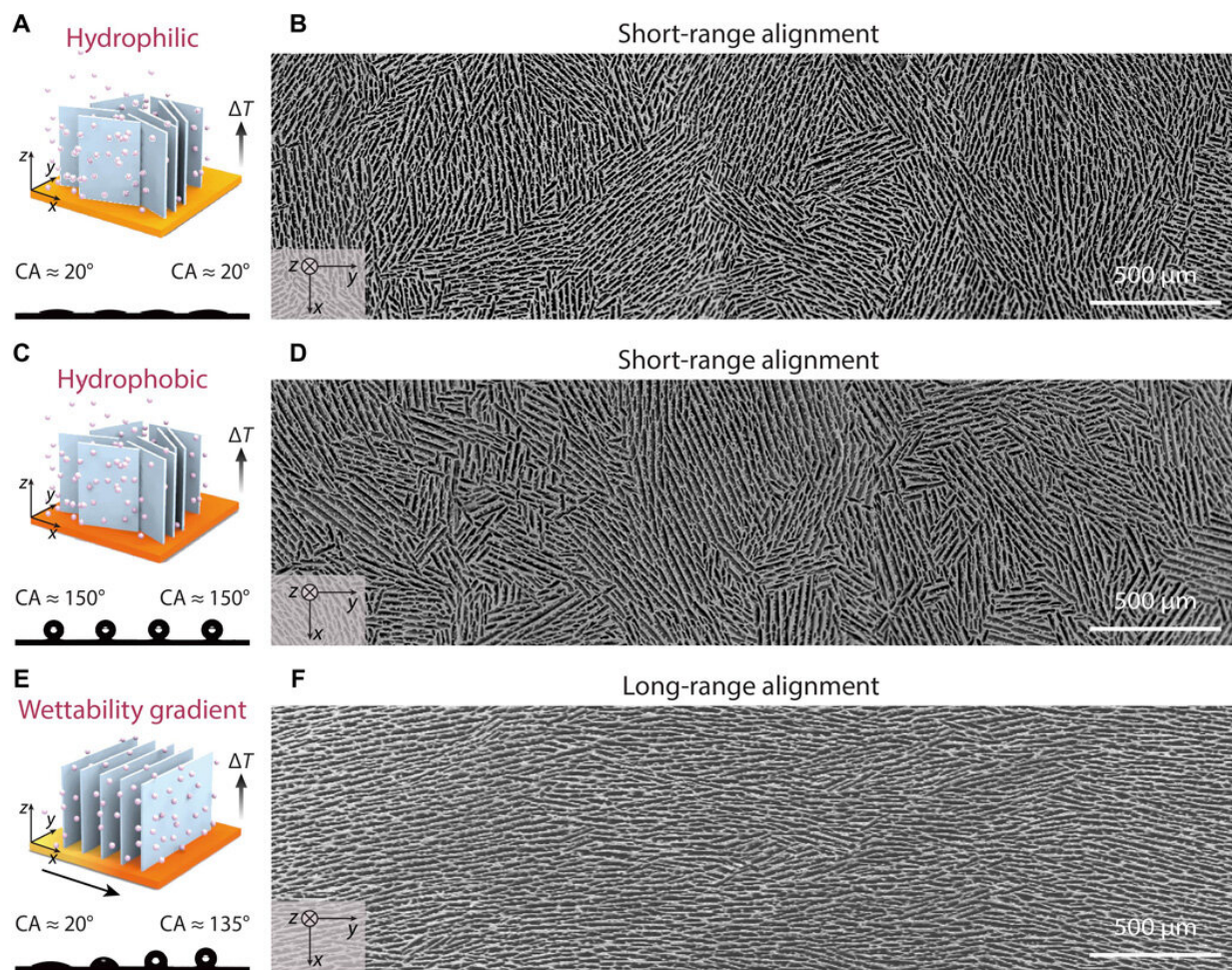


# Controlling ice formation on gradient wettability surfaces for high-performance bioinspired materials

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Freeze-casting technique using copper surfaces with different wettability and the resulting scaffolds. SEM images were taken from the cross section of 1-cm height parallel to the cold surface. (A to D) When freezing on the

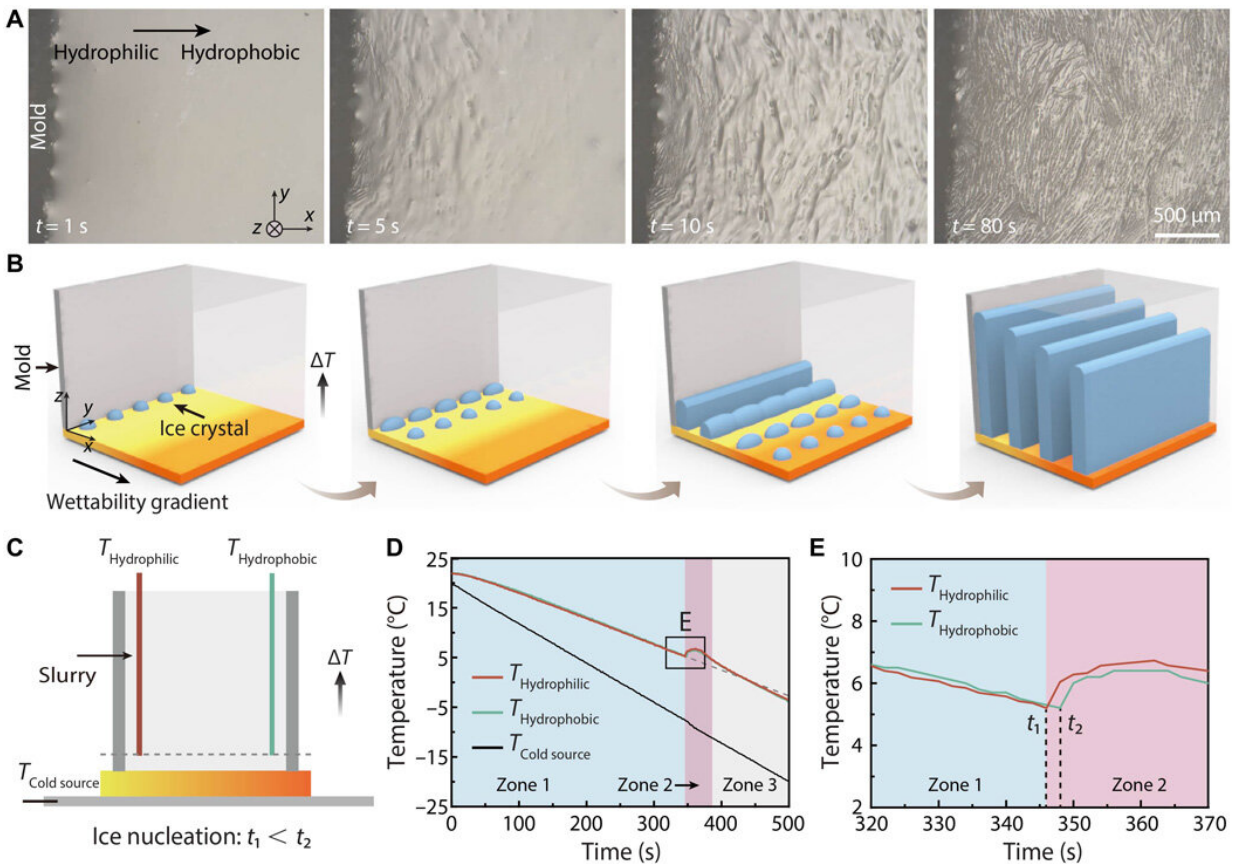
homogeneously hydrophilic and hydrophobic copper substrates, the ice crystals nucleate simultaneously over the surfaces and grow without a preferred direction, resulting in a short-range lamellar structure that contains various randomly oriented domains. (E and F) When freezing on a copper surface with a linear wettability gradient, the ice crystals align perpendicular to the gradient, resulting in a long-range lamellar structure with only a single domain. Credit: Science Advances, doi: 10.1126/sciadv.abb4712

Ice-templating is a powerful technique to construct biological materials using ice nucleation and growth to obtain frozen material architectures, but scientists have been unable to control these two factors with effective methods. In a new report on *Science Advances*, Nifang Zhao and a team of scientists in chemical and biological engineering at Zhejiang University in China, demonstrated successive ice nucleation and preferential growth by introducing a wettability gradient [on a cold finger](#) (a laboratory device used to generate a localized cold surface). The work highlighted the ability to harness the rich designability of surface wettability patterns to engineer high-performance bulk materials with bioinspired complex architectures.

## **Developing bioinspired materials in the lab**

Bioinspired materials based on nature, bone and teeth have long served as a source of inspiration to develop [high performance](#) structural materials. Biological materials can realize outstanding mechanical properties to build [sophisticated hierarchical architectures](#) at the nano/micro- and macroscopic levels. For example, bioengineers had developed various methods in the past to engineer [nacre](#) (iridescent layer of molluscan shell)-mimetic composites, which include [freeze-casting](#) and [three-dimensional \(3-D\) printing](#). Freeze-casting, also known as ice-templating is a powerful technique with precise, architectural control, low-cost and versatility to engineer high performance [nacre-mimetic](#)

[composites](#) and assemble a [variety of building blocks](#). During the process, ice crystals can nucleate on a cold [surface](#) and grow in a preferred direction along the [temperature gradient](#), and the team can control factors contributing to the process, to [model the architecture](#) of the resulting porous material. Zhao et al. therefore focused on surface engineering by modulating or controlling [surface wettability](#). To accomplish this, they introduced a wettability gradient to control ice nucleation and growth on a cold surface. The work showed how surface wettability allowed to engineer bulk materials with biomimetic sophisticated architectures.



Observation of the freezing process. (A) Top-view optical images showing successive nucleation of ice crystals from the hydrophilic to hydrophobic region and oriented growth perpendicular to the wettability gradient. (B) Schematic

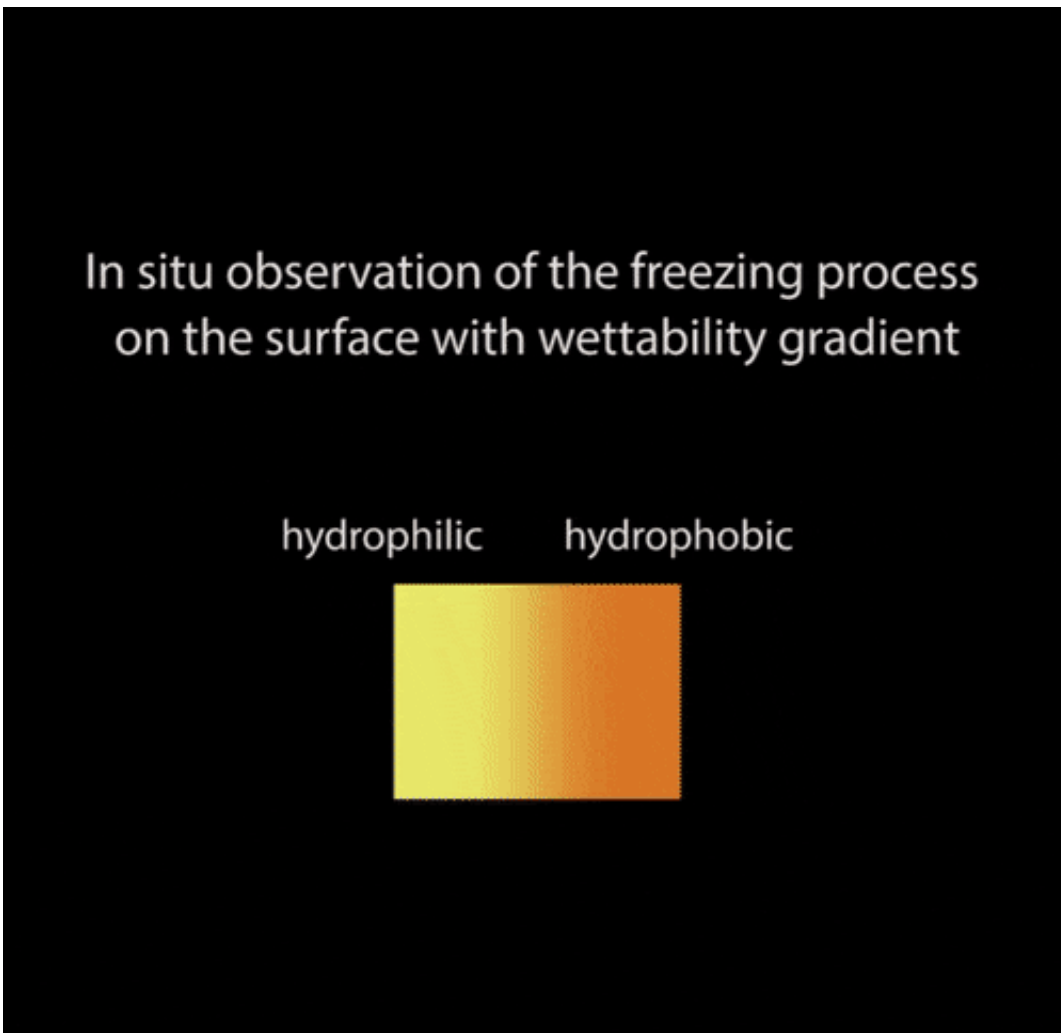
illustration of the freezing process showing successive nucleation and preferential growth. (C) Schematic illustration of thermocouples recording temperature variation above the hydrophilic and hydrophobic regions of the gradient surface. (D) Temperature variation of three zones over time. (E) Enlarged from (D) showing ice nucleation starts faster on the hydrophilic region. Credit: Science Advances, doi: 10.1126/sciadv.abb4712

## **Proof-of-concept freeze-casting technique**

As proof-of-concept, the team used an aqueous slurry of [hydroxyapatite \(HA\) particles](#) and compared freeze-casting processes on surfaces with various degrees of wettability to observe the resulting experimental microstructures. During traditional freeze-casting processes, the slurry was in direct contact with an unmodified, homogeneously hydrophilic copper substrate. Upon cooling, the team generated a vertical temperature gradient to guide the preferential growth of ice crystals from the bottom to the top. Due to the [hydrophilic \(water-loving\)](#) nature of the copper substrate, ice nucleation occurred simultaneously across the surface, which Zhao et al. observed using [scanning electron microscopy](#) (SEM). They then repeated the same freeze-casting process on a hydrophobic copper surface. Although the ice nucleation rate delayed on hydrophobic surfaces as expected, the process occurred randomly across the entire material. Based on the same idea, the scientists designed more complex patterns for freeze-casting including copper surface modifications with silane ([abbreviated POTS](#)) via programmed dip-coating to change the surface water contact angle and wettability.

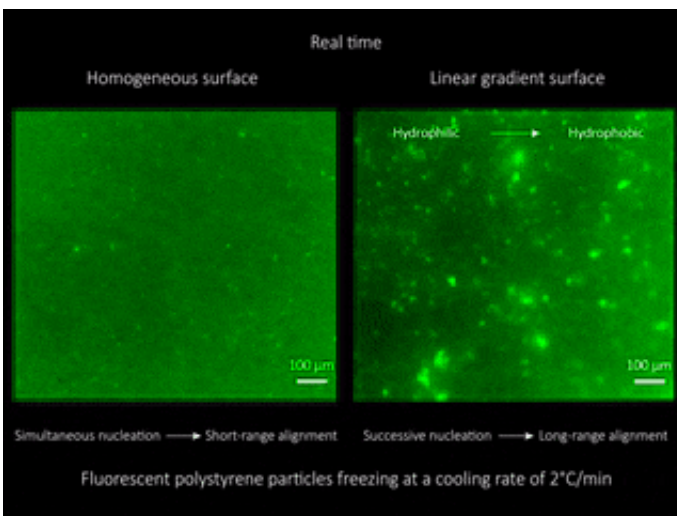
## **Observing the freezing process and proposing a freezing mechanism**

Zhao et al. observed the freezing-casting process using an optical microscope. During the experiments they sealed a Teflon mold to a copper substrate and poured a slurry with 20 percent HA particles into the mold to observe nucleation of ice crystals from the hydrophilic region to the hydrophobic region. They credited the phenomenon to nucleation rates induced by surface wettability and studied the effects of the wettability gradient including freezing velocity and particle concentration on the microstructure.



Observing the freezing process with the wettability gradient. Credit: Science Advances, doi: [10.1126/sciadv.abb4712](https://doi.org/10.1126/sciadv.abb4712)

They proposed a possible mechanism to control freeze-casted structures by controlling surface wettability. For this, the team studied the key assumptions of ice crystal nucleation and preferential growth and combined the two mechanisms to realize complex architectures in freeze-casted materials. The scientists visualized the process using a [fluorescence microscope](#) after mixing the HA slurry with a small amount of fluorescent polystyrene microspheres. The aligned particles in the medium then forced successive ice crystals to grow in similar orientations and form a long-range lamellar structure. The work suggested that surface wettability rather than the type of material determined the orientation of ice crystals.



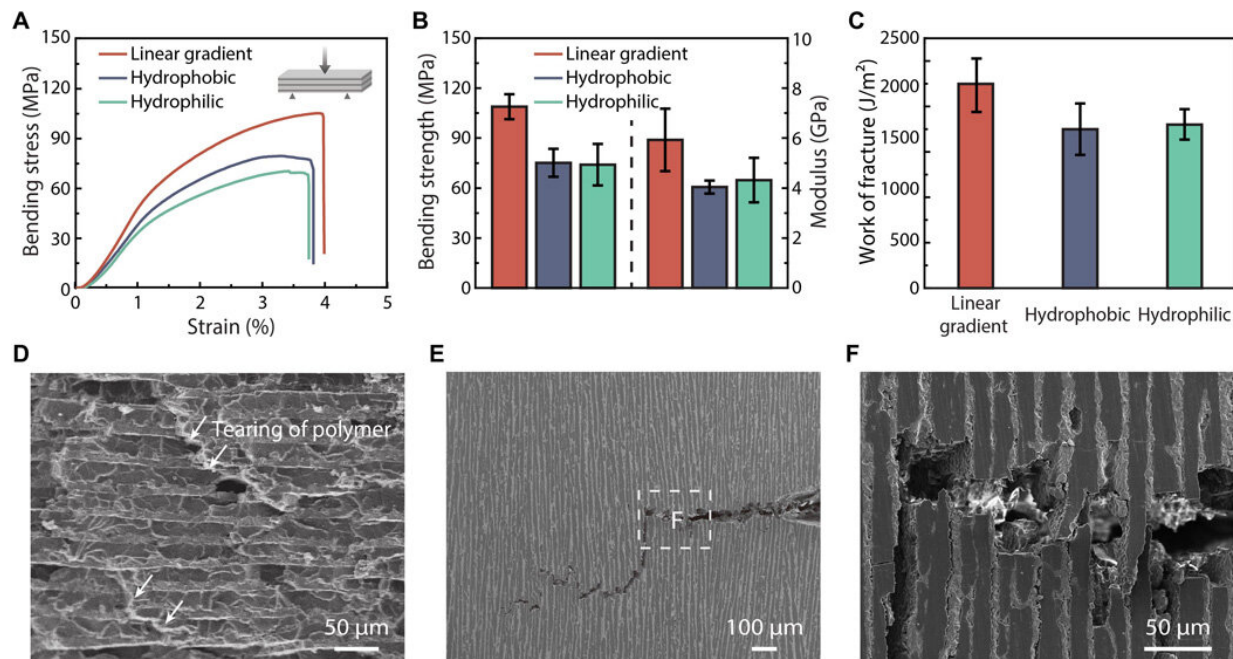
Observing the freezing process across a homogenous surface vs. a linear gradient surface. Credit: Science Advances, doi: 10.1126/sciadv.abb4712

## Developing a high-performance nacre-mimetic composite and testing its mechanical properties

The scientists sintered and compounded the HA scaffold containing a

long-range aligned lamellar structure with a polymer material, to generate high performance nacre-mimetic composites. The well-oriented structure mimicked the brick-and-mortar architecture of natural nacre, as confirmed with [micro-computed tomography](#). Zhao et al. maintained the particle concentration and ice growth velocity during the entire freeze-casting process to obtain large size samples with uniform structure.

To detect the mechanical properties of the resulting structure, the team compared flexural properties of the HA/polymer composites developed by freeze-casting on gradient and homogenous surfaces. The mechanical properties of nacre-mimetic composites were superior to those prepared on homogeneously hydrophobic or hydrophilic surfaces. The work showed the advantage of the long-range lamellar structure and verified freeze-casting on a gradient surface to be an effective approach to form high-performance nacre-mimetic composites.



Mechanical properties of the nacre-mimetic composite. (A) Three-point bending curves of the HA/PMMA composites prepared with the three types of surfaces.

(B and C) The bending strength, Young's modulus, and work of fracture of the nacre-mimetic composite are better than those prepared with homogeneously hydrophilic and hydrophobic surfaces. (D to F) SEM images showing that the nacre-mimetic composite shares the same toughening mechanism with natural nacre. (D) Fracture surface showing the tearing of the PMMA layers. (E) Under the single-edge notched bending test, the crack initiates from the notch and propagates along a tortuous path. (F) Enlarged SEM image of (E) showing interface failure, crack bridging, and ceramic defects. Credit: Science Advances, doi: 10.1126/sciadv.abb4712

## Designing a surface-wettability pattern

The team also showed the ability to design a surface wettability pattern by freeze-casting on copper surfaces containing a bilayer linear wettability gradient and radial wettability gradient. They obtained two representative structures with cross-aligned and circular lamellar patterns, not previously possible with conventional freeze-casting techniques. Zhao et al. then analyzed the mechanical properties of the composites to understand their performance and the results confirmed the possibility of harnessing the rich designability of surface wettability patterns to build high-performance bulk materials with complex bioinspired architecture.

In this way, Nifang Zhao and colleagues showed how [ice nucleation](#) and growth could be controlled by introducing a wettability gradient onto a cold surface to control the orientation of ice crystals and the architecture of the resulting porous material. Using the concept, they obtained a long-range aligned lamellar structure and infiltrated the porous scaffold to generate a high-performance bulk nacre-mimetic composite with excellent strength and toughness. The work highlights the potential of surface [wettability](#) and its rich designability to build patterns for bioinspired complex architectures with high performance.



**More information:** 1. Zhao N. et al. Controlling ice formation on gradient wettability surface for high-performance bioinspired materials, *Science Advances*, 10.1126/sciadv.abb4712

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3. Zhao N. et al. Superstretchable nacre-mimetic graphene/poly(vinyl alcohol) composite film based on interfacial architectural engineering, *ACS Nano*, [doi.org/10.1021/acsnano.7b01089](https://doi.org/10.1021/acsnano.7b01089)

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