Flexible, Low-cost and Scalable Nanostructured Conductive Paper-Based, Efficient Hygroelectric Generator

Kelly S. Moreira[a], Diana Lermen[a], Leandra P. dos Santos[c], Fernando Galembeck[c] and Thiago A. L. Burgo,*[,a,b]

[a]*Department of Chemistry and* [b]*Department of Physics, Federal University of Santa Maria, Santa Maria, RS, Brazil, 97105-900.*
[c]*Institute of Chemistry, University of Campinas, Campinas, SP, Brazil, 13083-970.*

1. EXPERIMENTAL PROCEDURES

1.1. ERG – coated paper preparation

Graphite powder was dispersed in an aqueous cellulose solution under stirring, to allow its dispersion, stabilization and exfoliation. The final composition of the aqueous dispersion was 4% cellulose, 7% NaOH and 20% graphite. This dispersion was painted on a sheet of Kraft paper and dried under ambient temperature and humidity (25 ± 3 °C and 50 ± 5 % RH, respectively). The resulting sample was used to produce different kinds of ERG-coated paper electrodes: S1 and S2. The former was made using the as-prepared ERG samples, but the latter was obtained after a finishing process: the ERG-coated paper was washed in water, followed by a second drying step under the same ambient temperature and RH and it was finally calendered in a MH300C (MH Equipamentos, Guarulhos SP) calender. Pictures of S1 and S2 electrodes are presented in Fig. S1.

1.2. Surface modification

ERG-HEG electrodes were made using the combinations of as-prepared (S1) and washed and calendered (S2) ERG-coated papers, either modified or not with aqueous NaOH and $Fe_2(SO_4)_3$ solutions. Electrode modification was done by wetting (8 x 2) cm^2 pieces with a 1% m/v aqueous NaOH or 10% m/v $Fe_2(SO_4)_3$ solutions. For both electrodes (S1-M and S2-M) only 1 ml of each solution were used. The wetted electrodes were allowed to dry at room temperature. The best results were obtained using the pairs formed by S1 modified with NaOH (S1-M) and S2 modified with $Fe_2(SO_4)_3$ (S2-M).

1.3. Fabrication of the hygroelectric nanogenerator (ERG-HEG)

The hygroelectric nanogenerator consists of two ERG-coated Kraft paper sheets (8 cm x 2 cm). Coin-shaped ERG electrodes were cut, piled-up and held with a plastic fastener, to obtain a series association.

1.4. Electric Measurements

The output voltage and the charging curves was measured by a Keithley 6514 system electrometer that was connected to the HEG devices through a triaxial cable. The data were acquired using an interface adapter (KUSB – 488B) to a notebook controlled by LabView software.

1.5. Humidity control

Humidity was controlled by changing the flow of two merging air currents: one is dry and the other is water- saturated, produced by bubbling air through distilled water. Temperature was controlled by an air conditioning system that kept

the room temperature at 23± 5 ºC. Both the temperature and the humidity inside the box were continuously monitored using a digital thermohygrometer (Akrom KR420).

1.6. Scanning electrostatic potential measurements

Measurements of electrostatic potential of the nanostructured carbon surfaces were done using a disc shaped 5 mm-diameter high sensitivity Kelvin probe (Trek, 3250) connected to a voltmeter (Trek, 320C). The probe is mounted on a mechanical arm that moves in the x-y plane, allowing the electrode to scan the sample holder upper area, at a constant height (probe-to-surface separation is 1 mm, as recommended by the manufacturer). The whole assembly is placed inside a grounded metal box, under controlled temperature and relative humidity. Fig. S2 shows a picture of the scanning electrostatic potential measurements apparatus.

1.7. Microscopy ~~Analysis~~

AFM topography and current maps (CP-AFM) were recorded on a Park NX10 microscope (Park Systems, Suwon – Korea) equipped with a SmartScan software version 1.0.RTM11a. The measurements were made using a 25Pt300B conductive probe with a nominal resonance frequency of 20 kHz and 18 N/m force constant. The current maps were obtained with a +0.5 V bias ~~was~~ applied to the metallic sample holder. All measurements were made under ambient conditions at room temperature of 23±5^{0}C and a relative humidity of 55±10% with a scanning rate of 0.25 Hz. Images were treated offline using XEI software version 4.3.4Build22.RTM1.

Scanning electron microscopy maps were obtained using a JSM 6260/JEOL microscope. Exfoliated graphite powder was dried and deposited on a carbon tape surface previously mounted on a sample holder.

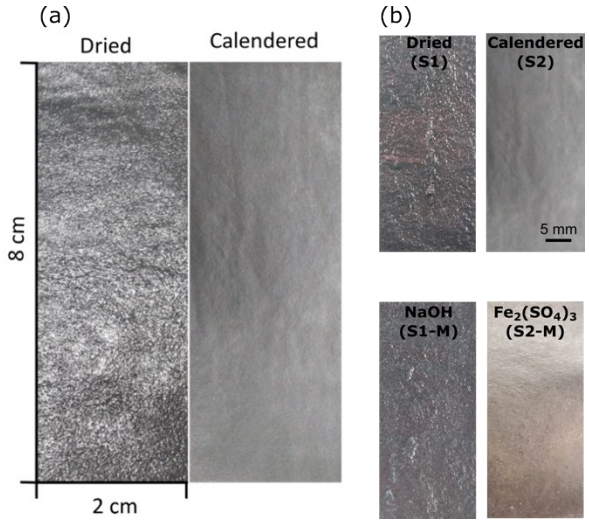

Fig. S1 – (a) Dried graphite electrode (S1, left) and calendered graphite electrode (S2, right). (b) Pictures of conductive paper electrodes, prepared using ERG-coated Kraft paper dried under air (S1) or following calendering (S2) and further modified with NaOH (S1-M) and $Fe_2(SO_4)_3$ (S2-M) solutions. As seen in Fig. S1b, the dried sample (S1) has a rough aspect that is maintained after NaOH modification (S1-M). The calendered ERG electrode has a smooth surface (S2), but with a brownish aspect characteristic of iron (III) oxohydroxides formed by $Fe_2(SO_4)_3$ hydrolysis (S2-M).

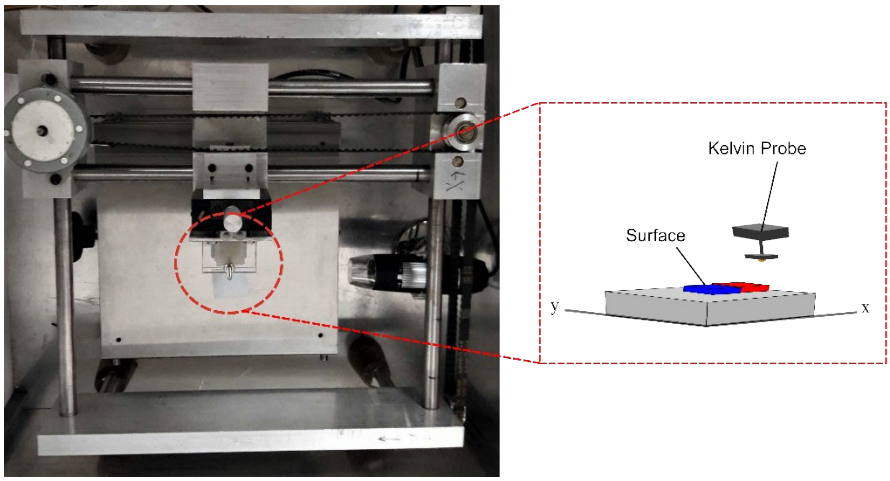

Fig. S2 Scanning electrostatic potential measurement apparatus.

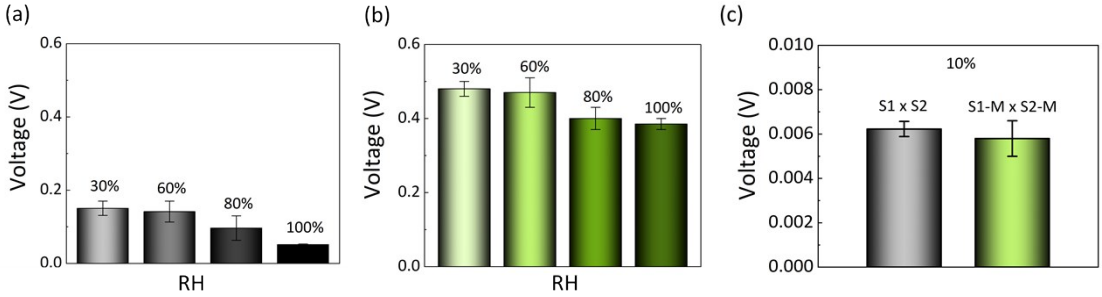

Fig. S3 – Average and standard deviation of the maximum voltage obtained when charging a 1.5 μF capacitor using (a) unmodified and (b) modified HEG at 30%, 60%, 80% and 100% RH. (c) Average and standard deviation of the maximum voltage achieved by the unmodified and modified hygroelectric generators at 10% RH.

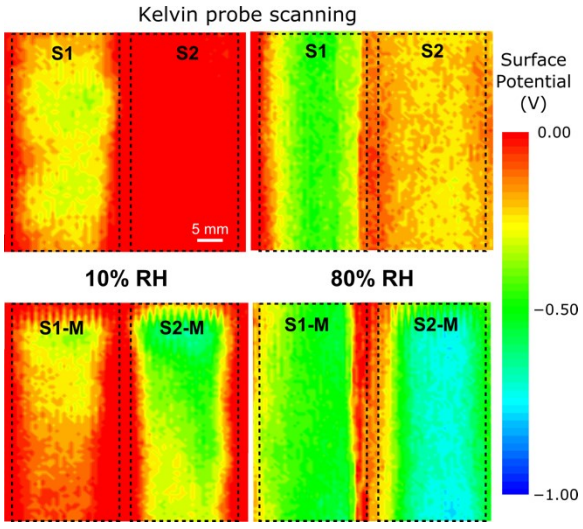

Fig. S4 – Electrostatic potential maps recorded with a Kelvin probe under 10% or 80% RH for unmodified and modified electrodes.

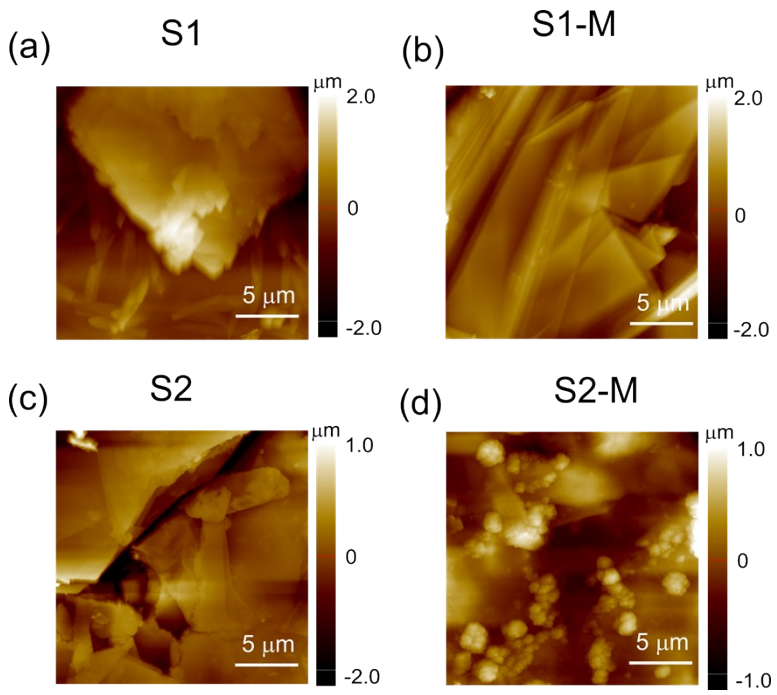

Fig. S5 – Topography maps obtained by AFM of (a) S1, (b) S1-M (non-calendered, modified with NaOH), (c) S2 and (d) S2-M (calendered, modified with $Fe_2(SO_4)_3$).

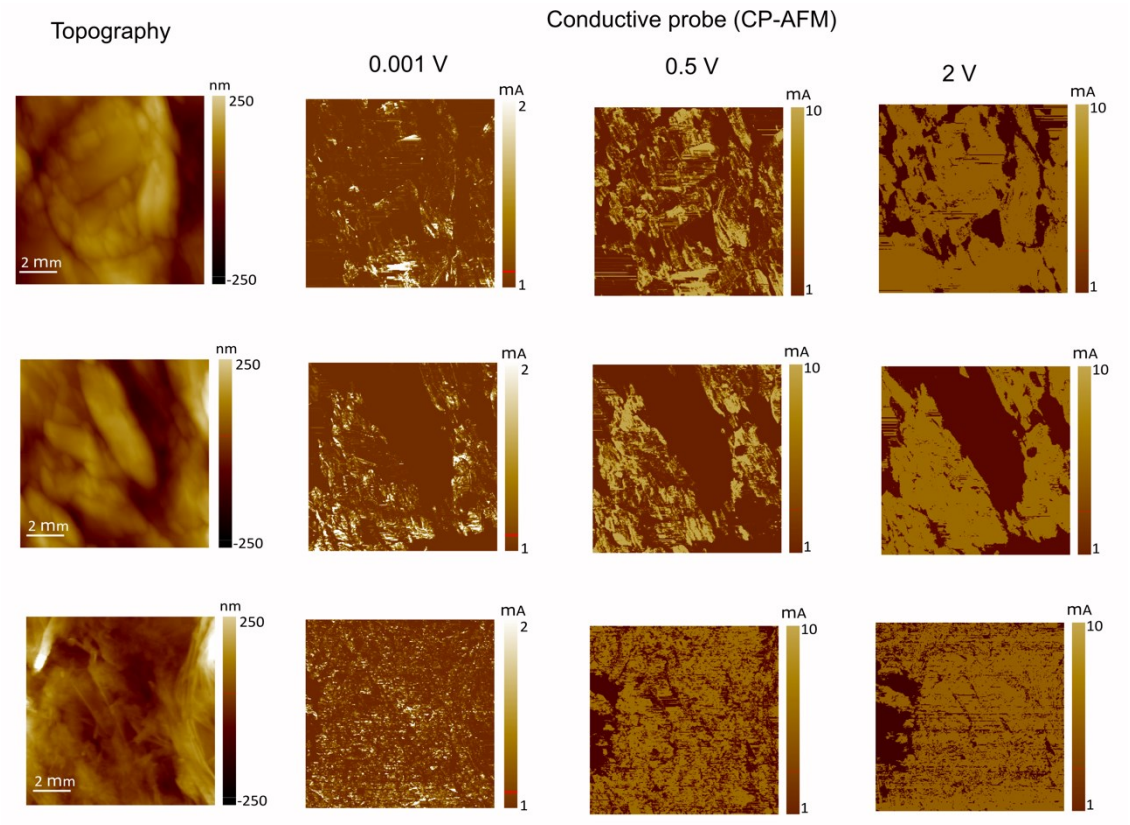

Fig. S6 – Conductive probe (CP-AFM): topography and current mode images of S1-M surface.

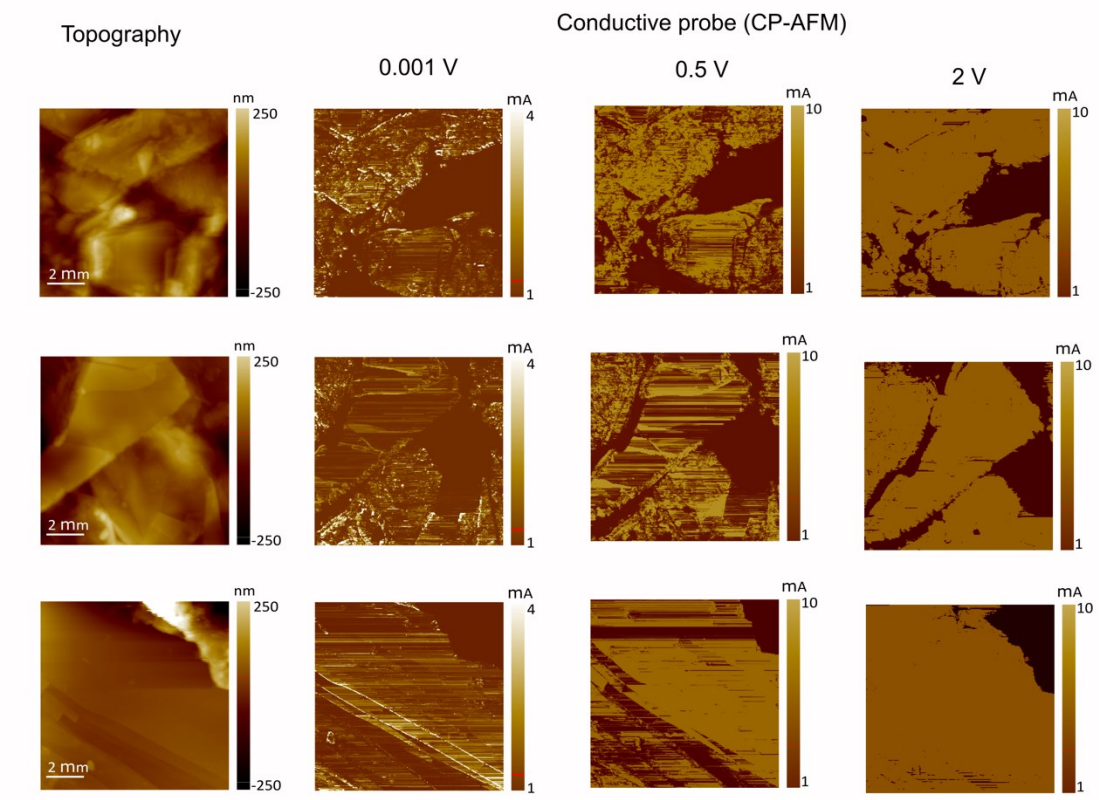

Fig. S7 – Conductive probe (CP-AFM): topography and current mode images of S2-M surface.

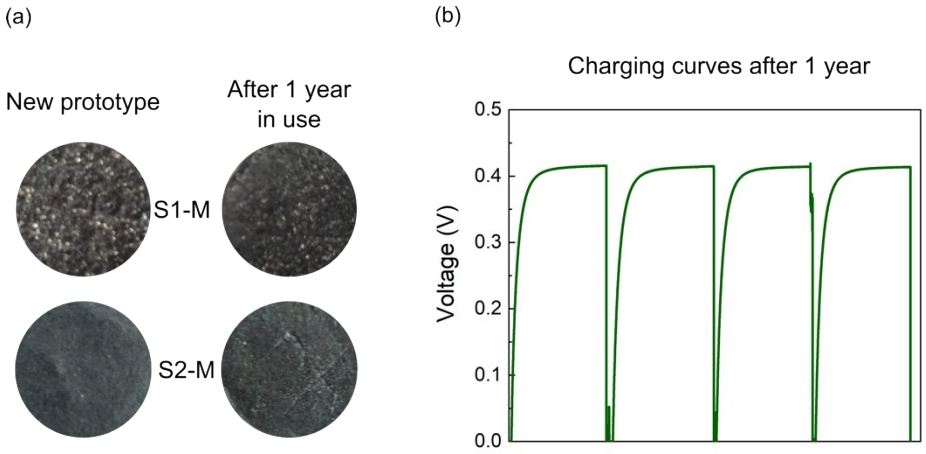

Fig. S8 – (a) Photography of a new and an old graphite-coated kraft paper sheet. (b) Charging curves of a 1.5 µF capacitor using an old prototype (after 1 year of use).

Table S1. Hygroelectric benchmarking.

Authors	Hygrogenerator materials	Voltage output/element	Current density/element	Power density	Advantages/Comments	Maximum current time
F. Zhao, H. Cheng, Z. Zhang, L. Jiang and L. Qu, *Adv. Mater.*, 2015, **27**, 4351–4357	Hygroscopic bulk of graphene oxide film (GOF) Gold electrodes	≈20 mV	≈5 μA cm^{-2}	4.2 mW m^{-2}	High sensitivity to moisture variation	≈ 3 s
F. Zhao, Y. Liang, H. Cheng, L. Jiang and L. Qu, *Energy Environ. Sci.*, 2016, **9**, 912–916.	3D GO frameworks with a preformed oxygen-containing group gradient Aluminum electrode	≈260 mV	≈3.2 mA cm^{-2}	1 mW cm^{-2}	High output power density	≈ 2.5 s
Y. Huang, H. Cheng, G. Shi and L. Qu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 38170–38175.	Graphene quantum dots (GQD) Gold electrodes	≈270 mV	≈27.7 mA cm^{-2}	1.68 mW cm^{-2} under 50 MΩ	High power generation performance	≈ 8 s
C. Shao, J. Gao, T. Xu, B. Ji, Y. Xiao, C. Gao, Y. Zhao and L. Qu, *Nano Energy*, 2018, **53**, 698–705.	Hygrogenerator based on GO fibers and Ag wire	≈300 mV	≈0.7 μA cm^{-1}	0.21 μW cm^{-1}	Can be molded into arbitrarily predesigned shapes and architectures.	≈ 0.5 s
H. Cheng, Y. Huang, F. Zhao, C. Yang, P. Zhang, L. Jiang, G. Shi and L. Qu, *Energy Environ. Sci.*, 2018, **11**, 2839–2845.	GO and reduced GO (r-GO) bulk Gold electrodes	≈450 mV	≈0.9 μA cm^{-2}	2 μW cm^{-2}	High output power density	≈ 20 s
Y. Huang, H. Cheng, C. Yang, P. Zhang, Q. Liao, H. Yao, G. Shi and L. Qu, Nature Comm., 2018, **9**, 4166.	Hygroscopic bulk graphene oxide with a heterogeneous structure and interface mediation between electrodes/materials	≈1.5 V	120 nA	32 mW cm^{-3} under 10 MΩ	Scalable, series association (18 V with 15 units) The metal-GO interfaces are Schottky junctions. The reported power output is peak power.	≈ 30 s
C. Yang, Y. Huang, H. Cheng, L. Jiang and L. Qu, *Adv. Mater.*, 2019, **31**, 1–7.	GO and r-GO film Au electrodes	≈180 mV	1.1 μA Area: 0.244 cm^2 ≈4.50 μA cm^{-2}	0.102 μW under 5 MΩ Area: 0.244 cm^2 ≈0.420 μW cm^{-2}	Diverse multidimensional HEGs deformation ability.	≈ 35 s
X. Liu, H. Gao, J. E. Ward, X. Liu, B. Yin, T. Fu, J. Chen, D. R. Lovley and J. Yao, *Nature*, 2020, **578**, 550–554.	Film of protein nanowires produced by the microorganism *Geobacter sulfurreducens* Gold electrodes	≈500 mV	17 μA cm^{-2} 100 nA through a 2 MΩ resistor gold electrode (with an area of around 25 mm^2)	4 mW cm^{-3}	Connecting several devices linearly scales up the voltage and current to power electronics.	≈ 50 h

Table S2. Capacitor charging time to reach 90% of maximum voltage at 30%, 60%, 80% and 100% RH.

	RH			
	30%	60%	80%	100%
Charging Curve	Time (s)	Time (s)	Time (s)	Time (s)
1	5.25	4.35	5.00	6.25
2	5.50	3.00	7.00	14.75
3	5.50	3.00	13.50	9.75
4	10.50	3.00	20.00	20.00
5	7.50	3.00	25.25	13.00
Mean	**6.85**	**3.25**	**14.15**	**12.75**
Mean deviation	**1.72**	**0.4**	**6.78**	**3.8**