Supporting Information

Graphene Nanoribbon Dielectric Passivation Layers for Graphene Electronics

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1. General

All materials including dry solvents were obtained from commercial suppliers and used without further purification. All reactions were performed with dry solvents under an atmosphere of nitrogen in oven-dried glassware using standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in the air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by a UV lamp (254 nm). Open column chromatography was performed with KANTO Silica Gel 60N (spherical, neutral, 40-100 μm). The metal scavenger was from Biotage Metal Scavenger Si-TMT. The developed chromatogram was analyzed under a UV lamp (254 nm and 365 nm). Preparative recycling gel permeation chromatography (GPC) was performed with an LC-9210II NEXT instrument (Japan Analytical Industry Ltd., Nishitama, Tokyo, Japan), equipped with an in-line JAIGEL-3H and 5H columns using CHCl3 as an eluent at a flow rate of 3.5 mL min⁻¹, UV, and RI detectors. The molecular weight and the distribution of the synthesized polymers were measured by size-exclusion chromatography (SEC) on a Shimadzu Prominence 2000 instrument equipped with two in-line linear polystyrene gel columns (TOSOH TSKgel Multipore HXL-M SEC columns 7.8 mm × 300 mm) at 40 °C. Tetrahydrofuran (THF), containing 0.1 wt% tetra-n-butylammonium bromide (TBAB), was used as the eluent at the flow rate of 1.0 mL min⁻¹. The molecular weight calibration curve was obtained with polystyrene standards (TOSOH TSKgel polystyrene standard). The absorption and fluorescence spectra were obtained in a 1 cm quartz cell at 25 °C using a JASCO V570 spectrophotometer and JASCO FP-6600. Fourier-transform infrared (FT-IR) spectra were recorded using a JASCO FT/IR-6100 spectrometer in attenuated total reflection (ATR) mode. The atomic force microscopy (AFM) measurements were performed using a Dimension FastScan (Bruker, Billerica, MA, USA) at room temperature and under atmospheric conditions with a silicon tip on silicon nitride cantilevers (FastScan-C, Bruker, Billerica, MA, USA) in tapping mode. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 (fast atom bombardment mass spectrometry, FAB-MS) with 3-nitrobenzyl alcohol (NBA) as a matrix. Nuclear magnetic resonance (NMR) spectra
were recorded on JEOL ECS-400 (1H 400 MHz, 13C 100 MHz), or JEOL ECS-600 (1H 600 MHz, 13C 150 MHz) spectrometer. Chemical shifts for 1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or C2D2Cl4 (δ 6.00 ppm). Chemical shifts for 13C NMR are expressed in ppm relative to CDCl3 (δ 77.0 ppm) or C2D2Cl4 (δ 73.78 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constant (Hz), and integration.

2. Synthesis of silicon-bridged phenanthrene 1

3-Chloro-3-ethylundecane was synthesized using a modified method reported in the previous study.51

A 200-mL two-necked round-bottom flask, containing a magnetic stirring bar with Mg turnings, was added (5.8 g, 240 mmol), and the reaction vessel was heated by a heat gun with stirring for 10 min under reduced pressure. After cooling the flask to room temperature, n-octyl bromide (37.1 mL, 225 mmol) and THF (100 mL) were added. To this reaction mixture, 1,2-dibromoethane (2 drops, for activation of Mg turning) was added and the reaction mixture was stirred at 40 °C for 1 h to prepare the corresponding Grignard reagent. Another 300-mL two-necked round-bottom flask, containing a magnetic stirring bar, was added to 3-pentanone (S1) (16.0 mL, 150 mmol) and THF (100 mL). To this ketone solution, the prepared Grignard reagent was added dropwise at 0 °C with vigorous stirring. Then, the reaction mixture was stirred at 40 °C for overnight. After checking the progress of the reaction by TLC, the reaction mixture was quenched with water. The organic layer was washed with saturated NH4Cl aq. and water dried over Na2SO4, filtered and concentrated under reduced pressure to give crude 3-ethyl-3-hydroxylundecane (S2). A 200-mL round-bottom flask, containing a magnetic stirring bar and the crude S2 concentrated HCl (35 mL), was added. The reaction mixture was stirred at a room temperature for 1 h before being extracted into Et2O (100 mL × 3). The combined organic layers were washed with brine and then dried over Na2SO4. After filtration, the solvents were removed under reduced
pressure. Purification by flash column chromatography on silica gel (eluent: hexane) afforded 3-chloro-3-ethylundecane (S3) (17.0 g, 76%).

A 100 mL two-necked round-bottom flask, containing a magnetic stirring bar, was added fluorene S4 (3.01 g, 18.1 mmol) and 3-chloro-3-ethylundecane S3 (9.58 g, 45.0 mmol) in CS₂ (50 mL) under an N₂ atmosphere. Then, FeCl₃ (5.86 g, 36.0 mmol) was added at room temperature. After stirring at room temperature overnight, the reaction was quenched with MeOH. The organic layer was washed with water, dried over Na₂SO₄, filtered and concentrated under the reduced pressure to give the crude product. Purification by open column chromatography on silica gel (eluent: hexane) afforded 2,7-di(3-ethyl-3-undecyl) fluorene S5 as a colorless oil (4.81 g, 50%).

A 50 mL two-necked round-bottom flask, containing a magnetic stirring bar 2,7-di(3-ethyl-3-undecyl) fluorene S5 (2.00 g, 3.77 mmol) and THF (20 mL), was added under an N₂ atmosphere. Then, n-BuLi in hexane (1.6 M, 2.35 mL, 3.77 mmol) was added dropwise at 0 °C. After stirring at 0 °C for 5 min, p-formaldehyde (0.12 g, 4.14 mmol) was added at this temperature. The reaction mixture was stirred at room temperature for 20 min before being quenched with water. The reaction mixture was extracted with Et₂O. The combined organic layers were washed with brine, and then dried over Na₂SO₄. After filtration, the solvents were removed under a reduced pressure to yield carbinol S6 as colorless oil. The crude product was directly used in the next step.
A 100 mL round-bottom flask, containing a magnetic stirring bar obtained from carbinol S6 and toluene (40 mL), was added under air. Then P2O5 (5.35 g, 37.7 mmol) was added at room temperature. After stirring at 100 °C for 1 h, the mixture was cooled at room temperature and the reaction was quenched with a saturated NH4Cl aqueous solution. The mixture was extracted with Et2O. The combined organic layers were washed with brine and then dried over Na2SO4. After filtration, the solvents were removed under reduced pressure to give the crude product. Purification by flash column chromatography on silica gel (eluent: hexane) afforded 2,7-bis(3-ethylundecan-3-yl) phenanthrene S7 as colorless oil. (0.98 g, 47%).

A 5 ml Schlenck-tube, containing a magnetic stirring bar 2,7-bis(3-ethylundecan-3-yl) phenanthrene S7 (0.11 g, 0.20 mmol) and TMEDA (119 mml, 0.8 mmol), were added under a N2 atmosphere. Then, n-BuLi (1.6 M, 228 mL, 0.8 mmol) was added dropwise at 0 °C. After stirring at 60 °C for 3 h, distilled dichlorodimethylsilane (72 mml, 0.4 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature for 24 h before being quenched with water. The reaction mixture was extracted with Et2O. The combined organic layers were washed with brine and then dried over Na2SO4. After filtration, the solvents were removed under reduced pressure to give the crude product. Purification by open column chromatography on silica gel (eluent: hexane) afforded monomer 1 as a colorless oil (42 mg, 35%).

2,6-Bis(3-ethylundecan-3-yl)-4,4-dimethyl-4H-phenanthro[4,5-b,c,d]silole (1)

1H-NMR (400 MHz, CDCl3) δ 7.90 (s, 2H), 7.82 (s, 2H), 7.69 (s, 2H), 1.81–1.89 (m, 8H), 1.37–1.47 (m, 22H), 1.20-1.36 (m, 18H), 0.86–0.90 (m, 6H), 0.55 (s, 6H).

13C-NMR (150 MHz, CDCl3) δ 149.6, 145.2, 138.6, 129.2, 128.3, 127.2, 120.1, 34.7, 31.9, 31.5, 29.71(2C), 29.68(3C), 29.3, 22.6, 14.1, −2.91.

HRMS (FAB⁺) m/z calcd for C42H67Si⁺ [M+H]⁺: 599.5006, found 599.5004.
Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) of 1.

Figure S2. $^{13}$C NMR (150 MHz, CDCl$_3$) of 1.
3. Synthesis of cove-type GNR 2 by APEX reaction of 1

A 5 mL Schlenck-tube containing a magnetic stirring bar 2,6-bis(3-ethylundecan-3-yl)-4,4-dimethyl-4H-phenanthro[4,5-b,c,d]silole 1 (100 mg, 167 µmol), AgSbF$_6$ (114 mg, 333 µmol), Pd(OOCF$_3$)$_2$ (55.1 mg, 167 µmol), and o-chloranil (81.2 mg, 333 µmol) in 1,2-dichloroethane (0.50 mL) were added under N$_2$ atmosphere. After stirring the mixture at 80 °C for 12 h, the reaction mixture was cooled down to room temperature, passed through a short pad of silica gel and then treated with the metal scavenger before washing with CH$_2$Cl$_2$. The solvent was removed under reduced pressure to give the crude product. The SEC analysis of the crude mixture showed the multimodal peaks around retention time (rt) = 10–25 min (Figure S3). The main peaks ($M_p = 1.5 \times 10^5$, $5.4 \times 10^4$, and $3.2 \times 10^4$) related to the GNRs were found between 11 min and 17 min. The separation at the larger molecular weight region (rt = 11–13 min) by SEC afforded the cove-type GNR 2 as a black powder with a relatively narrow polydispersity (35.0 mg, 35% yield, $M_n = 1.55 \times 10^5$, PDI ($M_w/M_n$) = 1.24, Figure S4).

**Figure S3.** SEC chart of the crude cove-type GNR 2. $M_p$ was determined by SEC analysis equipped with a polystyrene column eluted with THF containing 0.1 wt% of tetra-n-butylammonium bromide at a flow rate of 1.0 mL/min o at 40 °C, polystyrene standards were used for the calibration of the molecular weights.
Figure S4. SEC chart of purified cove-type GNR 2 with $M_n = 1.55 \times 10^5$, and PDI ($M_w/M_n$) = 1.24. $M_n$, PDI were determined by SEC analysis equipped with a polystyrene column eluted with THF, containing 0.1wt% of tetra-n-butylammonium bromide at a flow rate of 1.0 mL/min at 40 °C, polystyrene standards were used for the calibration of the molecular weights.

4. Characterization of cove-type GNR 2

Figure S5. IR spectra of cove-type GNR 2 with $M_n = 1.55 \times 10^5$, PDI = 1.24 (red) and the simulated tetramer S8 (blue) by DFT at the B3LYP/6-31G(d) level of theory.
Figure S6. $^1$H NMR (600 MHz, $\text{Cl}_2\text{CDCl}_2$, $120^\circ\text{C}$) of cove-type GNR 2 with $M_n = 1.55 \times 10^5$ and PDI $= 1.24$. 
Figure S7. $^{13}$C NMR (150 MHz, Cl$_2$C=DC=Cl$_2$, 120 °C) of cove-type GNR 2 with $M_n = 1.55 \times 10^5$ and PDI = 1.24.
5. DFT-calculations of tetramer S8 as a model compound for GNR 2

The Gaussian 09 program running on an SGI Altix4700 system was used for optimization (B3LYP/6-31G(d)). Structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. The harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Visualization of the results was performed by using GaussView 5.0 software.

**Table S1.** Uncorrected and thermal-corrected (298 K) energies of the stationary points (Hartree).

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$E$: electronic energy; $ZPE$: zero-point energy; $H = E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$: sum of electronic and thermal enthalpies; $G = H - TS$: sum of electronic and thermal free energies.

**Table S2.** Cartesian coordinates of S8.

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6. Interaction between GNRs and graphene

We found that the nanostructure of GNR 2 (hereafter, simply referred to as GNR) when adsorbed on graphene (GNRs/Gr) was highly dependent on the deposition temperature. AFM images of the GNRs/Gr formed at 60, 45, and 30 °C are shown in Figure S8. Trigonal patterns were found on graphene when the solution was evaporated at 60 °C (Figure S8a). The ~12 nm-wide and several hundred nanometers-long structures might be bundled GNRs because the width of an isolated GNR is ~3 nm. As the evaporation temperature decreased to 45 °C, the bundled GNRs aggregated further. Figure S8b showed the thicker GNR bundles whose width and length were ca. 40–50 and ca. 100–200 nm, respectively. The bundles found in Figure S8b also exhibited a trigonal pattern. The trigonal pattern was no longer observed when evaporated at 30 °C (Figure S8c). The GNRs formed bumpy structures with large variation in height. The interaction between GNRs at the upper side could differ from those at the lower side of GNRs/Gr.

This could be explained by the fact that the GNRs were strongly fixed to the graphene, while GNRs were interacting with each other in a weak form. We observed that the ~30-nm thick GNRs/Gr was further reduced to ~4-nm thick GNRs/Gr after immersion in 1,2,4-trichlorobenzene for 1 min (Figure S9). The first GNR layer was stably adsorbed on the graphene and could not be removed. The characteristic trigonal pattern, found in GNRs/Gr, indicates the existence of π–π interactions. The trigonal pattern remained on ~2-nm thick GNRs/Gr even after immersion in 1,2,4-trichlorobenzene for 12 h (Figure S10). The strong interaction between the GNRs and graphene was different from those observed for the alkyl-based molecules and graphene, where only CH–π interactions were dominant.\(^{S3}\) CH–π-interacting molecules could be washed away by solvents,\(^{S4}\) while π–π interacting molecules were hardly removed.\(^{S5,S6}\)

Mechanically exfoliated graphene could be used to demonstrate the π–π interaction between GNRs and graphene. The GNRs were aligned parallel and perpendicular to the edge; this indicated the AB stacking of GNRs against the zigzag and armchair edges of graphene (Figure 2). These facts indicated that the first GNR adlayer was stably fixed to the graphene by π–π interactions. As the GNRs have alkyl side chains, CH–π interaction also contributes to their adherence to the graphene. The domain size of the aligned GNR was larger than 200 nm (Figures 2, S8–S10).

The domain size of small molecules, such as cobalt phthalocyanine in adlayers on graphene cleaved on SiO\(_2\)/Si (Gr/SiO\(_2\)/Si), was normally limited to several tens of nanometers because of the corrugation of the graphene.\(^{S7}\) In contrast, a large area assembly of GNRs was found on our Gr/SiO\(_2\)/Si. The observed length of a single domain in Figure S8b roughly matched the calculated value of the average length of the GNR (~140 nm) based on the SEC analyses. On atomically flat highly oriented pyrolytic graphite, Narita et al. have reported that other types of organic synthetic GNRs, whose lengths were ca. 110–260 nm, have formed several hundreds of nanometer domains.\(^{S8}\) However, the surface roughness of our Gr/SiO\(_2\)/Si (root-mean-square roughness was ~0.7 nm) was much larger than that of graphite. Thus, our
result is the first to demonstrate the large-area assembly of synthetic GNRs on a relatively rough monolayer graphene surface.

**Figure S8.** AFM images of the GNRs/Gr deposited at (a) 60, (b) 45, and (c) 30 °C. (a) was taken at the boundary of the GNRs/Gr and SiO$_2$.

**Figure S9.** AFM image of the GNRs/Gr FET (a) before and (b) after immersion in 1,2,4-trichlorobenzene for 1 min. Inset in (b) shows the magnified image. (c) Cross-sectional height profiles were taken along the dotted and solid lines in (a) and (b), respectively.
Figure S10. AFM image of a ~2-nm-thick GNRs/Gr (a) before and (b) after immersion in 1,2,4-trichlorobenzene for 12 h.

7. I-V characteristics of the GNR thin film

Figure S11. Output curves of a ~100-nm-thick GNR film measured with applying various $V_{GS}$. Channel length and width are ~30 and ~1000 µm, respectively.

8. Temperature-dependent electrical conductivity of graphene and GNRs/Gr

Figure S12 shows the temperature dependence of conductivity obtained from two different FETs before and after the GNR deposition. Charge-neutral voltages $V_{CNP}$ were constant in device A regardless of temperature, while those of device B shifted to more positive voltages at higher temperatures because of $p$-type doping from the SiO$_2$ substrate due to the rippling at high temperatures. The difference in SiO$_2$ surface roughness in each device might be reflected in the observed results.
Figure S12. Temperature-dependent conductivity of a (a) graphene and (b) GNRs/Gr FET (device A). Fluctuation seen in the green curve at 343 K in (b) is extrinsic noise. Temperature-dependent conductivity of another (c) graphene and (d) GNRs/Gr FET (device B).

9. Gas desorption effect

The possibility of sample cleaning during the heating procedure is discussed. Figure 13a summarizes the results obtained from each experimental step. We performed the transfer curves measurement at 30 °C first (black) and then again at 90 °C (green). The sample was then cooled down to 30 °C (blue) and measured again. After these procedures, the GNRs were deposited on graphene and measured at 30 °C (red). The shift of $V_{CNP}$ could not be removed by cooling down the sample to 30 °C. We extracted charge-carrier mobility using equation 1 and found no significant increase when changing the temperature between 30 and 90 °C in graphene FET (Figure S13b). However, negative shifts in $V_{CNP}$ and increased mobility were confirmed after the GNR deposition. Thus, the observed improvement in mobility was not due to gas desorption during heating procedures, but to surface passivation and dielectric screening by the GNR deposition.
Figure S13. (a) Transfer curves of graphene and GNRs/Gr FET (device B). (b) Mobility extracted from the curves in (a).

Next, effect of ambient gas desorption in vacuum is discussed. Figure S14 shows the transfer curves measured in the ambient air and in vacuum conditions at room temperature. We confirmed slight increase in electron mobility and slight decrease in hole mobility when the FETs were put in vacuum, which were consistent with the previous report.\textsuperscript{10} This effect was explained by desorption of oxygen/water redox couple from graphene deosited on SiO\textsubscript{2}. Both the electron and hole mobility enhancement observed after the deposition of GNRs (Figures 3, 4, S12, S13) could not be explained by simply considering the gas desorption effect.

Figure S14. Transfer curves of (a) device C and (b) device D measured in the ambient air (solid curves) and in vacuum (dotted curves).

10. Density of impurities estimated from the charge-neutral point broadening

Density fluctuation $\delta n$ around the charge-neutral point universally exists in graphene in the presence of multiple impurities. We experimentally obtained $\delta n$ from the crossing points of linear fits of $\sigma(n)$ at large
carrier density \( n \) and minimum conductivity \( \sigma_{\text{min}} \) (Figure S15). Then, the number of impurities \( n_{\text{imp}} \) can be estimated by

\[
\sigma_{\text{min}} = \frac{20e^2 \delta n}{\hbar n_{\text{imp}}}
\]  

(S1)

where \( e \) and \( h \) are the elementary charges and Planck constant, respectively. We assumed \( \delta n = 2\delta n_h \), because we could not fit \( \sigma(n) \) at large \( n \) for electrons (Figures S15b, S15d). Application of gate-source voltage \( V_{GS} \) was limited to +80 V to prevent electrical breakdown of the SiO\(_2\); thus, we could not access the highly electron-doped region. From equation S1, \( n_{\text{imp}} \approx 4.07 \times 10^{12} \) (2.76\( \times \)10\(^{12} \)) cm\(^{-2} \) was obtained for the graphene (GNRs/Gr) device A (Table 1). These values were almost comparable with the values obtained from the charge-neutral point \( V_{\text{CNP}} \) shifts

\[
c_G \left( V_{GS} - V_{\text{CNP}} \right) = e \left( n - Zn_{\text{imp}} \right),
\]  

(S2)

where \( c_G \) is the gate capacitance per unit area (1.15 \( \times \) 10\(^{-4} \) F m\(^{-2} \)). Then \( n_{\text{imp}} \approx 3.01 \times 10^{12} \) (2.35 \( \times \) 10\(^{12} \)) cm\(^{-2} \) was obtained for the graphene (GNRs/Gr) FET using equation S2. We used \( Z = 1 \), which was valid for potassium deposited graphene in an ultra-high vacuum. Similar trend was also confirmed in the device B. The \( n_{\text{imp}} \) of 1.98 \( \times \) 10\(^{12} \) cm\(^{-2} \) in graphene was reduced to 6.46 \( \times \) 10\(^{11} \) cm\(^{-2} \) after the deposition of GNRs (Figure S15c).

**Figure S15.** Conductivities of graphene (black) and GNRs/Gr (red) as a function of (a) hole and (b) electron density (device A). The black and red arrows showed points to define the broadening of the
charge-neutral points, where the hole density fluctuation was $6.19 \times 10^{11}$ (black) and $3.68 \times 10^{11}$ cm$^{-2}$ (red), respectively. Corresponding data for (c) hole and (d) electron density obtained from the device B.

11. Dielectric screening by the GNR dielectric passivation layer

We consider a situation where the graphene channel is sandwiched between SiO$_2$ and a passivation layer (PL). The dielectric constant of these two layers is represented as $\kappa_{\text{SiO}_2}$ ($\approx 3.9$) and $\kappa_{\text{PL}}$ (Figure S16a). Adam et al. reported that the screening-dependent constant $C$ in equation 2 was obtained within random-phase approximation:$^{S12}$

$$C = \frac{2e}{hG(r_s)}, \quad \text{(S3)}$$

$$G(r_s) = \pi r_s^2 + 24r_s^3(1-\pi r_s) + \frac{16r_s^3(6r_s^2-1)\arccos\left[\frac{1}{2r_s}\right]}{\sqrt{4r_s^2-1}}, \quad \text{(S4)}$$

$$r_s = \frac{\gamma}{(\kappa_{\text{SiO}_2} + \kappa_{\text{PL}})d}, \quad \text{(S5)}$$

where $r_s$, $\gamma$, and $d$ represented the coupling constant, proportional constant ($\sim 3.97$ nm), and the average distance of impurities away from the graphene plane, respectively. $\gamma$ became smaller when the impurity potential was screened by a larger amount of charge density.$^{S14}$ In the last term in equation S4, both the numerator and the denominator are purely imaginary for $r_s < 0.5$; thus, $G(r_s)$ becomes a real number for all possible $r_s$. There is no way to directly observe $d$ experimentally; however, $d = 10$ Å is reported to reproduce the experimental results.$^{S12}$ Thus, we put $d = 10$ Å at first. In the case of graphene supported on SiO$_2$ ($\kappa_{\text{SiO}_2} = 3.9$), which was put in the air or in a vacuum (here we substituted $\kappa_{\text{PL}} = 1.0$), $r_s = 0.81$ and $C = 4.8 \times 10^{15}$ V$^{-1}$s$^{-1}$ were obtained successively. $C$ monotonically increased as $\kappa_{\text{PL}}$ increased, and represented the dielectric screening effect by the PL deposition (Figure S16b). When we assume impurities lie at the interlayer distance of graphite, $d = 3.4$ Å, $C$ becomes insensitive to $\kappa_{\text{PL}}$. Small changes in $d$ (<10 Å) drastically alter the efficiency of the dielectric screening.

The experimentally obtained improvement in $C$ by the GNR deposition is discussed hereafter. We use $\kappa_{\text{PL}} = 1.0$ for the pristine graphene and $\kappa_{\text{PL}} = 5.2$ for the GNRS/Gr (Figure S17). The experimentally obtained $\kappa_{\text{PL}}$ of $\sim 5.2$ was smaller than that of the theoretical value ($\sim 6.9$).$^{S15}$ The experimentally obtained $C$ for an electron ($C_e$) was well reproduced when $d = 9.8$ and 5.9 Å for the transfer curves obtained at 30 and 90 °C, respectively (Table S3). Graphene was reported to deform on SiO$_2$ at high temperatures, where $d$ became small because of the significant rippling.$^{S9}$ $C$ for holes ($C_h$) was much higher; thus, $d$ for holes was also assumed to be large. It should be noted that the application of $V_{\text{GS}}$ changes $d$ because the randomly charged
imperfections could be both positive and negative in unequal numbers.\textsuperscript{516} Local suspension of the GNRs/Gr on a rough SiO$_2$ surface also increased $C$ by directly enlarging $d$, which is suggested by the independent Raman spectroscopy measurements (Figure 2). The combination of all these effects might result in the observed increase in $C$.

\textbf{Figure S16.} (a) Schematic illustration of graphene sandwiched between SiO$_2$ and a PL. (b) $C$ as a function of $\kappa_{PL}$. Solid and dotted curves are obtained when $d = 10$ and 3.4 Å.

\textbf{Figure S17.} Schematic of the capacitors consisting of (a) SiO$_2$ and (b) GNRs/SiO$_2$. Layer thickness of the SiO$_2$ and the GNRs are $\sim$300 and $\sim$500 nm, respectively. (c) Measured capacitance of the samples (a) and (b) as a function of voltage. Measurements were done with AC voltage frequency of 0.1 Hz.

\textbf{Table S3.} $C_h$ and $C_e$ before and after GNR deposition at different $d$.

<table>
<thead>
<tr>
<th>$d$ (Å)</th>
<th>$C_h$ for graphene (V$^{-1}$s$^{-1}$)</th>
<th>$C_h$ for GNRs/Gr (V$^{-1}$s$^{-1}$)</th>
<th>$C_e$ for graphene (V$^{-1}$s$^{-1}$)</th>
<th>$C_e$ for GNRs/Gr (V$^{-1}$s$^{-1}$)</th>
</tr>
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<tr>
<td>$d = 32$ Å</td>
<td>$1.2 \times 10^{16}$</td>
<td>$2.5 \times 10^{16}$</td>
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<td></td>
</tr>
<tr>
<td>$d = 9.8$ Å (at 30 °C)</td>
<td></td>
<td></td>
<td>$4.8 \times 10^{15}$</td>
<td>$7.2 \times 10^{15}$</td>
</tr>
<tr>
<td>$d = 5.9$ Å (at 90 °C)</td>
<td></td>
<td></td>
<td>$3.8 \times 10^{15}$</td>
<td>$5.1 \times 10^{15}$</td>
</tr>
</tbody>
</table>
12. Transfer curves of graphene FETs with different channel lengths

We tested graphene FETs whose channel lengths $L$ were longer than 4 $\mu$m. All of them showed similar transfer curves as shown in Figure 3b, i.e., positively shifted charge-neutral points, higher conductivity in hole-doped regions and lower conductivity in electron-doped regions, regardless of their $L$ (Figure S18a). Such asymmetry was also interpreted previously in terms of charge-carrier doping from electrodes.\textsuperscript{S17,S18} The contact-doping effect extends from both ends of the graphene to several hundred nanometers from the neighboring electrodes,\textsuperscript{S19} and the contact-doping effect may overtake the impurity effect when the channel length of the FET is shorter than 3 $\mu$m.\textsuperscript{S17} However, the FETs used in this study had longer channels and showed width-normalized resistance $R_{tot}W$ nearly proportional to the $L$ (Figure S18b); this suggested that the channel resistance was dominantly larger than that by the contact-doping effect. A transmission line model was employed to extract the contact resistance $R_{con}$:

$$R_{tot}W = \rho_{Gr} L + 2R_{con}W,$$

where $\rho_{Gr}$ represents the resistivity of the graphene channel. $R_{con}$ was more than 10 times smaller in magnitude as compared with $R_{tot}$ (Figure S18b). An apparently large negative $R_{con}$ was reported when carrier doping from the metal contacts was more substantial than the actual contact resistance precisely at the contacts,\textsuperscript{S20} while no such phenomenon was confirmed in the present study. Thus, the observed electron-hole asymmetry was dominantly caused by the carrier doping to the graphene channel due to the oxygen/water redox couple and the SiO$_2$ substrate.

![Figure S18](image-url)

**Figure S18.** (a) Conductivities as a function of $V_{GS}$ and (b) $R_{tot}W$ as a function of $V_{GS}$ normalized with $V_{CNP}$ of three graphene FETs with different $L$ (solid curves). The dotted curve in (b) shows the calculated $R_{con}W$ using equation S6. Optical images of (c) 7.7-, (d) 4.6-, and (e) 4.2-$\mu$m-long channel devices.

13. References


(S18) Huard, B.; Stander, N.; Sulpizio, J. A.; Goldhaber-Gordon, D. Evidence of the role of contacts on the...
