

Supplementary Information

Investigating Electrochemical Deposition of Gold on Commercial Off-the-Shelf 3-D Printing Materials Towards Developing Sensing Applications

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Electrochemical (EC) measurements

Electrode chips were cleaned by rinsing with MQ water for 15 seconds. Glassware was cleaned by washing with soap and distilled water then MQ water 3-5 times and dried under a stream of N_2 . The EC set-up was inside a Faraday cage using an EC Multiplex Potentiostat/Galvanostat (Metrohm Autolab). The EC cell consists of a 3D printed working electrode (WE) on a glass chip as well as an external platinum counter electrode (CE) and reference electrode (RE, Ag/AgCl in 3 M KCl). The electrolyte solution is 5 mM $K_4Fe(CN)_6^{3-}$ /5 mM $K_3Fe(CN)_6^{4-}$ and 1 M $NaClO_4$; CE (Pt electrode), RE (Ag/AgCl in 3 M KCl). This solution and the RE are connected by a salt bridge. EC measurements were taken before and after gold deposition by submerging the WE on the glass chip into the electrolyte solution. Cyclic voltammograms (CV) were obtained always starting with open-circuit potential and using a window from -0.1 V to 0.6 V with a scan rate of 0.1 V/s for 6 cycles.

X-ray photoelectron spectroscopy (XPS) measurements

The XPS spectra were measured on a Kratos Axis Nova spectrometer equipped with an Al X-ray source. The sample was mounted onto a coated aluminum plate using double-sided adhesive copper tape, kept under high vacuum (10^{-8} Torr) overnight inside the preparation chamber, and then transferred into the analysis chamber (ultrahigh vacuum, 10^{-9} Torr) of the spectrometer.

The XPS data were collected using AlK_{α} radiation at 1486.69 eV (150 W, 10 mA), charge neutralizer and a delay-line detector (DLD) consisting of three multi-channel plates. Binding energies are referred to the amorphous/graphitic carbon C1s peak at 284.8 eV. Survey spectra were recorded from -5 to 1200 eV at a pass energy of 160 eV (number of sweeps/dwell time: 1/100 ms) using an energy step size of 1 eV and a dwell time of 100 ms. High resolution spectra for O 1s, C 1s and Au 4f were recorded in the appropriate regions at a pass energy of 20 eV (number of sweeps/dwell time: O 1s, 10/330 ms; C 1s 10/300 ms; Au 4f, 5/373 ms) using an energy step size of 0.1 eV. The analyzed area on the specimens was about $300 \times 700 \mu m^2$ (lens mode: FOV 1) at this position. The incident angle (X-ray source/sample) is the angle of 54.74° and the take-off angle (sample/detector) is 90° .

The spectra were measured using *ESCApe* software and converted to *.vms files for using the *CasaXPS* software. The data were corrected for background using the Shirley (wide scan, high resolution spectra for O 1s and C 1s) and the extrapolate Shirley algorithm (high resolution spectra for Au 4f). Peak fits were obtained using a symmetric line shape {Gaussina-Lorentzian – GL(30); for O 1s, C 1s) and an asymmetric line shape {Doniach Sunjic (DS); for Au 4f}.

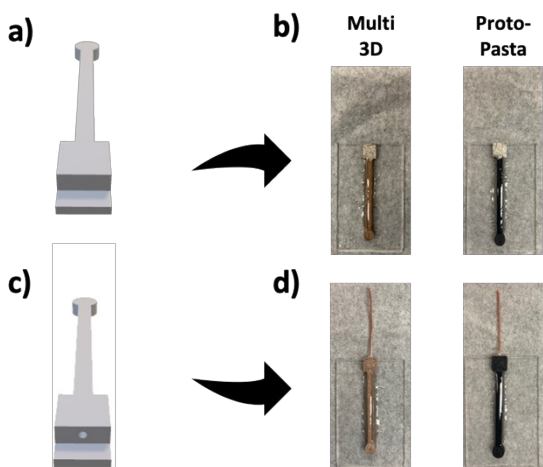


Figure S1 Two different electrode designs that were investigated using two conductive filaments; Electrifi Multi3D and Proto-pasta. (a,c) CAD designs that are to be 3-D printed. (b) 3-D printed electrodes from both filaments with no copper wire embedded. (d) 3-D printed electrodes from both filaments with an embedded copper wire. Spacer ledge not incorporated into final design.

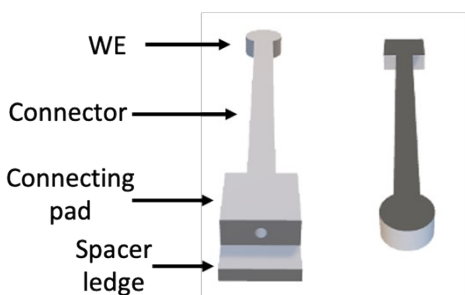


Figure S2 CAD drawing of final working electrode (WE) design that is 3-D printed onto a glass slide with a cut-out for copper wire to be embedded into design. Spacer ledge is incorporated into CAD drawing to insert glass slide into place but does not remain part of the final electrode design.

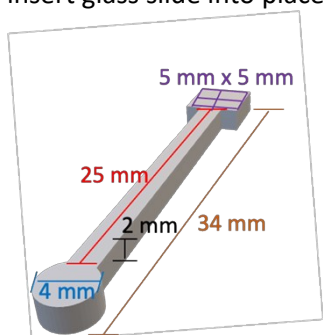


Figure S3 CAD drawing of working electrode (WE) design with dimensions. Values indicated in Table S1.

Table S1 Dimensions of both electrode designs that were investigated with no copper wire (E1) and with a copper wire (E2).

	WE diameter (mm)	Connector length (mm)	Connector width (mm)	Connecting pad length (mm)	Connecting pad width (mm)	Copper wire cut-out diameter (mm)	Electrode Height (mm)
E 1	4	25	2	5	5	N/A	2
E 2	4	25	2	5	5	0.75	2

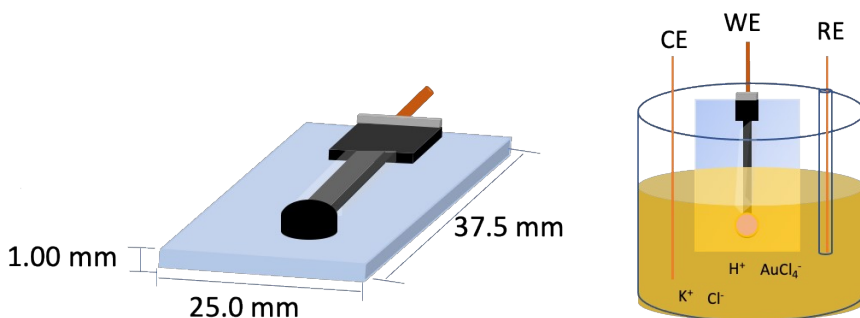


Figure S4 Illustration of gold deposition set-up and electrode design. Counter electrode (CE) dimensions: 1.00 mm diameter; 66.40 mm height. Reference electrode (RE) dimensions: 0.25 mm diameter of wire; 2.23 mm diameter of capillary tube; 43.75 mm height. Working electrode (WE) dimensions: 4 mm diameter; 2 mm height; 34 mm long. WE connector pad dimensions: 5.00 mm wide; 5.00 mm long.

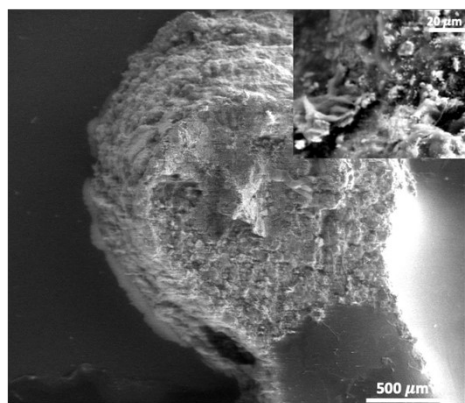


Figure S5 Scanning Electron Microscopy images from conductive Multi3D copper blend filament after gold deposition.

Table S2 Energy Dispersive X-ray Spectroscopy of elements present after gold deposition for Multi3D copper blend filament.

	Oxygen	Copper	Sodium	Iron	Gold	Chlorine	Silicon	Silver
Atomic %	56.24	19.47	7.95	4.28	4.16	3.95	2.88	1.08

Table S3 Oxidation current peak values obtained after potentials of -1.4 V, -1.5 V, -1.6 V with different gold deposition times of 0, 2, 15, 30 minutes using Proto-pasta conductive filament with embedded copper wire. Data values represent figure 5d.

	-1.4 V	-1.5 V	-1.6 V
0 mins	0.00385 mA	0.00303 mA	0.00304 mA
2 mins	0.550 mA	0.500 mA	0.556 mA
15 mins	0.590 mA	0.603 mA	0.613 mA
30 mins	0.616 mA	0.597 mA	0.637 mA

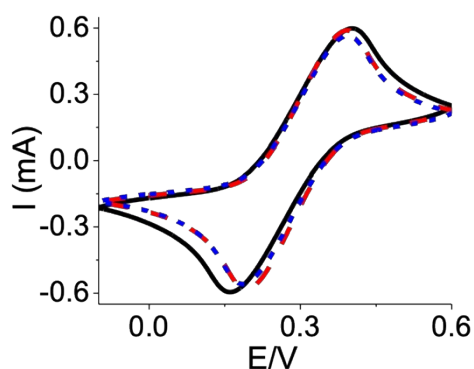


Figure S6 Reproducibility of three electrodes made from Proto-past filament with copper embedded wire using -1.4 V for gold deposition using chronoamperometry for 15 minutes.

Table S4 Values obtained from oxidation and reduction peak values from reproducibility of three electrodes shown in Figure S3 to calculate relative standard deviation to see how reproducible the fabricated electrodes are.

	Y-axis	X-axis
Mean oxidation peak	0.584 mA	0.397 V
Standard deviation	0.0180 mA	0.0050 V
Relative standard deviation (%)	2.84	1.26
Mean reduction peak	0.580 mA	0.180 V
Standard deviation	0.0200 mA	0.0170 V
Relative standard deviation (%)	3.45	9.46

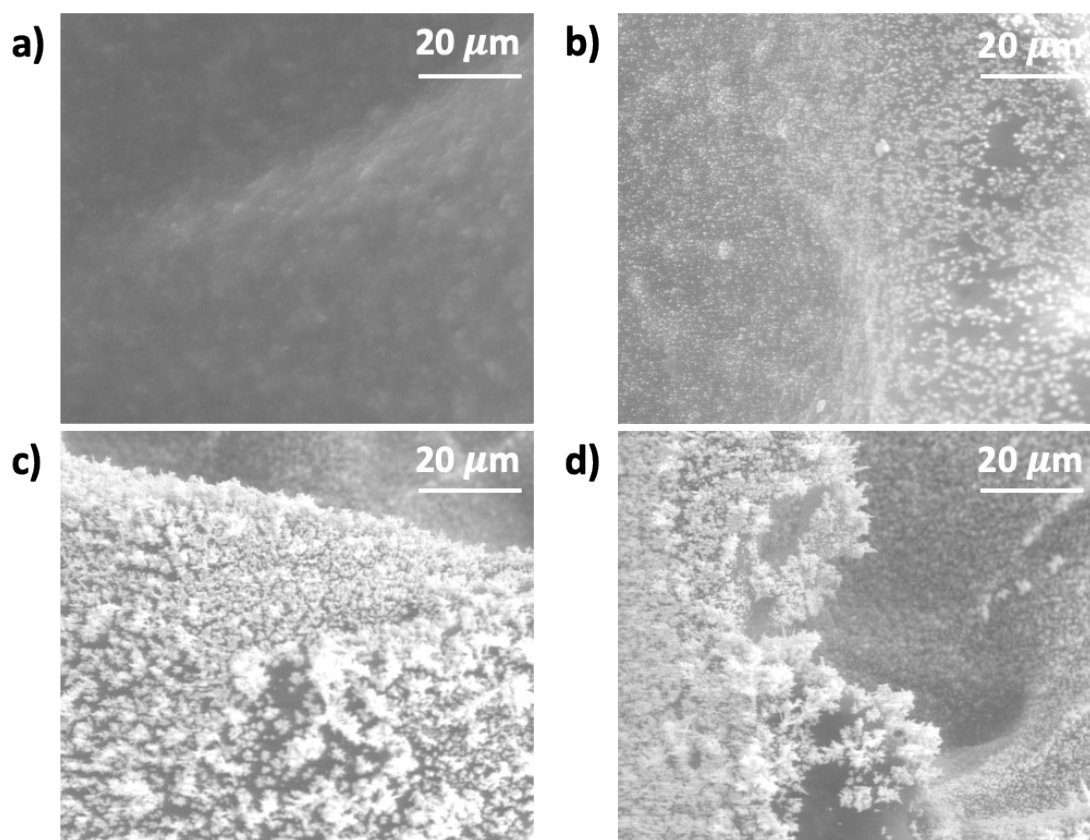


Figure S7 Enlarged SEM images of Protopasta electrode with Cu wire embedded after gold deposition at -1.4 V potential over deposition times of (a) 0 minutes; (b) 2 minutes; (c) 15 minutes; (d) 30 minutes.

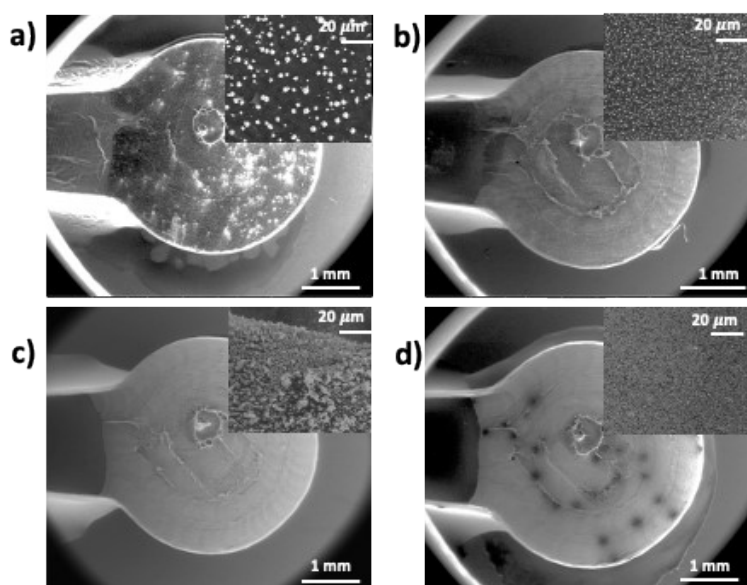


Figure S8 SEM images of Protopasta electrode with Cu wire embedded after gold deposition that was done over varying potentials held at 15 minutes including (a) -0.6 V; (b) -1.0 V; (c) -1.4 V; (d) -1.8 V.

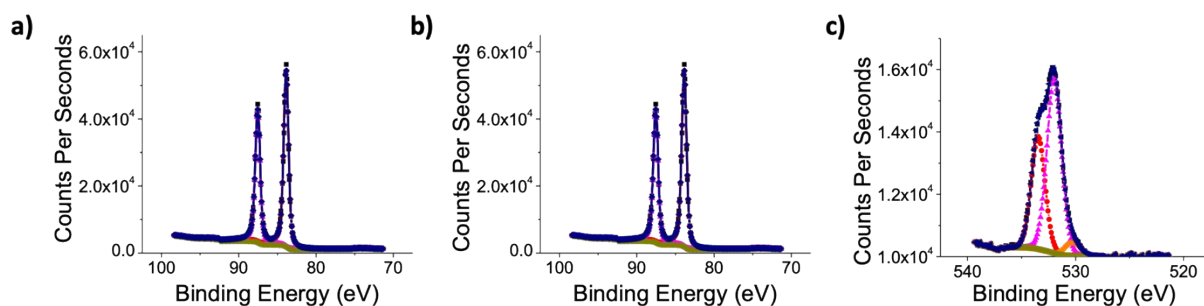


Figure S9 High resolution XPS scans, recorded for Protopasta electrode surface after electrodeposition of gold. Scans performed for regions corresponding to (a) Au 4f (Au 4f_{7/2}, red; Au 4f_{5/2}, magenta), (b) C 1s (O-C=O, red; C=O, magenta; C-O, orange; C-H, grey; C-C, maroon), and (c) O 1s (O-C=O, red; C-O, C=O, magenta; 1s oxide, orange). Counts per seconds (black), background (olive green), envelope (navy blue). Peak values and associations highlighted in Table S6 below. Gold deposition done at -1.4 V over 15 minutes.

Table S5 XPS peak values and associations for Protopasta electrode surface after electrodeposition of gold.

Region	Peak value (eV)	Association
Au 4f	83.87, 87.54	Corresponding to Au(0) being electrodeposited represented by Au 4f _{7/2} and Au 4f _{5/2} peaks respectively
C 1s	284.8, 285.02, 286.07, 286.92, 288.78	Corresponding to C-C, C-H, C-O, C=O, and O-C=O respectively that is present in polylactic acid polymer
O 1s	530.25, 531.97, 533.46	Corresponding to oxide, C-O, C=O, and O=C-O respectively due to polylactic acid polymer

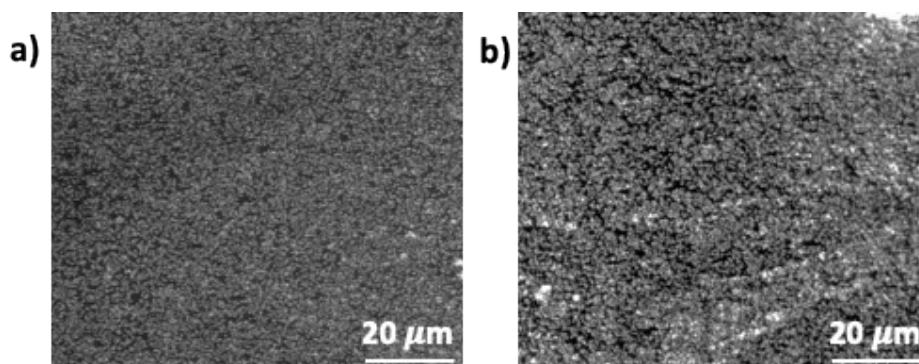


Figure S10 SEM images of Protopasta electrode with Cu wire embedded. (a) before electrochemically cleaning and (b) after electrochemically cleaning. EC cleaning done for 5 minutes in 0.5 M H₂SO₄.

Table S6 Energy Dispersive X-ray Spectroscopy of elements present before and after electrochemically cleaning the Protopast electrode with copper wire. EC cleaning done for 5 minutes in 0.5 M H₂SO₄.

	Carbon	Oxygen	Gold
Atomic % before	75.3	18.7	6.00
Atomic % after	71.1	20.6	8.30

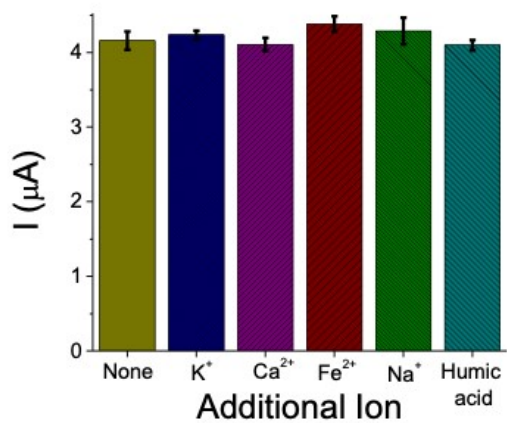


Figure S11 Interference study demonstrating peak currents vs. added interfering agents, including K⁺ (dark blue), Ca²⁺ (magenta), Fe²⁺ (maroon), Na⁺ (bright green), Humic acid (teal). Interfering agents (3 ppm) are added to 3 ppm Cu²⁺ in 0.05 M H₂SO₄.