Supporting Information

Fabrication of sub-nanometer pores on graphene membrane for

ion selective transport

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1. Experimental Methods

a. Si₃N₄ Substrate Fabrication Protocol

The process of fabrication silicon nitride (Si_3N_4) substrate is shown in Figure S1 (a). In the first step, a freestanding with100 nm thick Si_3N_4 membrane was deposited on both sides of the <100> silicon substrate by low-pressure chemical vapor deposition (LPCVD). Then, optical lithography and reactive ion etching (RIE) methods were used to etch a 720 µm × 720 µm square window at the center of the Si_3N_4 membrane on one side of the silicon wafer. In the third step, the wafer went through a Tetramethylammonium Hydroxide (TMAH) wet etching process from the Si_3N_4 window to expose a freestanding Si_3N_4 membrane on the opposite side. Then the Si_3N_4 membrane was sputtered using a Ga⁺ Focused Ion Beam (Helio NanolabTM 600i, FEI Company) to fabricate a single hole. The dose was calibrated to ensure that the diameter of the hole was consistently at 2 µm. The scanning electron microscope (SEM) image of the 2-µm-diameter Si_3N_4 hole is shown in Figure S1 (b). Prior to transfer graphene,

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nanopores were cleaned using freshly heated piranha solution (1:2 mixtures of H_2O_2 and H_2SO_4) for 10-15 min.



Figure S1. (a) The process of fabrication Si_3N_4 substrate; (b) The SEM of a 2-µmdiameter Si_3N_4 pore.

b. Graphene Transfer Protocol

To fabricate graphene-on-Si₃N₄, we used a mechanical transfer process (Figure S2). In our first step of sample preparation, monolayer graphene was obtained by micromechanical cleavage from bulk crystals and transferred to a Si wafer with a 300nm SiO₂ capping layer. Then, a thin layer of polymethyl methacrylate (PMMA) (4%) was spin-coated on the samples with film thickness at $\sim 1 \mu m$. Following the spin coating, a layer of polydimethylsiloxane (PDMS) with 2 mm hole was adhered to the sample. Afterwards, the sample was immersed in 45% KOH solutions. Once SiO₂ was etched, the Si substrate would sink to the bottom of the bath, leaving the membrane containing graphene, PMMA and PDMS floating on top. The membrane was cleaned using deionized water and adhered to a glass slide, which was clamped onto the arm of a micromanipulator mounted on an optical microscope. Using the microscope to optically locate the position of the graphene flake on the suspended PMMA, the graphene was precisely aligned to the Si_3N_4 microchip device with a single 2 μ m hole. Then the chip was immersed in acetone solutions to wash out the PMMA. Finally, scanning electron microscope imaging (Figure S3) was used to confirm that the graphene layer suspended over the hole was intact with no visible ruptures or tears.



Figure S2. The process of transferring graphene



Figure S3. The SEM of transferred monolayer graphene on the Si_3N_4 substrate from the view of (a) large window and (b) small window.

c. Plasma Etching

Nanopores were introduced on the transferred graphene by plasma etching. To

accurately control the defect density and retard the progress of defect introduction, the plasma power and pressure were maintained at 40 W and 20 Pa, respectively. In addition, in order to ensure the vacuum environment, we need to keep the chamber pressure lower than 0.1 Pa before filling with argon or oxygen gas. Graphene membrane was characterized with a Raman spectroscopy (a LabRAM HR800 Raman system with excitation laser light of 514.5 nm) before and after the plasma treatment to check the defects.

d. Measurement of Current - Voltage Characteristics

To measure current-voltage characteristics, we used a patch-clamp amplifier (MultiClamp 700B Amplifier) with silver/silver chloride electrodes to transduce the ionic current into an electronic current. The patch-clamp amplifier was operated in voltage-clamp mode, which allows for a fixed voltage to be applied across the graphene membrane while recording currents. Two PMMA cells were designed to mount the chip with a suspended nanoporous graphene membrane connecting the two liquid reservoirs filled with electrolytes. The chip was sealed in the groove of one cell, and the two cells were stuck together using PDMS. Ag/AgCl electrodes immersed in each chamber were connected to the patch clamp amplifier to measure ionic current. Voltage control and digitization of analog signals (Digidata 1550A) are both programmed using free automation software, AutoIT. Current traces (80 s long) were measured at steady state between -500 and 500 mV in voltage steps of 100 mV. The traces were lowpass-filtered with a 5 kHz four-pole Bessel filter and sampled at 25 kHz. All current data were fitted using Clampfit 10.5.



Figure S4. A schematic of the experimental device showing a nanopore sandwiched

between two PMMA reservoirs.

2. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations were conducted to determine the energy barriers for protons and Na⁺ ions transport through nanoporous graphene membranes with the Vienna Ab Initio Simulation Package¹. Energy cutoff of 520 eV was used as the plane wave basis sets in the method of projector augmented wave². Under the general gradient approximation, the exchange correlation interaction was treated with the Perdew-Burke-Ernzerhof parametrization³. Here, the energy barrier was used to describe the energy gap between states of immediate reaction and transition. At least 10 Å vacuum regions were performed in the z-direction, and periodic boundary conditions were also applied in the x and y directions. The Forces on atoms were converged to be smaller than 10^{-2} eV/Å , in order to keep fully optimized structures which would be calculated latter more accurate. Each atomic structure was fully optimized, namely pristine graphene membrane, graphene membrane with argon plasma treatment and graphene membrane with oxygen plasma treatment. During structural optimization, all of the atoms in each atomic structure were allowed to relax in order to make sure that each atomic structure had the lowest energy, which indicated that the most stable atomic structures were obtained. After structural optimization, the Protons and Na⁺ ions were set in the system with different distances away from each membrane respectively, and the total relative energy were calculated as a function of the distances. The effects of water molecules can be ignored because we only consider the change of energy barrier when the protons or Na⁺ ions transport across each membrane.



Figure S5. The energy barrier for the transport of protons and Na⁺ ions across oxygen plasma-treated graphene along the perpendicular direction. The dash line indicates the position of the oxygen atoms.



Figure S6. Current-voltage characteristics of graphene membranes treated with (a) oxygen plasma for 5 s and (b) argon plasma for 15 s.



Figure S7. (a) The conductance versus concentration at low bias and at high bias in HCl electrolyte; (b) The normalized I-V plots by the HCl concentration.

Reference

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