edge, vertex, or face-sharing octahedra. However, the three nickel atoms are crystallographically inequivalent with different Ni–O bond lengths. Combined with the trigonal symmetry of the crystal, this leads to an arrangement of 120° rotated triangles that are stacked on top of each other to form a helix.

In the figure, the blue triangles correspond to adjacent nickel octahedra while the red triangles correspond to nickel-tellurium. Importantly, the researchers were able to show that the chiralities of the red and blue helices do not cancel each other within a unit cell leading to a net left- or right-handedness. Also, the resulting spatial shift of the ions leads to a net polarization. Any optical domain wall that was not also a polar domain wall was found to disturb the ideal stacking for tellurium octahedra.

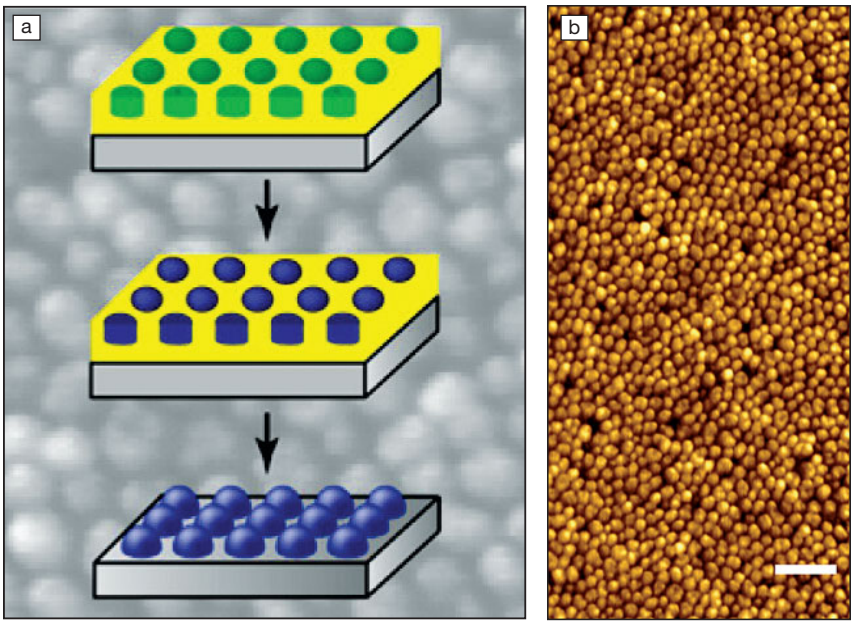
Most inorganic materials that have large optical activity have so far only shown chirality without polarity. NTO is the first known material that shows both. "Our findings unveil the rich coupling nature of chiral and polar order parameters and provide new insights into understanding and engineering domains in functional chiral and polar materials," the group states in their article. This understanding of the fundamental properties of polar domain boundaries is key to the development of new economically important materials according to Chris Stock of The University of Edinburgh, who adds, "This has been evidenced by fundamental developments in disordered ferroelectrics (such as the lead-based relaxors) resulting in recent applications of memory storage such as FRAM [ferroelectric random-access memory]. The observation of these highly structured domains is really a breakthrough in materials physics and will lead to new studies on similar materials and eventually new applications."

Vineet Venugopal

Nano Focus

Block copolymers enable nanoscale patterning of metal oxides

The size scale for semiconductor components such as metal oxide is soon expected to dip below the 10-nm-size range. Current top-down fabrication techniques such as lithography are being stretched to their limits. A bottom-up approach, such as self-assembly of a block copolymer (BCP) avoids some of the challenges inherent to lithography; however, current BCP materials and processes cannot produce ultrasmall features. Now, a joint research team including Morgan Schulze, a graduate student working with Marc Hillmyer at the University of Minnesota in collaboration with Christophe Sinturel from the Université d'Orléans, France, has surmounted these challenges, producing ordered arrays of metal oxide particles with diameters as small as 6 nm—all without the use of traditional lithography techniques.



(a) Scheme of templating process. Top: poly(cyclohexylethylene) (yellow)-*block*-poly(ethylene oxide) (green) template. Middle: poly(ethylene oxide) block infiltrated with inorganic precursor. Bottom: organic block polymer template is removed to reveal the metal oxide nanoarray. (b) Atomic force micrograph of titania nanoparticles produced by the block copolymer templating process. Scale bar is 100 nm.

The key advance, reported in *ACS Macro Letters* (DOI: 10.1021/acsmacrolett.5b00458), was the novel block polymer design and synthesis (see Schematic). "Our choice of blocks allowed us to not only achieve small sizes, but also allowed us to selectively incorporate metal oxide precursors into hydrophilic domains that enabled a simple pattern transfer process," Hillmyer says.

No top-down patterning is needed because the block copolymers self-assemble into the desired array of domains due to the incompatibility of the two polymer blocks. The process is analogous to the formation of an oil–water emulsion, except that because the polymer blocks are covalently joined, the domain size is very small (nanoscale). The problem, according to Hillmyer, is that "smaller feature sizes require smaller molecules, but the smaller the block polymer, the more incompatible the individual segments need to be." Motivated by this challenge, the team developed a route for the synthesis of highly incompatible poly(cyclohexylethylene)-*block*-poly(ethylene

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oxide). Block incompatibility, characterized by the interaction parameter of the blocks (χ), was estimated through dynamic mechanical spectroscopy and small-angle x-ray scattering experiments.

In order to fabricate arrays of silica, titania, and iron oxide particles, the team selectively infiltrated the hydrophilic (and also metallo-philic) poly(ethylene oxide) blocks with an inorganic precursor, and removed the polymer scaffold with a UV/ozone process. Atomic force micrographs showed arrays of circular oxide particles (see Figure). For samples fabricated using the 5.9 kg/mol block copolymer, the average diameter of the oxide particles was 13 nm and their heights ranged from 1 nm to 3 nm. To push feature sizes even smaller, the team prepared oxide arrays using a block copolymer with a lower molecular weight of 4.1 kg/mol, resulting in metal oxide particles of 6 nm in diameter. These are the smallest particles to be templated using this type of process.

Hillmyer envisions the future applications of the technology: "We hope that these kinds of materials will find applications where ultrasmall nanostructures are needed to achieve high-performance microelectronics or to meet high-density data storage demands." Building functional components at the single-digit nanometer size scale lies at the intersection of chemistry and materials science. This research advance exemplifies the fundamental progress needed to continue the trend of decreasing semiconductor feature sizes and increasing processor power.

Mary Nora Dickson

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