V_b yields the surface carrier concentration N_D, from which the location of the Fermi level can be determined.[51] With that, the conduction band edge E_c is known and, through the band gap, the valence band edge E_v. All of this information can be studied with and without the surface chemical modifier. Surface inhomogeneity can complicate the interpretation of Mott-Schottky plots, but at this level of screening, it is an ideal approach, and refinements can be made in the final step when optical characterization gives direct information on surface variability.

One of our primary tools to understand interfacial energy states and their modification through organic monolayers will be x-ray photoemission (XPS). This has proven to be a valuable tool in optimizing organic light-emitting diodes.[52] By watching the zinc 3d levels and the oxygen 1s states as functions of the chemical modification we can tell how the adsorbate has modified not only the overall sample surface, but also the individual ions. This will help to verify and clarify bonding configurations and to aid the interpretations of the electrochemical energy level experiments. In addition, through energy distribution difference methods,[53] we can directly measure the location of filled states in the molecular adsorbate and can identify the crucial highest occupied molecular orbital (HOMO).

Optical characterization of charge transfer: Considerable effort has been devoted to understanding the charge transfer process which occurs at the interface between polymers and inorganic materials both in PV and in OLED applications. Optical techniques have proven invaluable in this work. One routine signature of charge transfer in a broad range of hybrid inorganic and organic (polymer, bioligand, etc.) materials is photoluminescence quenching. An example is given in Fig. 4 which shows absorption and PL spectra for the semiconducting polymer poly(p-phenylene vinylene) (PPV) and for a two PPV/SnO_2 nanoparticle blends. We find there is very little change in the shapes of the PPV absorption spectra as a result of adding SnO_2, but quenching of the PL is quite evident as seen in the figure. This is strongly indicative of exciton dissociation and charge transfer at the interface between the PPV and the benzyl capped SnO_2 nanoparticles. Interestingly, solar cells made from these blends do not work well, often not producing a rectifying device. Since charge transfer is clearly occurring, and dispersion of the dots in the polymer matrix appears to be better than with other oxide polymer blends which did yield working devices, we are not sure why performance is so poor. This underscores the need for basic studies of these interfaces, and suggests the SnO_2 PPV system as another interesting place to work.

PL quenching has become a common diagnostic used by the organic PV community (and members of our team) to improve and develop new polymer/inorganic blends.[54,55] In organic/inorganic heterojunction PV devices, the inorganic typically acts as an electron acceptor from the polymer. One of the critical questions addressed by the PL work is the energetic alignment of the conduction band in the inorganic nanoparticle and the LUMO level of the organic. In the present study, changing the relative alignment of 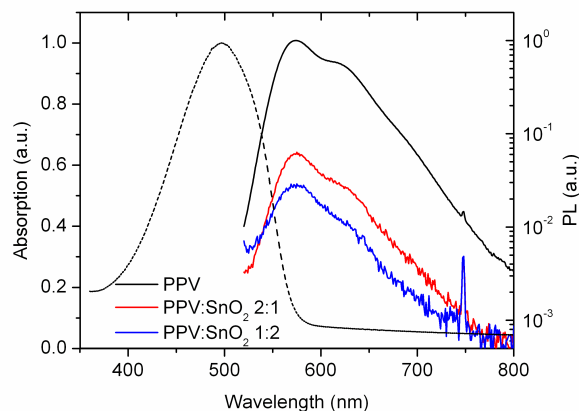these energies, or changing organic to inorganic coupling through surface functionalization, is expected to have a dramatic effect on charge transfer and hence on PL quenching. We note in passing such shifts also affect the operating voltages of PV devices. In organic PV studies, PL quenching is most easily observed in nanostructured systems such as the polymer quantum dot blend in Fig. 4 and polymer nanorod composites in Fig. 1. In the work proposed here we can test the effectiveness of surface functionalization by measuring quenching efficiency in such nanostructured systems.

Figure 4. Absorption (dashed) from poly(p-phenylene vinylene) (PPV) and PL (solid lines) from PPV and two SnO_2 nanoparticle PPV blends. The PL is on a log scale, and more than an order of magnitude quenching of the PPV luminescence is observed in the presence of the nanoparticles.

In systems where PL quenching is observed, photoinduced absorption (PIA) can help uncover the nature of the charge transfer process. In principle the experiment is straight forward. Spectrally resolved transmission is measured using standard techniques, e.g. FTIR or grating spectrophotometry. A pump source excites the sample, typically a laser with an energy above the fundamental optical transitions quenched in the PL experiment. The pump is modulated (or chopped) and the transmitted signal is detected synchronously with the pump to determine pump induced changes in the transmission spectrum. Polarization of pump and probe is controlled to produce both parallel and crossed geometries.

In quantum dot systems, PIA has identified photobleaching of interband transitions and associated appearance of infrared absorptions due to intersubband transitions between quantum confined states in the dots.[56] PIA in conjunction with other optical techniques has provided evidence for interaction of optically excited carriers with surface states in nanostructures.[57] In

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polymer/inorganic composites, changes in the PIA of the polymer in the absence or presence of inorganic acceptors has given a clear signature of exciton decomposition and charge transfer at the polymer interface.[58] In conjunction with PL quenching, this has helped identify potential alternative polymer/solid state nanostructure composites for high efficiency organic PVs. In analogy with the polymer work, in the study proposed here PIA of inorganic nanostructures (e.g. quantum dots and wires) will be measured with and without various surface terminations designed to enhance charge transfer. The goal will be to identify changes in the PIA spectrum that can be associated with the surface treatment and charge transfer. The spectral changes, and their dependence on excitation power and energy, temperature, and ambient (e.g. in a gas ambient or acid or base electrochemical solution), will assist in developing an understanding of the charge transfer process.

Ultimately, determining the kinetics of charge transport and the effect of the surface treatments on kinetics is a central goal of our work. Time resolved optical techniques have become routine in measurements of carrier kinetics in optically active systems. Time resolved PL lifetime measurements, for example, of nanostructured electrodes in the presence or absence of surface layers or the polymer matrix will help quantify the rate of PL quenching.

Transient absorption (TA) is a technique which has given information essential to our present understanding of charge separation in polymer/C60 blends.[59] TA is a time resolved form of PIA. A femtosecond laser pulse is split with one beam functioning as a pump, and the second used to produce a white light continuum which acts as a probe. After passing through the sample the probe is dispersed into a monochromator to give the transmission spectrum. The difference between the spectrum with and without the probe gives the photoinduced transmission. By delaying the arrival of the pump pulse with respect to the probe, time resolved photoinduced transmission (or absorption) spectra are obtained. In the polymer C60 system, photoinduced PIA was used to show charge separation occurs on a subpicosecond time scale, while reverse transfer, from the C60 back to the polymer occurs in the millisecond time domain.[59] In the present study, we can focus on PIA signatures that have already been identified in polymer/C60 and polymer/oxide nanoparticle systems. Changes in the characteristic time scale of transient absorption will then allow quantitative analysis of trends in exciton dissociation kinetics as a function of changes in surface treatments. These trends will be important, quantitative input into theoretical analysis of electronic coupling between the organic and inorganic interfaces

Detailed structural and bonding investigations: Using well-defined samples (primarily low-index surfaces of single crystals and off-axis-polished surfaces) with chemical modifiers deposited under controlled conditions, we will assay the best systems using optical spectroscopy, primarily those sensitive to vibrational modes. A vibrational spectrum provides a fingerprint of the molecular species at the interface. This is useful to determine bonding configurations, orientation distributions for specific molecular groups, the extent of order in larger molecules, molecule-molecule interactions, and environmental influences.

We will use high-sensitivity FTIR spectrometry to detect the vibrational spectra of monolayers adsorbed on polished and oriented single crystal wafers of ZnO. This will be accomplished with established differential transmission methods.[60] We will concentrate on aromatic carboxylic acids, which provide a rich collection of useful molecular group modes. The transmission IR technique also provides an excellent way to evaluate the influence of microstructure on the surface modification. That is, we can examine not only single crystals, but also polycrystalline thin films, as well as nanoparticles.[61] In the latter case, we would embed the particles in an IR-transparent host, such as an alkali halide pellet, by conventional sample preparation methods. We expect to identify surface attachment through carbonyl vibrations, to estimate molecular orientation with phenyl ring vibrations, and through these same modes to also evaluate the extent of orbital delocalization throughout the molecular layer.[62]

To obtain still more detailed insight about the surface modifiers, we will perform resonant surface vibrational sum frequency generation (SVSFG).[63] Nonlinear optical methods involve the combination, on the surface, of two intense optical fields from one or two laser beams. This leads to the generation of a third optical field, whose frequency is the sum of the input frequencies. The effect is driven by the second order optical susceptibility which is non-zero only in media where there is no inversion symmetry. Our prototype oxide, ZnO, has the wurtzite structure and consequently lacks inversion symmetry in its bulk. However, by using a well-oriented single crystal, the signal is a strong function of the directions of the optical fields. Conditions can be established under which the bulk contribution is zero.[64] This makes it possible to specifically study adsorbates.
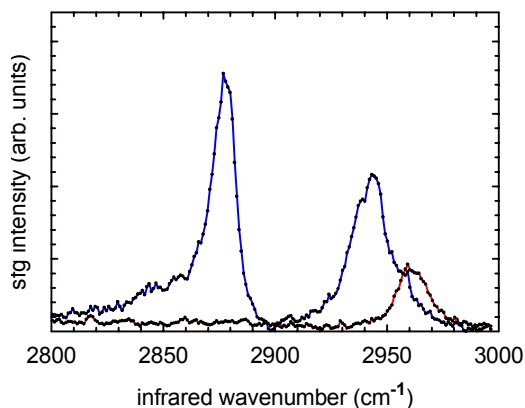

Figure 5. SFG spectrum of octadecylsiloxane on silica measured with two different optical polarization combinations. These modes come from the terminal methyl group.
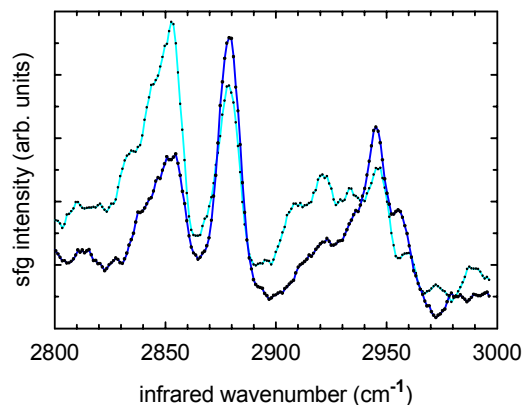
Figure 6. SFG spectrum of a defective octadecylsiloxane layer. Methylene modes associated with gauche defects are evident.

This experiment can provide information about the structure of the interfacial zone of not only a freely exposed surface, but also an oxide/electrolyte system, even one that contains the same molecular species in the liquid that is also adsorbed onto the surface. Through careful selection of the optical field directions, separate elements of the second order susceptibility can be determined, and, from these, average characteristics of a surface molecular distribution, such as the average angle of tilt (with respect to the surface normal) and the surface in-plane order parameter.[65] It is also important to note that the static electric field in the space charge region modifies the symmetry and can give rise to a new contribution to the nonlinear optical effect, which mixes coherently with the other parts of the signal. By minimizing this component, under electrochemical control, we can directly identify the flat band potential under a variety of conditions.[66] Sum-frequency generation spectroscopy is, therefore, an ideal tool with which to provide detailed information about the surface modifications that are critical to this project, including configurations in which band alignments can be adjusted. An example of this is shown in Fig. 5, which is the SVSFG spectrum of a silane coupled self-assembled monolayer recorded in our laboratory at CSM.[67] We learn from this that the chains are straight (all-trans), nearly vertical, and well-packed. If the layer is grown with a lower surface density then the alkane chains partially collapse. This breaks the inversion symmetry along the backbone where gauche defects are formed. Figure 6 shows a self-assembled layer in which these defects are prominent.

An additional measure of the modified surfaces will be gathered with variable angle spectroscopic ellipsometry (VASE). The method relies on careful modeling of the optical properties of not only the adsorbate, but also the substrate.[68] We expect to extract the photon energy dependence of the anisotropic complex dielectric function of the modifier layer. Comparisons

among the different types of molecules will be particularly valuable, and will help us to understand the interfacial energetics of charge transfer.

Theory and modeling

Molecular level theoretical understanding and computational analysis of the relationship between atomic structure and electronic properties at the interface are critical needs for the development of organic/inorganic composites. In the present case, theoretical modeling will help both with interpretation of experimental results, and with predictions of candidate surface terminations for improved interfacial charge transfer. This problem, however, is difficult because organic semiconductors, and interfaces involving these materials, are intermediate between ordered crystalline solids, which are described using the approaches of traditional condensed matter physics, and isolated molecules, which are described using the approaches of traditional quantum chemistry. Neither of these traditional approaches is completely adequate to describe these materials and new methods must be devised. Throughout the course of this project, we will collaborate closely with one of the few groups working at this boundary. It includes Darryl Smith, Ian Campbell, and Richard Martin at Los Alamos National Laboratory. In prior work this group has explored the effect on metal/organic Schottky barriers of attaching self assembled monolayers to the metal.[41,69] They were able to demonstrate barrier height shifts of over 1.0eV. They then applied *ab initio* quantum chemistry (Hartree-Fock) techniques to estimate the dipole moments of the monolayers. They showed that the dipole created at the surface drives the shift in barrier height. In the discussion above we have proposed similar approaches for controlling the workfunction of semiconducting oxides that provides a starting point for our work with the Los Alamos team. The PI has long history of collaboration with Darryl Smith at Los Alamos. In addition, the Los Alamos team has an active program in organic light emitting diodes that would profit significantly from the results of the proposed study. This strong overlap in interests will drive an effective collaboration. A letter of support from Darryl Smith has been included at the end of this grant. In the long term, the goal of this theory effort will be to develop a more general framework for modeling organic/inorganic composite interfaces that can be applied to the broad range of composites being developed.

Broader Impacts

Organic inorganic composites represent a novel new class of electronic materials which combine broadly tunable properties with low cost solution synthesis techniques. They hold the potential for advances in existing fields such as energy generation (photovoltaics and hydrogen production) and lighting (organic LEDs). They are also enabling for entirely new applications in, for example, computing (organic spintronics), biology (DNA identification and sorting), and even environmental cleanup where the possibility of creating optically active oxide nanoparticles which capture and then decompose organic contaminants through charge transfer driven oxidation or reduction is being explored. With all this promise, a key issue (in many instances *the* key issue) in these systems is the electronic nature of the interface and its impact on carrier transport. While the research proposed here is directed at particular organic/inorganic interfaces, the new techniques and systematic methodologies for characterizing and controlling interfaces that will be explored are aimed specifically at the charge transfer problem with the goal of accelerating the development of a much broader range of organic/inorganic electronic materials.

Education and Outreach

Outreach: CSM is well known for its support and active involvement in K-12 outreach. Through the Office of Special Programs and Continuing Education (SPACE), CSM reaches hundreds

of practicing teachers through an extensive short-course curriculum. Prof. Furtak participates in this effort through a class designed to familiarize middle and high school teachers with current aspects of science and technology in our everyday world. The course, called "How Things Work", has been very popular, as it provides teachers with ways they can reach their students through common phenomena and gadgets. The topics are based on light: emitters, controllers, detectors. The teachers learn about everything from light emitting diodes to liquid crystals. The best part is a kit of materials that the teachers use for classroom demonstrations.

The major portion of our education and outreach plan is a project under which our graduate and undergraduate students, with guidance from their faculty mentors, will develop hands-on classroom experiences targeting middle school students. The overriding goal will be to develop approaches for supplementing science education at this critical age both 1) to introduce the connection between the nanoscale structure, macroscopic properties, and applications of electronic materials and 2) to energize an interest in science and engineering at an early age. A secondary goal will be to improve the ability of involved graduate and undergraduate students to communicate the value and excitement of their fields to the public. Our work will build on and contribute to existing activities at CSM.

Module development (examples are described below) will take advantage of work by Dr. Laura Kosbar of IBM Research who has had considerable experience in middle school outreach programs at IBM. Her letter of support is included at the end of this proposal. After development, the modules will initially be implemented in conjunction with an NSF GK-12 Learning Partnerships project on the CSM campus. This project, run by Professor Barbara Moskal of the Department of Mathematics and Computer Science, has created collaborative teams that include a practicing teacher, a college faculty member, and a graduate student (referred to as a "Teaching Fellow"). The participating Denver area middle schools have large Hispanic student enrollment (55%), and the middle school teachers have a strong background in standards-based education and an expressed interest in bringing applications of mathematics, science and engineering to their students through hands-on classroom experiences. Each summer participating teachers and fellows attend a two-week summer workshop. These workshops are designed to provide the participants with content and pedagogical instruction in hands-on science, mathematics and engineering. Throughout the school year, the teaching fellows assist the participating teachers in implementing the hands-on activities in their classrooms.

The undergraduate and graduate students in the present project will work with Dr. Moskal's graduate fellows to implement the modules they develop. (A letter of support from Dr. Moskal has been included at the end of this grant). Drs. Moskal and Kosbar, who have worked with middle school teachers and have a strong knowledge of the middle school classroom, will provide on-going guidance to the Co-PIs and their students for the construction of units that are appropriate to the middle school classroom. It is important, for example, to align the module with the Colorado K-12 standards and benchmarks for science education. Colorado teachers must also be certified as "Highly Qualified" by 2006. The present GK-12 summer program provides five credit hours towards this certification and the new modules will be designed so this continues making participation much more attractive to the teachers.

Module development will begin in the 2006-2007 academic year. The professors and graduate students from the current proposal will present these units to the GK-12 teachers and fellows for the first time during the summer 2007 workshops. The investigators will further support the GK-12 project by: 1) holding follow-up sessions concerning microstructure and interfaces during Teaching Fellows workshops occurring throughout the academic year, 2) loaning materials to the teachers and teaching fellows to use in middle school classrooms and 3) having graduate students from the current proposal assist in implementing the new units at the local schools. The goal will be to provide sufficient assistance so the teachers will, subsequently, be able to implement the lessons

on their own. The researchers will also arrange for interested middle school teachers to visit the Co-PI's laboratories with their students. Many students from these schools have never visited a college campus, and we have found that the experience increases their interest in attending a university in the future.

An existing and classroom tested module that introduces the students to polymers will be extended to include properties of composite materials. Activities will include classroom participation exercises where students link hands to experience the mechanical implications of chain structure, cross-linking, and self-assembly found in common plastics. Students will then do a lab procedure mixing linear polymer vinyl acetate (Elmer's glue) with borax solution to produce a silly putty-like cross linked polymer. Other possible modules include: 1) exploration of sizes of "small things," where students rank a variety of objects in order of size (human hair, human cell, etc.) and are exposed to techniques used to make measurements from macro to nanosizes, 2) patterning materials where students are exposed to the technology of lithography including a lab procedure where they make their own mask from an overhead transparency and marker pens and lithographically transfer the pattern using photosensitive (blue) paper and sunlight, and 3) an exploration of Langmuir films where students dispense a known amount of oil onto the surface of water in a pan, measure the area of the oil on the surface (using equations for the area of a circle, etc.), and then calculate the surface area of each molecule in this very simple single monolayer system. Discussions leading from this simple experiment can include the size of molecules, the formation of monolayers, the chemical interactions leading to self-assembly, and the importance of this phenomenon for biological and nanoscale materials assembly.

Human Resource Development: The PIs have a history of positive experiences with undergraduate involvement in their research programs. Summer undergraduate (REU) support has been directly included in the budget to support this, and it is hoped more students may become involved through supplemental funding or support from the States of Colorado. In addition to participation in experiment design and discussion of results during group meetings, undergraduates will be asked to document their results at the end of the summer which helps hone their writing skills. In the past, undergraduates in our groups have participated in conferences such as the regional chapters of the AVS, APS, and ACS, and this will continue. Undergraduates in both of our groups have also been co-authors and, in some instances, principal authors on publications. We want to further encourage this in the present project. Development of communication skills, both for undergraduates and graduates, is a high priority for the Co-PIs. This will be emphasized in all aspects of the project extending from outreach activities to technical reporting in regular group meetings.

Undergraduate involvement also provides a unique learning experience for graduate students. Each undergraduate is paired with a graduate student who offers technical information and, ultimately, guidance to the direction of the work (in conjunction with supervision by the Co-PIs). Through this process, the graduate students gain experience with supervising someone who may be quite gifted, but does not possess their background. Former students often cite this experience as one of their best when reminiscing about their graduate career. Both undergraduates and graduates will learn to work in a team environment with members having a broad range of skill levels both in their research activities, and in the development of the K-12 outreach discussed above. The interdisciplinary nature of the present project, and ability to work not only in the PIs labs but also in laboratories at NREL, will make this team environment even more productive since students will be exposed to and work on problems that are outside of their traditional fields of expertise. Helping students develop a "bigger picture" view of science and training them to think beyond the facility restrictions of their own institutions is important to the co-PIs.

The Co-PI's are also firmly committed to diversity and have a history of involving women and minorities in their research programs. Both are actively involved in mentoring female faculty and graduate students as part of campus and departmental mentoring programs.

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Facilities and Equipment

A broad range of tools for materials growth, processing, electrical, optical, and nanoscale characterization are available through the Co-PI's laboratories at CSM, joint-use facilities in the Center for Solar and Electronic Materials, and shared CSM campus resources. Facilities particularly relevant to this project that are located at CSM are identified below:

1. Electronic materials processing lab with over 2000 sq-ft and facilities for thermal, e-beam, and sputter evaporation systems, oxide growth, dopant diffusion, RIE, probe stations, fume hoods, and a Class-1000 clean room with optical lithography tools, spin-on film deposition and programmable annealing stations.
2. Facilities for temperature dependent photoluminescence, electroluminescence and excitation spectroscopy including: High sensitivity LN2 cooled Si CCD detector. Roper Scientific and SPEX spectrometers. Close cycle and continuous flow cryostats. Lasers sources, including: CW Argon ion laser, CW tunable Ti-Sapphire laser, modelocked Nd:YAG laser, dye lasers, cavity dumper, a pulsed Nitrogen laser.
3. Gamry PCI4 potentiostat/impedance spectroscopy system for electrochemical control and capacitance measurements.
4. Vibrational sum-frequency generation spectrometer based on a nanosecond, Q-switched Nd YAG pulsed laser with a full set of frequency mixing crystals, coupled to a pulsed dye laser. The facility includes an 8-meter confocal cavity in a high-pressure hydrogen chamber for producing tunable coherent infrared radiation via the stimulated Raman effect.
5. Digital Instruments Nanoscope III AFM with contact, tapping, phase, electric and magnetic force modes.
6. Cary-V UV-Vis-NIR spectrophotometer for measurements of transmission, reflection, and absorption.
7. Bio-Rad FTS20/80 FTIR equipped with a liquid-nitrogen-cooled HgCdTe detector and an attenuated internal reflection attachment.
8. A Woollam variable-angle, spectroscopic ellipsometer designed for reflection and transmission polarimetry (to determine the full Jones matrix spectra) over a spectral range from 200 nm to 1700 nm.
9. Surface analysis including a Kratos Model HSi XPS with sample prep chamber.
10. Ultrafast science research laboratory. The laboratory features a broad array of laser systems, both for high-intensity laser science and nonlinear microscopy, coherent control of chemical processes, micromachining, spectroscopy, etc. With these laser sources ultrafast light is available across the spectrum-from 200 nm to 10 μm.
11. Near-Field Scanning Optical Microscopy. One system for transmission, reflection, photoluminescence, and photocurrent, and the second specialized for nanolithography and routine room temperature transmission and photocurrent studies. Facilities are available for preparing tips for the instruments.
12. Facilities for Raman spectroscopy include argon ion and krypton ion laser sources, Spex double pass and triple pass monchromators, high sensitivity CCD detectors, low dark count cooled photomultipliers, and a micro-Raman sampling
13. Micro-Transmission and Reflection Tool.
14. Microscopy facility including a FEI Quanta 600 ESEM with EDS, Philips CM200 STEM, and a SBT XLA2000 low angle ion mill. Funding for a new Field Emission SEM with nanolithography patterning capability has been awarded.

15. Thin film characterization equipment including a Tencor P10 surface profiler, a nanoindenter, and a Gaertner laser-based ellipsometer.
16. Electrical characterization including impedance spectroscopy and drive level capacitance profiling, Seebeck effect measurement system, two temperature-dependent Hall effect systems (Bio-Rad HL5500PC and Lakeshore 7507), I-V characterization, and PV quantum efficiency.
17. X-ray analysis facility, including small angle and glancing incidence measurements.
18. In addition to the above user facilities, the CSM Physics department maintains an electronics shop staffed by an electronics technician, and a well equipped machine shop which is operated by a highly skilled Instrument Maker.

In addition, through the National Renewable Energy Laboratory collaboration which is an integral part of this project, participants will have access to NREL facilities. Particularly important to the collaboration are:
1. Extensive synthesis and characterization capabilities for thin film oxides including pulsed laser and sputter deposition.
2. Expertise and tools for solution synthesis of oxide nanostructures (CSM team members already have a collaboration with the NREL group on oxide nanostructure fabrication).
3. Capability to produce and or modify films and nanostructures in a variety of controlled atmospheres. Several inert atmosphere dry boxes and vacuum lines are dedicated to this area. This allows deposition of polymeric films in controlled environments.
4. Extensive device/structure fabrication facilities and in particular, for fabrication of polymer solar cells and LEDs. This will allow optimized organic/inorganic composites generated in this study to be readily incorporated in test device structures. These devices can then be characterized providing direct feedback on the nature and quality of the structures generated.
5. In addition, the project will have access to a broad range of structural, optical, electronic, and analytical characterization equipment available in Dr. Ginley's group and as part of NREL user facilities.