Macromolecular Research

Article

DOI 10.1007/s13233-022-0085-x

www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

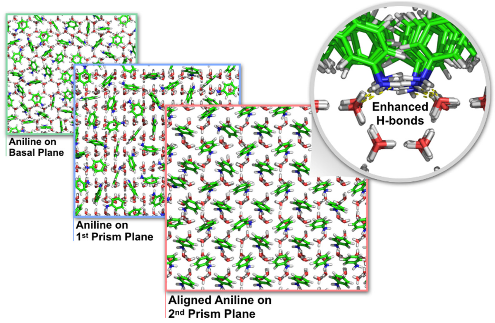
Directed Self-Assembly of Conducting Polymer Nanofilms on Single-Crystalline Ice Facets

Sang Yup Lee[†,1]
Sung Ryul Kim[†,1]
Dong June Ahn[*,1,2]

[1] KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Korea
[2] Deperatment of Chemical and Biological Engineering, Korea University, Seoul 02841, Korea

Received May 7, 2022 / Revised May 25, 2022 / Accepted June 2, 2022

Abstract: The assembly of aniline molecules was controlled using single-crystalline ice facets that have highly ordered but dissimilarly organized OH groups at the surface. We found a difference in electrical properties of polyaniline nanofilms synthesized on dissimilar ice surfaces; basal, primary prism, and secondary prism planes. We discovered through molecular dynamics that ice-directed self-assembly induced layered structures of aniline monomers depending on enhanced formation of hydrogen bonding network per ice facet. The anilines assembled better-ordered on secondary prism plane and their lattice coincided with a repeat distance of H_2O molecules on ice. This resulted in improved electrical properties of polyaniline nanofilms after subsequent polymerization.



Keywords: polyaniline, single-crystalline ice, degree of ordering, molecular dynamics, directed self-assembly.

1. Introduction

Conducting polymers have unique optical and electrical properties because they have a backbone with an extended π-conjugated system. The electrical conductivity of conducting polymers can be increased by doping, and different methods of synthesis and various applications for these electrically conductive compounds have been studied, including light-emitting diodes,[1] batteries,[2] electromagnetic shielding,[3] antistatic agents,[4,5] gas sensors,[6,7] biosensors,[8-10] and activators.[11] Common conducting polymers include polyacetylene, polyaniline, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene) (PEDOT). Polyaniline, among others, has high stability, ease of synthesis, low cost, and excellent mechanical properties.[12,13] Decades of research have shown that the electrical conductivity of polyaniline is affected by its nanostructure and crystallinity, and there is controlled using hard-templates such as graphene oxide[14] and gold substrate.[15] Recently, ice has been used as a template to synthesize polyaniline to improve its electrical conductivity by controlling the crystallinity.[16] In addition, this method can easily remove the template to obtain a pure film, easily patterned, and is environmentally friendly. The mechanism of ice-templating synthesis has been interpreted as the self-orientation of monomers by hydrogen bonding with the ice surface. Still, molecular interpretation at the atomic scale has not been elucidated yet.

Acknowledgment: This work was supported by the National Research Foundation of Korea (NRF-2021R1A2C3009955, 2017M3D1A1039421, 2020R1A6A3A13073854) and the Korea University Grant.

***Corresponding Author:** Dong June Ahn (ahn@korea.ac.kr)
[†]These authors equally contributed to this work.

On Earth at atmospheric pressure, ice and snow have a hexagonal crystal structure. Ice crystals form hexagonal columns or plates, where the top and bottom faces are the basal faces and the six side faces are the prism faces.[17] A novel feature of ice is that, by controlling the growth of different crystal faces, a monocrystalline system having various surfaces with different hydrogen bonding capacities can be formed. The well-ordered surface is a suitable environment for the organization of organic molecules into thin layers. In addition, an ice single crystal has a more ordered periodic arrangement of atoms than polycrystalline ice. There are several ways to grow ice single crystals in the laboratory. The well-known Bridgman method[18,19] and Czochralski method[20] can be used to grow a single-crystalline ice. Khusnatdinov and Petrenko also developed a technique that uses a vacuum chamber operated at room temperature to form bulk crystals.[21] In addition, Knight developed a method that mimics the natural formation of ice in lakes.[22]

In this work, we experimentally and theoretically show that well-controlled single-crystalline ice can align the aniline monomers *via* hydrogen bonding. Through this work, we expand the design of single-crystalline ice templates with various lattice structures, which in turn enrich the diversity of available materials.

2. Experimental

2.1. Materials

Aniline, ammonium persulfate (APS), hydrochloric acid (HCl), and deionized (DI) ultra-pure water were purchased from Sigma-Aldrich. The DI water was degassed by using membrane degassing units.