3D printed sensors based on modified-polylactic acid for electrochemical sensing

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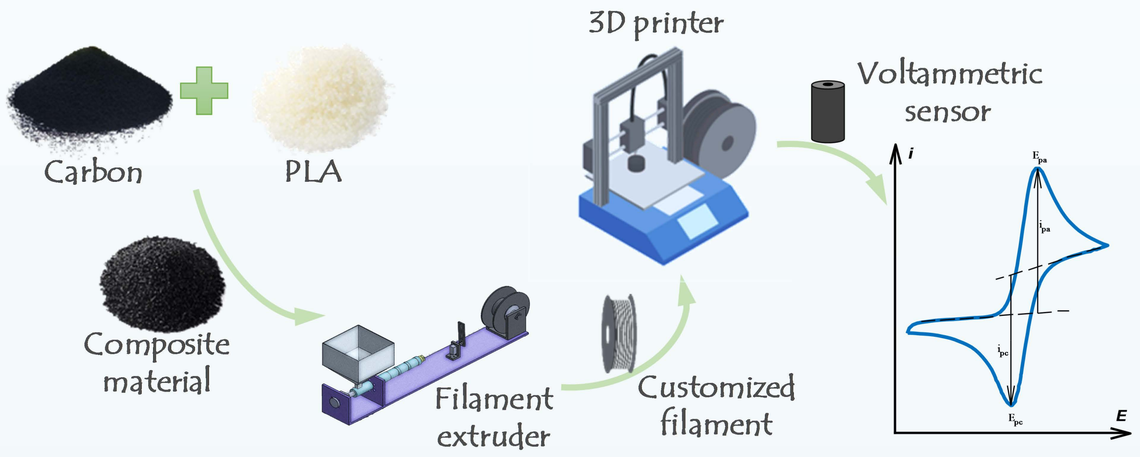

A wide variety of materials have historically been considered when developing electrochemical sensors. Initial studies relied on mercury electrodes, which were soon replaced by different inert metals (mainly Au and Pt) and carbon-based materials (*e.g.,* glassy carbon electrodes) [1]. However, the performance of such bare electrodes is usually limited, lacking the sensitivity and/or selectivity required for the analysis of complex real samples [2]. In this direction, modification of electrode surfaces with different electrocatalysts was explored as a solution. This lead to the popularization of chemically modified electrodes (CMEs), with carbon paste electrodes first, and screen printed electrodes later, as the most common choices.

Nowadays, 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, tunability and easy prototyping [3,4]. Concretely, electrodes are fabricated by fused deposition modelling from thermoplastics such as polylactic acid (PLA), commonly doped with different carbon-based materials to overcome its insulating nature. In this regard, herein we explore the preparation of bulk-modified conductive filaments through the incorporation of redox mediators/electrocatalysts for the manufacturing of 3D-printed voltammetric sensors. Developed electrodes were first characterized, next benchmarked against commercial electrodes and finally applied for the voltammetric detection of active pharmaceutical ingredients (APIs).

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). For the printing of the electrodes, a cylindrical geometry of 10 mm height and 6 mm of diameter was chosen. Lastly, after printing, the lateral surface of the cylinder was insulated to ensure that only the bottom was acting as the working electrode; limiting in this manner its geometric area to 28.3 mm2.

In a next step, upon confirmation of the suitability of the formulated composite, Prussian blue (PB) was mixed with CB and PLA prior to the extrusion, leading to the preparation of bulk-modified 3D-printed sensors.

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), as well as hydrogen peroxide by chronoamperometry (Fig. 10).

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 (insets of Figs. 7,8&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

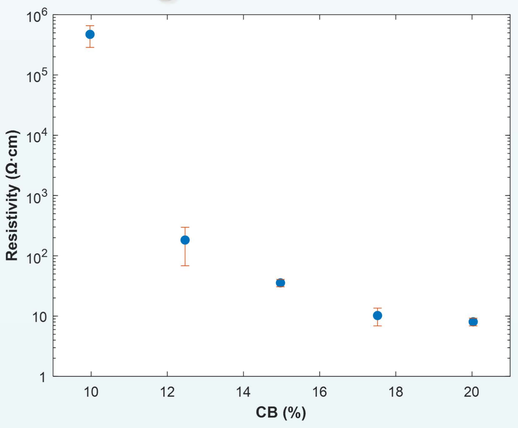

Fig. 1. Percolation curve obtained for CB and PLA composites during the optimization of the filament ratio. All mixtures were prepared in triplicate, with error bars corresponding to standard deviation.

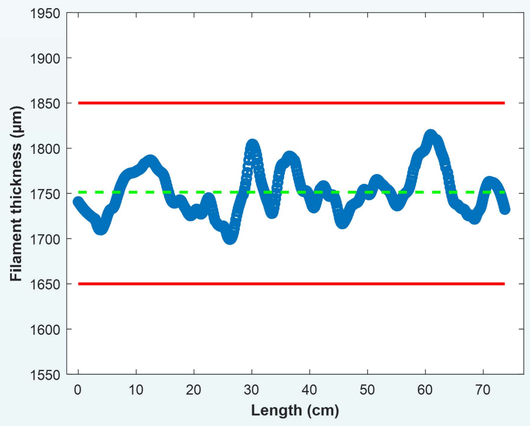

Fig. 2. Variation of the filament thickness during the extrusion process. Red lines correspond to the upper and lower specification limits, while the green line corresponds to the average value.

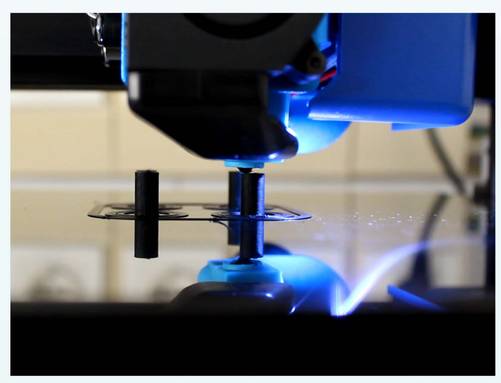

Fig. 3. Picture of the 3D-printing process, illustrating how the shape/size of the sensors can be easily tuned to fit the desired application.

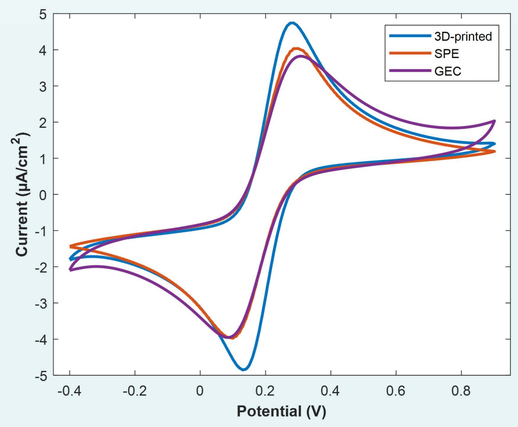

Fig. 4. Voltammetric response of a 3D-printed, screen printed (SPE) and graphite-epoxy composite (GEC) electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4). For comparison purposes, the currents have been normalized taking into account their respective geometric areas.

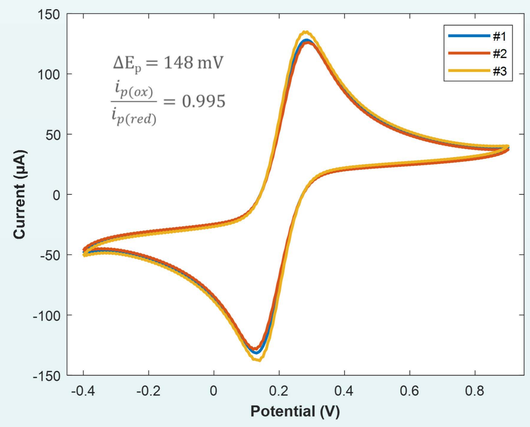

Fig. 5. Voltammetric responses of three different 3D-printed electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4) showcasing their good reproducibility.

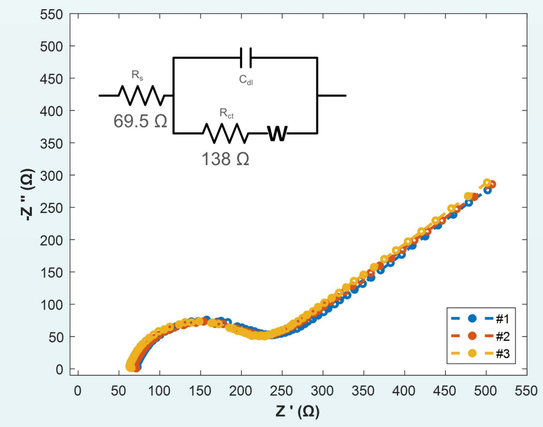

Fig. 6. Impedimetric responses of three different 3D-printed electrodes towards a 2 mM $[Fe(CN)_6]^{3/4-}$ in phosphate buffer (pH 7.4), showcasing the good reproducibility as well as the low charge transfer resistance.

Unmodified electrode – Analysis of ascorbic acid and Melatonin

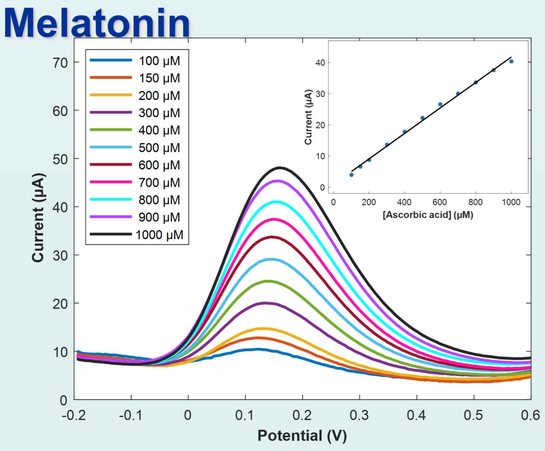

Fig. 7. Voltammetric response of the 3D-printed sensor towards increasing concentrations of ascorbic acid (100 to 1000 µM). Inset corresponds to the calibration curve obtained using three different sensors, with error bars corresponding to the standard deviation.

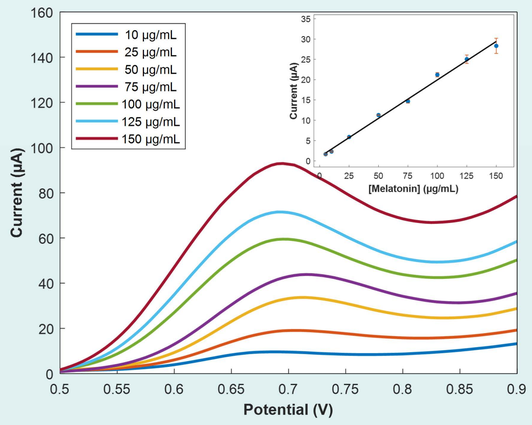

Fig. 8. Voltammetric response of the 3D-printed sensor towards increasing concentrations of melatonin (10 to 150 µg/mL). Inset corresponds to the calibration curve obtained using three different sensors, with error bars corresponding to the standard deviation.

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

Analyte	Potential	Sensitivity	R^2	LOD	Linear range
Ascorbic acid	~0.14 V	40.8 nA/µM	0.996	22.6 µM	100-1000 µM
Melatonin	~0.69 V	189 nA·mL/µg	0.989	6.08 µg/mL	10-150 µg/mL

PB-modified electrode – Analysis of H_2O_2

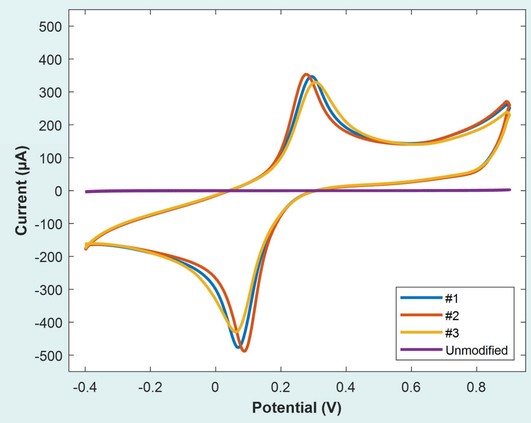

Fig. 9. Voltammetric responses of three different 3D-printed PB-modified sensors in phosphate buffer (pH 7.4) showcasing the successful incorporation of PB in the composite.

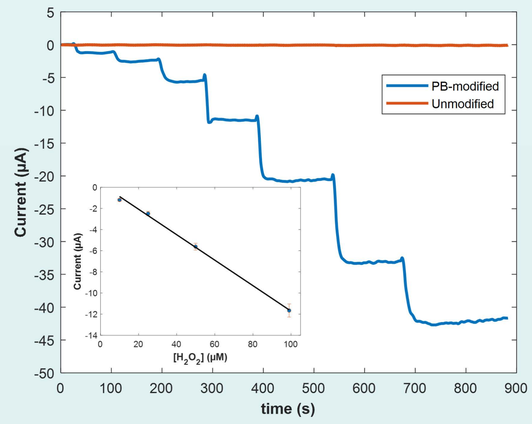

Fig. 10. Amperometric response at -0.2 V of a non- and a PB-modified 3D-printed sensor towards H_2O_2 (10 to 500 µM) in phosphate buffer (pH 7.4). Inset corresponds to the calibration curve obtained using three different sensors. Error bars correspond to the standard deviation.

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

Potential	Sensitivity	R^2	LOD	Linear range
-0.2 V	120 nA/µM	0.992	5.75 µM	10-100 µM

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 sensors have shown a good performance, slightly superior to that of carbon SPEs or other composite materials such 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. Additionally, the successful incorporation of electrocatalysts has been proved as a simple approach to further improve the performance of the built sensors.

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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