



## Supporting Information

for *Small*, DOI: 10.1002/sml.201502134

**Cross-Talk Between Ionic and Nanoribbon Current Signals in Graphene Nanoribbon-Nanopore Sensors for Single-Molecule Detection**

*Matthew Puster, Adrian Balan, Julio A. Rodríguez-Manzo, Gopinath Danda, Jae-Hyuk Ahn, William Parkin, and Marija Drndić\**

# Graphene Nanoribbon-Nanopore Sensors for Single Molecule Detection

Matthew Puster,<sup>1,2</sup> Adrian Balan,<sup>1</sup> Julio A. Rodríguez-Manzo,<sup>1</sup> Gopinath Danda,<sup>1,3</sup>

Jae-Hyuk Ahn,<sup>1</sup> William Parkin,<sup>1</sup> and Marija Drndić<sup>1</sup>

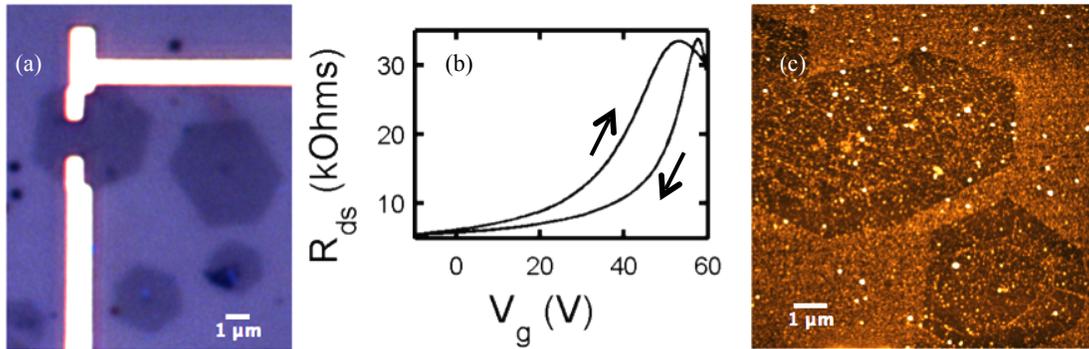
*<sup>1</sup>Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA.*

*<sup>2</sup>Department of Material Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA.*

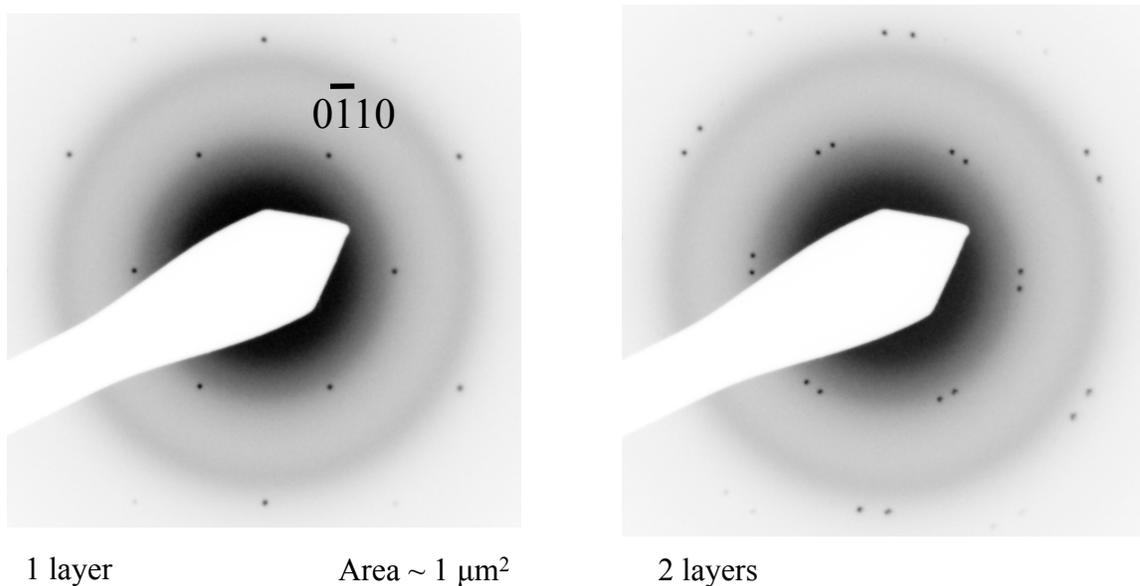
*<sup>3</sup>Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA.*

## **Table of Contents:**

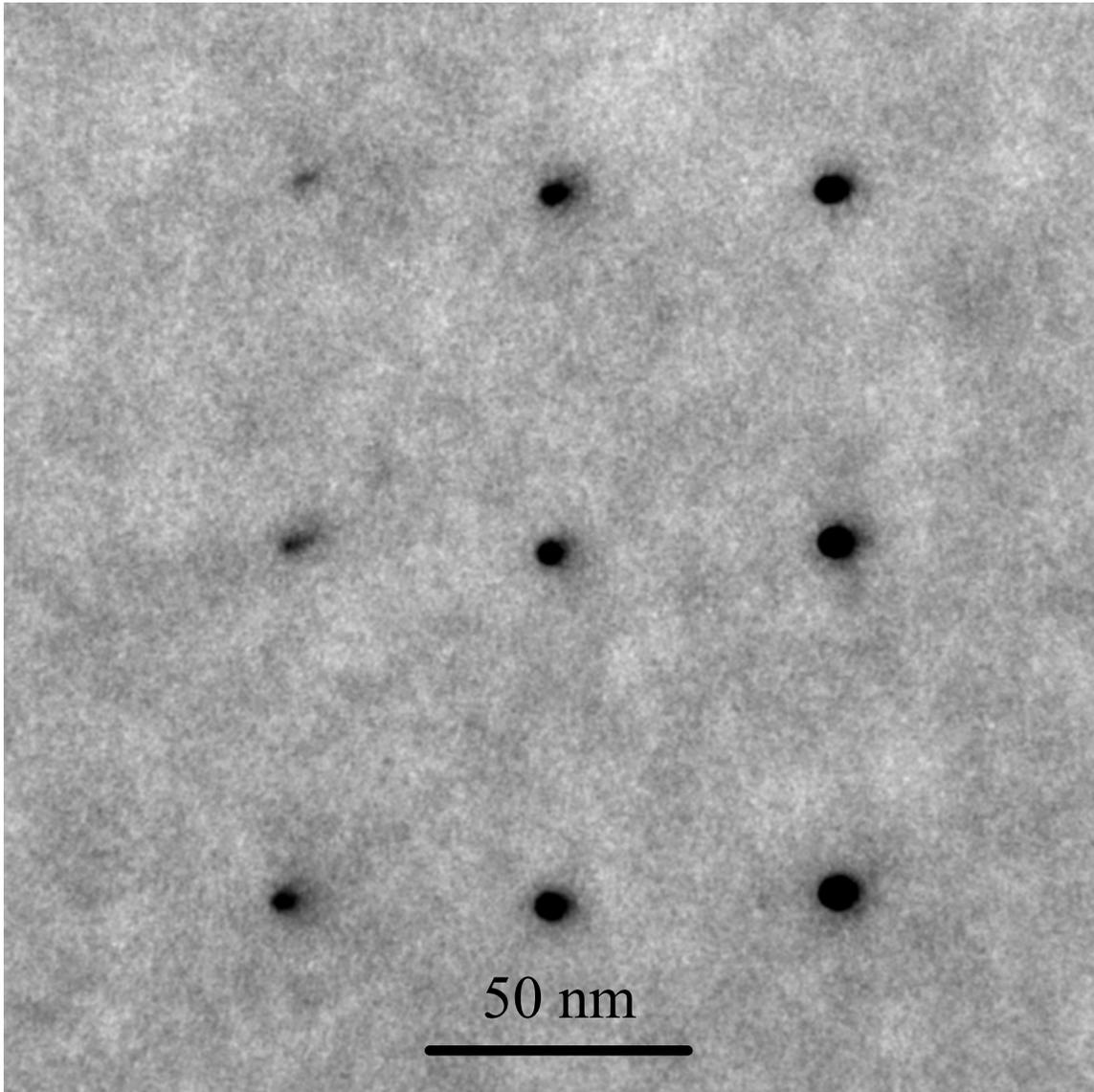
- Figure S1.** Devices made from CVD grown, single-crystal graphene hexagons
- Figure S2.** Electron diffraction of GNR-nanopore devices
- Figure S3.** Calibration and control of nanopore size in STEM mode
- Figure S4.** EELS signal to monitor material composition at nanopore
- Figure S5.** DNA translocation data from a nanopore next to a gold electrode
- Figure S6.** Comparison of analytic and COMSOL potential field calculations for GNR-nanopore device



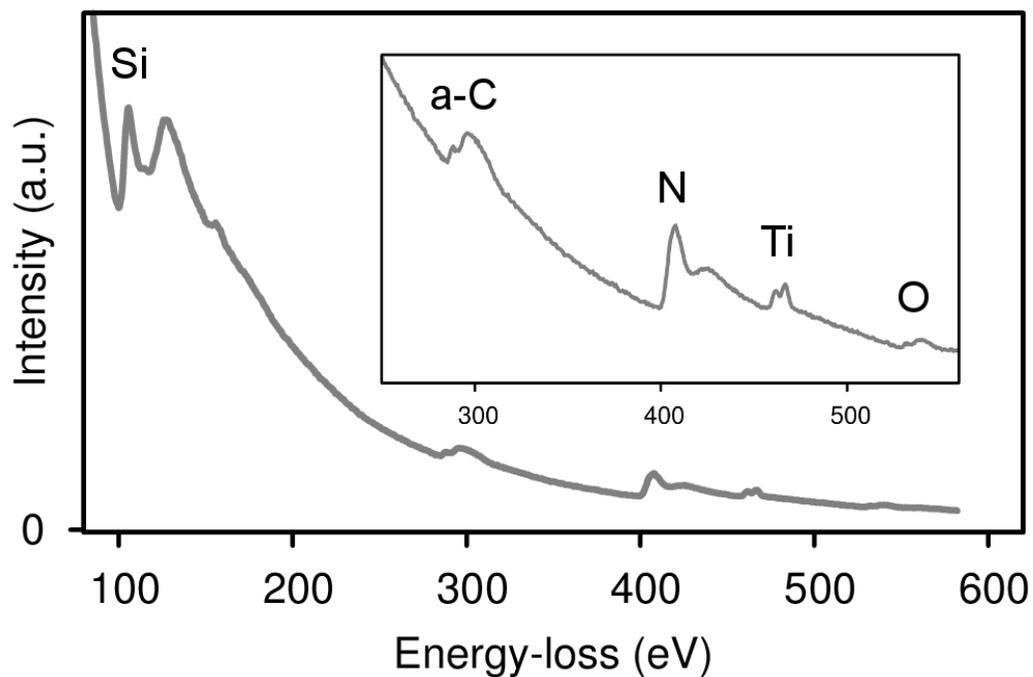
**Figure S1. Devices made from CVD grown, single-crystal graphene hexagons.** (a) CVD grown graphene hexagon device with two Au leads on 90nm SiO<sub>2</sub> (4" N/Ph <100> 1-10 Ωcm Si wafer) is shown. (b) Gate voltage was applied to the Si substrate of the device shown and the resistance of the flake was monitored. A hysteresis loop was obtained with a peak resistance value of  $R_{ds} \sim 33 \text{ k}\Omega$  at  $V_g = 50\text{-}55 \text{ V}$ . (c) AFM image of a graphene hexagon transferred onto a SiO<sub>2</sub> substrate is shown.



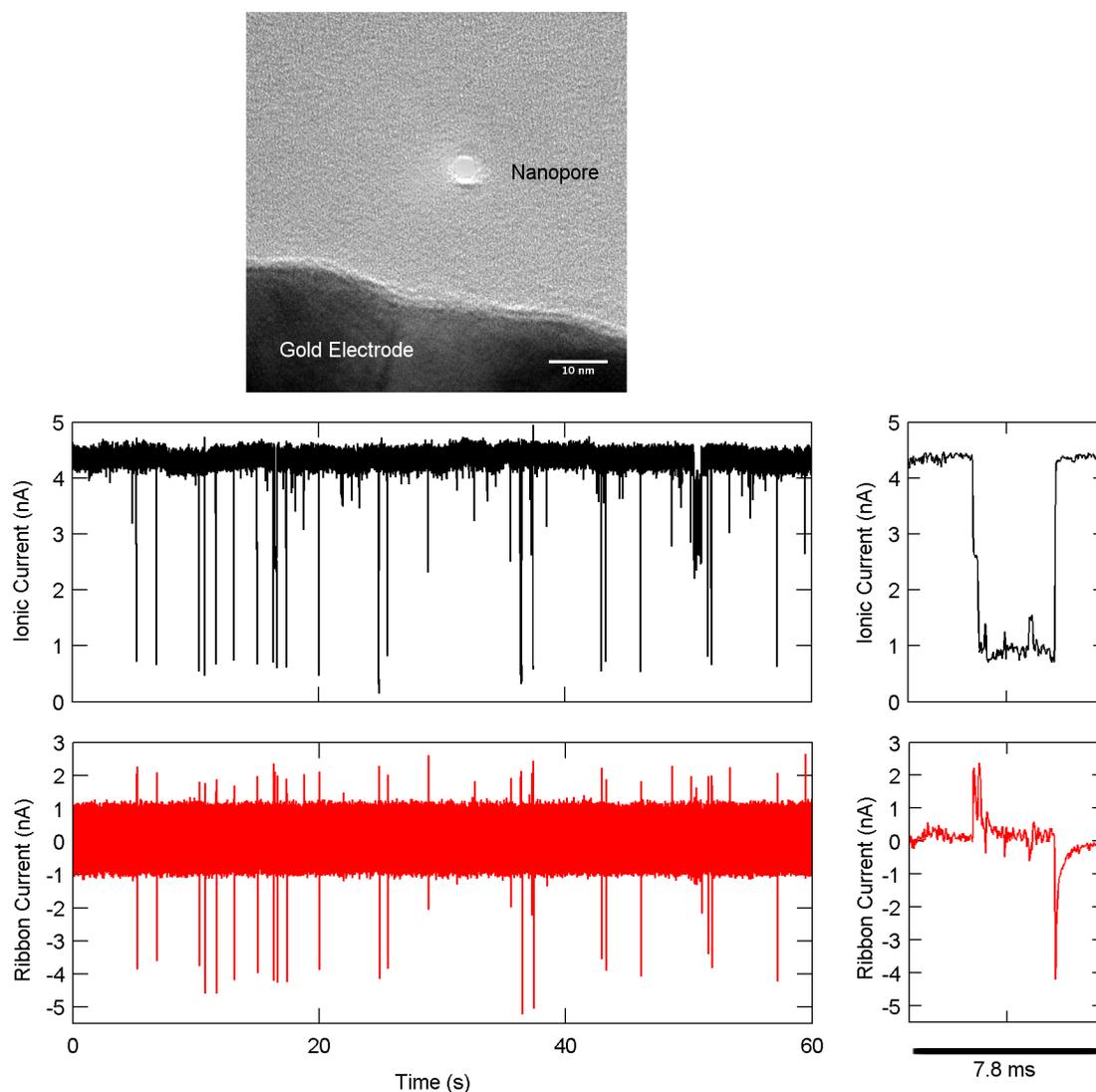
**Figure S2. Electron diffraction of GNR-nanopore devices.** Electron diffraction of graphene deposited on  $\text{SiN}_x$  membranes can be used as an aid to confirm the number of graphene layers and to characterize the crystal orientation of the GNR with respect to the electrodes. The left and right images correspond to electron diffraction patterns taken from approximately  $1 \mu\text{m}^2$  areas of one and two layers of graphene, respectively, on top of a  $\text{SiN}_x$  membrane.



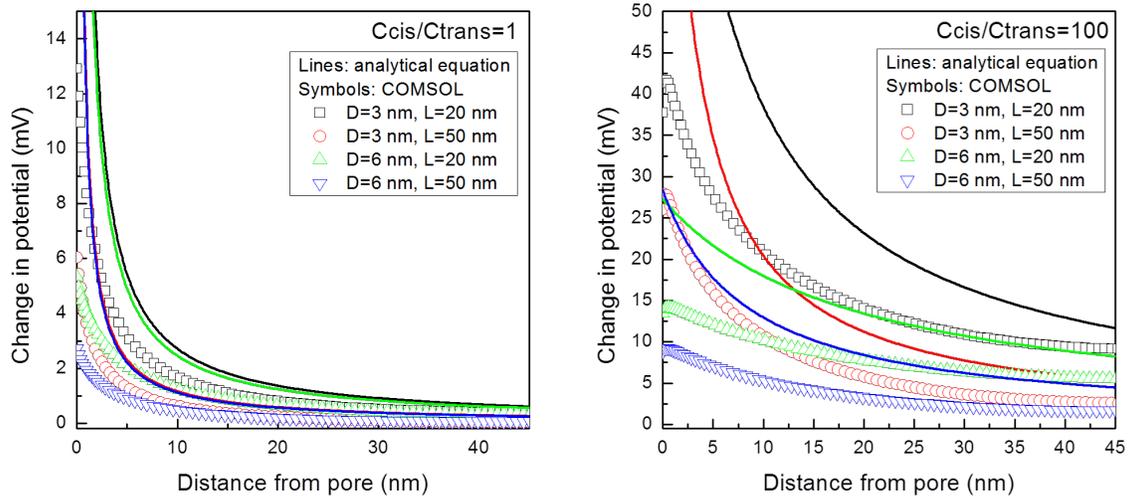
**Figure S3. Calibration and control of nanopore size in STEM mode.** In STEM mode the electron probe size, convergence angle and current density can be modified in order to produce solid-state nanopores with different sizes. Here we show a nine-point array made in a  $\text{Si}_3\text{N}_4$  membrane by varying the electron dose delivered with the same electron probe conditions. In this way, the size of nanopores made in solid-state membranes can be controlled and calibrated.



**Figure S4. EELS signal to monitor material composition at nanopore.** The EELS signal can be used not only to monitor the progress of the nanopore drilling as Figure 1f of the main manuscript shows but also to characterize the chemistry of the membrane surrounding the nanopore. The EELS spectrum shows ionization edges of Si, C, N, Ti and O. This corresponds to a  $\text{Si}_3\text{N}_4$  membrane with a passivation layer of  $\text{TiO}_2$ . The C edge does not correspond to graphene, but to electron-probe-induced amorphous C deposition, indicative of an unclean sample that is not optimal for nanopore drilling.



**Figure S5. DNA translocation data from a nanopore next to a gold electrode.** Top: TEM image of the nanopore next to the gold electrode. The spacing between the nanopore and the gold electrode is 20 nm. The nanopore diameter is 2.8 nm. The ionic current trace is in black, with a representative single translocation event shown on the right. The corresponding GNR current time trace is in red, below the ionic data. The salt concentration was 1 M KCl.  $V_{\text{ionic}} = 1$  V and  $V_{\text{ds}} = 0$  V.



**Figure S6. Comparison of analytic and numerical (COMSOL) potential field calculations for GNR-nanopore device.** Analytical calculations based on Xie, *et.al* and COMSOL Multiphysics simulation based on Poisson's equation and Nernst-Planck equation were used to estimate the potential field change near a nanopore when DNA translocates through it, measured along the topside of the membrane from the edge of nanopore. The  $C_{cis}/C_{trans}$  was varied and the effect of the potential drop as a function of distance and nanopore dimensions was calculated. The two models differ in the magnitude of potential change, which is more pronounced for  $C_{cis}/C_{trans} = 100$ . However, the trends of exponential drop in potential with distance from the nanopore edge, the increase in change in potential for higher  $C_{cis}/C_{trans}$  and smaller nanopore diameters, and larger decay length of the potential drop for smaller and thinner pores are the same in both the models. The difference in the results arises likely from the different assumptions made in each model. For the analytical calculations, no surface charge of the nanopore was considered, while for the COMSOL simulation a nanopore surface charge density of  $-20 \text{ mC/m}^2$  was assumed. All calculations were performed for an ionic voltage of 1 V.