# Ten-Minute Synthesis of Highly Conductive Polymer Nanosheets on Ice Surfaces: Role of Ice Crystallinity

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Abstract: Conducting polymers have been studied widely over the past decades for use as organic electrode materials owing to their high electrical conductivity and low-cost synthesis. Among the various synthesis methods reported, the recently established ice-assisted approach for developing conducting polymer nanosheets is regarded as an advanced technology that allows for easy fabrication in an eco-friendly manner. However, the role of the crystallinity of the underlying ice surface in determining the physicochemical properties of the conducting polymers remains unclear. Here, the electronic properties and packing structures of polyaniline (PANI) nanosheets formed on ice surfaces are studied by controlling the ice crystallinity. Intriguingly, the crystallinity of the PANI nanosheets resembles that of the ice surfaces, in that the anisotropic growth of the PANI crystals with a face-on orientation occurs preferentially on high-crystalline ice surfaces. In addition, it is found that the development of highly crystalline PANI nanosheets results in efficient charge transport, owing to polaron delocalization in PANI with extended chain conformations and the improvement in the degree of backbone ordering because of the preorganized aniline moieties on the ice surface.

### 1. Introduction

The ice-assisted synthesis of various functional materials has seen remarkable developments in the past few decades.<sup>[1-6]</sup> Owing to its advantages of a being simple technique (all that is involved in freezing and thawing), ice-related chemistry has been used successfully in various applications.<sup>[4-9]</sup> Representative examples of this include the design of ordered porous materials through the directional freezing technique,<sup>[2,10,11]</sup> with the aim of developing bioinspired materials with excellent mechanical properties<sup>[3,12]</sup> as well as high-performance electrodes with large surface areas for batteries and supercapacitors.<sup>[13,14]</sup>

In addition, the ice-induced nanoscale assembly of metal nanoparticles  $^{[15]}$  and nanowires  $^{[16,17]}$  into dimension-controlled

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superstructures has also attracted considerable attention. The confinement-driven dipole arrangements in ice grain boundaries enabled the exploitation of collective properties of individual nanocrystals. Through the two-dimensional assembly of inorganic nanowires developed using this method, advanced energy storage devices have also been established.<sup>[17]</sup>

Considering that ice inherently contains many impurities, ingenious approaches have been proposed for removing organic/inorganic contaminants from (ocean) water by freezing while controlling solute rejection and/or redistribution.<sup>[18,19]</sup> These research efforts have shown that freezing induces changes in the pH of salty water as cations and anions are rejected with different kinetics upon freezing, resulting in a charge imbalance, which is mitigated by the diffusion of protons and hydroxide ions.<sup>[20,21]</sup> This allows for unexpected chemical reactions to

occur under cold conditions. For example, the oxidative decomposition of gallic acid occurs in acidic aqueous solutions upon freezing.<sup>[22]</sup> Based on the freeze concentration effect, cases of accelerated chemical reactions/biological processes at the interfaces of ice crystals have also been reported.<sup>[1,23,24]</sup> This implies that ice interfaces can serve as a unique chemical environment in which unprecedented chemical reactions can occur.

In this context, quasi-liquid layers (QLLs) formed on ice surfaces have long attracted research interest.[25-27] Progressing from being able to explain how one can skate on ice based on the discovery of QLLs centuries ago,<sup>[25]</sup> it has now been shown that while QLLs exhibit most of the physiochemical characteristics between solid ice and liquid water, some of their other important properties, such as their refractive index, are similar to those of liquid water.<sup>[26]</sup> Theoretical studies based on molecular dynamics simulations have further revealed that the diffusion coefficient of water molecules is higher in QLLs than that in bulk water. This is attributable to the lower connectivity of the hydrogen-bonding networks at the air-QLL interface.<sup>[27]</sup> The reported thickness of QLLs on ice surfaces varies from several angstroms to tens of nanometers as determined by several experimental and theoretical studies.<sup>[28,29]</sup> However, the exact range is still a subject of debate. Their thickness was found to be primarily dependent on the temperature. However, QLLs can even exist at temperatures as low as -70 °C.<sup>[28]</sup> A recent study of ice surfaces using laser confocal microscopy coupled with differential interference contrast

K. Kim, M. J. Park

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Figure 1. Schematic illustration of the synthesis of PANI nanosheets on ice surfaces with controlled ice crystallinity.

microscopy revealed that the formation of QLLs is affected by the crystalline nature of the ice used.<sup>[30]</sup> While it is fair to say that many phenomena that occur on the ice surface are yet unknown, QLLs, which form spontaneously at different temperatures, have high potential as a reaction space for facilitating chemical reactions.

Recent works by Park et al. on the formation of twodimensional sheet-like conducting polymers on ice surfaces within a short reaction time (less than 5 min) are of significant importance in this regard. Nanosheets with high crystallinity and improved electrical conductivity (≈30 S cm<sup>-1</sup>) were established for ice-templated polyaniline (PANI)<sup>[31,32]</sup> and poly(3,4ethylenedioxythiophene): poly(styrenesulfonate).[33] This was in stark contrast to the results of previous studies, which reported the formation of one-dimensional nanofiber structures with low crystallinity and conductivity (less than 1 S cm<sup>-1</sup>).<sup>[34]</sup> However, the underlying mechanism responsible for the effects of the crystallinity of the ice surface on the packing structure and electrical properties of the ice-templated conducting polymer nanosheets remains unknown. Here, we report the synthesis of PANI nanosheets on ice surfaces by controlling the crystallinity of the ice. Defect-free PANI nanosheets were obtained regardless of the crystallinity of the ice template. However, their electrical properties, packing structure, and crystal orientation could be significantly modulated by varying the crystallinity. Highly conducting PANI nanosheets were formed on highly crystalline ice surfaces, owing to polaron delocalization in PANI with extended chain conformations and the improved backbone ordering because of the ice-induced  $\pi$ - $\pi$  stacking interactions.

## 2. Results and Discussions

**Figure 1** shows the process for synthesizing PANI nanosheets on ice surfaces. First, a 0.25  $\,$ M aniline solution in 1  $\,$ M HCl was cast onto the ice surface at -5 °C. This was followed by the addition of a 0.25  $\,$ M ammonium persulfate solution in 1  $\,$ M HCl. After 5 min of the chemical oxidative polymerization of PANI on the ice surface at a constant temperature of -5 °C, it was observed that the colorless ice surface gradually turned blue, indicating the formation of pernigraniline salt. When the reaction was allowed to last for 10 min, the blue surface layer turned green, and PANI in the emeraldine salt state was formed.

The modulation of the crystallinity of the ice template used was the key strategy for controlling the electronic properties of the formed PANI nanosheets. For this, polyethylene glycol (PEG,  $M_n = 4600 \text{ g mol}^{-1}$ ) was introduced as an oncotic agent during the freezing of the ice at -20 °C.<sup>[35]</sup> Although the molecular weight and amount of PEG added were varied systematically to control the crystallinity of the ice, for brevity, we will discuss only the representative data obtained for an ice sample containing 2.5 wt% PEG (hereafter referred to as PEG-ice), which allowed for the defect-free synthesis of PANI nanosheets. Detailed information on the PANI morphologies developed on PEG-ice with varied ice crystallinity is provided in Table S1 of Supporting Information. Differential scanning calorimetry showed that the heat of melting and crystallization temperature of PEG-ice were lower than those of pure ice, resulting in a decrease in the degree of crystallinity from 92.4% (pure ice) to 76.0% (PEG-ice) (Figure S1, Supporting Information). This was indicative of the cryoprotective effect of the added PEG.<sup>[35]</sup> Despite these differences in the ice crystallinities, the polymerization kinetics of PANI were not significantly affected. Thus, all the PANI nanosheets discussed in this study were obtained through a reaction performed at -5 °C for 10 min.

The optical micrographs in Figure 2a,b show the crystal grains formed on the pure ice and PEG-ice surfaces; it can be seen that the average grain size is approximately 10–20 µm. The PEG mapping of PEG-ice was performed using low-temperature Raman spectroscopy based on the CH<sub>2</sub> scissoring vibrations of PEG at 1475 cm<sup>-1</sup>; the exposure time was 0.1 s, and a 532 nm laser was used for the measurements. It was evident that PEG was highly localized in the liquid-like region at the grain boundaries of the ice crystals. As can be seen from Figure 2c, despite the difference in their crystallinities, both the pure ice and PEG-ice templates prepared at -20 °C have smooth surfaces that are free of cracks. Bright-field transmission electron microscopy (TEM) images of the PANI nanosheets formed on pure ice and PEG-ice are shown in Figure 2d,e, respectively. It can be seen that, qualitatively, the sheets have the same morphology and are free of nanofiber structures. Scanning electron micrographs of the PANI nanosheets examined over a large area are also provided in Figure S2, Supporting Information. We would like to mention that we deliberately show the parts with marked defects; otherwise, it would be difficult to distinguish the presence of thin sheets over a large area.

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**Figure 2.** Optical micrographs of a) pure ice and b) PEG-ice surfaces. The image shown at bottom of (b) represents PEG-map obtained using Raman spectroscopy. c) Digital photographs of pure ice and PEG-ice showing smooth surfaces. TEM images of PANI with sheet-like morphology formed on d) pure ice and e) PEG-ice.

Next, we investigated the electrical properties of the icetemplated PANI nanosheets. The synthesized PANI nanosheets were transferred from the ice surfaces onto Si/SiO<sub>2</sub> wafers with gold electrodes (10 µm width and 10 µm gap) via the floating-off method, and their current-voltage profiles were evaluated. Figure 3a shows representative linear sweep voltammograms of the PANI nanosheets, measured in the voltage range of -1.0 to 1.0 V at room temperature. The thickness of each PANI film was measured from the height profile of a scanning probe microscope (SPM). Given a reaction time of 10 min, the average thickness was  $70 \pm 4$  nm, regardless of the type of ice template used (reaction time-dependent thickness of PANI nanosheets is shown in Figure S3, Supporting Information). The representative height profile of a PANI nanosheet formed on pure ice is shown in the inset. The current values were normalized based on the thickness and area of the PANI nanosheets. As can be seen from the figure, the pure-ice-templated PANI nanosheet showed a high current

flow of 19.6 A cm<sup>-1</sup> at 1.0 V, which was three times higher than that (6.7 A cm<sup>-1</sup>) of its PEG-ice-templated counterpart. The result of the conventional PANI thin film is also shown in Figure 3a for a comparison, which revealed a considerably low current flow of  $1.1 \text{ A cm}^{-1}$ ; the film was prepared by chemical oxidative polymerization of aniline solution at -5 °C for 2h.

The electrical conductivity of each PANI nanosheet was calculated using the following equation:

$$\sigma = \frac{LI}{VA} \tag{1}$$

where *L* is the distance between the gold electrodes (10  $\mu$ m), *I* is the current value, *V* is the applied voltage, and *A* is the cross-sectional area of the sample placed between the gap of the gold electrodes. The conductivities of the PANI sheets formed on pure ice and PEG-ice were highly dissimilar at 19.6 and





**Figure 3.** a) Normalized currents of PANI nanosheets formed on pure ice and PEG-ice for voltage sweep in range of -1 V to 1 V. Thickness of each film as estimated using SPM was  $\approx$ 70 nm. b) UV–visible spectra of icetemplated PANI nanosheets formed on pure ice and PEG-ice. As a control, the current-voltage profile and UV–Vis spectrum of PANI synthesized by conventional chemical oxidative polymerization of aniline solution at -5 °C for 2h are also shown in (a) and (b), respectively.

6.7 S cm<sup>-1</sup>, respectively, indicating that the electrical conductivity of ice-templated PANI decreases with a decrease in the crystallinity of the ice template used. Nevertheless, considering that the commonly reported electrical conductivity of HCl-doped PANI is around 1 S cm<sup>-1</sup>, (conductivity of our PANI calculated from Figure 3a is 1.1 S cm<sup>-1</sup>)<sup>[34]</sup> it is likely that fast electron transfer occurs in ice-templated PANI nanosheets. It should also be noted that when PANI was synthesized by the chemical oxidative polymerization of an aniline solution containing PEG, typical nanofiber structure was formed, and the electrical conductivity was as low as 0.9 S cm<sup>-1</sup> (Figure S4, Supporting Information). This confirms that the effect of the added PEG on the synthesis and electrical properties of PANI is not significant because the  $\pi$ - $\pi$  stacking interactions of PANI are stronger than the interchain hydrogen bonding interactions of PEG and PANI.

To elucidate the mechanism responsible for the icecrystallinity dependence of the electrical conductivity of PANI, the UV–visible spectra of the PANI nanosheets were measured.  
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**Figure 4.** a) FT-IR spectra and b) low-temperature in-situ Raman spectra of PANI nanosheets formed on pure ice and PEG-ice.

As shown in Figure 3b, the absorption peaks at 360, 432, and 877 nm seen in the case of PANI on pure ice correspond to  $\pi$ - $\pi$ \* transitions, polaron- $\pi$ \* transitions, and  $\pi$ -polaron transitions, respectively, indicating that the synthesized PANI nanosheets were in the emeraldine salt state.<sup>[36]</sup> While PANI on PEG-ice also showed analogous peaks related to  $\pi$ - $\pi$ \* transitions and polaron- $\pi$ \* transitions at 360 nm and 432 nm, respectively, the peak related to  $\pi$ -polaron transitions was significantly blue-shifted to 820 nm. For conventional PANI, a more shifted peak of 819 nm was observed. This indicates that the polaron band of PANI on PEG-ice is narrow; this conclusion is in keeping with the conductivity results. Thus, the electronic structure of PANI nanosheets can be tuned through a simple but powerful ice-templated method based on the control of the crystallinity of the ice template.

Next, we examined the chemical structures of the icetemplated PANI nanosheets. As shown in **Figure 4**a, the PANI nanosheets showed similar FT-IR spectra, regardless of the type of ice template used. In addition, there was no noticeable difference in the doping levels of the PANI nanosheets, with all the



peaks showing a similar peak ratio (approximately 1) for the peak related to quinoid at 1564 cm<sup>-1</sup> and that related to benzenoid at 1482 cm<sup>-1</sup>. This indicated that both types of PANI nanosheets were in the emeraldine salt state.<sup>[37]</sup> A peak related to the C–N stretching vibrations in the quinoid-benzenoid-quinoid unit was seen at 1385 cm<sup>-1</sup> along with peaks related to secondary amines at 1296 and 1240 cm<sup>-1</sup> and a peak related to the C–H bending vibrations at 1122 cm<sup>-1</sup>. Moreover, the intensities of the peaks of the two samples were similar. Hence, the higher conductivity of PANI on pure ice than that of PANI on PEG-ice does not have a chemical origin. It was also confirmed that an undetectable amount of PEG remained in the PANI formed on PEG-ice.

The mechanism underlying the variations in the conductivity of PANI with the crystallinity of the ice template used was explored using low-temperature in-situ Raman spectroscopy. Figure 4b shows representative Raman spectra of the PANI nanosheets formed on pure ice and PEG-ice as measured after a 10-min reaction at -5 °C (without transferring steps onto other substrates). The characteristic peaks of PANI are assigned in the figure. Overall, the Raman intensities of the PANI nanosheets formed on PEG-ice were low. This was presumably owing to the low crystallinity of PANI on PEG-ice (see X-ray diffraction patterns in Figure S5, Supporting Information), given that the Raman spectrum of a material is largely determined by its degree of ordering. This hypothesis was confirmed through Raman measurements performed on PANI films of similar thicknesses prepared by the conventional chemical oxidative polymerization of an aniline solution (Figure S6, Supporting Information). The spectra were poorly resolved to the extent that it was difficult to assign the characteristic peaks.

Intriguingly, the Raman spectra of the PANI nanosheets formed on the different ice templates exhibited markedly different characteristic peaks. The two peaks at 1373 and 1630 cm<sup>-1</sup> correspond to the delocalized polarons in PANI.<sup>[38,39]</sup> These peaks were considerably weaker in the case of PANI on PEG-ice:  $I_{1373}$  / $I_{1174}$  of 0.69 (pure ice),  $I_{1364}$  / $I_{1166}$  of 0.24 (PEG-ice),  $I_{1630}$  / $I_{1174}$  of 1.30 (pure ice), and  $I_{1630}$  / $I_{1166}$  of 0.53 (PEG-ice). Nevertheless, given the fact that the Raman peaks of the delocalized polarons have rarely been observed in the case of PANI nanosheets synthesized through conventional methods (Figure S6, Supporting Information), it can be assumed that polaron delocalization in the ice-templated PANI nanosheets has a determining effect on their conductivity, highlighting the unique advantages of ice surfaces as chemical reactors.

The appearance of these two peaks related to delocalized polarons can be attributed to the fact that the extended chain conformations improve the degree of ordering of the PANI backbones. It has been reported previously that PANI/graphene composites show polaron delocalization, which is attributable to grapheneinduced  $\pi$ – $\pi$  stacking interactions.<sup>[40,41]</sup> Moreover, in the case of solvent-treated camphorsulfonic acid-doped PANI, the molecular packing of the PANI units is transformed from a random one to an ordered one.<sup>[39]</sup> Thus, ice templates play a crucial role in modulating the packing structure of the PANI units, resulting in a more planar structure with reduced backbone distortion. In addition, this effect becomes more pronounced when highly crystalline ice is used. We believe that the adsorption of aniline monomers onto the ice surface via hydrogen-bonding interactions at the beginning of the reaction is important for ensuring the packing of the preorganized monomers prior to polymerization.

To prove this, we performed in-situ grazing-incidence X-ray scattering (GIXS) experiments to elucidate the ordering of aniline on ice surfaces. For this, a thin ice substrate was prepared using Peltier modules to allow for both the reflection and transmission of the X-ray beam at the ice surfaces. Figure S7, Supporting Information, shows a representative GIXS pattern, which was measured 5 min after casting the aniline monomer onto the ice surfaces at -5 °C. Intriguingly, a broad arc was observed at a q value of 17.5 nm<sup>-1</sup> in the out-of-plane direction; this corresponded to the  $\pi$ - $\pi$  stacking of the aniline monomers before the addition of ammonium persulfate. Thus, it can be inferred that the preorganization of the aniline moieties in QLLs occurs before polymerization, as stated above, and that the face-on orientation forms preferentially under the reaction conditions investigated in this study.

We further investigated the crystal orientations and packing structures of the ice-templated PANI nanosheets after their synthesis. For this, the PANI films were transferred onto Si wafers from the ice surfaces after a reaction time of 10 min via the floatoff method. The GIXS patterns of the PANI nanosheets formed on pure ice and PEG-ice are shown in Figure 5a,b, respectively. For comparison, the results for solution-cast PANI formed on a Si wafer are also shown in Figure 5c; the solution was prepared by the conventional chemical oxidative polymerization of aniline. Scattering peaks were observed at *q* values of 6.3, 10.2, 14.4, and 17.6 nm<sup>-1</sup> in the case of all three samples; these corresponded to the (200), (201), (002), and (020) reflections of the PANI crystals.<sup>[31]</sup> Interestingly, a high-intensity arc pattern in the out-of-plane direction was again observed in the spectrum of the ice-templated PANI nanosheets. This indicated  $\pi - \pi$  stacked PANI molecules with a distance of 3.5 Å from an ice surface to the air to have face-on orientation. In addition, the strong in-plane peak related to the (200) plane with a spacing of 9.9 Å seen in the case of the ice-templated PANI nanosheets was indicative of laterally stacked lamellar crystals. The anisotropic orientation of the PANI crystals was in sharp contrast to the isotropic orientation of the conventional PANI structure.

To elucidate the role of the crystallinity of the ice substrate used on the crystalline structure of the formed PANI nanosheets, the 1D scattering intensity profiles of the three samples are shown in **Figure 5**d–e. The (020)  $\pi$ - $\pi$  stacking peak was only visible in the out-of-plane direction in the case of the PANI nanosheets formed on pure ice (Figure 5d). On the other hand, although anisotropy was still observed, the PANI nanosheets formed on PEG-ice showed a  $\pi - \pi$  stacking peak in both the in-plane and out-of-plane directions (Figure 5e), as indicated by shading. Moreover, the scattering intensities of the (201) and (002) peaks were relatively stronger in the in-plane profile of the PANI nanosheets formed on pure ice compared with those of the PEG-ice-templated PANI nanosheets. Hence, one can conclude that the anisotropic growth of PANI crystals occurs predominantly on highly crystalline ice surfaces with a face-on orientation. With respect to the isotropic GIXS pattern of the conventional PANI films, the peak intensities in both the in-plane and out-of-plane profiles were similar, as shown in Figure 5f. This meant that the PANI nanosheets were www.advancedsciencenews.com

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**Figure 5.** 2D GIXS patterns and 1D scattering profiles of PANI nanosheets formed on a,d) pure ice and b,e) PEG-ice and c,f) those of conventional PANI. In-plane (020) peaks are shaded to highlight the difference in  $\pi$ - $\pi$  stacking intensities along in-plane direction.

randomly oriented and suggested that the use of an ice template is the key to synthesizing anisotropically arranged PANI crystals, as their orientation and packing structure are affected by the crystallinity of the underlying ice surface.

The proportion of the crystals with a face-on orientation was assessed for each PANI sample by analyzing the azimuthal pole figure of the (020)  $\pi$ - $\pi$  stacking peak (Figure S8, Supporting Information).<sup>[42]</sup> The ratios of the proportion of crystals with the face-on orientation to that of the crystals with the edge-on orientation were calculated to be 3.7 and 3.0 for the PANI nanosheets formed on pure ice and PEG-ice, respectively; in contrast, the ratio was close to unity for conventional PANI.

Note in passing that most literature on sub-zero temperature synthesis of PANI is concerning the freeze concentration effects.<sup>[43,44]</sup> Ubiquitous particle-like<sup>[43]</sup> or nanofiber morphologies<sup>[44]</sup> have been reported for resultant PANIs. The synthesis of two-dimensional sheet-like PANIs on ice surfaces was first reported by our group in 2015, stemmed from the selforganization of PANIs in the QLL layer on the ice surfaces.<sup>[31]</sup> The main contribution of this work to the literature is that it is the first elucidation of the effect of ice crystallinity on electrical properties and morphologies of ice-templated PANIs.

It is also noted here that in our previous study,<sup>[31]</sup> we had set the reaction temperature to 0°C. However, we had observed significant surface melting of PEG-ice at this temperature. Therefore, the reaction temperature was lowered to -5 °C in the present study. However, this meant that more time was required to ensure that the aniline monomer uniformly covered the ice surfaces before the oxidizing agent was drop-cast on them (this was important for the formation of defect-free PANI nanosheets). We found that this caused a radical change in the  $\pi$ - $\pi$  stacking direction, as we observed a dominant edge-on orientation in the case of the

PANI nanosheets formed on ice surfaces at 0 °C. The predominant face-on orientation of PANI on pure ice at -5 °C (this study) lowered the electrical conductivity of PANI nanosheets compared to edge-on-oriented counterparts developed at 0 °C,<sup>[31]</sup> in good agreement with the literature disclosing high electron mobility for conducting polymers with edge-on orientation.<sup>[45–47]</sup>

To explore the applicability of ice-templated PANI nanosheets in practical applications, PANI nanosheet on pure ice was applied to two different electromechanical and electrochemical devices. First, we fabricated electroactive polymer actuators with PANI nanosheet electrodes. As shown in Figure S9a, Supporting Information, the actuators demonstrated excellent low-voltage-driven mechanical deformation with bending strains greater than 0.4% at ±1.5 V. This is attributed to the high-conductivity, defect-free two-dimensional structure, and flexibility of PANI nanosheet. Next, we investigated lithium batteries with Si nanoparticle anodes fabricated with PANI nanosheet binder. More than 20% increased specific capacities and considerably reduced cell polarization were obtained from the lithium cell with the PANI nanosheet binder (Figure S9b, Supporting Information), as it effectively enclosed the low-conductivity Si active materials, thereby helping with fast electron transfer. A more in-depth device study will be the scope of our future research.

### 3. Conclusions

We studied the electrical properties, morphologies, and packing structures of PANI nanosheets formed on different types of ice surfaces with a focus on the effect of the crystallinity of the ice template used. By introducing 2.5 wt% PEG during the freezing of the ice at -20 °C, its crystallinity was lowered by 16%. This ice was then used as a template, and the results obtained



were compared with those obtained with pure ice. The PANI nanosheets synthesized on both pure ice and PEG-ice exhibited a thickness of  $\approx$ 70 nm and had qualitatively similar morphologies, which were free of nanofiber structures. Furthermore, both types of nanosheets had a dominant face-on orientation and consisted of PANI crystals that showed anisotropic growth. In addition, the sheets showed high electrical conductivity, which was at least six times higher than the values commonly reported in the literature. Intriguingly, the electronic structure and crystal orientation appeared to be modulated by the crystallinity of the ice template used. The PANI nanosheets formed on pure ice showed a high conductivity of 19.6 S cm<sup>-1</sup> while the PEG-ice-templated PANI nanosheets showed a value that was three times lower (6.7 S cm<sup>-1</sup>). This enhancement can be attributed to the widening of the polaron band as well as the strong delocalized polarons in the PANI nanosheets formed on the highly crystalline ice surface, which is unprecedented. This results in an extended chain conformation and improvements in the backbone ordering of the PANI crystals because of the strong  $\pi - \pi$  stacking interactions, leading to a more planar structure. It was determined that the simple preorganization of the aniline monomers on the ice template surface before polymerization is the key to the development of this packing structure. Thus, the proposed method should allow for the easy tuning of the electrical properties of conducting polymer films through a simple but powerful ice-assisted approach.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

Research data are not shared.

### **Keywords**

conducting polymers, electronic properties, ice crystallinity, ice-template, polyaniline

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