Parallelization of ThermoChemical NanoLithography

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S.1 Thermal Array Details

The thermal array contains five tips as shown in Figure S.1. All arrays were fabricated by the Professor William P. King's lab at the University of Illinois at Urbana Champaign. The electronic and thermal responses of the tips are the same as single thermal tips described in literature [1]. Each tip is individually addressable which means that tip 1 can be held at one temperature, while tips 2-5 are at different, unique temperatures. While thermal cross talk among different tips in an array has been reported in the literature [2], in this work, we neglected this effect.

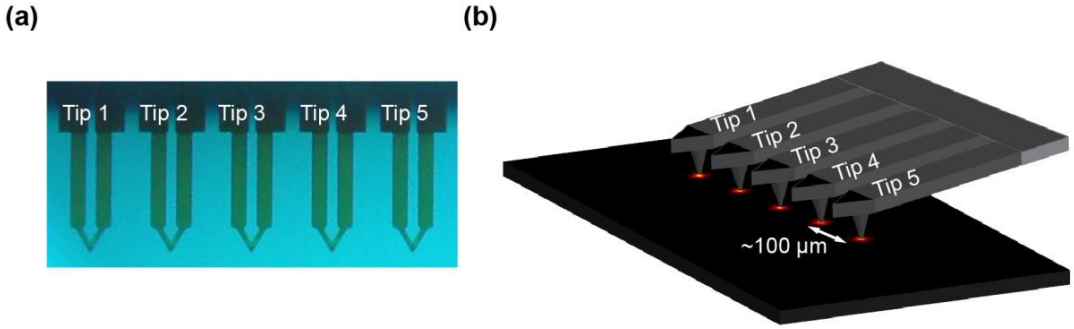

Figure S.1 Geometry of the array

S.2 Leveling

In order to compensate for misalignment between the tips and the sample, an optical leveling device was introduced to simultaneously (within 200 nm) bring all five tips into contact with the sample. To check the alignment, the resistance of each cantilever was monitored as a function of the tip-sample distance. The resistance across the cantilever is a function of the temperature of the heater+tip. By applying a voltage to each cantilever (i.e. heating the tip), the sudden change in resistance (i.e. temperature of the tip) detects when a tip touches the sample (see Fig. S.2). Figure S.2 illustrates the basic procedures, in particular in figure S.2a, tip 1 is in contact with the surface first, followed by tip 2, 3, 4, and 5 respectively. This suggests that the substrate is not well aligned with respect to the array in the same manner as suggested on the right of figure S.2a. The red arrow indicates how to compensate the optical leveling device against this tilt. After several iterations, the tips can be simultaneously brought into contact; the final result is shown in figure S.2b.

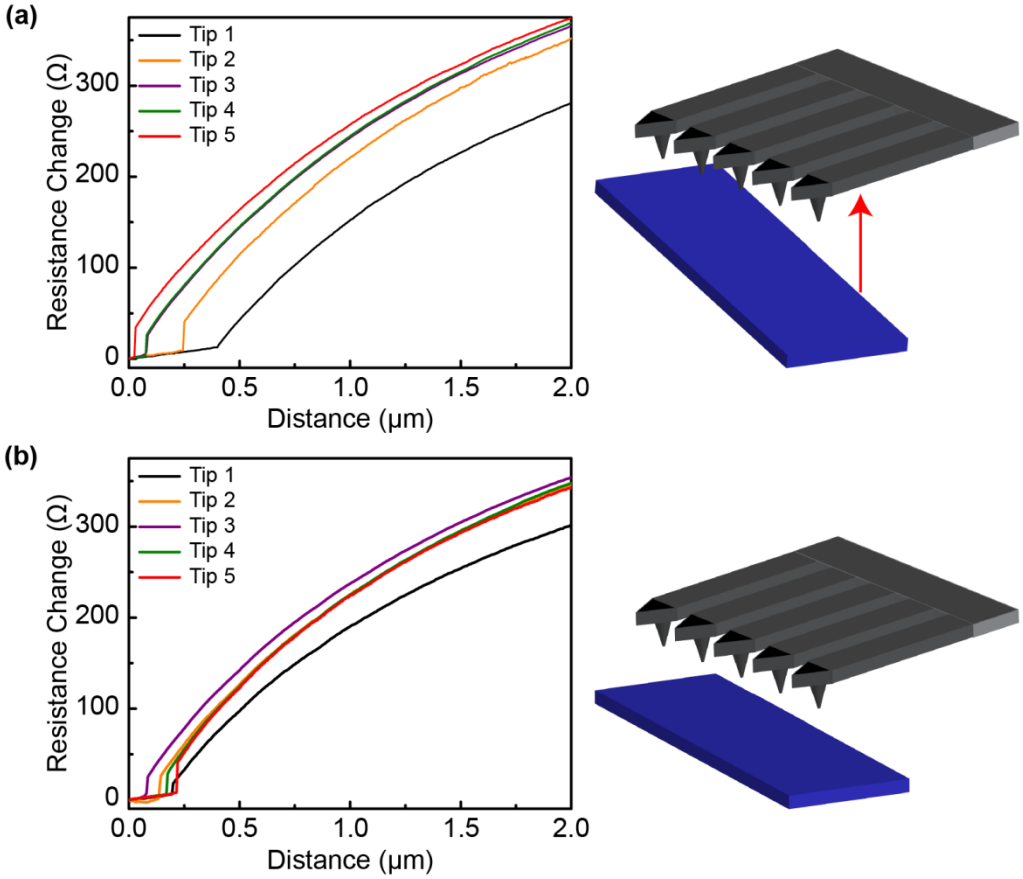

Figure S.2 (a) Uneven alignment between the substrate and the arrays; as shown in the graph, tip 1 comes into contact with the substrate first, followed by tip 2, 3, 4, and 5 respectively. (b) Almost even alignment of the tips with the substrate.

S.3 Reaction of PXT to PPV

The reaction from the precursor film (poly(*p*-xylene tetrahydrothiophenium chloride)) to poly(p-phenylene vinylene) (PPV) is shown in figure S.3. While it is unclear what exactly causes the change in topography; one reasonable hypothesis is material loss resulting from the cleavage of the tetrahydrothiophene (THT) side group. This change in topography is reproducible rendering the 3-D replica of the *Mona Lisa*.

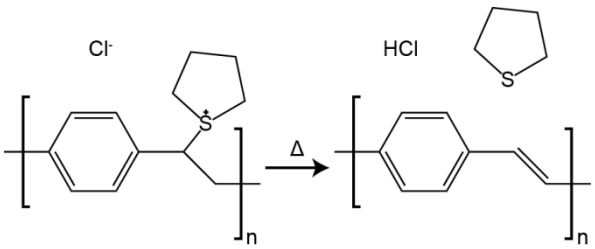

Figure S.3 PXT to PPV reaction.

S.4 Graphene Oxide Film Preparation

The graphene oxide (GO) film (thickness ~ 50 nm) was prepared by drop casting colloidal GO dispersion on a Si chip and leaving it to dry at 70°C. Stable colloidal GO dispersions were produced by modified Hummers method [3]. Briefly, graphite flakes (0.3 g, Sigma Aldrich), $NaNO_3$ (0.6 g, Sigma Aldrich), and H_2SO_4 (23 mL, 98%, Sigma Aldrich) were stirred for 15 minutes. $KMnO_4$ (3 g, Sigma Aldrich) was then slowly added and the mixture was stirred for 6 hours at 30°C. Subsequently, 40 mL of deionized (DI) H_2O was added to stop the oxidation reaction, leading to a rapid rise of temperature (~ 70°C). After 30 minutes at this temperature, 100 mL of DI H_2O and 3 mL of H_2O_2 solution (30%) were added to dissolve the insoluble manganese species, turning the color of the mixture to yellow.

Once the reaction was terminated, the oxidized portion was separated and cleaned from unoxidized graphite and other residual species. The cleaning was performed by centrifugation of the obtained suspension at 7800 rpm for 30 minutes in order to remove both the acidic content and ions. The solid content was collected and redispersed with DI H_20. This operation was repeated in sequence until the pH of the supernatant raised close to neutrality. At that point, the exfoliation of graphite oxide was performed by prolonged and vigorous shaking, forming a brownish colloidal suspension of GO flakes. Finally, solid unoxidized graphite was removed by mild centrifugation (~ 2000 rpm for 20 minutes). The subsequent collection of the purified supernatant resulted in stable aqueous GO suspensions.

S.5 TCNL of Graphene Oxide Film

Figure S.4a shown an optical image of the five cantilevers array used to locally reduce GO. Each of the five tips wrote four zigzag nanostructures in the graphene oxide thin film, as shown in Fug. S.4b. The writing speed was 0.2 μm/s for all these nanostructures.

The AFM topography and friction images of the rGO nanostructures (Figure S.5) were obtained with a Veeco Nanoscope IV AFM. The scans were performed with a "NanoAndMore" Pt/Ir coated tip in contact mode. The cross section of a line in the zoom-in topography image shows a half maximum width of 50 nm. Figure S.5 (c) shows that the rGO nanostructures have a lower friction than GO. The topography of rGO nanostructures made by tip 1 is shown in figure S.5 (a), whereas the nanostructures made by tip 2, 3, 4, and 5 are shown in Figure S.6. The topography images in Figure S.6 were obtained with the cantilevers in the array, using an Agilent 5600 LS AFM.

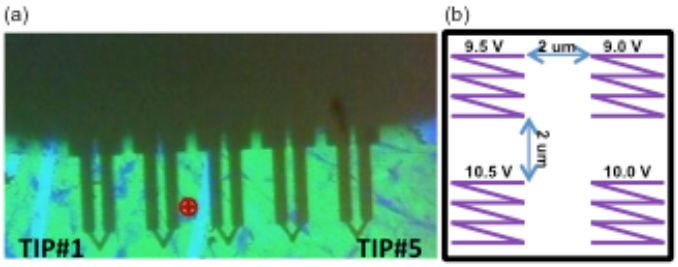

FIG. S4. (a) Optical view of the tip array above the sample. (b) A cartoon of the four nanostructures that each tip made using different temperatures for each nanostructure, corresponding to the range of voltages, 9.0 to 10.5 V.

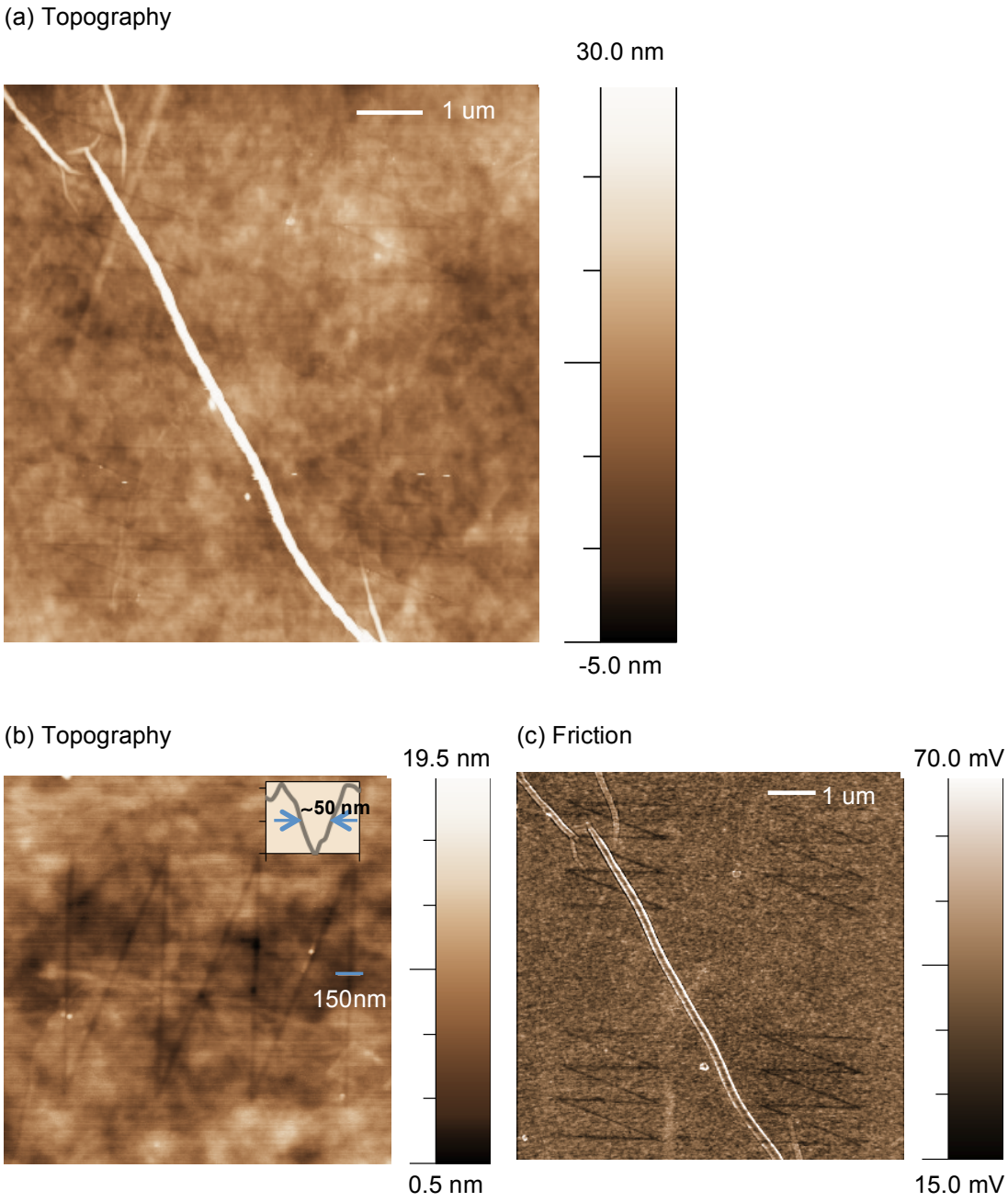

FIG. S5. (a) Topography of the four rGO zig-zag nanostructures made by tip 1. (b) Zoomed in and 90^{o} turned topography image of the bottom left nanostructure in (a). (c) Friction of the four nanostructures made by tip 1.

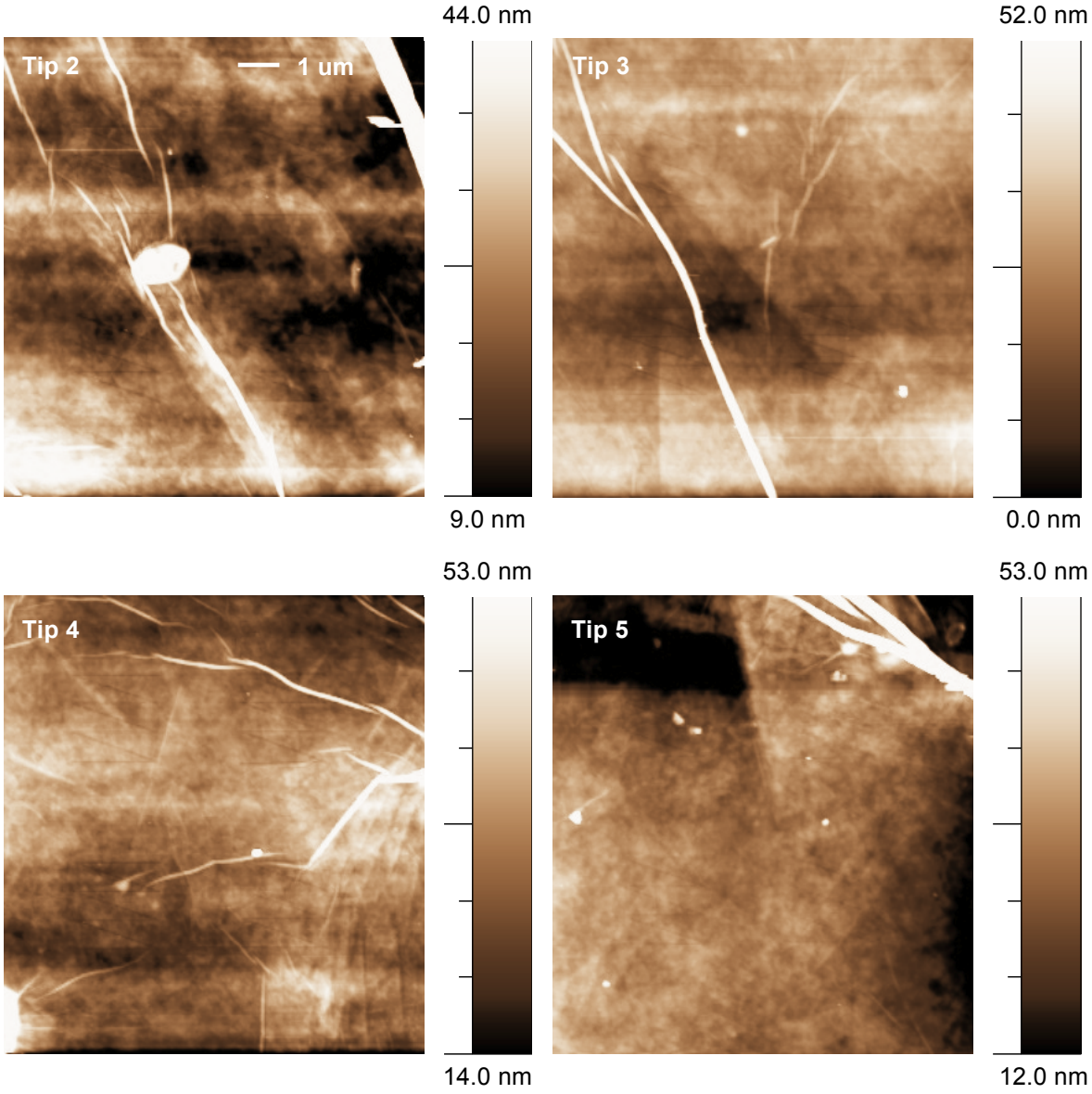

FIG. S6. Topography of rGO nanostructures made by tip 2, 3, 4, and 5, and measured by one of the cantilevers in the array.

Notes and references

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1. Nelson, B. A.; King, W. P., Temperature Calibration of Heated Silicon Atomic Force Microscope Cantilevers. *Sens. Actuators, A* **2007,** *140*, 51-59.
2. Kim, H. J.; Dai, Z.; King, W. P., Thermal Crosstalk in Heated Microcantilever Arrays. *Journal of Micromechanics and Microengineering* **2013,** *23*, 025001. And, S.

Somnath, H.J. Kim, H. Hu, W.P. King, Parallel Nanoimaging and Nanolithography using a Heated Microcantilever Array, Nanotechnology, 25 (2014) (accepted).

3. Hummers, W. S.; Offman, R. E., Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958,** *80*, 1339-1339.