Preparation and characterization of in-lab formulated carbon-black/polylactic acid (CB/PLA) 3D-printed sensors

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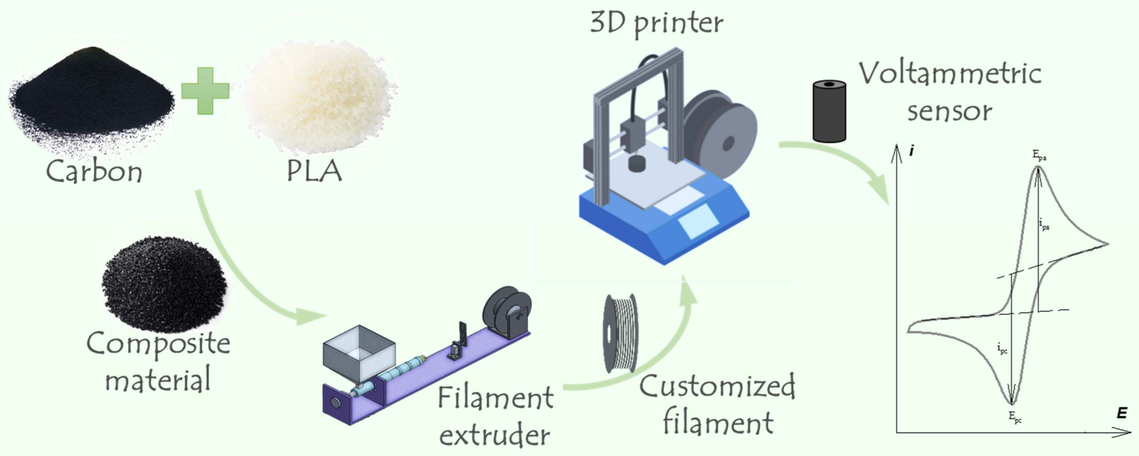

Additive manufacturing (commonly known as 3D printing) is emerging as an alternative approach for the fabrication of customized electrochemical sensors, owing to their many unique advantages such as its low-cost (both of the material and equipment), tunability and easy prototyping [1,2]. Concretely, electrodes are fabricated by fused deposition modelling (FDM) from thermoplastics such as polylactic acid (PLA), commonly doped with different carbon-based materials such as carbon black (CB) or graphene to overcome the insulating nature of PLA. Furthermore, the ease of fabrication of composite materials (through the incorporation of electrocatalysts during the extrusion of customized filaments) combined with the automatized fabrication and miniaturization makes 3D printing even more appealing.

In this direction, the development of a simple protocol for the preparation of bulk-modified conductive filaments for the printing of voltammetric sensors is explored herein. Firstly, optimum proportions of the composite material were found by percolation theory [3]. Next, the process for the printing and activation of the filament were also optimized to ensure the highest reproducibility, sensitivity, stability and fast response. To this aim, devices were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), and their performance was benchmarked against commercial electrodes. Finally, the potential of the approach is demonstrated in the analysis of ascorbic acid and melatonin.

Experimental

Sensor preparation

Preparation of the in-lab formulated filament started with the optimization of the carbon black (CB) and polylactic acid (PLA) mixture (Fig. 1), followed by its extrusion with a filament maker (Fig. 2). Electrodes were designed employing AutoCAD software (Autodesk, San Rafael, CA, USA) and 3D printed employing a 3D Artillery Genius printer (XuegangLu, China) (Fig. 3).

The chosen geometry was that of a cylinder of 10 mm height and 6 mm of diameter, with a 2.1 mm hole on the top side to allow the connection to the potentiostat with a banana. After printing, the lateral surface of the cylinder was insulated to ensure that only the bottom of the cylinder was acting as the working electrode; limiting in this manner its geometric area to 28.3 mm^2.

Electrochemical measurements

Electrochemical measurements were performed at room temperature employing a Palmsens MultiEmStat4 potentiostat (PalmSens, Houten, The Netherlands) and a standard three-electrode set up. The cell was composed of an Ag/AgCl (3 M KCl) reference electrode, a Pt wire as counter electrode and the developed 3d printed as the working electrode.

Characterization of the electrodes was performed employing cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with $[Fe(CN)_6]^{3/4-}$ as the redox probe. Concretely, the response towards a 2 mM solution in phosphate buffer (pH 7.4) was evaluated (Figs. 4-6).

The analytical performance of the sensor was also evaluated towards the determination of ascorbic acid (Fig. 7) and melatonin (Fig. 9) employing square wave voltammetry (SWV).

Data analysis

Analysis of the voltammetric and impedimetric signals was done with MultiTrace software (PalmSens; Houten, The Netherlands), which allowed to extract the conventional electrochemical parameters.

For CV and SWV, the peak heights and peak positions were calculated, from which the calibration curves were built (Figs. 8&10). For EIS spectra, the data was fitted to the Randles equivalent circuit (inset of Fig. 6), from which the charge transfer resistance between the solution and the electrode surface (R_{ct}) was the main parameter taken into account.

Printing and Characterization

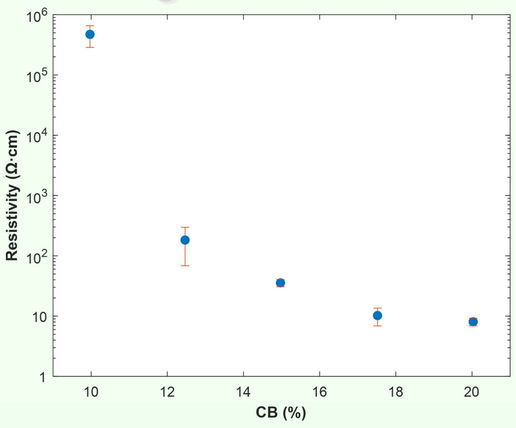

Fig. 1. Percolation curve obtained for CB and PLA composites during the optimization of the filament ratio. All mixtures were prepared in triplicate, with error bars corresponding to standard deviation.

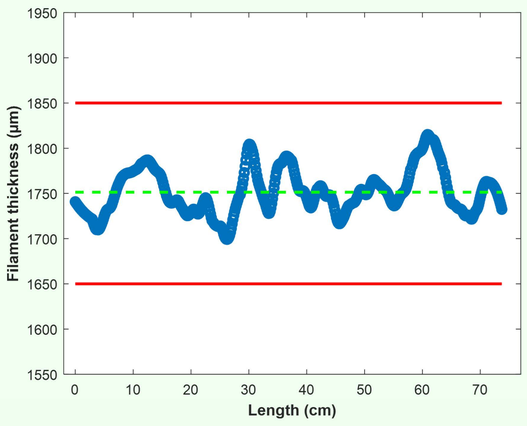

Fig. 2. Variation of the filament thickness during the extrusion process. Red lines correspond to the upper and lower specification limits, while the green line corresponds to the average value.

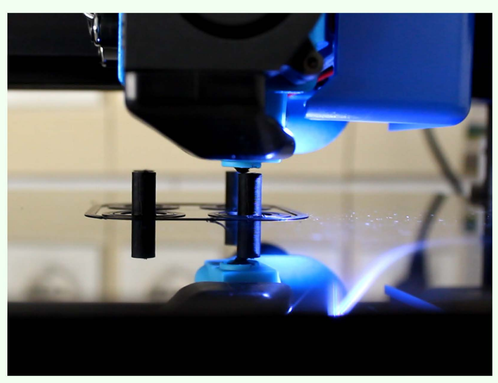

Fig. 3. Picture of the 3D-printing process, illustrating how the shape/size of the sensors can be easily tuned to fit the desired application.

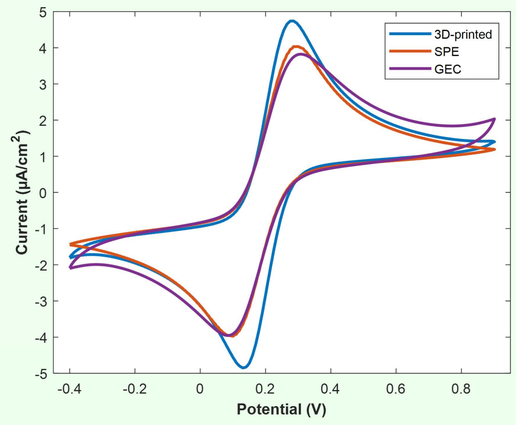

Fig. 4. Voltammetric response of a 3D-printed, screen printed (SPE) and graphite-epoxy composite (GEC) electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4). For comparison purposes, the currents have been normalized taking into account their respective geometric areas.

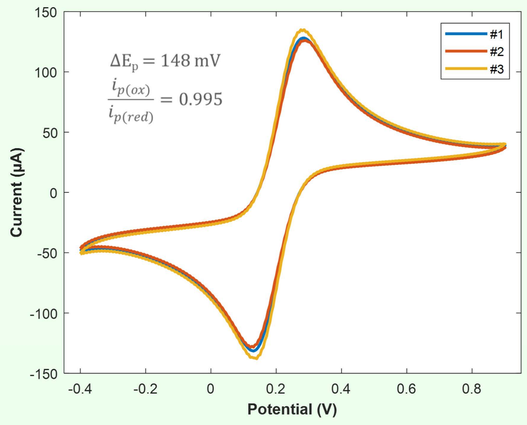

Fig. 5. Voltammetric responses of three different 3D-printed electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4) showcasing their good reproducibility.

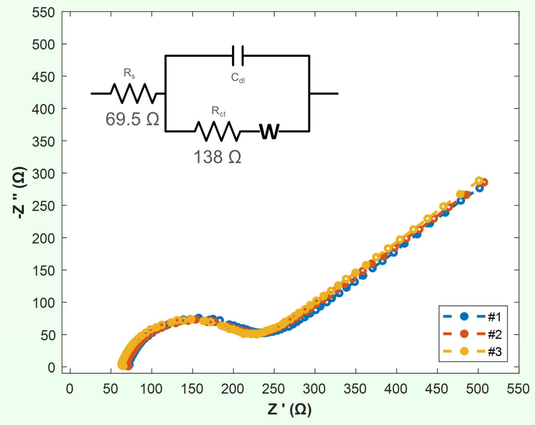

Fig. 6. Impedimetric responses of three different 3D-printed electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4), showcasing the good reproducibility as well as the low charge transfer resistance.

Ascorbic acid analysis

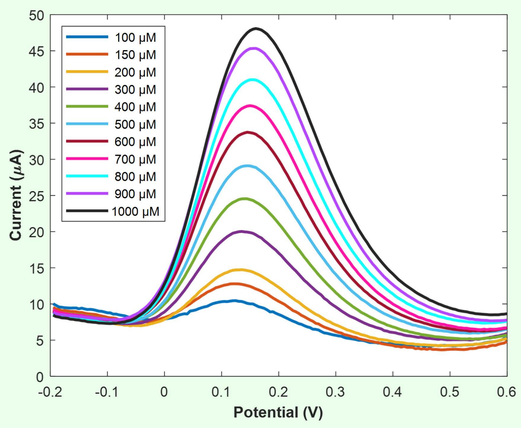

Fig. 7. Voltammetric response of the 3D-printed sensor towards ascorbic acid. Series of plots correspond to increasing concentrations from 100 to 1000 μM.

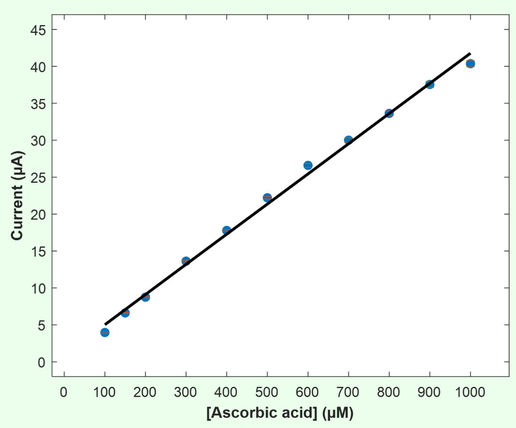

Fig. 8. Calibration curve for ascorbic acid obtained from the peak height of the voltammetric responses shown in Fig. 7 using three different sensors. Error bars correspond to the standard deviation.

Table 1. Summary of the performance of the developed sensor for the determination of ascorbic acid.

Potential (V)	Sensitivity (nA/ mM)	R^2	LOD (μM)	Linear range (μM)
~0.14	40.8	0.996	22.6	100-1000

Melatonin analysis

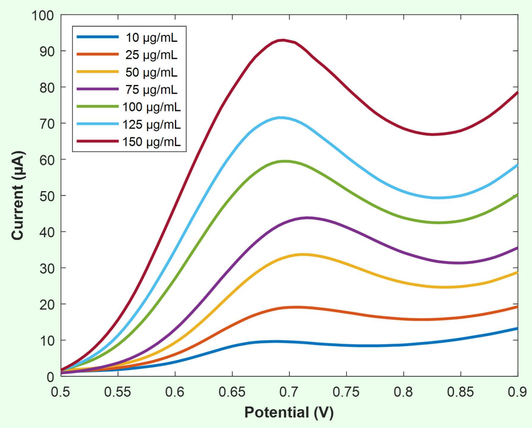

Fig. 9. Voltammetric response of the 3D-printed sensor towards melatonin. Series of plots correspond to increasing concentrations from 10 to 150 μg/mL.

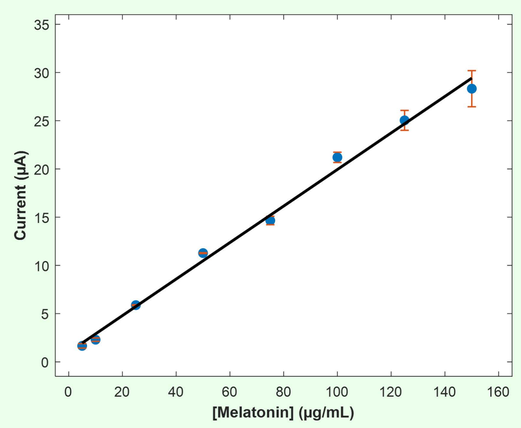

Fig. 10. Calibration curve for melatonin obtained from the peak height of the voltammetric responses shown in Fig. 9 using three different sensors. Error bars correspond to the standard deviation.

Table 2. Summary of the performance of the developed sensor for the determination of melatonin.

Potential (V)	Sensitivity (nA·mL/μg)	R^2	LOD (μg/mL)	Linear range (μg/mL)
~0.69	189	0.989	6.08	10-150

Conclusions

The preparation, characterization and application of in-lab formulated carbon-black/polylactic acid (CB/PLA) 3D-printed sensors has been reported herein. The developed sensor has shown a good performance, slightly superior to that of carbon screen printed electrodes (SPE) or other composite materials such as graphite-epoxy composites (GECs). More importantly, the sensors exhibits a good repeatability and reproducibility, and can be used for a large number of measurements without showing degradation signs.

Overall, the reported approach herein demonstrates the potential of 3D-printing as a viable option for the preparation of customized voltammetric sensors, with many added advantages as are the automation, simplicity and low cost of both the system and the materials. Furthermore, the versatility and high-adaptability of the design combined with the excellent performance of the material have to be highlighted.

References

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Acknowledgments

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