University of Wisconsin
Nanoscale Science and Engineering Center
on Templated Synthesis and Assembly at the Nanoscale

Thrust 1: Directed Assembly of Block Copolymer Materials

Thrust 1 explores and develops new materials and processes for advanced lithography, in which self-assembling block copolymers are directed to adopt morphologies that advance the performance of nanomanufacturing processes.

Molecular Transfer Printing Using Block Copolymers

S. Ji, C.C. Liu, G. Liu and P.F. Nealey

Photolithography allows for the patterning of billions of nanoscopic structures and parts of the devices with virtually no defects over macroscopic areas. As fundamental barriers emerge for use of traditional photolithographic materials and processes for patterned features smaller than 20 nm, the cost of traditional patterning will become prohibitively expensive. A team of researchers at the University of Wisconsin Nanoscale Science and Engineering Center have recently developed an approach to replicating geometrically complex pattern over macroscopic areas with feature dimensions on the order of 10 nm. The technique, called "molecular transfer printing" (MTP), takes advantage of patterns in the domain structure at the surface of block copolymer films and transfers those patterns with high fidelity to substrates placed in contact with the copolymer film. In MTP, reservoirs of inks in copolymer domains promote saturation of molecular transfer at the replica surface. The resulting pattern on the replicas mirrors the domain pattern present at the original film surface and can direct the assembly of new thin films of block copolymers. Technologically useful patterns such as bends, jogs, T-junctions, and hexagonal arrays of cylinders were successfully replicated in high fidelity (see Figure). The pattern from which transfer occurs (and thus the resulting pattern by MTP) is of superior quality (perfection, registration, uniformity of feature dimensions) and at higher resolution than the initial lithographically defined pre-pattern.

The ease of this technique to produce well-defined nanoscale patterns over macroscopic areas holds potential for many applications across the physical, engineering, and life sciences. It may also have profound implications for augmenting and advancing the performance and capabilities of the current lithographic process.

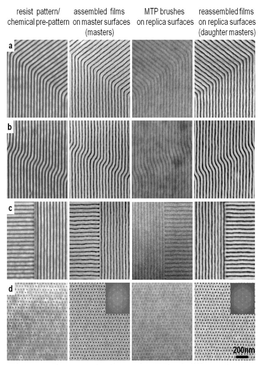


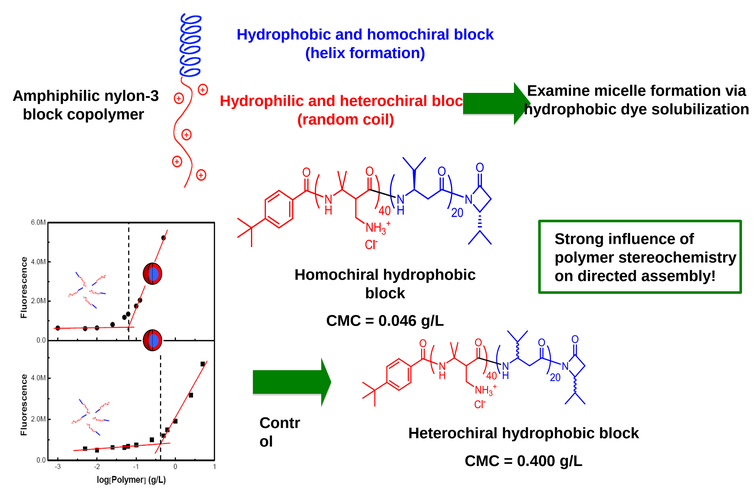
Figure. Demonstration of MTP of different pattern geometries using ternary blends of block copolymers. (a–d) SEM images of the photoresist pattern, indicative of chemical pre-patterns, blend films assembled on the master surfaces (masters), transferred brushes on replica surfaces, and reassembled blend films on replica surfaces (daughter masters). MTP replicates arrays of (a) 120° bends, (b) jogs, (c) T-junctions, and (d) dot arrays with high fidelity. The patterns of the brushes transferred by MTP and the daughter masters are mirror images of the masters.

Thrust 2: Sequence-Directed Assembly of Organic Nanostructures

Thrust 2 explores directed assembly at the nanoscale through the synthesis of biologically-inspired organic nanostructures in which functional side-chains display unique ordering, in terms of both sequence along a backbone and three-dimensional arrangement in space.

Directed Assembly in Aqueous Solution with Block Nylon-3 Copolymers Role of Polymer Stereochemistry

J. Zhang, and D. M. Lynn



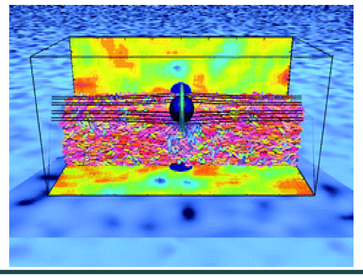
Thrust 3: Driven Assembly at the Nanoscale

Thrust 3 explores and harnesses non-equilibrium processes, including the use of external fields, for manipulating the assembly of nanoscale objects, including particles and macromolecules.

Flow Induced Deformation of Defects Around Nanoparticles and Nanodroplets Suspended in Liquid Crystals

[a]B. T. Gettelfinger, [a]J. A. Moreno-Razo, [a]G. M. Koenig Jr, [b]J. P. Hernández-Ortiz, [a]N. L. Abbott and [a]J. J. de Pablo
[a]University of Wisconsin - Madison, [b]Universidad Nacional de Colombia, Sede Medell´ın, Columbia

A three-dimensional molecular theory is used to describe the effect of flow on the defects that arise around nanoparticles and nanodroplets suspended in a nematic liquid crystal. It is observed that flow displaces the Saturn ring line defect that forms around a nanoparticle at equilibrium in the upstream direction; it is eventually closed by the flow and becomes a Hedgehog point defect. In contrast, the Saturn ring that forms around a nanodroplet is slightly displaced in the downstream direction. Experimental measurements of defects around nanoparticles have not been reported in the literature. In the absence of experiments, the validity of theoretical predictions is assessed through a direct comparison to results of many-body molecular dynamics simulations of a coarse grain liquid crystal model. Theoretical predictions and molecular simulations are in quantitative agreement, thereby lending credibility to the predictions presented in this work and suggesting that flow can be used to manipulate defect structure and aggregation of nanoparticles in nematic liquid crystals.



BT Gettelfinger, JA Moreno-Razo, GM. Koenig Jr, JP. Hernández-Ortiz, NL. Abbott and JJ de Pablo, *Soft Matter*, **6**, 896-901 (2010)

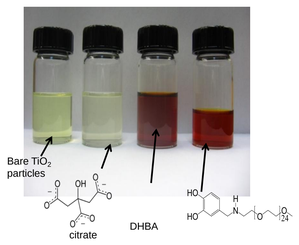
Thrust 4: Environmental Health & Safety Implications of Nanotechnology

Thrust 4 elucidates the environmental fate and toxicity of nanomaterials.

Chemical and Photo-toxicity of Metal Oxide Nanoparticles

J. A. Pedersen, R. J. Hamers, W. Heideman, and R. E. Peterson

Metal oxide nanoparticles such as TiO_2 are of increasing interest for applications in renewable energy and as potentially safer alternatives to organic compounds in topical application as sunscreens. Thrust 4 is investigated the fate and toxicity of metal oxides such as TiO_2 in the environment, including the role of natural organic matter in stabilizing nanoparticles in aqueous media. Thrust 4 is investigating the toxicity of metal oxide nanoparticles and how exposure to light and the concomitant formation of reactive oxygen species impacts development and toxcity of zebrafish. Because toxicity is closely connected with aggregation of nanoparticles, we have also studied the influence of organic ligands on nanoparticle aggregation, generation of reactive oxygen species, and toxicity. These organic ligands are designed to simulate the effects of natural organic material.



Ligand-modified nanoparticles used as model systems for understanding influence of ligands on the environmental alteration, bioavailability, and toxicity of nanoparticles

As a baseline, we investigated commercially available TiO2 nanoparticles consisting of a mixture of anatase and rutile TiO2. Ongoing experiments are focusing on monodisperse nanoparticles with the anatase form synthesized at UW and examining the effects of size and surface chemistry. Results thus far show that the commercially available TiO2 nanoparticles left in the dark are toxic only at very high concentrations, but upon illumination with above-bandgap light the particles exhibit much higher levels of toxicity and induce morphological endpoints of toxicity at sub-lethal levels. Measurements show that nanoparticle size influences toxicity in a complex manner, with nanoparticle of intermediate sizes (~20 nm) having higher toxicity than either small or larger nanoparticles. Ongoing experiments are targeted toward a mechanistic understanding of this size dependence.

Societal Implications Group

The Societal Implications Group analyzes the potential of the online environment for effective public communication and engagement in nanomaterials related issues.

Narrowing the Nano Discourse? The Web Changes How and What Citizens Learn About Emerging Technologies

P. Ladwig, A. Anderson, D. Brossard, D. Scheufele, and B. Shaw

Audiences for science and technology news in traditional news outlets are shrinking, and recent data suggest that citizens increasingly turn to online sources for information about emerging technologies, such as nanotechnology. This raises a number of related questions. How do they approach this wealth of online information about nanotechnology, i.e., what kinds of keywords searches are most frequently used by citizens? And what kinds of content are they likely to encounter, based on these searches? As

Based on analyses of Google Keyword data, Google Suggestions data and nano related Web sites content data, our results suggest that the terms audiences search for and the content they encounter during these searches increasingly shift the public debate about nanotechnology away from economic or scientific considerations. Instead, the web is directing the public toward a framing of the issue around health and medical considerations. This may have an impact on public's perception of the science and the range of its applications. In 2009, Google users are searching less for economic terms relating to nanotechnology than they were in 2008, and current Google suggestions highlight more health-related than economic terms. Plant biotechnology experienced a similar trend as U.S. media coverage initially focused on technological and economic development, but, by the late 1990s, focused on health and ethical risks. Although this shift in frames did not affect regulatory policy, it slowed industry growth. The trend we are seeing in online searching and content of nanotechnology could adversely affect future investments in nanotechnology in a similar fashion.

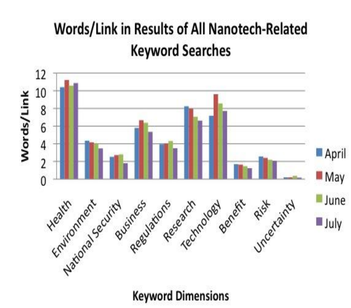


Figure 1: We searched for "nanotechnology" and several other keywords on Google and analyzed the content of the resultant websites by searching for a set number of words/link on the sites. We found that overall, most online nanotechnology content is health themed.

Education / Outreach Group

The Educational Outreach Group develops new scaleable teaching and learning programs, methods, and communities, aimed at cultivating a diverse next generation of nanoscientists and engineers.

Teaching Nanoscale Science and Engineering with Technology: Webquests for Middle and High School Students

J. W. Moore, and A. E. Greenberg

The NSF supported Nanoscale Science and Engineering Center (NSEC) at the University of Wisconsin – Madison has authored a series of highly evaluated nanoscale science and engineering focused webquests for teaching K-12 students about nano related topics. The webquests ask students to explore nanoscience topics ranging from nanoscience and materials found naturally to economic impacts of nanotechnology. The task based inquiry lessons allow students to use their creativity while learning about cutting edge science and technology research. Each webquest includes detailed national and local content standards, student assessments, and directions for classroom implementation.

Students share the outcomes of their tasks with other students through an online database. The series of lessons was recently added to the Middle School Portal of the National Science Digital Library for national dissemination.

Primary Strategic Outcome Goal:

Learning: Cultivate a world-class, broadly inclusive science and engineering workforce, and expand the scientific literacy of all citizens.

Secondary Strategic Outcome Goals:
How does this highlight address the strategic outcome goal(s) as described in the NSF Strategic Plan 2006-2011?

Learning – Nanoscience wequests helps students to learn about modern research and its broad implications on society.

Screenshots of four of the NSEC developed webquests.

University of Wisconsin–Madison NSEC Nanoscale Science & Engineering Center

Nanoscale Science and Engineering Center on Templated Synthesis and Assembly at the Nanoscale

We gratefully acknowledge funding from the National Science Foundation, DMR-0832760

THE UNIVERSITY of WISCONSIN MADISON