SUPPLEMENTARY INFORMATION

High Mobility, Printable and Solution-Processed Graphene Electronics

Shuai Wang,[1] Priscilla Kailian Ang,[1,2] Ziqian Wang,[3] Ai Ling Lena Tang,[1] , T. T. L. John [3] & Kian Ping Loh[1,*]

[1]Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543. [2]NUS Graduate School for Integrative Sciences and Engineering, Singapore 117597. [3]Department of Electrical & Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576.

*Corresponding author rmail: chmlohkp@nus.edu.sg

METHODS

Synthesis of BSGO. 1.5 g of graphite, 1.5 g of NaNO3 and 69 ml of H2SO4 were first mixed and stirred in an ice bath. Next, 9 g of KMnO4 was slowly added. The solution was kept in room temperature and stirred for 1 h. After which, 100 ml of water was added and the temperature was increased to 90 °C. After 30 mins, 300 ml of water followed by 10 ml of H_2O_2 were slowly added. The resultant mixture was filtered and washed by water until the solution pH was about 6. The synthesized GO sheets were dispersed in water: methanol (1:5) mixture and purified with 3 repeated centrifugation steps at 12,000 rpm for 30 mins. The purified sample was centrifuged at 8 krpm for 30 min to remove the smaller sized GO sheets. Then the remaining solution was redispersed in water/methanol mixture with the ratio of 1:5 and centrifuged at 2,500 rpm to recover the big sized graphite oxide (BSGO) sheets.

The synthesis of big sized graphene sheet and films by annealing at 1000 °C in H_2. The samples were annealed in a furnace at 1000 °C for one hour in 27 mBar of H2 gas. The base pressure of the vacuum (before admitting H2 gas) is 1E-5 mBar. H2 flow rate is 67 sccm.

Fabrication and electrical measurements of graphene FET. Electrodes were patterned by electron beam lithography using polymethylmethacrylate (PMMA) as the e-beam resist. Two-point probe configuration was used for graphene thin film FET while four-point probe configuration was used for graphene single sheet FET. 0.5 mg/ml and 1 mg/ml GO solution was spin coated onto SiO2/Si substrate to form single sheet and film, respectively. GO sheets were spin coated to form a film on oxidized silicon substrates (285 nm SiO2 with pre-fabricated marker), and heated in H_2 at 1000 °C. 100 μL 3% PMMA (molecular mass, 950 K) chlorobenzene solution was spin coated on substrates at 6000 rpm using Spincoater® Model P6700 Series (Specialty Coating Systems, INC), and baked at 120 °C for 15 min. The thickness of PMMA is about 200 nm. Electron-beam patterning was done using a Philips XL30 FEGSEM at 30 kV with a Raith Elphy Plus controller, with an exposure dosage 280 □A/cm2. The PMMA was then developed with a methyl isobutyl keton (MIBK) and isopropyl alcohol (1:3) solution. 10 nm chromium and 100 nm were deposited in the substrate through vacuum thermal evaporation. The films were then lifted off in acetone for 1h at room temperature and rinsed with isopropyl alcohol. The sample was annealed at 300 °C in tube-furnace at a hydrogen/argon (5/95 sccm) for 1hr at a pressure of 0.3 mBar to improve the contacts between metal and graphene. Electrodes were wire-bonded by a 4523AD Manual Wedge Bonder (Kulicke&Soffa®) to a 24-pin Side-Brazed Dual In-Line Ceramic Package (Spectrum Semiconductor Materials, Inc). The device was measured in a B1500A Semiconductor Device Analyzer (Agilent Technologies®) using the in-built R-I Kelvin measurement software.

Printable graphene electronics. 4 mg/ml and 1mg/ml GO solutions were drop-casted or printed on SiO_2/Si substrates to make the electrodes and active layers, respectively. The area surrounding graphene active channel was removed by oxygen plasma etching to prevent the gate leakage of graphene FETs. The devices were then heated at 1000 °C in H_2 for 1 h. Epoxy resin was used to insulate metal contacts from the NaF electrolyte. I-V_g measurements were obrained in air using B1500A Semiconductor Device Analyzer (Agilent Technologies®) using the in-built R-I Kelvin measurement software.

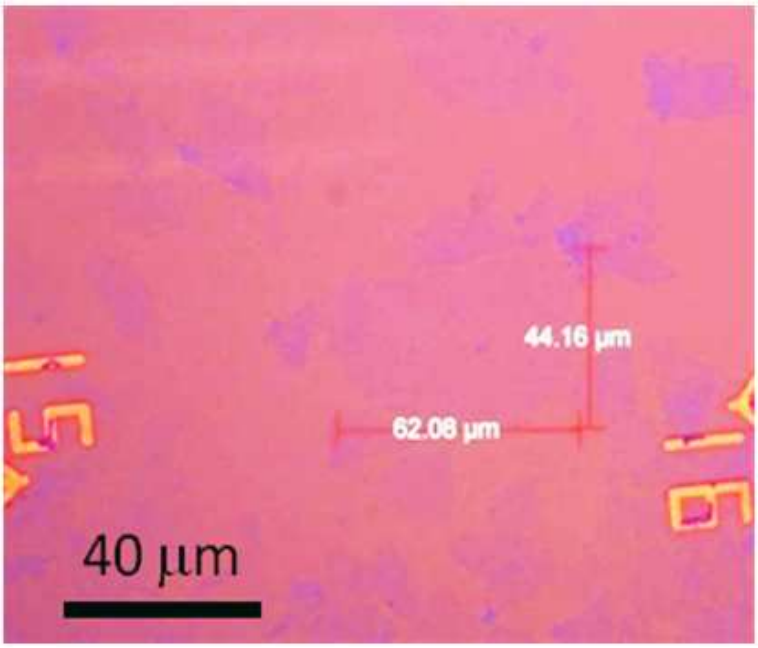

Figure S1. Optical micrograph of big sized GO.

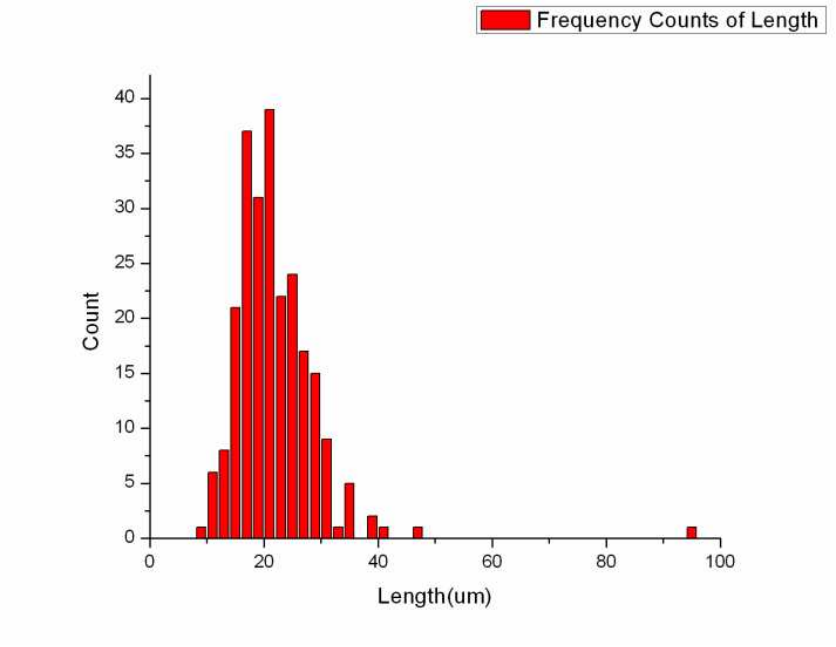

Figure S2. Size distribution of GO sheets.

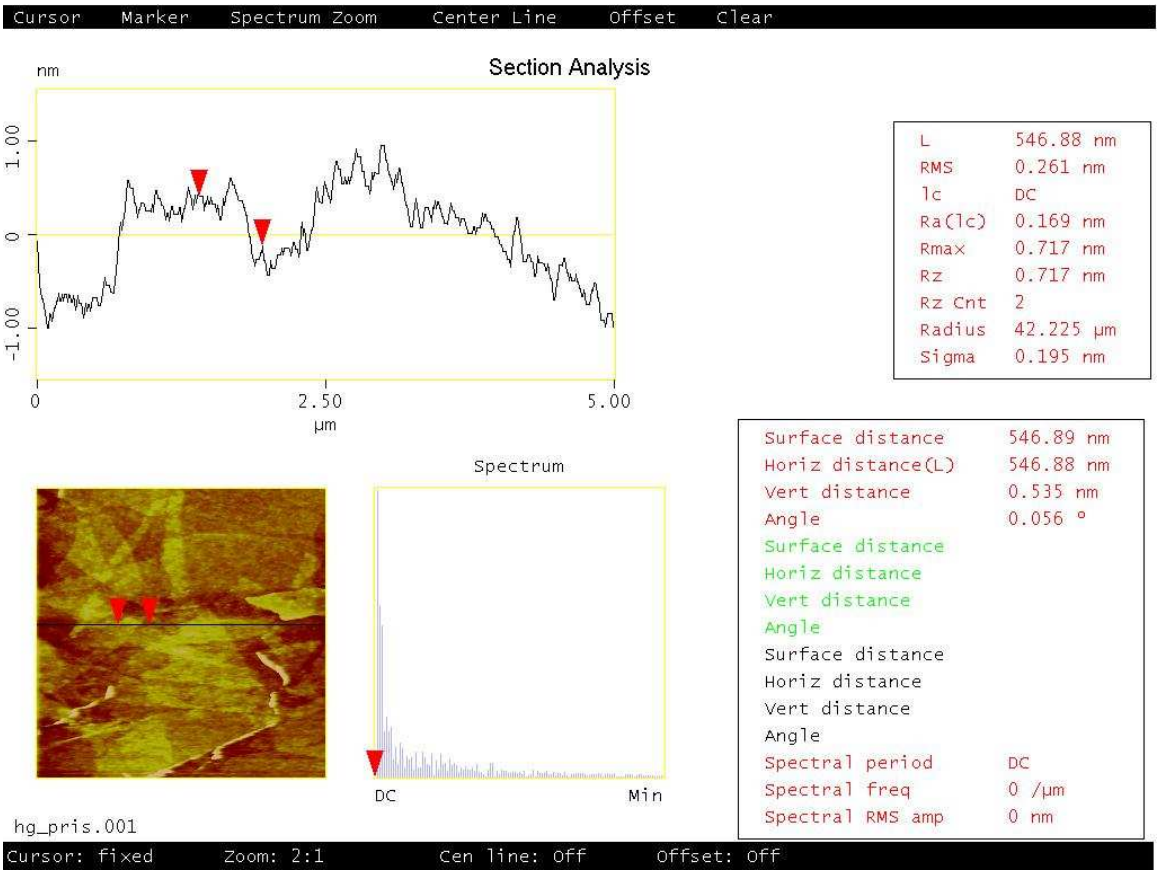

Figure S3. AFM of thermally reduced GO at 1000 °C sheets with thickness of 0.535 nm.

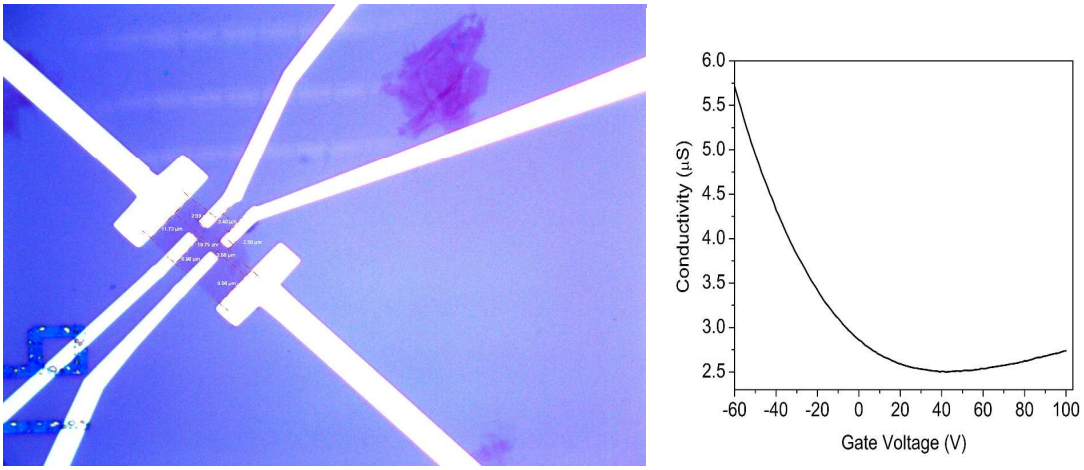

Figure S4. The 4-point probe measurement on one thermally reduced GO sheet with channel of 3.40 μm length and 2.99 μm width, which shows resistance of 27876 Ohm. Hole and electron mobility is 5.2 cm^2/Vs and 1.3 cm^2/Vs respectively.

4pt resistance on the lower left 2 electrodes: 12 336Ohm.
W = 6.98 um, L = 3.40 um, conductivity = 74 503S/m.
4pt resistance on the upper right 2 electrodes: 27 876Ohm.
W = 2.99 um, L = 3.40 um, conductivity = **76 966S/m.**

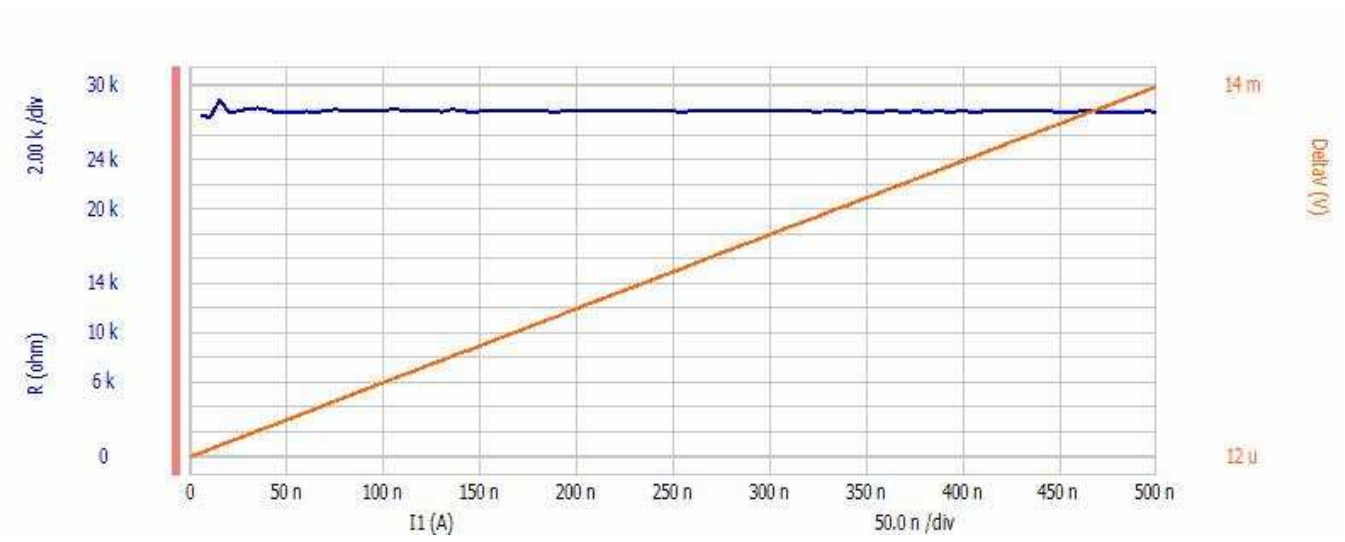

Figure S5. The I-V curve of one 4-point probe resistance measurement on one thermally reduced GO with channel of 3.40 um length and 2.99 um width. This graphene sheet demonstrated high conductivity of 76966 S/m.

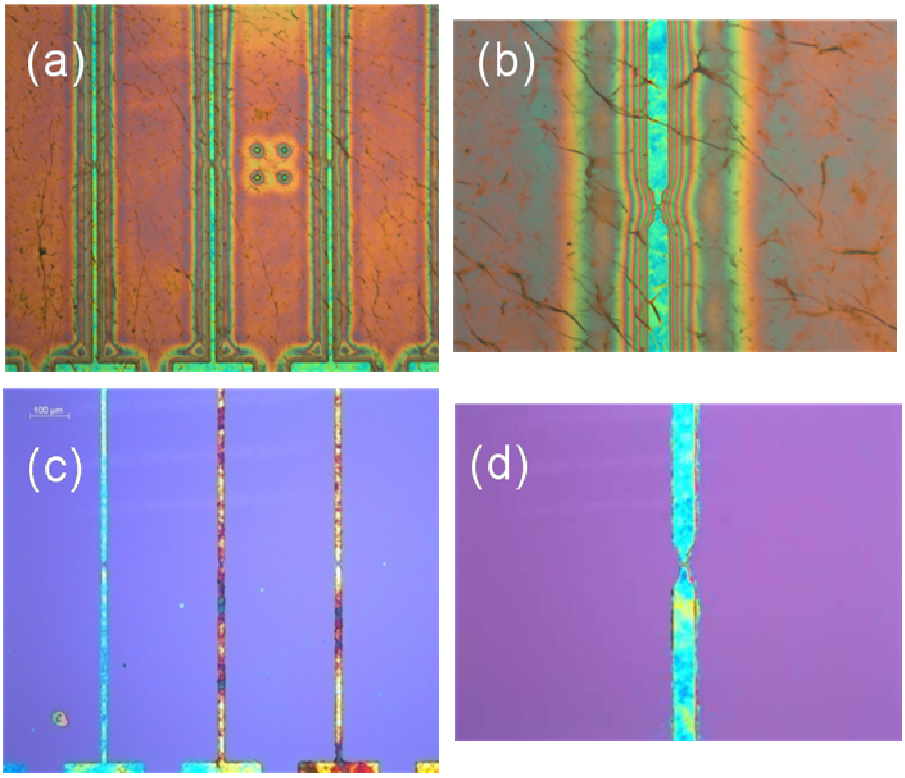

Figure S6. (a) and (b) Optical micrograph of the graphene oxide patterns formed in the channels defined by photoresistance. (c) and (d) Optical micrograph of the printable electrodes with channel of 2 um length and 4 um width.

Optical contrast spectroscopy

The contrast spectra were obtained with a WITEC CRM200 Raman system. The excitation source is 532 nm laser (2.33 eV) with laser power below 0.1 mW to avoid laser-induced heating. The laser spot size at focus was around 500 nm in diameter with a 100× objective lens (NA = 0.95). The sample was placed on an x-y piezostage to perform contrast imaging across the active channel region. The contrast spectra of graphene film are obtained by

$$C(\lambda) = (R_0(\lambda) - R(\lambda)) / R_0(\lambda)$$

where $R_0(\lambda)$ is the reflection spectrum from SiO_2/Si substrate of SiO_2 thickness of 285 nm and $R(\lambda)$ is the reflection spectrum from graphene sheet illuminated by normal white light source.

Figure S7 shows the contrast spectra for 1 to 5 layers of reduced graphene sheets across the active channels, which have a peak centered at 550 nm and does not vary with increasing layers up to 10.

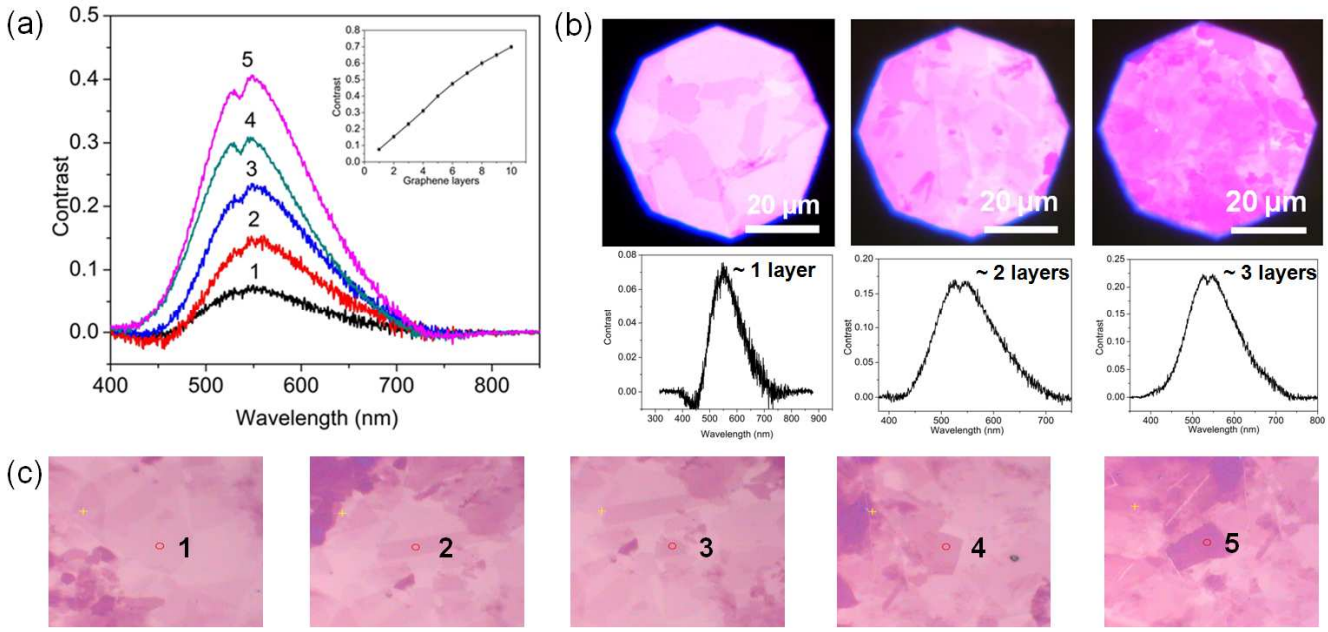

Figure S7. Optical contrast spectra of different number of graphene layers. **a.** Contrast spectra of 1 to 5 layer. Inset shows the calibration curve of contrast as a function of the number of layers. The contrast values obtained are 0.076 ± 0.005 (one layer), 0.153 ± 0.010 (two layers), 0.230 ± 0.013 (three layers), 0.311 ± 0.012 (four layers), 0.405 ± 0.015 (five layers) which increases approximately linearly and shows saturation after 10 layers. **b.** Contrast spectra for graphene active channels with an average of ~1 (left), ~2 (centre) and ~ 3 layers (right). **c.** Optical micrographs of representative 1, 2, 3, 4 and 5 layer(s) of reduced BSGO deposited onto 285 nm SiO_2.

AFM analysis of graphene films used in this study

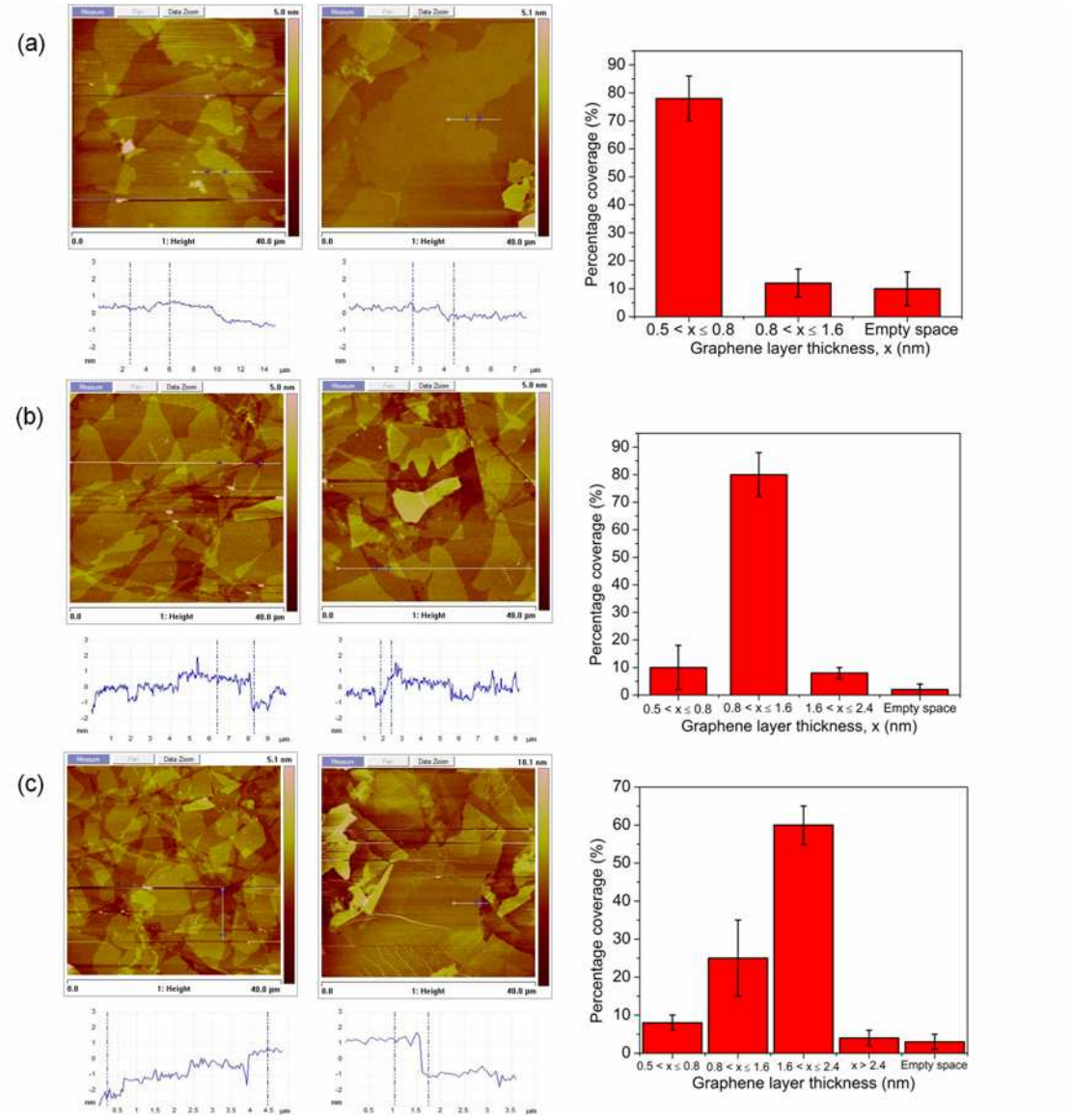

Fig. S8. AFM section analysis of graphene film thickness and their corresponding surface area coverage. (a) Single layer graphene film (b) Bilayer graphene film (c) Trilayer graphene film

Besides optical contrast microscopy, AFM section analysis (on average 10 per substrate) was done randomly on different areas of a 1 cm×1 cm SiO_2/Si substrate with different layers of graphene deposited.

The section analysis of the thickness of graphene film spin-coated on substrate and the corresponding surface area coverage were computed as shown in Fig. S8. For single-layer graphene film, about 78 ± 8 % of the substrate was covered with single layer graphene and the rest consisted of overlapped edges of individual graphene sheets and empty spaces. For bilayer graphene film, about 80 ± 7 % of the substrate was covered with bilayer graphene sheets while a trilayer graphene film had 60 ± 5 % of the substrate surface area covered with trilayer graphene sheets. Graphene layer thickness, x, for single layer graphene is $0.5 < x \leq 0.8$ nm, bilayer graphene is $0.8 < x \leq 1.6$ nm, trilayer graphene is $1.6 < x \leq 2.4$ nm and x for four layers and above is > 2.4 nm.