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Graphene transmembrane nanofluidic devices: fabrication strategies and ion transport

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Chapter 7

Summary, Conclusions, and Outlook

Summary.

This thesis investigates the fabrication, stabilization, and functionalization of a graphene nanofluidic device for ion-selective transport. Through five experimental chapters, we address key challenges in integrating graphene into practical devices by introducing strategies that improve their stability, scalability, and ion selectivity.

Fabrication challenges (Chapter 2): This study systematically evaluates mechanically exfoliated graphene, known for its pristine crystallinity and no grain boundary defects, for use in nanofluidic ion transport studies aiming at understanding the fundamental transmembrane properties of graphene. However, the fabrication and measurement success rate of these devices is very low. This work focuses on characterizing graphene damage, poor wetting, contamination, and delamination. Through statistical analysis of over a hundred devices, we identify the factors causing failure and propose optimized protocols and solutions to improve the reliability and yield, paving the way for more consistent experimental results and robust datasets.

Stabilization of graphene nanofluidic devices (Chapter 3): As discussed in Chapter 2, free-standing graphene faces critical stability challenges in aqueous environments, with delamination limiting its practical application in nanofluidics. To address this issue, a pyrene-based adhesion layer was introduced, forming strong π-π interactions with graphene and significantly enhancing graphene-chip adhesion. This approach highly increases the successful device yield from a mere 4% to 76.2%, and maintains stability for up to 11 days in electrolytes. This study highlights the importance of preventing delamination from the substrate, ensuring the operational longevity of graphene nanofluidic devices for applications such as sensing, filtration, and molecular separations.

Chemical functionalization for selective proton transport (Chapter 4): Building on Chapters 2 and 3, we have achieved stable graphene nanofludic devices. In this chapter, we focus on using graphene to achieve ion selectivity. However, pristine graphene has been reported to allow only minimal proton transport, though ripples and wrinkles area. To enhance proton conductivity and selectivity, we covalently functionalized graphene with 4-sulfonato benzenediazonium. This functionalization process generated precisely sized pores (sp^3-hybridized expanded ring) grafted with sulfonate groups, which enhanced local proton concentrations via electrostatic interaction and Grotthuss-like hopping mechanisms, while steric effects restricted potassium ion diffusion. As a result, proton conductivity increased from 0.08 S cm^{-2} in pristine graphene up to ~64 S cm^{-2} in the sulfonatophenylated graphene. This study

offers a chemical functionalization for creating highly selective and efficient proton-conducting graphene membranes, opening opportunities in proton-exchange membranes and energy conversion technologies.

Diazotization of porous graphene (Chapter 5): As shown in Chapter 4, sulfonatophenylated graphene enhances proton transport. Since the porous graphene can further increase the ion flux compared to pristine graphene, and has higher chemical reactivity of its pore edges. In this study, porous graphene was created via oxygen plasma treatment, followed by covalent functionalization with 4-SBD to achieve improved ion flux and selectivity. The resulting functionalized porous graphene exhibited monovalent ion selectivity, with an H^+/K^+ selectivity ratio of 1.5 and a K^+/Cl^- selectivity ratio of 75.4 ± 14.3 under a 10-fold KCl concentration gradient. These graphene-based membranes outperform other ion-selective membranes, such as graphene oxide-based and polymeric membranes, in both ion selectivity and energy harvesting performance. This performance highlights the significant potential of graphene for energy harvesting applications and advanced separation technologies.

Graphene Nanoribbons (GNRs) *via* ultramicrotomy (Chapter 6): In this chapter, edge-aligned, width-tunable GNRs are fabricated through ultramicrotomy. By embedding monolayer graphene in a polymeric resin and controlling blade angles during sectioning, we achieved precise control over nanoribbon dimensions (width and inter-edge spacing). This scalable technique bypasses traditional lithographic limitations, offering a platform to explore edge-specific chemistry and quantum-confined electronic properties in graphene nanoribbon-based sensors.

Outlook.

Building on the progress demonstrated in this dissertation, several promising research directions emerge for advancing graphene-based technologies:

1. Impact of adhesion layers: While pyrene-based adhesion layers significantly improve device stability through π-π interactions, their influence on the in-plane doping and transport properties of graphene requires careful evaluation. The pyrene functionalization process we used, which makes multilayers, may introduce unintended doping effects that could alter charge carrier concentrations and mobility in the graphene membrane. Additionally, potential conduction pathways through the pyrene layers themselves must be characterized to fully understand their impact on transmembrane transport. Systematic studies combining gate-dependent electrical measurements, thickness-controlled adhesion layers, and surface potential mapping will be essential to decouple stability enhancement from electronic modifications.

2. Theoretical insights: While sulfophenyl-functionalized graphene demonstrates remarkable proton conductivity improvements (from 0.08 to 64.2 S cm^{-2}), the underlying mechanisms require deeper investigation. In particular, the increased proton conductivity upon sulfonatophenylation may arise from multiple synergistic phenomena: enhanced surface hydrophilicity, the introduction of negative charge through sulfonate groups, the generation of sp^3 structural defects, and potential electronic doping effects. Currently, we cannot pinpoint exactly which factor (or combination of factors) is most responsible for the improved conductivity. Future research should focus on carefully separating these individual factors. This will involve using advanced theoretical simulations to better understand the mechanisms governing proton permeation.

3. Detailed characterization of functionalized graphene: Although Raman spectroscopy confirms the formation of sp^3 defects, there is still a gap in understanding and imaging the structure of functionalized graphene. Key challenges include visualizing sp^3 defects at atomic resolution, mapping sulfophenyl group distribution, and quantifying graft density correlations with ion transport. Advanced techniques, such as atomic-resolution TEM, Fourier-transform infrared (FTIR) spectroscopy, and tip-enhanced Raman, could provide nanoscale structural insights. Complementary surface analysis and *in situ* transport measurements should be coupled with simulations to establish design principles for optimized membranes. Overcoming these characterization limitations will enable rational engineering of graphene-based membranes with precisely tailored ion selectivity and conductivity.

4. Functionalization strategies: Exploring a range of chemical functionalization approaches presents significant opportunities to engineer graphene membranes with tailored ion permselectivity properties. Strategic modification of the surface chemistry of graphene could enable precise control over ion selectivity, particularly for challenging separations involving similarly sized ions (*e.g.*, Na^+/K^+ or Li^+/Mg^{2+}). Both covalent (*e.g.*, diazonium, aryl) and non-covalent (*e.g.*, π-stacked, electrostatic) modification routes should be systematically evaluated to establish structure-property relationships. Additionally, the correlation between ion transport and the degree of functionalization, including reaction time and kinetics, requires further investigation.

5. Graphene nanoribbon fabrication challenges and optimization: Although the nanoskiving approach shows great promise for the scalable production of graphene nanoribbons (GNRs), current fabrication challenges limit the production of GNRs with widths below 100 nm. Reducing the width of GNRs to below 100 nm is crucial,

as it enables the opening of the graphene bandgap, enabling applications in fields such as electronic devices, optoelectronics, and logic circuits. However, the resin matrix currently used in the nanoskiving process cannot be sectioned to below 100 nm while maintaining a continuous film. Additionally, weak bonding between the resin matrix and graphene results in poor adhesion, causing the graphene to detach during sectioning at these thin thicknesses. Therefore, developing a resin with stronger adhesion properties is essential to fully realize the potential of graphene nanoribbons.