Materials Science

Highly Ordered, Multilayered Polymer Composite Films

With the growing demand for unique multifunctional composite materials for a range of advanced applications that require controlled optical, mechanical or electrical properties, there is a need for scalable fabrication processes that would allow for precise nanostructure control. PRINT is a viable approach for this type of fabrication as it provides complete tunability of the filler particle parameters: shape, size (nanometer to micron), orientation and composition. As the molded particles are in an initially non-aggregated state either in the mold or on a substrate, strategies can be employed to transfer the particles to a matrix without aggregating the particles. Using a layering approach, particles are uniformly dispersed in a polymer matrix to generate complex three-dimensional architectures, where particles cannot aggregate. Both polymer-polymer and polymer-ceramic composites have been generated using this technique, with particle inclusions ranging in size from 7 micron to 200 nm.

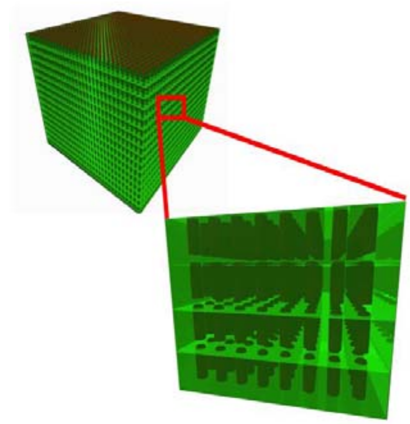

Figure 1. Cartoon depicting layered assemblies of polymer composite films.

Nano-Patterned PEM Fuel Cells

Fuel cells provide a means to consume alternative, renewable energy sources and produce significantly fewer environmentally malign byproducts. A promising fuel cell technology is the proton exchange membrane fuel cell, at the center of which is the proton exchange membrane, the target of our research project. Conventional proton exchange membranes are composed of high molecular weight linear polymers that undergo an undesirable balancing of performance and durability and are limited to flat, two-dimensional geometries. The nature of flat membranes provides a restraint on the contact with the adjacent catalyst layer, where the electrochemical processes occur, which limits the performance of the fuel cell.

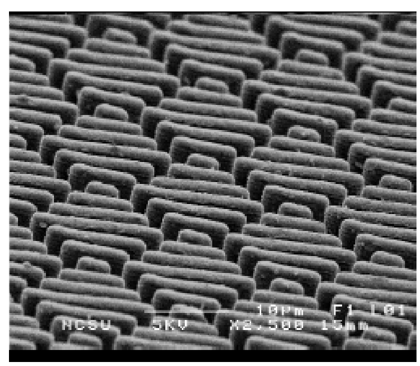

Figure 2. SEM image of a patterned proton exchange membrane.

The approach undertaken by the DeSimone group is to synthesize crosslinked membranes directly from liquid precursors. Because the membranes are crosslinked, the balancing act between performance and durability does not exist and patterned higher surface area membranes can be prepared using PRINT technology. These high surface area membranes have greater contact with the catalyst layer and, as a result, have demonstrated significantly better performance than commercially available standards.

Polymerization in Supercritical Carbon Dioxide

A cornerstone of our efforts has been to synthesize and process highly desirable polymeric products in an environmentally responsible way using liquid and supercritical CO_2 technologies. For the past several years, our goal has been to utilize the unique properties of supercritical fluids to improve the production of important specialty polymers based on tetrafluoroethylene such as TeflonTM, Teflon-AFTM, KalrezTM fluoroelastomers, NafionTM and other fluorinated high performance materials. We have recently carried out fluoropolymer synthesis in CO_2 expanded organic solvents, especially some hydrocarbon solvents. We are also interested in making new functional fluoropolymers with improved or tunable surface and binding properties in CO_2 medium. Polymerization methods examined in our laboratory include homogeneous, precipitation, dispersion polymerizations, as well as continuous polymerization methods.

Antifouling Coatings

Figure 3. PFPE/PEG blends for antibiofouling applications.

Current antifouling coatings are responsible for alarming increases in the levels of organotin and other toxic compounds in the vicinity of dry-docks, harbors and shipping lanes. Perfluoropolyethers (PFPE) with unique properties were exploited as safe, nontoxic, environmentally benign alternatives to antifouling technologies. As a unique class of fluoropolymers, PFPE have been established as high performance materials, which combine low surface tensions (8 - 15 mN/m), tunable moduli (1 – 100 MPa), as well as excellent thermal and chemical stabilities with the practical ease of solventless processibility. A multifaceted approach is being utilized in order to investigate how fundamental changes in molecular structure correlate to bulk properties, surface properties and the fouling resistance of these materials. In particular the effects of the surface dynamics and chemistries, which effect interfacial interactions, surface topologies (through lithographic techniques), curing chemistries, and the inclusion of comonomers, which inhibit protein adsorption, are being investigated.

Colloidal Assembly of Anisotropic Particles

Colloidal assembly is a fascinating field of materials science that the DeSimone group has recently begun to contribute to. Using PRINT, particles can be synthesized with remarkable control over shape, size and composition. With this capability, the colloidal assembly of such particles can be systematically studied as a function of these parameters. Shape is a particularly important factor in colloidal assembly, as it would control the type of crystal lattices that result, which in turn affects macroscopic properties, such as optical properties. We have shown the alignment and crystallization of a variety of unique anisotropic particles that were fabricated using the PRINT process. This directed assembly was accomplished using dielectrophoresis, where the colloidal suspension was subjected to a nonuniform AC electric field. (See Figure 4) Continued efforts in this research are focused on exploring the effects of composition and shape on colloidal assembly directed by electric and magnetic fields.

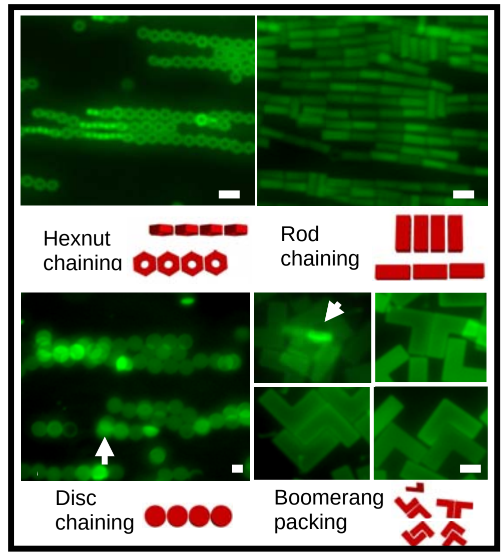

Figure 4. Anisotropic particles aligned in an AC electric field.

Nanopatterned Photovoltaic Devices

With global energy demands increasing yearly and current energy production dependent on a finite supply of fossil fuels, solar energy provides a sustainable energy alternative to traditional energy sources. Recent advances in solar energy research have shown organic-based photovoltaic cells, when configured into bulk heterojunction (BHJ) morphologies, exhibit high collection efficiencies if the morphology of phase separation is controlled to the extent that any point in the network is within the exciton diffusion length of a donor/acceptor junction and the network is bicontinuous. In this research effort, we have fabricated bulk heterojunction photovoltaic (PV) cells using a PFPE stamp to control the morphology of the donor-acceptor interface within devices. Devices were fabricated using the PRINT process to have nanoscale control over the bulk heterojunction device architecture. The low-surface energy, chemically resistant, variable modulus, fluoropolymer based molds used in PRINT provide a route to patterning, with nanometer resolution, general polymeric donor materials such as polythiophene and polyphenylenvinylene derivatives and 'hard' inorganic oxide structures typically used as acceptor materials in hybrid organic solar cells such as TiO_2, ZnO, and CdSe. This "top-down" approach allows for patterning over large areas and for the functionalization of the donor/acceptor interface.

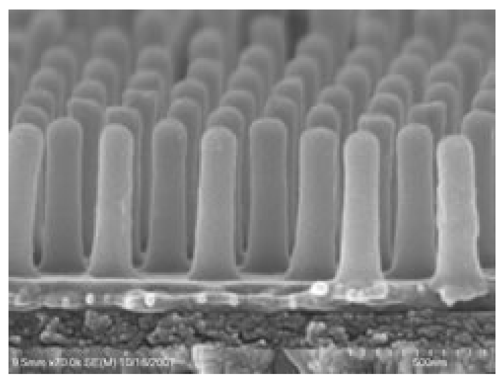

Figure 5. SEM of patterned semiconducting polymer nano-towers for new photovoltaic devices.