

Supporting information

Deep eutectic solvent-based manganese molybdate nanosheets for sensitive and simultaneous detection of human lethal compounds: Comparing the electrochemical performances of M-molybdate (M= Mg, Fe, and Mn) electrocatalysts

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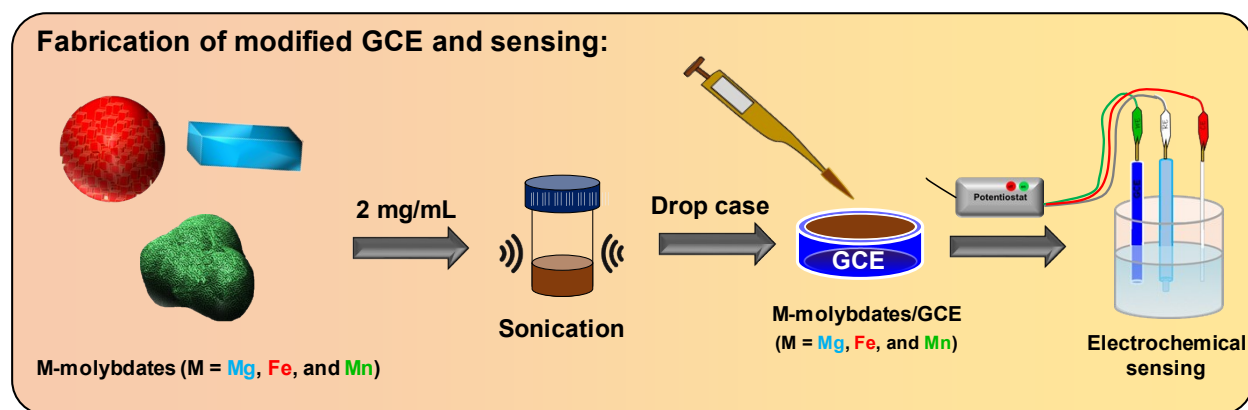
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Chemicals and Reagents

All the chemicals used in the study are of analytical grade and are received from Sigma-Aldrich and Merck. Ultrapure fresh water is obtained from a millipore water purification system (Milli-Q, specific resistivity $>18\text{ M}\Omega\text{cm}$, S.A.; Molsheim, France) and is used in all the experiments. Sodium phosphate dibasic and sodium dihydrogen phosphate (Na_2HPO_4 and NaH_2PO_4) are utilized to prepare 0.05 M (pH 7) PB (phosphate buffer). All the electrochemical experiments are carried out using 0.05 M PB (pH 7) as the supporting electrolyte.

Fabrication of Modified Electrodes.



Scheme S1. Fabrication of M-molybdate ($M = \text{Mg}, \text{Fe}$ and Mn) modified electrodes and sensing of HQ, Hg^{2+} and NO_2^-

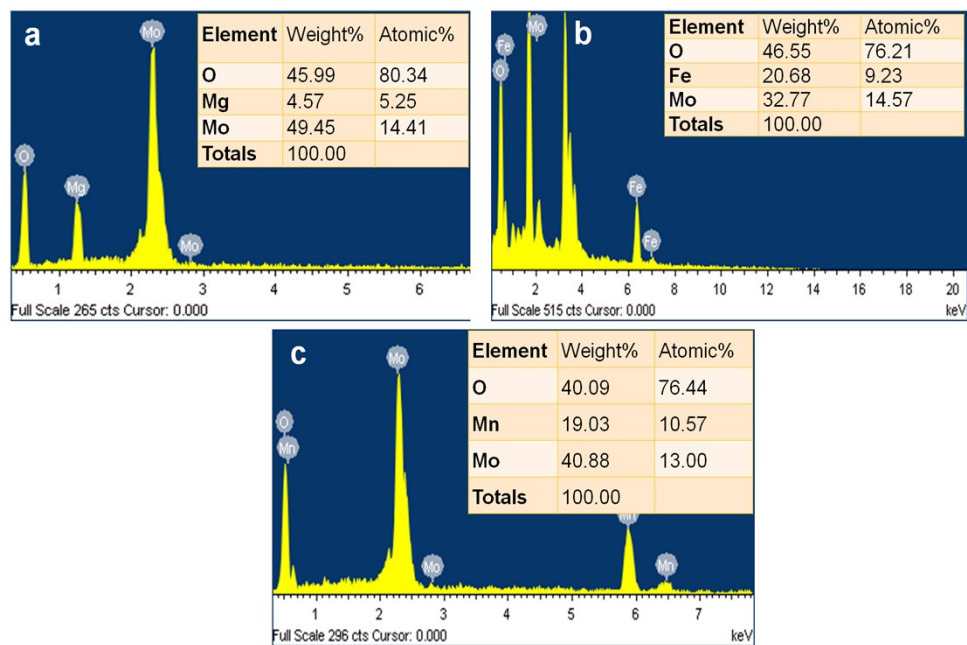


Fig. S1. EDS of (a) MgMoO₄ NRs (b) Fe₂(MoO₄)₃ Ys and (c) MnMoO₄ BC.

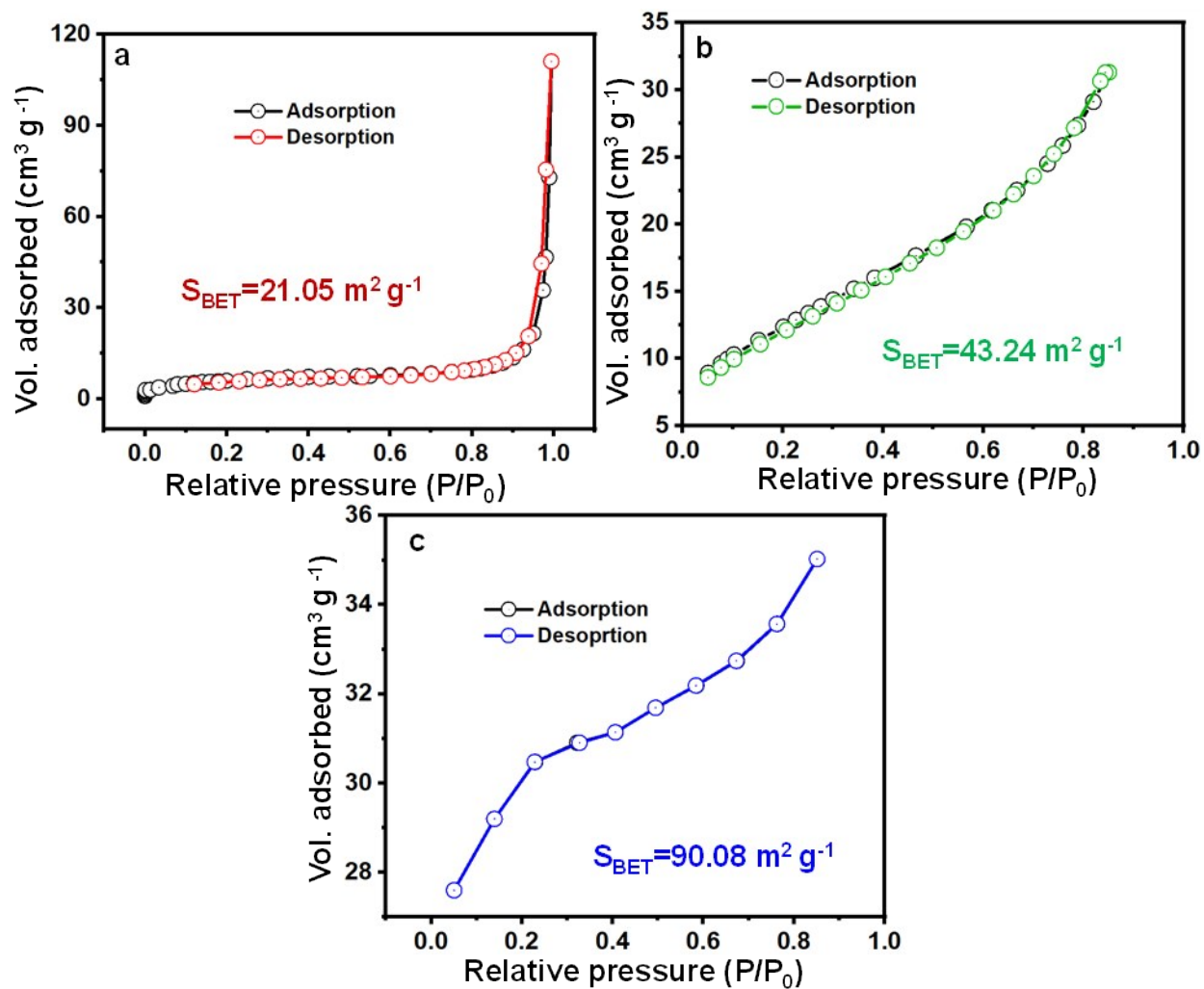


Fig. S2. BET isotherms of (a) MgMoO₄ (b) Fe₂(MoO₄)₃ and (c) MnMoO₄.

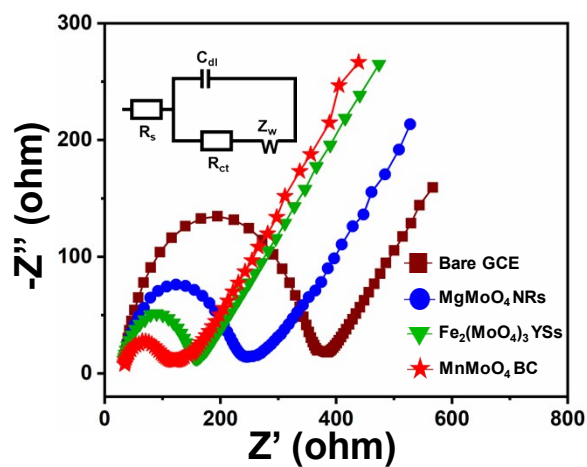


Fig. S3. Nyquist plot of various electrodes: bare GCE, MgMoO₄ NRs/GCE, Fe₂(MoO₄)₃ YSSs/GCE and MnMoO₄ BC/GCE; inset: diagram of Randles equivalent circuit model.

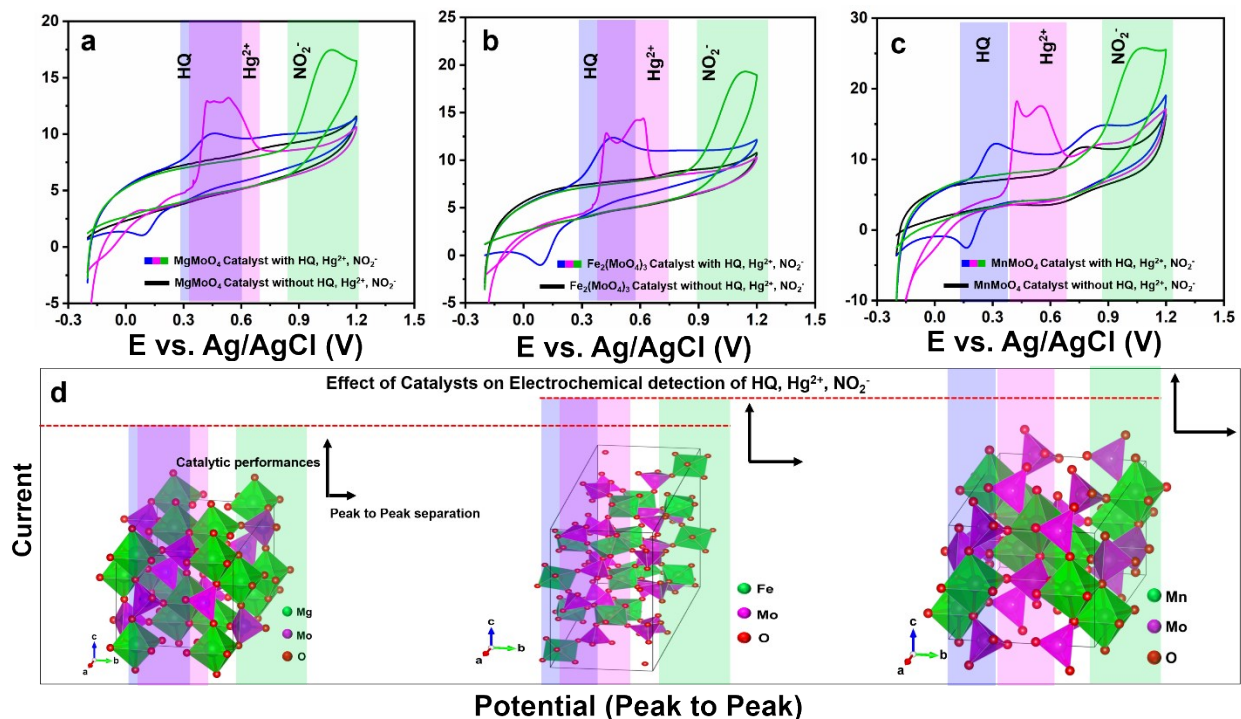


Fig.S4. CV profiles of background, unmodified and modified MgMoO₄ NRs (a), Fe₂(MoO₄)₃ YSSs (b), and MnMoO₄ BC (c) electrodes towards 100 μM of HQ, Hg²⁺ and NO₂⁻. All measurements were recorded in electrolyte: 0.05 M PB (pH 7.0) at a scan rate of 50 mV s⁻¹. (d), Crystal structures of MgMoO₄ (a), Fe₂(MoO₄)₃ (b), and MnMoO₄ with catalytic performances towards Electrochemical detection of HQ, Hg²⁺ and NO₂⁻.

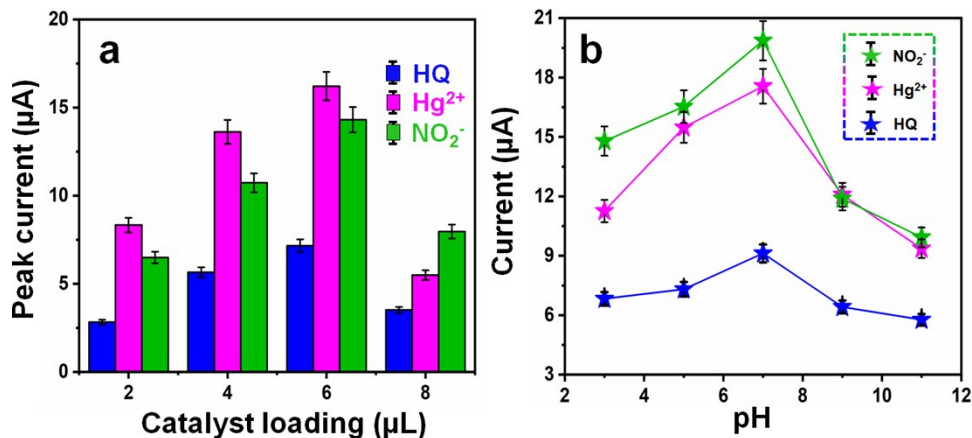


Fig. S5. (a) Effect of catalyst loading on GCEs (μL) vs. relative peak current in presence of HQ, Hg^{2+} and NO_2^- . **(b)** Plot of MnMoO_4 BC/GCE obtained in supporting electrolyte at different pH containing $100 \mu\text{M}$ HQ, Hg^{2+} and NO_2^- (plot between current vs pH).

Real sample preparation

Face cream was obtained from local shop market. Tuna fish & Salami are brought from Zhnogshan fish market, Taipei, Taiwan. Certain amount of fishes is weighed for about 6g and is been homogenized with 3.0 mL of 0.1 mol L^{-1} EDTA and merged with 2.0 mL in pH 7.0 Mclavine buffer solution by utilizing HY-4 homogenizer model instrument with a lateral speed of 5000 rpm for nearly 30 mins. Afterwards it is shaken vigorously for almost 10 mins with 3 m mL of acetonitrile. Continuing, it is centrifuged at a speed of 5000 rpm for 10 mins, transferred to a clean polypropylene tube. Moreover, using 3.0 mL of aliquot acetonitrile fish residues were extracted. Later, both the extracts are combined further evaporated by drying in nitrogen atmosphere. Obtained dried extract is re-formed in $200 \mu\text{L}$ of methanol, centrifuged in 5000 rpm for 5 mins and then stored for further use in 40C dark area.

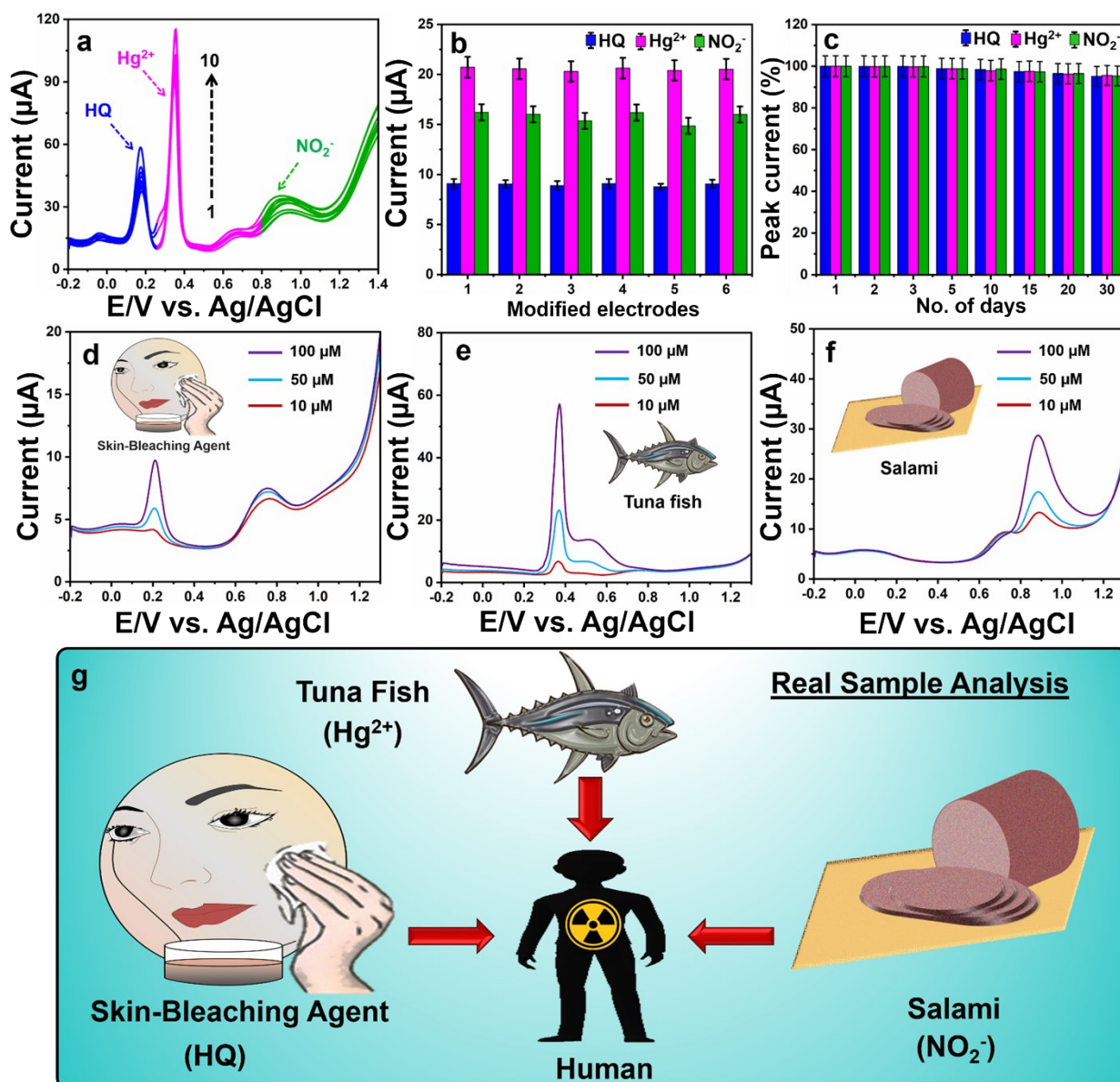


Fig. S6. (a) DPV profiles of selectivity of the MnMoO₄ modified GCE containing simultaneous addition HQ Hg²⁺ and NO₂⁻ in the presence of an excess concentration (1–9) of CC, RC, Cd²⁺, Pb²⁺, NaAc, ascorbic acid, NaCl, bisphenol A, and glucose. (b and c) Reproducibility and stability of the MnMoO₄ modified GCE in 0.05 M pH 7.0. DPV profiles of different real samples of the MnMoO₄ modified GCE containing (d) HQ, (e) Hg²⁺ and (f) NO₂⁻. (g) Schematic representation of real-time analysis of analytes causing metabolic toxication.

Table S1. Structural, BET and BJH parameters of MgMoO₄, Fe₂(MoO₄)₃ and MnMoO₄.

| Sample | Lattice parameters (Å) | | | | Scherrer method D (nm) | Lattice strain | Surface area (m ² /g) | Pore volume (cc/g) | Pore diameter (nm) |
|--|------------------------|-------------|-------------|--------------|---------------------------|----------------|----------------------------------|--------------------|--------------------|
| | a | b | c | β | | | | | |
| MgMoO ₄ | 10.15 | 9.24 | 7.03 | 105.9 | 27.55 | 0.0102 | 21.05 | 0.078 | 8.91 |
| Fe ₂ (MoO ₄) ₃ | 15.70 | 9.23 | 18.2 | 125.2 | 22.95 | 0.0122 | 45.24 | 0.046 | 6.19 |
| MnMoO ₄ | 10.46 | 9.51 | 7.14 | 106.2 | 13.45 | 0.0105 | 90.08 | 0.019 | 2.88 |

Table S2. Comparison of analytical confines for the determination of HQ at MnMoO₄ BC modified electrode with previous reports.

| Electrode materials | Methods | Linear range (μM) | LOD (μM) | Interfering species | Ref |
|---|------------------|-------------------|--------------|---|------------------|
| PANI/MnO ₂ | DPV | 0.2–100 | 0.13 | CC and RC | S1 |
| CD ^a /r-GO | DPV | 0.5–1000 | 0.17 | CC and RC | S2 |
| AuNPs/Fe ₃ O ₄ - ^b APTES-GO | Amperometric i-t | 3–137 | 1.1 | CC | S3 |
| GR ^c -La(OH) ₃ | DPV | 5–300 | 0.015 | CC | S4 |
| Pt–Au– ^d OSi@CS | Amperometric i-t | 0.06–90.98 | 0.02 | CC | S5 |
| Graphene– chitosan | DPV | 1.0–200 | 0.75 | CC | S6 |
| NA-COGH ^e | DPV | 0.8–500 | 0.034 | CC | S7 |
| Polydopamine- RGO | DPV | 1.0–2300 | 0.074 | CC | S8 |
| P-rGO | DPV | 5-120 | 0.18 | CC | S9 |
| GMC | DPV | 2-70 | 0.31 | CC | S10 |
| Nitrogen- doped CNT | DPV | 20–1000 | 2.71 | CC | S11 |
| MnMoO₄ BC | DPV | 0.9-591.2 | 0.026 | Hg²⁺ and NO₂⁻ | This work |

a- Carbon dot, *b-* (3-Aminopropyl) triethoxysilane, *c-* Graphene, *d-* Organosilica@chitosan composites, *e-* Nanopore array derived cysteine oxide/gold hybrids.

Table S3. Comparison of analytical limitations for the determination of Hg²⁺ at MnMoO₄ BC modified electrode with previous reports.

| Electrode Materials | Methods | Linear Range | LOD | Interfering Species | Ref. |
|---|--------------------|---------------------|----------------|--|------------------|
| Pd _{1.5} / ^a PAC-900 | DPV | 0.24–7.5 μM | 0.054 μM | Cd ²⁺ , Pb ²⁺ , and Cu ²⁺ | S12 |
| ^b NH ₂ -CMS | SWASV ^c | 0.4–1.2 μM | 0.098 μM | Cd ²⁺ , Pb ²⁺ , and Cu ²⁺ | S13 |
| DNA Modified Fe ₃ O ₄ @Au NPs | SWV | 10–100 nM | 1.7 nM | Ag ⁺ | S14 |
| SnO ₂ /RGO | SWASV | 0.4–1.2 μM | 0.279 nM | Cd ²⁺ , Pb ²⁺ , and Cu ²⁺ | S15 |
| NG ^d | DPSV ^e | 0.2–9 μM | 0.05 μM | Cd ²⁺ , Pb ²⁺ , and Cu ²⁺ | S16 |
| MnFe ₂ O ₄ NAs ^f | DPV | 100 nM–872.3 μM | 0.14 nM | - | S17 |
| ^g Alk-Ti ₃ C ₂ | SWASV | 0.1–1.5 μM | 0.130 | Cd ²⁺ , Pb ²⁺ , and Cu ²⁺ | S18 |
| MnMoO₄ BC | DPV | 0.9-591.2 μM | 0.05 μM | HQ and NO₂⁻ | This work |

a- Porous activated carbons, b- Amino-functionalized carbon microsphere, c- Square wave anodic stripping voltammetry, d- N-doped graphene e- Differential pulse stripping voltammetry, f- Nano-agglomerates g- Alkaline intercalation of Ti₃C₂ MXene

Table S4. Comparison of analytical limitations for the determination of NO₂⁻ at MnMoO₄ BC modified electrode with previous reports.

| Electrode Materials | Methods | Linear Range | LOD (μM) | Interfering Species | Ref. |
|------------------------------|----------------------------|---------------------|-------------|-------------------------------|------------------|
| La-MWCNTs | Chronoamperometry | 0.4–710 μM | 0.13 | AA, DA and UA | S19 |
| HOOC-MWCNT | DPV | 100 μM to 0.7 mM | 0.56 | SO ₃ ²⁻ | S20 |
| Cu/MWCNT/RGO | SWV | 0.1–75 μM | 0.03 | NO ₃ ⁻ | S21 |
| AgZEGE ^a | CV | 100–1000 μM | 0.005 | NO ₃ ⁻ | S22 |
| G-PLA ^b | Multiple-pulse amperometry | 0.5–250 μM | 0.03 | Uric Acid | S23 |
| NRCu ^c /rGO | DPV | 0.3–131.5 μM | 0.1 | HQ, CC and RS | S24 |
| ^d 2,4-DDMA-NiO/NP | SWVs | 10.0–700.0 μM | 5.0 | TS and 4-CPe | S25 |
| MnMoO₄ BC | DPV | 0.9-453.1 μM | 0.01 | HQ and Hg²⁺ | This work |

a- Zeolite-expanded graphite-epoxy composite electrode, b-Polylactic acid containing graphene, c- Nanoraspberry-like copper, d- 2,4-dimethyl-N'-[1-(2,3- dihydroxyphenyl)methylidene]aniline, e- Thiosulfate and 4-chlorophenol

Table S5. Results of determination of HQ, Hg²⁺ and NO₂⁻ in face cream, tuna fish, and salami samples towards MnMoO₄ BC/GCE.

| Samples | Added* (μM) | Detected (μM) ^a HPLC | Detection Rate (%) (Mean \pm RSD) (n=3) |
|-------------------|--------------------------|---|--|
| Face cream | 0 | - | - |
| | 10 | 09.86 | 98.60 \pm 0.017 |
| | 50 | 49.90 | 99.80 \pm 0.011 |
| | 100 | 99.70 | 99.70 \pm 0.005 |
| Tuna fish | 0 | - | - |
| | 10 | 09.73 | 97.30 \pm 0.014 |
| | 50 | 49.50 | 99.00 \pm 0.008 |
| | 100 | 99.17 | 99.17 \pm 0.019 |
| Salami | 0 | - | - |
| | 10 | 09.82 | 98.20 \pm 0.012 |
| | 50 | 49.27 | 98.54 \pm 0.018 |
| | 100 | 99.16 | 99.16 \pm 0.017 |

^aStandard addition method. Relative standard deviation deduced from three separate measurements.

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