Supporting Information

Inkjet Printing of Conductive Inks with High Lateral Resolution on Omniphobic "R^F Paper" for Paper-Based Electronics and MEMS.

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Experimental

Fabrication of R^H and R^F papers. The silanizing reagents: tris(dimethylamino)silane (TDAS), tricholoromethylsilane (CH_3SiCl_3, "$C_1{}^H$"), trichlorodecylsilane ($CH_3(CH_2)_9SiCl_3$, "$C_{10}{}^H$"), trichloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane ($CF_3(CF_2)_7CH_2$-CH_2SiCl_3, "$C_{10}{}^F$"), were purchased from Gelest Inc (Morrisville, PA). All chemicals were used as received without further purification. Canson tracing paper, Model No. 702-321, and Canson Vellum paper, Model No. 702-442 were purchased from Blick Art (Cambridge, MA, USA) and used as received. Whatman #1 Chromatography Paper was purchased from GE Healthcare (NJ, USA) and used as received.

The silanization reaction was conducted in a chamber with a volume of 0.01 m^3 at a temperature set at 105 °C. The silanizing reagent was transferred into a glass vial and placed inside the chamber together with the samples. Each experiment typically required ~100 mg of silane in 5 mL of anhydrous toluene. The silane was vaporized at 105 °C under reduced pressure (~30 mbar, ~0.03 atm) and allowed to react for 5 minutes. Diffusion inside the reaction chamber was sufficient for an even distribution of the silane within the chamber.

Inkjet printing: All inkjet printing was performed using a Fuji Dimatix DMP-2831 which dispensed inks using the Fuji Dimatix model waveform. Droplets were dispensed from a 10 pL cartridge; drop spacing was set at 20 μm and printing frequency at 5-10 kHz (except for the electroadhesive pad which used a 1 pL cartridge with a drop spacing of 9 μm). The Fuji Dimatix model waveform used an ejection voltage of 40V (except for the minimum wire resolution test that used an ejection voltage of 18-24V). The nozzles were heated to 30-33°C with a vacuum of 4 in H_2O for silver inks and 5 in H_2O for Methode 3801 carbon ink.

Characterization of the solvent resistance of printed conductive features on omniphobic R^F paper. Solvents were used as received: anhydrous ethanol (Pharmco-Aaper, 200 proof, absolute), *n*-hexadecane (Sigma-Aldrich, anhydrous, ≥99%), chloroform (Sigma-Aldrich, anhydrous, ≥99%), acetone (Sigma-Aldrich, anhydrous, ≥99%), acetic acid (Sigma-Aldrich, glacial), (DMSO (Sigma-Aldrich, anhydrous, ≥99%), glycerin (Sigma-Aldrich, anhydrous, ≥99%), toluene (Acros, spectrophotometric grade 99+%), dimethylsulfoxide (DMSO, Sigma-Aldrich, anhydrous 99.9%). Water is ultrapure and deionized (resistivity = 18.2 MΩ-cm).

In each solvent test, 10 distinct drops (volume = 50 μL) were added along the conductive path of each individual printed wire. The resistance of the wire was measured before the addition

of the drops, and 30 minutes after it, using the test leads of a digital multimeter. For each solvent, the procedure was repeated for seven distinct wires.

Contact angle measurements. The contact angle measurements were performed using a contact angle measurement system (Ramé-Hart model 500-F1, Ramé-Hart Instrument Co.) at room temperature (20 – 25 °C) with ~20% relative humidity. The droplet volume for the measurement was ~10 µL (unless otherwise specified). The droplet profile was fitted to a spherical profile using the software provided by the system (DROPimage Advanced, v. 2.0).

Polymeric films used as substrates for printing: The Melinex ST506/500 films were provided by DuPont Teijin Films.

Inkjet inks: The following inks were printed on Melinex ST506/500, C_1^H treated Canson tracing paper and C_{10}^F treated Canson tracing paper to compare the resistance of different combinations of substrate and ink: DGP 40-LT-15C (Advanced Nano Products), reactive silver ink (Electroninks Inc.), and carbon ink 3801 (Methode Electronics Inc.).

Scanning electron microscopy: SEM data was collected on unmetalized samples using a Zeiss Ultra Plus FESEM with an Extra High Tension of 2kV and a working distance ranging from 8.9 mm-9.7 mm collected with a positively biased Everhart-Thornley detector.

Resistance measurements: The resistance of the wires was measured using the test leads of a digital multimeter.

MEMS. The MEMS pattern was printed in three passes. For the MEMS deflection sensor, we manually applied Ercon 3456 silver ink to the ends of each cantilever to improve electrical connections with the voltage sensing pins of the testing apparatus.

Theory of wetting. The wettability of the substrate dictates how well the inkjet printed fluids will wet and spread. The spreading parameter (Equation 1), where γ_{SV}, γ_{LV}, and γ_{SL} are the solid–vapor, liquid–vapor, and solid–liquid surface energies per unit area, respectively, describes the thermodynamic criterion for equilibrium wetting of chemically homogenous smooth solid substrates. When $S \geq 0$, the process is accompanied by a decrease in free energy and the liquid displaces the vapor phase, wetting the substrate completely; when $S < 0$, the liquid forms a drop with a definite angle of contact between the liquid phase and the solid substrate. [1]

$$S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (1)$$

The interfacial interaction leading to the formation of a drop on the surface is described by Young´s equation (Equation 2): [1]

$$cos\,\theta_s = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

[1] A. W. Adamson, A. P. U. Gast, *Physical Chemistry of Surfaces*, Wiley, 1997.

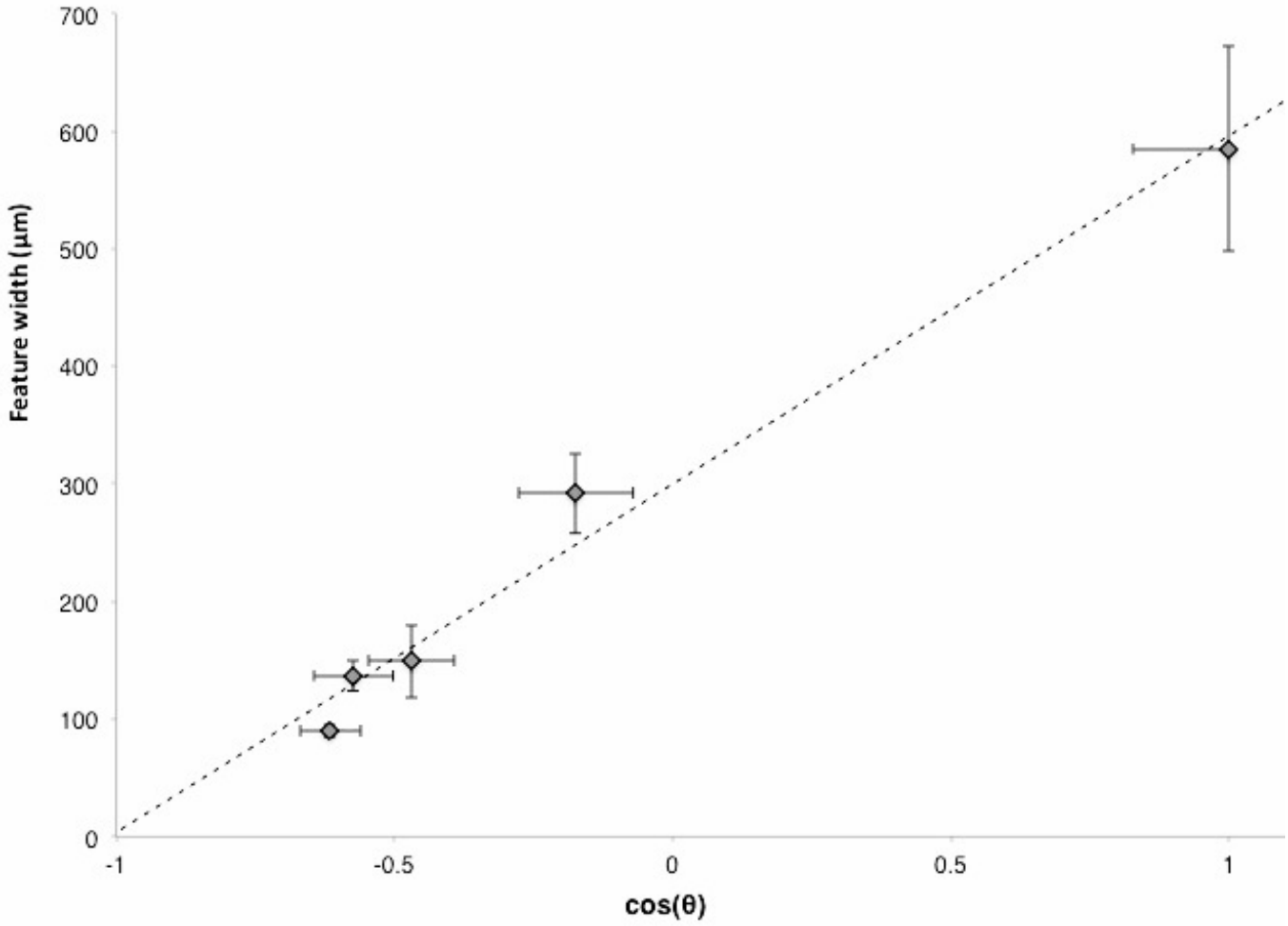


Figure S1: Relationship between the width of features printed on a modified or unmodified paper, and the contact angle of water on the respective surface. The data is fitted to a linear trendline with the equation: $y = 296.12x + 299.9$, $R^2=0.98$.

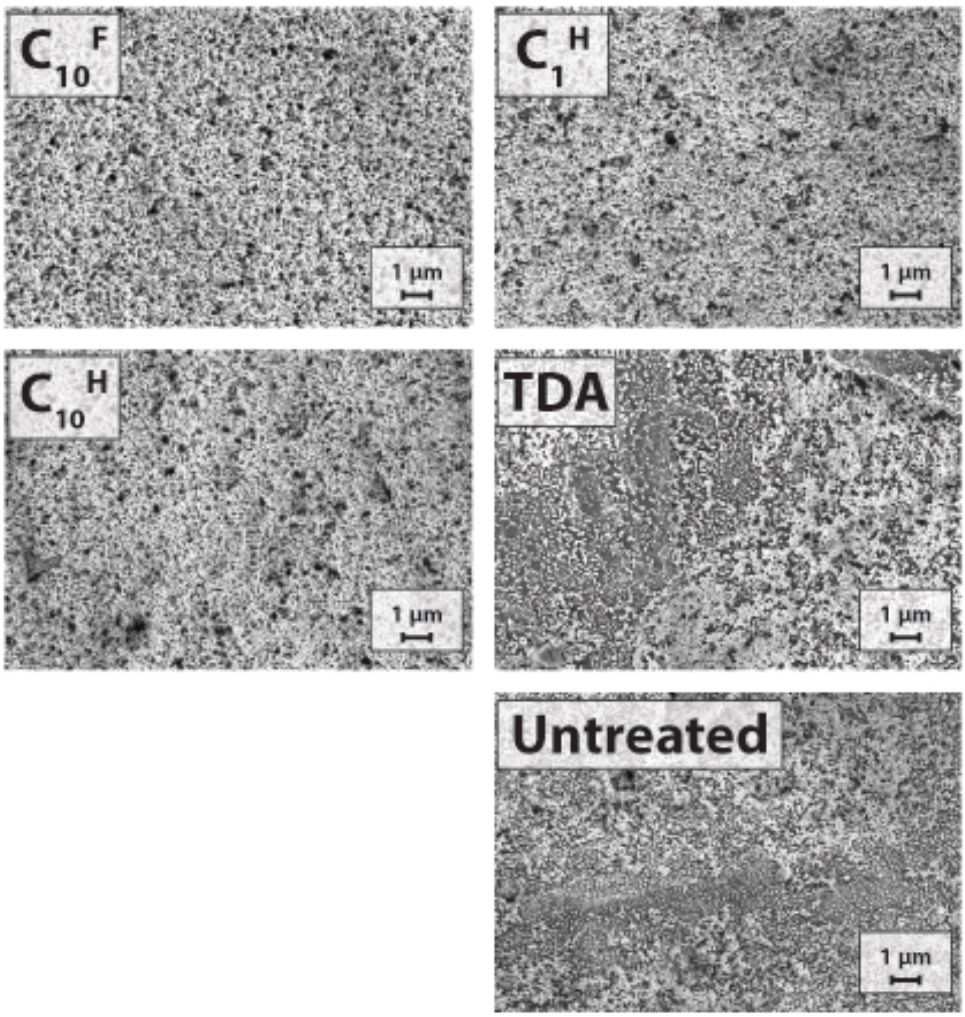


Figure S2. SEM images of reactive silver ink printed on treated and untreated papers.

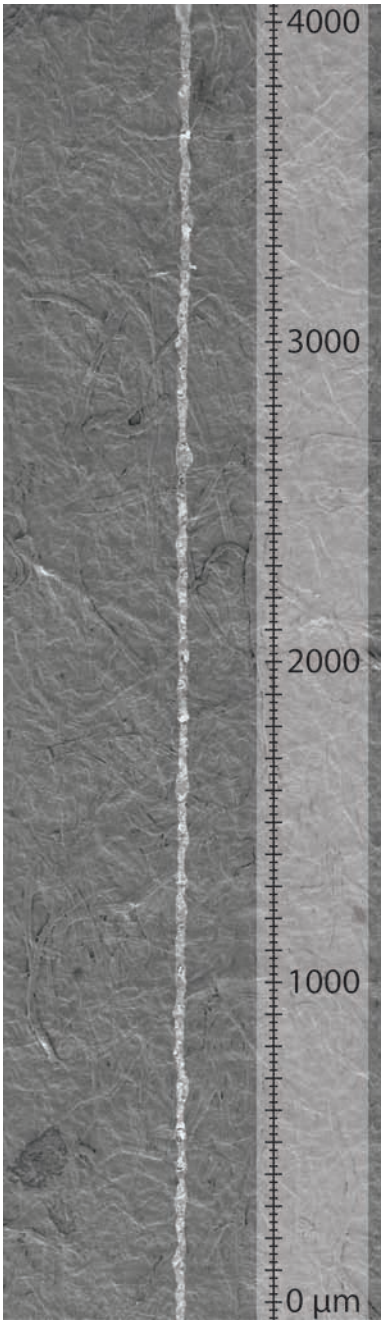
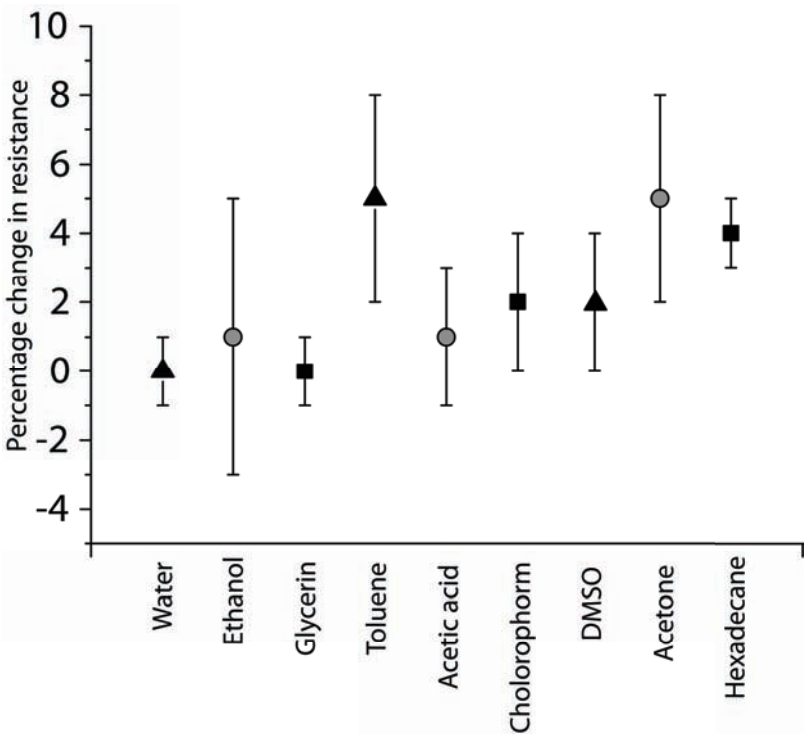


Figure S3: SEM image of a 4 mm-long silver feature printed using 10 pL droplets of reactive silver ink, with 20 µm spacing between drops, on C_{10}^{F}–treated Canson tracing paper. The feature depicted here has an average width of 28 ± 5 µm (*n*=41) and a line edge roughness of



σ_{LER} = 6 μm (*n*=41).

Figure S4: Percentage change in resistance following exposure of wires printed on C_{10}^{F} omniphobic paper to solvent. Ten 50 μL drops of solvent were deposited along the path of each 1 mm wide, 10 cm-long wire (*n*=7 wires were tested per solvent) printed with reactive silver ink, and the end to end resistance was measured before and after solvent exposure.

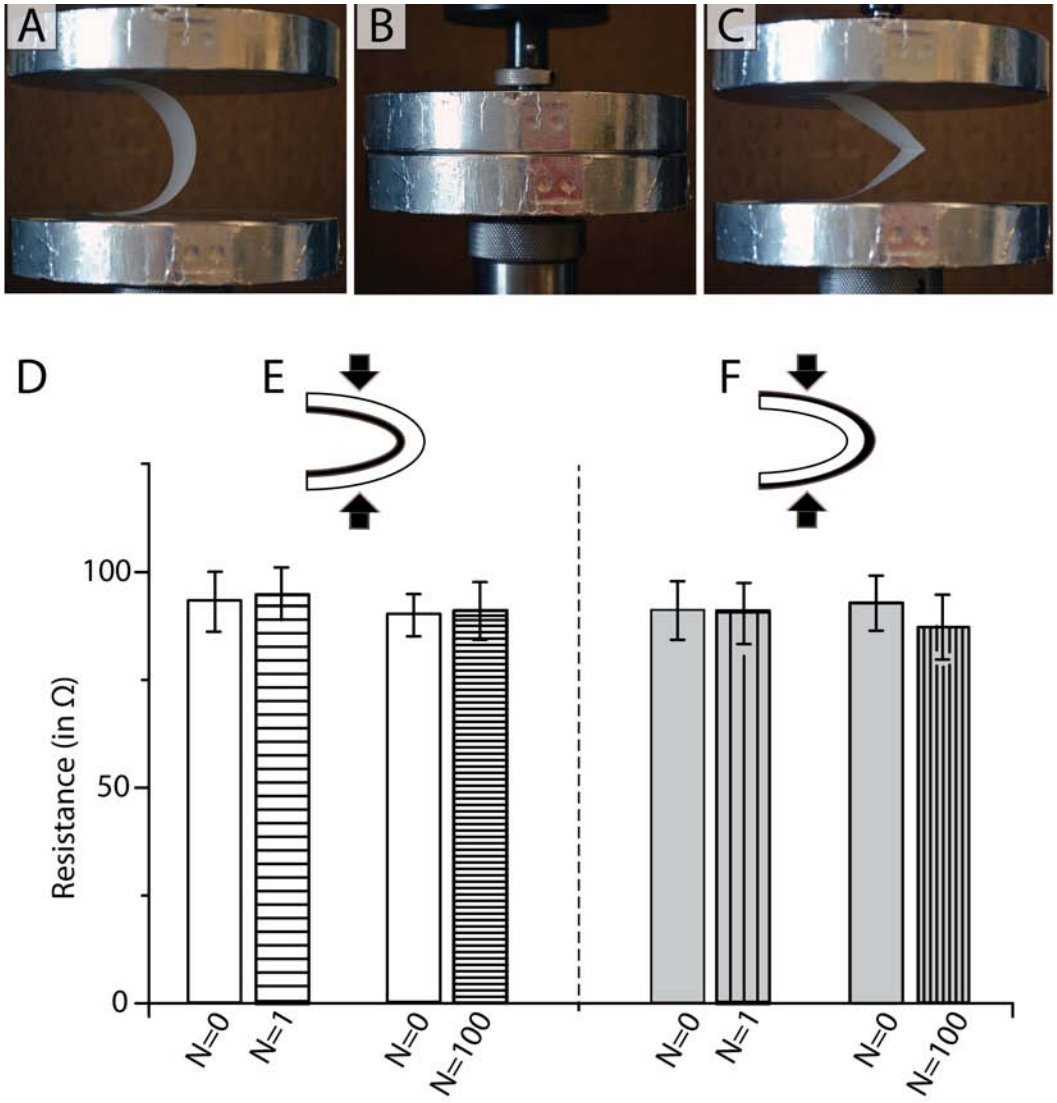


Figure S5: Resistance to creasing of printed conductive features: (A, B, C) Images of the test specimens undergoing a creasing cycle. (D) No significant increase in the respective electrical resistance was observed for the conductive prints relative to their initial, as-printed state, when the creasing occurs with the silver features either in (E) compression or in (F) extension.