Supporting information for:

Anodic Stripping Voltammetry with the Hanging Mercury Drop Electrode for Trace Metal Detection in Soils Samples

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Table S1. Comparison of analytical parameters between different electrodes.

Electrode	Repeatibility	Reproducibility	LOD	Ref
PdNPs – PACs modified GCE	NS	NS	Cd^{2+}: 41 nM Pb^{2+}: 50 nM Cu^{2+}: 66 nM Hg^{2+}: 54 nM	[1]
AuNPs modified GCE	5%-15%	NS	Cd^{2+}: 300 nM Pb^{2+}: 300 nM Cu^{2+}: 300 nM Hg^{2+}: 300 nM	[2]
GCE	NS	Zn^{2+} is not reproducible at pH >4	Zn^{2+}: 0.225 μM Cd^{2+}: 0.085 μM Pb^{2+}: 0.080 μM Cu^{2+}: 0.614 μM	[3]
Amino acid modified GCE	< 2%	< 5%	Zn^{2+}: 8.92 pM Cd^{2+}: 5.77 pM Cu^{2+}: 3.01 pM Hg^{2+}: 5.89 pM	[4]
GA-MOF modified GCE	Cd^{2+}: 6.9% Pb^{2+}: 2.9% Cu^{2+}: 4.8% Hg^{2+}: 0.8%	NS	Cd^{2+}: 9 nM Pb^{2+}: 1 nM Cu^{2+}: 8 nM Hg^{2+}: 0.9 nM	[5]
SnO_2/rGO modified GCE	NS	NS	Cd^{2+}: 0.102 nM Pb^{2+}: 0.184 nM Cu^{2+}: 0.227 nM Hg^{2+}: 0.279 nM	[6]
IL dopped with Mg(II)/Al(III) LDHs modified GCE	Cd^{2+}: 4.1% Pb^{2+}: 2.5% Cu^{2+}: 3.6% Hg^{2+}: 4.6%	Cd^{2+}: 4.7% Pb^{2+}: 4.5% Cu^{2+}: 3.8% Hg^{2+}: 5.6%	Cd^{2+}: 2.230 nM Pb^{2+}: 0.077 nM Cu^{2+}: 0.394 nM Hg^{2+}: 1.246 nM	[7]
Stainless steel	Cd^{2+}: 5.14% Pb^{2+}: 3.15%	NS	Cd^{2+}: 230 nM Pb^{2+}: 33 nM	[8]

	Cu^{2+}: 2.56% Hg^{2+}: 2.47%		Cu^{2+}: 7.3 nM Hg^{2+}: 28 nM	
rGO/SnO2/PPy modified GCE	NS	NS	Cd^{2+}: 0.75 pM Pb^{2+}: 0.83 pM Cu^{2+}: 0.83 pM Hg^{2+}: 0.81 pM	[9]
P1,2-DAAQ modified GCE	Pb^{2+}: 2.31% Hg^{2+}: 3.71% Cu^{2+}: 9.69% Cd^{2+}: 2.76%	NS	Cd^{2+}: 2.67 nM Pb^{2+}: 2.8 nM Cu^{2+}: 30.6 nM Hg^{2+}: 1.3 nM	[10]
Metallophthalocyanine modified GCE	No observable peak position and height	No observable peak position and height	Cd^{2+}: 347.06 nM Pb^{2+}: 55.87 nM Cu^{2+}: 327.71 nM Hg^{2+}: 81.94 nM	[11]
FGO modified GCE	NS	NS	Cd^{2+}: 10 nM[a] Pb^{2+}: 10 nM[a] Cu^{2+}:NS Hg^{2+}: NS	[12]
AgNps/rGO modified magnetic GCE	1.902%	NS	Cd^{2+}: 0.245 μM Pb^{2+}: 0.287 μM Cu^{2+}: 0.171 μM Hg^{2+}: 0.180 μM	[13]
rGO/$NiWO_4$ modified CPE	< 4%	< 4%	Cd^{2+}: 0.10 nM Pb^{2+}: 0.18 nM Cu^{2+}: 0.23 nM Hg^{2+}: 0.28 nM	[14]
HAP-Nafion modified GCE	NS	Cd^{2+}: 5.9% Pb^{2+}: 4.8% Cu^{2+}: 3.1% Hg^{2+}: 6.1%	Cd^{2+}: 35 nM Pb^{2+}: 49 nM Cu^{2+}: 21 nM Hg^{2+}: 30 nM	[15]
GO/CeO_2 modified GCE	NS	NS	Cd^{2+}: 0.194 nM Pb^{2+}: 0.106 nM Cu^{2+}: 0.164 nM Hg^{2+}: 0.277 nM	[16]
Cys/rGO modified GCE	NS	NS	Cd^{2+}: 3.26 nM Pb^{2+}: 2.01 nM Cu^{2+}: 4.11 nM Hg^{2+}: 5.55 nM	[17]

[a]LOD calculated for the individual determination of each metal

AuNPs: gold nanoparticles; CPE: carbon paste electrode; Cys: cysteine; FGO: Fluorinated graphene oxide; GA: graphene aerogel; GCE: glassy carbon electrode; GO: graphene oxide; HAP: hydroxyapatite; IL: ionic liquid LDH: layered double hydroxide; MOF: metal–organic framework; P1,2-DAAQ: poly(1,2-diaminoan-thraquinone); PACs: porous activated carbon; PdNPs: Palladium nanoparticles; PPy: polypyrrole; rGO: reduced graphene oxide; individual refers to no simultaneous results can be obtained from the original paper

Table S2. Metal concentration values determined by ASV and ICP-AES in soil samples.

Sample	Zn^{2+}			Pb^{2+}			Cd^{2+}		
	ASV (ppm)	**ICP-AES (ppm)**	**Difference (%)**	**ASV (ppm)**	**ICP-AES (ppm)**	**Difference (%)**	**ASV (ppm)**	**ICP-AES (ppm)**	**Difference (%)**
1	7.90	8.24	4.09	4.33	4.30	0.60	4.57	4.73	3.35
2	5.30	5.28	0.44	2.38	2.35	1.45	1.51	1.59	4.94
3	21.79	31.66	31.17	22.64	23.78	4.79	7.73	8.20	5.79
4	20.32	18.99	7.00	15.00	14.27	5.10	5.25	4.92	6.62
5	13.33	12.74	4.64	18.29	17.15	6.63	16.09	14.64	9.89
6	12.79	13.51	5.32	14.85	16.26	8.63	5.59	6.10	8.33
7	104.36	128.0	18.47	46.31	45.10	2.68	17.43	16.79	3.82
8	80.01	55.28	44.75	48.64	36.69	32.58	49.69	36.22	37.19
9	116.90	107.5	8.74	10.28	7.81	31.73	4.06	3.81	6.66
S0	11.04	10.84	1.86	7.34	6.99	5.09	5.66	5.48	3.32
11	14.80	12.33	20.03	6.98	6.43	8.55	4.09	3.80	7.58
12	9.57	9.48	0.90	5.79	5.67	2.09	5.37	4.97	8.12
13	17.23	8.22	109.64	6.20	4.16	49.10	2.96	2.58	14.77
14	35.94	36.18	0.67	66.77	69.53	3.97	70.29	66.42	5.83
15	126.61	122.6	3.3.	15.93	13.96	14.08	6.24	4.63	34.80
16	19.52	21.13	7.65	24.97	27.23	8.33	7.68	8.18	6.12
17	23.35	24.47	4.57	18.83	18.81	0.07	8.79	9.52	7.70
18	26.01	25.96	0.20	19.94	20.02	0.37	13.06	13.49	3.18
19	15.14	13.97	8.36	0.35	9.73	6.43	9.13	9.01	1.35

References

1. Veerakumar, P.; Veeramani, V.; Chen, S.-M.; Madhu, R.; Liu, S.-B. Palladium nanoparticle incorporated porous activated carbon: electrochemical detection of toxic metal ions. *ACS applied materials & interfaces* **2016**, *8*, 1319-1326.
2. Xu, X.; Duan, G.; Li, Y.; Liu, G.; Wang, J.; Zhang, H.; Dai, Z.; Cai, W. Fabrication of gold nanoparticles by laser ablation in liquid and their application for simultaneous electrochemical detection of Cd2+, Pb2+, Cu2+, Hg2+. *ACS applied materials & interfaces* **2014**, *6*, 65-71.
3. Van Staden, J.; Matoetoe, M. Simultaneous determination of copper, lead, cadmium and zinc using differential pulse anodic stripping voltammetry in a flow system. *Analytica Chimica Acta* **2000**, *411*, 201-207.
4. Kokab, T.; Shah, A.; Iftikhar, F.J.; Nisar, J.; Akhter, M.S.; Khan, S.B. Amino acid-fabricated glassy carbon electrode for efficient simultaneous sensing of zinc (II), cadmium (II), copper (II), and mercury (II) ions. *ACS omega* **2019**, *4*, 22057-22068.
5. Lu, M.; Deng, Y.; Luo, Y.; Lv, J.; Li, T.; Xu, J.; Chen, S.-W.; Wang, J. Graphene aerogel–metal–organic framework-based electrochemical method for simultaneous detection of multiple heavy-metal ions. *Analytical chemistry* **2018**, *91*, 888-895.
6. Wei, Y.; Gao, C.; Meng, F.-L.; Li, H.-H.; Wang, L.; Liu, J.-H.; Huang, X.-J. SnO2/reduced graphene oxide nanocomposite for the simultaneous electrochemical detection of cadmium (II), lead (II), copper (II), and mercury (II): an interesting favorable mutual interference. *The journal of physical chemistry C* **2012**, *116*, 1034-1041.
7. Zhou, J.; Sun, G.; Pan, J.; Pan, Y.; Wang, S.; Zhai, H. A nanocomposite consisting of ionic liquid-functionalized layered Mg (II)/Al (III) double hydroxides for simultaneous electrochemical determination of cadmium (II), copper (II), mercury (II) and lead (II). *Microchimica Acta* **2019**, *186*, 1-7.
8. Kitte, S.A.; Li, S.; Nsabimana, A.; Gao, W.; Lai, J.; Liu, Z.; Xu, G. Stainless steel electrode for simultaneous stripping analysis of Cd (II), Pb (II), Cu (II) and Hg (II). *Talanta* **2019**, *191*, 485-490.
9. Rehman, A.U.; Ikram, M.; Kan, K.; Zhao, Y.; Zhang, W.J.; Zhang, J.; Liu, Y.; Wang, Y.; Du, L.; Shi, K. 3D interlayer nanohybrids composed of reduced graphenescheme oxide/SnO2/PPy grown from expanded graphite for the detection of ultra-trace Cd2+, Cu2+, Hg2+ and Pb2+ ions. *Sensors and Actuators B: Chemical* **2018**, *274*, 285-295.
10. Hassan, K.M.; Gaber, S.E.; Altahan, M.F.; Azzem, M.A. Novel Sensor Based on Poly (1, 2-Diaminoanthraquinone) for Individual and Simultaneous Anodic Stripping Voltammetry of Cd2+, Pb2+, Cu2+ and Hg2+. *Electroanalysis* **2018**, *30*, 1155-1162.
11. Fomo, G.; Nwaji, N.; Nyokong, T. Low symmetric metallophthalocyanine modified electrode via click chemistry for simultaneous detection of heavy metals. *Journal of Electroanalytical Chemistry* **2018**, *813*, 58-66.
12. Thiruppathi, A.R.; Sidhureddy, B.; Keeler, W.; Chen, A. Facile one-pot synthesis of fluorinated graphene oxide for electrochemical sensing of heavy metal ions. *Electrochemistry Communications* **2017**, *76*, 42-46.
13. Sang, S.; Li, D.; Zhang, H.; Sun, Y.; Jian, A.; Zhang, Q.; Zhang, W. Facile synthesis of AgNPs on reduced graphene oxide for highly sensitive simultaneous detection of heavy metal ions. *RSC advances* **2017**, *7*, 21618-21624.
14. Kumar, R.; Bhuvana, T.; Sharma, A. Nickel tungstate–graphene nanocomposite for simultaneous electrochemical detection of heavy metal ions with application to complex aqueous media. *RSC advances* **2017**, *7*, 42146-42158.
15. Gao, F.; Gao, N.; Nishitani, A.; Tanaka, H. Rod-like hydroxyapatite and Nafion nanocomposite as an electrochemical matrix for simultaneous and sensitive detection of Hg2+, Cu2+, Pb2+ and Cd2+. *Journal of Electroanalytical Chemistry* **2016**, *775*, 212-218.
16. Xie, Y.-L.; Zhao, S.-Q.; Ye, H.-L.; Yuan, J.; Song, P.; Hu, S.-Q. Graphene/CeO2 hybrid materials for the simultaneous electrochemical detection of cadmium (II), lead (II), copper (II), and mercury (II). *Journal of Electroanalytical Chemistry* **2015**, *757*, 235-242.
17. Muralikrishna, S.; Sureshkumar, K.; Varley, T.S.; Nagaraju, D.H.; Ramakrishnappa, T. In situ reduction and functionalization of graphene oxide with L-cysteine for simultaneous electrochemical determination of cadmium (II), lead (II), copper (II), and mercury (II) ions. *Analytical Methods* **2014**, *6*, 8698-8705.