

A simple and industrially contable method for making a PANI-modified cellulose touch sensor / Ragazzini I.; Gualandi I.; Selli S.; Polizzi G.; Cassani M.C.; Alandi D; Cardbassi F. Tarderin D; Tarderin D; Scavetta E.; Ballarin B.. - In: CARBOHY DRATE POLYMERS - ISSN 0144-8617 - STAMPA. - 254:(2021), pp. 117304.1-117304.9. [10.1016/].carbpoli2020.117304] DELLA RICERCA

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

A simple and industrially scalable method for making a PANI-modified cellulose touch sensor

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Availability: This version is available at: https://hdl.handle.net/11585/800978 since: 2023-02-28

Published:

DOI: http://doi.org/10.1016/j.carbpol.2020.117304

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (https://cris.unibo.it/). When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Ragazzini I., Gualandi I., Selli S., Polizzi C., Cassani M.C., Nanni D., Gambassi F., Tarterini F., Tonelli D., Scavetta E., Ballarin B. "A simple and industrially scalable method for making a PANI-modified cellulose touch sensor", in Carbohydrate Polymers, 2021, 254

Thefinalpublishedversionisavailableonlineat:https://doi.org/10.1016/j.carbpol.2020.117304

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<u>https://cris.unibo.it/</u>)

When citing, please refer to the published version.

19 Graphical abstract



23

24

A simple and industrially scalable method for making a PANI-

modified cellulose touch sensor

25 I. Ragazzini^a, I. Gualandi^{a*}, S. Selli^b, C. Polizzi^a, M. C. Cassani^a, D. Nanni^a, F. Gambassi^a, D. Tonelli^a,

26 E. Scavetta^a, B. Ballarin^{a*}

^aDepartment of Industrial Chemistry "Toso Montanari", Bologna University, Via Risorgimento 4, I40136, Bologna, Italy.
^b Cromatos s.r.l., via G. Cardano, 6B/C/D – 47122 Forlì, Italy.

30

*To whom correspondence should be addressed. E-mail: <u>barbara.ballarin@unibo.it</u> (B.B), tel: +39 051 2093700;
 <u>isacco.gualandi2@unibo.it</u> (I.G.), tel: +39 051 2093386.

33

34 Abstract

In this work we present a simple, inexpensive, and easily scalable industrial paper process to prepare 35 sheets of conductive cellulose fibers coated with polyanilines. First, bare fibers were coated by in situ 36 oxidative polymerization of polyaniline then, the resulting composite fibers were used to fabricate 37 electroactive sheets. The resistivity of the sheets is $14 \pm 1 \Omega$ sq⁻¹, a value around 1000 times lower 38 than those reported in literature. The superior electronic proprieties of the sheets were demonstrated 39 40 by assembling a capacitive touch sensor device with optimized geometry. The touch sensor shows an increase of 3-4 % of the starting electric capacity after compression and a fast response time of 52 41 ms. To our knowledge this is the first time that a device is prepared in this way and therefore, the 42 43 herein presented results can bring an significant improvement in the development of low-cost, green and high-tech electronic devices. 44

45

46 Keywords: electro-active paper; PANI; cellulose; transducers; touch sensor

48 1. INTRODUCTION

In the current world, many action is eased by the presence of electrical devices but only 20% of these appliances is correctly recycled. Many landfills continue to be stuffed with unwanted electronics and workers are exposed to hazardous and carcinogenic substances during informally recycling processes in developing countries. As new products are consumed by hungry customers wanting the latest and greatest technology, the sheer volume of these daily produced discarded materials makes this task apparently insurmountable (EU Report).

55 Research efforts are focused on the development of an alternative to traditional electronics that should be low-cost, degradable, compostable, and made from environmentally nontoxic 56 substances. As a candidate, cellulose is one of the most investigated raw materials, mainly because 57 of high abundance on Earth, biocompatibility, porosity, high flexibility and light-weight (Khan, Abas, 58 Kim, & Kim, 2016) (Luo & Huang, 2014). In addition, its low price (about 0.1 cent dm⁻²) (Tobjörk 59 & Österbacka, 2011) and its recyclability make cellulose an economically very viable option (John, 60 Mahadeva, & Kim, 2010) (Kanaparthi & Badhulika, 2017) (Tian, Qu, & Zeng, 2017). Despite its 61 high surface resistivity at relative humidity of 20-40 % (typically 10^{11} - $10^{15} \Omega$ sq⁻¹) (Tobjörk & 62 63 Österbacka, 2011), it can be used as support to produce conductive paper that can be exploited in a 64 wide range of applications, including supercapacitors, microfluidic systems, diagnostic devices, actuators and sensors (Luo & Huang, 2014) (Kanaparthi & Badhulika, 2017) (Sanandiya, Vijay, 65 Dimopoulou, Dritsas, & Fernandez, 2018) (Q. Wang et al., 2018). 66

Two different approaches to prepare conductive paper are described in literature. In the first one, organic or inorganic conductive, semi-conductive and dielectric printable materials is deposited on paper employing screen, inkjet printing or flexographic techniques (Tobjörk & Österbacka, 2011). The second approach consists in embedding conductive materials such as functionalized multi-walled carbon nanotubes, inorganic nanoparticles and conducting polymers (CPs) in cellulose fibers making them conductive (Khan et al., 2016) (Tobjörk & Österbacka, 2011) (John et al., 2010) (Yan et al.,

2016) (Pang et al., 2016) (Gu & Huang, 2013) (Rafatmah & Hemmateenejad, 2020) (Das, Mai, &
Duan, 2019) (Y. Zhang et al., 2019) (Silva et al., 2019) (Sharma, Pareek, Rohan, & Kumar, 2019)
(W. Zhang et al., 2019) (Zang et al., 2018). Conducting cellulosic fibers produced by coating with
CPs (i.e. polyaniline (PANI), polypirrole (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT) etc.)
are being explored for various applications including supercapacitors, batteries, transistors,
conductive wires, actuators and touch sensors (Tobjörk & Österbacka, 2011) (Aguado, Murtinho, &
Valente, 2019) (Ma, Wang, & Yu, 2020).

In this scenario PANI is particularly interesting because of its low cost, easy preparation, good environmental stability and tunable electrical properties by varying its oxidation state (Tobjörk & Österbacka, 2011)(Singh & Shukla, 2020)(Yanmin Wang, Liu, Han, & Li, 2019)(Tanguy, Thompson, & Yan, 2018)(Yanmin Wang et al., 2019)(Shoaie et al., 2019). In situ polymerization is the most popular way of depositing PANI on cellulosic fibers. Different methods can be employed depending on the types of fiber, oxidants, medium, dopants, monomers, concentration used, processing steps and parameters (John et al., 2010) (Ma et al., 2020) (Singh & Shukla, 2020) (Ke et al., 2019).

Herein we first report the preparation of cellulose/PANI fibers (Cell/PANI-F) in which PANI, 87 in the form of protonated conductive emeraldine salt, was obtained by a simple in situ oxidative 88 polymerization of aniline on bare cellulose fibers in acidic media (Ma et al., 2020) (Ke et al., 2019) 89 90 (Masood et al., 2019). Successively, the fibers were assembled to give electroactive sheets (Cell/PANI-S) with different thickness and resistivity: 1.25 mm with a resistivity of $14 \pm 1 \Omega$ sq⁻¹ 91 (0.5 S cm^{-1}) or 0.4 mm with a resistivity of $237 \pm 9 \Omega \text{ sq}^{-1}$ (0.1 S cm⁻¹). Finally, differently from those 92 reported in the literature which are normally of resistive type (Tao et al., 2017) (Shao et al., 2014), 93 capacitive touch sensors (Cell/PANI-TS) with an optimized geometry were assembled. Both 94 95 electroactive sheets and touch sensors were prepared using an industrially and easily scalable paper process provided by the industrial group Cromatos s.r.l. (https://www.cromatos.com). 96

97 The capacitive touch sensors were finally interfaced with Arduino UNO developed board to98 investigate their dynamic response. All the measures have been conducted at room temperature and

99 in natural environment humidity after that the Cell/PANI-S or the Cell/PANI-TS were subjected to100 air at room temperature for the time of 24 h.

101

102 2. RESULTS AND DISCUSSION

103 2.1. Preparation and characterization of Cell/PANI-F and Cell/PANI-S

- 104 The modification of bare cellulosic fibers with PANI was obtained via a simple in situ oxidative
- polymerization of aniline in acid media, as described in the experimental section (Fig. 1).



106

Fig. 1. A) Schematic representation of the oxidative polymerization of aniline with ammonium
persulfate [(NH₄)₂S₂O₈, APS] in acid media; B) Image of Bare Cell-F (white) and Cell/PANI-F
(black) after filtration and drying.

110

Scanning electron microscopy (SEM) images of bare cellulose fibers and Cell/PANI-F arereported in Fig. 2.



Fig. 2. Scanning electron microscopy (SEM) of bare Cell-F (A, A', A'') and Cell/PANI-F (B, B',
B'') at 1000 X, 6000 X and 5000 X magnification, respectively; C) Cross-section of Cell/PANI-F at
10000 X magnification.

113

117 It can be seen from the SEM images that the pure Cell-F (Figs. 2A-A'') displayed a very clean and 118 smooth morphology, whereas the Cell/PANI-F displayed relatively rough surface (Figs. 2B-B''). 119 Compared the surface morphology the Cell/PANI-F is significantly different due to the deposition of 120 PANI on the surface. All the cellulose surface results covered by a rough film that is ascribed to 121 PANI. The PANI layer showed a relative compact morphology and well wrapped the cellulose fibers 122 with a thickness around 4.4 μ m, as observable in Fig. 2C.

SEM image and EDS element mappings of Cell/PANI-F sample are presented in Fig. 3. Within the

124 elemental maps, the C signal originates from the cellulose fiber and PANI; O signal comes from

cellulose fiber and the N signals uniquely indicate the PANI regions. N was observed only in theouter space of cellulose fibers.

127





Fig. 3. EDS elemental mapping of CELL/PANI-F for Carbon, Oxygen and Nitrogen.

130

131 The PANI average amount on cellulose fibers was measured using the Kjeldahl method after132 digestion of the Cell/PANI-F sample and resulted 22.3 wt%.

The conductive sheets Cell/PANI-S were prepared from the Cell/PANI-F, using a protocol commonly employed for coloring paper with acid dyes (Supplementary Information, SI and Scheme S1) (Cartari, 2003). In order to maintain the polyaniline in the oxidized state (emeraldine salt), the modified fibers were immersed in a 25% Al₂(SO₄)₃ aqueous solution kept at *ca*. pH 3.0. Successively, after being partially dried in a square sieve and kept in a press at 50 bar for 10 s, sheets of 200 grams for square meter (200 gsm) and a thickness of 0.40 mm were obtained. Alternatively, thicker sheets (1.25 mm; 630 gsm) were prepared in a similar fashion.

The ATR-FTIR spectra of Cell/PANI-S (Fig. 4) show all the characteristic peaks attributed to PANI: the stretching vibrations of benzoid N-B-N and quinoid N=Q=N structures show up at 1443 and 1564 cm⁻¹, separately. The absorption band at 1290 is ascribed to protonation of PANI. Bare cellulose shows the characteristic absorption peaks at ca. 3300 cm⁻¹ attributed to the stretching of
hydroxyl groups v(-OH) and 2900 cm⁻¹ attributed to the stretching of C-H groups; moreover, in the
region of 1300 cm⁻¹ the -OH bending and the C-O antisymmetric bridge stretching are present and
the strong bands around 1000 cm⁻¹ due to the C-O-C pyranose ring skeletal vibration are observed
(Chougale, Thombare, Fulari, & Kadam, 2013) (Cases, Huerta, Garcés, Morallón, & Vázquez, 2001)
(Liu et al., 2005) (Dhibar & Das, 2014).



- Fig. 4. ATR-FTIR spectra of bare Cellulose (black), PANI (red) and Cell/PANI-S (blue); inset:
 enlargement in the range 1900-700 cm⁻¹.
- 153 **2.2 Cell/PANI-S electrical features**

The Cell/PANI-S conductivity was evaluated by 4-line-probe measurements with a home-made 154 sample holder (Fig. S2) to avoid the contribution due to contact resistances. In order to evaluate the 155 reproducibility of the system, the effect of different morphology and the influence of the 156 environmental condition during the real use, the electrical characterization was performed at different 157 times, for each thickness, on three different paper sheets at room temperature and balanced with the 158 surrounding atmosphere. As expected, it was found that the conductivity of Cell/PANI-S depends on 159 the sheet thickness being 0.105 ± 0.004 S cm⁻¹ for a thickness of 0.40 mm and 0.56 ± 0.06 S cm⁻¹ for 160 a thickness of 1.25 mm; in the latter the value is only one order of magnitude lower than the highest 161 values reported for pristine PANI. It is important to underline that our preparation method allows to 162 163 obtain conductivity values higher (or similar, depending from the thickness) than those achievable by all the conductive papers presented in literature, as evident from the data reported in Table 1. The 164 small standard deviation obtained suggested the low influence of the external environmental variation 165 166 (i.e. humidity).

Material	Synthesis	Conductivity (S cm ⁻¹)	Ref.
Cell/PANI-S	In situ synthesis on the cellulose pulp	$5.6 \pm 0.6 \ 10^{-1}$	This work
	(1.25 mm thickness)		
Cell/PANI-S	In situ synthesis on the cellulose pulp	$1.05 \pm 0.04 \ 10^{-1}$	This work
	(0.4 mm thickness)		
Rice pulp/PANI	In situ synthesis on the cellulose pulp	2.5 10-5	(Youssef, El-Samahy, &
			Abdel Rehim, 2012)
Pineapple fibers/PANI	In situ synthesis on the cellulose pulp	3.0 10-4	(S. I. A. Razak, N. F. A.
			Sharif, 2014)
Cellulose pulp/PANI	In situ synthesis on the cellulose pulp.	1.5 10-2	(Sharifi, Zabihzadeh, &
	Chemiometric optimization		Ghorbani, 2018)
CA electrospun/PANI	In situ polymerization onto electrospun cellulose	1.0 10-1	(Baptista et al., 2018))
	membrane		
Cellulose/PANI	Dispersed Cellulose + PANI	4.7 10-8	(John et al., 2010)
Ink-jet printed PANI	Ink composed by PANI nanoparticles	4.0 10-4	(Ngamna et al., 2007)

167	Table 1.	Comparison	of the	conductivity	v of different	samples bas	sed on PANI
					/	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	

Thin PANI film on filter	In situ polymerizzation on masked paper sheet	1.0 10-3	(Gao, Ota, Kiriya, Takei, &
paper			Javey, 2019)
PANI bulk		1-5	(Teo et al., 2019)

168

- 169 In order to clearly demonstrate the excellent conductivity of Cell/PANI-S, two 1.25 mm thick paper 170 sheets were successfully used as wires to transport the current necessary to power a LED with an
- applied voltage of 2.0 V (Fig. 5).



172

- **Fig. 5.** Experimental setup with Cell/PANI-S (1.25 mm) and LED.
- 174

175 **2.3 Cell/PANI-TS assembling and performance**

176	Cell/PANI-TS was prepared by an industrial assembling method coupling a Cell/PANI-S (0.4 mm,
177	200 gsm) suitably cut with scissors in the required shape and a cellulose sheet (0.4 mm, 200 gsm), as
178	described in the experimental section. By maintaining the composite under a 50 bar pressure for 10

- s, a device with a thickness of 0.80 mm has been obtained as reported in Figure 6 and Scheme S2.
- 180 Dimensions and shape of the built circuit can be easily varied as reported in Fig. S3.

181



182

183

Fig. 6. Cell/PANI-TS: SEM image of the cross section and assembled circuit.

184

To understand the functionality of the capacitive touch sensor, an experimental test has been set up using a home-made equipment which allows to exercise and control the pressure given on the touch sensor with a step by step motor. The pressure was applied by keeping the position unchanged, and the whole area of the touch sensor was stimulated. Then the force-weight at each single advance step of the motor was measured and the capacity was recorded at the same time with Arduino UNO board (see Figs. S4-S8 and Scheme S3 for details).

Three Cell/PANI-TS samples with different geometries were tested (Fig. 7). For each, the 191 192 capacitive component was measured without any touch interaction and during the dynamically induced increasing pressure up to a maximum value of 22 kPa (saturation level). The Cell/PANI-TS 193 was excited by a square wave through the Weight Force Generator (WFG) while the out-put signal 194 was observed with the oscilloscope and acquired with Arduino UNO development board, as described 195 in SI. All three touch sensors have a starting capacity of about 93-94 pF and different saturation 196 197 capacity depending on the geometry employed, however an increase of 3-4 % of the initial value after pressure exertion is always obtained. Fig. 7 shows the results of the tests reporting $\Delta C/C_0$ % vs 198 pressure, where ΔC is (C_P-C₀), C_P and C₀ correspond to the capacity with and without pressure (Zang 199 200 et al., 2018) (Tao et al., 2017) (Yu, Tang, Cai, Ren, & Tang, 2019) (Cataldi et al., 2018).



201

Fig. 7. Cell/PANI-TS with different geometry and related change of capacity with pressure curves.

203

From the data comparison, it can be observed that the geometry heavily affects the response as shown in Fig. 7. A-type sensor shows two different linear trends with a sensitivity, defined by (C_P- C_0)/C₀/P where P is the used pressure (Zang et al., 2018) (Tao et al., 2017) (Yu et al., 2019), of 0.66 kPa⁻¹ in a small pressure range (0 to 2 kPa) and 0.012 kPa⁻¹ in a large pressure range (2 to 20 kPa) (Figure S9). On the contrary, the C-type sensor curve follows a logarithmic trend with equation y = 209 $0.598 \ln(x) + 1.724$; R² = 0.954 (Fig. S10) and shows sensitivities of 2.34 (0.45 σ %), 1.37 (0.44 σ %) and 0.19 (0.44 σ %) kPa⁻¹ at pressures of 0.5, 2 and 20 kPa, respectively (average of five different 210 measurements). Under each pressure both sensors display a good and stable response. Finally, B-type 211 sensor present a different behavior which cannot be traced back to a simple mathematical expression. 212 Due to its logarithmic behavior, we have chosen to carry out the repeatability and stability tests only 213 on C-type sensors, recording, for each device, six independent $\Delta C/C_0$ % vs pressure curves, at 214 different data. The results shown in Fig. S11, indicate a good reproducibility under all pressure range 215 without a noticeable degradation of the performances. 216

Finally, a pressure around 6 kPa was used to examine the sensors time response revealing a response time of 52 ± 1 ms.

219

220 **3. CONCLUSIONS**

To the best of our knowledge, for the first time, an easily scalable industrial paper process is here 221 proposed to produce conductive paper sheets with excellent electrical performances as demonstrated 222 by the success of their use in the fabrication of capacitive touch sensors. This method can provide an 223 224 enormous improvement in the field of low-cost electronic technology. The electroactive sheets exhibit a conductivity around five times higher than those reported in literature for similar systems and can 225 be employed to light a LED with an applied potential of 2.0 V, highlighting the outstanding electrical 226 performances of these composite materials. The capacitive touch sensors show a very quick response 227 228 time (52 ms) and a sensibility that can be easily modulated by changing the geometry of the device.

229

230 4. EXPERIMENTAL SECTION

231 4.1 Materials

All chemicals and solvents are ACS reagent grade, were purchased from commercial vendors and 232 233 used directly unless otherwise stated. Sulfuric acid (H₂SO₄, 95.0-98.0%), ammonium persulfate $[(NH_4)_2S_2O_8), \ge 98\%]$ and aniline ($\ge 99\%$), were purchased from Sigma-Aldrich (now Merck KGaA, 234 Darmstadt, Germany); aniline was distilled under nitrogen prior to use. Citric acid ($\geq 99.5\%$) was 235 purchased from VWR Chemicals (Vienna, Austria); a solution of ca. 25 wt% of Al₂(SO₄)₃ in water 236 (commercial name FLOCLINE S8C) was purchased from Bio-Line s.r.l. (Milano, Italy). Bare 237 cellulose fibers (pine tree long fiber with sulfate treatment) were kindly provided by Cromatos s.r.l. 238 (Forlì, Italy). 239

240 4.2 Preparation of Cell/PANI-F

In a 1 L round bottom flask, 2.5 g of bare cellulose fibers were dispersed in demineralized water (250 mL) for 30 min; successively a solution made of 2.5 mL of aniline in 150 mL of 1.0 M citric acid ($C_6H_8O_7$) was added to the fiber suspension and stirred for 3 h at room temperature. In turn, the oxidative polymerization was carried out adding dropwise to the stirred suspension, previously cooled to 0 °C in an ice bath, a solution of 7 g of (NH_4)₂S₂O₈ dissolved in 200 mL of 1.0 M citric acid. After 24 h the coated fibers were filtered in a Buchner funnel and washed several times with 1.0 M citric acid solution. The conductive fibers were dried in air atmosphere for 24 h; see Scheme 1 for details.



Scheme 1. Preparation steps for Cell/PANI-F.

250 4.3 Preparation of Cell/PANI-S

10 g of Cell/PANI-F were added to 1.0 L of an acid solution (ca. pH 3.0, 25 wt% Al₂(SO₄)₃ in demineralized water) and stirred for 5 min. The fibers were partially dried in a square sieve (21.0 cm x 14.8 cm size). The sheet was pressed at 50 bar pressure (P50 AXA manual hydraulic press) for 10 s to obtain the Cell/PANI-S (200 gsm, 0.40 mm thickness). Similarly, a 1.25 mm thick sheet was prepared by using 30 g of fibres (see Scheme S1 for the industrial steps details).

256 4.4 Preparation of Cell/PANI-TS

The wet coupling method employed in the paper industry to produce sheets of paper with variable thicknesses or with greater resistance was used to prepare the Cell/PANI-TS samples. A Cell/PANI-S of 0.40 mm thickness was cut in the desired shape and coupled with a cellulose sheet (th. 0.40 mm) moistened with water. The two sheets were then pressed (50 bar, 10 s) and dried at 80 °C for 10 min. The electrical connections were made afterwards with copper adhesive tape and silver glue, see Scheme S2 for details. The whole six-steps preparation from fibers to touch sensor is reported in Scheme 2.



265

266

Scheme 2. Six-steps preparation for cellulose/PANI touch sensor preparation.

267 4.5 Instruments

ATR-FTIR analyses were performed using a Perkin Elmer Spectrum Two spectrophotometer, equipped with a Universal ATR accessory, with a resolution of 0.5 cm⁻¹ in the range 4000-400 cm⁻¹. The samples were directly analyzed performing 40 scans for any analysis.

The determination of PANI amount in Cell/PANI-F was performed with an automatic Kjeldahl Nitrogen Analyzer (Gerhardt Bonn). The Kjeldahl analysis was carried out on four Cell/PANI-F samples and a blank sample (cellulose bare fibre treated exactly as the Cell/PANI-F) using the following protocol. 1.0 g of each sample was put in a glass weighing flask and placed in a Kjeldahl test tube. A catalyst tablet (1 tablet contains 3.5 g of K₂SO₄ and 3.5 mg of Se) (Kjeldahl tablets, 1.18649 Supelco, Merck), 20 mL of concentrated H₂SO₄ (sulfuric acid 95-98%, ACS reagent, 277 258105 Sigma-Aldrich) and 4 glass spheres were then added. The test tubes were heated to 350 ° C
278 for 5 h. The final solution must be clear and colourless. Finally, the test tubes were inserted in the
279 Kjeldahl titration instrument and the potentiometric titration automatically start with 0.100 M HCl in
280 presence of an acid basic indicator (a mixture of methyl red and bromocresol green).

SEM images were recorded at 25 kV with a Sem Zeiss EVO 50 EP equipped with Oxford INCA 350; EDS Sprectrometer equipped with a Bruker Z200 energy dispersive microanalysis (EDX) system was used for semi-quantitative chemical analysis and mapping.

284 4.6 Electrical measurements

Cell/PANI-S resistance was measured with a keysight B2902A source meter units in a 4-line-285 286 probe configuration by exploiting a home-made holder that is composed by 4 parallel copper electrodes on a glass slide (Figure S1). The sample was prepared with a rectangular shape and was 287 held down with an insulating material by exerting a uniform pressure on all the surface. The inner 288 289 electrodes measure the difference of potential while a constant current flow was forced between the two outer electrodes. The measurements were performed at different current values (100, 200, 300 290 µA) and a line passing from the origin was always obtained. The resistance (R) was calculated with 291 the Ohm's law and the sheet resistance (R_{\bullet}) is equal to: 292

$$R_{\bullet} = R \frac{W}{L}$$

294 Where W and L are the width and the length, respectively.

295 The specific resistance (ρ) can be calculated by:

 $\rho = R_{\bullet} t$

297 Where t is the thickness. The specific conductance (κ) is calculated by:

298
$$\kappa = \frac{1}{\rho}$$

299 4.7 Test execution for capacitive vs pressure curves

In order to standardize the measurements, a nitrile rubber (Buna-N, Perbunan - NBR) was chosen as dielectric material and was interposed between the pressure generator and the sensor (P.Cataldi et al., 2018). The sensor was housed in the appropriate seat apparatus reported in Figure S4 and a forceweight was exerted with an increase step of 1.0 g (subsequently converted into Pascal) on the whole sensor surface and the capacity was recorded at the same time.

305

306 ASSOCIATED CONTENT

307 Supporting informatio	n
---------------------------	---

308 The Supporting Information is available free of charge on the Publication website at DOI:

309 AUTHOR INFORMATION

310 Corresponding Autors

- ***Barbara Ballarin**, Dipartimento di Chimica Industriale Toso Montanari, UNIBO, Viale
 Risorgimento 4, 40136 Bologna-IT
- orcid.org/0000-0003-3698-2352; E-mail: <u>barbara.ballarin@unibo.it</u>
- 314 *Isacco Gualandi, Dipartimento di Chimica Industriale Toso Montanari, UNIBO, Viale
- Risorgimento 4, 40136 Bologna-IT
- 316 orcid.org/0000-0002-6823-7501; E-mail: isacco.gualandi2@unibo.it
- 317
- 318

319 Author contributions

B.B., E.S., I.G., I.R., conceived the project, supervised the preparation and analysis of the samples, analysed the data and wrote the paper. C.P. designed and developed the electronic experiments setup. S.S. helped to assemble the sheets and the touch sensors. M.C.C. and F.G. participated in analytical data collection and analysis. D.T. and D.N. revised the manuscript.

324 ACKNOWLEDGEMENTS

325 The authors thank the University of Bologna for financial support. The authors gratefully thank Dr.

326 Sandra Stipa and Dr. Fabrizio Tarterini for the SEM images and Kjeldahl analyses. Finally the authors

- 327 especially thank Cromatos s.r.l. and Roberto Bezzi for the sheets preparation.
- 328

329 **REFERENCES**

- 10° Corso di Tecnologia per Tecnici Cartari, edizione 2002/2003; Scuola Interregionale di
 Tecnologia per Tecnici Cartari, Via Don G. Minzoni, 50 37138 Verona
- Aguado, R., Murtinho, D., & Valente, A. J. M. (2019). A broad overview on innovative
- functionalized paper solutions. *Nordic Pulp and Paper Research Journal*, *34*(4), 395–416.
- 334 https://doi.org/10.1515/npprj-2019-0036
- Baptista, A. C., Ropio, I., Romba, B., Nobre, J. P., Henriques, C., Silva, J. C., Ferreira, I. (2018).
- Cellulose-based electrospun fibers functionalized with polypyrrole and polyaniline for fully
- 337 organic batteries. *Journal of Material Chemistry A*, *6*(1), 256–265.
- 338 https://doi.org/10.1039/c7ta06457h
- Cataldi, P.; Dussoni, S.; Ceseracciu, L.; Maggiali, M.; Natale, L.; Metta, G.; Athanassiou, A.;
- Bayer, I. S. (2018) Carbon nanofiber versus graphene-based stretchable capacitive touch
 sensors for artificial electronic skin, *Advanced Science*, *5*, 1700587-1700597.
- 342 Cases, F., Huerta, F., Garcés, P., Morallón, E., & Vázquez, J. L. (2001). Voltammetric and in situ
- 343 FTIRS study of the electrochemical oxidation of aniline from aqueous solutions buffered at pH
- 344 5. Journal of Electroanalytical Chemistry, 501(1–2), 186–192. https://doi.org/10.1016/S0022-

- 345 0728(00)00526-X
- Chougale, U. M., Thombare, J. V., Fulari, V. J., & Kadam, A. B. (2013). Synthesis of polyaniline
- nanofibres by SILAR method for supercapacitor application. 2013 International Conference
- 348 on Energy Efficient Technologies for Sustainability, ICEETS 2013, (April), 1078–1083.
- 349 https://doi.org/10.1109/ICEETS.2013.6533537
- 350 Cromatos s.r.l. is an industrial group operating worldwide dedicated to the production, formulation
 and marketing of dyes, pigments and chemical products for industry.
- 352 (https://www.cromatos.com).
- 353 Das, P., Mai, V. C., & Duan, H. (2019). Flexible bioinspired ternary nanocomposites based on
- 354 carboxymethyl cellulose/nanoclay/graphene oxide. ACS Applied Polymer Materials, 1(6),

355 1505–1513. research-article. https://doi.org/10.1021/acsapm.9b00245

- Dhibar, S., & Das, C. K. (2014). Silver nanoparticles decorated polyaniline/multiwalled carbon
 nanotubes nanocomposite for high-performance supercapacitor electrode. *Industrial and*
- 358 *Engineering Chemistry Research*, *53*(9), 3495–3508. https://doi.org/10.1021/ie402161e
- Gao, W., Ota, H., Kiriya, D., Takei, K., & Javey, A. (2019). Flexible Electronics toward Wearable
 Sensing. *Accounts of Chemical Research*, *52*(3), 523–533.
- 361 https://doi.org/10.1021/acs.accounts.8b00500
- Gu, Y., & Huang, J. (2013). Colorimetric detection of gaseous ammonia by polyaniline nanocoating
- 363 of natural cellulose substances. *Colloids and Surfaces A: Physicochemical and Engineering*

364 *Aspects*, *433*, 166–172. https://doi.org/10.1016/j.colsurfa.2013.05.016

- John, A., Mahadeva, S. K., & Kim, J. (2010). The preparation, characterization and actuation
- behavior of polyaniline and cellulose blended electro-active paper. *Smart Materials and*
- 367 *Structures*, *19*(4). https://doi.org/10.1088/0964-1726/19/4/045011
- 368 Kanaparthi, S., & Badhulika, S. (2017). Low cost, flexible and biodegradable touch sensor
- fabricated by solvent-free processing of graphite on cellulose paper. *Sensors and Actuators, B:*
- 370 *Chemical*, 242, 857–864. https://doi.org/10.1016/j.snb.2016.09.172

- Ke, S., Ouyang, T., Zhang, K., Nong, Y., Mo, Y., Mo, Q., Cheng, F. (2019). Highly conductive 371
- 372 cellulose network/polyaniline composites prepared by wood fractionation and in situ
- polymerization of aniline. *Macromolecular Materials and Engineering*, 304(7), 1–10. 373
- 374 https://doi.org/10.1002/mame.201900112
- 375 Khan, A., Abas, Z., Kim, H. S., & Kim, J. (2016). Recent progress on cellulose-based electro-active
- paper, its hybrid nanocomposites and applications. Sensors (Switzerland), 16(8), 1–30. 376

https://doi.org/10.3390/s16081172 377

- Liu, X. X., Zhang, L., Li, Y. B., Bian, L. J., Su, Z., & Zhang, L. J. (2005). Electropolymerization of 378
- aniline in aqueous solutions at pH 2 to 12. Journal of Materials Science, 40(17), 4511-4515. 379
- 380 https://doi.org/10.1007/s10853-005-0854-x
- Luo, Y., & Huang, J. (2014). Surface modification of natural cellulose substances: Toward 381 functional materials and applications. Science China Chemistry, 57(12), 1672–1682. 382
- 383 https://doi.org/10.1007/s11426-014-5226-4
- Ma, Z., Wang, W., & Yu, D. (2020). Assembled wearable mechanical sensor prepared based on 384 cotton fabric. Journal of Materials Science, 55(2), 796-805. https://doi.org/10.1007/s10853-385 019-04035-0
- 386
- Masood, A., Shoukat, Z., Yousaf, Z., Sana, M., Faisal Iqbal, M., Rehman, A. R., Razaq, A. (2019). 387
- 388 High capacity natural fiber coated conductive and electroactive composite papers electrode for
- energy storage applications. Journal of Applied Polymer Science, 136(13), 1–6. 389
- https://doi.org/10.1002/app.47282 390
- 391 Ngamna, O., Morrin, A., Killard, A. J., Moulton, S. E., Smyth, M. R., & Wallace, G. G. (2007).
- Inkjet printable polyaniline nanoformulations. Langmuir, 23(16), 8569–8574. 392
- https://doi.org/10.1021/la700540g 393
- Pang, Z., Yang, Z., Chen, Y., Zhang, J., Wang, Q., Huang, F., & Wei, Q. (2016). A room 394
- temperature ammonia gas sensor based on cellulose/TiO₂/PANI composite nanofibers. 395
- 396 Colloids and Surfaces A: Physicochemical and Engineering Aspects, 494, 248–255.

- 397 https://doi.org/10.1016/j.colsurfa.2016.01.024
- Rafatmah, E., & Hemmateenejad, B. (2020). Dendrite gold nanostructures electrodeposited on
- 399 paper fibers: Application to electrochemical non-enzymatic determination of glucose. *Sensors*
- 400 *and Actuators, B: Chemical, 304*(October 2019), 127335.
- 401 https://doi.org/10.1016/j.snb.2019.127335
- Razak S. I. A, Sharif, N. H. M. N. (2014). Elect rically Conductive Paper of Polyaniline Modified
 Pineapple Leaf Fiber. *Fibers and Polymers*, *15*, 1107. https://doi.org/10.1007/s12221-0141107-x
- 405 Report EU. (n.d.). Retrieved from https://www.unenvironment.org/news-and-stories/press-

406 release/un-report-time-seize-opportunity-tackle-challenge-e-waste

- 407 Sanandiya, N. D., Vijay, Y., Dimopoulou, M., Dritsas, S., & Fernandez, J. G. (2018). Large-scale
 408 additive manufacturing with bioinspired cellulosic materials. *Scientific Reports*, 8(1), 1–8.
 409 https://doi.org/10.1038/s41598-018-26985-2
- 410 Shao, Q., Niu, Z., Hirtz, M., Jiang, L., Liu, Y., Wang, Z., & Chen, X. (2014). High-performance
- 411 and tailorable pressure sensor based on ultrathin conductive polymer film. *Small*, 10(8), 1466–
- 412 1472. https://doi.org/10.1002/smll.201303601
- 413 Sharifi, H., Zabihzadeh, M., & Ghorbani, M. (2018). The application of response surface
- 414 methodology on the synthesis of conductive polyaniline/cellulosic fiber nanocomposites.
- 415 *Carbohydrate Polymers*, *194*(February), 384–394.
- 416 https://doi.org/10.1016/j.carbpol.2018.04.083
- 417 Sharma, K., Pareek, K., Rohan, R., & Kumar, P. (2019). Flexible supercapacitor based on three-
- 418 dimensional cellulose/graphite/polyaniline composite. *International Journal of Energy*
- 419 *Research*, 43(1), 604–611. https://doi.org/10.1002/er.4277
- 420 Shoaie, N., Daneshpour, M., Azimzadeh, M., Mahshid, S., Khoshfetrat, S. M., Jahanpeyma, F., ...
- 421 Foruzandeh, M. (2019). Electrochemical sensors and biosensors based on the use of
- 422 polyaniline and its nanocomposites: a review on recent advances. *Microchimica Acta*, 186(7).

423 https://doi.org/10.1007/s00604-019-3588-1

- 424 Silva, L. E., Cunha Claro, P. I., Sanfelice, R. C., Guimarães, M., de Oliveira, J. E., Ugucioni, J. C.,
- 425 Denzin Tonoli, G. H. (2019). Cellulose nanofibrils modification with polyaniline aiming at
- 426 enhancing electrical properties for application in flexible electronics. *Cellulose Chemistry and*
- 427 *Technology*, *53*(7–8), 775–786. https://doi.org/10.35812/CelluloseChemTechnol.2019.53.76
- 428 Singh, P., & Shukla, S. K. (2020). Advances in polyaniline-based nanocomposites. *Journal of*

429 *Materials Science*, 55(4), 1331–1365. https://doi.org/10.1007/s10853-019-04141-z

- 430 Tanguy, N. R., Thompson, M., & Yan, N. (2018). A review on advances in application of
- 431 polyaniline for ammonia detection. *Sensors and Actuators, B: Chemical*, 257, 1044–1064.
- 432 https://doi.org/10.1016/j.snb.2017.11.008
- 433 Tao, L. Q., Zhang, K. N., Tian, H., Liu, Y., Wang, D. Y., Chen, Y. Q., Ren, T. L. (2017). Graphene-
- 434 Paper Pressure Sensor for Detecting Human Motions. *ACS Nano*, *11*(9), 8790–8795.
- 435 https://doi.org/10.1021/acsnano.7b02826
- 436 Teo, M. Y., Stuart, L., Devaraj, H., Liu, C. Y., Aw, K. C., & Stringer, J. (2019). The: In situ
- 437 synthesis of conductive polyaniline patterns using micro-reactive inkjet printing. *Journal of*

438 *Materials Chemistry C*, 7(8), 2219–2224. https://doi.org/10.1039/c8tc06485g

- Tian, Y., Qu, K., & Zeng, X. (2017). Investigation into the ring-substituted polyanilines and their
- 440 application for the detection and adsorption of sulfur dioxide. *Sensors and Actuators, B:*

441 *Chemical*, 249, 423–430. https://doi.org/10.1016/j.snb.2017.04.057

- 442 Tobjörk, D., & Österbacka, R. (2011). Paper electronics. *Advanced Materials*, 23(17), 1935–1961.
 443 https://doi.org/10.1002/adma.201004692
- 444 Wang, Q., Sun, J., Yao, Q., Ji, C., Liu, J., & Zhu, Q. (2018). 3D printing with cellulose materials.
- 445 *Cellulose*, 25(8), 4275–4301. https://doi.org/10.1007/s10570-018-1888-y
- 446 Wang, Yanhu, Zhang, L., Zhao, P., Ge, S., Yan, M., & Yu, J. (2019). Visual distance readout to
- display the level of energy generation in paper-based biofuel cells: application to enzymatic
- 448 sensing of glucose. *Microchimica Acta*, *186*(5). https://doi.org/10.1007/s00604-019-3374-0

Wang, Yanmin, Liu, A., Han, Y., & Li, T. (2019). Sensors based on conductive polymers and their
composites: a review. *Polymer International*, (September 2019).

451 https://doi.org/10.1002/pi.5907

- 452 Yan, H., Guo, Y., Lai, S., Sun, X., Niu, Z., & Wan, P. (2016). Flexible Room-Temperature Gas
- 453 Sensors of Nanocomposite Network-Coated Papers. *ChemistrySelect*, *1*(11), 2816–2820.
- 454 https://doi.org/10.1002/slct.201600648
- Youssef, A. M., El-Samahy, M. A., & Abdel Rehim, M. H. (2012). Preparation of conductive paper
 composites based on natural cellulosic fibers for packaging applications. *Carbohydrate*

457 *Polymers*, 89(4), 1027–1032. https://doi.org/10.1016/j.carbpol.2012.03.044

- 458 Yu, Z., Tang, Y., Cai, G., Ren, R., & Tang, D. (2019). Paper Electrode-Based Flexible Pressure
- 459 Sensor for Point-of-Care Immunoassay with Digital Multimeter. *Analytical Chemistry*, 91(2),

460 1222–1226. https://doi.org/10.1021/acs.analchem.8b04635

- 461 Zang, X., Jiang, Y., Wang, X., Wang, X., Ji, J., & Xue, M. (2018). Highly sensitive pressure
- sensors based on conducting polymer-coated paper. Sensors and Actuators, B: Chemical,

463 273(July), 1195–1201. https://doi.org/10.1016/j.snb.2018.06.132

- Zhang, W., Wu, Z., Hu, J., Cao, Y., Guo, J., Long, M., ... Jia, D. (2019). Flexible chemiresistive
- sensor of polyaniline coated filter paper prepared by spraying for fast and non-contact
- detection of nitroaromatic explosives. *Sensors and Actuators B: Chemical*, 127233.
- 467 https://doi.org/10.1016/j.snb.2019.127233
- Zhang, Y., Yang, Z., Yu, Y., Wen, B., Liu, Y., & Qiu, M. (2019). Tunable electromagnetic
- interference shielding ability in a one-dimensional bagasse fiber/polyaniline heterostructure.
- 470 *ACS Applied Polymer Materials*, *1*(4), 737–745. https://doi.org/10.1021/acsapm.8b00025