

Supporting Information

Wet Transfer of Inkjet Printed Graphene for Microsupercapacitors on Arbitrary Substrates

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Experimental Methods

Formulation of graphene inks

The graphene inks were formulated through the electrochemical exfoliation of graphite as previously reported.^{1,2} Briefly, a graphite sheet as positive electrode and platinum as negative electrode were inserted in 0.1 M (NH₄)₂SO₄ solution and biased at a DC voltage of 10 V for 40 min. The so-obtained graphite flakes were rinsed first with deionized water and then with dimethylformamide (DMF) for 3 times each. Next, the graphite flakes were collected in DMF and dispersed through ultrasonication for 2 hours. The graphene flakes were then separated from the heavier graphite flakes with centrifugation (3 000 rpm for 10 minutes). Finally, after a second centrifugation (10 000 rpm for 10 minutes), the supernatant was removed and the solvent exchanged with a 75:25 v/v mixture of cyclohexanone (Sigma-Aldrich, product number: 398241) and terpineol (Sigma-Aldrich, product number: 86480) containing 20 mg ml⁻¹ of ethyl cellulose (4 cp for 5 w/v% in 80:20 toluene:ethanol, Sigma-Aldrich, product number: 200646), followed by redispersion of the graphene flakes through ultrasonication. The final ink concentration was found to be 1.5 mg ml⁻¹.

Printing

The graphene honeycomb patterns and the micro-supercapacitors (MSCs) were fabricated by inkjet printing of the graphene inks on a copper substrate. The inkjet printer used was a DMP 2800, Dimatix-Fujifilm Inc. equipped with a 10 pL cartridge (DMC-11610). All the printed MSCs were printed with 20 printing passes, drop spacing of 30 μm, platen temperature of 50°C and 20 V of nozzle firing voltage. After printing, the MSCs were annealed in nitrogen atmosphere for 2 hours at 400°C.

Since the MSCs include a gap between the interdigitated fingers causing the structure to drift apart during the transfer process, before printing the graphene flakes two lines were printed with a polyimide ink (UTDPI-IJ, UtDots Inc.) with 3 printing passes, drop spacing of 30 μm, platen temperature of 55°C and nozzle firing voltage of 20 V. The polyimide lines were then cured at 130°C for 1 hour and at 250°C for 1 hour.

Graphene film transfer

The so-obtained graphene structures were transferred on the desired substrate with a wet transfer process. First, the devices were let float on a FeCl₃ solution (6% w/v FeCl₃ in deionized water) until the copper substrate completely dissolved. Then, the patterns were collected with a glass slide and placed into deionized water. In order to remove any FeCl₃ residue, the patterns were then moved into an HCl solution (25% v/v HCl in deionized water) and then placed in deionized water. In case the target substrate was hydrophobic, the sample was placed in an isopropyl alcohol solution (up to 15% v/v isopropyl alcohol in deionized water). Except plants and fruits, all the substrates used were supplied by Modulor GmbH.

Electrochemical measurements

Cyclic voltammetry (CV), galvanostatic-charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed in a 2 terminal configuration using a Biologic VMP2 potentiostat. Silver glue and copper tape were used to improve the contact between the graphene electrodes and the external connection to the potentiostat. Also, like in most research in literature, no packaging was used during the characterization since the interdigitated structure of the electrodes prevents short circuits and the electrolyte is solid and leak-free.

The areal capacitance was calculated from the CV and GCD curves. In the first case, Equation 1 was used:

$$C_A = \frac{\int_0^{\Delta V} (I_c - I_D) dV}{2Av\Delta V} \quad (1)$$

Where I_c and I_d are the charging and discharging curves respectively, A is the device area (excluding finger gaps), v is the scan rate and ΔV is the voltage window.

In the case of areal capacitance from GCD curves, Equation 2 was used:

$$C_A = \frac{I\Delta T}{A\Delta V} \quad (2)$$

Where I is the charging and discharging current density, A is the device area (excluding finger gaps), ΔT is the discharging time and ΔV is the voltage window.

The cycle life of the MSC on polystyrene was determined with GCD for 11 000 cycles at a current density of $50 \mu\text{A cm}^{-2}$. The areal capacitance was extracted for each 500th cycle with Eq. 2. The data acquisition started from the first cycle with no stabilization period.

Contact angle measurements

The contact angle measurements were performed with a CAM200 contact angle meter (KSV Instruments Ltd) and the drop shape analysis was performed with the OneAttension software (Biolin Scientific AB). The analysis was performed by computing the average of the contact angles on the right and left side of a $3 \mu\text{l}$ H_2O droplet 10s after it touched the substrate. For each substrate, at least 3 measurements were performed and their average was extracted.

Transfer misalignment estimation

The accuracy of our wet transfer technique was assessed on a 100 mm silicon wafer with SiO₂ as shown in Fig. S1. First, five frames were inkjet printed on SiO₂ with gold nanoink (UTDAu40, UtDots Inc.) and cured thermally at 250°C for 2 hours. Five graphene MSCs were then carefully transferred into each of these frames and dried at 70°C.

Because the gold frames have inner width and length slightly larger (330 μ m and 200 μ m respectively) than the total width and length of the MSCs, a perfect alignment would require the MSC to be placed exactly 165 μ m in the x direction and 100 μ m in the y direction from the top-left inner corner of the frame as shown in Fig. S2. The misalignment of each MSC was then calculated accordingly, with the results reported in Table S1. With this method we found the accuracy to be $\sim$ 300 μ m, corresponding to the maximum misalignment.

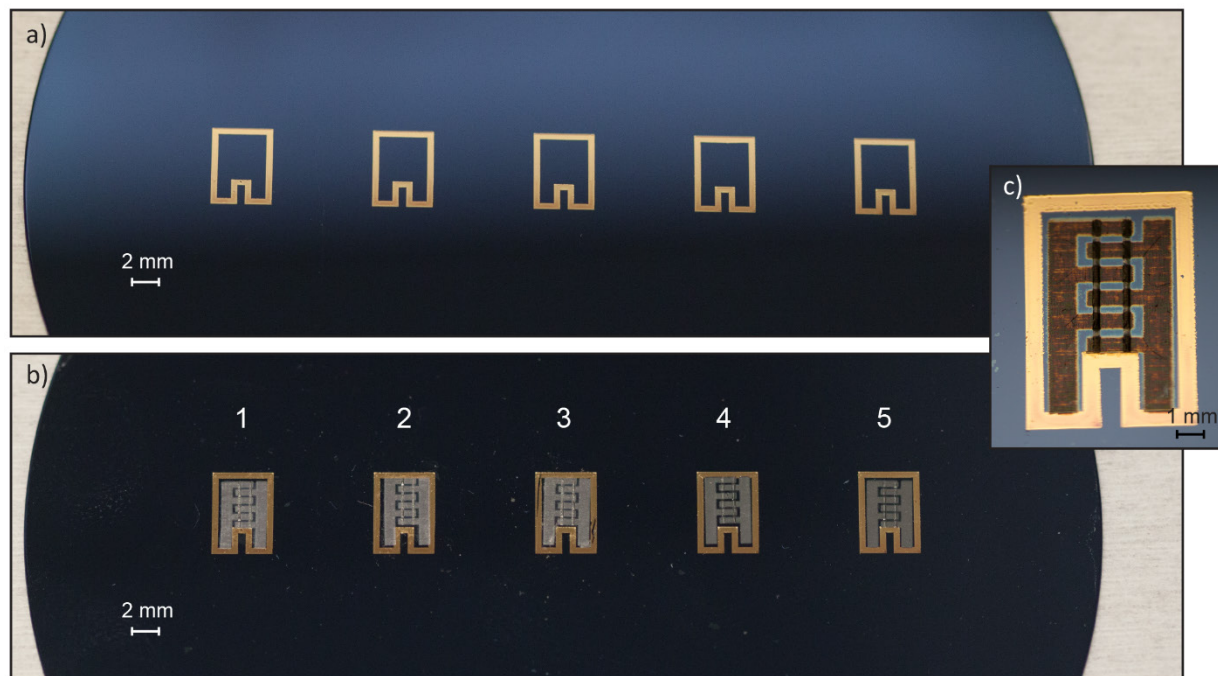


Figure S1. Optical images of the silicon wafer with gold frames used for the transfer accuracy assessment. a) Inkjet printed gold frames before MSC transfer. b) MSCs transferred into each gold frame (devices from 1 to 5). c) Close-up view of device 5.

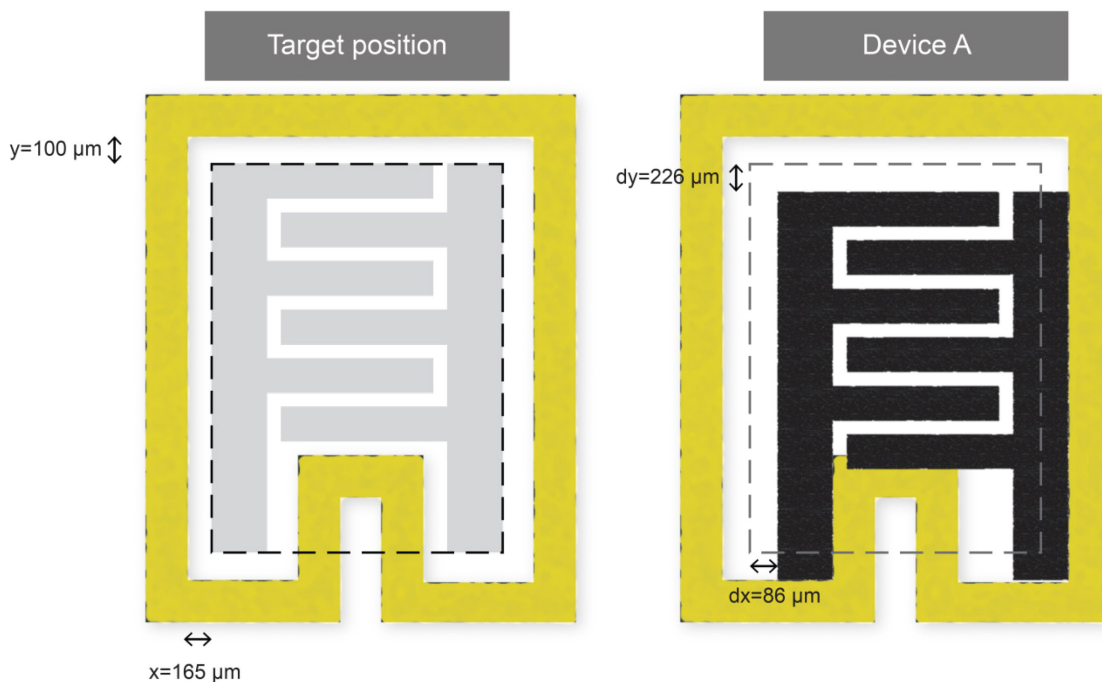


Figure S2. Diagram depicting the misalignment estimation of the MSCs enclosed in the gold frames. Since the MSCs are smaller than the inner perimeter of the gold frames, a perfectly aligned device would be placed $165\ \mu\text{m}$ in the x direction and $100\ \mu\text{m}$ in the y direction from the top-left inner corner of the gold frame. The position of each transferred MSC relative to the target position (dashed square) was then found.

Table S1. Summary of the misalignment of each MSC relative to the target position in the gold frame.

	A	B	C	D	E	Max
dx (μm)	86	257	121	28	43	257
dy (μm)	226	-108	-187	-268	137	268

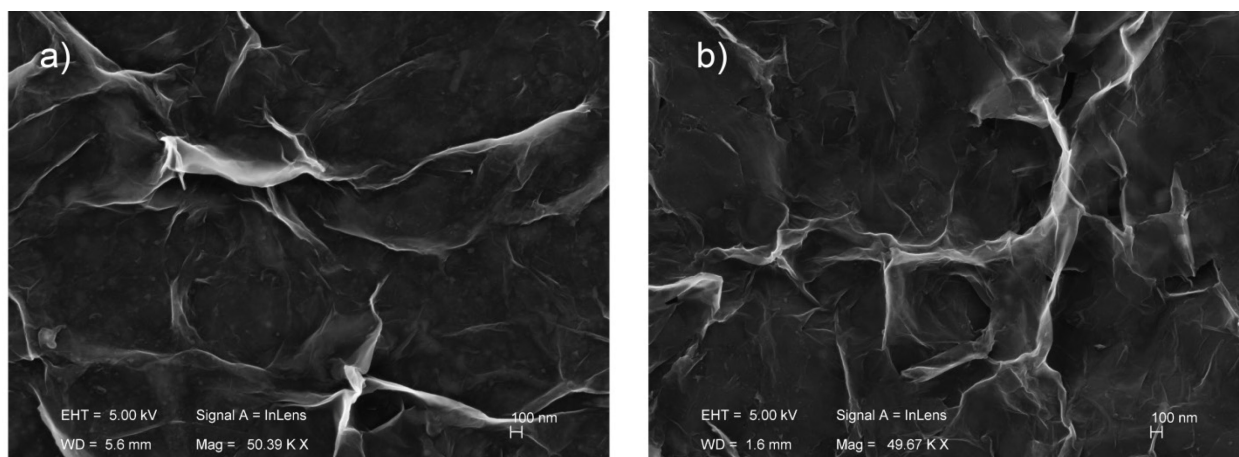


Figure S3. SEM images comparison between graphene films a) printed directly on silicon dioxide and b) printed and then transferred on silicon dioxide.

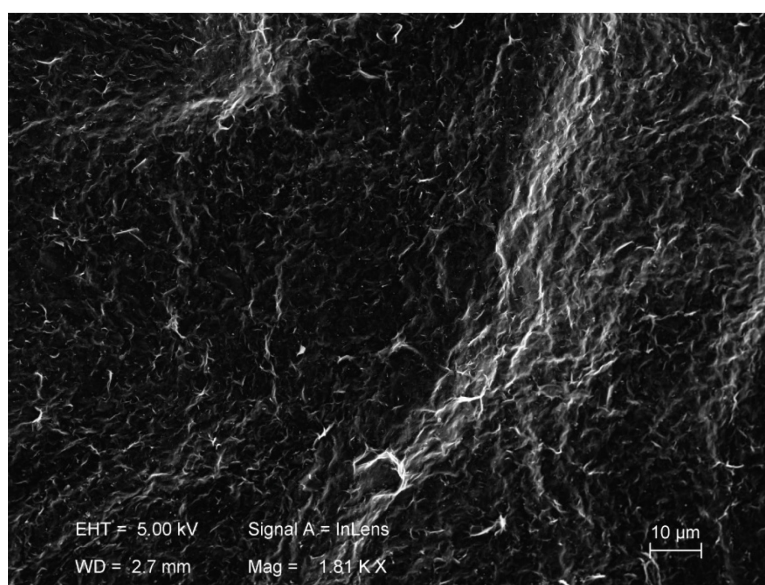


Figure S4. SEM image of a graphene film on paper. The graphene films retain the morphology of the underlying substrate, as seen by the ripples originating from the wavy texture of the paper substrate.

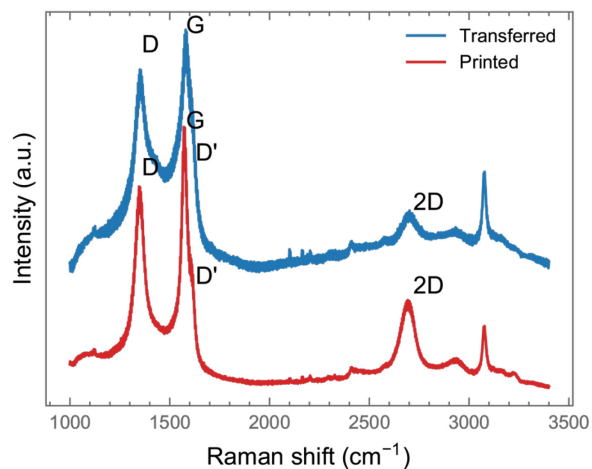


Figure S5. Comparison of Raman spectra between graphene films printed directly on silicon dioxide (red line) and printed and then transferred on silicon dioxide (blue line).

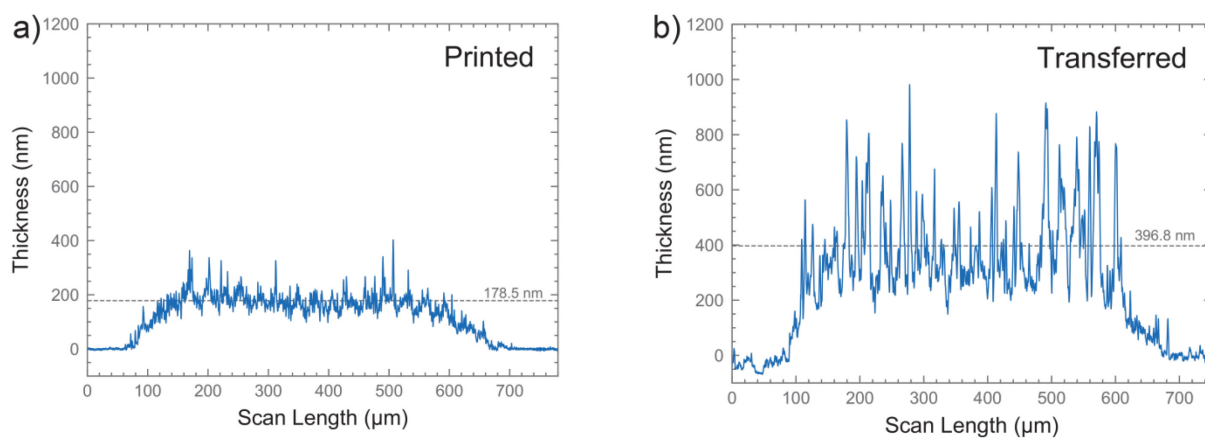


Figure S6. Profiles obtained with a profilometer showing the average thickness of the graphene films a) directly printed on silicon dioxide and b) printed and transferred on silicon dioxide. The curves are a typical profile of the graphene films.

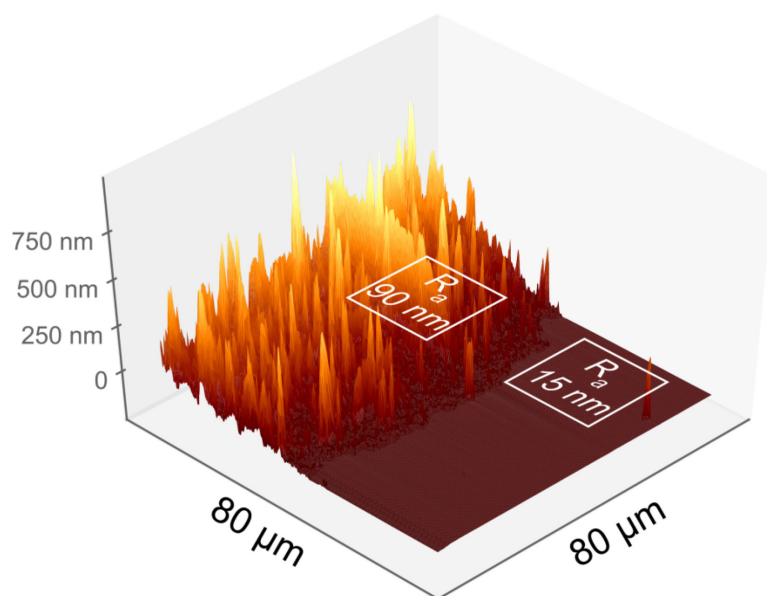


Figure S7. AFM image of a transferred graphene film on silicon dioxide comparing the roughness of the graphene film with silicon dioxide.

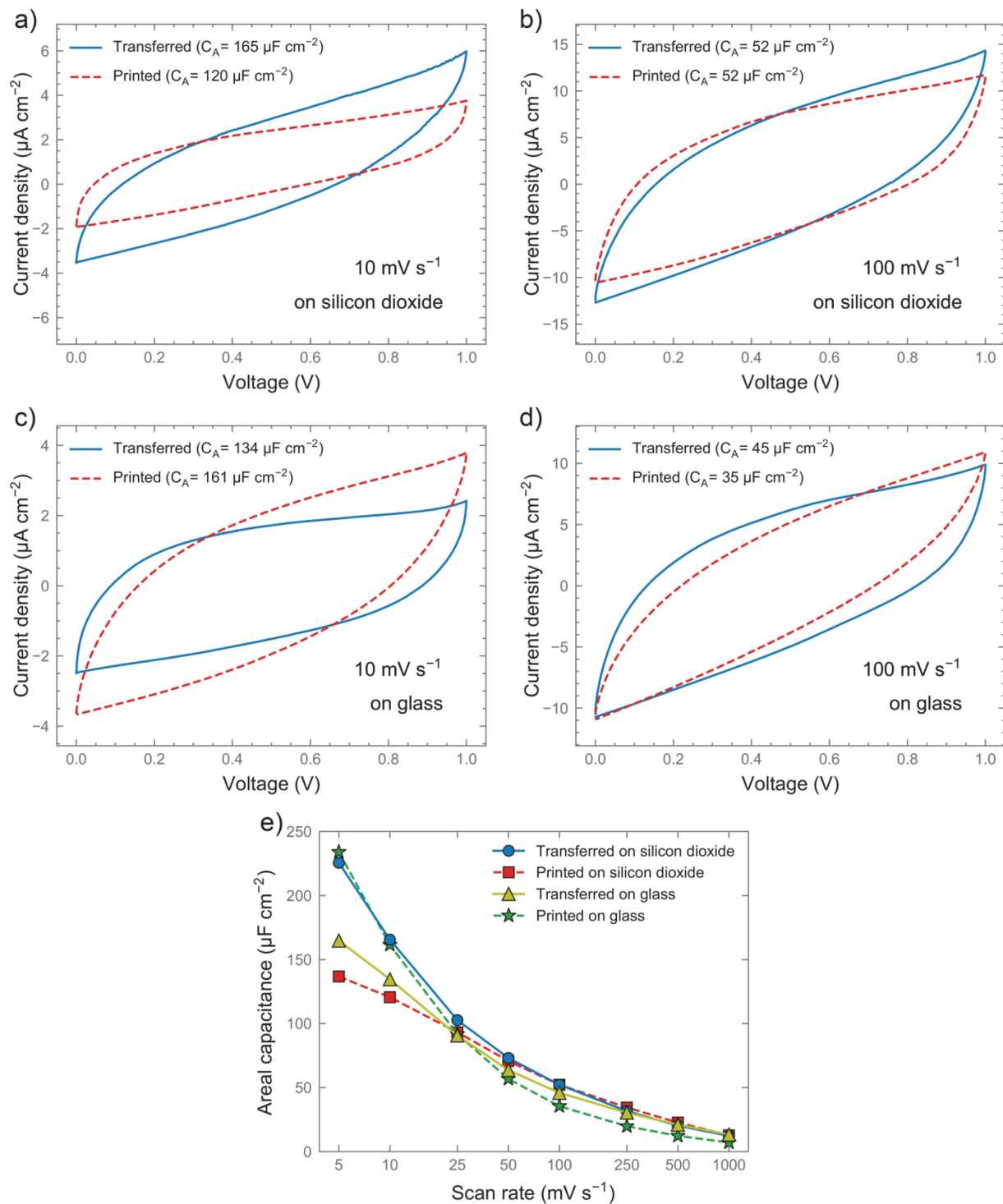


Figure S8. Cyclic voltammetry curves of micro-supercapacitors printed directly and transferred on different substrates at different scan rates. a) Devices on silicon dioxide, at scan rate of 10 mV s^{-1} . b) Devices on silicon dioxide, at scan rate of 100 mV s^{-1} . c) Devices on a microscope glass slide, at scan rate of 10 mV s^{-1} . d) Devices on a microscope glass slide, at scan rate of 100 mV s^{-1} . e) Areal capacitance of the devices (either printed directly or printed and transferred on the substrate) on silicon dioxide or glass, at scan rates from 5 mV s^{-1} to 1 V s^{-1} .

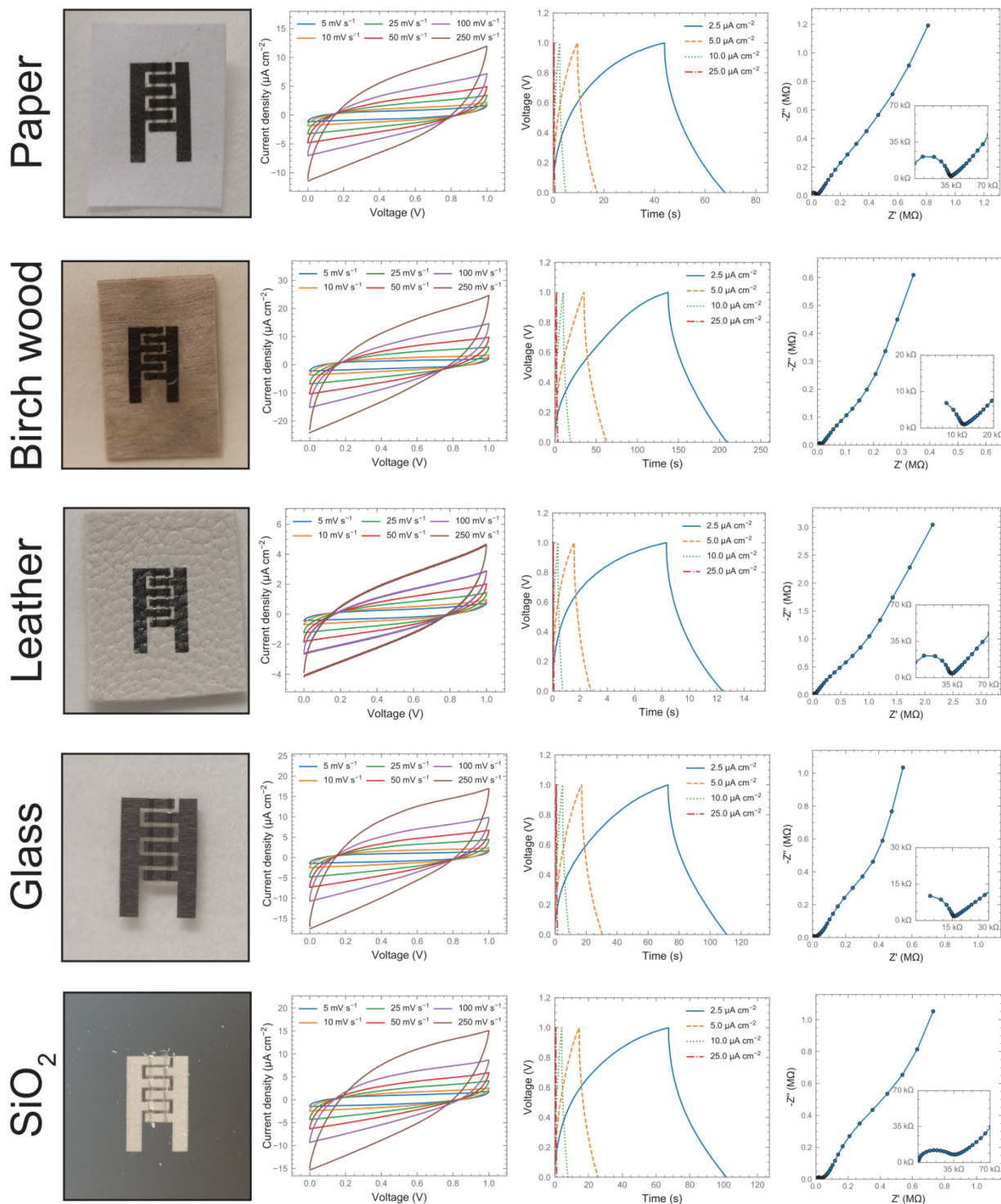


Figure S9. Summary of the electrochemical characterization of devices on various substrates. For each device, cyclic voltammetry was performed at scan rates from 5 mV s^{-1} to 250 mV s^{-1} , galvanostatic charge-discharge was performed at current densities from 2.5 $\mu\text{A cm}^{-2}$ to 25 $\mu\text{A cm}^{-2}$ and electrochemical impedance spectroscopy from 200 kHz to 10 mHz. The micro-supercapacitors were transferred on the following substrates: paper, birch wood, leather, a microscope glass slide and silicon dioxide.

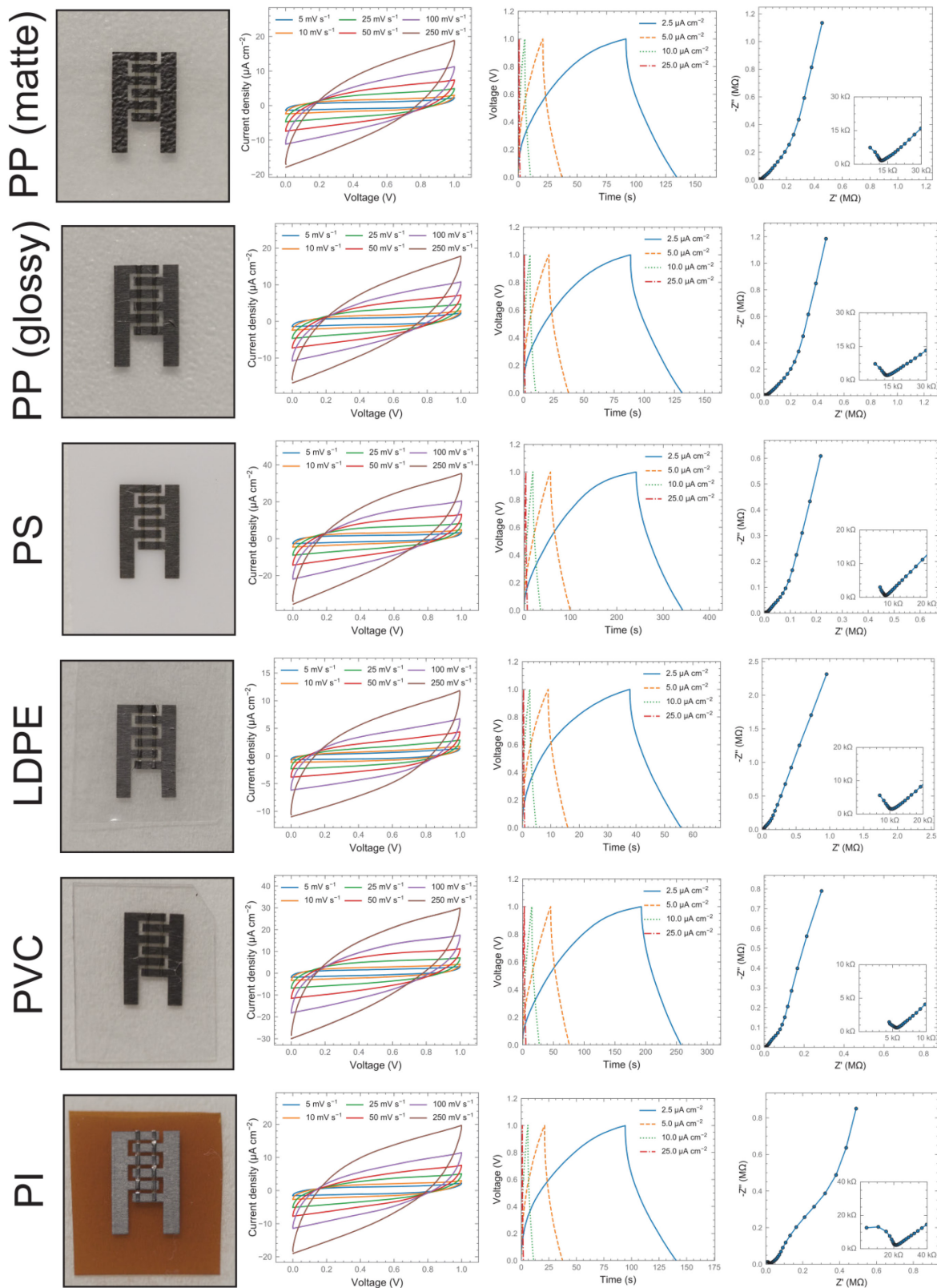


Figure S10. Summary of the electrochemical characterization of devices on various substrates. The micro-supercapacitors were transferred on the following substrates: polypropylene (matte and glossy), polystyrene, low-density polypropylene, polyvinyl chloride and polyimide (Kapton).

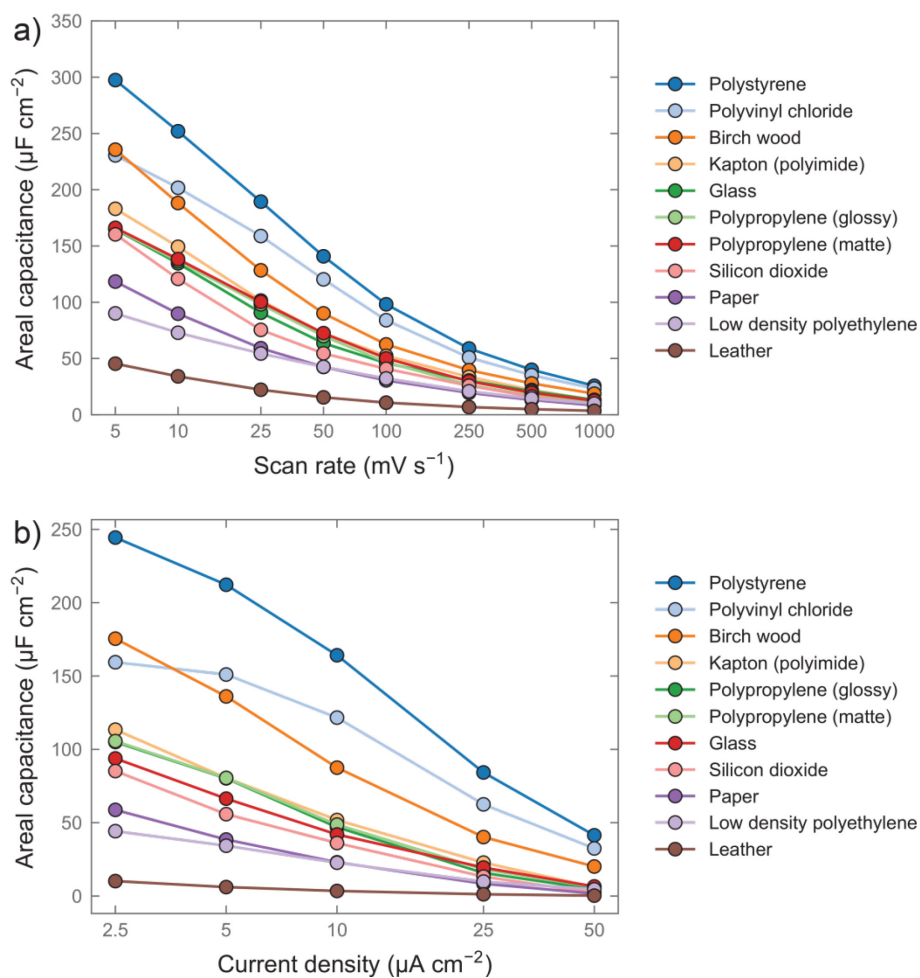


Figure S11. Areal capacitances extracted from a) cyclic voltammetry and b) galvanostatic charge-discharge of devices on various substrates.

Table S2. Contact angle measurements of non-absorbent substrates.

Substrate	Contact angle (°)	Substrate	Contact angle (°)
Glass	31.97 ± 4.89	Polypropylene (glossy)	98.16 ± 4.39
Silicon dioxide	45.71 ± 3.72	Polyvinyl chloride	98.47 ± 1.07
Kapton (polyimide)	75.45 ± 2.99	Low density polyethylene	103.23 ± 0.73
Polystyrene	94.47 ± 4.61	Leather	103.43 ± 2.40
Polypropylene (matte)	97.75 ± 3.82		

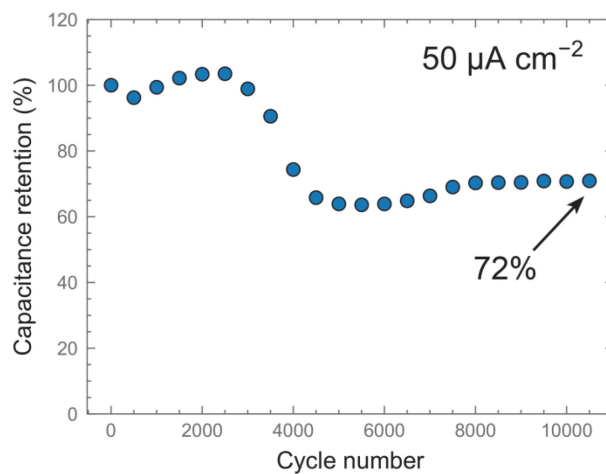


Figure S12. Cycle life of a micro-supercapacitor on polystyrene. The capacitance was extracted from galvanostatic charge-discharge measurements at current density of $50 \mu\text{A cm}^{-2}$. No stabilizing period was accounted for during this measurement, so the data were acquired from the 1st cycle.

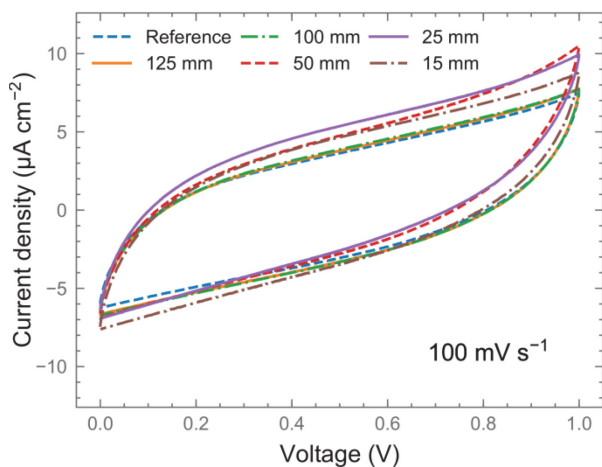


Figure S13. Cyclic voltammetry performance of a micro-supercapacitor on paper during bending at a scan rate of 100 mV s^{-1} . The legend indicates the bending radii.

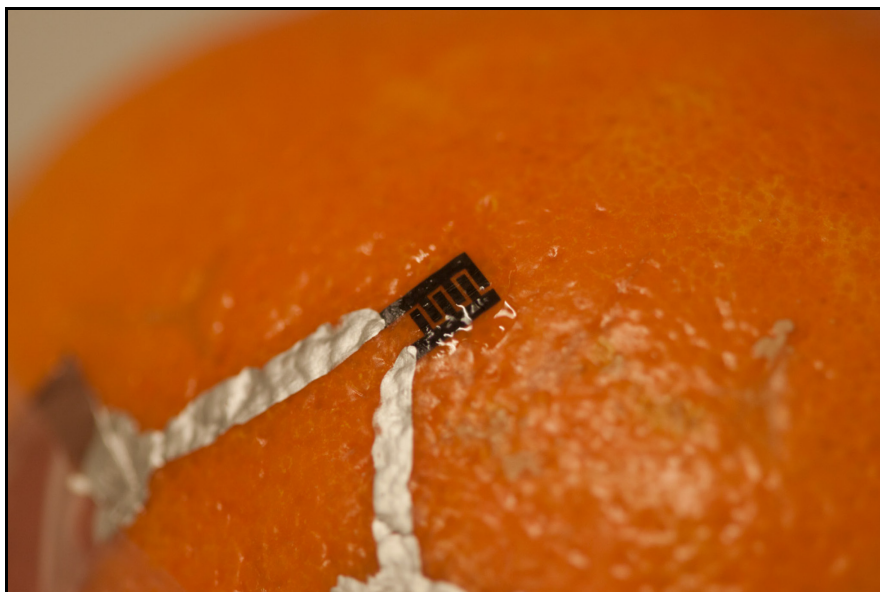


Figure S14. Photograph of a full micro-supercapacitor (transferred graphene electrodes with drop-casted gel electrolyte) on an orange during electrochemical characterization.

Table S3. Comparison of our work with the performance of supercapacitors found in literature. Only supercapacitors based on graphene and on a gel electrolyte were considered.

Material	Electrolyte	C_A ($\mu\text{F cm}^{-2}$)	C_V (F cm^{-3})	Ref.
Graphene	PVA/ H_3PO_4	80		3
Reduced multilayer graphene oxide	PVA/ H_3PO_4	394		3
Laser-scribed graphene	PVA/ H_3PO_4		0.46	4
Laser-scribed graphene	PVA/ H_2SO_4	2300	3.05	5
Graphene films	PVA/ H_2SO_4	80.7	17.9	6
Graphene	PVA/ H_3PO_4	3700		7
Printed graphene	PVA/ H_3PO_4		17.8	8
Printed graphene	Ion gel	268		9
3D printed graphene	PVA/ H_2SO_4	74310	0.83	10
Printed graphene	Printed PSSH	700		11
Printed graphene	PVA/ H_3PO_4	140		12
Inkjet printed + transferred graphene films (orchid leaf)	PVA/ H_3PO_4	441	1.16	This work

Table S4. Comparison of our work with graphene transfer techniques found in literature.

Method	Patterning	Carrier	Treatment on substrate	Substrate(s)	Graphene form	Devices	Year	Ref.
G/Ni transfer + PDMS stamping	pre	PDMS	-	PET, SiO ₂ /Si	CVD	-	2008	13
Roll-to-roll	-	thermal release tape	heat (90-120°C)	PET		transparent conducting films, touch screen panels	2010	14
Dry G/Cu transfer	-	PDMS + PMMA	heat (150°C) + Ar and N ₂ anneal + acetone bath	SiO ₂ /Si		-	2011	15
Biotransfer onto silk	-	PDMS	-	silk		wireless biosensors	2012	16
Laser-assisted transfer-printing	pre	PMMA or PDMS	not given	SiO ₂ /Si, PDMS		transparent strain sensors	2012	17
Transfer on SiO ₂ /Si + pattern + transfer on target	pre	SU-8	carrier is not removed	Textiles		GFETs, strain sensors	2014	18
PDMS stamping	pre	PDMS	carrier is not removed	PDMS		transparent strain sensors	2013	19
Multilayer G/Cu transfer	-	P(VDF-TrFE)	carrier is not removed	P(VDF-TrFE)		acoustic actuators, nanogenerators	2013	20
Clean lifting G/Cu transfer	-	-	electrostatic discharging	PET, SiO ₂ /Si, glass		GFETs, OLEDs	2013	21
G/Cu transfer	post	PMMA	heat (80°C) or hot acetone	PET/PI/SiO ₂		touch sensors	2014	22
Roll-to-Roll delamination	-	EVA/PET	carrier is not removed	EVA/PET		triboelectric nanogenerators	2015	23
Modified RCA clean G/Cu transfer	-	PMMA	heat (150°C) + acetone + isopropanol + heat (200°C)	SiO ₂		GFETs	2011	24
Support-free G/Cu transfer mediated by F-SAMs	during	-	F-SAM treatment	SiO ₂ /Si, glass, PET		GFETs	2016	25
PDMS stamping	pre	PDMS	-	PVP		OFETs	2011	26
G/Cu transfer	post	EVA	heat (80°C) + boiling xylene	SiO ₂ /Si		GFETs	2016	27
Transfer patterning with a pen	post	PTFE (membrane filter)	-	Paper	Exfoliated	various graphene circuits	2013	28
Graphene-Nanocellulose embedded in PDMS	-	PDMS	-	PDMS		strain sensors	2014	29
Transfer Printing	pre	Cytop/Si mold	O ₂ plasma + UV light curing	PET + adhesive		electrolyte gated transistors	2017	30
Wet transfer of inkjet printed graphene	pre	-	-	various (flat, rough, 2D, 3D, biological)		micro-supercapacitors	2018	This work

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