



Bio Focus

Gold nanoparticles enable instant colorimetric hydration sensor

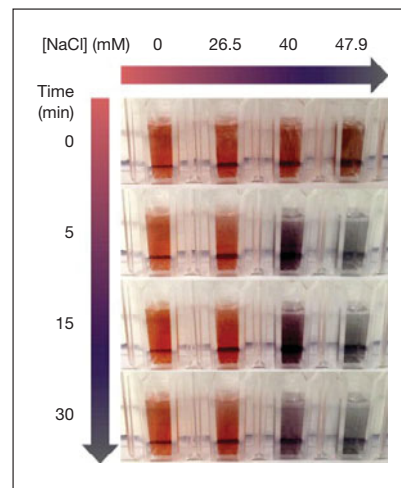
During sports activities, monitoring hydration status before, during, and after exercise is essential for both performance and safety. Y. Zhou of Nanyang Technological University, Souhir Boujday of Sorbonne Universités in Paris, and their colleagues have now developed a gold nanoparticle-based colorimetric sensor that makes it possible to detect hydration balance and overhydration within minutes. They reported their work in the journal *Materials & Design* (DOI: 10.1016/j.matdes.2015.06.078).

The researchers used ascorbic acid-stabilized gold nanoparticles (AuNPs) in this work. To obtain a model mixture with the necessary concentration of the AuNPs, 100 μL of 100 g L^{-1} chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was mixed with 25 mL of de-ionized water and 1.5 mL of 21.2 g L^{-1} sodium carbonate solution. To

complete the synthesis, 2 mL of 7 g L^{-1} ascorbic acid underwent vigorous stirring at 1000 rpm on a magnetic stirrer for 15 min. The mixed solution was chilled with ice at about 0–2°C. The designed mixture model had the concentration range of human body fluid.

Different colors were obtained at NaCl concentrations of 26.5 mM, 40 mM, and 47.9 mM, which indicate that the sensor can distinguish between hydration imbalance situations. As the concentration of NaCl increased from 26.5 mM to 40 mM and 47.9 mM, the A650/A520 ratio increased, indicating a decrease in dispersed particles and an increase in AuNP aggregates. The ratio of absorbance at 650–520 nm (A650/A520) is a good indicator of the aggregation state of the AuNPs. The particles' aggregation/dispersion state occurred in the desired range of salt concentration.

The researchers envision this type of sensor to be used for detection of hydration levels with many desirable properties, including simple detection display,



The different color of AuNPs solution in the presence of different concentrations of NaCl. Credit: *Materials & Design*.

high stability, and fast response time. Furthermore, this model of sensor may be useful in detecting small changes in biological substances in excreted fluids.

Jean Njoroge

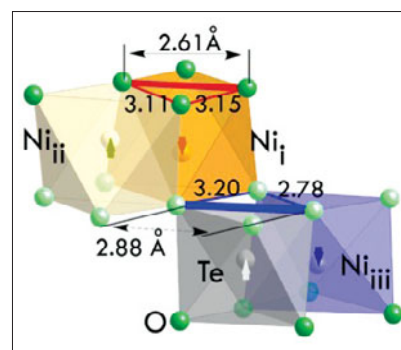
Ni_3TeO_6 crystal structure exhibits interlocked chiral and polar domain walls

Coexisting optical and polar domains have been found in single-crystal Ni_3TeO_6 . Furthermore, these domains are intertwined—the optical orientation, directly related to structural chirality, determines the polar orientation and vice versa. A group at Rutgers, The State University of New Jersey led by Sang-Wook Cheong reports these findings in *APL Materials* (DOI: 10.1063/1.4927232). This is the first known report of a crystal that has been found to show intertwined optical and polar domains.

“After getting high-quality single crystals of Ni_3TeO_6 (NTO), we happened to observe domain inversion under a transmission polarized optical microscope,” Cheong tells *MRS Bulletin*. “Since the crystal group Ni_3TeO_6 is non-centrosymmetric, it’s natural to test the piezoresponse by PFM [piezo force

microscope] scanning.” Such crystals have no center of symmetry, and show charge polarization, which is necessary for the piezoelectric effect—the propensity of certain materials to develop a surface charge when squeezed. PFM is a method of directly observing this behavior using an atomic force microscope. Optical activity is the rotation of plane-polarized light as it passes through a material.

Most crystals are found to be divided into smaller regions based on their polar/optical responses. The macroscopic behavior of a crystal is then the average behavior of all these domains. Some optical domains may rotate light counterclockwise while other domains rotate it clockwise. Similarly, polar domains have dipoles orientated in different directions. In NTO, if adjacent domains rotate light right-left, the corresponding polarization is found to be either up-down or down-up. Thus, an optical domain in NTO is also a polar domain and vice versa since their domain walls coincide. The polar



The basic building block of Ni_3TeO_6 . Credit: *APL Materials*.

domains in a hexagonal single crystal of NTO resemble the trefoil symbol for radiation danger.

The group explains this correlation through the crystal structure of the material. NTO has a corundum (Al_2O_3) crystal structure with nickel and tellurium occupying the sites traditionally reserved for aluminum. Each of the metal ions is surrounded by six oxygen atoms forming

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 nano-scale patterning of metal oxides

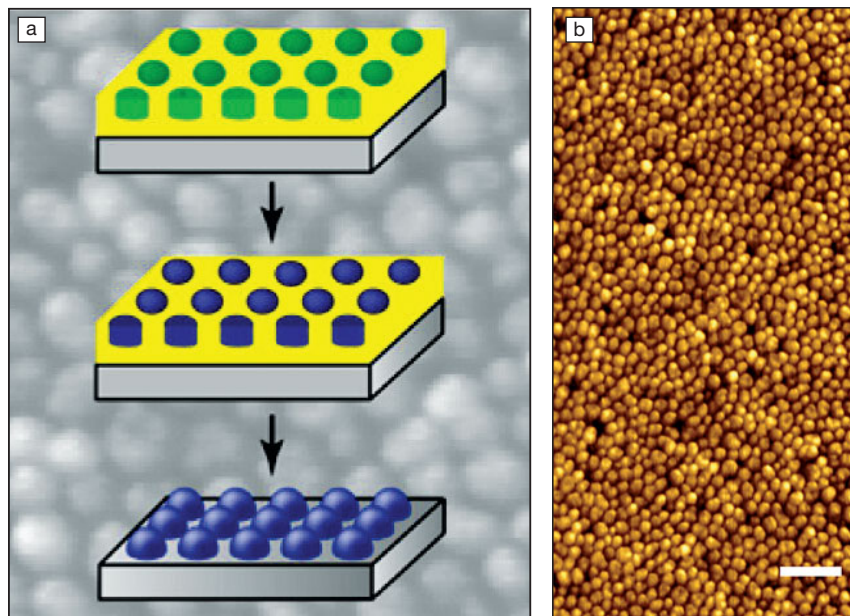
The size scale for semiconductor components such as metal oxide is soon expected to dip below the 10-nm-size range. Current top-down fabrication

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.

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



(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.