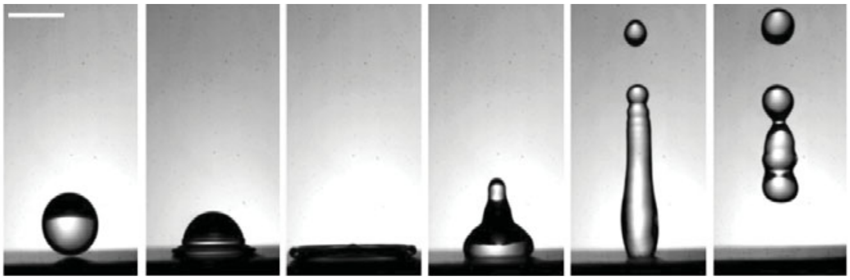
Rare-earth oxide ceramics found to be robustly hydrophobic

Understanding and controlling the hydrophobicity/-philicity of surfaces is critical for a range of applications. Traditional hydrophobic surfaces consisting of a polymer coating over a roughened surface often deteriorate in harsh environments, giving rise to increased wettability. Recently, however, researchers from the Massachusetts Institute of Technology (MIT) have shown that a series of rare-earth oxides ceramics (REOs) are intrinsically hydrophobic, a property related to unique structuring of water molecules at the oxide surfaces.

As described in the January 20 online edition of *Nature Materials* (DOI: 10.1038/NMAT3545), G. Azimi and co-workers sintered REO pellets of the lanthanide series including ceria and lutecia. Upon subjecting them to thermal and abrasive testing, the REOs show minimal change to their hydrophobic nature. Superhydrophobic surfaces were generated by texturing the REOs using a range of techniques, such as sputter-coating onto smooth and microstructured silica surfaces. Contact angles as large as 160° were measured and video snapshots of water droplets falling onto the microstructured surface show the droplets bouncing off the surface.



Sequential snapshots of a water droplet impinging on a surface coated with a thin layer of ceria (~200 nm thick); the droplet cannot form hydrogen bonding with the REO and surface tension causes the water droplet to bounce off the coating illustrating the superhydrophobic nature of these materials. Scale bar 2.5 mm. Reproduced with permission from *Nature Mater*. (DOI: 10.1038/NMAT3545). © 2013 Macmillan Publishers Ltd.

The origin of the hydrophobicity of the REOs can be attributed to their electronic structure. While most ceramics and metals are hydrophilic, due to coordinative unsaturation which allows water to form bonds with available valence orbitals, the 4*f* orbitals of rare-earth atoms are completely shielded by the electrons in the filled 5*s* and 5*p* orbitals. They are thus not available to hydrogen bond with water molecules. This causes the water adjacent to the REO surface to exhibit a hydrophobic hydration structure.

This work highlights the flexibility and scalability of these intrinsically hydrophobic REOs, where they can be fabricated using standard ceramic processing methods. The research also addresses problems of robustness, and may lead to new hydrophobic applications in harsh environments.

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Energy Focus

Charge-density waves may be competing with superconductivity

Researchers have been trying to identify the mechanisms underlying high-temperature superconductivity (HTS) in cuprate superconductors, typically attributed to charge-density waves (CDWs). Researchers at the Massachusetts Institute of Technology (MIT) and Brookhaven National Laboratory (BNL) have revealed that CDWs cannot be the root cause of the unparalleled power conveyance in cuprate HTS materials. In fact, CDW formation is likely an independent and competing instability according to the researchers, as reported in the February 24 online edition of *Nature Materials* (DOI: 10.1038/NMAT3571).

In describing charge-density waves, co-author Ivan Božovíc of BNL said, "They resemble waves rolling across the surface of a lake under a breeze, except that instead of water, here we actually have a sea of mobile electrons." Once a CDW forms, the electron density loses uniformity as the ripples rise and fall. Detecting CDWs typically requires high-intensity x-rays, but even then, the technique works only if the waves are essentially frozen upon formation. However, if CDWs actually fluctuate rapidly, they may escape detection by x-ray diffraction, which typically requires a long exposure time that blurs fast motion.

For their experiment, the researchers grew thin films of $La_{1.9}Sr_{0.1}CuO_4$, a HTS cuprate compound. The metallic cuprates, assembled one atomic layer at a time, are separated by insulating planes of lanthanum and strontium oxides, resulting in a quasi-two-dimensional conductor. When cooled down to less than 100 K, electron waves began to ripple through the 2D matrix. At even lower temperatures, these films became superconducting.

To catch CDWs in action, the research group at MIT, led by Nuh Gedik, used an advanced ultrafast pump-probe spectroscopy technique. Intense laser pulses, "pumps," cause excitations in the superconducting films, which are then probed by measuring the film reflectance with a second light pulse. The second pulse is delayed by precise time intervals, and the series of measurements allows the lifetime of the excitation to be determined. In a more sophisticated variant of the technique, the researchers replaced the standard single pump beam by two beams hitting the surface from different sides simultaneously. This generated a standing wave of controlled wavelength in the film, but it disappeared