Fig. 1 | Schematic of the polar structure and atomic-resolution images of the Sm-doped PMN-PT relaxor-ferroelectric. The sketch shows a tetragonal ferroelectric domain (yellow) spontaneously polarized in the (001) pseudo-cubic direction (red arrow), embedding local polar nanoregions (blue circles). This hypothetical picture is consistent with the results that the authors obtained when using atomic-resolution dark-field imaging. The dark-field images adjacent to the schematics show the tetragonal domain (matrix) and a polar nanoregion (local) with different crystallographic symmetries (see arrows). Sm doping is expected to further enhance the local disorder otherwise inherent in PMN-PT, leading to a flatter thermodynamic energy landscape for polarization rotation under external fields. Such a landscape is illustrated for arbitrary polarization directions (P_i) below the schematic. Adapted from ref. [2], Macmillan Publishers Ltd.

rare earths apparently enhances disorder in PMN-PT, further flattening the energy landscape for polarization rotation. The largest effect was observed with a samarium (Sm) donor dopant, resulting in spectacular piezoelectric coefficients of ~1,500 pC N^{-1}, the highest ever reported in polycrystalline ceramics. The existence of polar nanoregions inside tetragonal ferroelectric domains with a different symmetry was confirmed in Sm-doped PMN-PT by atomic resolution electron microscopy (Fig. 1).

Common to all sciences is that discoveries always raise additional questions. What is so special about Sm that it gives rise to the largest effect among the many dopants tested? What is the defect structure of the material? How do the donor-dopant sites

and the compensating defects (probably lead vacancies) distribute locally and how does this affect polarity at the nanoscale? To what extent does processing come into play when considering the dopant distribution in the ceramic matrix? Some of these questions may be answered by first-principles atomistic computations combined with advanced experimental approaches — for example, atomic-resolution microscopy with in situ field biasing — which could provide a mechanistic background to further develop and apply this discovery.

The modelling studies performed by the authors suggest the possibility of manipulating interfaces, and thus interfacial energies, between normal ferroelectric phases to enhance piezoelectric response

via nanoscale engineering. It would be interesting to see if superlattices could be one such case, and we could easily imagine and engineer a variety of nanocomposites with different levels of connectivity.

Although the maximum temperature up to which these materials can be utilized remains low (Curie temperature of ~90 °C), the authors show remarkable stability of piezoelectric response for temperatures almost up to this value. It is possible to imagine relaxor-ferroelectric ceramics with extremely high piezoelectric coefficients of ~1,500 pC N^{-1} replacing single crystals in piezoelectric devices, with the advantage of exhibiting comparable performance, but at a lower cost and with up-scalable processing, yielding a variety of sizes and shapes. When completely understood and verified, it would be interesting to determine whether nanoscale-engineered enhancement of piezoelectric response could be transferred to other groups of ferroelectrics. Implementing this approach in lead-free piezoelectric ceramics, which in many applications are currently outperformed by lead-based ferroelectrics, could certainly aid the sustainability of these devices. ❏

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SUPERHYDROPHOBICITY

Multilevel robustness

A combination of hard, soft and nanoscale organic components results in robust superhydrophobic surfaces that can withstand mechanical abrasion and chemical oxidation, and exhibit excellent substrate adhesion.

Henri-Louis Girard, Sami Khan and Kripa K. Varanasi

Superhydrophobic surfaces, on which water beads up and rolls away with very little adhesion[1], have generated a broad range of interest because of their promising use in self-cleaning[2], antifouling[3], anti-icing[4], drag reduction[5] and oil–water separation[6] applications. However, their practical implementation has been limited by the need for resistance to physical
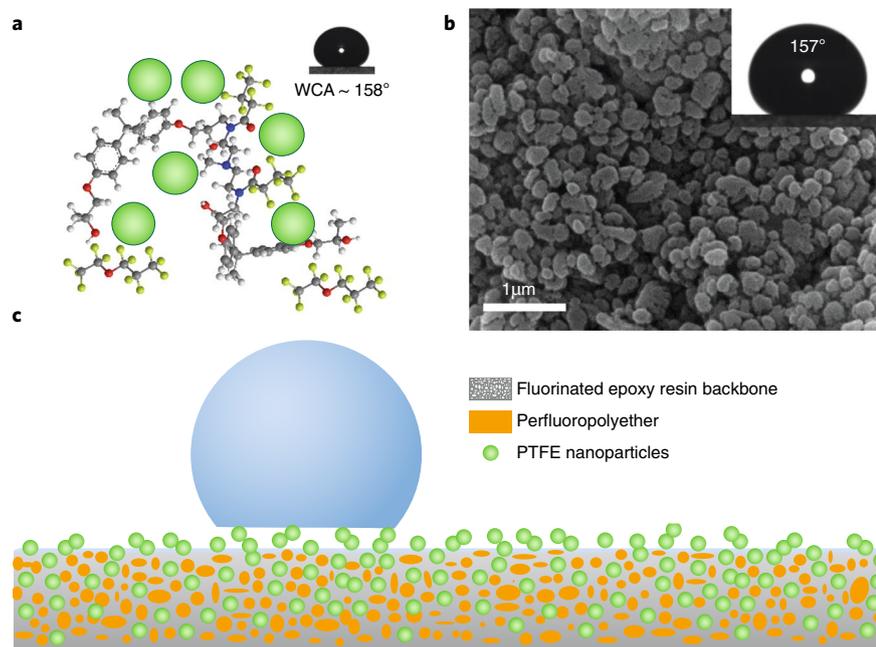
Fig. 1 | Multicomponent superhydrophobic coating. a, Illustration of the superhydrophobic coating composite structure, showing the epoxy resin backbone functionalized with fluorinated groups blended with perfluoropolyether and dispersed polytetrafluoroethylene (PTFE) nanoparticles (green circles), and the resulting water contact angle (WCA) of this material. **b**, SEM image of the coating surface after 12 hours in a sodium hydroxide solution, showing no physical damage and a high WCA (inset). Scale bar, 1 μm. **c**, Schematic of the multicomponent coating illustrating the different components of the system. Adapted from ref. [11], Macmillan Publishers Ltd (**a**,**b**).

abrasion, erosion, chemical exposure, high temperatures and ultraviolet radiation. Moreover, these materials should display good substrate adhesion and be easy to manufacture. Studies using ceramic coatings[7], candle soot templates[8], metallic nanonails[9] or initiated chemical vapour deposition (iCVD)[10] have reported surfaces with some of these characteristics. Yet a coating that simultaneously retains all of these properties has proven out of reach.

Now, writing in *Nature Materials*, Manish Tiwari and colleagues[11] describe a multilevel organic coating that resists chemical and physical abrasion while retaining high water repellency and mobility. This composite material is simultaneously mechanically robust, flexible, displays a self-similar nanoroughness that enables it to withstand damage and can be used to coat distinct surfaces by industrial application methods. The authors follow a multicomponent approach to robustness (Fig. 1), combining a fluorinated epoxy scaffold with a perfluoropolyether oil to create a flexible hydrophobic substrate. The further inclusion of up to 75 wt% of polytetrafluoroethylene (PTFE) nanoparticles provides the nanoroughness necessary to render the material superhydrophobic. This coating can be

mixed in a liquid form to be sprayed or brushed before the epoxy resin has hardened, making it easy to apply to a variety of substrates such as glass or metals.

Tiwari and colleagues demonstrate the mechanical adhesion of their superhydrophobic material to a substrate via a tape peel test. After 30 cycles of peeling, the water contact angle remains above 150° and the hysteresis below 5°, indicating a high mobility of water droplets. The commercially available superhydrophobic coatings NeverWet, Ultra-Ever Dry, Capstone C8 and HIREC 450 all fail after fewer than 10 cycles. A loaded-wheel abrasion test further demonstrates the enhanced resistance of the multilevel coating but also highlights the eventual failure of the nanoroughness of the coating under high external load. Nonetheless, because each level of the formulation exhibits intrinsic hydrophobicity, the coating retains highly hydrophobic characteristics even after the nanoparticles are flattened. The authors also show that the superhydrophobic material exhibits resistance to oxidation by aqua regia and degradation by sodium hydroxide. In these instances, the physical characteristics of its surface were unchanged, but defects in the chemical modifiers eventually appeared,

leading to a lowering of the contact angle and a small increase of the hysteresis. Moreover, the coating presents a great resistance to water impalement from drop impacts and high-speed jets with speeds up to 35 m s⁻¹. This feature was attributed to the flexibility of the material, which enables it to dissipate some of the impacting pressure felt at the surface.

The composite material reported by Tiwari and co-workers exhibits an impressive multipronged robustness, which could complement existing durable hydrophobic treatments[8–10,12] and broaden their window of applicability. It could also lead to advancements in a variety of non-wetting applications. For instance, by tuning the fabrication process, it may be possible to create structures fine enough to prevent nucleation within the pores[13] thereby making the coating applicable to anti-icing on external structures, methane-hydrate mitigation in oil and gas pipelines, and enhancing dropwise condensation for power condensers. These surfaces could also provide good corrosion protection because of the defect tolerance inherent to their multilevel structure. Nonetheless, the practical implementation of the coating in these applications needs to be fully evaluated. It will be interesting to investigate the resistance of the formulation to prolonged exposure to high temperatures and fatigue, and develop routes that bypass the intrinsic vulnerability of superhydrophobic coatings relying on nanoroughness that can be ground and polished via mechanical abrasion. A possibility would be to combine the multilevel approach developed by the authors with a sacrificial self-similar coating of nanoparticles, where the top layer of particles is removed by abrasion instead of being flattened, thus giving the resulting coating a higher resistance to occasional abrasion. Regardless of these limitations, the combined chemical and physical robustness, high substrate adhesion, flexibility and ease of application of the superhydrophobic coating described by Tiwari and colleagues constitutes a significant advancement over other materials of this sort. A future where these are used in commercial applications might not be so far away. ❑

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MATERIAL WITNESS

Chain reaction

In the 1950s J. Desmond Bernal sought to understand the structure of liquids by considering them as random packings of incompressible spheres, which he modelled using steel ball bearings. Bernal's model raised the question of how far the behaviour of a molecular system, agitated by thermal fluctuations, can be considered analogous to a collection of macroscopic particles in static equilibrium at zero effective temperature.

In the ensuing decades, Sam Edwards at Cambridge took that idea further by developing explicit analogies between the statistical mechanics of matter at the microscopic scale and the behaviour of granular media. Edwards and Oakeshott suggested that the volume for a granular material can play a role analogous to energy in statistical mechanics, and that a quantity called the compactivity, related to the packing fraction, is the analogue of temperature[1].

This hypothesis is still debated. It implies a definition of an effective entropy for granular media that seems to hold at least at the special point where a granular pile becomes 'jammed' into immobility[2]. This jamming transition has been proposed as the analogue of the transition from a liquid to a glass.

Much of Edwards's focus, however, was not simple liquids but polymers. Here the equivalent of a granular system of hard spheres is a chain of beads. The mechanical behaviour of such a system is complicated by the fact that, while the beads may still

jam against one another by friction, their motion is also restricted by the bonds between beads. Does Edwards's correspondence of macro and micro work for polymers too?

It does indeed, according to Zou et al., who showed that metal bead chains of the kind commonly used for window-shade pulls, when shaken in a container to produce dense packing, exhibit jamming in a manner that supports an equivalence between the final (maximal) random-packing density and the inverse of a polymer's glass transition temperature[3]. As those authors pointed out, this implies that condensed matter may be governed by geometry and symmetry beyond any details of microscopic interaction.

Dumont et al. have now taken this comparison further[4]. Using similar shaken bead chains of varying length, they explored how the resistance to indentation for chains packed within soft-sided containers (to allow for dilation and reduce the formation of load-bearing 'arches') varies with the number of beads per chain. This enabled them to investigate the changes in behaviour from Bernal-style 'ball-bearing liquids' to analogues of long-chain polymer melts.

Using ideas from polymer physics, the researchers predict that the resistance force due to friction is self-amplifying, increasing exponentially with the applied load, and that the exponent is proportional to the square root of the chain length. That's a relationship closely borne out by the data using a mechanical indenter.

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They also consider the case of a 'dilute polymer' in a solvent of single beads, where, by analogy with real polymer solutions, the chains are expected to be more or less self-avoiding, blob-like random coils. Again, polymer theory suggests a dependence of the exponent on the volume fraction of chain beads to the power 11/8, which is close to the measured value.

As well as lending further credence to the correspondence between microscopic molecules and macroscopic grains and chains, the work suggests that powders might be given greater mechanical integrity by interspersing a low concentration of chain-like structures, which may help to bind the grains together purely by friction. ❑

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