

Supplementary information

Self-Assembled Electrical Biodetector Based on Reduced Graphene Oxide

Tetiana Kurkina^{1}, Subramanian Sundaram^{1§}, Ravi Shankar Sundaram^{1#}, Francesca Re²,
Massimo Masserini², Klaus Kern^{1,3}, Kannan Balasubramanian^{1*}*

¹Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany.

*²Dipartimento di Medicina Sperimentale, Università degli Studi di Milano-Bicocca, Via Cadore 48, I-
20052 Monza, Italy.*

*³Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, CH-1015
Lausanne, Switzerland.*

*[§] (present address) Department of Electrical Engineering and Computer Science, Massachusetts Institute
of Technology, Cambridge, MA 02139 USA.*

*[#] (present address) Center for Advanced Photonics and Electronics (CAPE), Engineering Department,
University of Cambridge, 9, JJ Thomson Avenue, Cambridge, CB3 0FA, UK.*

Preparation of graphene solution

Graphene oxide solution was prepared using Hummers method¹. 1 g of graphite powder (200µm grain size) was added under constant stirring to the flask with 23 ml of 98% sulfuric acid. 0.5 g of NaNO₃ was added and the speed of stirring was increased. After that 3 g of KMnO₄ was added carefully. The above mentioned procedures were performed in the ice bath with temperature

control of the solution. The temperature of the mixture was kept below 20°C. Upon removing the iced water bath, the temperature was increased to 35°C in 30 minutes, leaving a brownish grey paste. 46 ml of deionized water was then added and the temperature was increased to 98°C where it was maintained for 15 minutes. Then 70 ml of warm water was poured into the mixture. 3% H₂O₂ was added slowly until the solution turned bright yellow. The suspension was vacuum filtered resulting in a yellow brown filtrate which was washed several times with dilute HCl and warm water. The exfoliation was performed by a mild ultrasonication. The obtained graphite oxide suspensions in water were placed in an ultrasonic bath for 10 minutes and then centrifuged at 3000 rpm for 3-4 minutes.

Site-specificity of GO deposition

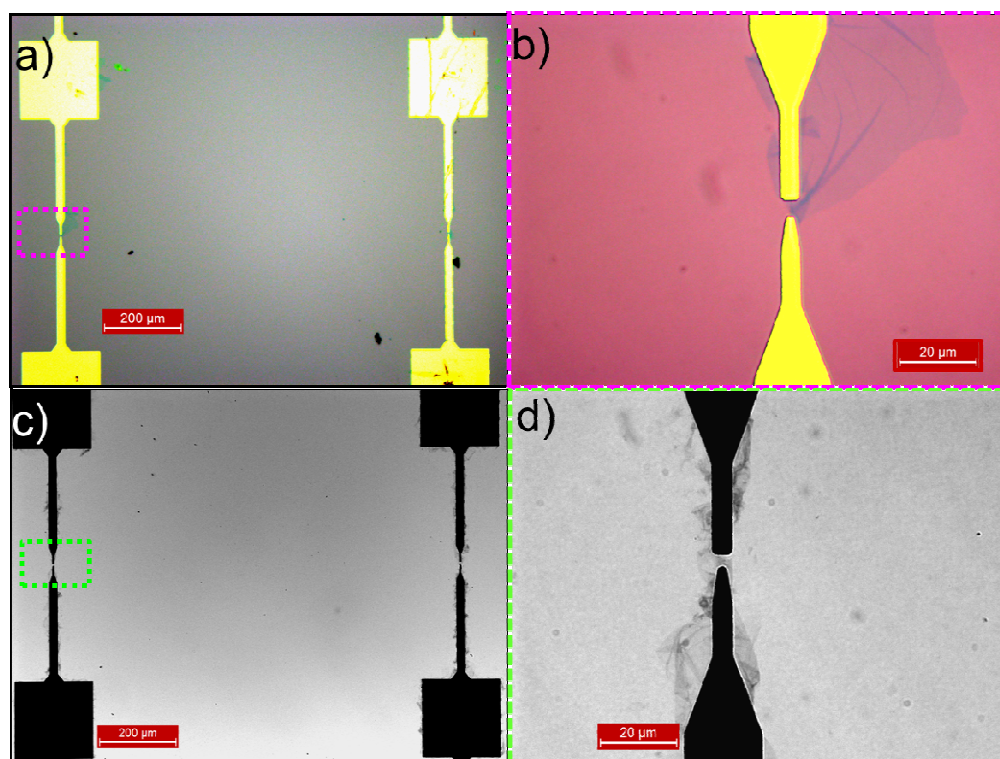


Figure S1. Site-specificity of GO deposition on electrochemically modified electrodes. (a) optical microscope image (reflected light) of two pairs of electrodes on Si/SiO₂ substrate, (b) detailed view of the marked area in (a), (c) optical microscope image (transmitted light) of two pairs of electrodes on glass substrates, (d) detailed view of the left electrode marked in (c). It is clearly visible that after 1 h of incubation of substrates in graphene oxide solution, the flakes are deposited exclusively on the electrodes.

Thermal annealing of the samples

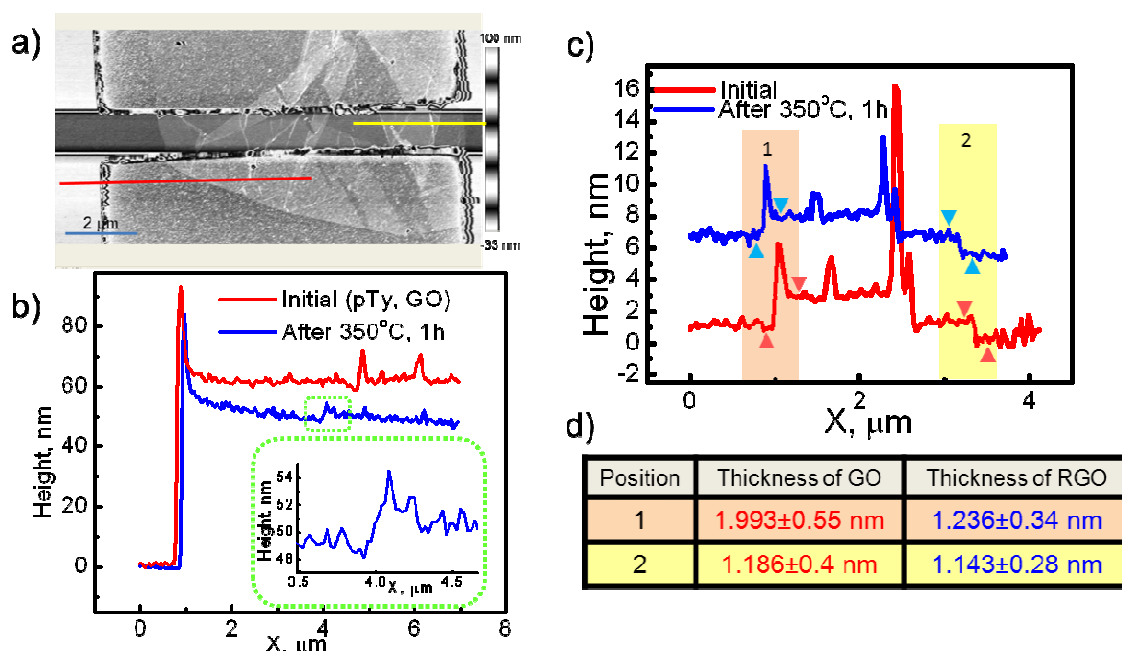


Figure S2. The influence of thermal annealing on the thickness of polytyramine and graphene oxide. (a) AFM image of RGO device prepared using site-specific chemical anchoring, (b) height profiles taken along the red line in Fig. S2a before and after thermal annealing in argon at 350°C for 1 h. The inset shows a detailed view of the step corresponding to the RGO flake. Due to the roughness of the polymer layer this step is not visible in the height profile of this area before annealing. The height profiles confirm the decrease of the polymer layer after annealing on both areas covered and not covered with the flakes. (c) height profile of GO flake taken along the yellow line in Fig. S2a before and after thermal reduction. (d) table showing the comparison of the heights of few layers of GO (position 1) and monolayer of GO (position 2). The thickness is calculated using Gwyddion 2.27. The reduction of the thickness of few layers (folded) GO is clearly observed. This effect may be attributed to the disappearance of the water trapped between the layers in the fold and elimination of oxygen containing groups in multiple layers of graphene oxide. However due to the high roughness of the surface we do not observe the distinct changes in the thickness of the monolayer flake.

KPFM characterization of the samples

To confirm the successful reduction of graphene oxide we studied the obtained devices using Kelvin probe force microscopy (KPFM). The resulting surface potential maps are depicted in Figures S3(b) and S3(c). In the former case, there is no conducting pathway measurable in the device before annealing, consistent with its insulating behavior. By contrast, after annealing the

current carrying flake can be clearly identified in figure S3 (c), analogous to recent results on individually contacted RGO flakes.² KPFM images also show the variation of the potential on the electrode surface in both cases. This result can be attributed to the inhomogeneity of the electrode surface coverage with pTy, GO and RGO. It is possible that electrical contact of RGO with the electrodes happens only in certain parts and/or it is not identical everywhere. However the electrical current flow pathway is clearly observed in the presented KPFM images. This leads us to conclude that the annealing procedure serves as a single processing step that results in a graphene-like backbone of the GO flakes, while simultaneously removing the polytyramine layer to provide good contacts.

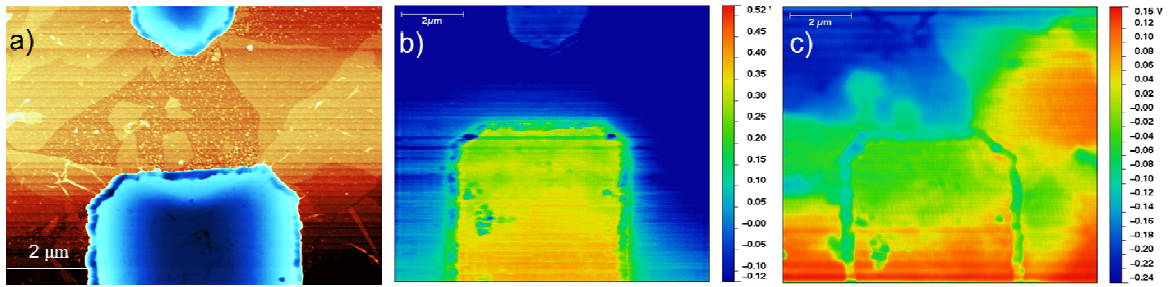


Figure S3. (a) Tapping mode AFM height image of the same device. (b) and (c) Surface potential maps of the same device before (b) and after (c) the thermal annealing step. The tip was grounded while a fixed bias (0.5 V for (b) and 0.25 V for (c)) was applied across the gap.

Alternative substrates and commercially available graphene oxide for RGO devices fabrication

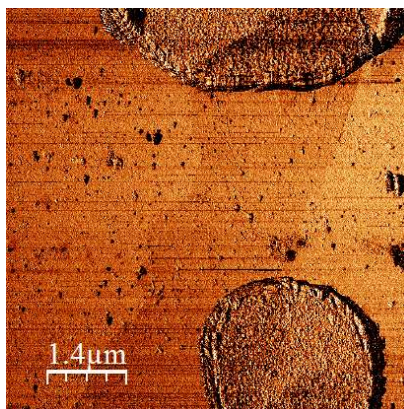


Figure S4. AFM image (phase mode) of graphene oxide coupled to electrochemically modified electrodes on flexible kapton substrate.

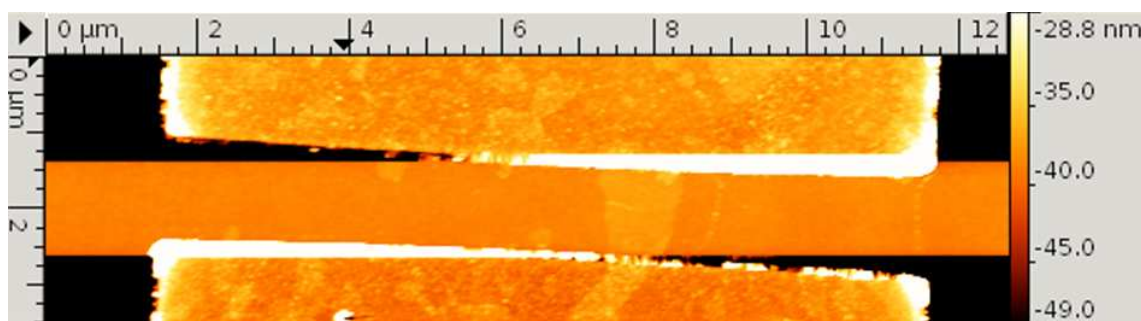


Figure S5. Commercially available graphene oxide (Graphene supermarket, USA) coupled to the electrodes.

Biochemical functionalization of reduced graphene oxide

0.1 M N-Hydroxysuccinimide (Acros organics) and 0.1 M 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (Sigma) in 10mM Phosphate buffer pH 6 were mixed (1:1 ratio) and immediately added to the PDMS well above RGO. After 15 min the solution in the well was exchanged for 100 μg/ml Protein A from *Staphylococcus aureus* (Sigma) in 10mM acetate buffer pH 5. After 25 min at the well was washed with acetate buffer pH 5 and phosphate buffer pH 7.4. Then 100mM ethanolamine in 10mM phosphate buffer pH 7.4 was introduced to the well for 15 min.

Oriented immobilization of anti-A β -antibodies (Invitrogen) on RGO was performed by introducing 10 μ M antibody solution in 10mM phosphate buffer pH 7.4 containing 100mM NaCl to the well with Protein A-functionalized RGO.

Preparation of amyloid beta (1-42) oligomers

Amyloid beta peptide (Invitrogen) was dissolved in DMSO to obtain 5mM concentration. Then it was diluted to 100 μ M concentration with 10 mM potassium phosphate buffer pH 7.4 containing 100mM NaCl. This solution was incubated for 12 h at 4°C. The obtained stock solution of amyloid-beta oligomers was stored at -40°C. Before use the solution was defreezed at room temperature and diluted to required concentration with 10mM potassium phosphate buffer pH 7.4 containing 100mM NaCl.

Comparison of chemical anchoring approach and dielectrophoretic trapping for RGO devices fabrication

Simultaneous dielectrophoretic (DEP) deposition of the graphene derivatives have been previously demonstrated by several groups for the fabrication of the arrays of nanodevices³⁻⁵. It requires the application of AC voltage to the connected electrodes. The second (counter) electrode in each pair has to be capacitively coupled to the ground (back gate)^{3,5}. This limits the choice of the substrate for the devices fabrication. To use the dielectric substrates (glass, kapton) for dielectrophoresis, AC-voltage has to be applied between two electrodes in a pair. However, in this case the trapping on the multiple positions can be realized only serially⁴.

It is also known that geometry of the electrodes plays important role for dielectrophoretic deposition of nanomaterials⁵. In some situations this makes it difficult to establish the optimal DEP conditions. The presented approach relies on the unique chemical properties of GO (namely

oxygen containing groups) and in comparison to dielectrophoresis it is less dependent on the kind of substrate and the electrodes. The only limiting factor is the size of the flakes in the GO solution which should not be less than the gap between the electrodes.

Another important aspect is the area of the wafer over which the simultaneous fabrication of the devices was performed. In this work we use 4" wafer. The area of 15 chips is 9*3 cm² in total excluding the narrow areas between separate chips required for cutting the wafer. The gap between two neighboring pairs of electrodes on the chip is 1 mm. To our knowledge DEP has only been used until now for the fabrication of RGO devices on much smaller substrate areas (few mm scale or less).

References

1. Hummers, W.S.; Offeman, R.E. Preparation of Graphitic Oxide. *J. American Chemical Society*, **1958**, *80*, 1339–1339.
2. Yan, L.; Punckt, C.; Aksay, I.A.; Mertin, W.; Bacher, G. Local Voltage Drop in a Single Functionalized Graphene Sheet Characterized by Kelvin Probe Force Microscopy. *Nano Lett.* **2011**, *11*, 3543–354.
3. Vijayaraghavan, A.; Sciascia, C.; Dehm, S.; Lombardo, A.; Bonetti, A.; Ferrari, A.C.; Krupke, R. Dielectrophoretic Assembly of High-Density Arrays of Individual Graphene Devices for Rapid Screening. *ACS Nano* **2009**, *3*, 1729-1734.
4. Joung, D.; Chunder, A.; Zhai, L.; Khondaker, S.I. High Yield Fabrication of Chemically Reduced Graphene Oxide Field Effect Transistors by Dielectrophoresis. *Nanotechnology*, **2010**, *21*, 165202-6.
5. Burg, B.R.; Lütolf, F.; Schneider, J.; Schirmer, N.C.; Schwamb, T.; Poulidakos, D. High-Yield Dielectrophoretic Assembly of Two-Dimensional Graphene Nanostructures. *Applied Physics Letters*, **2009**, *94*, 053110
6. Xu, D.; Subramanian, A.; Dong, L. Shaping Nanoelectrodes for High-Precision Dielectrophoretic Assembly of Carbon Nanotubes. *IEEE Transactions on Nanotechnology*, **2009**, *8*, 449-456