Electronic Supplementary Material (ESI) for Nanoscale.

Fully Inkjet Printed Ultrathin Microsupercapacitors Based on Graphene Electrodes and Nano-Graphene Oxide Electrolyte

Szymon Sollami Delekta,[1] Karin H. Adolfsson,[2] Nejla B. Erdal,[2] Minna Hakkarainen,[2] Mikael Östling[1] and Jiantong Li[1,]*

[1]KTH Royal Institute of Technology, School of Electrical Engineering and Computer Science, Division of Electronics, Electrum 229, SE-164 40 Kista, Sweden.

[2]KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, Teknikringen 58, SE 11428 Stockholm, Sweden

Corresponding Author

*E-mail: jiantong@kth.se

Electronic Supplementary Information

Experimental section

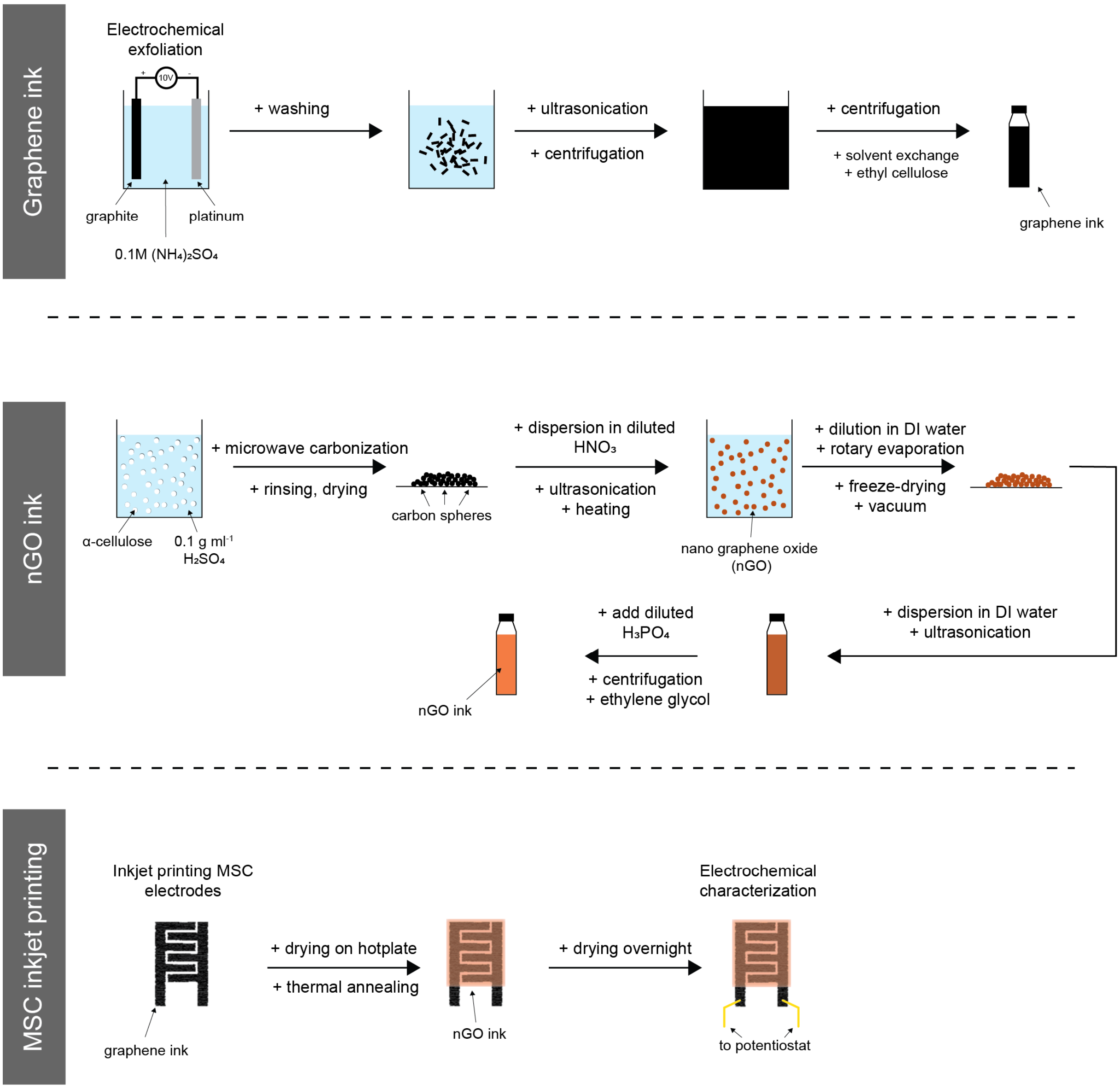

Fig. S1. Process flow showing the main formulation steps of graphene and nGO inks and the microsupercapacitor (MSC) fabrication by inkjet printing.

Graphene ink formulation. Graphene flakes were obtained through the electrochemical exfoliation of graphite in 0.1 M $(NH_4)_2SO_4$ as previously reported.[1,2] They were then collected and rinsed with deionized water and dimethylformamide (DMF). After ultrasonication for 30 min, the graphene flakes were separated from the heavier graphite powders with a centrifugation at 4 000 rpm for 10 min. Then, a high-speed centrifugation at 10 000 rpm for 10 min was used to separate the graphene flakes from the supernatant (DMF). Next, the graphene flakes were redispersed in a mixture of cyclohexanone and terpineol (volume ratio 3:1) together with ethyl cellulose (20 mg ml^{-1}) as the binder. Finally, after ultrasonication for 30 min and centrifugation at 2 000 rpm for 3 min to further remove big graphene flakes, the graphene inks were obtained. The concentration of graphene flakes was measured with a UV-Vis spectrophotometer (Lambda 750 UV/Vis/NIR spectrophotometer, PerkinElmer) to be approximately 1.8 mg ml^{-1} (**Fig. S1**).

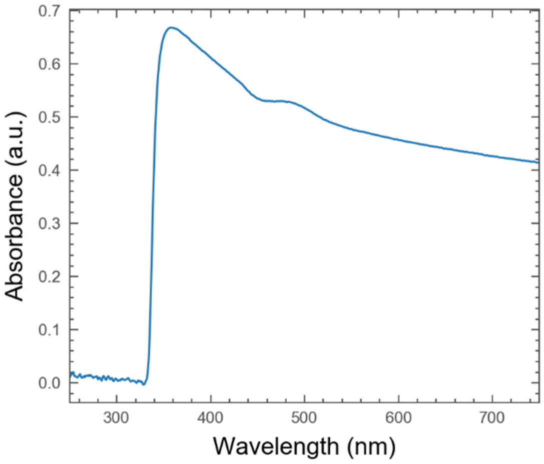

Fig. S2. Absorbance spectra of 100x diluted EG ink obtained with a UV-Vis spectrophotometer from which the concentration was calculated. The path length is 1 cm.

Nano-graphene oxide synthesis. The nGO was synthesized from cellulose derived carbon spheres (CS) according to previously reported studies.[3,4] Briefly, α-cellulose was carbonized in diluted acidic medium (0.1 g ml^{-1} H_2SO_4) using microwave technology (flexiWAVE, Milestone Inc.) for 2 h at 220°C, with a ramp time of 20 min. The resulting CS was rinsed with water and dried. To synthesize nGO, CS was bath sonicated in 70% nitric acid (HNO_3) solution (1:100 w/w) for 30 min and then placed in 90°C for 30 min under constant stirring. The reaction mixture was diluted by pouring the dispersion into cold deionized water and the red-orange solids were collected by evaporating the acidic medium via rotary evaporation. The nGO was then freeze-dried and stored in vacuum at room temperature for the removal of any residues of water or acid.

Nano-graphene oxide ink formulation. The nano-graphene oxide (nGO) was dispersed in deionized water (20 mg ml^{-1}) and sonicated for 10 min. The nGO dispersion was then mixed with a 20 mg ml^{-1} solution of H_3PO_4 in deionized water at a volume ratio of 1:1 and centrifuged at 2 000 rpm for 3 min to remove a negligible amount of sediment. Finally, the nGO inks were obtained from mixing the collected supernatant with ethylene glycol at a volume ratio of 1:1.

Device fabrication. First, the two interdigitated electrodes of the MSCs were inkjet printed with the graphene inks using a DMP 2800 (Dimatix-Fujifilm Inc.) equipped with a 10 pL cartridge (DMC-11610). While the thickness of the electrodes was controlled by varying the number of overwritten printing layers, the following printing settings were held constant: drop spacing of 30 µm, cartridge temperature of 36°C, nozzle firing voltage of 22 V, platen temperature of 45°C and printing height of 800 µm. The print was then dried at 120°C for 30 min to evaporate the solvent followed by thermal annealing at 320°C for 2 hours on a hot plate. Next, the electrolyte was printed with the nGO ink with varying number of printing layers with the following printing settings: drop spacing of 30 µm, cartridge temperature of 30°C, nozzle firing voltage of 21 V, platen temperature of 45°C, printing height of 800 µm and delay in-between printing passes of 120 s. After printing the electrolyte, the samples were dried overnight at 80°C to evaporate the solvents.

Electrochemical characterization

All the electrochemical measurements (cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy) were performed with the use of a Gamry Interface 1010E potentiostat (Gamry Instruments Inc., Warminster PA, USA) at a relative humidity of ~20% and temperature of 20°C. To improve the contact between the graphene electrodes and the potentiostat, we used a Signatone S-1160 probe station equipped with S-725-PRM micropositioners (Signatone Corporation, Gilroy CA, USA). The areal capacitance extracted from cyclic voltammetry was obtained with **Equation S1**:

$$C_{A,CV} = \frac{\int_0^{\Delta V} (I_C - I_D) dV}{2 A_{el} v \Delta V} \tag{S1}$$

where I_C and I_D are the charging and discharging currents respectively, ΔV is the voltage window (1 V), v is the scan rate and A_{el} is the geometrical area of the electrodes excluding finger gaps (0.16 cm^2). The areal capacitance was also extracted from the galvanostatic charge-discharge measurements with **Equation S2**:

$$C_{A,GCD} = \frac{|I_D| \Delta t}{A_{el} \Delta V} \tag{S2}$$

where I_D is the discharging current and Δt is the discharging time.

The power and energy densities in the Ragone plots were obtained with **Equations S3** to **S6**:

$$E_{d,el} = \frac{1}{2} \cdot \frac{C_{CV} \Delta V^2}{A_{el} / \delta_{el}} \tag{S3}$$

$$P_{d,el} = \frac{E_{d,el}}{t} \tag{S4}$$

$$E_{d,full} = \frac{1}{2} \cdot \frac{C_{CV} \Delta V^2}{A_{full} / \delta_{full}} \tag{S5}$$

$$P_{d,full} = \frac{E_{d,full}}{t} \tag{S6}$$

where C_{CV} is the capacitance extracted from the cyclic voltammetry curves, A_{el} is the area of the electrodes (0.16 cm^2), A_{full} is the area of the full device (=area of the electrolyte, 0.24 cm^2), δ_{el} is the thickness of the electrodes, δ_{full} is the thickness of the device (=thickness of the electrolyte) and $t = {}^{\Delta V}/_{v}$ is the discharging time.

Transmission Electron Microscopy (TEM) characterization

TEM was performed by preparing solution of nGO and nGO ink in deionized water at a concentration of 0.01 mg ml^{-1}. The solutions were then drop-casted on an ultrathin carbon coated copper TEM grid (Ted Pella, Inc.) and images were captured using a transmission electron microscopy HITACHI HT7700 instrument.

X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was performed using a PHI Quantera II from Physical Electronics (Chanhassen, MN, US) and the obtained spectra are shown in **Fig. S3**. The EG ink and a dispersion of nGO in deionized water were drop-cast on a silicon wafer with 100 nm SiO_2. Then, the EG sample was dried at 80°C for 30 min and annealed at 320°C for 2h while the nGO sample was dried at 80°C for 2h. The XPS spectra were acquired with the following parameters: beam size of 100 µm, power of 25 W, voltage of 15 kV, pass energy level of 55 eV, time per step of 50 ms and step of 0.1 eV. After the analysis, the baseline was removed, curve fitting was performed on the multiple peaks and the areas of each peak were found.

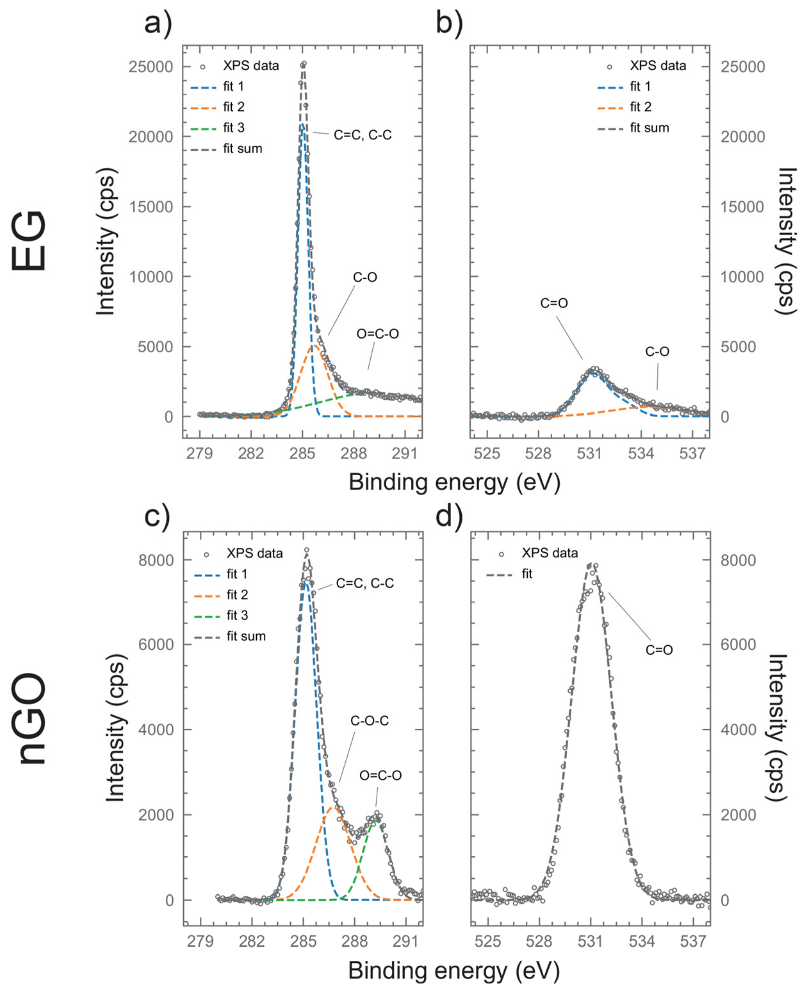

Fig. S3. X-ray photoelectron spectroscopy (XPS) analysis. Top: XPS peaks of EG in the a) C1s and b) O1s region. Bottom: XPS peaks of nGO dispersion in the c) C1s and d) O1s region. Due to a different chemical environment, the C1s peak in c) was located at 283 eV so it needed to be shifted by 2 eV for this analysis.

To find the C/O ratio of the samples, the sum of the areas of the curves (equal to the area of the fit sum curve) was found and **Equation S7** was used:

$$C/_{O} = \frac{\frac{A_{fit\ sum,C1s}}{ASF_{c1s}}}{\frac{A_{fit\ sum,O1s}}{ASF_{O1s}}} \qquad \text{(S7)}$$

where $A_{fit\ sum,C1s}$ and $A_{fit\ sum,O1s}$ are the areas under the C1s fit sum and the O1s fit sum curves respectively, while ASF_{c1s} and ASF_{O1s} are the atomic sensitivity factors of C1s and O1s respectively.

The results (**Table S1**) indicate the EG sample has a C/O ratio of 7.78 which is comparable to the literature[1], although it is not extraordinary. Possible causes are: (1) the small lateral size of the graphene flakes causing large areas of the flake to be likely oxidized because close to the edges and (2) eventual –OH groups which originate from the moisture in air and remain on the surface of the sample even under vacuum.
On the other hand, the nGO sample shows an expected nGO ratio of 2.15.[3]

Table S1. Results of XPS peak analysis, showing the C/O ratios of the EG and nGO samples.

Sample	$A_{fit\ sum,C1s}$	ASF_{c1s}	$A_{fit\ sum,O1s}$	ASF_{O1s}	C/O
EG	38773	0.296	11970	0.711	7.78
nGO	20704		23088		2.15

Zeta potential measurements

Zeta potential was measured using a Zetasizer Nano ZS from Malvern Instrument (Malvern, U.K). The nGO dispersion was prepared in deionized water (1 mg ml^{-1}).

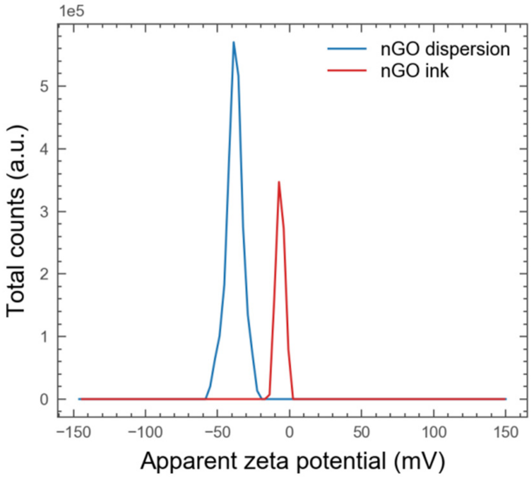

Fig. S4. Zeta potential measurements of nGO dispersion (blue line) and nGO ink (red line) showing that both samples have negative zeta potential.

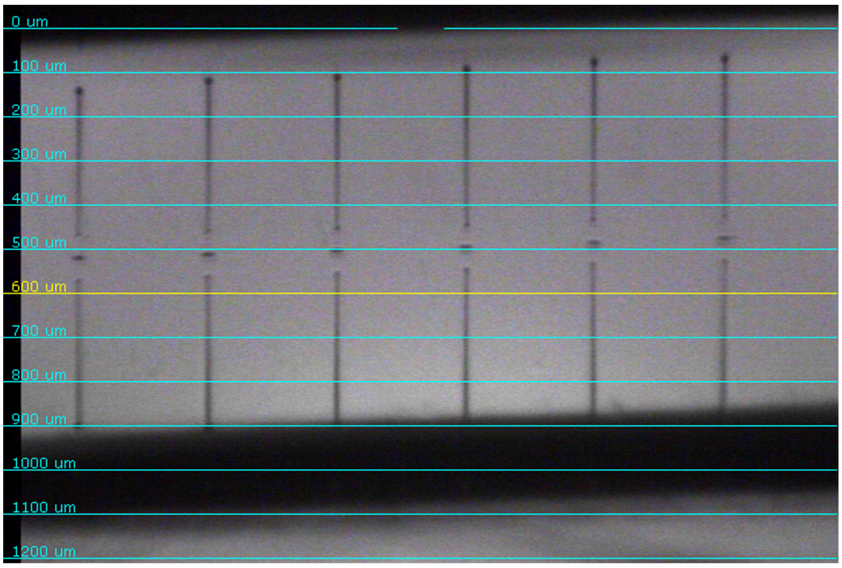

Fig. S5. Optical image from the Drop watcher camera equipped on the Dimatix DMP-2800 inkjet printer showing the jetting performance of the nGO inks.

Influence of humidity on ionic conductivity of nGO

To investigate the influence of humidity on the ionic conductivity of nano-graphene oxide (nGO), we performed electrochemical impedance spectroscopy (EIS) measurements of drop-cast nGO ink in-between two conductive lines placed in a Faraday cage. The two lines were spaced 350 µm and were obtained by inkjet printing of gold nanoink (UT Dots, Inc.) followed by sintering at 200°C for 2 hours. The resultant nGO films had width of 1700 µm and thickness of 2 µm. The ionic conductivity was obtained by fitting the EIS curves to a corresponding equivalent circuit with the Gamry Echem Analyst software. The equivalent circuit model consisted of electrode resistance in series with a parallel combination of a constant phase element (CPE) and electrolyte resistance in series with a Warburg element. The humidity was controlled with a commercial humidifier or by introducing dry air in the Faraday cage. The EIS measurements were performed after 20 minutes since a constant humidity baseline was established. A reference humidity sensor (HIH-4000, Honeywell International Inc.) was used for reading the humidity.

Equation S8 was used to calculate the ionic conductivity:

$$\sigma = \frac{1}{R_e}\frac{L}{A} \qquad \text{(S8)}$$

where R_e is the resistance of the electrolyte obtained by fitting the EIS curve, L is the spacing between the two Au lines and A is the area of the nGO film in-between the two Au lines. For example, the ionic conductivity at RH=22% was extracted as follows:

$$\sigma = \frac{1}{2.8 \times 10^{5}\ [\Omega]} \frac{3.5 \times 10^{-2}\ [cm]}{0.17\ [cm] \times 2 \times 10^{-4}\ [cm]} = 3.6 \times 10^{-3}\ [S \cdot cm^{-1}]$$

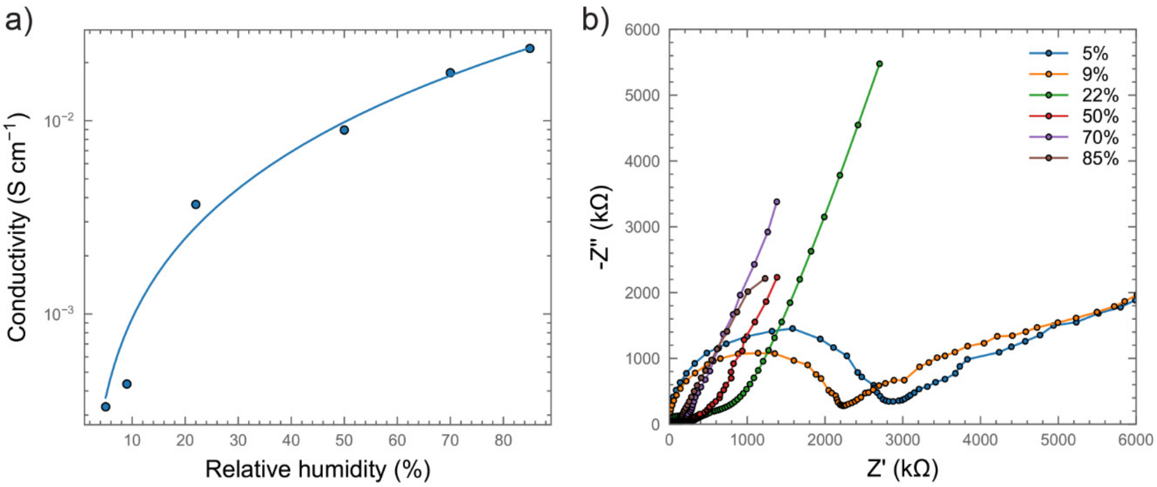

Fig. S6. Ionic conductivity measurements with varying humidity levels. The values in a) were extracted from the electrochemical impedance spectra in b).

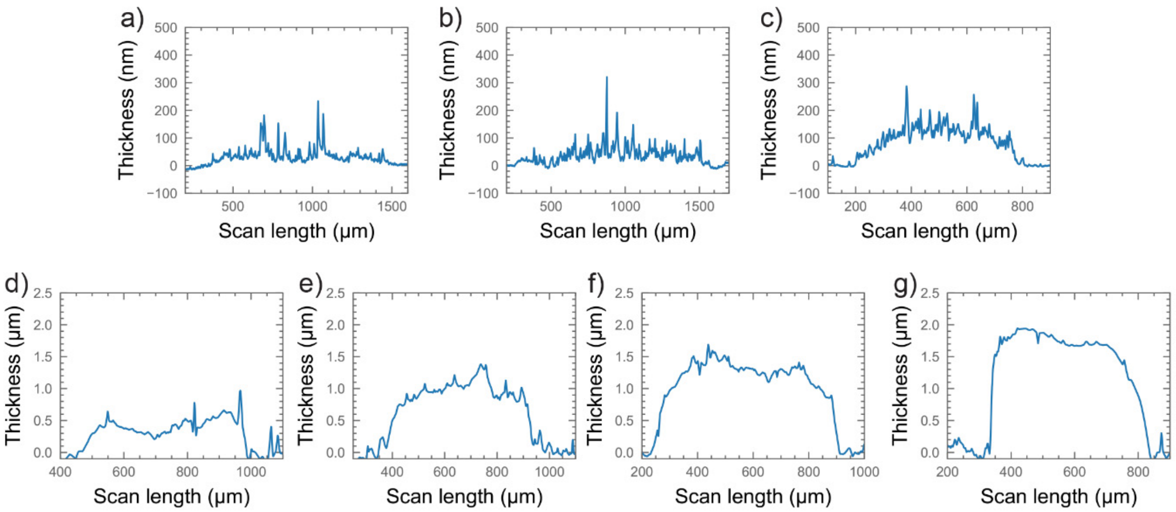

Fig. S7. Profiles of the films constituting the microsupercapacitors. The scans were performed on the samples a) EG5L, b) EG10L, c) EG20L, d) nGO5L, e) nGO10L, f) nGO20L and g) nGO30L.

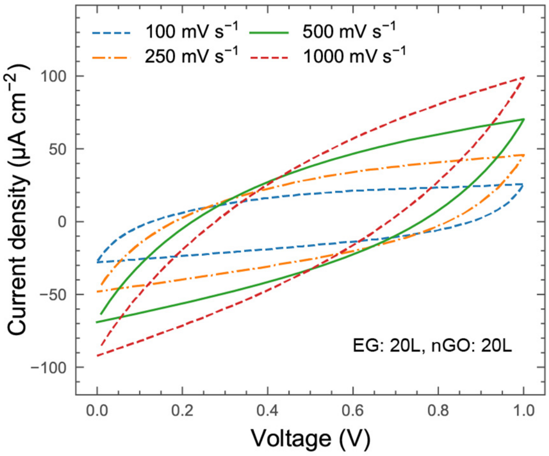

Fig. S8. Cyclic voltammetry curves of EG20L/nGO20L device at high scan rates from 100 mV s^{-1} to 1000 mV s^{-1}.

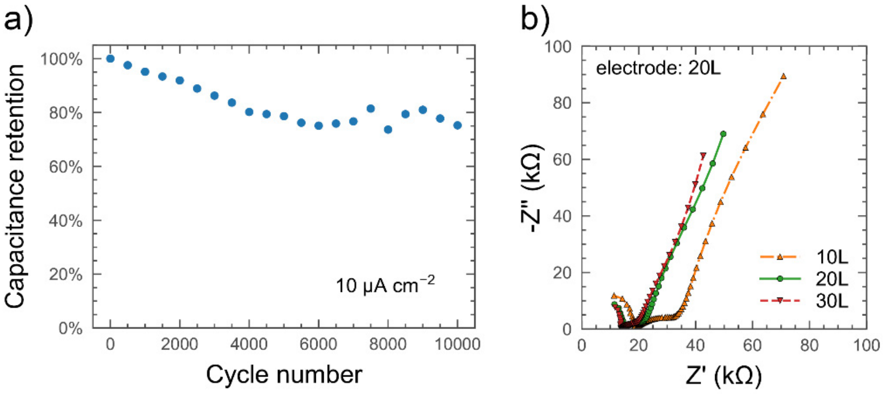

Fig. S9. a) Capacitance retention of EG20L/nGO20L device over 11 0000 cycles of GCD at 10 µA cm^{-2}. b) Electrochemical impedance spectroscopy of devices with electrode thickness 20L and electrolyte thickness 10L, 20L and 30L.

Table S2. Areal capacitances, power densities and energy densities extracted from cyclic voltammetry measurements on device EG20L/nGO20L at scan rates from 5 to 1000 mV s^{-1}.

Scan rate (mV s^{-1})	$C_{A,CV}$ (µF cm^{-2}) with A=0.16 cm^2	$P_{d,el}$ (mW cm^{-3})	$E_{d,el}$ (mWh cm^{-3})	$P_{d,full}$ (mW cm^{-3})	$E_{d,full}$ (mWh cm^{-3})
5	313	78	4.33	4.33	0.24
10	274	136.5	3.79	7.58	0.21
25	233	290.63	3.23	16.15	0.18
50	191	476.25	2.65	26.46	0.15
100	141	705	1.96	39.17	0.11
250	83	1031.25	1.15	57.29	0.06
500	51	1275	0.71	70.83	0.04
1000	27	1350	0.38	75	0.02

References

1 K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2014, **136**, 6083–6091.

2 J. Li, S. Sollami Delekta, P. Zhang, S. Yang, M. R. Lohe, X. Zhuang, X. Feng and M. Östling, *ACS Nano*, 2017, **11**, 8249–8256.

3 K. H. Adolfsson, S. Hassanzadeh and M. Hakkarainen, *RSC Adv.*, 2015, **5**, 26550–26558.

4 S. Hassanzadeh, N. Aminlashgari and M. Hakkarainen, *ACS Sustain. Chem. Eng.*, 2015, **3**, 177–185.