ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Revealing the Direct Effect of Individual Intercalations on DNA Conductance toward Single-Molecule Electrical Biodetection

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Supporting Information

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1. Materials

The oligonucleotides were synthesized by Takara Biotechnology Co., Ltd. (Dalian, China) and used as received. The oligonucleotide sequences were as follows:

H_2N-$(CH_2)_3$-Pi-5′-TGTCGTCTTACACCATTGAG-3′-Pi-$(CH_2)_3$-NH_2

5′-ACAGCAGAATGTGGTAACTC-3′

The first DNA sequence is a single-stranded 20-mer with NH_2 on both 3′ and 5′ termini. The second DNA sequence is a 20-mer oligonucleotide that is complementary to the first sequence. N-Hydroxysulfosuccinimide sodium salt (Sulfo-NHS) and N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) were purchased from Sigma-Aldrich, Inc. (Beijing, China). Ultrapure water with an electrical resistivity larger than 18.2 MΩ cm was used.

2. Device Fabrication

Device Fabrication: The cut graphene devices were fabricated by a dash-line lithographic (DLL) method, described in detail elsewhere.[1] In brief, after the initial electrical characterization of the pristine graphene devices, a polymethylmethacrylate (PMMA) layer (950, A2) was spincast (4000 RPM, 45 s) on the surface and then baked at 170 °C for 2 min. We applied a DesignCAD file with a 5-nm-wide dash line at the specific position using e-beam lithography to obtain the window precursor. The graphenes were then cut locally through the open window by oxygen plasma ion etching. The devices were then soaked in acetone solution overnight and dried with a stream of nitrogen gas. Finally, these devices were treated by Triton X–100 (1%, V/V) by immersion in the solution overnight, to produce a blocking layer that prevents nonspecific absorption.

DNA connection: dsDNA was grafted into the gaps using a previously published strategy.[2] Briefly, the freshly cut single-layer graphene (SLG) devices were immersed in a 50-mM 2-(N-morpholino)ethanesulfonic acid (MES) buffer solution (pH = 4.7) containing 5 mM activating agents (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI)) and 10 mM amide coupling agent Sulfo- N-Hydroxysuccinimide (Sulfo-NHS) overnight. The devices were then removed from the solution, washed with fresh buffer solution, and dried with a stream of nitrogen gas. The activated SLG devices termini were then reacted with amine-modified DNAs (10 μM) dissolved in phosphate-buffered saline solution (pH = 7.2) to covalently bridge the gap. After 24 h, the devices were taken out of the solution, washed with H_2O, and then dried with a stream of nitrogen gas.

EB and SG treatments: Ethidium bromide (EB) was dissolved in H_2O to prepare solutions with different concentrations, ranging from 1.0×10^{-4} mol/L to 5.0×10^{-13} mol/L. SYBR Green I (SG) was dissolved in H_2O to prepare solutions with different concentrations, ranging from 2.0×10^{-12} mol/L to 1.96×10^{-14} mol/L. For EB or SG intercalating experiments, the newly rejoined devices were immersed in EB or SG solutions. After incubation for 30 min, the devices were removed from the solution, washed with H_2O, and dried with a stream of nitrogen gas for device characterization. All device characterizations were performed using a Karl Suss probe station equipped with the semiconducting parameter analyzer (Agilent 4155C), under room temperature ambient conditions with a constant moisture content (30%).

3. Control Experiments

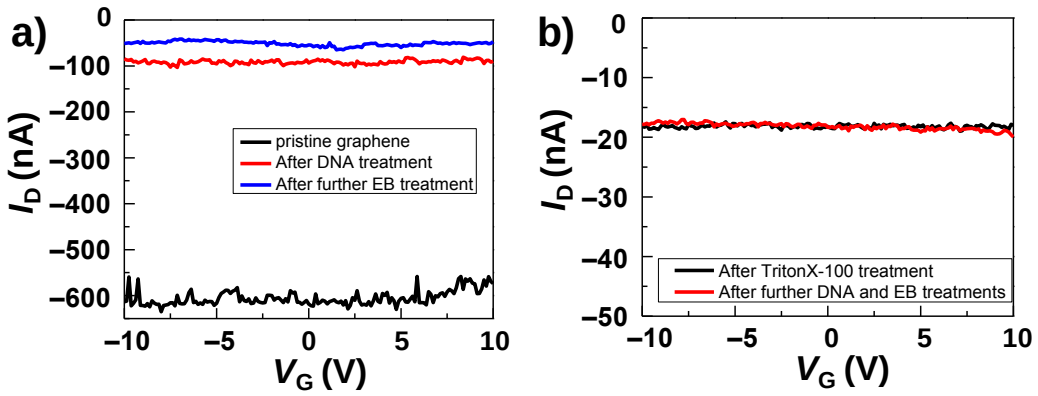

Figure S1. (a) *I*–*V* curves of a pristine graphene device at different stages: black for pristine graphene; red for DNA treatments (10 μM); blue for further EB treatments (1×10^{-4} mol/L). (b) *I*–*V* curves of another pristine graphene device after Triton X-100 treatment and after further DNA (10 μM) and EB (1×10^{-4} mol/L) treatments. All measurements were performed at V_D= –50 mV.

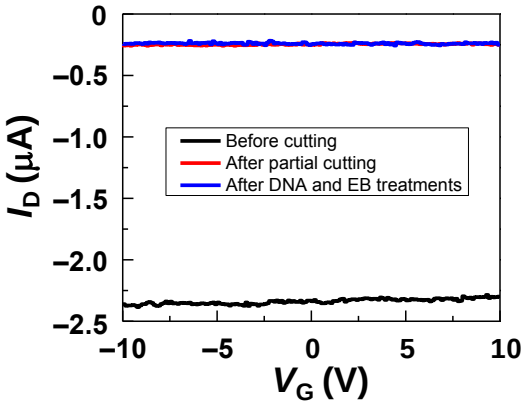

Figure S2. Control experiments using partially cut graphene devices at different stages: black, before cutting; red, after cutting; blue, after further DNA (10 μM) and EB (1×10^{-4} mol/L) treatments. All measurements were performed at V_D= –50 mV.

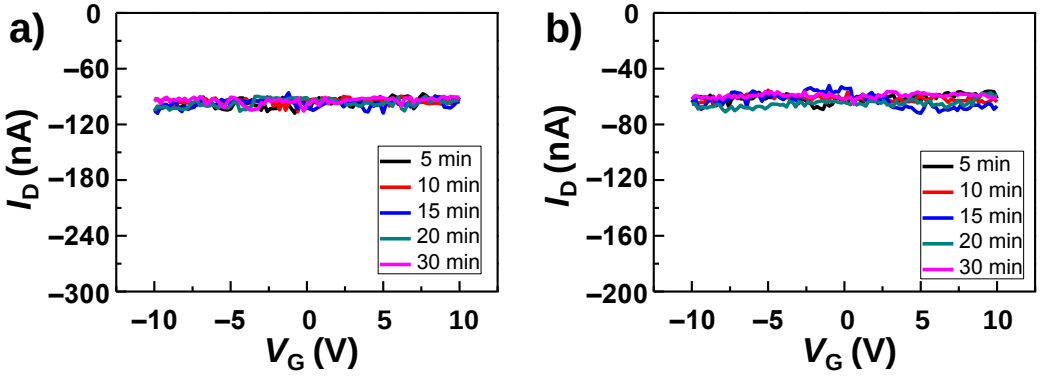

Figure S3. Conductance stabilities of the working devices reconnected by DNAs in an ambient environment (a) and after further water treatments (b). All measurements were performed at V_D= –50 mV.

References:

(1) Y. Cao, S. Dong, S. Liu, L. He, L. Gan, X. Yu, M. L. Steigerwald, X. Wu, Z. Liu and X. Guo, *Angew. Chem. Int. Ed.*, 2012, **51**, 12228.

(2) X. Guo, A. A. Gorodetsky, J. Hone, J. K. Barton and C. Nuckolls, *Nat. Nanotechnol.*, 2008, **3**, 163.