Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019



Journal of Materials Chemistry A

COMMUNICATION

Supporting Information

Wearable Binary Cooperative Polypyrrole Nanofilms for Chemical Mapping on the Skin

Vitória Brito de Morais, ^a Cátia Crispilho Corrêa, ^a Evandro Martin Lanzoni, ^a Carlos Alberto Rodrigues Costa, ^a Carlos César Bof Bufon, ^a Murilo Santhiago* ^a

^aBrazilian Nanotechnology National Laboratory (LNNano), CNPEM, 13083-970, Campinas, Brazil. *murilo.santhiago@lnnano.cnpem.br

S1) Procedure for PPy nanofilm electrical measurements

The nanofilm resistance measurements were all conducted using a DC mode multimeter. The

positioning of the probes during the measurements is shown in Figure S1.



Figure S1. Electrical measurements of the PPy nanofilms using (a) silver contact pads and (b) directly on the conductive spot.

S2) Cross-sectional SEM image of the PPy nanofilm and thickness measurements

The Figure S2 below shows the cross-sectional SEM image and the arrows indicates the PPy nanofilm. The material was cleaved under liquid nitrogen. The thickness of the nanofilm was approximately $148 (\pm 34)$.



Figure S2. Cross-sectional SEM image of the PPy nanofilm. The white arrows indicate the PPy nanofilm.

S3) XPS additional informations

PPy exhibits a higher intensity peak in the high-resolution spectrum of N1s at a binding energy of approximately 399.7 eV, characteristic of pyrrole nitrogen (-NH-), which is present with a percentage of 50% relative to the total of nitrogen species in the material. In addition, a high binding energy tail attributed to positively charged nitrogen species, namely polarons and bipolarons, is also observed. The chemical treatment with NaOH results in the formation of deprotonated Py nitrogens. It is possible to note that the chemical step significantly enhances the formation of imine-like structures (-N=), as confirmed by the increase of the peak at lower binding energy of 397.7 eV.^{1–3}

Figure S3a shows the percentage of chemical structures at each chemical step. The predominant species on each step are in good agreement with our electrical measurements. For instance, high and low percentages of imine-like and polaron/bipolaron structures, respectively, should be observed in the deprotonation step (NaOH treatment). Moreover, the deprotonation step causes the remotion of counter ions, which was confirmed by the low atomic percentage of chloride on the surface (Figure S3b).



Figure S3. (a) Percentage of occurence for nitrogen especies after each treatment step. (b) Atomic percentual in the XPS survey to the elements after each treatment step.

 Table S1. Binding energies and atomic percentual obtained of N1s high resolution XPS analysis for PPy nanofilm after each step of treatment.

| | PPy | -AG | PPy-1 | NaOH | PPy | -HCl |
|------------|-----------|----------|-----------|----------|-----------|----------|
| Assignment | B.E. (eV) | % Atomic | B.E. (eV) | % Atomic | B.E. (eV) | % Atomic |
| N-H | 399.57 | 52.62 | 399.56 | 47.02 | 399.72 | 52.40 |
| -N= | 398.05 | 20.25 | 397.77 | 41.49 | 398.21 | 7.17 |
| Polaron | 400.80 | 21.63 | 401.00 | 6.33 | 400.50 | 28.47 |
| Bipolaron | 402.50 | 5.50 | 402.00 | 5.16 | 402.07 | 11.96 |

S4) Partially reversible electrical response

Initially, PPy nanofilms have an average electrical resistance of $2.8 \pm 0.9 \text{ k}\Omega$. The mechanism of response of the wearable device is based on the protonation of the PPy nanofilms chemically treated with NaOH. After the chemical process the resistance of the PPy nanofilms increases (100.1±38.6 k Ω) and the functional material becomes sensitive to acids. By exposing the chemically treated PPy nanofilms to HCl (either in liquid, vapor or vapor adsorbed onto solids), systematically decreases the resistance (9.0±4.7 k Ω), and this variation from step 2 to step 3 is the fundamental basis of the electrical response of the wearable devices (Figure S4).



Figure S4. Schematic principle of operation of the device. Electrical response after each step: (1) as-grown PPy nanofilm, (2) after NaOH treatment, and (3) after HCl vapor exposure. Error bars correspond to the standard deviation of 10 independent devices.

S5) Bending test additional informations and electrical measurements of the crumpled device

The curves shown in the manuscript (Figures 2i and 2j) represent a small portion of the curves shown in Figures S4a and S4b. The devices were able to perform (1201 ± 207) cycles considering a positive bend (Figure S4a) and (1932 ± 690) cycles considering a negative bend (Figure S4b). We also inserted the control curve without bending the devices (Figure S4c). By taking into account the control curve, the bending tests do not have a significant impact on the electric response of the devices.



Figure S5. (a) Positive (+ 180) and (b) negative (-180) bending curves. (c) control curve. The black arrows in Figures (a) and (b) shows the time in which the bending process started.

J. Mater. Chem. A

We measured the electrical resistance before and after the device was completely crumpled. Table S2 below shows the obtained values.

| Table S2. Electrical resistance obtained before and after crumpling the devices. | | | | |
|----------------------------------------------------------------------------------|------------------------|-----------------------|--------------------|--|
| Sample | $R_{before} (k\Omega)$ | $R_{after} (k\Omega)$ | $\Delta R/R_0$ (%) | |
| 1 | 90.7 | 92.2 | 1.7 | |
| 2 | 75.0 | 77.2 | 2.9 | |
| 3 | 130.4 | 132.4 | 1.5 | |
| 4 | 102.3 | 105.1 | 2.7 | |
| 5 | 90.0 | 92.8 | 3.1 | |
| 6 | 122.4 | 126.2 | 3.1 | |
| 7 | 110.3 | 111.2 | 0.8 | |
| 8 | 98.5 | 99.0 | 0.5 | |
| 9 | 115.1 | 116.4 | 1.1 | |
| 10 | 86.7 | 88.2 | 1.7 | |
| | | mean | 1.9 | |
| | | s.d. | 1.0 | |

Communication

S6) FTIR discussion and PPy nanofilm stability test

By comparing the band intensities located in 1570 and 1480 cm⁻¹ after the NaOH treatment in Figure 3a, it is possible to note that the predominant intensity belongs to the band at 1480 cm⁻¹, while for the as-grown material the band in 1570 cm⁻¹ was higher. These results are in good agreement with previous studies regarding the influence of pH on the structural and electrical properties of PPy.^{4,5} The deprotonation process resulting from the NaOH treatment causes a reorganization in the structure of the polymer chains, reducing the occurrence of the charge carriers responsible for the conductive character of the polymer, namely polarons and bipolarons, which are directly responsible for the decrease in the conductivity of the material. After exposing the devices to HCl, another change in the IR spectra that is in agreement with the literature can be observed. ⁶ There is a maximum intensity switch between the bands in 1570 and 1480 cm⁻¹, being the former more intense than the later, as shown in Fig. 3a.

In order to investigate the stability of the PPy nanofilms we monitored the electrical resistance over days using two groups of experiments (sealed samples and control). The sealed samples were fully-enclosed with tape and aluminum foil to minimize the influence of oxygen, humidity and UV light. These factors have been responsible for altering the electrical properties of PPy nanofilms.^{1,6–8} For comparison, a unsealed sample (control group) was kept next to the sealed sample at the same ambient conditions. The assay was conducted for approximately two months and the electrical resistance of both groups of devices were monitored weekly, as can be seen in Figure S6.

As illustrated in Figure S6, the electrical resistance of the control group sharply increases over time. However, we observed that the electrical resistance decreased in a similar way after exposure to HCl. Particularly, 95% of the initial electrical response was restored in both cases, indicating minimal irreversible damage of the PPy nanofilms.



Figure S6. Graph of resistance vs. time for the sealed and unsealed samples (control). The green and yellow markers shows the electrical response after exposing the device to HCl.

The influence of humidity was studied in three different levels. The Table S3 below shows the relative response for each condition studied. As can be observed, the relative response barely changed for different humidity levels.

| $\Delta R/R_0$ (%)* | - |
|---------------------|-----------------------------------------------------------------------------------------|
| 94.0 (± 1.1) | - |
| 93.9 (± 2.0) | |
| 92.3 (± 1.7) | |
| | Δ R / R ₀ (%)* 94.0 (± 1.1) 93.9 (± 2.0) 92.3 (± 1.7) |

Table S3. Mean relative electrical resistance of devices submitted to different levels of relative humidity

* The standard deviation represents 5 independent devices.

We also investigated the influence of the temperature. The Table S4 below shows the relative response measured at two different temperatures.

| Temperature (°C) | Δ R / R ₀ (%)* | | |
|------------------|-----------------------------------------|--|--|
| 21.0 | 93.9 (± 2.0) | | |
| 45.9 | 93.7 (± 3.0) | | |

* The standard deviation represents 5 independent devices.

S7) EDS of nanofilm surface

The energy-dispersive (EDS) detector was used to monitor the chemical composition of the nanoparticulates. The small black marker in the SEM image illustrated in Figure S7a shows the region of the image where the spectrum was collected. From the EDS spectrum illustrated in Figure S7b it is possible to confirm that copper is present in the nanoparticulate.



Figure S7. (a) SEM image of the PPy nanofilm surface. The EDS spectrum of the indicated nanoparticulate is presented in (b). The scale bar is $1\mu m$.

Considering that the concentration of $CuCl_2$ 4M solution used as oxidizing agent is very close to the solubility limit of this salt in water (4.48 M)⁹ and that during the polymerization the occurrence of evaporation is imminent to the process, precipitation of the salt on the PPy film polymer may be considered an explanation for the presence of copper on the surface, as shown above.

S8) AFM measurements of the PPy nanofilm surface

Figure S8a and S8b shows the AFM topographic image of cellulose acetate and the as-grown PPy nanofilm, respectively. It is possible note the presence of some nanoparticulates in the nanofilm. Figure S8c and S8d illustrate the dc/dz images for the substrate and the PPy-AG. As can be observed, all the higher regions formed by the nanoparticulates in Figure S8b have poor electrical properties. These nanoparticulates have copper in their structure and are probably formed due to high concentrations of copper chloride used in this work. Such residues of oxidants can also be observed in other substrates¹⁰. The results are consistent with the AFM-IR image obtained for the PPy-AG nanofilm (Figure 3), which indicates less PPy on the higher regions of the nanofilm.



Figure S8. AFM topographic images of (a) the CA and (b) PPy-AG. AFM dc/dz images of (c) CA and (d) PPy-AG. All scale bars are 1 μ m. The AFM images were taken in the same region of the sample, as indicated by the dashed white squares.

S9) Surface roughness of the PPy nanofilm

Figure S9 shows the topography obtained by AFM after each treatment step. It is possible to observe the formation of characteristic globular structures of the material after polymerization (PPy-AG) in Figure S9a. The roughness obtained for the nanofilm surface at this stage was approximately 2.9 nm, considering an area of 2.7 μ m². It is possible to note that alkaline treatment increases the surface roughness (R_q=8.3 nm), as can be seen in Figure S9b. After exposure to HCl vapor, no significant variation in the surface roughness was observed, as shown in Figure S9c.



Figure S9. AFM topographic images of (a) PPy-AG, (b) PPy-NaOH and (c) PPy-HCl. These images were extracted from Figure 3c. The roughness (Rq) was obtained in the same area for all steps illustrated. The scale bars are 1 µm.

S10) Static contact angle measurements and additional information about the "chemical chessboard"

Static contact angle (CA) measurements were performed on the nanofilm samples at different steps of the process. The average contact angle obtained (for 8 samples) for the surface of the cellulose acetate substrate as a control group was (71±2)°. As shown in Figure S10a, the wettability of the as-grown PPy nanofilm is similar to the substrate. After treatment with NaOH the contact angle decreases. It is well known that surface chemistry can promote wettability changes, however, due to differences in roughness observed in Figure S10 we cannot exclude this effect on the contact angles. When the PPy-NaOH films are exposed to HCl the contact angle did not go back to initial values observed in the as-grown sample. Since we confirmed by XPS that the chemical composition in PPy-AG and PPy-HCl is practically the same, the alteration in roughness caused by the NaOH treatment could lead to this difference. The results shows that water-based droplets will wet the nanofilms in a similar fashion. This is an important feature when the goal is to map droplets using an array of PPy nanofilms.



Figure S10. Static contact angle measurements of (a) PPy-AG, (b) PPy-NaOH and (c) PPy-HCl nanofilms.

In order to complement the information presented in the graphs of Figure 4b (i-iii), Table S5 shows the mean values obtained for different samples, as well as their respective standard deviations after exposure to solutions with different pH values.

| | $\Delta \mathbf{R}/\mathbf{R}_{0}$ (%) | | |
|--------------------|--------------------------------------------------|----------------------------------------------|--|
| рН | PPy-AG | PPy-NaOH | |
| 2.0 | -25.7 (± 9.8) | -90.3 (± 3.8) | |
| 7.0 | 50.8 (± 20.7) | 23.0 (± 3.9) | |
| 12.0 | 118.3 (± 28.8) | 6.6 (± 4.2) | |
| 2.0 7.0 12.0 | -25.7 (± 9.8) 50.8 (± 20.7) 118.3 (± 28.8) | -90.3 (± 3.8) 23.0 (± 3.9) 6.6 (± 4.2) | |

Table S5. Mean and s.d. values obtained for the "chemical chessboard"

J. Mater. Chem. A

Communication

S11) Functional devices attached on the skin or gloves

Figure S11a and S11b shows that the devices can be attached on the skin and laboratory gloves, respectively.



Figure S11. Pictures of the biocompatible, lightweight and conformable device attached on (a) skin and (b) laboratory glove.

S12) Electrical response to other compounds

Figure S12 below shows the normalized electrical response to HCl, nitric acid, acetic acid, ammonia, water vapor (control), and 2-mercaptoethanol.



Figure S12. Electrical response of PPy-NaOH nanofilm to inorganic and organic compounds.

S13) Integration procedure and recognition of the QR code

The QR code can be generated on a free website (in this case, QR Code Generator®) whose link is related to the code (Figure S13a). The code can be read using free apps, as illustrated in Figure S13b and S13c. We used a free app named QR Barcode Scanner®.

| а | Create your Q | R Code for fre | e | | | |
|----|-----------------|-------------------------------------------------------------------------------|--------------------------------------------------------|--------------------------|--|--|
| | 🗉 URL 🗉 VCard 🚍 | Text @ E-mail 戻 SMS | 🖞 Facebook 🛛 PDF | ာ MP3 i O App stores | | |
| | Images | | | | | |
| | Text QR Code | | | | | |
| | Message: | Name: Vitória Brito de Morais Company: CNPEM LNNano Check in: 8:00 AM | RG/Passport: 12.345.678-9 Phone: +55 11 9 9221-3393 | | | |
| | | | 0 | ~ | | |
| | | CREATE | QR CODE | | | |
| b | P | | c | - | | |
| - | The | | | SUNO | | |
| | 1 Bin 2 | | Name: Vit RG/Passpo Composition | TEXT Oria Brito de La | | |
| a | | | Phone: (11) Check In: 8:0 | 9 9221 - LNNano | | |
| IJ | | O SUNO | | | | |
| U | C | 8 | | | | |
| | +0 | ELE | Carry | | | |
| T | - | 000 | | 31 | | |

Figure S13. (a) Website interface for generating QR code from user information. (b) Positioning the cellphone to read the code. (c) Reading the information of the QR code.

S14) Device thermal resistance test

The average electrical resistance values were obtained for 5 samples before and after printing. The temperature inside the printer remains between 50 and 80°C during printing and after the process there is an increase in electrical resistance of less than 5%. Thus, both the PPy-NaOH nanofilm and the cellulose acetate substrate can withstand the process without compromising the electrical response of the assembly.

S15) Supplementary experimental procedure

Device fabrication: The flexible substrate was prepared by dissolving 0.15 g of CA (Sigma-Aldrich) in 2.85 g of a mixture of acetone (LabSynth 99.5%)/cyclohexanone (Sigma-Aldrich 99%) in a ratio of 1:1, with constant stirring for 2 hours. Then 1 mL of the mixture was transferred to a mold made of poly (ethylene terephthalate) and let it dry overnight at 21°C. After evaporation of the solvent, the film was removed from the mold for the fabrication of the PPy arrays. We used patterned SAL to control the dimensions of the polymerized area. The adhesive layers (3M Scotch®810) were patterned with a knife plotter (Silhouette Curio) and attached to the substrate. Then, 10 μ L of a 4.0 M CuCl₂.H₂O solution (Emsure) was dispensed into the delimited area. The system was closed (Figure S15) and then exposed to Py monomer vapor (Alfa-Aesar 98%) for a certain time. A similar polymerization process have been described by us.^{11–14} After polymerization, the devices were washed with deionized water, and the SAL removed, leaving on the substrate a nanometer thick PPy film. In order to estimate the thickness of the PPy nanofilm we cleaved the samples in liquid nitrogen to obtain a good cross-section. We used the software of the SEM microscope to estimate the thickness of the nanofilms.

The electrical contact pads were also fabricated using the SAL method. Silver conductive inks (SPI Supplies) were spread on patterned SAL layers and carefully removed after the ink was dried. The alkaline treatment consisted of keeping aliquots of 0.5 M NaOH (Emsure 99%) solution on the PPy structures. After the reaction time, the devices were washed with deionized water. Finally, the devices were exposed to HCl (vapor, liquid, and vapor adsorbed onto solids) and the electrical resistance was measured, as shown in Figure S1.



Points 1-4: Py monomer vapor source

Figure S15. Gas phase polymerization process setup. (a) Illustrative scheme of the components used during the polymerization. (b) the location of the pyrrole monomer.

Characterization: A 3D laser scanning confocal microscope (LSCM) from Keyence, model VK-X200 series, Osaka, Japan was used to obtain a thickness of the substrate. Static contact angles were measured by sessile drop technique using an Attension THeTa L (Finland) under ambient laboratory conditions. A 2 μ L drop of deionized water was placed on the surface, and the contact angle was measured after 10 seconds. The One Attension® software was used for contact angle measurements. The measurements were repeated on eight samples, and the average value was reported with standard deviation. AFM topographical images were obtained using the intermittent contact mode in a Park NX10 microscope with an NCHR NanoWorld silicone tip (resonance frequency=75 kHz and force constant = 2.8 N·m⁻¹). AFM-IR absorption images were obtained using the contact mode in an Anasys NanoIR2-s microscope with a fixed wavenumber of 1570 cm⁻¹. XPS was performed with a Thermo Scientific K α micro-focused monochromatized source with a resolution of 0.100 eV, pass energy of 50 eV with a spot size of 300 µm and 10 scans. The SEM images of the cross-sectional view of a structure and its respective nitrogen maps (EDS) were performed using FEI® Inspect 50FEG Scanning Electron Microscope. Fourier transform infrared spectra were recorded in absorption mode by a Nicolet 6700 (Thermo Scientific) spectrometer in the range 4.000-400 cm⁻¹ at 100 scans per spectrum with a resolution of 2 cm⁻¹ in ATR (Attenuated Total Reflectance) mode. All of the characterizations were performed on freshly prepared samples. The scotch tape test was performed using the NaOH treated device and after each cycle (apply and remove tape) the electrical resistance was measured. The bending test was conducted on a lab-made apparatus by measuring the resistance as a

function of the time during the test. The bending cycle was ten seconds. QR-codes were printed on the substrate containing the PPy-NaOH nanofilms using a conventional toner printer (Lexmark® MX711de).

Multimedia supplementary files

Video S1) Sensitivity test to HCl vapor

In the video presented in the supplementary material it is possible to observe the device detecting HCl vapor. In one of the Petri dishes we have pure water and in the other, concentrated HCl, both colorless. When the hand of the user reaches the Petri dish containing HCl the LED instantly lights up. After the treatment with NaOH, the PPy-NaOH nanofilm presents high electrical resistance to the passage of the current, thus preventing the LED from lighting up. By exposing the device to HCl vapor, the semiconductor is doped, decreasing the resistance and thus allowing the passage of current to turn on the LED.

Video S2) HCl vapor adsorbed on solid surfaces

This video shows the array of PPy nanofilms being protonated by a glove that contains HCl vapor adsorbed on it. By using the PPy nanofilm array it is possible to precisely map the region that was touched by the finger containing HCl adsorbed.

Video S3) QR code reading

In this video it is possible to observe the QR code reading step. Any person can obtain information about the user or visitor at any time.

Video S4) Demonstration of the capacity to move freely when wearing the device

Once attached on the skin the device does not compromise user movement. In this video it is possible to observe that after natural movements, such as opening and closing hands or even fist movements, the device remains attached to the glove.

Video S5) Electrical measurements during movements

We inserted a new video showing how the electrical resistance changes during the movements. The device was connected to a multimeter via electrical contacts, as can be seen in the video. The PPy nanofilm was treated with 0.5 M NaOH as described in the manuscript. The electrical resistance of the material remains practically unchanged during movements.

Supplementary references

- 1 C. Malitesta, I. Losito, L. Sabbatini and P. G. Zambonin, J. Electron Spectrosc. Relat. Phenom., 1995, 76, 629–634.
- 2 D. K. Hwang, D. Song, S. S. Jeon, T. H. Han, Y. S. Kang and S. S. Im, *J Mater Chem A*, 2014, **2**, 859–865.
- 3 K. L. Tan, B. T. G. Tan, E. T. Kang and K. G. Neoh, J. Mater. Sci., 1992, 27, 4056-4060.
- 4 J. Stejskal, M. Trchová, P. Bober, Z. Morávková, D. Kopecký, M. Vrňata, J. Prokeš, M. Varga and E. Watzlová, *RSC Adv.*, 2016, **6**, 88382–88391.
- 5 N. Costantini and J. M. Lupton, Phys. Chem. Chem. Phys., 2003, 5, 749-757.
- 6 D. N. Huyen, N. T. Tung, T. D. Vinh and N. D. Thien, Sensors, 2012, 12, 7965–7974.
- 7 K. Kanemoto and J. Yamauchi, J. Phys. Chem. B, 2001, 105, 2117-2121.
- 8 W.-D. Lin, H.-M. Chang and R.-J. Wu, Sens. Actuators B Chem., 2013, 181, 326-331.
- 9 J. A. Dean and N. A. Lange, Eds., *Lange's handbook of chemistry*, McGraw-Hill, New York, NY, 15. ed., 1999.
- 10 M. Santhiago, P. Costa, M. P. Pereira, C. C. Corrêa, V. B. Morais and C. C. B. Bufon, *ACS Appl. Mater. Interfaces*, DOI:10.1021/acsami.8b12780.
- 11 C. C. Bof Bufon and T. Heinzel, Appl. Phys. Lett., 2006, 89, 012104.
- 12 S. Barnoss, H. Shanak, C. C. Bof Bufon and T. Heinzel, *Sens. Actuators Phys.*, 2009, **154**, 79–84.
- 13 C. C. Bof Bufon and T. Heinzel, *Phys. Rev. B*, DOI:10.1103/PhysRevB.76.245206.
- 14 M. Santhiago, J. Bettini, S. R. Araújo and C. C. B. Bufon, *ACS Appl. Mater. Interfaces*, 2016, **8**, 10661–10664.