Letter from the Center Director

With the projected increase in worldwide population to approximately 9 billion by 2040, and related infrastructural demands coupled with improvements in the quality of life of individuals around the globe, the consumption rate of energy promises to be more rapid than in prior decades. Most of this demand will come from the less developed nations, and less so from Europe and the US. The consumption portfolio between renewable and fossil fuel-based sources will differ from one part of the world to another and from country to country. This usage manifests a combination of drivers that include availability of resources, economics, scientific capabilities, technological and manufacturing infrastructure and public policy. Solar energy will play an important role in the future, due its natural abundance. Technologies such as thermoelectrics, which enable the capture of waste heat for subsequent use as electricity, will become increasingly important. Indeed enhancements in efficiencies of energy conversion technologies that are readily adaptable in any environment will continue to increase, thereby contributing cost reductions, and hence increased availability. Scientific progress around the world in areas including solar energy conversion and thermoelectrics has been quite significant during last few years; this is primarily due to significant investments in scientific research. Researchers in our energy frontier research center (EFRC),

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the Center for Solar and Thermal Energy Conversion (CSTEC), have been making important contributions to these areas, with notable scientific and technological breakthroughs.

Research at CSTEC is conducted in three areas, or thrusts: structure absorption and carrier transport in inorganic nanostructures (Thrust Area 1); thermal/electronic processes in inorganic systems (Thrust Area 2) and energy transport in organic and hybrid systems (Thrust Area 3). Several research themes cut across these main thrust areas, including organic and hybrid systems for TE, inorganic PV and TE materials, organic and hybrid PV and structure and transport at the nanoscale. To date CSTEC researchers have published over 150 papers in the best scientific journals in the world. These publications, encompassing aspects of organic and inorganic materials for photovoltaics and thermoelectrics, have been the result of a highly collaborative environment. At its inception, the goal of our center was the design and synthesis of new materials, based on the discovery of new phenomena, for high-efficiency PV and TE devices; our progress to date has enabled us to realize this goal.

This newsletter includes articles that describe examples of the discoveries of new phenomena and the associated development of new materials for efficient energy conversion. In order to provide a context for this information, one should recall that in thermoelectric devices, the primary goal is to minimize the thermal conductivity, $\kappa$, of the material and to maximize the combination of the charge carrier conductivity, $\sigma$, and the thermopower, $S$, such that $S^2\sigma$ is as large as possible. In this regard, the goal is to maximize the Figure of Merit $ZT=S^2\sigma/\kappa$. Significant challenges arise largely because the parameters $S$, $\sigma$ and $\kappa$ are interrelated. In the case of solar cells, the highest efficiencies for converting sunlight to electricity would be achieved by understanding and controlling fundamental mechanisms of the conversion process in order to minimize parasitic energy losses. For organic and inorganic materials in these devices, the challenges are fundamentally different due to differences between the nature of the interactions (bonding) and the structure, which influence the manner in which charges and energy are transported and indeed manipulated. When this center was established four years ago, we established a goal that through a collaboration between researchers working on organic and inorganic materials, and others working primarily on energy conversion devices, we would make major fundamental discoveries that would compel researchers to redefine the limits that would be achievable for energy conversion applications.

One of the major advances in our center occurred on two fronts. First, we can now literally control aspects of the molecular structure of the inorganic TE materials to maximize the efficiency. This is the result of theoretical and experimental advances, which were not possible even a year ago. Second, we also developed a new understanding of carrier transport processes in organic materials that enable us to understand how to develop organic-based thermoelectrics; this was not believed to be possible a few years ago. Other advances include the development of new organic materials, as well as processes to control the nanoscale morphology and hence device efficiencies. This newsletter highlights some of our discoveries and advances within CSTEC.

I conclude my letter by mentioning that researchers in the center conducted frequent and regularly scheduled collaborative meetings throughout the years; this culminated in three “all hands meetings” during the Spring of this year, 2013. These meetings, entirely organized by graduate students and postdocs, discussed scientific and technical advances developed within the center. The meetings provided a medium that enabled researchers in the center to plan effectively for the future.

Peter Green
Paint-on Plastic Electronics: Aligning Polymers for High Performance

Semiconducting polymers are an unruly bunch, but a new method for getting them in line could pave the way for cheaper, greener, “paint-on” plastic electronics. Prof. Jinsang Kim’s group recently developed and demonstrated a technique for creating high-performance semiconducting surfaces.

Semiconductors are the key ingredient for computer processors, solar cells, and LED displays, but they are expensive. Inorganic semiconductors like silicon require high temperatures in excess of 2,000 degrees Fahrenheit and costly vacuum systems for processing into electronics, but organic and plastic semiconductors can be prepared on a basic lab bench. The trouble is that charge carriers, like electrons, can’t move through plastics nearly as easily as they can move through inorganic semiconductors.

A semiconducting polymer molecule is like a short wire; together, these wires are randomly arranged in a thin film. Because charge mobility along the polymer chains is much faster than between the polymer molecules, research groups have been trying to align them into a charge-carrying freeway to take advantage of the good conduction along the polymer chains. However, it’s a bit like trying to arrange nanoscopic linguine.

Kim’s group approached the problem by making smarter semiconducting polymers. They wanted a liquid polymer solution that they could brush over a surface, and the molecules would automatically align with one another in the direction of the stroke, assembling into high-performance semiconducting thin-layer films.

Kim’s group of researchers designed the polymers to be slippery—ordinary polymers glom together like flat noodles left in the fridge. By choosing polymers with a natural twist, polymers do not stick to one another in the solution. But they didn’t want the polymers to be slippery all the time, so the polymer was also designed to untwist as the solvent dried up, becoming flat and ready to interact with adjacent polymers. In addition, they designed polymers not to form large chunks by adding flexible arms that extended off to the sides of the flat, wire-like polymer. These arms prevented too much close contact among the polymers while their bulkiness kept the arms from snagging on one another.

This molecular design principle for directed alignment of semiconducting polymer works very well indeed. Researchers made molecules that matched their design and built a device for spreading the polymer solution over surfaces such as glass or a flexible plastic film. The force from the silicon blade, moving at a constant speed across the liquid polymer, was enough to align the polymers. The team then built the semiconducting film into a simple transistor, a version of the electronic components that make up computer processors. The device demonstrated the importance of polymer alignment by showing that charge carriers moved 1,600 times faster in the direction parallel to the silicon blade’s brush-stroke than they did when crossing the direction of the stroke.

Even with this first attempt, using a polymer that wasn’t optimized for moving charges quickly, the charge carrier mobility was on par with the best reported plastic semiconductors. By combining the established molecular design principle with a polymer that has very good intrinsic charge carrier mobility, Kim’s group believes that a huge improvement in organic electronics can be achieved.

Further information may be found: Bong-Gi Kim, Eun Jeong Jeong, JongWon Chung, Sungbaek Seo, Bonwon Koo, and Jinsang Kim, “A molecular design principle of lyotropic liquid-crystalline conjugated polymers with directed alignment capability for plastic electronics,” Nature Mater. 12, 659 (2013). This article is based on U-M news article written by Kate McAlpine (kmca@umich.edu) http://www.ns.umich.edu/new/multimedia/slideshows/21325-paint-on-plastic-electronics-aligning-polymers-for-high-performance
Two-way Mirrors for Molecules

Invented in 1986 at Kodak, organic light emitting devices (OLEDs) are now increasingly finding applications in the newest generation of displays and, as the costs come down, in energy-efficient general illumination. In these applications, a voltage is applied to the OLED, electrical current flows in, and light comes out. A University of Michigan CSTEC team has discovered that for some configurations of the OLED, a kind of nanoscale two-way mirror can be built to electrically detect when new molecules enter the nanoscale surroundings of the device. This finding suggests a new generation of advanced sensors for biomedical, metrology, and other applications.

Typical OLEDs consist of extremely thin (~10-100 nanometers) organic films, layered between two similarly thin electrical conductors. As electrical current flows through the stack, with positive and negative charge injected from opposite electrodes, the organic molecules inside are excited, emitting light and heat. The proximity of excited molecules to the metal leads to efficient transfer of electromagnetic energy to the nanoscale “sea” of electrons in the metal contacts (creating “plasmon polaritons”), which in turn vibrate and create their own electromagnetic field that extends into the space directly adjacent to the metal surface (also termed “evanescent field”). For some material compositions and layer thicknesses, the electromagnetic field extends both inward and outward; the excited organic molecules inside the OLED can “see” themselves reflected in the mirror of the electrode, and receive information from the outside via electromagnetic interaction with the metal electrode.

By selecting the green-emitting aluminum tris-quinoline as the organic molecule to excite, and silver electrode layers of appropriate thickness (Figure 1), Agrawal, Sykes, and coworkers were able to achieve resonant coupling, a specific interaction between the excited molecules in the organic layer and the electrons in the electrodes, with the strength of the resonance being extremely sensitive to the environment on the air side of the outer metal electrode. When new molecules or other materials are introduced into the immediate (nanoscale) environment of the OLED, they perturb the evanescent electromagnetic field generated by the metal film. Through a complex physical mechanism suggested by the team, the proportion of electromagnetic radiation generated by the interior molecules that is reflected inward versus funneled into the metal electrode shifts and the effective electrical conduction properties of the organic layers change. As a result, the electrical current through the device changes in a detectable manner. The dynamic mechanism described above relies on optical interference inside the layered structure of the device, and exhibits oscillations that are predicted and experimentally measured by Agrawal, et al., with accompanying oscillations in the total electrical current at constant applied voltage (Figure 2). The scale of these oscillations amounts to nearly 15 percent of the total current, which is quite significant.

These findings suggest that a single probe can be built to both set off and monitor close-range energy exchange between the probe and the sample, potentially allowing researchers to build more compact and robust sensors with extremely high imaging resolution.

Additional information on this research can be found in the following publication:
Organic photovoltaic cells are often touted for their potential for extremely low-cost energy production, but the physics governing the energy conversion is still being discovered. These photovoltaics often suffer from either a low photocurrent or open circuit voltage; either deficiency severely limits the efficiency, and therefore, the usefulness of the technology. The Forrest group recently led an investigation that has revealed fundamental explanations for why a tradeoff in current and voltage is generally observed, and more importantly, has discovered a method for avoiding these losses.

Specifically, the Forrest group studied a class of strongly absorbing dye molecules called “squaraines” that can be made either amorphous or crystalline depending on how they are processed. These squaraines are paired with a fullerene to create a “heterojunction.” Devices made from highly disordered squaraine films tend to produce small currents and large voltages. When the same squaraine is crystallized (and hence very ordered), the current increases but the voltage drops. The result of these two situations is the well-known tradeoff between increased current and reduced voltage. The increase in photocurrent occurs because amorphous materials have poor molecular excited state (e.g. an “exciton”) and charge transport, while crystalline materials have greatly improved exciton and charge transport. A consequence of the efficient charge transport is that positive and negative charges concentrate at the heterojunction, which leads to encounters with each that reduces voltage following their recombination.

The trick is to understand how to decouple charge transport from recombination. A nanostructure that is crystalline in the bulk but disordered at the interface allows for efficient exciton transport, and hence a large current, while the disorder at the interface helps prevent positive and negative charges from easily finding each other, maintaining a large open circuit voltage.

Using nanostructural control methods developed in the Forrest lab, this optimum morphology was achieved in several squaraine-based solar cells. Inserting these cells into a tandem device consisting of two solar cells stacked in series results in solar power conversion efficiencies of 8.3 percent, which is among the highest published efficiency for a small molecule-based tandem photovoltaic cell to date. The improved efficiency of this rather counterintuitive structure marks a change in our understanding of the underlying physical processes governing solar-to-electrical energy conversion in organic solar cells.

Further information:
http://www.umich.edu/~ocm/
A New Processing Protocol for Polymer/Fullerene Organic Photovoltaic Devices

Despite the increasing use of inorganic semiconductors in photovoltaic cells, organic semiconductors have the potential for the fabrication of lightweight, flexible and low-cost photovoltaic devices. Organic photovoltaic devices based on a polymer/fullerene blend bulk heterojunction (BHJ) concept have received considerable attention. The BHJ consists of a mixture of donor (polymer)/acceptor (fullerene) materials cast from a common solvent. The performance of these devices is sensitive to the spatial organizational structure, length-scales and purity of the donor-rich and acceptor-rich phases of the photoactive layer. Several processing techniques that include thermal annealing, solvent annealing and solvent additives have been employed to control the nanoscale three-dimensional structure.

Recently, we proposed using supercritical carbon dioxide (scCO₂) as a processing technique—an environmentally friendly low-temperature alternative to the conventional high-temperature procedure for controlling the structure and morphology of the benchmark polymer solar cell system consisting of poly(3-hexylthiophene) (P3HT)/phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM).

In industry, scCO₂ has emerged as a viable and sustainable alternative to toxic organic solvents in polymer processing and synthesis because it is a nontoxic compressible solvent with tunable solvent properties. In addition, with a critical temperature of 31.1°C and critical pressure of 7.38 MPa, its supercritical region can be accessed quite easily. Furthermore, the solvent strength of scCO₂ can be regulated with fine changes to pressure and/or temperature, making it appealing for controlling the morphology of polymer thin films. This is one of the main reasons scCO₂ was used for this study.

Changes in the pressure and temperature in the range 6.2 MPa – 13.8 MPa and 35°C – 70°C respectively afforded the ability to achieve various morphological structures, characterized using a combination of energy filtered transmission electron microscopy, UV-vis spectroscopy and atomic force microscopy, of varying power conversion efficiencies. An optimum condition of 50°C, 10.34 MPa processed for 45 min, was achieved for the P3HT/PC₆₁BM system. While other scCO₂ conditions within the pressure and temperature ranges noted did not yield optimal performances, their efficiencies were better than those of the as-cast device, demonstrating the effectiveness of scCO₂ processing in improving device performance. In comparison with the conventional thermal annealed device at 150°C, the device at the optimum scCO₂ condition showed comparable device performance with similar nanoscale morphology and possessed larger fractions of photoactive regions.

This work indicates that low-temperature scCO₂ annealing can be used as a new strategy for improving device performance of polymer BHJ solar cells.

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Researchers from CSTEC have proposed a new way of achieving efficient thermoelectric materials through exploring the self-organizing nature of atoms and their bonding to block heat transfer. By integrating theoretical, computational and experimental approaches, new strategies to achieve low thermal conductivity in thermoelectric materials were identified and experimentally verified. The approach relies on disrupting atomic vibrations that govern heat transport by creating local atomic disorder through alloying on specific atomic sites. Suppression of heat transfer is one of the bottlenecks to achieving high efficiency in thermoelectric energy conversion devices. Increasing the efficiency of thermoelectric materials opens economical opportunities to collect waste heat in cars, trucks, and industrial processes and directly convert it to electricity. Efficient conversion of waste heat of cars and trucks would lead to improved gas mileage, with significant savings of fossil fuels.

The scientists have demonstrated that a specific group of atoms can be manipulated to yield particularly low values of thermal conductivity for the case of a particular family of prospective thermoelectric materials known as skutterudites, e.g., CoSb$_3$. The skutterudite structure is typified by the presence of near square rings of pnictogen (Sb) atoms, the vibrations of which represent the dominant contribution to the heat flow of the compound. They found out that replacing two Sb atoms with one atom each from the column IV and column VI elements, to achieve an average charge of two Sb atoms, is a very effective approach.

Quantum mechanical calculations were used to identify the most stable configurations of the structure. Subsequent molecular and lattice dynamics simulations established both the extent to which atoms can move at high temperatures and the values of the thermal conductivity. These efforts confirmed the decisive role of atomic order on heat transport, which was subsequently verified by experimental studies. This approach and resulting insights can be extended to other families of thermoelectric materials.

“The unique, collaborative environment made possible and nurtured by the Energy Frontier Research Center (EFRC) at the University of Michigan resulted in the identification of new opportunities to reduce heat conduction in thermoelectric materials,” said Ctirad Uher, C. Wilbur Peters Collegiate Professor of Physics.

“In this project, we identify that Ge/Te double substitution on the pnictogen rings in CoSb$_3$ is very effective in lowering the materials’ thermal conductivity and thus increasing their thermoelectric conversion efficiency.”

The research involves strong collaboration between experiment and theory, where the group led by Associate Professor Anton Van der Ven from Materials Science and Engineering computed the most stable configurations of the material, the group of Professor Massoud Kaviany from Mechanical Engineering carried out computations and simulations of the heat transport, and the group of Professor Uher from Physics synthesized the compounds and measured their thermal conductivity.

Please see the following paper for further information:
Thermoelectric materials can be used to turn waste heat into electricity and provide refrigeration without any liquid coolants, making them a very reliable means for energy conversion. Recently a CSTEC research team (Prof. Kevin Pipe and students Gunho Kim, Lei Shao and Kejia Zhang) has found a way to nearly double the energy conversion efficiency of a particular class of thermoelectric materials that is made with organic semiconductors.

Organic semiconductors are carbon-rich compounds that are relatively cheap, abundant, lightweight and tough, yet haven’t traditionally been considered candidate thermoelectric materials because they have been inefficient in carrying out the essential heat-to-electricity conversion process.

Today’s most efficient thermoelectric materials are made of relatively rare inorganic semiconductors such as bismuth, tellurium and selenium that are expensive, brittle and often toxic. Still, they manage to convert heat into electricity more than four times as efficiently as organic semiconductors created to date. This greater efficiency is reflected in a metric known by researchers as the thermoelectric figure-of-merit. This metric is approximately 1 near room temperature for state-of-the-art inorganic thermoelectric materials, but only 0.25 for organic semiconductors.

CSTEC researchers improved upon the state-of-the-art in organic semiconductors by 70 percent, achieving a figure-of-merit of 0.42 in PEDOT:PSS, which is nearly half as efficient as current inorganic semiconductor based thermoelectric materials.

PEDOT:PSS is a mixture of two polymers: the conjugated polymer PEDOT and the polyelectrolyte PSS. It has previously been used as a transparent electrode for devices such as organic LEDs and solar cells, as well as an antistatic agent for materials such as photographic films.

One of the ways scientists and engineers increase a material’s capacity for conducting electricity is to add impurities to it in a process known as doping. When these added ingredients, called dopants, bond to the host material, they give it an electrical carrier. Each of these additional carriers enhances the material’s electrical conductivity.

In PEDOT doped by PSS, however, only a small fraction of the PSS molecules actually bond to the host PEDOT; the rest of the PSS molecules do not become ionized and are inactive. Through a sophisticated model they developed for thermoelectric transport in organic semiconductors, the researchers found that these excess PSS molecules dramatically inhibit both the electrical conductivity and the thermoelectric performance of the material by pushing the PEDOT molecules further apart, making it harder for electrons to jump between PEDOT molecules. While ionized PSS molecules improve electrical conductivity, non-ionized PSS molecules reduce it.

To improve the material’s thermoelectric efficiency, the researchers restructured it at the nanoscale. They developed a method to use certain solvents to remove some of the non-ionized PSS dopant molecules from the mixture, leading to large increases in both the electrical conductivity and the thermoelectric energy conversion efficiency.

This particular organic thermoelectric material would be effective at temperatures up to approximately 250 degrees Fahrenheit.

Eventually this technology could lead to a flexible sheet—think of Saran Wrap—that can be rolled out or wrapped around a hot object to generate electricity or provide cooling.

New Polymers Efficiently Convert Heat to Electricity and Vice-Versa

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Combined figure shows an efficient 2-dimensional dedoping trajectory that not only optimizes carrier concentration but also reduces dopant volume.

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Figure shows the steep ascent of the dedoping trajectory along both n/N₀ and r_κ axes in the direction of maximum S²/σ.
Probing Atomic-Scale Heat Dissipation

In findings that could help overcome a major technological hurdle in the road toward smaller and more powerful electronics, an international research team involving CSTEC researchers, has elucidated the unique ways in which heat dissipates at the atomic scale.

A paper on the research is published in the June 13 edition of Nature.

When a current passes through a material that conducts electricity, it generates heat. Understanding where the temperature will rise in an electronic system helps engineers design reliable, high-performing computers, batteries and energy conversion devices, among others. While heat generation in larger circuits is well understood, classical physics can’t describe the relationship between heat and electricity at the ultimate end of the nanoscale—where devices have atomic-scale dimensions (~1 nanometer).

Using custom-fabricated scanning probes with integrated nanoscale thermocouples (shown in the first two panels of the figure), Prof. Reddy and colleagues elucidated atomic-scale heat dissipation phenomena for the first time and related the electronic structure of atomic-scale junctions to their heat dissipation characteristics. In order to accomplish this, researchers in Reddy’s lab—Woochul Lee, a doctoral student; Kyeongtae Kim, a postdoctoral fellow; and Wonho Jeong, a doctoral student—developed scanning probe techniques to create stable atomic-scale devices and designed and fabricated a stiff scanning probe with an integrated nanoscale thermometer that is capable of resolving sub milliKelvin temperature changes and sub nanowatt heat currents. Using this scanning probe, single molecules or atoms were trapped between the exterior gold layer of the probe and a thin film of gold deposited on a rigid substrate to study heat dissipation in prototypical molecular-scale circuits.

The last panel of the figure shows one of the key results obtained in this work: The heat dissipation in the electrodes of a molecular junction is asymmetric, i.e. unequal and dependent on the bias polarity. These asymmetries were also related to the identity of majority charge carriers (electrons vs. holes) in the molecular junctions using first principles density functional theory based calculations. This work established the validity of using the Landauer formalism, a mathematical approach for describing transport in nanoscale devices, to describe heat dissipation in several nano-/meso-scale systems where transport is predominantly elastic. Such systems include semiconductor nanowires, two-dimensional electron gases, semiconductor heterostructures, carbon nanotubes and graphene, among others, and are widely expected to play a central role in the creation of novel computing and information processing devices.

Researchers from the Universidad Autónoma de Madrid in Spain and the University of Konstanz in Germany also contributed to the work.

Publication:
A novel concept recently developed within the Kaviany group predicts that electricity-generated heat in a semiconductor can boost electric potential in a circuit, taking the processes that traditionally produce resistive losses and turning it into a gain in voltage.

In order to understand this idea, it helps to first know a little terminology. Electricity consists of electrons flowing along in the conduction band of a material. These electrons are free to move along because they have been given just enough extra energy to move from their normal home in the valence band up to the conduction band. This amount of energy is known as the band gap, and it is material-dependent. Heat, on a fundamental level, is simply interatomic vibrations that are known as phonons. A phonon can interact with an electron, boosting the electron’s energy for a short time, making it “excited.” The excited electron will only keep its extra energy for a very short period of time before it gives it off again and drops to its previous energy level.

This is where the usefulness of the heterobarrier comes in. If an excited electron traveling along in a semiconductor material of a given composition meets a sudden variation in material composition, a phonon absorption populates high-energy electrons, and this energy is converted to electric potential in barrier transition. The heterobarrier is higher than it was initially. This material architecture is called a heterobarrier—“hetero-” for the different material composition and “-barrier” for the energy barrier that the excited electrons are boosted over, creating a sudden change in the bandgap. After the sudden change in composition, a continued, gradual change in material composition keeps the electron moving along at this higher energy level, though the cost of moving the electron along does mean that the potential is decreasing slightly. If additional heterobarriers are introduced downstream, however, the electric potential can be further raised. Another especially useful facet of this energy conversion technique is that the type of phonons that are produced as heat in an electrical circuit (optical phonons) are the same type of phonons that work well to energize the electrons. Finally, an additional benefit is that heat is recycled, leaving less to be removed.

The Kaviany group used first principle calculations to develop their result, using gallium arsenide (GaAs) as the semiconductor and substituting aluminum for gallium in the compound to create the new material for the heterobarrier. Simulations show that 19 percent of phonon energy converts to electric potential.

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This work was supported as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences. Prof. Jinsang Kim’s group, also members of CSTEC, provided helpful assistance and discussions regarding sample preparation.


This work was also supported by a grant from the National Science Foundation.

This article is based on a U-M news release written by Nicole Casal Moore (ncmoore@umich.edu): http://www.ns.umich.edu/new/releases/21442-improving-materials-that-convert-heat-to-electricity-and-vice-versa


Probing Geometrically Unique Silsesquioxanes with Ultra-Fast Laser Spectroscopy

Silsesquioxanes (SQs), or small cages of alternating silicon and oxygen atoms, are of considerable interest for hybrid electronic and photonic materials applications for multiple reasons including high thermal stability, resistance to oxygen and 3D uniform structure. However, to date, their photophysical (e.g. light absorption, energy transport and fluorescence) properties and influence in solar cells have not been studied extensively, thus their potential remains conjecture. Their properties are important because they have the ability to improve current molecular-based solar devices, which suffer from short usage lifetimes, due to oxidation. As part of CSTEC, the Goodson and Laine groups have set out to understand these properties through advanced methods of synthesizing and separating molecules and characterizing them using spectroscopy. Here we describe the first known efforts to map structure-photophysical property relationships as a function of cage symmetry and size (e.g. 8, 10, 12 Si atoms). This work can be considered the first phase of mapping to establish baseline behavior in model systems before moving to more complex systems that build on the structure-property relationships shown here, for example, 9,9-dimethylfluorene polymeric systems.

Our initial experiments on synthesizing and characterizing silsesquioxanes explored the synthesis and photophysical properties of stilbene moieties (segments of molecules attached to corners) of mixed 8- and 10/12-Si cages of stilbenevinylSQs, where we saw unique results. Our research interests have since turned to the separation of the individual cage sizes (10 and 12 silicon, Figure 1), which was achieved through selective solubility/precipitation methods. We have now set out to understand the photophysical properties of those stilbenevinylSQs, characterized using single photon absorption, two-photon absorption, fluorescence emission and fluorescence lifetime kinetics—all tools for understanding energy transfer characteristics in these materials.

This first detailed photophysical study of the larger pure 10 and 12 silsesquioxane reveals that cage size and/or symmetry can strongly affect photophysical properties. The fluorescence behavior shows that these SQs offer excitation wavelength dependent emission (evidence of rare “red-edge” effects, Figure 2), which can be important for white light emission in light emitting diodes.

Figure 3 shows our observation of a decrease in the amount of energy transfer that is occurring in molecules with larger versus smaller cages, which is unexpected for an increasing number of chromophores (light absorbing/emitting groups off the corners of the cage). Discoveries like this are important in determining molecular design principles that would be optimal for these materials. Another interesting finding is that the 10 stilbenevinylSQ offers up to a 10-fold increase in two-photon absorption cross-section per chromophore over a free chromophore (no cage), signifying an increased ability to separate charges in the absorption process. This charge separation process is a vital characteristic of photovoltaic materials. In initial studies SQs have shown some promise as additives for stabilizing test solar...

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One of the key challenges being addressed by researchers at the Center for Solar and Thermal Energy Conversion is the 31 percent efficiency limit of conventional planar single-junction solar cells. Center researchers are pursuing several design strategies based on inorganic materials that could exceed that 31 percent efficiency limit, known collectively as third-generation designs. One such third-generation design is the hot carrier solar cell. In conventional solar cells based on inorganic semiconductors, only photons (packets of light) with certain energies can produce electrons that become useful for producing energy. Unfortunately, much of the light energy given to the electrons is rapidly lost to heat, limiting the efficiency of the solar cell. The principle of a hot carrier solar cell is to extract charge carriers (electrons and holes) prior to these thermal losses, so that each carrier extracted has a higher energy. This type of solar cell has the potential to achieve efficiencies in excess of 60 percent.

One requirement for hot carrier solar cells is that the electrons and holes must be extracted through energy selective contacts, which allow transport of carriers only within a very narrow range of energies. These energy selective contacts have usually been made using structures called “quantum dots.” Quantum dots are small chunks of semiconductor material, with dimensions in the range of 5–50 nanometers (1 nanometer = 10^9 m). The quantum dots are grown using a technique known as selective area epitaxy, in which the position and size of the quantum dots are controlled by making an array of holes through which the quantum dots can grow from gaseous precursors. For the hot carrier solar cells under investigation in CSTEC, the energy-selective contacts are made from periodic arrays of quantum dots made from the semiconductor material called gallium nitride (GaN). The actual carrier transport is controlled by an “active layer” of the semiconductor indium gallium nitride embedded in each quantum dot. Indium gallium nitride (InGaN) is similar to gallium nitride, but indium atoms take the place of approximately 15 percent of the gallium atoms in this case. To make sure these energy-selective contacts would work effectively, their ability to transport carriers within a narrow range of energies was probed using a technique called photoluminescence, in which photons of a higher energy shine on the quantum dots. This causes lower-energy photons to be emitted from the active layers, with a spread in energies that is a measure of how well the contacts will perform (a narrow range of energies is better). This testing showed that the range in energies was about twice as broad as expected based on the assumed shape of the active layers. Because of this difference, CSTEC researchers suspected the shape of the active layers might be different than they had assumed.

To develop a more realistic understanding of the active layer shape, a phase-field computational model was developed to simulate the growth of the quantum dots and embedded active layers. Phase-field models represent which phase the system is in at each point of the simulation volume using a variable known as an order parameter; in this model, the order parameter is used to determine whether the system is in the solid (GaN/InGaN) or vapor phase. Simulation parameters were varied until the best match was observed between simulation and experiments in order to calibrate the model. Then the simulation parameters were varied in a parametric study to investigate the effect of selective area epitaxy growth conditions on thickness.
cell devices. These findings show that the size and geometric orientation of these cages drive their different and specific properties, identifying SQs as a separate class of compounds/materials that can be anticipated to offer novel properties of value in developing new components for electronic and photonic applications.

Our future work will continue to build up the understanding of synthetic methods for made-to-order SQ cage sizes and functionality, as well as develop new materials toward many applications. These materials may include polymeric derivatives, which would allow for better processing for incorporation in devices, or alterations to the corner groups attached to the cages containing more complex systems.

For further information please see:

Jae Hwan Jung, Joseph C. Furgal, Sarah Clark, Matthew C. Schwartz, Kathleen Chou, and Richard M. Laine, “Beads on a Chain (BoC) Polymers with Model Dendronized Beads. Copolymerization of t-[4-NH2C6H4SiO1.5]6(IPhSiO1.5)2 with 1,4-Diethynylbenzene (DEB) Gives Through Chain, Extended 3-D Conjugation in the Excited State That is an Average of the Corresponding Homopolymers,” Macromolecules 46, 7580 (2013).

For more information, see:
Third Annual CSTEC External Workshop
October 2, 2012

External workshops serve as a catalyst for optimizing CSTEC’s research focus through the insights communicated by the advisory board members in attendance. Our most recent review featured overview talks by thrust group leaders, presentations by graduate students and post-doctoral fellows, and a poster session.

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Dr. Sheila G. Bailey*, Senior Physicist at NASA Glenn Research Center

Dr. David Eaglesham, CEO at Pellion Technologies

Dr. Alex K.-Y. Jen*, Boeing/Johnson Professor of Materials Science and Engineering and Director, Institute of Advanced Materials and Technology at the University of Washington

Dr. Lawrence Kazmerski*, Executive Director of Science and Technology Partnerships at the US National Renewable Energy Laboratory

Dr. Venkatesh Narayanamurti, Benjamin Peirce Professor of Technology and Public Policy and Professor of Physics, Director of Science, Technology and Public Policy program at Belfer Center, Harvard Kennedy School at Harvard University

Dr. Ali Shakouri*, Mary Jo and Robert L. Kirk Director of the Birck Nanotechnology Center, Professor of Electrical and Computer Engineering at Purdue University

Dr. Jeff Y. Tsao*, Principal scientist at Sandia National Laboratories.

CSTEC All-Hands Meetings
February, April, and May 2013

CSTEC incorporated three internal meetings into its schedule this year, with each researcher in CSTEC encouraged to attend every meeting. The focus in February was on energy transport in organic and hybrid systems. In April, presentations discussed thermal/electronic processes in inorganic systems. The gathering in May emphasized carrier transport and absorption in inorganic nanostructures. Every meeting began with a tutorial lecture that presented the foundational principles integral to the topic of the day. Then, following lunch, seven to eight graduate students or post-doctoral fellows talked about their projects. Investigators enthusiastically listened to some groundbreaking research and to the efforts of collaborations between research groups that crossed disciplines and campuses. Some of the efforts discussed at these All-Hands meetings are also featured in this newsletter.

Graduate students and postdoctoral fellows presented talks at both the external and internal workshops.
Awards

Awards and Recognition

Stephen R. Forrest was named the Thompson-Reuters Top 100 Cited Materials Scientists 2000–2010 (Rank #13). In addition, the Stephen R. Forrest chair in Electrical Engineering was established at Princeton University.

Rachel S. Goldman was elected Fellow of the American Vacuum Society and Fellow of the American Physical Society.

Peter Green was elected a Fellow of the Royal Society of Chemistry (FRSC) and was Chair of the Panel on Neutron Research, National Academy of Sciences.

Massoud Kaviany was awarded the 75th Anniversary Medal, Heat Transfer Division, American Society of Mechanical Engineers.

Manos Kioupakis received an Early Faculty Career Development (CAREER) Award from the National Science Foundation.

Nicholas A. Kotov was elected Fellow of the Royal Society of Chemistry (RSC) and received the Langmuir Lecturer Award from the American Chemical Society (ACS).

Richard M. Laine received the International Award from the Society for Polymer Science of Japan (SPSJ).

Anne McNeil received the Camille and Henry Dreyfus Teacher Scholar Award from the Camille and Henry Dreyfus Foundation.

University of Michigan Awards

Jinsang Kim received the Outstanding Accomplishment Award from the Materials Science and Engineering Department.

Anne McNeil received the Class of 1923 Memorial Teaching Award.

Graduate Student Awards

Joong Hwan Bahng won the MRS Science as Art award (Gran Prix).

Kyeongwoon Chung received 2013 Rackham International Student Fellowship.

Brian Roberts won the best poster award from the 39th IEEE Photovoltaic Specialists Conference.

Seid Sadat was awarded U-M’s Richard and Eleanor Towner Prize for Outstanding PhD Research.

2013–14
CSTEC Colloquium


Oct. 28 Dr. Jihui Yang, University of Washington The Tale of Minority Carriers for Thermoelectrics

Nov. 4 Dr. Manos Kioupakis, University of Michigan Electronic Structure Calculations of Materials for Energy

Dec. 12 Dr. Mercouri Kanatzidis, Northwestern University All-scale Thermoelectrics for Power Generation from Heat

Jan. 16 Dr. Peter Rossky, University of Texas Exciton Migration and Dissociation in Conjugated Molecular Materials

Feb. 13 Dr. Alberto Salleo, Stanford University How does Microstructure Affect Charge Generation and Transport in Polymer-based Photovoltaics?

Feb. 27 Dr. Else Reichmanis, Georgia Institute of Technology Charge Transport and Polymeric Semiconductors: The Role of Molecular Ordering

Mar. 13 Dr. Malika Jeffries-El, Iowa State University Tuning the Properties of Organic Semiconductors via Atomic Engineering

Mar. 27 Dr. Ali Shakouri, Purdue University Ballistic and Diffusive Thermal and Thermoelectric Transport