

Large-Scale 2D-Confined Self-Assembly of Colloidal Nanoparticles via Dynamic Ice Crystal Templates

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When confined between directionally growing ice crystals, colloidal nanoparticles can be assembled into large 2D nanosheets.

Two-dimensional inorganic nanosheet materials with nanometer-level thickness play an increasingly important role in applications such as nanoelectronics, energy harvesting/conversion/storage, membrane separations, etc. In addition to the conventional top-down exfoliation of agglomerates of intrinsic 2D materials and bottom-up synthesis from atomic/molecular-level precursors, self-assembly of nanosize colloidal building blocks with desired properties offers a new option for preparing nanosheets. In this issue of *ACS Central Science*, Yu and co-workers utilized directionally growing ice crystals as a confining template to assemble colloidal nanoparticles into large 2D nanosheets (Figure 1).¹ This method represents an exciting addition to the toolbox of large-scale 2D self-assembly of nanoparticles.

In the formation of large 2D nanoarchitectures, the interparticle interactions alone are insufficient to maintain a long-range order assembly. Therefore, external fields, responsive and interactive units, and templates are often required to construct a macrostructure.² Among various 2D self-assembly techniques, directional freezing (also known as ice templating or freeze casting) is promising but less explored.³ This method is relatively simple, low cost, and highly scalable. Most importantly, it is a universal method for a wide variety of particle building blocks.⁴ By manipulating the particle solutions/suspensions and the freezing conditions, the particle building blocks (typically dispersed in water) are pushed to the side by the directionally growing ice front, oriented by the ice–water interface, and subsequently confined in the planar spaces between ice crystals

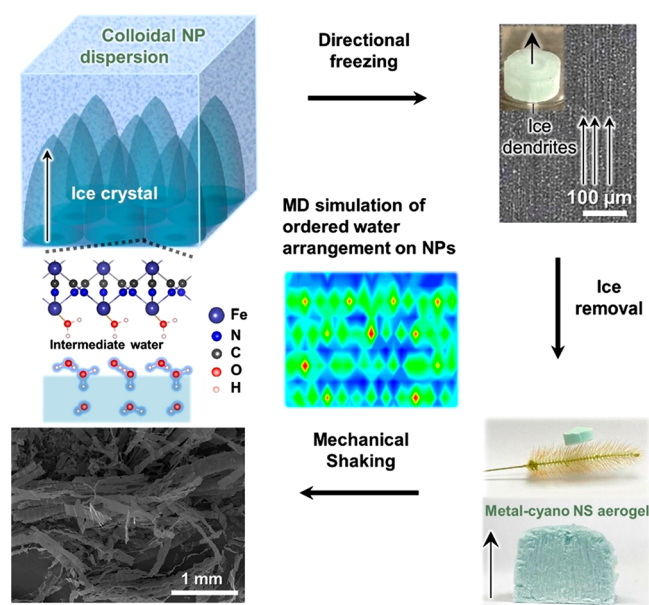
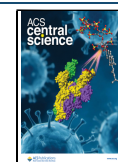


Figure 1. Schematic illustration of the synthesis of large-size nanosheets through the 2D-confined assembly of colloidal nanoparticles with directionally growing ice crystal templates. Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.

during freezing. The length of the 2D assembly progresses along with the growing ice crystal template. After simple sublimation of ice and mechanical separations, large freestanding sheets composed of particles can be obtained.

Directional freezing is a powerful and versatile tool to assemble colloidal nanoparticles into large 2D porous nanostructures without complicated template removal steps.

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Yu and co-workers demonstrated, for the first time, the use of this technique to synthesize millimeter-sized nanosheets based on colloidal metal-cyano nanoparticles. Through a set of comparisons, they found that an even distribution of colloidal nanoparticles along the ice solidification front requires a homogeneous colloidal dispersion. Therefore, maintaining a smaller hydrodynamic diameter and a more negative ζ potential to prevent aggregation is critical to the success of the method. These two material properties can be optimized by controlled variation of solvent and salt and the combination of metal ions in metal-cyano particles.

Directional freezing is a powerful and versatile tool to assemble colloidal nanoparticles into large 2D porous nanostructures without complicated template removal steps.

In addition to the proper ζ potential and hydrodynamic diameter, the 2D assembly of metal-cyanogel also depends on the critical velocity, which is determined by a number of factors, including the particle radius, the distance between the particle and the ice, and the mean distance between particles (particle concentration). The critical velocity is a descriptor of the assembly behavior of the particles during directional freezing. Lamellar assembly can only be realized when the velocity of the ice solidification front is slightly smaller than the critical velocity. For example, while having a small radius of the colloidal nanoparticles and a low concentration can avoid agglomeration, the critical velocity tends to be much larger than the velocity of ice crystal growth, leading to the segregation of particles from ice. The authors pointed out that the successful 2D assembly of metal-cyanogels is attributed to the large particle–ice distance that substantially lowers the critical velocity to a suitable level. Furthermore, differential scanning calorimetry analysis and molecular dynamics simulations confirmed the critical role of the freezable bound water (intermediate water) bonded with the coordinated water on the unsaturated metal sites. The intermediate water not only increases the thickness of the interfacial water layer between the metal-cyano nanoparticles and ice crystals but also facilitates the particle–ice interaction to guide the formation of surface water with an icelike crystal structure, which enables homogeneous dispersion and oriented arrangement of nanoparticles along the anisotropically growing ice template.

This report on directionally growing ice crystal templates for confined assembly of colloidal nanoparticles into large-scale freestanding nanosheets will open up new opportunities

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for 2D self-assembly. By optimizing the colloidal suspension and directional freezing techniques, it is expected that a 2D-confined assembly of other types of nanoparticles can also be achieved.^{5,6} This demonstration illustrates the importance of strong particle–water interfacial interactions (intermediate water in this work). We believe that the library of colloidal nanoparticles feasible for 2D assembly through directional freezing can be further expanded through proper surface functionalization and solvent/solution selection.⁷ Besides, if the particle building blocks are large suspensions (such as Fe_2O_3 and Al_2O_3 nanoparticles), ultrathin 2D nanosheets could possibly be obtained via the conversion of 2D nanosheets assembled with their colloidal precursors [such as $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$].⁸ Finally, the concept of a 2D-confined assembly could be further extended to multiple building blocks, exploring the assembly behaviors and the properties of the composite nanosheets.⁹ This represents a unique direction for nanomaterial synthesis.

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