Electrical pulse fabrication of graphene nanopores in electrolyte solution

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Nanopores in graphene membranes can potentially offer unprecedented spatial resolution for single molecule sensing, but their fabrication has thus far been difficult, poorly scalable, and prone to contamination. We demonstrate an *in-situ* fabrication method that nucleates and controllably enlarges nanopores in electrolyte solution by applying ultra-short, high-voltage pulses across the graphene membrane. This method can be used to rapidly produce graphene nanopores with subnanometer size accuracy in an apparatus free of nanoscale beams or tips. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921620>]

Graphene membranes are the thinnest possible barrier to ions or molecules, and are mechanically robust enough to withstand fluidic or pressurized environments. Recently, intense interest has been focused on using graphene for nanopore applications, because its extreme thinness confers unique advantages such as superior spatial resolution for nanopore DNA sequencing^{1,2} and low flow resistance for nanofiltration^{3,4} and gas separation.^{5,6} However, the fabrication of single graphene nanopores has thus far only been achieved via transmission electron microscope (TEM) drilling,^{2,7–12} an expensive and challenging process that is highly susceptible to hydrocarbon contamination. Here, we demonstrate an electrical pulse fabrication method that requires only a simple fluidic cell and modest electronics, yet dramatically increases the accuracy and reliability of graphene nanopore production, allowing consistent production of single nanopores down to subnanometer sizes.

Fabrication of single nanopores in silicon nitride (SiN_x) membranes via controlled dielectric breakdown has recently been demonstrated^{13–16} as a viable alternative to other fabrication techniques such as TEM drilling^{17,18} or ion beam sculpting.^{19–21} While it might be expected that exposure to high voltages would similarly induce damage in graphene membranes, it is not immediately obvious that the distinct physical and chemical properties of graphene would allow single pores to be fabricated with any degree of control. In particular, the dielectric breakdown mechanism responsible for pore fabrication in SiN_x depends on the slow accumulation of structural defects throughout the membrane thickness over 10¹–10⁵ s,^{13,16} whereas the removal of any atoms from a graphene membrane immediately creates pores within 10^{–6} s. It is actually quite surprising that single pores can be reliably formed and enlarged in graphene, as the formation of multiple pores or catastrophic failure of the membrane might initially seem more likely. Because experimental studies of nanopores in graphene (as well as other 2D materials such as boron nitride²² and molybdenum disulfide²³) are currently dependent on TEM drilling, which is particularly challenging and contamination-prone for atomically thin

membranes, we anticipate the results shown here to be of considerable practical usefulness and to contribute to the widespread interest in the chemical and physical properties of graphene.^{24,25}

A schematic of the experimental setup is shown in Fig. 1(a). Suspended single layer graphene membranes²⁶ are loaded into a fluidic cell and wet on both sides with 1 M KCl solution. Ag/AgCl electrodes are used to monitor transmembrane current (at 100 mV DC bias) or apply short, 250 ns

FIG. 1. Electrical pulse method. (a) Experimental setup for electrical pulse fabrication of a nanopore in a suspended graphene membrane. The transmembrane current (at 100 mV in 1 M KCl solution) is measured to monitor the pore size. 250 ns, high voltage electrical pulses are applied across the membrane to nucleate or enlarge the pore. (b) Experimental current data from a representative example of pore fabrication resulting in a 2.2 nm pore. Electrical pulses are indicated by vertical bars (including 1 s measurement pauses). Pore nucleation is indicated by a sharp increase in current after a 7 V pulse. The pore is then enlarged with the repeated application of 5 V enlarging pulses until the desired pore size (right-hand vertical axis) is achieved.

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voltage pulses across the membrane that create or enlarge nanopores in the membrane. Such short pulses were used to minimize the amount of membrane material removed during each pulse, which translates into accurate control over nanopore size. The pulse length of 250 ns was selected to be as short as possible while still being long compared to the RC charging time of the device.²⁶ Fig. 1(b) shows a representative experimental example of pore nucleation (creation of a very small nanopore) and progressive enlargement culminating in a 2.2 nm pore. At first, the membrane exhibits very little leakage current ($\ll 1$ nA), indicating that it is defect-free.¹⁰ 7 V nucleation pulses are repeatedly applied until a discernable jump in current is observed, indicating the nucleation of a nanopore. Since it usually takes several pulses before a pore is nucleated, it is unlikely that more than one pore will be created in the first successful nucleation pulse. After pore nucleation, lower voltage enlargement pulses of 5 V are successively applied to controllably increase the pore size. The measured transmembrane current can be converted into a real-time measure of the pore diameter (right-hand vertical axis, Fig. 1(b)) using the analytical approximation^{27,28}

$$D = \frac{G}{2\sigma} \left(1 + \sqrt{1 + \frac{16\sigma T}{\pi G}} \right), \quad (1)$$

where D is the pore diameter (nm), G is the trans-membrane conductance (nS), σ is the solution conductivity (S/m), and $T = 0.6$ nm (Ref. 10) is the effective thickness of the graphene. While 5 V pulses are usually ineffective for nucleating pores, their ability to enlarge pores once they have been nucleated is perhaps due to the increased reactivity at graphene edges,^{29,30} weaker bonding of edge atoms compared to bulk,³¹ or elevated temperatures in the pore due to Ohmic heating.³² The change in diameter for each enlarging pulse is generally independent of the size of the pore before the pulse is applied.²⁶ After the electrical pulsing process, nanopores show approximately linear I-V curves²⁶ with stable conductance. The as-fabricated graphene nanopores display considerable low frequency noise with a $1/f$ -like spectrum,²⁶ the reduction of which remains an important technological challenge. However, the noise levels of electrically fabricated graphene nanopores are not significantly different from those of TEM drilled graphene nanopores in other studies^{2,11,33,34} and seem to be intrinsic to graphene nanopores rather than a consequence of fabrication method.

To determine the accuracy of control over nanopore size, we gathered statistics on the electrical pulse fabrication process for many nanopores. The distributions of changes in nanopore diameter due to successful nucleation and enlarging pulses (ΔD_N and ΔD_E , respectively) calculated from conductance measurements are plotted in Fig. 2(a). These data suggest that pores as small as $\Delta D_N = 0.5 \pm 0.3$ nm (mean $\pm$ S.D.) can be nucleated and enlarged in steps of $\Delta D_E = 0.1 \pm 0.3$ nm. Note that ΔD_E was sometimes negative, which suggests that pulses may sometimes induce rearrangement or addition of atoms at the pore edge, decreasing the size of the pore. When attempting to fabricate a pore of a given size, there is always a small chance that a large ΔD_E can overshoot the target

FIG. 2. Electrical pulse statistics. (a) Histograms of changes in pore diameter due to successful 7 V nucleation (ΔD_N) and 5 V enlargement pulses (ΔD_E). Dotted lines indicate averages, which suggest that pores as small as $\Delta D_N = 0.5 \pm 0.3$ nm (mean $\pm$ S.D.) can be nucleated and enlarged in steps of $\Delta D_E = 0.1 \pm 0.3$ nm. (b) Simulation of pore fabrication generated by randomly choosing values ΔD_N and ΔD_E from the distributions shown in (c) until the target diameter is reached or exceeded. Inset: median error in diameter is 0.2 nm for pores larger than 0.5 nm.

diameter. To understand these statistics, we simulated fabrication pulses by randomly choosing values of ΔD_N and ΔD_E from the distributions shown in Fig. 2(a), applying successive pulses until a target diameter was reached or exceeded (Fig. 2(b)). The simulation shows that pores can be reliably fabricated within 0.2 nm (inset). Given that bond lengths in graphene are about 0.14 nm, these results suggest that enlargement pulses usually remove less than a single ring of atoms from the pore edge, allowing atomic-scale control of nanopore size.

DNA translocation experiments were performed after electrical pulse fabrication to confirm that only a single pore of the appropriate size is created and to demonstrate the suitability of these nanopores for single molecule measurements. To prevent DNA from adhering to the graphene surfaces, the membranes containing a nanopore were first coated on both sides with a self-assembled coating consisting of aminopyrene “foot” molecules that adhere to the graphene surface and tethered polyethylene glycol 4-mer (PEG₄) “brushes” that render the surface hydrophilic and discourage DNA sticking (developed by Schneider *et al.*,⁹ Fig. 3(a)). The coating reduces the conductivity of the pore, which can be approximated by^{9,27,28}

$$G' = \sigma \left[\frac{4T'}{\pi(D')^2} + \frac{1}{D'} \right]^{-1} \\ = \sigma \left[\frac{4(T + 2L)}{\pi(D - 2\Delta R)^2} + \frac{1}{(D - 2\Delta R)} \right]^{-1}, \quad (2)$$

where L is the effective length of the polymer, ΔR is a measure of how much the coating obscures the pore opening, $T = 0.6$ nm is the effective thickness of the graphene,¹⁰ and D is the diameter of the pore before coating given by Eq. (1) (Fig. 3(b)). A least squares fit of Eq. (2) to measured pore conductances (Fig. 3(c)) gives $L = 1.7 \pm 0.5$ nm (mean $\pm$ S.D.) and $\Delta R = 0.1 \pm 0.2$ nm, both physically reasonable values given the length of the PEG₄ brush (1.56 nm)

FIG. 3. Pore coating. (a) Self-assembled hydrophilic coating used to prevent DNA from sticking to graphene membranes (developed by Schneider *et al.*⁹). Two step pore coating chemistry combines aminopyrene “foot” and polyethylene glycol 4-mer (PEG₄) “brush” molecules. (b) Diagram of coated pore, illustrating increased thickness L and reduced diameter ΔR . (c) Measured pore conductances before and after coating, shown with predictions from an analytical model (Eq. (2)) with best fit coating parameters $L = 1.7 \pm 0.5$ nm and $\Delta R = 0.1 \pm 0.2$ nm. Dashed lines show predictions for multiple equally sized pores, confirming that the electrical pulse method consistently produces a single pore.

and the pyrene-graphene spacing (0.35 nm (Ref. 35)). It is worth noting that these conductance measurements can already distinguish a single nanopore from multiple smaller ones, since smaller pores are affected more substantially by the coating. Indeed, generalizations of Eq. (2) to include multiple pores produce predictions inconsistent with the data (Fig. 3(c), dashed lines), indicating that the fabrication method reliably produces a single pore.

After pore coating, 10 kbp double stranded DNA (dsDNA) fragments were injected on the grounded side of the membrane and electrophoretically driven through the pore with a 200 mV DC voltage bias in 3 M KCl.^{2,10} The threading of a DNA molecule as it passes through the pore causes a transient reduction in the current through the pore, known as a translocation event. The magnitude of the current blockage is associated with the cross-sectional diameter of dsDNA (~ 2.3 nm), whereas the duration depends on the length of the DNA fragment ($\sim 6 \mu\text{m}$). A scatter plot of more than 200 translocation events through a representative nanopore (Fig. 4(a)) shows that most of the events have similar current blockages and durations corresponding to the monodisperse sample of injected DNA fragments. The tail in the

FIG. 4. DNA translocations. (a) Scatter plot of current blockages and translocation durations for dsDNA translocations through an 8.0 nm coated graphene nanopore (10 kbp fragments, 3 M KCl, 200 mV bias, $n = 202$). (b) DNA translocation blockages as a function of open pore current for eight pores of different diameters. Calculated pore diameters are shown on the upper horizontal axis. Individual translocation events are plotted as small dots; large markers indicate pore averages, with error bars indicating the median 50% of events. The solid line indicates computational predictions from a finite element model of a pore threaded by dsDNA.²⁶ This is not a fit to the data, as all free parameters have already been determined from Fig. 3(c). Agreement between data and model confirms that calculated pore diameters are accurate.

distribution of translocation durations suggests that dsDNA sometimes temporarily sticks to the pore or membrane despite the polymer coating.

To confirm that the nanopores match the sizes computed from their conductances, we performed DNA translocation experiments with several pores of different diameters and compared the current blockages to computational predictions from a finite element model of appropriately sized pores²⁶ (Fig. 4(b)). For such thin nanopores, the current blockage is quite sensitive to the diameter of the pore, allowing this measurement to serve as a consistency check on the nanopore diameters. It is important to note that the predicted curve in Fig. 4(b) is not a fit, as all model parameters have been determined via Eq. (2). Although the model is only a simple approximation of the physical system, the data lie close to the predicted curve, verifying that the model accurately encapsulates the geometry of the fabricated pores. The slight deviations from the model predictions may be due to interactions between the DNA and the PEG brushes or other complications not included in the model. TEM imaging was also

attempted to directly verify the pore sizes,²⁶ but turned out not to be a precise measure of pore size due to hydrocarbon contamination and/or damage from the electron beam.

Determining the mechanisms responsible for electrical pulse nanopore formation and enlargement is a difficult problem. Redox reactions between graphene and water are likely responsible for removing carbon atoms from the lattice,³⁶ but in this context, oxidation and reduction half-reactions could act from opposite sides of the membrane, supporting an electrochemical current. Since the membrane is atomically thin, it is even possible that the half-reactions are coupled through the graphene and occur simultaneously. The fact that the method produces predominantly single nanopores suggests that the process is initiated via a fluctuation that randomly selects a site for a nanopore nucleation and then is limited to that site during enlargement. Given the extremely small amount of material being removed from the membrane (<100 atoms per pulse), it is unlikely that direct studies of reaction products will be feasible to study the mechanisms of nanopore formation. In this work, we have already exploited the acute sensitivity of transmembrane current measurements to the removal of such small numbers of atoms from the membrane. Perhaps careful electrical measurements during the pulsing process could provide additional information. Nevertheless, a full mechanistic understanding of electrical pulse fabrication probably must await further fundamental research on graphene chemistry under high electric fields.

We have shown that graphene nanopores can be readily fabricated with subnanometer accuracy in electrolyte solution using electrical pulses. Analysis of data from pore coating and DNA translocation experiments indicates that single pores are preferentially formed and are well-suited for DNA sequencing devices or single-molecule biophysics experiments. By dramatically increasing the accuracy, reliability, and ease of graphene nanopore production, this electrical pulse method will help unlock the technological and scientific potential of graphene nanopores.

100 nm circular apertures were milled in 300 nm thick SiN membranes using a FIB (FEI/Micron Vectra 980, 50 kV Ga⁺). Single layer graphene was grown on 25 μ m Cu foil (Alpha Aesar) at 1000 °C under 10 sccm H₂ and 4 sccm CH₄ (40 min) and transferred onto the SiN apertures using standard wet transfer techniques³⁷ (using Methyl methacrylate (MMA) as the transfer polymer and 1 M FeCl₃ as the copper etchant). MMA transfer polymer was removed using acetone, then samples were washed in ethanol and critical point dried. Samples were annealed at 250 °C under 400 sccm Ar and 200 sccm H₂ for at least 2 h prior to experiments to remove surface contamination. After annealing, typical samples exhibit characteristic stripes of surface contamination, but reliably showed >50% atomically clean area in TEM images.²⁶ Samples imaged in TEM were not used for fluidic cell experiments. Possible failure modes for sample preparation include improperly sized SiN apertures, surface contamination on graphene membranes, and ripped or damaged graphene membranes. Including these failure modes, the yield of successful samples for electrical pulsing was about 50%.

Graphene membranes were loaded into custom Polyether Ether Ketone (PEEK) fluidic cells that allow wetting and

electrical contact via Ag/AgCl electrodes to both sides of the graphene membrane. Polydimethylsiloxane (PDMS) gaskets were used to create a fluid tight seal. The fluidic cells were submerged in deionized water and ultrapure CO₂ gas (99.999%) was flowed through both sides for 5 min to replace any air contacting the graphene membrane with CO₂. Degassed 1 M KCl solution (10 mM Tris buffer, 1 mM EDTA, titrated with KOH to pH 10) was then flowed through both sides of the cell with syringes (still underwater so that no air is introduced). The cell was then removed from the water, dried off with an N₂ gun, and connected to a current amplifier (Axopatch 200B). Any residual CO₂ bubbles on the graphene surface are removed by hydroxyl ions in solution (CO₂ + 2OH⁻ → CO₃²⁻ + H₂O), allowing the graphene to wet completely. Nominally defect-free graphene membranes display a very small leakage conductance (0.1–1 nS) that is not well understood, but is negligible compared to pore conductance for pores larger than 1 nm (>6 nS). Experiments were performed in 1 M (11.2 S/m at 25 °C) or 3 M KCl (24.5 S/m at 25 °C) at pH 10.

A patch clamp amplifier (Axopatch 200B) was used to monitor transmembrane conductance at 100 mV and a pulse generator (HP8110A) was used to apply 250 ns long voltage pulses across the membrane. In order to protect the amplifier from large input voltages, a mechanical relay was used to disconnect the amplifier before pulses were applied and reconnect it 1 s after each pulse. Pulse triggering was performed via an Arduino Uno board with manual pushbutton control. Samples were fabricated using a 7 V/5 V protocol, in which 7 V pulses were applied repeatedly until nucleation and 5 V used thereafter for enlarging (Fig. 1(b)). The voltages were selected empirically as approximately the lowest voltage to reliably nucleate pores (7 V) and the lowest voltage to reliably enlarge nucleated pores (5 V).

After pore nucleation and enlargement, the fluidic cell was flushed with deionized water, followed by methanol. The cell was then filled with 1-aminopyrene (10 mg/ml in methanol) on both sides for 10 min to allow full binding of the aminopyrene to the graphene. After flushing again with methanol, the cell was filled with Methyl-PEG₄-NHS-Ester (Pierce Biotech, 10 mg/ml in methanol) on both sides to react with the amine groups on the aminopyrene coating. After 10 min, the cell was flushed with methanol, water, and then 1 M KCl at pH 10. The coated nanopores show a lower conductance due to the increased thickness and reduced diameter of the membrane. Coated nanopores usually exhibited stable conductance for at least several days. The fit in Fig. 3(c) was obtained using a least squares minimization with the model function given in Eq. (2), with the graphene thickness taken to be 0.6 nm.¹⁰ The confidence intervals were obtained using a Monte Carlo bootstrap method.³⁸

Translocation experiments were performed in 3 M KCl at pH 10 on PEG₄ coated nanopores to prevent DNA from sticking the graphene membrane and clogging the pore.^{2,9,10} 10 kbp fragments of dsDNA (~25 ng/ μ l) were injected in the grounded side of the fluidic cell (Fig. 1(a)) and 200 mV was applied to electrophoretically drive the DNA through the pore. Current measurements were taken at 500 kHz sampling rate with a 20 kHz hardware low-pass filter. Translocation events were identified using a custom script interfacing with

the PoreView software engine (<https://github.com/tszalay/PoreView>). The script applied a 50 Hz–10 kHz bandpass filter to center the baseline current at zero and identified candidate events via a current threshold (−1 to −1.5 nA, depending on noise level). The script then examined candidates in the original (unfiltered) data to more accurately determine the event durations and current blockages (defined as the integral of the current divided by the duration of the event). Finally, events were manually screened to reject obviously spurious noise artifacts.

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