


Biomimetic Nacrelike Membranes for Selective Ion Transport

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Biomimetic nacrelike designs not only present a rational strategy for preparing robust materials but also open the avenue for regulating nanofluidic ion transport.

Two-dimensional (2D) materials have natural advantages for constructing layered nanofluidics, which have been a hot topic for mimicking the fantastic functions of the biological ion channels. However, simple stacking of pristine nanosheets normally results in an unstable layered structure and poor mechanical strength, inducing inadequate selective ion transport. In their latest pioneering work published in this issue of *ACS Central Science*, Liping Wen et al. highlight the promise of biomimetic nacrelike design as nanofluidic devices for selective ion transport and sustainable energy conversion.¹

Ion transport regulated by ion channels plays a foundational role in the physiological activities of live beings, such as sensing, energy conversion, and information transmission.^{2–4} Artificial ion channels with nanoscale confined spaces are expected to be an ideal model for exploring future nanofluidic devices.⁵ The blooming 2D materials have shown great potential in building layered system stemming from their planar structures and provide the possibility of realizing large-scale integration for practical applications. Specifically, the angstrom-scale nanochannels formed by 2D materials, which are comparable to the biological channels, guarantee efficient ion selectivity. Nevertheless, nanofluidic devices fabricated by 2D materials are always confronted with uncontrollable swelling that results in an unstable nanoconfined system and, therefore, a solely uncontrollable ion transport. Currently, the inadequate charged functional groups contributing to the charge screening effects also become a shortcoming for the layered biomimetic nanochannels.

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In this work,¹ Liping Wen and the team drew inspiration from nature when approaching their materials design, and introduced one dimensional (1D) charged aramid nanofibers (ANFs) into 2D graphene oxide (GO) nanosheets (Figure 1). To overcome the instability of the layered system, Wen et al. took inspiration from the natural nacrelike “brick-and-mortar” structure and constructed GO/ANF membranes with hard GO nanosheets as the “brick” and soft ANFs as the “mortar”, which represent a robust nanofluidic system with superior structural stability. The ANF in their system function as a soft chain to cross-link the GO nanosheets, which are beneficial for constraining the swelling of the interlayer space and the slip of the GO nanosheets in order to realize a stable nanoconfinement configuration. Also, the nacrelike structure improves the mechanical strength of the employed ANFs, which are then able to withstand interfacial stresses.^{6,7} Therefore, this work presents a facile and scalable method to fabricate biomimetic nanocomposite membranes with improved chemical and physical robustness.⁸

Notably, ANFs not only serve as cross-linkers to ensure stable and tough integration but also work as space charge donors for the enhanced charge screening effect. The electric double layer in nanochannels completely overlaps

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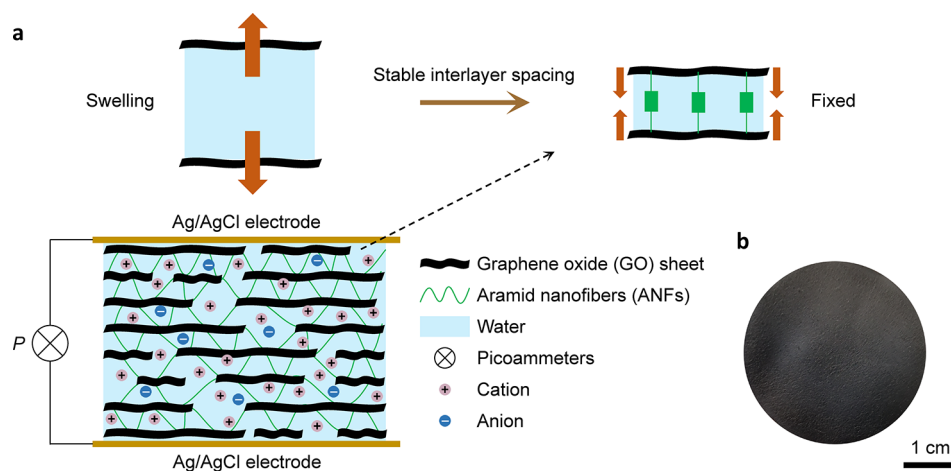


Figure 1. (a) Schematic of the experimental setup for ion transport. The GO/ANF membrane separates two electrolyte-filled reservoirs, with Ag/AgCl electrodes in the reservoir to monitor the flowing of ionic currents. The cross-linked structure can prevent the plane swelling and, thus, achieve a stable interlayer spacing. SNFs also provide active sites such as various oxygenated functional groups. (b) Freestanding GO/ANF composite membrane obtained by vacuum-assisted filtration. Reproduced with permission from ref 1. Copyright 2021 The Authors. Published by American Chemical Society.

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materials for converting osmotic energy and present a superb osmotic power conversion performance with an output power density up to 5.06 W m^{-2} by mixing artificial seawater and river water.

The electric double layer in nanochannels completely overlaps due to the coupling of surface charge and space charge. This promotes the ionic selectivity of the membrane and thus enhances the ionic transport across the membrane.

due to the coupling of surface charge and space charge. This promotes the ionic selectivity of the membrane and thus enhances the ionic transport across the membrane. Thereby, the GO/ANF composite membranes address the issue of insufficient surface charge densities of the state-of-the-art 2D

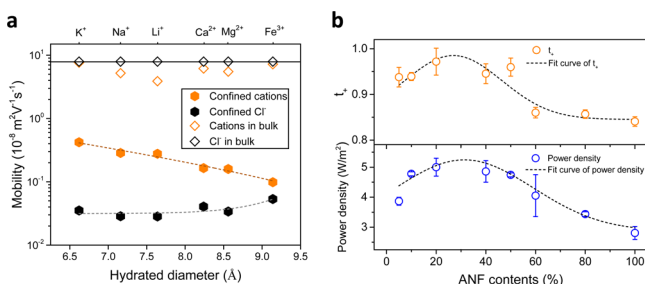


Figure 2. (a) Ion mobility under the nanoconfinement versus D_H . (b) Ion selectivity of the composite membrane, defined as transmembrane ion transference number versus ANF contents (top). Power density of the membrane versus ANF contents (bottom). Reproduced with permission from ref 1. Copyright 2021 The Authors. Published by American Chemical Society.

Further, the ultrahigh selectivity of the proposed system was investigated by conducting a drift diffusion experiment to reveal its physical mechanism.⁹ By using the Henderson equation, the cation/anion mobility is calculated (Figure 2a). The ion mobility in the nanoconfinements deviates from the ion mobility in bulk solution. The activated size exclusion was observed, and the cation mobility decreases with increasing the hydrated diameter (D_H). Besides, the mobility of Cl^- is lower than that of the cations due to electrostatic repulsion. Thus, the electrostatic repulsion and activated size exclusion together contribute to the ion selectively transport.

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The application of the biomimetic nacrel-like membrane reported by Wen et al. is engaging for broadening the family of artificial nacrel-like materials. Both the mechanical property and the ion transport property are closely associated with the material structure, which has been simultaneously optimized in a biomimetic design. The successful combination of structural reliability and improved functionality is instructive for developing future functional materials, such as energy storage and energy conversion materials.

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