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Nanostructured Layer Based on Intrinsically Conductive Polymers for Optimizing Carbon Electrodes' Surface: Electrospray and Ultrasonic Spray Coating †

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Abstract: In this work, we focused on Electrospray (ES) and Ultrasonic Spray Coating (USC) as two promising and innovative fabrication techniques for the optimization of carbon electrodes' surface to be employed in Bio-Electrochemical Systems. We performed, on commercial carbon paper electrodes, controlled depositions of a nanostructured layer containing PEO and PEDOT:PSS. We then employed electron microscopy and Raman spectroscopy to characterize the morphology and superficial uniformity of the so-obtained electrodes. Together with electrochemical characterizations and experiments in bio-electrochemical devices, we demonstrated how ES and USC represent promising techniques for the optimization of carbon electrodes' surface obtained with the deposition of a conductive nanostructured layer.

Keywords: Microbial Fuel Cells; Microbial Electrolysis Cells; surface decoration; electrospray; Ultrasonic Spray Coating

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1. Introduction

Nowadays, Bio-Electrochemical System such as Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) draw increasing attention for their potential application in sustainable energy production. In both MFCs and MECs systems, the anode electrode plays a crucial role in improving overall devices' performances, and numerous studies aimed at increasing the electrode's surface hydrophilicity, porosity and electrical conductivity [1]. To this end, promising results were obtained by electrodes' surface optimization with both Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and Polyethylene oxide (PEO) [1,2]. Indeed, PEDOT:PSS is a well-known conductive polymer, and already finds applications in many sectors, among which energy conversion and storage. In addition, other works demonstrated how the surface decoration with PEO increased electrodes' surface hydrophilicity and, in MFCs, promoted the proliferation of the biofilm that is crucial for the proper functioning of such devices [2]. In this work, we focus on Electrospray and Ultrasonic Spray Coating as two promising and innovative fabrication techniques for the deposition of PEO and PEDOT:PSS solutions on commercial carbon paper. Both techniques are scalable and offer fine-control over the deposition of nanostructured layers. While previous works already processed PEDOT:PSS with electrochemical methods [1], it is the first time such material is deposited on MFC electrodes with ES or USC techniques.

Employing both ES and USC, we fabricated samples on which we then characterized the morphology and the electrochemical properties provided by the nanostructured layer. In addition, we investigated the use of Raman spectroscopy to quantitatively validate and

map spatial uniformity of such layers. Finally, we assessed performance improvements and stability in laboratory MFC devices.

2. Materials and Methods

2.1. Materials and Electrodes Fabrication

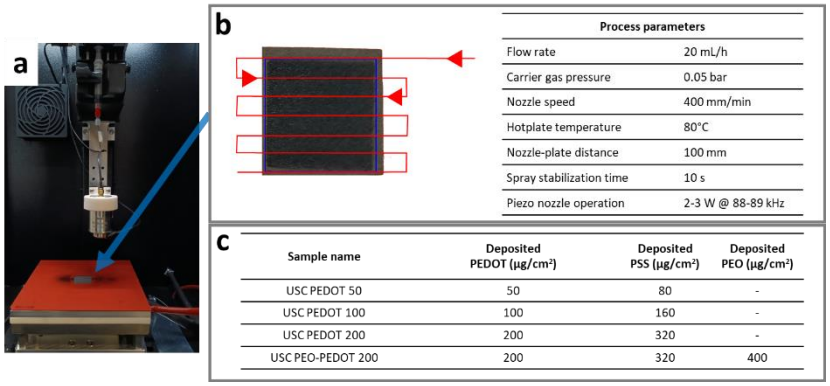
We fabricated all electrodes starting from as-purchased commercial Carbon Paper (AvCarb, Lowell, MA, USA). To realize the nanostructured coating, we prepared spraying solutions containing Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 1.3 wt.% water dispersion, purchased from Sigma Aldrich), Polyethylene oxide (PEO, 600 kDa average molecular weight, purchased from Sigma Aldrich), and de-ionized water (Merck Millipore, Darmstadt, Germany).

Electrolyte solution for electrochemical characterization contained sodium acetate, ammonium chloride, potassium chloride and sodium dihydrogen phosphate, all purchased from Sigma Aldrich.

2.1.1. Anodes Fabrication via Ultrasonic Spray Coating (USC)

We employed a Nadetech Ultrasonic Spray Coater (Nadetech Innovations, Navarra, Spain) to deposit the PEDOT:PSS nanostructured layer on bare carbon paper. The sprayed solution consisted in commercial PEDOT:PSS aqueous dispersion (0.5 wt.% PEDOT, 0.8 wt.% PSS), diluted in de-ionized water (2/8 volume ratio). As a result, the final solution contained 1 mg/mL of PEDOT and 1.6 mg/mL of PSS, providing us a finer control over the deposited material amount respect to pure commercial solution. Instead, in order to deposit both PEO and PEDOT:PSS, we prepared a spraying solution suitable for USC starting from the same PEDOT:PSS commercial aqueous dispersion, adding PEO (1 wt.%) and then diluting in deionized water (1/9 volume ratio). Prior use, we stirred the solution overnight to ensure uniform mixing.

Figure 1a-b describes the process condition and parameters. Fabricated samples, here named *USC PEDOT 50/100/200* or *USC PEO-PEDOT 200*, are described in Figure 1c alongside with details on the deposited material amount.



Process parameters	
Flow rate	20 mL/h
Carrier gas pressure	0.05 bar
Nozzle speed	400 mm/min
Hotplate temperature	80°C
Nozzle-plate distance	100 mm
Spray stabilization time	10 s
Piezo nozzle operation	2-3 W @ 88-89 kHz

Sample name	Deposited PEDOT (µg/cm²)	Deposited PSS (µg/cm²)	Deposited PEO (µg/cm²)
USC PEDOT 50	50	80	-
USC PEDOT 100	100	160	-
USC PEDOT 200	200	320	-
USC PEO-PEDOT 200	200	320	400

Figure 1. (**a**) detail of the USC equipment, (**b**) pattern and process parameters employed to perform PEDOT:PSS and PEO depositions. (**c**) overview of anode electrodes fabricated by USC.

We obtained each electrode sample from a 30 × 30 mm carbon paper square, held in place on the heated deposition plate by vacuum suction and a silicone mask. The deposition duration ranged within 2–6 min, with the spray nozzle following a pattern that aimed at maximizing surface uniformity of deposited material (Figure 1b).

2.1.2. Anodes Fabrication via Electrospray (ES)

We employed a NANON 01A electrospray device (MECC Co. Ltd., Fukuoka, Japan) to deposit PEO and PEDOT:PSS on carbon paper. The spraying solution consisted of pure commercial PEDOT:PSS commercial aqueous dispersion, with the addition of PEO (1

wt.%). Prior use, we stirred the solution overnight to ensure uniform mixing. As a result, the final solution contained 5 mg/mL of PEDOT, 8 mg/mL of PSS and 10 mg/mL of PEO, and it was properly loaded into a syringe. ES process was obtained by applying a voltage value of 30 kV, thus guaranteeing the direct deposition of nanodrops onto carbon paper used as collector substrate. The deposition lasted about 40 min, with a flow rate of 1 mL/h and nozzle-plate distance of 90 mm. The fabricated electrodes, here called *ES PEO-PEDOT 200*, contained 200 μg/cm^2 of PEDOT, 320 μg/cm^2 of PSS and 400 μg/cm^2 of PEO. Thus, samples *USC PEO-PEDOT 200* and *ES PEO-PEDOT 200* allow us to compare ES and USC as fabrication techniques, being equal the deposited material amount.

2.2. Characterization Techniques

2.2.1. Morphological and Physical-Chemical Characterizations

To analyse the surface morphology of anode electrodes, we employed a Field Emission Scanning Electron Microscope (FESEM, ZEISS Supra 40), also featuring a detector for energy-dispersive x-ray (EDX) spectroscopy.

We examined the surface of fabricated anodes using Raman spectroscopy to highlight the presence of PEDOT:PSS by observing its fingerprint peaks. In this work, we also tried to assess how Raman spectroscopy could provide information on the uniformity of the deposited PEDOT:PSS layer. To this end, we analysed our as-fabricated samples employing a Renishaw inVia™ Qontor Raman Microscope (532 nm laser excitation wavelength). Over the whole samples' surface, we acquired multiple single-point spectra, and a 300 × 250 μm^2 map (31 × 17 pixels).

2.2.2. Electrochemical Characterization and Operation in MFCs

We conducted all electrochemical characterizations using a PalmSens 4 (PalmSens BV, Municipality, The Netherlands) potentiostat. To assess the performance of fabricated electrodes in their intended environment of use, we performed both electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in an electrolyte solution commonly used in microbial fuel cells. Such solution contained sodium acetate ($C_2H_3NaO_2$, 1 g/L), ammonium chloride (NH_4Cl, 0.31 g/L), potassium chloride (KCl, 0.13 g/L) and sodium dihydrogen phosphate (NaH_2PO_4, 2.450 g/L).

We performed EIS characterizations to investigate the interfaces arising at the anode electrode: the fabricated anodes were analysed in a three-electrode configuration, where they served as working electrodes in contact with the standard MFC electrolyte solution. A platinum wire acted as counter electrode, while reference was an Ag/AgCl electrode. For EIS, we applied a 0 V DC bias, and an AC sinusoidal signal with a 10 mV amplitude and frequency ranging from 200 mHz to 150 kHz. Employing the same setup, we then conducted CV characterizations, applying potentials from −0.5 V to 0.9 V, at 100 mV/s, for 5 cycles.

Finally, to study performances of fabricated electrodes as anodes in MFC devices, we employed a setup and procedures analogous to those described in [3].

3. Results and Discussion

3.1. Morphological and Physical-Chemical Characterizations

We analysed the morphology of the samples fabricated in comparison with bare commercial carbon paper (Figure 2a–f). As the amount of the deposited material increases, the PEDOT:PSS layer becomes more evenly distributed over the surface. Also, it is possible to observe a preferential accumulation of deposited material on the most superficial fibres. The samples containing both PEO and PEDOT:PSS confirmed a similar superficial uniformity.

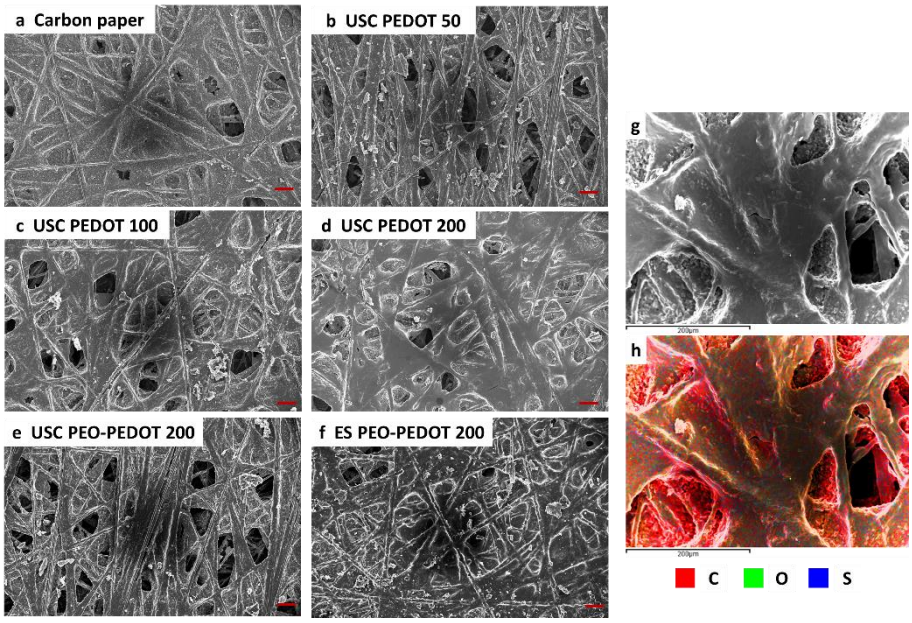


Figure 2. (**a**–**f**) FESEM images of the fabricated anodes surfaces. All images display a 75× magnification, with the marker corresponding to 100 μm. (**g**) FESEM image of a detail on a *USC PEDOT 200* electrode and (**h**) map of the elemental composition (EDX spectroscopy Kα1 peaks, represented elements: carbon, oxygen, sulphur).

Also, the EDX characterization (Figure 2g,h) allowed to distinguish the regions on the samples' surface where mainly carbon is present (uncovered carbon paper surface) from those also containing oxygen and sulphur (belonging to the deposited PEDOT:PSS).

Raman Characterization

The Raman spectrum of carbon paper (Figure 3) presents the two peaks typical of carbon-based materials (D band around 1347 cm^{-1} related with the presence of defects, vacancies and bent sp^2 bonds in the graphitic structure and G band around 1573 cm^{-1}, which is related with in-plane vibration of sp^2 hybridized C-C bonds). When analysing fabricated anodes, the main peaks located at 1256, 1360, and 1437 cm^{-1} can be associated to the presence of PEDOT:PSS on top of the carbon paper substrate (respectively, to Cα–Cα′ inter-ring stretching, Cβ–Cβ′ stretching, and Cα=Cβ symmetric stretching vibrations [4,5]). The other observed, weaker intensity peaks are also in good agreement with those described in detail by Kong et al. [4].

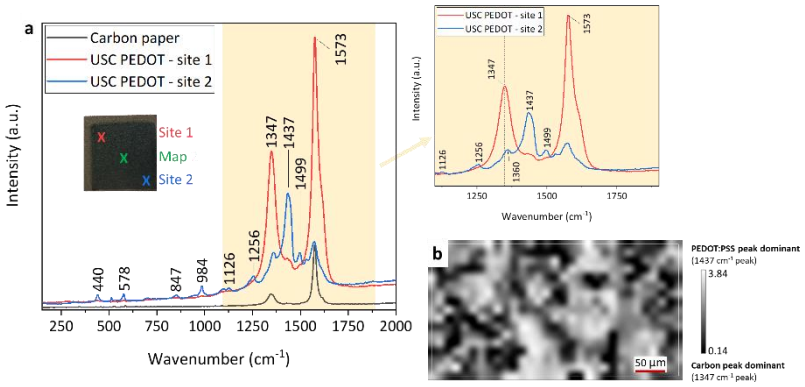


Figure 3. (**a**) Raman spectra acquired at two different sites on a *USC PEDOT 200* sample, compared with that of bare carbon paper. (**b**) false-colour map representing the relative abundance of PEDOT:PSS on carbon paper.

As shown in Figure 3a, the two selected Raman spectra acquired at different sites on the sample feature different intensity of characteristic peaks, which hint a carbon-dominated (*site 1*) or PEDOT:PSS-dominated (*site 2*) response. Such macroscopic non-uniformity led us to further investigate potential inhomogeneities observable at the micro-scale. To this end, as previously described, we acquired a matrix of single-point measurements producing a 300 × 250 μm² map. Then, by computing the ration between the intensity of a PEDOT:PSS characteristic peak (1437 cm^{-1}) respect to that of a carbon characteristic peak (1347 cm^{-1}), we obtained a false-colour image representing the relative abundance of PEDOT:PSS (Figure 3b).

Indeed, this technique can only provide relative abundance information, and is not sufficient to quantify the deposited material amount. Nonetheless, we believe Raman mapping technique deserves further investigation as might prove useful to compare deposition uniformity, both at the mm- and μ-meter scale, across several repeated samples, or to compare different deposition techniques.

3.2. Electrochemical Characterization and Operation in MFCs

The cyclic voltammetry characterizations demonstrated an electric double-layer capacitance (EDLC) behaviour for all samples (Figure 4a).

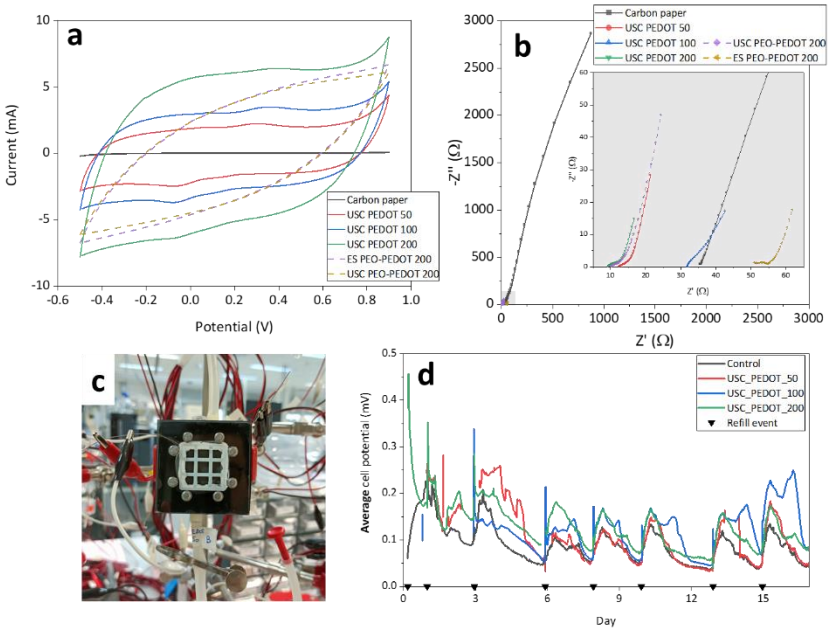


Figure 4. (**a**) EIS and (**b**) CV characteristics acquired on fabricated samples; (**c**) MFC device employed to study fabricated electrodes and (**d**) average performance recorded on MFC experiments.

In particular, electrodes fabricated via USC exhibited a direct correlation between the deposited PEDOT:PSS amount and the capacitive response. Compared to bare carbon paper, PEDOT:PSS-modified electrodes feature an increased electrical conductivity thanks to the presence of intrinsically conductive PEDOT. Also, the enhanced electric double-layer capacitance can be attributed to the hydrophilic PSS, which increases surface's wettability and thus the electrically active area. Noticeably, samples containing both PEO and PEDOT:PSS presented a further deviation from the rectangular response of the EDLC. This could be attributed to an increase in interface resistance induced by the presence of PEO, as well as to the high scan rate employed [5].

Cyclic voltammograms resulted reproducible between scans, symmetric between forward and reverse scan, and presented no faradic response. Such characteristics indicate

that so-fabricated electrodes are inactive in electrolyte in microbial fuel cell electrolyte and represent good candidates to be employed in MFC.

The EIS characteristics (Figure 4b), which could be physically modeled with a Randles circuit, featured a distorted arc at high frequencies, while mass transfer impedances dominated at lower frequencies. The arc distortion is associated with the non-ideal capacitance characteristic of the complex electrode-electrolyte interface. For the *USC PEDOT* samples, these results confirmed both the direct correlation between EDLC and deposited material amount, and that PEDOT:PSS deposition effectively reduced electrodes' impedances.

Finally, starting from these promising electrochemical results, we assessed the performances of fabricated electrodes as anodes in microbial fuel cell devices as described in [3] (and represented in Figure 4c), assembling a triplet of devices for each deposition previously described. Figure 4d displays the output potential measured from MFCs, containing *USC PEDOT* anode electrodes, during the first 16 days of activity. Each curve represents the average potential of each triplet of MFCs, highlighting how devices containing PEDOT:PSS nanostructured anodes systematically provided a higher potential output compared to bare carbon paper electrodes.

4. Conclusions

In this work we investigated the use of Electrospray (ES) and Ultrasonic Spray Coating (USC) as innovative fabrication techniques to obtain nanostructured layer for optimizing carbon electrodes' surface. Starting from commercially available polymers, PEO and PEDOT:PSS, we obtained solutions that can be conveniently employed to deposit a nanostructured conductive layer on carbon paper using ES and USC techniques. Both techniques allowed us to finely control the deposited material amount, while requiring processing times ranging from less than one hour down to few minutes. To the best of our knowledge, this is the first time such techniques have been employed to deposit PEDOT:PSS on anodes for Bio-Electrochemical systems.

Employing electron microscopy, we analysed the morphology and uniformity of the nanostructured layer as function of the material amount deposited with both ES and USC techniques. In addition, we investigated the potential of Raman spectroscopy as a tool to validate and map the relative spatial uniformity of PEDOT:PSS depositions, both across multiple samples and different fabrication techniques.

The electrochemical characterizations demonstrated the improvements given by electrodes' surface modification previously described, both in terms of reduced electrical impedances and of increased capacitive properties respect to bare carbon paper.

Finally, experiments performed in MFC devices highlighted, since the early operative stages, the performance improvements provided by ES and USC optimized anodes.

Author Contributions: Conceptualization, all authors; methodology, G.S., G.M. and M.Q; validation, G.M. and M.Q; formal analysis, G.S.; investigation, G.S.; resources, C.F.P. and M.Q.; data curation, G.S., G.M. and S.B.; writing—original draft preparation, G.S.; writing—review and editing, all authors; supervision, G.M., S.B. and M.Q.; project administration, C.F.P., S.B. and M.Q.; funding acquisition, C.F.P., S.B. and M.Q. All authors have read and agreed to the published version of the manuscript.

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References

1. Cai, T.; Meng, L.; Chen, G.; Xi, Y.; Jiang, N.; Song, J.; Zheng, S.; Liu, Y.; Zhen, G.; Huang, M. Application of Advanced Anodes in Microbial Fuel Cells for Power Generation: A Review. *Chemosphere* **2020**, *248*, 125985. https://doi.org/10.1016/j.chemosphere.2020.125985.
2. Massaglia, G.; Frascella, F.; Chiadò, A.; Sacco, A.; Marasso, S.L.; Cocuzza, M.; Pirri, C.F.; Quaglio, M. Electrospun Nanofibers: From Food to Energy by Engineered Electrodes in Microbial Fuel Cells. *Nanomaterials* **2020**, *10*, 523. https://doi.org/10.3390/nano10030523.
3. Massaglia, G.; Margaria, V.; Fiorentin, M.R.; Pasha, K.; Sacco, A.; Castellino, M.; Chiodoni, A.; Bianco, S.; Pirri, F.C.; Quaglio, M. Nonwoven Mats of N-Doped Carbon Nanofibers as High-Performing Anodes in Microbial Fuel Cells. *Mater. Today Energy* **2020**, *16*, 100385. https://doi.org/10.1016/j.mtener.2020.100385.
4. Kong, M.; Garriga, M.; Reparaz, J.S.; Alonso, M.I. Advanced Optical Characterization of PEDOT:PSS by Combining Spectroscopic Ellipsometry and Raman Scattering. *ACS Omega* **2022**, *7*, 39429–39436. https://doi.org/10.1021/acsomega.2c05945.
5. Park, S.-G.; Rhee, C.; Jadhav, D.A.; Eisa, T.; Al-Mayyahi, R.B.; Shin, S.G.; Abdelkareem, M.A.; Chae, K.-J. Tailoring a Highly Conductive and Super-Hydrophilic Electrode for Biocatalytic Performance of Microbial Electrolysis Cells. *Sci. Total Environ.* **2023**, *856*, 159105. https://doi.org/10.1016/j.scitotenv.2022.159105.