

[1]

Plastic Scintillators based on Polystyrene-TADF-Bismuth Ternary Systems for Gamma- Spectroscopy

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Abstract

To advance autonomous radiological and nuclear (RN) search capabilities for countering nuclear threats, we have developed a series of plastic scintillators based on polystyrene loaded with high-Z material-triphenylbismuth, and a light-emitting molecule-2CZPN, displaying thermally activated delayed fluorescence (TADF). TADF-emitters can harvest 100% of the excitons produced in them through efficient reverse intersystem crossing at room temperature. This makes them an attractive class of materials for the development of low-cost plastic scintillators. Preliminary investigations explore the polymerization of styrene monomer mixed with different compositions of a standard fluorophore- 9,10-diphenylanthracene, 2CZPN and triphenylbismuth, reveal the phase stability of the plastic scintillators. UV excitation experiments on scintillators show that they are blue emitting and could be potential candidates for gamma-spectroscopy.

[2]

Titanium Oxide Hydrates as Optically Versatile Species in Inorganic-Organic Hybrid Materials

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Abstract

Inorganic-organic hybrids allow for the modification of physical properties and the addition of new features in polymer-based systems, and thus have received great interest. For example, the addition of a higher refractive index inorganic species into an organic polymer allows for the increase of the refractive index of the final material beyond that of the indices reached with polymers alone. Most hybrids (or nanocomposites), however, commonly suffer from absorption and/or scattering losses due to the nature and size of the inorganic species. We demonstrate here that titanium oxide hydrates are highly versatile inorganic 'fillers' in polymer-based hybrids. Titanium oxide hydrates are typically used as precursors for crystalline TiO₂, a well-known material used in a wide range of applications due to its moderate price, biocompatibility, and efficient photo-catalytic property. Beneficially, using the hydrate also allows for the creation of versatile, low-temperature, sol-gel processed hybrids. We show that these hydrates increase the refractive index of hybrid materials with no or minimal optical loss. Using organic species that contain several hydroxyl moieties appear, thereby, to have a stabilizing effect on the titanium oxide hydrates. Such 'matrices' can also create an oxygen barrier to the Ti-species. This oxygen barrier is advantageous for inducing a strong photo-catalytic response of Ti(IV) to Ti(III) in such hybrid films because it limits the re-oxidation of Ti(III) in air. The high transparency in the visible and near-infrared range could also prove useful for producing low-loss photonic structures to aid and improve light management. Because of the solution-processability of the hybrids, such light-management structures promise to be readily implemented in devices such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs), providing pathways to increase their overall performance, device efficiency and, potentially, long term stability.

[3]

Organic Photodiodes for Wearable Sensing Platforms

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Abstract

We demonstrate a high-performance photodetector using organic photodiodes (OPDs) with ultra-low dark current values. The OPDs achieve a shot-noise dominated specific value of 10^{14} Jones that are comparable to those of low-noise inorganic counterparts but at lower voltage and room temperature operation. In addition, rigid inorganic photodetectors introduce challenges for developing reliable and soft wearable electronics. OPDs can be fabricated into devices with a flexible form factor using coating and printing techniques that are scalable with ease of process.

[4]

Color Control in Ultra High Contrast Anodically Coloring Electrochromics

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Abstract

Electrochromism is the change of a material's color upon the application of an electrochemical potential. These materials have prospective uses in full color passive displays, energy saving tinted windows, and dimmable visors for military and/or recreational use. Organic polymer electrochromes have the benefits of being solution processable, lightweight, and flexible, however, most of these materials are cathodically coloring (colored in the neutral state and oxidize to be transmissive). This approach gives an inherent limit to the materials' optical contrasts due to broad absorbance of the oxidized state. Anodically coloring organic electrochromic materials are comprised of discrete chromophores that are UV absorbing in the neutral state which upon oxidation form broadly absorbing, colored radical species. In this work we examine how color can be controlled in these systems. We show that in anodically coloring systems color control is achieved by adjusting the singly occupied molecular orbitals (SOMO). Here we introduce novel UV absorbing discrete chromophores based on a 2-thiomethyl-dioxythiophene coupled to a 4-methoxyphenylene. We show that SOMO control is achieved by readily tuning the substitution pattern on the phenylene moiety, leading to radical cations that absorb across the visible spectrum.

[5]

Effect of Heteroatom and Doping on the Thermoelectric Properties of Poly(3-alkylchalcogenophenes)

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Abstract

Polymer thermoelectric materials have garnered interest for energy harvesting applications and solid-state cooling because they are lightweight, flexible, and have an inherently low thermal conductivity. Despite these advantages, many intrinsic semiconducting polymers are not electrically conducting enough for thermoelectric applications. To our knowledge, there has not been a systematic study correlating the identity of the heteroatom in polyheterocycles with (i) the doping process, (ii) the resulting thermoelectric properties, and (iii) the charge transport mechanism. We report on the thermoelectric properties of poly(3-alkylchalcogenophene) as a function of heteroatom (sulfur, selenium, tellurium), and how these properties change with dopant (ferric chloride) concentration. UV-Vis-NIR spectroscopy shows that polaronic charge carriers are formed upon doping. Poly(3-alkyltellurophene) (P3RTe) is most easily doped followed by poly(3-alkylselenophene) (P3RSe) and poly(3-alkylthiophene) (P3RT). Thermoelectric properties vary as functions of the heteroatom and doping level. At low dopant concentrations (~1 mM), P3RTe shows the highest power factor of $10 \mu\text{W m}^{-1} \text{K}^{-2}$, while, at higher dopant concentrations (~5 mM), P3RSe shows the highest power factor of $13 \mu\text{W m}^{-1} \text{K}^{-2}$. Most notably, we find that the measured properties are consistent with Mott's polaron hopping model and not consistent with other transport models. Additionally, temperature dependent conductivity measurements show that for a given dopant concentration, the activation energies for electronic transport decrease as the heteroatom is changed from sulfur to selenium to tellurium. Overall, this work presents a systematic study of poly(chalcogenophenes) and indicates the potential of polymers beyond P3HT by tuning the heteroatom and doping level for optimized thermoelectric performance.

[6]

Novel Organic Field Effect Transistor (OFET)-Based Photodetector for Radiation Detection

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Abstract

We have demonstrated a new concept of organic photodetector based on organic field-effect transistors (OFETs), which show remarkable thermal, environmental, and long-term operational stability that is comparable or superior to that of commercial inorganic FET technologies. This novel organic photodetector achieves hundreds of times higher responsivity than the state-of-the-art organic photodiode at low optical power (below 10 nW). By calculating the responsivity using the theoretical model, we believe that when combined with plastic scintillators there is a simple path to develop large-area, low-cost, and light-weight radiation detectors.

[7]

Effect of Counterion Exchange of Conjugated Polyelectrolytes in Organic Electrochemical TransistorsBrian Khau and Elsa ReichmanisGeorgia Institute of Technology
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The palette of mixed ionic-electronic materials for organic electrochemical transistors (OECTs) can be divided into three types: PEDOT-PSS and its derivatives, semiconducting polymers with nonionic polar chains, and conjugated polyelectrolytes (CPEs). To date, the relative amount of literature on CPEs-based OECTs dwindles in comparison to PEDOT:PSS-based devices. We assert that CPEs provide a useful pedagogical system for understanding mechanisms of ionic and electronic transport in OECTs. Through ion-exchange on an anionic polythiophene with a pendant carboxyl group, poly[3-(4-carboxypropyl)thiophene-2,5-diyl] (PCPT), a series of analogues are produced with the same conjugated backbone, only differing in their cations. This procedure clearly elucidates how the choice of counter-ion dictates operation of an accumulation-mode OECT. Firstly, we highlight how these analogues differ in microstructure and phase morphology at various length scales, characterized via optical microscopy and scattering techniques. Secondly, we investigate the photophysical processes of the cast films through ultra-fast spectroscopic methods to understand the effect of counter-ion on charge transport. Lastly, we demonstrate that the counter-ion plays a crucial role in modulating electrolytic ion injection into the polymer film during OECT operation, via cyclic voltammetry and spectroelectrochemistry.

[8]

High Electron Mobility Naphthalene Diimides as n Dopable MaterialsKhaled Al Kurdi, Ragunath Reddy Dasari, Stephen Barlow, and Seth R. MarderDepartment of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332
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Organic semiconductor research has been on the rise aiming to discover materials that are superior to their inorganic counterparts for use in common day applications (OLEDs, TEGs, etc.). This is due to their low cost of fabrication, solution processability, and property tunability via molecular design. Naphthalene diimide (NDI) derivatives have been explored over the last two decades in several applications as semiconducting materials. Albeit NDIs high electron affinity and widely investigated high electron mobility, as shown by OFET devices, n-doped NDI derivatives are still not as explored. Moreover, the literature reported high mobility does not necessarily translate into high conductivity in many instances. This work aims at a structure-processing-property relationship study to understand how to obtain high conductivity materials utilizing n-doped NDIs. In addition, it aims to understand the nature of charge carriers in those materials while generating a database for accelerated materials discovery. Having the synthetic routes used to synthesize the target molecules as a starting point, the poster will also provide an overview of the dopant choice, doping results (both in solution and in thin film), along with solution processing and device fabrication.

[9]

Every Atom Counts: Elucidating the Fundamental Impact of Structural Change in Conjugated Polymers for Organic Photovoltaics

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ABSTRACT

As many conjugated polymer-based organic photovoltaic materials provide substantial solar power conversion efficiencies, it is important to develop a deeper understanding of how the primary repeat unit structures impact device performance. We have varied the Group 14 atom (C, Si, Ge) at the center of a bithiophene fused ring to elucidate the impact of a minimal repeat unit structure change on the optical, transport, and morphological properties, which ultimately control device performance. DFT calculation, absorption, and solution NMR results indicate that the polymers exhibit different rotational conformations. Solid-state ¹H MAS NMR experiments reveal that the greater probability of the anti-conformation in P(DTS-TPD) and P(DTG-TPD) prevail in the solid phase. This conformational variation in turn affects the polymer stacking and intermolecular interaction. Using grazing incidence wide angle x-ray scattering (GIWAXS), we observe the π -face of the conjugated backbones of P(DTC-TPD) aligned edge-on, while in contrast P(DTS-TPD) and P(DTG-TPD) align parallel to the surface. These differences in polymer conformations and backbone orientations lead to variations in the device performance with the device containing P(DTC-TPD):PCBM having a lower fill factor and a lower power conversion efficiency. Ultrafast transient absorption spectroscopy shows the P(DTC-TPD):PCBM blend to have a more pronounced triplet formation from bimolecular recombination of initially separated charges. With a combination of sub-bandgap external quantum efficiency measurements and DFT calculations, we present evidence that the greater charge recombination loss is the result of a lower lying triplet energy level for P(DTC-TPD), leading to a higher rate of recombination and lower device performance.

[10]

The Field-effect Electron Mobility of The Non-fullerene Acceptor ITIC

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Abstract

Non-fullerene acceptor, 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC), has generated significant interest for its use in photoactive layers in high-performance polymer solar cells. We report on the fabrication and characterization of organic field-effect transistors using ITIC. These experiments yield average field-effect electron mobility value of 1.4×10^{-2} cm²/Vs, which corresponds to one order of magnitude larger than those reported previously from space-charge limited current experiments and lower than previous reports using ambipolar OFETs. We believe that our results provide a better reference for the electron mobility of the non-fullerene acceptor ITIC using unipolar n-channel only devices.

[11]

Structural Tuning of Charge Transport Properties in Dioxythiophene Polymers for Electrochemical Device ApplicationsSandra L. Pittelli^[a], Melony Ochieng^[a], James Ponder^[b], Michel de Keersmaeker^[a], and John R. Reynolds^[a]

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Conjugated, redox-active polymers are unique materials, as they can effectively transport both electronic and ionic charge. Because of this ability, they are being evaluated as active materials in electrochemical applications ranging from charge storage, to electrochromism, to sensors and bioelectronics. Our group has developed a family of soluble, and therefore printable, dioxythiophene-based polymers to suit these applications. To induce solubility, the polymers are functionalized with long hydrocarbon chains. Previously, it was thought that these side chains had little impact on the redox properties of the polymer; however recently, there has been more effort put towards understanding how these side chains can affect the material properties of the conjugated systems. While these side chains do not induce any redox functionality, they do influence polymer morphology and intermolecular interactions that can affect the polymer's redox properties. Here, we evaluate how choice of dioxythiophene repeat unit and the side chain substitution pattern affect the material properties such as conductivity, charge mobility, charge capacity, ion diffusion, and morphology, and how these properties can influence the performance of electrochemical devices. In addition to these properties, we will discuss how the nature of side chain and repeat unit govern the frontier molecular orbitals the polymer, which can be modeled by DFT calculations, and how this relates to the degree of twisting of the conjugated backbone and ultimately the redox properties of the material. The film morphology and molecular ordering is analyzed by both Atomic Force Microscopy on microscale and by Grazing-Incidence Wide-Angle X-Ray Scattering, which is a technique that provides information about intermolecular interactions in the film.

[12]

A reevaluation of emissive layer design for high performance blue-emitting organic light-emitting diodes from thermally activated delayed fluorescenceXiaoqing Zhang,^[a] Canek Fuentes-Hernandez,^[a] Yadong Zhang,^[b] Matthew W. Cooper,^[b] Stephen Barlow,^[b] Seth R. Marder,^[b] and Bernard Kippelen^[a]

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Due to the small concentration dependent fluorescence quenching and ambipolar charge transport properties, thermally activated delayed fluorescence (TADF) offer new paradigms for the design of emissive layers (EMLs) which are contrary to the conventional wisdom. We demonstrate that OLEDs with an EML having an oBFCzTrz concentration of 50 wt. % in DPEPO yield a maximum external quantum efficiency (EQE) of 25.5% with an EQE roll-off of 10% in the range from 10 to 1,000 cd/m². OLEDs with a neat oBFCzTrz EML display a maximum EQE of 14.0%. Time-resolved electroluminescent decay studies, and analysis using a simple model, reveal significant differences in transport, trapping, and recombination in their EMLs.

[13]

Functionalized nanocellulose as stable supports for crystallizing small molecule pharmaceuticalsManali Banerjee and Blair BrettmannSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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Nanocellulose, an abundant biopolymer with high strength and surface area has been earning recognition in biomedical applications, especially those benefiting from its mechanical properties. Its porosity and highly tunable surface also provides excellent potential for applications in drug delivery. For example, nanocellulose-derived hydrogels have been used for controlled release of hydrophilic drugs such as carbazochrome sodium sulfonate. Hydrogels leaves a large number of drugs inaccessible to the system due to hydrophobicity. Here, we designed a supramolecular organogel system based on nanocellulose derivatives to be used as a favorable environment for crystallizing small molecule pharmaceuticals. We investigated the optimization of network formation within the nanocellulose gel to create a stable support for drug nucleation. By using molecular interactions between nanocellulose and active pharmaceutical ingredients, combined with the high number of interaction sites and the small size of the excipient particles, this work was focused on developing a drug production system wherein we can direct the growth of specific drug polymorphs by changing the functional group on the nanocellulose surface to tune the particle interaction with the drugs. These new drug polymorphs not only show different physical characteristics but also present with different release behaviors than the as-received material, opening up new avenues for pharmaceutical applications.

[14]

Incorporation of Cellulose with Polyelectrolyte Complex Coacervates for Paper-makingNasreen Khan, Carly Travis, and Blair BrettmannDepartment of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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The Forest Products Industry has a goal to reduce water consumption and energy usage in the papermaking process. One approach is to optimize the chemistry of paper furnishes. By utilizing oppositely charged polyelectrolytes to form complex coacervates (PECs) in paper formulation, we can increase the percent solids that reach the drying step. The goal is to formulate with new and commercially available polyelectrolytes to decrease inherent water content. We have studied two polyelectrolyte systems of anionic poly(acrylic acid) (PAA)/ cationic poly (allylamine) (PAH) and anionic polystyrene sulfonate (PSS)/cationic poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) and tested their ability to form precipitate, coacervate, or soluble phase with added salt using turbidity and microscopy measurements. The PAA-PAH was found to produce the desired coacervate formation, which are then used to study the association with cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNC). The order of addition of the polycation, PAH and polyanion, PAA has also shown an observable difference on the association of the coacervates with fibers at short time scales. PECs are already known to be used in the paper-making industry but by systematically studying the fundamental mechanisms of PEC phase behavior with coacervates we aim to improve sustainability in the paper-making process.

[15]

Rheology and characterization of high-solids slurries for direct ink writing applicationsHannah K. Woods, Zachary Adams, Elizabeth Sinner, and Blair BrettmannSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30318
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Additive manufacturing has revolutionized product fabrication, showing promise in industries where customization is either advantageous or completely essential. As the technology has advanced beyond basic resin or thermoplastic prototyping, it is finding its place in niche areas where more specialized materials are required. Direct ink writing (DIW), also known as robocasting, is a form of additive manufacturing in which a paste-like ink is extruded through a nozzle to produce the desired geometry. This method makes it possible to print with customizable inks comprised of high volume percentages of powders or solid particulate (here termed “high-solids slurries”). The ability to manufacture such thick, paste-like inks has the potential to be valuable in industries involving pharmaceuticals, energetic materials, ceramics, and more. This work focuses on understanding the ways in which filler content, size, morphology, surface properties, as well as binder chemistry and viscosity affect the properties and performance of DIW inks. We focus on two primary modes of solidification – ultraviolet curing (UV) and solvent evaporation (SE). Formulations of bisphenol A glycerolate dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) as the UV binder system are compared to those from a polyvinylpyrrolidone (PVP) and methanol (MeOH) SE binder system, with glass spheres of varying sizes as the solid filler (diameters ranging from 9-170 μm). Rheological data from the base binders and inks of varying filler percentages is analyzed in conjunction with 3D printing flow test results and compared to basic print quality to evaluate the overall success of the high-solids slurries as DIW inks.

[16]

In silico Prediction of Racemic Porous Organic Cage CrystalsYang Liu and David S. ShollSchool of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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Porous organic cage (POC) solids are porous materials made up of individual porous molecules held together by non-covalent forces. Chirality within POC materials can play an important role in controlling the crystalline assembly. For instance, a relatively low-cost synthesis route for POC crystals (CC3-racemic) synthesized from a racemic mixture of diaminocyclohexane and triformylbenzene has been demonstrated. This material has been reported to have improved sorption properties and stability relative to homochiral CC3 crystals. It is challenging to fully resolve the structure of this racemic crystal experimentally because only subtle differences exist between the racemic structure and the known crystal structure of homochiral CC3. Here we introduce an *in silico* prediction method to predict the structure of CC3-racemic. We first enumerate types of cage molecules that can be present in this material and establish their concentrations. A key observation from these calculations is that CC3-racemic is not made up of only CC3-R and CC3-S molecules; an additional class of heterochiral POCs is also present. By studying the packing energy of cage pairs in CC3-racemic, a lattice model representations of the racemic crystal is developed and used in MC simulations to assess the structure of extended crystals. By expanding the lattice model into atomic detail, fully detailed CC3-racemic crystal models are obtained. We show that these models are fully consistent with experimental powder XRD patterns of CC3-racemic, but that the resulting structures give insights into the packing of this interesting material that are not currently available from experiments alone.

[17]

Robust Folding Mechanisms of Rigid, Thin SheetsJames McInerney and Zeb RocklinSchool of Physics, Georgia Institute of Technology, Atlanta, GA
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Deploying technology where control is limited, for example sub-micron scales or in space, can be a long, expensive process. On the other hand, engineering materials which utilize actuation mechanisms to self-assemble provides a means of rapid, mass production. Thin sheets are particularly suited for this type of design due to the preference to bend out-of-plane as opposed to stretching. By restricting folding to occur about specified edges called creases – motivated by the ancient Japanese art of origami – success has been achieved at both the microscopic and macroscopic scales with various materials indicating a predominately scale-free theory. The allowed folding mechanisms, and hence paths between flat and deployed states, are entirely determined by the crease pattern. However, it is generally difficult to determine how many, if any, of these mechanisms exist as well as the shapes a given crease pattern can form. We investigate the entire class of periodically triangulated crease patterns. By relating the lattice symmetries of the system to the length preservation constraint of rigid origami folding, we show these patterns always exhibit two unique rigid folding mechanisms. As a result, any periodically triangulated crease pattern continually transforms between cylindrical sections with different radii and rotation axes.

[18]

The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor NanowiresMaritza Mujica, Gozde Tutuncuoglu, Sven H. Behrens, Victor Breedveld, and Michael A. FillerSchool of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, unfortunately, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize semiconductor nanowires at throughputs orders of magnitude beyond the state-of-the-art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica hollow microcapsules, whose interior surface serves as a high-surface area growth substrate. Hollow microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microcapsule structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires on the microcapsule interior.

[19]

Differential Dynamic Microscopy in Electron Microscope EnvironmentsGraham Parkinson, Jessica Stelzel, and Paul Russo

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Abstract

Differential dynamic microscopy [DDM] is a novel analysis technique that allows for determination of diffusion and particle sizing data through the use of only an optical microscope and video capture equipment. Unlike traditional particle tracking and particle sizing in optical systems, DDM functions even when the particles are below the Abbe limit—they cannot be resolved optically. It has seen utility in most soft materials including polymer solutions and colloids and has even been extended to use in tracking bacteria and cells. In this work, we extend this technique to electron microscope environments in both scanning electron microscopes and transmission electron microscope samples. While the use of electrons in place of photons is transferable to this analysis technique, the technique is not entirely directly transferable and has its unique challenges.

[20]

Controlling the Softness of Metamaterials: Corner Modes via TopologyAdrien Saremi and Zeb Rocklin

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Abstract

The structure of a vast range of soft materials determines how they deform under external forces. In particular, systems that are robust/soft because they are at the point of mechanical stability have been shown to have topological properties that lead to new deformations. Here we extend this topological softness to otherwise rigid periodic mechanical structures. A higher order topological invariant creates, directs and protects modes on their boundaries. We introduce a model system consisting of rigid quadrilaterals joined at their corners. This bulk structure generates a topological linear deformation mode exponentially localized in one corner, as investigated numerically and via experimental prototype. Unlike previous topological mechanical systems, these structures select a single desired mode, which controls variable stiffness and mechanical amplification that can be incorporated into soft materials at any scale.

[21]

Potential atypical mechanical and sensor applications of polystyrene sulfonate solids and solutions prepared via aqueous ATRP that benefit from no Cu catalyst removal.Paul Balding^[a] and Paul R. Russo^[a,b]

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Abstract

Polyelectrolyte materials are seldom used for common everyday products that typically made from neutral polymers such as polyethylene, polystyrene and polyethylene terephthalate. Here we describe some potential applications based on the mechanical and thermal properties of solid polystyrene sulfonate homopolymer synthesized from aqueous ATRP. This material benefits from a greener synthesis (water solvent and low input energy) and the ability to be easily re dissolved in water for later re use compared to the aforementioned neutral polymers. The salty Cu catalyst used in ATRP has been described as problematic due to the unwanted impurity and obvious blue-green color of the final

product. But this characteristic benefits the glassy polyelectrolyte solid formation and the tensile strength and modulus of the material exhibit a catalyst concentration dependence. The solutions obtained by dissolving Cu catalyst containing polystyrene sulfonate in water also exhibit a color marker phenomenon based on the Cu(I) (brown-grey) or Cu(II) (blue-green) state of the catalyst which can be a dissolved oxygen or temperature indicator.

[22]

Transition Studies of Thermoresponsive Polypeptides

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Abstract

Stimuli-responsive core-shell particles can find many uses in drug delivery and separation applications. Materials such as silica polypeptide composite particles (PCPs), consisting of an inorganic colloidal silica core and an organic polypeptide shell, can be used as model systems for studying biological and physical particle interactions. The polypeptide shell is comprised of a homopolypeptide, poly (ϵ -carbobenzyloxy-L-lysine) (PCBL), which is known to exhibit a reversible coil-helix transition when dissolved as a pure polymer in m-cresol. Optical rotatory dispersion and a density and sound velocity meter were used to study the conformational transition of PCBL, tethered and untethered, to determine how tethering the polypeptide to a surface affected the transition from a random coil to alpha helix. The conjunction of these two methods allows a new way to monitor the transition and to calculate the helicity of the polypeptide during the transition. This will provide a better understanding of the polypeptide transition in differing environments, which can be applied to other systems used in drug delivery and separations.

[23]

Solving Materials' Small Data Problem with Dynamic Experimental Databases

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Abstract

The traditional paradigm in materials process optimization is energy-intensive and time consuming. Generally, single factor, trial-and-error based experimentation is used to screen a wide array of complex processing conditions and results are difficult to reproduce because of a lack of standardization due to the exploratory nature of the field. Thus, it is challenging to develop global, robust process-structure-property relationships to generate novel material formulations. Instead, informatics-based methodologies can leverage existing knowledge from the literature to guide high-throughput screening of promising candidate experimental conditions. In this work two case studies of applying materials informatics methodologies to polymer systems will be presented. In the first study, the impact of processing conditions on the organic field effect mobility of the semiconducting polymer, poly(3-hexylthiophene) (P3HT), will be presented. A database of over 200 devices was created to identify significant trends and to identify an optimal operating space. Both integer and categorical processing conditions resulting in mobility values exceeding $0.1 \text{ cm}^2/\text{V-s}$ were identified to reduce the dimensionality of the design space. This enabled the generation of new hypotheses for future high-throughput experimentation. In the second study, a database with over 140 entries quantifying the development of polypropylene and talc composites for high strength materials was created. However, this database suffered from inconsistent reporting of processing conditions. Varying thresholds of Young's Modulus were applied to identify the span of processing conditions that result in high strength composites. In both studies quantified analysis of all processing conditions has identified key design spaces to enable high through-put experimentation.

[24]

Engineering Polymer-Nanoparticle Systems Towards Sustainable Devices and SensorsBailey Risteen^[a], Justin Zoppe^[b], Mohan Srinivasarao^[c], Paul Russo^[c,d], and Elsa Reichmanis^[a,c,d]

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Abstract

The future of organic electronics relies not only on the synthesis of new, high-performing polymers but also on engineering systems where the polymer structure and interactions can be controlled. Furthermore, there has been a push to incorporate renewable materials into device architectures for improved sustainability and recyclability. Here, we discuss efforts to utilize rodlike, bio-derived particles called cellulose nanocrystals (CNCs) and their liquid crystal phases in the design of polymer systems for device and sensor applications. First, CNCs were used to induce long-range order in a semiconducting polymer, poly[3-(potassium-4-butanoate) thiophene-2,5-diyl] (PPBT). When mixed with CNCs, PPBT was incorporated into the liquid crystal “template” to form ordered structures. The $\pi - \pi$ interactions between polymer chains, which contribute considerably to the energetics of the semiconducting system, were directly influenced by the presence and packing of the liquid crystal phase. The results of this study led to exploring a temperature “switchable” liquid crystal system. The thermoresponsive polymer, poly(N-isopropylacrylamide) (PNIPAM) was grafted from the surface of CNCs via surface-initiated atom transfer radical polymerization (SI-ATRP). These PNIPAM-modified particles formed a liquid crystal phase at room temperature but when brought above the lower critical solution temperature of PNIPAM ($\sim 32^\circ\text{C}$), the sample became dark under crossed polarizers and the liquid crystal was switched “off”. This “switchable” liquid crystal system could provide a basis for a sustainable sensor in smart packaging or other applications that require a response to temperature.

[25]

Molecularly-mixed composite membranes for advanced separation processesGuanghui Zhu^[a], Fengyi Zhang^[a], Xunxiang Hu^[b], Guoyan Zhang^[a], Christopher W. Jones^[a], and Ryan P. Lively^[a]

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[b] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
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Porous organic cages (POCs) are individual soluble, porous molecules. Compared to their extended framework counterparts, such as zeolites and metal-organic frameworks (MOFs), POCs offer the distinct advantage of solution processability. Moreover, when fabricated into mixed-matrix membranes (MMMs), the soluble POC molecules have the potential to exhibit intimate molecular-level mixing with the matrix polymer. In this work, we utilize vertex functionalized amorphous scrambled porous organic cages (ASPOCs) as membrane performance enhancers. The dispersion of ASPOC mixtures within a polymer matrix is visually probed using scanning electron microscopy (SEM), Raman imaging, and Energy Dispersive X-ray (EDX) mapping. Glass transition analysis suggests molecular-level mixing between the amorphous ASPOC cages and the polymer chains. Positron annihilation lifetime spectroscopy measurements reveal that the porosity of the molecularly-mixed cages is retained. A 340 % permeability increase was observed for N_2 , CO_2 , and CH_4 in the molecularly-mixed ASPOC membranes compared to pure polymer membrane. Moreover, an apparent molecular sieving effect was observed for SF_6 , resulting in a 150 % increase in N_2/SF_6 selectivity compared to the pure polymer membrane. The membranes were further examined in organic solvent nanofiltration experiments using a cross-flow permeation approach and polystyrene oligomers as markers. The amorphous ASPOC membranes exhibited unprecedented performance with over 95 % rejection of polystyrene solutes with molecular weights ranging from 200 to 1800 Dalton. Overall, membranes based on non-particle forming ASPOC materials resulted in the homogeneous mixing between the ASPOC molecules and the polymer matrix, which resulted in significant increases in both membrane permeability and selectivity.

[26]

Integrative Systems Biology LabSiarhei Hladyshau^[a,b], Anastasia Zhurikhina^[a], William Pilcher^[a], and Denis V Tsygankov^[a,b]

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shladyshau3@gatech.edu, denis.tsygankov@bme.gatech.edu**Abstract**

The Integrative Systems Biology Lab focuses on combining novel experimental and computational methods (involving modeling, simulations, and computer vision techniques) to gain a systems-level understanding of complex biological processes. The emphasis is made on biomechanical aspects of physiological phenomena across scales from molecules (signal transduction, actomyosin regulation) to cells (morphodynamics, polarization, and motility) to tissues (multicellular patterning, collective cell behavior).

[27]

Open Polymer Active Learning Laboratory: Advanced Student-led Training within STAMI/GTPN

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The Open Polymer Active Learning Laboratory (OPALL) trains juniors, seniors and beginning graduate students by providing hands-on experience on industry-grade equipment for polymer and colloid characterization, ideally solving problems of industrial relevance. Operationally, OPALL is a flat space based on knowledge and merit. What students can do depends on their training and proven ability to work safely. *Masters* will be able field strip a piece of equipment, and might very well be inventing a new instrument superior to commercially available devices. *Associates* can operate equipment safely and understand the theory of operation. Less advanced participants, called *Learning Assistants*, are drawn from GT's freshman and sophomore classes, plus area high schools. They may not understand the theory behind how a piece of equipment works, but are capable of safely performing limited and routine operations. These may include assistance to students of GT's potent polymer curriculum, as OPALL runs "parallel" to courses such as polymer synthesis, polymer characterization, and polymer physics. Industrial partners can access OPALL through the MSE Design course, through contracts to Georgia Tech investigators, or by providing research fellowships to students at any level, or to postdocs. Pedagogically positioned between GT's Maker Spaces (especially MSE's Materials Innovation Learning Laboratory) and GT's potent Institute and Center research facilities (e.g., Renewable Bioproducts Institute, Institute for Electronics and Nanotechnology, STAMI's Shared Lab) OPALL blends "hacker" culture with formal training in the proper conduct of experiments. OPALL enhances educational quality and equipment availability for juniors, seniors and beginning graduate students who wish to master core techniques vital to the global polymer community. OPALL is particularly interested in outreach to under-represented groups and the economically disadvantaged.

[100]

Additive Manufacturing of Energetic Material Surrogates via Direct-Ink Writing

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Abstract

Additive manufacturing (AM) has been transformative for a number of industries, providing personalized medical implants, allowing for cost-effective prototyping, and improving production of specialized aerospace parts, among others. For energetic materials, AM provides a unique fabrication opportunity in geometries that are traditionally difficult or impossible to manufacture via subtractive means. Though effort has been made to use AM to prepare energetic materials, the high solids loadings required for these materials prove to be significant challenges to processing, and defects and voids in the printed material change shockwave propagation of resulting detonations. Direct Ink Writing (DIW) is one method of additive manufacturing capable of producing parts from these high solid slurries. DIW requires precise control of the precursor material in a flow condition, with the deposited material then solidifying to maintain its shape. There are two methods of solidification studied in this work: solvent evaporation (SE) and ultraviolet cure (UV). SE cured materials harden after 3D printing due to solvent evaporation from the material, while the UV materials harden from UV exposure. As the start to a collaborative project studying heterogeneities in additively manufactured energetic materials, we examine the material mixing, rheology as a function of solid loading, flow in a nozzle and 3D printing of polymer/surrogate particle/solvent mixtures.

[28]

Minimally Substituted Acceptor Polymers for OPV

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Abstract

An organic photovoltaic (OPV) is a type of solar cell that uses organic dyes, typically conjugated polymers, as the active component to produce electricity from sunlight. These devices have several potential advantages over silicon-based devices, such as – being lightweight, flexible, inexpensive, and easy to fabricate by roll-to-roll processing. Current OPV research focuses on tuning chemical structures and optimizing processing parameters to produce higher device power conversion efficiencies (PCE) (percentage of produced power to theoretical maximum). A primary area of research is the design of donor-acceptor (DA) polymers. Recent work by Graham *et al.* indicates that higher PCEs can be achieved by molecular (steric) control of fullerene-polymer interactions. In this work, it was hypothesized that better fullerene “docking” on the acceptor units facilitated the more efficient charge transfer from donor unit to acceptor unit to fullerene. Based on this work, we hypothesize that placement of less bulky side chains on the acceptor can lead to improved OPV performance. To explore the concept of fullerene “docking” on the acceptor unit, we looked at state-of-the-art OPV polymers and found that the high-performing polymer PCE-11 fit our “minimally substituted acceptor” hypothesis. PCE-11 is a high performing solar polymer, but unlike other solar polymers, its acceptor unit lacks sidechains. To test our hypothesis, analogs of PCE-11 were proposed utilizing minimally substituted versions of various acceptor units (methylated forms of isoindigo, TPD, and DPP). The de-bulking of the acceptor units is hypothesized to promote fullerene-acceptor unit interactions leading to improved device performance.

[29]

Strategic Design of Solution-Processable N-Channel Polymeric Semiconductors for Sustainable Next-Generation Electronic Technologies

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Abstract

The development of semiconducting conjugated polymers for organic thin film transistors (OTFTs) has been the focus of intense research efforts for their key role in plastic electronics, as well as a vision of solution processability leading to reduced costs in device fabrication relative to their inorganic counterparts. The pursuit of high-performance *n*-channel (electron-transporting) polymer semiconductors vital to the development of robust low-cost organic integrated circuits has faced significant challenges, mainly for poor ambient operational stability and OTFT device performance lagging far behind that of *p*-channel organic semiconductors (OSCs). As an alternative to the ubiquitous donor-acceptor (DA) molecular design strategy, a novel conjugated *n*-channel copolymer has been fabricated using an all-acceptor (AA) unipolar approach. In order to further understand the impact of electron withdrawing moieties to conjugated polymer device performance and the utility of the AA molecular design, we have synthesized a new conjugated polymer, poly(2-(2-decyltetradecyl)-6-(5-(5'-methyl-[2,2'-bithialo]-5-yl)-3-(5-methylpyridin-2-yl)-5-(tricosan-11-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**PDBPyBTz**). In incorporating **PDBPyBTz** into an OFET device, unipolar electron transport was observed with an average FET mobility of 1.07 (± 0.018) $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. In addition to developing a high-performance *n*-channel polymer, this study allowed for an investigation of structure-property

relationships crucial to the design of electronic materials in high demand for sustainable and solution-processable technologies.

[30]

2D COFs with Impactful Optoelectronic Properties

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Abstract

Two-dimensional covalent organic frameworks (2D COFs) are crystalline and porous networks, which are being synthesized from the custom-designed organic linkers with periodic bonding in two orthogonal directions. The regular arrangement of the organic units and their linkage make COFs potential candidates for optoelectronic applications that depend on charge-transport. However, as synthesized COFs are multi-layer networks, as analogous to graphite, preparation of monolayer COFs would provide an opportunity to study the intrinsic properties of materials. Here, we show synthesis approaches to realize highly delocalized COFs that may exhibit potentially interesting charge-transport properties, as per the band structure calculations. We also present the synthesis of monolayer COF structures on a metal substrate.

[31]

PEDOT:PSS films in redox-active devices

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Abstract

We present new designs for fast and reversibly switchable redox-active devices using PEDOT:PSS both as a transparent electrode material and an interface film exploiting its capacitive properties. Thin PEDOT:PSS films have been incorporated in window-type purple-to-transmissive electrochromic devices and symmetric electrodes as part of charge storage devices. We reached a conductivity up to 2000 S cm⁻¹ when post-treating PEDOT:PSS films using different (in)organic acids on different substrates, enough to reversibly switch multiple ECPs made in the Reynolds Group depending on the targeted application. We will demonstrate how the device construction, charge-balancing and electrode conductivity have an influence on the device performance focusing on switching speed and capacitive behavior. We combine our device design with a fundamental study of the mixed electron and ion transport processes occurring in the ECP films at the electrodes looking for links to electrode and device performance. Using these new device structures, we have developed an easy way to produce both electrochromic and charge storage devices using solution processable polymers and roll-to-roll compatible coating techniques.

[32]

Metallic-Type Transport in Polymers: Towards Establishing Structure/Property Interrelationships

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Abstract

Current organic electronics research aims at exploiting the unique property matrix of “plastic” semiconductors, including their chemical tunability, straight-forward processability and mechanical flexibility, to create new applications. While much knowledge has been developed in the design of semiconducting/conducting conjugated organic materials, there are still immense opportunities to establish design guidelines for highly conductive macromolecular matters. The chemical versatility and the multitude of possibilities for “plastic” semiconductors to order over different length scales creates, however, a daunting task to establish comprehensive structure/processing/property interrelations. Here, we present a multidisciplinary approach towards a framework that should allow us to predict the structure/property interrelations of such systems by developing versatile processing methods for the assembly of organic materials with metallic-type transport. We will focus on poly(thiophene) derivatives as model systems, including poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT), to gain insight into how the spatial arrangement, controlled through intercalation and co-crystal formation, affects charge transport. The detailed structural control that especially PBTTT and its oligomers provide, should allow us to develop a detailed picture of the complex electronic landscape that we will use to obtain deep understanding of the design of conducting “plastics”.

[33]

Cosolvent processing of a low-solubility material for polymer:fullerene organic photovoltaics, and hyperspectral microscopy characterization

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Abstract

This report covers the morphological development of an ambient processed polymer:fullerene blend system deposited via blade coating. The high molecular weight polymer DT-PDPP2T-TT, despite having dual large decyl-tetradecyl side chains on the DPP acceptor unit, exhibits remarkably low solubility in halogenated solvents like chloroform and 1,2-dichlorobenzene that are commonly used to dissolve and process similar polymers. As a result, several different cosolvents are able to induce ideal phase separation as the films solidify into a bulk-heterojunction (BHJ), leading to enhanced photovoltaic properties when integrated into a device. The emergence of isotropic nanofibrillar texture was seen in all cosolvent cast films, where 7.5%_v of 1,2-dichlorobenzene (DCB), 1,8-diiodooctane (DIO), or diphenyl ether (DPE) was added to the chloroform host solvent. To understand the origin of these morphological changes as a result of the addition of cosolvent, real-time optical reflection and X-ray scattering methods were used to understand how the morphology evolves with time during coating. We find that all three cosolvents act as nucleating agents, which increases the nucleation density leading to reduced domain size and enhanced polymer crystallinity in thin films relative to films cast from chloroform alone. This results in a percolated bulk-heterojunction network that performs well with relatively thick films, making this system amenable to continuous roll-to-roll processing methods. Furthermore, we make use of hyperspectral microscopy, a novel technique to acquire spatially resolved absorption and fluorescence data on thin films, to confirm that chloroform-only cast films are strongly phase separated relative to the cosolvent cast films.

[34]

A fullerene derivative for solution-processed perovskite solar cells

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Abstract

Due to their optoelectronic properties and ease of processing, metal halide perovskites are an attractive class of materials for large scale, low-cost photovoltaic applications. The power conversion efficiencies (PCEs) of perovskite solar cells have soared from just 3.8% at their inception, to certified values of over 23% less than a decade later. One of the central challenges in pushing the photovoltaic performance of perovskite solar cells closer to the thermodynamic limit is eliminating non-radiative recombination pathways. These losses primarily occur because of trap-assisted recombination sites, most likely located at the interfaces between the charge selective contacts and the perovskite absorber. Fullerenes appear to be good candidates as electron-selective contacts, since they do not appear to induce a high density of defects responsible for charge recombination. However, fullerenes can be dissolved by solvents, such as DMF, from which the perovskite layer is usually cast. Here, we present an approach to limit dissolution of fullerenes and to prevent migration of dopants commonly used to increase the conductivity of such electron-transporting materials. We synthesized a thermally-oligomerizable fullerene derivative, PCBCB, which is solution processable but, after thermal treatment, is not dissolved by DMF. A smooth, thin and continuous electron-transporting layer can be obtained and can be n-doped, leading to an increase in conductivity of PCBCB by five orders of magnitude and an increase in PCE by 5%. Dopant diffusion studies are currently in progress.

[35]

Organic Photodetectors (OPDs) with Near-Infrared (NIR) Response

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Abstract

Near-Infrared (NIR) photodetectors with high detectivity are desirable. High detectivity enables photodetectors to distinguish the NIR signal from noise at low optical intensities. Therefore, the electric power required by the optical source (e.g. LED) is less, decreasing the power consumption requirements of a sensing system. If shot noise is dominant, high-detectivity photodetectors are attainable for devices with low dark current in reverse bias. In this work, we demonstrate various NIR organic photodetectors (OPDs) with low dark currents ($< 1 \text{ nA/cm}^2$) by using different carbon-based materials such as polymers, fullerenes and small molecules. In contrast to inorganic photodetectors, OPDs offer advantages in applications that require flexibility, semitransparency and large detection areas. NIR OPDs can have a high impact in specific fields such as night vision, biomedical sensing, internet of things, or wearable electronics.

[36]

The Design of New Donor-Acceptor Polymers for Organic PhotovoltaicsAudrey Scholz^[a], Carolyn Buckley^[b], and Elsa Reichmanis^[a,b]

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Abstract

Organic semiconducting polymers are a popular topic of research for their use in photovoltaics, such as solar cells. Relative to inorganic semiconductors, organic semiconductors have the advantage of higher affordability, sustainability, and easier large-scale fabrication. Unfortunately, the overall efficiency of organic solar cells still lags behind its counterparts due to weak oxidation stability and poor charge carrier transport resulting from low charge carrier mobility. Therefore, development of new donor-acceptor (D-A) polymers is aimed at increasing ambient stability, charge carrier mobilities, and effective π - π interactions, while decreasing bandgaps. Previously, we have shown that replacing thiophene with thiazole in DPP-based polymers resulted in decreased electron density, lowering the HOMO and LUMO levels. This resulted in an increased charge carrier mobility, leading to the design of new DPP-based D-A polymers. A common donor moiety, benzodithiophene (BDT) is being used in conjunction with diketopyrrolopyrrole (DPP) in a series of polymers to investigate the change in charge carrier mobility as different structural aspects of the polymer change. The aspects changing include the aromatic groups surrounding DPP and the extended conjugation on the BDT unit. Similarly, known high performing DPP-based polymers will be synthesized with partially fluorinated alkyl chains to improve crystallinity and decrease HOMO energy levels, thus increasing ambient stability.

[37]

Design of Hybrid Metamaterials with Large Modulation of Plasmonic Resonances and QD PhotoluminescenceJing Zhou, Ju-Won Jeon, Jeffrey A. Geldmeier, James F. Ponder Jr., Mahmoud A. Mahmoud, Young Jun Yoon, Jaehan Jung, Lexy Rile, Mostafa El-Sayed, John R. Reynolds, Zhiqun Lin, Vladimir V. Tsukruk

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Abstract

Assembling optical active nanostructures into polymer matrices holds promise for the design of functional materials with controlled light-matter interactions, which finds applications such as sensors and flexible photovoltaics. We present various methodologies for the control of the plasmonic properties of gold nanorods and the photoluminescence of quantum dot (QD). First, electrochromic hybrid systems with electrochemical modulation of plasmon resonance were designed by direct polymerizing electroactive polymers around gold nanorods. The plasmon tuning behavior, resulted from polymer's refractive index change, varied when different electroactive polymers were used. For example, a dual-responsive system with the plasmon mode reversibly modulated through electric potential and pH was realized when polyaniline served as the outer shell and a maximum shift of the longitudinal plasmon mode of 149 nm was obtained. Another electrochemical modulated plasmon tuning system with narrow visible-near infrared absorption bands was also demonstrated using a transmissive polymer poly[(3,4-propylenedioxy)pyrrole]. Overall, these core-shell nanostructures with electrochemical plasmonic tunability allow for the fine control of the optical and electrochemical properties of plasmon response. Second, we developed a new method for enhancing photoluminescence from QDs/polymer nanocomposite through the control of the degree of film dewetting. The dewetted films were found to have increased amounts of scattering, which resulted in up to a 5-fold enhancement of the film emission. A unique photopatterning strategy was also presented based on the aforementioned method.

[38]

Utilizing Cyclodextrin to Compatibilize the Polymer and CNC InterfaceKrista K. Bullard^[a], Will R. Gutekunst^[a], and Mohan Srinivasarao^[b]

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As environmental concerns increase, the interest in using cellulose and cellulose nanocrystals (CNC) for the creation of new materials also grows larger. This poster presents preliminary data towards realizing this strategy by grafting cyclodextrins onto the surface of the CNCs through two different strategies and the characterization of the resulting CNCs. The first strategy uses a difunctional linker to modify CNC then attach the cyclodextrin. The second strategy couples functionalized CNC with a monosubstituted cyclodextrin. The ultimate goal is to develop a CD functionalized CNC that acts as a universal precursor for a wide range of traditionally incompatible polymer systems.

[39]

Transparent Wood Smart WindowsAugustus W. Lang^[a], Yuanyuan Li^[b], Michel De Keersmaecker^[c], D. Eric Shen^[c], Anna M. Österholm^[c], Lars Berglund^[c], and John R. Reynolds^[a,c]

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Transparent wood composites are composed of a delignified birch skeleton infiltrated with poly(methyl methacrylate) giving a material with high strength and optical transparency. These materials also exhibit a toughness 30 times higher than glass and a low thermal conductivity making them promising candidates for diffusely transmitting windows/roofs. Here, transparent wood electrodes based on solution processed PEDOT:PSS are demonstrated to enable electrochromic "smart windows". With a mild acid treatment, the PEDOT:PSS is rendered highly conductive (1200 S cm⁻¹). The transparent wood electrode conductivity is retained over a 1.3 V potential window enabling their application for a variety of cathodically coloring electrochromic polymers. Electrochromic devices based on these materials exhibit a vibrant magenta-to-clear color change ($\Delta E^* = 43$, $\Delta\%T = 38\%$) with a highly color-neutral bleached state resulting from the light diffusion through the transparent wood. These devices are energy efficient (3 mWh m⁻² per switch) and can maintain each optical state (colored or bleached) without power for an hour. This solution-based approach offers a route to fabricate mechanically robust, energy-efficient, smart windows.

[40]

Printable circuits and solution-processed electronics on paper for the Internet of Things (IoT)Cheng-Yin Wang^[a], Felipe A. Larrain^[a], C. Fuentes-Hernandez^[a], Robert J. Moon^[b] and B. Kippelen^[a]

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Abstract

Energy savings and healthcare tracking are among the many benefits that the Internet of Things (IoT) provides today, as it fulfills its promise of ubiquitous connection between people and objects. However, the biggest challenge to deploy IoT is bringing it to unpowered objects that lack an internet connection. A potential solution is to use a short-range wireless communication technology called Near Field Communications (NFC). Indeed, NFCs offer the intuitive experience of touching two devices, getting the convenience of wireless communication without the need of an explicit user interface. Still, conventional silicon-based electronics are a poor match to NFCs due to their intrinsic manufacturing costs and mechanical properties. Here, we discuss how printed electronics provides the building blocks for a new generation of low-cost and high-volume NFCs, which may enable further deployment of the IoT. In particular, we report on state-of-the-art organic field-effect transistors, light harvesting devices built on paper substrates and instant inkjet-printable circuits compatible with paper for scalable NFC prototyping.

[41]

Recyclable Biobased Furan-Epoxy Thermoset via Diels-Alder Crosslink and Reinforced by Nanocellulose Crystal for Lighter and Stronger CompositesLuc Le^[a], Karl Jacob^[a], and Kyriaki Kalaitzidou^[b]

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Abstract

Strong and light weight thermoset polymeric composite can be used for many structural applications. However, thermoset composite materials may cause significant environmental problems since many of such materials cannot be recycled and have to be stored in landfills. Thus, thermoset composites that can be recycled, or even renewed will have substantial impact on reducing the adverse environmental impact of such materials. Renewable polymer composite is a promising path for reducing environment pollution while improving sustainability of such materials for the long future. By introducing the thermo-reversible covalent bonds in the molecular network, the thermoset material can be reprocessed upon a suitable thermal trigger. One of the most effective reversible covalent bonds is the Diels Alder bond in the synthesis of a furan and a maleimide thank to its relatively fast kinetics and mild reaction conditions. For other aspect of enhancing mechanical and thermal properties of material, incorporation of mechanically robust nanoscale fillers can significantly improve a composite's strength and stiffness. Nano-cellulose crystals (CNC), extracted from cellulose fiber abundant from plant sources, has high aspect ratio, high percentage of crystallinity and high elastic modulus that makes them highly suitable as reinforcements in such composites. In addition, CNC has large active surface area of hydroxyl group not only improves interface contact of filler and polymer matrix to enhance interfacial shear strength and toughness, but also is able to modify to have better bonding with polymer matrices. The aim of the work presented here is to provide a proof of principle for the use of DA chemistry as a thermoreversible cross-linking and the reinforcement effect of abundant green nanocellulose filler.

[42]

Vapor Phase Modification of Cellulosic Free-Standing Film

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Abstract

Surface modification of cellulosic film is potentially useful for packaging, printing, flexible substrate and separation films. Most surface modification research has focused on wet chemistry (fluorine, polymer and saline coatings). In this presentation, we will discuss a vapor phase modification technique that is simple but gives somewhat surprising results. We have examined vapor phase modification of cellulose film with trimethylaluminum (TMA) and water. These are self-limiting reactions that provide atomic level control over the amount of Al_2O_3 that is deposited. We observed differences in the hydrophobicity behavior depending on the post-heat treatments that are done. Pure cellulosic film that is made of nanocellulose and microcellulose composite is found to remain hydrophilic after a single TMA/ H_2O dose (immediately dispense in water), but once heated to a modest temperature (~ 150 °C) in air, it becomes hydrophobic (~ 130 ° water contact angle) and shown good water resistance performance even after long time harsh sonication. Electron microscopy and IR spectroscopy do not detect any significant difference in the bulk chemical and structural properties. However, XPS measurements suggest a difference in the surface chemistry that is permitting greater uptake of adventitious carbon. The effect of this surface chemistry on the difference in observed wetting properties will be discussed.

[43]

Rheological Characterization of Nanocellulose Materials for Quality ControlJianshan Liao^[a,b] and Victor Breedveld^[a,b]

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Abstract

Cellulose nanomaterial (cellulose nanocrystals and cellulose nanofibrils), can be fabricated from abundant and renewable cellulose materials. Its unique properties make it appealing to many industry applications. Nevertheless, one of the most urgent issues that needs to be addressed is the lack of standardized, rapid and reliable characterization methods to achieve quality control for these nanomaterials. Rheology provides a fast and cost-effective way to characterize nanocellulose in bulk quantity. Understanding the relationships between nanocellulose's intrinsic properties and its rheological behaviors will lay a solid foundation for establishment of testing standards. In this work, we will show how rheological properties are influenced by concentration, temperature, salt content, and sample preparation methods. Several rheological testing protocols were performed. Oscillatory rheology and recovery tests were performed to investigate gel forming dynamics. Moreover, the experimental rheological data was fitted to rheological models to establish benchmarks for cellulose materials.

[44]

Comparison of Nanocellulose Sources through Organogel Production and CharacterizationSisira Saraswatula, Manali Banerjee, and Blair BrettmannDepartment of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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Cellulose is a natural substance commonly extracted from trees, algae, and bacteria. Cellulose at the nanoscale, nanocellulose, consists of repetitive amorphous and crystalline segments. Once cellulose undergoes acid hydrolysis, the resulting cellulose nanocrystals (CNCs) have favorable properties including high tensile strength, stiffness, biodegradability, and low toxicity. Such properties allow CNC to be a useful natural material for a wide variety of applications, particularly the formation of organogels. Organogels have several uses such as the controlled release of drugs and cell encapsulation. Moreover, the tunability of the CNC surface allows for optimization of organogels for these applications. In this work, we attempt to determine if the method of production of CNC from two different producers, Celluforce and the Forest Products Laboratory, affects the gel network strength. While both producers hydrolyze their CNC in a similar manner, the method with which they dilute and stabilize their CNC varies. Oxidized forms of either CNC will be used to produce organogels. The thermal and colloidal stability of the organogels is tested to determine if the method of CNC production affects gel strength.

[45]

Vapor Phase Modification (VPM) of Cellulosic Materials for Use in Polymer CompositesJamie P. Wooding^[a], Kyriaki Kalaitzidou^[b], Mark D. Losego^[a]

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[b] The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30313
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Automotive and aerospace industries are increasing their demand for lightweight materials to further improve fuel efficiency via vehicle weight reduction. A common approach to light-weighting employs glass or carbon fibers as reinforcing agents in polymer composites; we aim to replace these reinforcing agents with lighter, but equally strong, nanocellulose. Traditional challenges in incorporating cellulose nanocrystals in polymer resins stem from the inability to (1) uniformly disperse hydrophilic cellulose within hydrophobic thermosetting polymers and to (2) establish favorable reinforcing agent and polymer matrix interactions at the interface. Here, we employ a nanocellulose-network preform to remediate issues of dispersion and homogeneous distribution and perform atomic layer deposition (ALD) to alter the nanocellulose surface chemistry, thereby establishing favorable cellulose-polymer interfacial interaction. To assess viability, we measure contact angle and wicking properties of cellulose substrates, and determine mechanical properties of the resulting cellulose-resin composites.

[46]

Electrospinning of Microparticles at High Loading.Ian Campbell, Elena Ewaldz, and Blair BrettmannDepartment of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332
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Electrospinning is a method for processing polymers which forms fibers by submitting solution droplets to an electric field. Correct utilization of this technique can produce fibers on the nanoscale whose utility can apply to filtration, textile manufacturing, and the development of high-performing composites. To implement innovative applications of this process, such as wearable devices and pharmaceuticals, this work examines the effects and implications of introducing significant additives into the spun polymer solution. Increasing concentrations of foreign particles have effects first and foremost on the spinnability of the solution; effective spinning is harder to establish at higher concentrations. It is observed that a more viscous solution may whip less under the influence of the field, causing less fiber drying and overdamp mats. We show additionally that varying the solution composition affects the physical properties of the mat, as demonstrated through mechanical testing. FTIR testing allows us to investigate if these variations are caused by induced bonding within the mat. The increase in understanding of the impact of a high-loading of electrospun microparticles contained herein allow us to deduce possible improvements for our future work.

[47]

Impact of Large Particles at High Loadings in ElectrospinningElena Ewaldz, Riddhi Patel, Manali Banerjee, and Blair BrettmannDepartment of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30318
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Electrospinning is a valuable production method for nanoscale polymeric fibers. A major limitation of the technology is the requirement for high molecular weight polymers as a major part of the matrix. Many applications would benefit from flexibility in the materials for electrospinning, including pharmaceuticals, wearable devices and diagnostics, and structured fibers with particles included that are larger than the fiber size. To realize these more advanced functional composites, a strong understanding of how particle inclusion affects the electrospinning process and mat properties is essential. In this work, we examine materials systems containing polymers and microparticles, focusing on how inclusion of particles affects the electrospinnability and morphology of the fiber. The primary factors that influence electrospinnability and morphology are the particle density, particle aggregation, and size ratio of the fibers to the particles. These results provide a platform for product design for new electrospun materials with high loadings of functional particles.

[48]

Tailorable Regenerating Hyaluronan Polymer Brushes: A Novel Class of Biointerfaces

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Abstract

Polymer brushes are relevant to a wide range of industrial and biomedical applications. This makes understanding their fundamental properties crucial to optimizing their design for specific applications. We introduce novel methods to generate microns-thick hyaluronan polymer brushes and characterize their properties. These brushes are regenerative, easily tuned, and one of the thickest brushes ever reported for any type of polymer, synthetic or natural. We also demonstrate modulation of the effective grafting density of the brush via patterning achieved by application of a near UV laser beam which enables binary patterning of the brush with microscopic features and the generation of more complex brushes with height gradients. These interfaces show promise in a variety of applications from stimulus responsive biomaterials, anti-microbial surfaces, filtration, drug delivery, and the potential for implants or other surfaces. This new experimental platform represents a unique approach to fabricating polymer brushes, provides opportunities for fundamental studies, and ultimately applications in the design of functional interfaces.

[49]

Selective Patterning of Si/Ge Nanostructures for High Performance, Flexible Electronics

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Abstract

Functional devices (e.g., transistors) contain one or more features with nanoscale dimensions. When such devices are to be produced at very large manufacturing rates (e.g., for large-area integrated circuitry), an alternative to top-down patterning is necessary to define key features. In this study, we show how Si and Ge surfaces can be selectively masked using the surface-initiated growth of polymer films. Our approach is particularly useful for patterning axially-encoded Si/Ge nanowire heterostructures. Surface masking of Si, but not Ge, is accomplished in a two-step procedure. Atom transfer radical polymerization (ATRP) of polymethylmethacrylate (PMMA) first occurs from a surface-tethered initiator. The selectivity of initiator attachment leads to thick and thin PMMA layers on Si and Ge surfaces, respectively. Unwanted PMMA on the Ge surface is subsequently removed by a clean-up etch that targets GeO_x, but not SiO_x, to yield nearly 100% polymerization selectivity. We investigate the role of Si/Ge surface pre-treatment, PMMA polymerization, and post-polymerization cleaning on the resulting polymer properties and surface selectivity with a suite of spectroscopy and microscopy techniques. We also show that selective polymerization is possible on Si/Ge nanowire heterostructures. The ability to mask nanoscale objects in a bottom-up fashion opens up the possibility of nanoscale patterning in a truly scalable manner.

[50]

Engineering Si nanowires for next generation thermoelectric applications

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Abstract

Expanding our understanding of thermal transport will enable exciting future technologies such as electronics cooling, next generation refrigeration and thermoelectrics. Owing to their precisely engineered nanoscale structures, semiconductor nanowires unlock new methods to control thermal transport. Initial demonstrations show that morphology, diameter, and surface roughness can modify the thermal conductivity of Si nanowires. However, these effects remain poorly understood and difficult to rationally engineer. In this work, we combine state-of-the-art nanowire synthesis, thermal transport characterization, and modeling to understand, predict, and control heat transport in Si nanowires. The synthesis of nanowires with axially-modulated diameters is accomplished by the combination of nanowire growth in a chemical vapor deposition system and post-growth dopant selective etching. Thermal conductivity of Si nanowires is measured by a suspended four bridge technique which eliminates the impact of the contact resistance. Simulations using the complete frequency- and temperature-dependent solution to the phonon-Boltzmann equation, which accurately describe phonon-surface interactions, are consistent with our experimental results. We demonstrate that the thermal conductivity of Si nanowires can be engineered by altering the diameter of the thinnest section along the nanowire and the relative lengths of the each diameter modulated section. By connecting local nanowire diameter and morphology to phonon mean-free-path and the resulting thermal properties, our work paves the way for the rational design of future thermal materials.

[51]

Multivalent Antimicrobial Additives for Silicone Systems

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Abstract

Typically, silicone is made surface antimicrobial via free additives that have a propensity to leach or through surface coatings that, if damaged, expose defects that could be subject to microbial growth. Additionally, the process of surface coating requires an added manufacturing step. One way to potentially circumvent these challenges is to create a non-leaching antimicrobial additive that would render the surface antimicrobial whilst still maintaining antimicrobial activity in the bulk. Previous research shows that in amorphous polymer systems, bulky chain ends self-segregate to the air-surface interface, minimizing the free energy of the system. Because of this, it is possible to alter the surface properties of a polymeric material in a gradient fashion through the use of an additive. In this research, we propose the use of a PDMS (Polydimethylsiloxane) additive that is chain-end modified with multivalent dendritic bulky chain ends containing antimicrobial quaternary ammonium groups. Here we show the synthesis of PDMS additives with two types of dendritic chain ends, each with varying degrees of branching and subsequent quaternization. The dendrimers we use are PAMAM (Poly(amidoamine), a dendrimer with repetitive amide and amine subunits, and Bis-MPA type, a dendrimer based on a bis-MPA (2,2-bis(hydroxymethyl)propionic acid) building block. The dendrimers are modified with quaternary ammonium groups of C16 alkyl chain length. We will use these additives in future antimicrobial and materials testing of cured silicone systems.

[52]

Creation of Solvent Stable Microporous Membranes via Vapor Phase InfiltrationEmily K. McGuinness^[a], Fengyi Zhang^[b], Ryan P. Lively^[b], Mark D. Losego^[a]

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Abstract

Membrane separation is a promising alternative to traditional energy intensive distillation separation, but requires materials that exhibit stable and reliable operation in demanding environments. Existing membranes used for chemically aggressive environments (e.g., inorganic membranes) are associated with high cost and difficult scale-up and are thus less attractive than intrinsically scalable polymeric membranes. Developing methods to improve polymeric membrane stability while leveraging the scalability of polymer membrane technology will broaden the opportunities for membrane separation deployment. Traditional methods for improving polymer membrane stability include crosslinking and pyrolysis. However, these processes significantly alter the polymer's chemical and physical properties. This poster will discuss a new post-synthesis modification technique called vapor phase infiltration (VPI) that protects polymer of intrinsic microporosity-1 (PIM-1) from swelling and dissolution while maintaining its characteristic narrow pore size distribution, high surface area, and membrane morphology (properties that make PIM-1 attractive for use in membrane separations). During the VPI process, metalorganic precursors sorb into the polymer surface, diffuse through the bulk, and become entrapped either physically or chemically. Through purposeful control of VPI processing parameters, complete infiltration of PIM-1 (and other polymers) with metal oxides can be achieved with minimal changes to polymer microstructure. Resulting hybrid PIM-1/Al₂O₃ membranes exhibit 81% less swelling in ethanol, solvent resistance in THF on the order of 6 months, and effective separation capabilities in traditionally challenging environments.

[53]

Degradable Polymers from Thionolactone Radical Ring-Opening Copolymerization

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Abstract

Radical ring-opening polymerization (rROP) utilizes strained cyclic monomers which react with a radical source to ring open resulting in a stabilized radical species allowing for further propagation. This method is attractive, as it enables new types of functional groups to be incorporated into the backbone of radical polymers, such as esters that permit degradation. The nature of rROP in principle permits these features to be incorporated into any existing radical polymer family systems; however, the poor reactivity ratios with several important monomer families (styrene, acrylates, and acrylamides), inability to polymerize via living polymerization techniques, and difficulty in monomer synthesis have prevented widespread adoption of this polymerization strategy. In this work, we have developed a new class of rROP monomers that uses a thiocarbonyl as a radical acceptor to overcome classical issues of monomer reactivity. Further, the thionolactone ring can be synthesized in two steps and has a structure amenable to further structural modification. This has resulted in a robust method to copolymerize acrylates using controlled radical polymerization methods and leads to the incorporation of reactive thioester functional groups into the polymer backbone.

[54]

Halide Rebound Polymerization of Twisted AmidesMizhi Xu, Jiyao Yu, and Will R. Gutekunst

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Abstract

Twisted amides are a special class of molecules that have distorted, non-planar amide bonds as a result of the geometric constraints imposed by the bicyclic framework. The weakened resonance from C-N bond rotation causes the nitrogen to become more nucleophilic and the carbonyl group more electrophilic. The reactivity can be correlated to the degree of distortion found in the amide, described by the twist angle and the pyramidalization of the nitrogen atom. Here, we demonstrate the potential of twisted amides to polymerize through a new mechanism for controlled, living polymerization termed "halide rebound polymerization." Initiated by alkyl halides, the polymerization of twisted amides is a unique case of electrophilic polymerization that has stable, isolable chain ends which is demonstrated through chain extension experiments. The twisted angles of new twisted amide systems can be readily calculated to identify future monomer designs with heightened reactivity.

[55]

Enyne Functionalization of ROMP PolymersTianqi Zhang, Liangbing Fu, and Will R. Gutekunst

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Abstract

Ring-opening metathesis polymerization (ROMP) has become a powerful and broadly applicable method to synthesize well-defined functional polymers because of its high functional tolerance and reliability.¹ However, efficient methods for chain-end functionalization of ROMP polymers still remains a significant challenge.² This work presents a new strategy to modify ruthenium carbenoids through the use of enyne molecules. In these systems, a terminal alkyne serves as a directing group that rapidly reacts with the ruthenium alkylidene or benzylidene and promotes ring-closing metathesis onto an unreactive, hindered cinnamyl olefin. Using this general relay strategy, molecules can be designed to give polymer termination or to generate functional initiators that permit the modification of either end of the metathesis-derived polymer chain. Due to the speed and robustness of the alkyne addition, this can be used for rapid polymer-polymer coupling of living metathesis polymers. This greatly expedites the creation of functional ROMP materials and is expected to lead to further applications in bioconjugation, surface functionalization, and branched polymer synthesis.