Supporting Information for:

Eco-friendly integration of gold nanoparticles into additive manufacturing filaments: Advancing conductivity and electrochemical performance for lead detection in water

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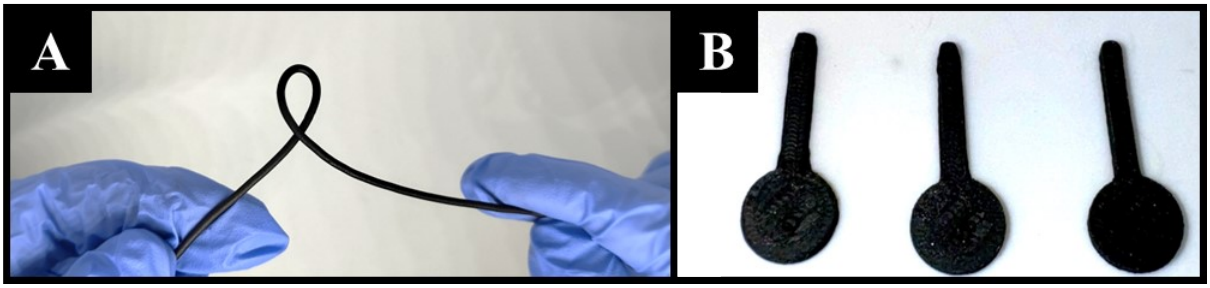

Figure S1. Photographs of bespoke (A) AuNP-G filament, highlighting the flexibility and (B) three additive manufactured electrodes printed from this filament.

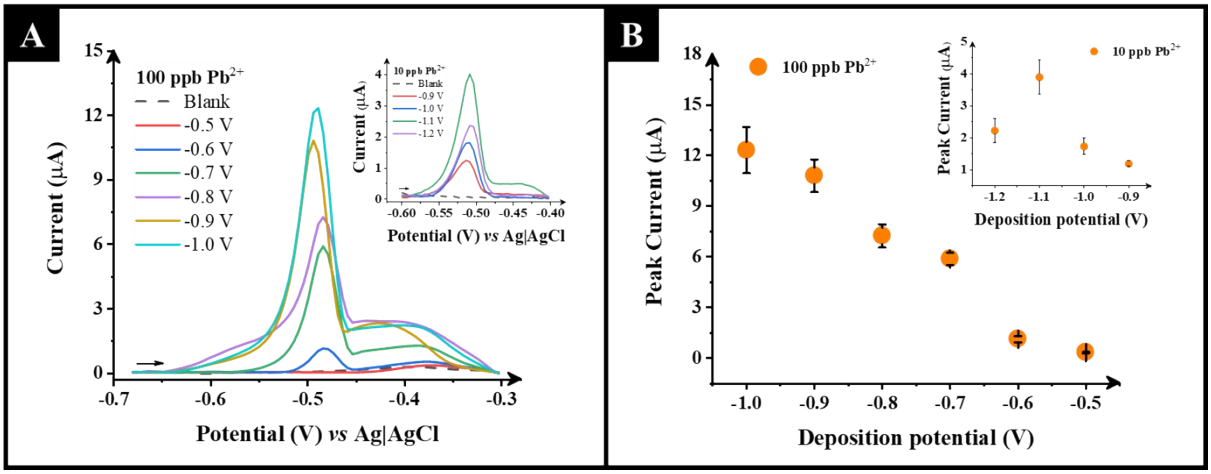

Figure S2. (A) SWASV performed at the AuNP-G electrode in 0.1 M HCl using 100 ppb of Pb^{2+} at different deposition potentials (−1.0, − 0.9, − 0.8, −0.7, − 0.6, and −0.5 V) for 60 seconds. SWV parameters: a = 20 mV, f = 25 Hz, ΔE = 5 mV, and $t_{deposition}$ = 60s. Inset: 10 ppb of Pb^{2+}. (B) Results obtained for repetitive measurements (n=3) for different deposition potentials (−1.0, − 0.9, − 0.8, −0.7, − 0.6, and −0.5 V) using 100 ppb of Pb^{2+}. Inset: 10 ppb of Pb^{2+}.

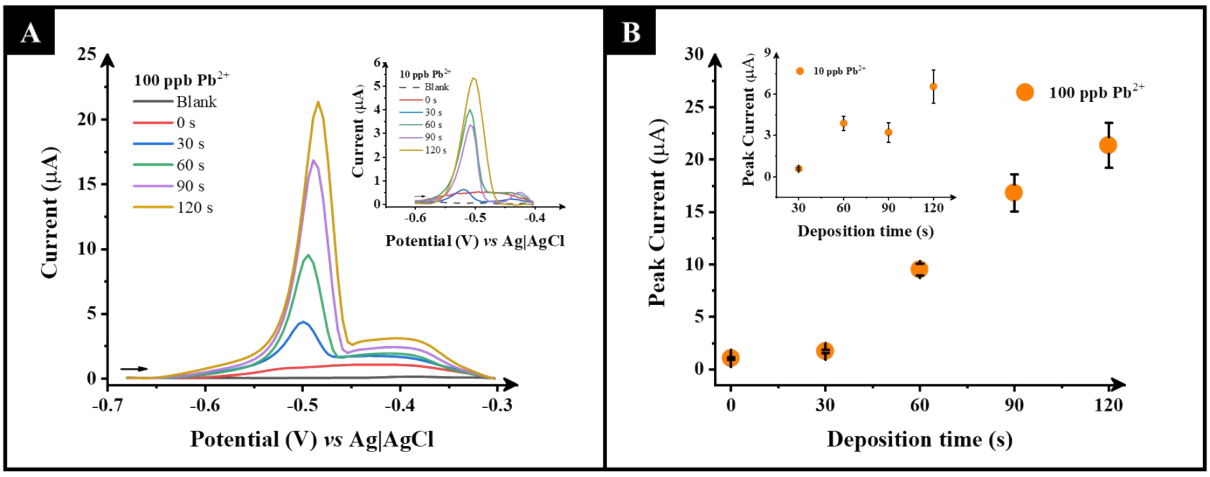

Figure S3. (A) SWASV performed at the AuNP-G electrode in 0.1 M HCl using 100 ppb of Pb^{2+} at different deposition times (0, 30, 60, 90, and 120 s). SWV parameters: a = 20 mV, f = 25 Hz, ΔE = 5 mV, and $E_{deposition}$ = –0.90 V. Inset: 10 ppb of Pb^{2+}. (B) Results obtained for repetitive measurements (n=3) for different deposition times (0, 30, 60, 90, and 120 s) using 100 ppb of Pb^{2+}. Inset: 10 ppb of Pb^{2+}.

Table S1. SWASV optimisation of instrumental parameters involved in detection of Pb^{2+}

Technique parameter	Studied range	Selected value
Step potential (V)	0.001 — 0.010	0.009
Amplitude (mV)	10 —100	60
Frequency (Hz)	5 — 45	40
Deposition potential (V)	–1.2 — −0.5	–0.9[a] (–1.1[b])
Deposition time (s)	0 – 120	90[a] (120[b])

[a]Optimal values for 100 pbb Pb^{2+}; [b]Optimal values for 10 ppb Pb^{2+}

Table S2. Comparisons between the electrode in this work and the literature for Pb^{2+} detection, including the electrode type used, electroanalytical technique, the real samples analysed, the obtained linear range, and the limit of detection (LOD)

Electrode	Technique	Sample	Linear range (ppb)	LOD (ppb)	Reference
2D Bismuthene-graphene/GCE	SWASV	Tap water	1 - 30	0.3	[1]
Bi Oxycarbide /GCE	DPASV	Deionized and tap water.	10 - 50	3.97	[2]
G/PANI/PS nanoporous fiber/SPCE	SWASV	River water	10 - 500	3.30	[3]
G/MWCNTs/Bi	DPASV	Water samples	0.5 - 30	0.2	[4]
NCQDs-GO/GCE	SWASV	Lake and tap water	20.72 - 10360	1.17	[5]
Carbon black/PLA 3D-printed sensor	SWASV	Spiked tap water and fuel ethanol samples	10 - 870	0.8	[6]
Additive manufactured AuNP-Graphite/PLA (AuNP-G)	SWASV	River water	1 - 75	0.89	This work

Key: 2D bismuthene-graphene/GCE: glassy carbon electrode modified with a bismuthene/graphene composite film; Bi oxycarbide /GCE: bismuth oxycarbide modified glassy carbon electrode; G/PANI/PS nanoporous fiber/SPCE: graphene/polyaniline/polystyrene nanoporous fibers modified screen-printed carbon electrode; G/MWCNTs/Bi: glassy carbon modified with three-dimensional graphene-MWCNTs nanocomposites and bismuth film; NCQDs-GO/GCE: N-doped carbon quantum dots-graphene oxide hybrid functionalized glass carbon electrode; Carbon black/PLA 3D-printed sensor: 3D-pen fabricated electrochemical sensor using carbon black/polylactic acid (PLA) filament.

Reference

[1] A.C. Lazanas, K. Tsirka, A.S. Paipetis, M.I. Prodromidis, 2D bismuthene/graphene modified electrodes for the ultra-sensitive stripping voltammetric determination of lead and cadmium, Electrochim Acta 336 (2020) 135726. https://doi.org/10.1016/J.ELECTACTA.2020.135726.

[2] Y. Zhang, C. Li, Y. Su, W. Mu, X. Han, Simultaneous detection of trace Cd(II) and Pb(II) by differential pulse anodic stripping voltammetry using a bismuth oxycarbide/nafion electrode, Inorg Chem Commun 111 (2020) 107672. https://doi.org/10.1016/J.INOCHE.2019.107672.

[3] N. Promphet, P. Rattanarat, R. Rangkupan, O. Chailapakul, N. Rodthongkum, An electrochemical sensor based on graphene/polyaniline/polystyrene nanoporous fibers modified electrode for simultaneous determination of lead and cadmium, Sens Actuators B Chem 207 (2015) 526–534. https://doi.org/10.1016/J.SNB.2014.10.126.

[4] H. Huang, T. Chen, X. Liu, H. Ma, Ultrasensitive and simultaneous detection of heavy metal ions based on three-dimensional graphene-carbon nanotubes hybrid electrode materials, Anal Chim Acta 852 (2014) 45–54. https://doi.org/10.1016/J.ACA.2014.09.010.

[5] L. Li, D. Liu, A. Shi, T. You, Simultaneous stripping determination of cadmium and lead ions based on the N-doped carbon quantum dots-graphene oxide hybrid, Sens Actuators B Chem 255 (2018) 1762–1770. https://doi.org/10.1016/J.SNB.2017.08.190.

[6] A.F. João, S.V.F. Castro, R.M. Cardoso, R.R. Gamela, D.P. Rocha, E.M. Richter, R.A.A. Muñoz, 3D printing pen using conductive filaments to fabricate affordable electrochemical sensors for trace metal monitoring, Journal of Electroanalytical Chemistry 876 (2020) 114701. https://doi.org/10.1016/J.JELECHEM.2020.114701.