General Synthesis of Large Inorganic Nanosheets via 2D Confinement Assembly of Nanoparticles

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ABSTRACT: Assembling nanoparticles to spatially well-defined functional nanomaterials and sophisticated architectures has been an intriguing goal for scientists. However, maintaining a long-range order of assembly to create macrostructures remains a challenge, owing to the reliance on purely interparticle interactions. Here, we present a general strategy to synthesize a class of inorganic nanosheets via a bottom-up directional freezing method. We demonstrate that, by confining a homogeneously dispersed metal-cyano colloidal suspension at the ice–water interface, followed by removal of ice crystals, large nanosheets with a lateral scale of up to several millimeters can be produced. The formation of millimeter-sized nanosheets is attributed to balanced electrostatic forces between dispersed nanoparticles, coupled with an appropriate hydrodynamic size of nanoparticles, potentially favorable lattice matching between nanoparticles and ice crystals, and the intermediate water at the ice–particle interface. The highly anisotropic growth of ice crystals can therefore guide the 2D confined assembly of nanoparticles in a long-range order, leading to well-defined 2D nanosheets. This contribution sheds light on the potential of nanoparticle assembly at larger length scales in designing families of large 2D nanoarchitectures for practical applications.

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The bottom-up assembly of colloidal nanocrystals to engineer hierarchical nanoarchitectures with enhanced physicochemical properties has been an intriguing topic.1−3 In particular, large nanosheets are more desirable for their mechanical, electronic, and optical properties.4−7 Currently, most reports on the synthesis of large inorganic nanosheets are top-down strategies such as micromechanical cleavage,8 phase exfoliation,9 and intercalation exfoliation.10,11 Similar to the limitation of top-down strategies, typical bottom-up assembly approaches such as chemical vapor deposition12 and solvothermal methods13 lack the ability to achieve a general assembly of various nanoscale units with different properties. Moreover, reports on the high-yield synthesis of nanosheets of hundreds of micrometers or even millimeters in size are scarce. Nanoparticle (NP) assembly is a highly programmable approach toward building micro- and macroscopic materials, and it is largely contingent upon manipulating interparticle interactions such as van der Waals and Coulombic forces.2,3 Solely relying on particle interactions, however, is less effective in maintaining a long-range order toward assembling macrostructures.7

Directional freezing, also known as ice templating, is a versatile process that can drive building block assembly by guiding and confining NPs between ice crystals.14 It is suitable for a variety of building blocks across different types of materials and all dimensions, owing to the ice–liquid interface generated during the ice crystallization and growth. Such versatility has enabled the synthesis of various kinds of supracolloidal structures, such as porous films,15 porous microfibers,16 and polymeric hybrid materials.17 A fundamental reason for the versatility is the highly anisotropic nature of ice growth, during which building blocks are rejected and sequestered at the ice–liquid interface.18 This process is highly tunable by controlling the freezing direction, temperature, and solvent compositions.19 However, such a technique has rarely been used in constructing self-standing porous nanosheets which are of considerable interest in energy- and environmental-related areas.

Graphene, metal oxides, and metal chalcogenides are layered materials that have already been widely studied as nanosheets.4,20,21 However, nonlayered materials are rarely used to construct 2D nanostructures.22 Inorganic metal-cyanogel is an emerging class of nonlayered, coordination polymer materials that are promising candidates for energy applications owing to their hierarchical frameworks,23−25 complementing the current pool of popular energy materials. The molecular formula of metal-cyanogel consists of a cyanide bridge connecting two metals (−M′−CN−M″−). The multimetal nature of the nanoparticles endows the building block with high compositional tunability.26 The gel-like feature of metal-cyano
Figure 1. Step-by-step process of metal-cyano nanosheet (NS) synthesis. (a) Schematic illustration of the mechanism of NS formation via directional freezing. (b) Optical image of aligned ice dendrite growth. Inset: frozen cyanosol. (c) Cross-section view of metal-cyano NS aerogel. (d) Scanning electron microscopy (SEM) image of bulk metal-cyano NS aerogel. Vertical arrows in parts a–c represent the direction of ice crystal growth.

Figure 2. Images of cyanosol and structural characterizations of selected metal-cyano nanosheets. From left to right for each row: pictures of the dispersed colloidal suspension, SEM, STEM, and energy-dispersive X-ray spectroscopy (EDS) mapping of (a) Fe$^{III}$–Fe$^{II}$ nanosheets, (b) Al–Fe$^{II}$ nanosheets, (c) Ni–Co nanosheets, and (d) Ni–Fe$^{II}$ nanosheets.
Inorganic metal-cyano colloidal NPs were used as the building blocks for nanosheet synthesis (Figure 1, Figure S1). The metal-cyano colloidal solution (metal-cyanosol) can be prepared via a simple ligand substitution between the metal chloride salt and potassium metal cyanide at room temperature. The resulting product is two metals connected by a cyanide bridge, \( \text{M}^+\text{CN}^−\text{M}^+\) (abbreviated as \( \text{M}^+\text{M}^+\) in this Article), which is the polymeric unit.\(^\text{25}\) After removing excess salt, which is usually KCl in our study, and redispersing in water, a stable colloidal suspension will form, due to the electrostatic repulsion between NP building blocks. The principles of interactions between NPs and their surrounding liquid and lattice matching between NPs and ice crystals can be extra considerations for future NP assembly at a large scale. We also present a demonstration showing that as-synthesized nanosheets can be efficient electrocatalysts for oxygen evolution reactions.

### RESULTS AND DISCUSSION

Inorganic metal-cyano colloidal NPs were used as the building blocks for nanosheet synthesis (Figure 1, Figure S1). The metal-cyano colloidal solution (metal-cyanosol) can be prepared via a simple ligand substitution between the metal chloride salt and potassium metal cyanide at room temperature. The resulting product is two metals connected by a cyanide bridge, \( \text{M}^+\text{CN}^−\text{M}^+\) (abbreviated as \( \text{M}^+\text{M}^+\) in this Article), which is the polymeric unit.\(^\text{25}\) After removing excess salt, which is usually KCl in our study, and redispersing in water, a stable colloidal suspension will form, due to the electrostatic repulsion between NP building blocks. The principles of interactions between NPs and their surrounding liquid and lattice matching between NPs and ice crystals can be extra considerations for future NP assembly at a large scale. We also present a demonstration showing that as-synthesized nanosheets can be efficient electrocatalysts for oxygen evolution reactions.

Although the carbon of the cyanide bridge often connects to a metal other than iron, the signature peaks of non-Prussian blue materials are consistent with those of Prussian blue. Therefore, regardless of the type of metals or amount of coordinated water or vacancies, these inorganic polymers share the same crystal structure. XRD reveals that nanosheets placed under ambient conditions for 3 months remained chemically stable (Figure S8). STEM also shows that morphologies of these nanosheets did not have significant differences (Figure S9). The above characterizations indicated the high chemical and structural stability of metal-cyano nanosheets. We also measured the optical properties of the colloidal solution via
UV–vis spectroscopy (Figure 3b, Figure S10). We observed that when the transition metal salt was used, there was absorption in the 400–500 nm range (except for iron, where the only absorption is located around 700 nm), which may correlate to the photoinduced metal-to-metal charge transfer through the cyanide bond bridge in metal-cyano materials.27 An X-ray absorption fine structure (XAFS) analysis was performed to study the chemical configuration of metal-cyano materials. Fe K-edge X-ray absorption near-edge spectroscopy (XANES, Figure 3c, Figure S11) of In–FeIII-cyano NPs and In–FeII-cyano NPs (denoted as FeII-cyano NPs and FeIII-cyano NPs) was conducted to unravel the local geometry around the selected absorber, using the standard Fe foil, FeO, and Fe2O3 as control references. A small energy shift was detected from FeII to FeIII-cyano colloidal NPs. Figure 3d shows the Fourier transforms (FTs) of the extended X-ray absorption fine structure (EXAFS), displaying two major peaks with the first (1–2 Å) due to carbon atoms and the second (2–3 Å) due to nitrogen atoms, indicating similar Fe–C–N structures and bond lengths in Fe-cyano NPs with different states of transition metals. Thermogravimetric analysis (TGA) shows that, typically, nanosheets can be thermally stable up to 300 °C (Figure S12).

To investigate particle–particle interaction, the ζ potential of NPs was measured, which is an indicator of surface charges and stability of the colloidal suspension (Figure 4a). Generally, a ζ potential at least as negative as −30 mV indicates that the NP has sufficient negative charges around the outer electrical layer to induce repulsion with other NPs, a prerequisite for a well-dispersed stable colloidal solution. As ζ potential approaches zero, in which case the charge state around the nanoparticle approaches neutrality, aggregation of nanoparticles becomes inevitable, and it is not possible for nanoparticles to evenly distribute along the ice solidification front. It is therefore important to remove the salt byproducts from the colloidal system, since excess salt ions such as K+ will neutralize the negative charges of the nanoparticle. For example, the ζ potential of a PB suspension containing KCl is significantly less negative (−2.7 mV) than that with less KCl (Figure 4b, Figure S13). ζ potential alone cannot fully explain the assembly behavior of nanoparticles, however. For instance, Ni–FeII and In–FeII have comparable ζ potentials (−~40 mV) (Figure 4c), but Ni–FeII NPs assembled to larger, more continuous layered nanostructures (Figure 2d, Figure S2a). We therefore resorted to other points of view.

For most particle suspensions, the ice front is planar during the freeze–drying process, displacing particles and increasing the solid loading of the unfrozen region. To yield aligned porous structures via directional freezing, it is critical that colloidal particles are rejected by the solidification front.19 In a single-particle model, the energy requirement (Δσ) for a suspended particle to be rejected by the solidification front can be expressed as

$$\Delta \sigma = \sigma_{PS} - \sigma_{PL} - \sigma_{SL} > 0$$

where Δσ is the energy balance between particle–ice (σPS), particle–liquid (σPL), and ice–liquid (σSL) interfaces (Figure S14). A nanoparticle at the ice crystallization interface experiences both an attraction force given by

$$F_{attraction} = 2 \pi R \Delta \sigma \left( \frac{a_0}{d} \right)^n$$

and a repulsion force given by

$$F_{repulsion} = \frac{6 \pi n \eta R^2}{d}$$

Solving for v gives the critical freezing velocity which is the velocity of the ice solidification front

$$v_{critical} = \frac{\Delta \sigma d \left( \frac{a_0}{d} \right)^n}{3 \eta R}$$

where R is the radius of a nanoparticle, d is the thickness of the liquid layer between the solid–liquid interface and the nanoparticle (i.e., distance between the particle and the ice), a0 is the mean distance between the nanoparticles, η is the viscosity of the liquid, and n is an empirical correction factor for the repulsive forces that generally ranges from 1 to 4 (Figure S14).19,28

To form lamellar structures, the velocity of the ice solidification front needs to be slightly smaller than the critical freezing velocity (v < v_{critical}), so that particles will generally be rejected and form lamellar walls within the freeze-cast scaffold.19 However, experimental ice front velocities using liquid nitrogen as the cold source are typically in the range 5–30 μm s⁻¹, significantly lower than the critical freezing velocities (v < v_{critical}) of most particle dispersions. In this case,
the ice front will be planar instead of forming a scaffold, which means that nanoparticles will only pile up in the unfrozen region and form a complete segregation from the bulk ice crystals. On the other hand, if the velocity is larger than the critical freezing velocity \( v \geq v_{cr} \), a fraction of particles will create bridges between lamellar walls, producing a 3D “freeze-cast” structure. Therefore, based on the \( v_{cr} \) equation, \( R \), \( d \), and \( a_0 \) will be the dominant factors to tune the critical freezing velocities (assuming that \( \eta \) and \( n \) are constants for a specific type of nanoparticle dispersion), so that the critical freezing velocity can be lowered, optimized to be only slightly higher than the experimental freezing velocity. To study the radius of nanoparticle \( R \) and the thickness \( d \) of the liquid layer between the solid–liquid interface and the nanoparticle, we measured the hydrodynamic diameter of a series of inorganic NPs via dynamic light scattering (DLS). The hydrodynamic diameter describes the “true” solvated particle size in the liquid, including the diameters of both the nanoparticle and the particle–water interface (Figure S15); its value also roughly corresponds to the thickness of nanosheets. Moreover, such a diameter is correlated with \( \zeta \) potential: a larger hydrodynamic size typically corresponds to a less negative \( \zeta \) potential (Figure 4c), which to some extent can reflect the interfacial interaction between particles and liquid as well as the dispersity of particles. Interestingly, although the \( \zeta \) potential of FeIII–FeII is relatively negative (\( \sim -30 \text{ mV} \)) in ethanol, the hydrodynamic diameter is too large for the colloidal dispersion to be stable, which is probably due to the lack of hydrogen bonding between NPs and ethanol. We then plotted the hydrodynamic diameter of NPs versus their \( \zeta \) potential (Figure 4c). The trend in the plot aligns with our observation that large nanosheets such as FeIII–FeII and Al–FeII are built from NPs with large \( \zeta \) potential (absolute value) and small hydrodynamic diameter, whereas those with reasonably negative \( \zeta \) potential yet large diameter (such as In–FeII) yield discontinuous 2D nanostructures. On the top right of the distribution map, NPs flocculate in the aqueous solution and only yield aggregates after freeze-drying. Therefore, a homogeneous dispersion possessing a sufficiently negative \( \zeta \) potential and nanoparticles of small hydrodynamic radius is the critical prerequisite for directional freezing-driven assembly. Moreover, even for NPs of the same element compositions, their dispersity can vary owing to different element ratios. With FeIII–FeII as an example, as the ratio of FeIII to Fe(CN)64− increases from 1:1 to 4:3 and 2:1, the \( \zeta \) potential becomes less negative, and the hydrodynamic diameter increases (Figure 4c), resulting in a less homogeneous suspension (Figure S16), which may relate to the increased amount of K+ ions and more neutralized total charge. As predicted based on the aforementioned trend, FeIII–FeII with a less negative \( \zeta \) potential and larger hydrodynamic diameter yields a 2D architecture with smaller size and larger thickness (Figure S17).

We also found that the morphology of the assembled architecture is tunable via manipulating the concentration of homogeneous colloidal solution, which is relevant to the distance between nanoparticles \( (a_0) \) involved in the equations (Figure S18). When the colloidal solution was dilute (0.1 wt %), NPs assembled to a fiber-/beltlike morphology. When the concentration was increased to 0.5 wt %, a two-dimensional morphology started to appear. When the concentration was increased to 1.5 wt %, nanosheets formed with continuous order. We attribute this control parameter to the distance between NPs \( (a_0) \) necessary to maintain a certain level of interaction and packing coherency. For an inhomogeneous dispersion, on the other hand, such as Fe3O4 or FeIII–FeII (2:1) aqueous suspension, particles will precipitate, causing a concentration gradient which leads to a less uniform assembled structure. In this case, \( a_0 \) becomes very small, and \( R \) will be
very large, resulting in a small $v_d$ ($v_d < v$) that produces a random “freeze-cast” structure. We also experimentally compared the effect of freezing velocity ($v$) on the formation of nanosheets (Figure S19). When the freezing velocity of ice growth was significantly decreased to less than the critical velocity ($v \ll v_d$), the majority of nanoparticles cannot be rejected from the ice solidification front, only accumulating in the unfrozen region and forming bulk structures (Figure S19a,b).39 Therefore, according to the above experiments and analysis, to design a 2D lamellar nanostructure via direction-freezing, a uniform colloidal particle dispersion is the prerequisite, and many factors, including particle size ($R$), distance between particle and ice ($d$), dispersibility, and concentration of particles (mean distance between particles $a_0$), need to be optimized.

The aforementioned interfacial studies demonstrate that a sufficiently negative $\zeta$ potential and small hydrodynamic radius of nanoparticles are the critical prerequisites in directional freezing-induced 2D confined NP assembly. To further understand the interactions on a molecular level between metal-cyano NPs and water molecules, the melting behavior of the frozen suspension was investigated via differential scanning calorimetry (DSC) (Figure 5a). There are three types of water molecules (free water, freezable bound water, and nonfreezable bound water) during the freezing process, each interacting differently with their surroundings.29,30 As the bound water molecules have local environments different from the bulk water, they acquire a different phase transition temperature.31

Typically, freezable free water (normal hydrogen bonding) exhibits an endothermic peak above 0 °C. Nonfreezable bound water (such as coordinated water, strong bonding with polymers) loses the ability to interact with nearby water molecules to crystallize below 0 °C, due to the strong interaction between water molecules and polymers.31,32 Distinct from the nonfreezable bound water, the appearance of an endothermic peak below 0 °C can usually be ascribed to freezable bound water (intermediate water with weakened hydrogen bonding).29,33 To further understand the underlying interfacial interaction between metal-cyano NPs and water molecules, possible hydrogen bonds between metal-cyano NPs and water molecules were proposed in FeIII–FeII-cyano materials (Figure S20). Due to the abundant coordinatively unsaturated Fe sites in FeIII–FeII-cyano (denoted as Fe-cyano or PB) NPs,23 hydrogen bonds are widely present between coordinated water on N-coordinated Fe sites and the intermediate water. The endothermic peak near 0 °C results from bulklike free water away from the Fe-cyano NPs (Figure 5a). Interestingly, Fe-cyano NPs possess an additional peak below 0 °C, which indicates the presence of nonfreezable bound water (intermediate water) in the Fe-cyano NP colloidal dispersion. As a reference, Fe3O4 NPs solely exhibit one peak, and the nonfreezable bound water is absent, which means that intermediate water is missing in normal metal oxide NPs. In comparison, the existence of intermediate water on Fe-cyano NPs suggests the stronger water-binding ability of metal-cyano NPs and longer distance, $d$, between the particle and the ice. Moreover, the Fe-cyano sample with a 2:1 ratio (FeIII:FeII = 2:1) shows a larger hydrodynamic diameter ($R + d$) (Figure 4c), even though it possesses the intermediate water peak and thus smaller $d$, and is still unable to form an ordered 2D architecture due to poor dispersibility (Figure S17).

DSC results also confirm that the particle–water interfacial interaction has a critical impact on the dispersity of metal-cyano NPs in water and the formation of a 2D confined assembly of NPs during directional freezing. Based on the crystal symmetry of the ice crystal face (001) with an atomic arrangement of 3-fold symmetry, the interfacial interaction between ice molecules and (111) crystal facets of Prussian blue was studied. The Prussian blue (111) facet consists of plenty of N-coordinated Fe sites with dangling bonds due to the Fe(CN)6 defects.23 This scaffold structure arranges the coordinated water on Fe-sites to match with the ice crystal lattice (Figure 5b),35 which is similar to the organization of hydroxy groups on the ice-binding surface of GOs and antifreeze proteins.36,37 A strong particle–water interaction attributes metal-cyano NPs with high solvation (Figure S20), resulting in a larger $d$ and lower $v_d$. In this way, the system switches from $v_d \gg v$ to $v_d > v$, and particles will be rejected and form lamellar walls within the ice scaffold.36,38 In comparison, Fe3O4 NPs with weak particle–water interaction possess smaller $d$ and higher $v_d$, and thus, there is a lack of lamellar structure with long-range order (Figure S21).

To further explore the particle–water interaction on different PB crystal facets, the radial distribution function (RDF) of O–O, defined as the probability of finding an oxygen atom at a certain distance from another tagged oxygen atom (Figure 5c), is calculated for the surface water molecules on both (111) and (001) crystal facets of PB without K+ (Figures S22 and S23). In order to mimic the PB samples in our experimental study, four types of molecular dynamics simulation models are built: pristine PB (type i, KFeFe(CN)6),22 uncharged, PB without K+ (type ii, Fe3[Fe(CN)6] with a negative charge), PB with K+ and insufficient Fe3+ (type iii, K1FeFe[Fe(CN)6]2.5 with a minor negative charge, $x = 0.16$), and PB without K+ and insufficient Fe3+ (type iv, Fe3[Fe(CN)6] with a negative charge) (Figure S24). On PB without K+ (types ii and iv), the distances between two adjacent coordinate water molecules are about 2.6 and 4.5 Å, respectively, exactly equal to the peak position of the first and second peaks in Figure 5d. The high intensity of the first and second peaks indicates that the unique surface structure of metal-cyano materials contributes to the formation of surface water with an icelike structure. It is well-noted that the second peak is more obvious for negatively charged PB with N-coordinated Fe defects (type iv), as shown in the zoom-in view of Figure 5e, which may originate from the hydrogen bonding between exposed hydrophilic cyano groups (Fe–CN) and intermediate waters. Moreover, there is a higher intensity on (111) than on the (100) crystal facet, which is relevant to the lattice matching between PB (111) and ice crystals. We further studied the water arrangement and hydrogen bond formation on PB materials and elucidate the effects of charge and composition of PB (Figures S22–S24). The results demonstrate that PB with a negative charge can potentially arrange surface water molecules to match with the ice lattice, suggesting strong interaction between negatively charged metal-cyano NPs and water molecules. Based on the above molecular-level studies via DSC and MD simulations, particle–water interactions can be attributed to the intermediate water and lattice matching between metal-cyano NPs and ice crystals, allowing homogeneously dispersed metal-cyano NPs and an optimal arrangement along the ice solidification front. Thanks to the strong interaction between metal-cyano particles and water molecules, the critical freezing velocity decreases so NPs can be rejected and assembled into a 2D lamellar structure with long-range order.
The high surface area enabled by long-range order and the tunable metallic compositions inspire us to do a preliminary study on the electrocatalytic properties of these 2D nanosheets. We investigated the OER activities of a series of metal-cyano NSs, including FeIII–FeII cyano NSs, Al–FeIII cyano NSs, and Ni–FeII cyano NSs (Figure S25). After activation (Figure S26), Ni–FeII cyano NSs show the highest current density and lowest overpotential with 320 mV at 50 mA cm\(^{-2}\), even better than commercial RuO\(_2\) OER electrocatalysts. Interestingly, compared with FeIII–FeII cyano NSs, FeII cyano NSs exhibited less desirable OER activities with higher overpotential and lower current density.

**CONCLUSION**

In summary, we describe a general bottom-up strategy to assemble millimeter-size inorganic nanosheets by confining colloidal NPs along the ice crystallization front. We demonstrate that a sufficiently negative ζ potential and small hydrodynamic radius combined contribute to a homogeneous colloidal dispersion that is critical for even distribution along the ice crystal front. By taking advantage of the highly anisotropic growth of ice crystals, facilitated by potential lattice matching between metal-cyano NPs and ice crystals, intermediate water at the particle–ice interface, and optimized critical velocity, homogeneously dispersed nanoparticles are able to be continuously sequestered along the ice solidification front, resulting in nanosheets with long-range order. This contribution sheds light on large-scale nanoparticle assembly beyond particle–particle interactions, bringing in extra potential lattice matching. In addition, we provide new control parameters such as metal substitution and ratio, concentration, and freezing velocity. The aforementioned principles can potentially be extended to other types of nanoparticles with distinct functions, enabling the synthesis of large nanosheets with various applications.

**METHODS**

**General Synthesis of Inorganic Metal-Cyano Nanosheets.** A metal-cyano colloidal solution was prepared by mixing 0.05 M metal salts and 0.05 M metal cyanide. The solution was left to stir for 2 h at ambient temperature. The reaction mixture was then washed with ethanol (equal volume with reaction mixture) and centrifuged. The process was repeated 2 times, until the liquid phase was relatively clear. Washed sample was redispersed in water at 1.5 wt %. Then, the aqueous solution was subjected to a directional freezing process. The colloidal suspension was added to a cylinder mold with the bottom copper plate precooled in liquid nitrogen (−196 °C) to form frozen cyanosol. The cross-section view (parallel to the z-axis) of frozen cyanosol showing the aligned ice dendrite can be observed from optical microscopy. After ice freeze-drying, metal-cyano nanosheet aerogels were dispersed in hexane using a laboratory shaker for 10 min. As a reference, controlled sample was directly frozen in a commercial refrigerator. Frozen samples were then dried in a freeze-dryer. FeO\(_3\) NPs were synthesized by the annealing of FeIII–FeII–FeII–cyano NPs at 400 °C in the air for 2 h with a heating rate of 0.5 °C min\(^{-1}\) from room temperature.

**Imaging Characterization.** Scanning electron microscopy (SEM) images were obtained by an FEI Quanta 650 ESEM instrument. Higher-magnification SEM and scanning transmission electron microscopy (STEM) images and an energy-dispersive X-ray spectroscopy (EDS) pattern were collected by a Hitachi S5500 instrument.

**Composition Characterization.** Powder X-ray diffraction (XRD) patterns were collected on Rigaku Miniflex 600 diffractometer. Ultraviolet–visible (UV–vis) spectroscopy data were obtained using a UV–vis–NIR spectrometer (Cary 5000) with an integrating sphere unit and automation of reflectance measurement unit. XAFS measurements were recorded in the fluorescence mode at the U7C beamline in the National Synchrotron Radiation Laboratory, China, and 1W1B beamline of Beijing Synchrotron Radiation Facility.

**ζ Potential and DLS.** The hydrodynamic radius and ζ potential of colloidal nanoparticles were measured with a Malvern Zetasizer instrument.

**Differential Scanning Calorimetry.** Metal-cyano nanoparticles with a water ratio of around 60% were tightly sealed in an aluminum crucible to prevent the evaporation of water and kept at −30 °C for 5 min to be fully frozen. Then, the measurement was performed with scans at a linear heating rate of 2 °C min\(^{-1}\) under a nitrogen flow flux at 50 mL min\(^{-1}\), with temperature ranging from −25 to 25 °C.

**Molecular Dynamics Simulation of Interfacial Water on Prussian Blue (PB, Fe-Cyano).** Molecular dynamics (MD) simulations are performed implemented by the large-scale atomic/molecular massively parallel simulator (LAMMPS) package. The interatomic interactions in PB molecules are described based on the all-atom force field developed by Giacomo et al. The SPC/FW water model is adopted in our simulations; the intermolecular interactions were modeled by the 12-6 LJ potential. The dimensional sizes of simulation cells for PB (111) and (001) crystal facets models are 49.80 Å × 28.75 Å × 100.00 Å and 50.83 Å × 50.49 Å × 100.00 Å, respectively (Figure S22). The periodic boundary conditions were applied along three directions. The Newtonian equations of motion are integrated by a velocity Verlet algorithm with a time step of 0.2 fs. The cutoff radius of 14 Å was employed for the long-range interactions of van der Waals (VDW) and long-distance electrostatic forces calculated by the particle–particle–particle–mesh (PPPM) method. In our simulations, the PB nanoparticle was fixed to model the interfacial water arrangement. The NVE ensemble and Berendsen thermostat with a coupling constant of 20 fs were applied to the water molecules to keep the temperature at 265 K. The MD simulations are performed for 3 ns, where the system is relaxed for 1 ns to reach a steady state of the system, and in the last 2 ns, the density and structural parameters are recorded to analyze the water morphology on the interface of metal-cyano nanoparticles.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.2c00252.

Additional UV–vis spectra, XRD patterns, SEM images, TEM images, AFM image, BET spectra, XAFS spectra, TGA spectra, schematic diagrams, electrochemical characterizations, and computational results (PDF)
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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. Science 2002, 295 (5564), 2418.
(2) Santos, P. J.; Gabrys, P. A.; Zornberg, L. Z.; Lee, M. S.; Macfarlane, R. J. Macroscopic materials assembled from nanoparticle superlattices. Nature 2021, 591 (7851), 586–591.
(3) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O’Brien, S.; Murray, C. B. Structural diversity in binary nanoparticle superlattices. Nature 2006, 439 (7072), 55–59.
(4) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 2012, 7 (11), 699–712.
(5) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Adv. Mater. 2010, 22 (35), 3906–3924.
(6) Ghohamvand, Z.; McAteer, D.; Harvey, A.; Backes, C.; Coleman, J. N. Electrochemical Applications of Two-Dimensional Nanosheets: The Effect of Nanosheet Length and Thickness. Chem. Mater. 2016, 28 (8), 2641–2651.
(7) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X. Van der Waals heterostructures and devices. Nat. Rev. Mater. 2016, 1 (9), 16042.
(8) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. Proc. Natl. Acad. Sci. U. S. A. 2005, 102 (30), 10451.
(9) Zhang, X.; Xie, Y. Recent advances in free-standing two-dimensional crystals with atomic thickness: design, assembly and transfer strategies. Chem. Soc. Rev. 2013, 42 (21), 8187–8199.
(10) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 2013, 5 (4), 263–275.
(11) Ma, R.; Sasaki, T. Two-Dimensional Oxide and Hydroxide Nanosheets: Controllable High-Quality Exfoliation, Molecular Assembly, and Exploration of Functionality. Acc. Chem. Res. 2015, 48 (1), 136–143.
(12) Duan, X.; Wang, C.; Pan, A.; Yu, R.; Duan, X. Two-dimensional transition metal dichalcogenides as atomically thin semiconductors: opportunities and challenges. Chem. Soc. Rev. 2015, 44 (24), 8859–8876.
(13) Sun, Y.; Gao, S.; Lei, F.; Xie, Y. Atomically-thin two-dimensional sheets for understanding active sites in catalysis. Chem. Soc. Rev. 2015, 44 (3), 623–636.
(14) Shahbazi, M.-A.; Chalkhami, M.; Maleki, H. Directional Freeze-Casting: A Bioinspired Method to Assemble Multifunctional Aligned Porous Structures for Advanced Applications. Adv. Eng. Mater. 2020, 22 (7), 200033.
(15) Shao, Y.; El-Kady, M. F.; Lin, C.-W.; Zhu, G.; Marsh, K. L.; Hwang, J. Y.; Zhang, Q.; Li, Y.; Wang, H.; Kaner, R. B. 3D Freeze-Casting of Cellular Graphene Films for Ultrahigh-Power-Density Supercapacitors. Adv. Mater. 2016, 28 (31), 6719–6726.
(16) Qiu, L.; Liu, J. Z.; Chang, S. L. Y.; Wu, Y.; Li, D. Biomimetic superelastic graphene-based cellular monoliths. Nat. Commun. 2012, 3 (1), 1241.
(17) Zhang, X.; Ju, Z.; Housel, L. M.; Wang, L.; Zhu, Y.; Singh, G.; Sadique, N.; Takeuchi, K. J.; Takeuchi, E. S.; Marschilok, A. C.; Yu, G. Promoting Transport Kinetics in Li-Ion Battery with Aligned Porous Electrode Architectures. Nano Lett. 2019, 19 (11), 8255–8261.
(18) Hua, M.; Wu, S.; Ma, Y.; Zhao, Y.; Chen, Z.; Frenkel, I.; Strzalka, J.; Zhou, H.; Zhu, X.; He, X. Strong tough hydrogels via the synergy of freeze-casting and salting-out. Nature 2021, 590 (7847), 594–599.
(19) Shao, G.; Hanaor, D. A. H.; Shen, X.; Gurlo, A. Freeze Casting: From Low-Dimensional Building Blocks to Aligned Porous Structures—A Review of Novel Materials, Methods, and Applications. Adv. Mater. 2020, 32 (17), 1907176.
(20) Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tozzi, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V. Graphene, Related Two-Dimensional Crystals, and Hybrid Systems for Energy Conversion and Storage. Science 2015, 347 (6217), 1246501.
(21) Tan, C.; Cao, X.; Wu, X.-J.; He, Q.; Yang, J.; Zhang, X.; Chen, J.; Zhao, W.; Han, S.; Nam, G.-H.; Sindoro, M.; Zhang, H. Recent Advances in Ultrathin Two-Dimensional Nanomaterials. Chem. Rev. 2017, 117 (9), 6225–6331.
(22) Peng, L.; Xiong, P.; Ma, L.; Yuan, Y.; Zhu, Y.; Chen, D.; Luo, X.; Lu, J.; Amine, K.; Yu, G. Holey two-dimensional transition metal oxide nanosheets for efficient energy storage. Nat. Commun. 2017, 8, 15139.
(23) Fang, Z.; Zhang, A.; Wu, P.; Yu, G. Inorganic Cyanogels and Their Derivatives for Electrochemical Energy Storage and Conversion. ACS Mater. Lett. 2019, 1 (1), 158–170.
(24) Vondrova, M.; Burgess, C. M.; Bocarsly, A. B. Cyanogel Coordination Polymers as Precursors to Transition Metal Alloys and Intermetallics - from Traditional Heating to Microwave Processing. Chem. Mater. 2007, 19 (9), 2203–2212.
(25) Pfennig, B. W.; Bocarsly, A. B.; Prud’homme, R. K. Synthesis of a novel hydrogel based on a coordinate covalent polymer network. J. Am. Chem. Soc. 1993, 115 (7), 2661–2665.
(26) Alexandrov, E. V.; Virovets, A. V.; Blatov, V. A.; Peresypkina, E. V. Topological Motifs in Cyanometallates: From Building Units to Three-Periodic Frameworks. Chem. Rev. 2015, 115 (22), 12286–12319.

https://doi.org/10.1021/acscentsci.2c00252
ACS Cent. Sci. 2022, 8, 627–635
(27) Ohkoshi, S.-i.; Tokoro, H. Photomagnetism in Cyano-Bridged Bimetal Assemblies. *Acc. Chem. Res.* 2012, 45 (10), 1749−1758.

(28) Zhang, H.; Hussain, I.; Brust, M.; Butler, M. F.; Rannard, S. P.; Cooper, A. I. Aligned two- and three-dimensional structures by directional freezing of polymers and nanoparticles. *Nat. Mater.* 2005, 4 (10), 787−793.

(29) Zhao, F.; Guo, Y.; Zhou, X.; Shi, W.; Yu, G. Materials for solar-powered water evaporation. *Nat. Rev. Mater.* 2020, 5 (5), 388−401.

(30) Bag, M. A.; Valenzuela, L. M. Impact of the Hydration States of Polymers on Their Hemocompatibility for Medical Applications: A Review. *Int. J. Mol. Sci.* 2017, 18 (8), 1422.

(31) Zhou, J.; Lin, S.; Zeng, H.; Liu, J.; Li, B.; Xu, Y.; Zhao, X.; Chen, G. Dynamic intermolecular interactions through hydrogen bonding of water promote heat conduction in hydrogels. *Mater. Horiz.* 2020, 7 (11), 2936−2943.

(32) Zhou, X.; Zhao, F.; Guo, Y.; Rosenberger, B.; Yu, G. Architecting highly hydratable polymer networks to tune the water state for solar water purification. *Sci. Adv.* 2019, 5 (6), eaaw5484.

(33) Tai, Z.; Wei, J.; Zhou, J.; Liao, Y.; Wu, C.; Shang, Y.; Wang, B.; Wang, Q. Water-mediated crystallohydrate−polymer composite as a phase-change electrolyte. *Nat. Commun.* 2020, 11 (1), 1843.

(34) Li, C.-Y.; Le, J.-B.; Wang, Y.-H.; Chen, S.; Yang, Z.-L.; Li, J.-F.; Cheng, J.; Tian, Z.-Q. In situ probing electrified interfacial water structures at atomically flat surfaces. *Nat. Mater.* 2019, 18 (7), 697−701.

(35) Ruan, C.-Y.; Lobastov, V. A.; Vigliotti, F.; Chen, S.; Zewail, A. H. Ultrafast Electron Crystallography of Interfacial Water. *Science* 2004, 304 (5667), 80.

(36) Geng, H.; Liu, X.; Shi, G.; Bai, G.; Ma, J.; Chen, J.; Wu, Z.; Song, Y.; Fang, H.; Wang, J. Graphene Oxide Restricts Growth and Recrystallization of Ice Crystals. *Angew. Chem., Int. Ed.* 2017, 56 (4), 997−1001.

(37) Zheng, Y.; Su, C.; Lu, J.; Loh, K. P. Room-Temperature Ice Growth on Graphite Seeded by Nano-Graphene Oxide. *Angew. Chem., Int. Ed.* 2013, 52 (33), 8708−8712.

(38) Knight, C. A. Adding to the antifreeze agenda. *Nature* 2000, 406 (6793), 249−251.