Making complex nanomaterials with molecular stencils

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A new approach to fabricating nanomaterials combines molecular recognition with self-assembly to synthesize materials comprised of ordered, nanostructured functional features.

Nanomaterials can impact innumerable applications ranging from high-performance composites to energy-conversion technologies. The challenge lies in finding ways of efficiently fabricating these nanomaterials. One approach consists of starting with a large object and carefully removing material until the required structure is obtained. But as features become smaller, this approach becomes prohibitively slow or expensive. Alternatively, we can work from the bottom up using building blocks to assemble—or ideally self-assemble—the desired nanostructure. This method can be powerful but, in many cases, the most effective self-assembly materials do not have the properties desired for target applications, such as magnetic or metallic behavior.

Many different approaches to making nanomaterials have been demonstrated. These include lithographic techniques such as electron beam lithography and nanoimprint lithography, as well as bottom-up techniques such as DNA origami and block copolymer self-assembly. In many cases, however, these approaches are either costly or do not exhibit functional properties of interest. Electron beam lithography, for example, is serial in nature, meaning that each piece of the pattern is written one at a time. This makes the process slow and, therefore, expensive. On the other hand, techniques such as block copolymer self-assembly are low-cost, but the polymers themselves often do not exhibit the physical properties of interest.

We have developed a new approach called sequential infiltration synthesis (SIS) that can simultaneously take advantage of the low-cost assembly associated with soft matter (materials such as polymers) and the physical properties associated with hard matter (ceramics, for example). SIS begins with the self-assembly of a film of block copolymers. Due to the chemistry of these long-chain molecules, which are comprised of segments of two or more polymer materials, such copolymers can organize themselves into highly ordered and tunable nanoscale structures: see Figure 1(a). These structures have many potential applications. However, in most cases, realizing these uses requires a broader range of functionality than is available in the native polymers.

We have discovered that a technique called atomic layer deposition, in which reactants flow over a surface and grow materials in a highly controlled manner, can be applied to block copolymer films. In this case, though, the material does not grow on top of the polymer. Instead, the reactants infiltrate into the film. Careful selection of reactants and polymer chemistries can provide highly selective interactions such that deposition occurs only within one of the polymer domains: see Figure 1(b).

The size of the individual domains of inorganic material can be tuned with high precision by performing a specific number of atomic layer deposition cycles, with each cycle adding a little

Figure 1. Steps involved in the sequential infiltration synthesis (SIS) process. (a) First, a block copolymer film self-assembles into nanoscale domains (of PS and PMMA) on the substrate forming the pattern stencil. (b) Next, selective gas-phase reactions deposit inorganic material only within one of the two block copolymer phases, the PMMA domain. (c) Finally, the residual organic material (PS) can be removed to leave behind inorganic features that mimic the self-assembled structure of the original stencil. PS: Polystyrene. PMMA: Poly(methyl methacrylate).

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more material to each domain. Once the growth is completed, the remaining polymeric can be removed either by simple heating or by plasma etching. What remains is a pattern of inorganic material that perfectly mimics the pattern present in the original self-assembled block copolymer film: see Figure 1(c).

Starting with a poly(styrene-block-methyl methacrylate) block copolymer, we have used this approach to grow arrays of a variety of nanomaterials, including aluminum oxide, titanium dioxide (see Figure 2), silicon dioxide, zinc oxide, and tungsten. This progress represents only a small fraction of the available materials and structures accessible via SIS. It is possible to alter the block copolymer chemistry and/or the atomic layer deposition reactants to achieve different morphologies (spheres, stacked layers, etc.) or materials. Each combination of material and shape could have a different potential application, including photovoltaics, photonic crystals, or catalysts.

Nanomaterials have great promise, but traditional means of fabricating these materials often run into seemingly insurmountable challenges. We have added a tool to the arsenal of ways in which scientists can fabricate nanostructures. This tool, SIS, captures the combined advantages of molecular recognition and self-assembly to provide a pathway to many complex nanomaterials. Much work remains to optimize the methodology for specific applications and to test its limits. Our next step is to explore stepping out of the 2D world into the third dimension with SIS.

The use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract number DE-AC02-06CH11357. This work was supported in part by the Argonne-Northwestern Solar Energy Research Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001785.

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