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Exploration of defined 2-dimensional working electrode shapes through additive manufacturing†

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In this work, the electrochemical response of different morphologies (shapes) and dimensions of additively manufactured (3D-printing) carbon black (CB)/poly-lactic acid (PLA) electrodes are reported. The working electrodes (WE) are printed using standard non-conductive PLA based filament for the housing and commercial Protopasta (carbon black/PLA) filament for the electrode and connection parts. Discs, squares, equilateral triangles and six-point stars with varying working electrode (WE) widths from 2 to 10 mm are evaluated herein towards the well-known near-ideal outer sphere redox probe hexaamineruthenium(III) chloride (RuHex). The results obtained show that triangular and squared electrodes exhibit a faster heterogeneous electron transfer (HET) rate constant (k^0) than those of discs and stars, the latter being the slowest one. The results reported here also show a trend between the WE dimension and the reversibility of the electrochemical reaction, which decreases as the WE size increases. It is also observed that the ratio of the geometrical and electroactive area ($\%real_{area}$) decreases as the overall WE size increases. On the other hand, these four WE shapes were applied toward the well-known and benchmarking detection of ascorbic acid (AA), uric acid (UA), β -nicotinamide adenine dinucleotide (NADH) and dopamine (DA). Moreover, electroanalytical detection of real acetaminophen (ACOP) samples is also showcased. The different designs for the working electrode proposed in this manuscript are easily changed to any other desired shapes thanks to the additive manufacturing methodology, these four shapes being just an example of what additive manufacturing can offer to experimentalists and to electrochemists in particular. Additive manufacturing is shown here as a versatile and rapid prototyping tool for the production of novel electrochemical sensing platforms, with scope for this work to be able to impact a wide variety of electroanalytical applications.

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Introduction

Additive manufacturing (AM)/3D-printing has become recently popular in research due to its ability to create intricate designs, quick and affordable prototyping turnaround, and its bespoke capabilities. In electrochemistry research, additive manufacturing has been reported for the production of tailored cell designs,^{1,2} flow cells,³ thermal sensing,^{4,5} fully printed all-in-one setups^{6,7} and many others. Most of the work regarding the manufacture of tailored electrodes has been focusing on fused filament fabrication (FFF) methods, which allows a very affordable point of entry, low-waste and rapid prototyping.⁸ FFF feeds a heated thermoplastic filament continu-

ously through an extruder which will allow for the controlled deposition of the final product layer-by-layer.⁹

Historically, mercury electrodes were one of the first choices for working electrode materials in the last century; however, in the last decades, they have been replaced due to their known dangers¹⁰ by solid precious metals (gold (Au), silver (Ag) and platinum (Pt)) and later carbon/graphitic electrodes, which are known by their overall low background currents, wide potential range and chemical inertness.^{11,12} It is because of these features that graphite, in its many forms, is a great material of choice when designing conductive filaments for AM applications. These can be manufactured by embedding carbon black or graphene into a thermoplastic filament matrix, such as PLA or acrylonitrile butadiene styrene (ABS). Conductive FFF filaments can be widely purchased, however it is becoming a trend the bespoke production of them for some applications such as batteries,¹³ water splitting¹⁴ and electrochemical sensing.¹⁵ It is important to also note that, when applied to electroanalytical sensing, the performance of these

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Analyst, 2022, **147**, 5121–5129 | **5123**

Electrochemical characterisation

As mentioned before, circular disc, square, equilateral triangle and (6 point) star were the chosen WE's shapes as shown in Fig. S1.[†] These designs were manufactured in the following 5 different dimensions: 2, 2.5, 5, 7.5 and 10 mm of WE widths, respectively.

A

i) ii) iii) iv)

Current / μA

Potential / V (vs Ag/AgCl)

2 mm
2.5 mm
5 mm
7.5 mm
10 mm

B

Current density / $\mu\text{A cm}^{-2}$

Potential / V (vs Ag/AgCl)

222.2 mV
210.0 mV
191.2 mV
169.4 mV

Disc
Square
Triangle
Star

C

HET k^0 / $\mu\text{A cm}^{-1} \text{s}^{-1}$

Diameter / mm

Disc
Square
Triangle
Star

Fig. 2 (A) Voltammetric comparison of 1 mM RuHex (in 0.1 M KCl) using the range of electrodes shapes (disc (i), square (ii), triangle (iii) and star (iv)) and dimensions. (B) Current density comparison of 1 mM RuHex (0.1 M KCl). (C) Heterogeneous electron transfer (HET) rate constant (k^0) comparison for range of electrode dimensions. Voltammograms extracted from full scan rate studies, 50 mV s⁻¹ shown herein (vs. Ag/AgCl).

Fig. 2C, it is evident the decrease of the k^o values when the dimension of the electrode increases despite their shape. The highest k^o value ($10.1 \times 10^{-3} \text{ cm s}^{-1}$) was recorded for the 2 mm width square, while the lowest k^o value ($1.51 \times 10^{-3} \text{ cm s}^{-1}$) was recorded for the 10 mm star AME. This could also be due to the increase in the internal pathway of the graphite composite electrodes, leading to an increase in their internal resistance.²⁹ Please note that these differences do not seem to be statistically significant to draw any conclusive difference among the different AME shapes.

Attention was next turned to calculating the electroactive area (A_{real}) of the range of different AM electrodes using their respective Randles–Ševčík equation³⁷ (see Experimental Section for further details). The A_{real} for the different electrodes is included in Table 1, including the ratio between the geometrical and electroactive area expressed as a percentage (% $\text{real}_{\text{area}}$). The overall % $\text{real}_{\text{area}}$ values follow a decreasing trend when the dimensions of the electrode increase for all the different shapes, meaning that the electroactive area does not increase as much as the geometric one. This could be due to the internal electrode resistance and polymeric nature of the graphite/PLA filament, where PLA is electrochemically inactive (in contrast to traditional electrodes such as glassy carbon, where all the material is active and a linear increase of % $\text{real}_{\text{area}}$ would be expected). Overall, the above results indicate that as the dimension of the working electrode increases, the reversibility of the electrochemical reaction (and therefore its HET kinetics) decreases, so does the electroactive area for all the four electrodes' shapes tested herein. The AME shape with the

Table 1 Electrochemical characterisation of disc, square, triangle and star AM electrodes determined from cyclic voltammetry using 1 mM RuHex probe in 0.1 M KCl ($N = 3$) (vs. Ag/AgCl)

	WE Ø/mm	Disc	Square	Triangle	Star
$a_{\text{geo}}/\text{cm}^2$	2	0.0314	0.0314	0.0314	NP ^a
	2.5	0.0491	0.491	0.492	0.491
	5	0.196	0.196	0.196	0.196
	7.5	0.466	0.466	0.466	0.466
	10	0.785	0.785	0.785	0.785
Avg. $k^0/\text{cm s}^{-1}$	2	$8.49 (\pm 0.49) \times 10^{-3}$	$1.01 (\pm 0.073) \times 10^{-2}$	$9.32 (\pm 0.70) \times 10^{-3}$	NP ^a
	2.5	$7.85 (\pm 1.14) \times 10^{-3}$	$9.90 (\pm 1.43) \times 10^{-3}$	$9.42 (\pm 0.85) \times 10^{-3}$	$9.99 (\pm 0.075) \times 10^{-3}$
	5	$5.03 (\pm 0.25) \times 10^{-3}$	$6.69 (\pm 0.089) \times 10^{-3}$	$8.04 (\pm 0.88) \times 10^{-3}$	$4.19 (\pm 0.43) \times 10^{-3}$
	7.5	$2.89 (\pm 0.040) \times 10^{-3}$	$3.51 (\pm 0.020) \times 10^{-3}$	$6.30 (\pm 1.81) \times 10^{-3}$	$2.65 (\pm 0.24) \times 10^{-3}$
	10	$1.73 (\pm 0.031) \times 10^{-3}$	$3.13 (\pm 0.18) \times 10^{-3}$	$3.46 (\pm 2.31) \times 10^{-3}$	$1.55 (\pm 0.98) \times 10^{-3}$
$\Delta E_p/\text{mV}$ (at 50 mV s^{-1})	2	125	112	129	NP ^a
	2.5	130	132	127	111
	5	200	168	162	225
	7.5	286	260	231	394
	10	374	341	315	413
Avg. $A_{\text{real}}/\text{cm}^2$	2	0.030 (± 0.0018)	0.023 (± 0.0043)	0.023 (± 0.0014)	NP ^a
	2.5	0.049 (± 0.0027)	0.037 (± 0.0042)	0.038 (± 0.0038)	0.038 (± 0.00083)
	5	0.200 (± 0.0059)	0.159 (± 0.010)	0.145 (± 0.0059)	0.153 (± 0.012)
	7.5	0.433 (± 0.015)	0.321 (± 0.0029)	0.345 (± 0.0043)	0.311 (± 0.029)
	10	0.636 (± 0.057)	0.536 (± 0.0027)	0.559 (± 0.016)	0.503 (± 0.042)
%Real _{area}	2	94.8 (± 5.6)	72.7 (± 13.8)	74.7 (± 4.5)	NP ^a
	2.5	99.5 (± 5.5)	75.1 (± 8.6)	77.3 (± 7.6)	78.4 (± 1.7)
	5	102.1 (± 3.0)	80.9 (± 5.3)	73.7 (± 3.0)	77.7 (± 6.3)
	7.5	93.0 (± 3.2)	68.9 (± 0.6)	74.1 (± 0.9)	66.7 (± 6.2)
	10	80.9 (± 7.3)	68.2 (± 0.3)	71.2 (± 1.9)	64.0 (± 5.4)

^a NP = not printable.

highest %real_{area} across all sizes is the disc (varying from 80.9 to 102.1%), while the lowest %real_{area} is exhibited by the star electrode (ranging from 64.0 to 78.4%).

Electroanalytical applications

We now turn to exploring the electroanalytical performance of the AMEs towards the detection of relevant biological analytes, namely ascorbic acid (AA), uric acid (UA), β -nicotinamide adenine dinucleotide (NADH) and dopamine (DA) using the 2.5 mm width electrodes, as it was almost the one exhibiting the faster HET values for all geometric forms and it could be successfully 3D-printed for all shapes. Like for other carbon electrodes,⁴⁷ it is described in the literature the need of a post-printing enhancement of the electrochemical properties so called “activation method” prior the utilisation of AMEs in electroanalytical applications. Note that this method is unnecessary for the above RuHex studies, due to the near ideal outer-sphere nature of the redox probe, being this method only beneficial for the further electroanalytical sensing applications. Several literature reports have addressed this pre-conditioning of the electrode's surface by chemical, physical or electrochemical treatments to successfully increase the active surface area and its electron transfer rates.^{6,7} Herein, we apply the method developed by Kalinke *et al.*⁸ Such method is based on the use of NaOH while a potential-controlled electrochemical method (namely chronoamperometry) is applied to

promote PLA's saponification, which exposes the active material's active sites and electrochemical active area. This results in the increasing of the C/O ratio and therefore the improvement of the electrochemical performance of inner-sphere redox probes.

The calibration plots for AA, UA, NADH and DA using all the electrode shapes are depicted in Fig. 3, with examples of the respective calibration voltammograms as insets. These were AA with disc electrodes, UA with square electrodes, NADH with triangle electrodes and DA with star electrodes. Fig. S2† includes all the voltammograms for each of the four analytes and each of the four electrodes shapes. The electrochemical sensitivity, limit of detection (LOD) and coefficient of determination (R^2) values are included in Table 2. A very good linear behaviour is observed for all AMEs in all redox probes as R^2 values are successfully ranged between 0.994 and 0.999. Moreover, it is observed that there are no significant differences between the four electrodes shapes in terms of their electroanalytical performance towards AA, UA, and DA. This is likely to indicate that the observed differences can be attributed to their respective calculated deviations. It is detected, however, a higher variation in the sensitivity of the four AMEs in the detection of NADH possibly due to the more complexity of the redox process of this molecule. Note that no significant differences between the four electrode shapes are observed herein, and, although small LOD differences are observed



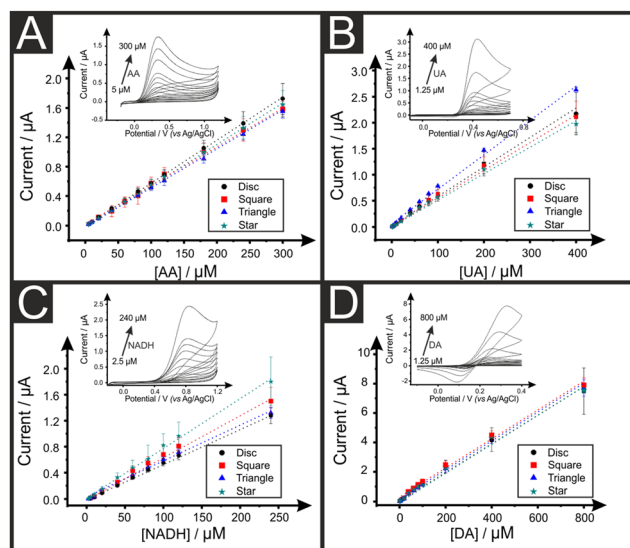


Fig. 3 Calibration plots of ascorbic acid (A; AA), uric acid (B; UA), NADH (C) and dopamine (DA; D) in PBS pH 7.4 using the range of disc, square, triangle and star 2.5 mm electrodes. Scan rate 50 mV s^{-1} (vs. Ag/AgCl). Insets are the respective voltammograms from the calibration plots for AA with disc electrodes, UA with square electrodes, NADH with triangle electrodes and DA with star electrodes.

between the different electrode shapes, the higher LODs are reported when using square electrodes, which are likely due to their slightly higher background noise in their recorded voltammograms. These observations could be due to the sizes of the electrodes and their current distributions, in addition to the diffusion regimes where the AMEs being big enough that planar diffusion governs the electrochemical process and therefore the shape of the electrode does not play a relevant part with these dimensions.⁴⁵ Also again, please note that these differences do not seem to be statistically significant.

Lastly, we apply the AMEs to the electrochemical determination of acetaminophen (ACOP) and the analysis of this compound in a commercial tablet accordingly diluted in PBS (0.01

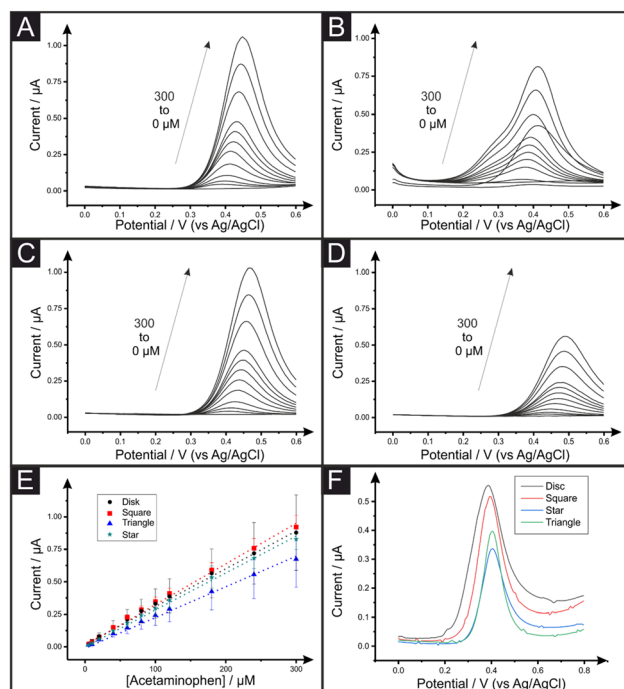


Fig. 4 (A) Differential pulse voltammetry for the detection of ACOP (5–300 μM ; $N = 3$) in PBS (0.01 M; pH = 7.4) for the square (A), triangle (B), disc (C) and star (D) shaped AMEs. (E) Calibration curves corresponding to the voltammetric determination of ACOP for these AMEs. (F) Differential pulse voltammograms for the diluted ACOP tablet sample with the AMEs.

M, pH = 7.4). A series of calibration plots was performed for each AME shape by differential pulse voltammetry (DPV). Fig. 4 shows the DPV signals of increasing amounts of ACOP for the square (A), triangle (B), disc (C) and star (D) shaped electrodes and their respective calibration plot of ACOP (E). The analytical sensitivity, limit of detection (LOD) and coefficient of determination (R^2) are reported in Table 3. The analytical sensitivity for the ACOP determination varies from 5.89×10^{-3} to $6.55 \times 10^{-3} \mu\text{A } \mu\text{M}^{-1}$ with star and disc electrodes

Table 2 Comparison of the analytical sensitivities (in $\mu\text{A } \mu\text{M}^{-1}$), limit of detection (LOD; ($3 \times \text{Sy/S}$)) and coefficient of determination (R^2) obtained at the various electrode shapes towards the detection of ascorbic acid, uric acid, NADH and dopamine in PBS pH 7.4 (calculated from gradient of calibration plots depicted in Fig. 3); scan rate 50 mV s^{-1} (vs. Ag/AgCl) ($N = 3$)

Analyte		Shape			
		Disc	Square	Triangle	Star
AA	Sensitivity/ $\mu\text{A } \mu\text{M}^{-1}$	6.55×10^{-3}	6.01×10^{-3}	6.33×10^{-3}	5.89×10^{-3}
	LOD/ μM	0.54	2.13	0.75	0.64
	R^2	0.999	0.998	0.999	0.999
UA	Sensitivity/ $\mu\text{A } \mu\text{M}^{-1}$	5.51×10^{-3}	5.35×10^{-3}	5.03×10^{-3}	6.65×10^{-3}
	LOD/ μM	0.12	0.36	0.26	0.19
	R^2	0.996	0.995	0.995	0.995
NADH	Sensitivity/ $\mu\text{A } \mu\text{M}^{-1}$	5.44×10^{-3}	6.40×10^{-3}	7.64×10^{-3}	5.60×10^{-3}
	LOD/ μM	0.79	0.53	0.50	0.48
	R^2	0.998	0.995	0.997	0.996
DA	Sensitivity/ $\mu\text{A } \mu\text{M}^{-1}$	9.43×10^{-3}	9.91×10^{-3}	9.52×10^{-3}	9.74×10^{-3}
	LOD/ μM	0.37	1.29	0.50	0.64
	R^2	0.994	0.993	0.994	0.997



		Shape			
		Disc	Square	Triangle	Star
ACOP	Sensitivity/ $\mu\text{A } \mu\text{M}^{-1}$	6.55×10^{-3}	6.01×10^{-3}	6.33×10^{-3}	5.89×10^{-3}
	LOD/ μM	0.54	2.13	0.75	0.64
	R^2	0.999	0.998	0.999	0.999
	Sample recovery/%	102.3	96.9	122.6	80.3

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