Supporting information

High Performance Mercury Sensing Enabled by the Synergistic Effect of rGO–MnO_2 Nanocomposites

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1. Calculation of Electroactive Surface Area, A (cm²) of the GCE

Randles–Sevcik equation was used to calculate the electroactive surface area. The Randles–Sevcik equation can be expressed as, $I_p = 2.69 \times 10^5\, n^{3/2}\, A\, D^{1/2}\, C\, \nu^{1/2}$. Where A is the electroactive surface area (cm²), D is the diffusion coefficient of the redox species (7.6×10^{-6} cm²/s), C is the bulk concentration of the redox probe (5.0×10^{-6} mol/cm³), v is the scan rate (V/s), I_p is the peak current (A) and n is the number of electrons transferred, normally n = 1, for $K_3[Fe(CN)_6]$.

Table S1. Active Surface Area Calculation of the GCE

Measurement No.	Scan Rate, v (mV/s)	Peak Current, *I*p (µA)	*I*p, (A)	v (V/s)	$v^{1/2}$	Calculated Active Area, A (cm²)
1	10	83.6	8.36×10^{-5}	0.01	0.100	0.225
2	20	119.3	11.93×10^{-5}	0.02	0.141	0.228
3	40	168.4	16.84×10^{-5}	0.04	0.200	0.227
4	60	205.5	20.55×10^{-5}	0.06	0.245	0.226

5	80	237.6	23.76×10^{-5}	0.08	0.283	0.229
6	100	261.3	26.13×10^{-5}	0.10	0.316	0.226

Calculated Average Electroactive Surface Area, A = 0.227 cm^2

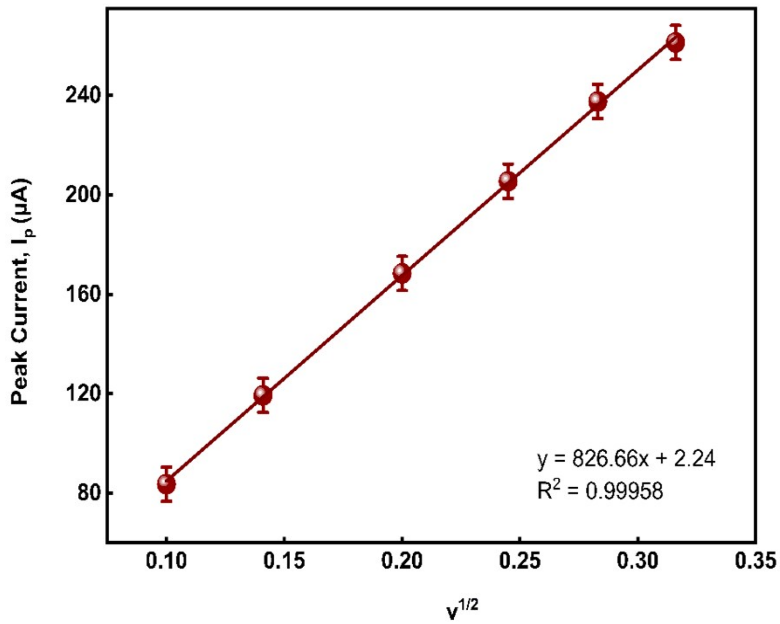

Figure S1. Anodic peak current (I_p) vs the square root of the scan rate ($v^{1/2}$).

2. Calculation of σ, LOD, and LOQ for the rGO–MnO_2/GCE Sensor

The limit of detection (LOD) and limit of quantification (LOQ) were evaluated using the standard deviation of the blank signal (σ) and the slope (S) of the calibration curve, following the well-established relations LOD = 3.3σ/S and LOQ = 10σ/S.

The value of slope, S (μA/nM) = 6.81 (From the calibration curve)

Table S2. Calculation of σ

Measurement No.	Blank Current Response, x_i (μA)	Deviation from Mean, ($x_i - \bar{x}$) (μA)	Deviations, $(x_i - \bar{x})^2$
1	1.45	–0.31	0.0961
2	2.05	+0.29	0.0841
3	1.80	+0.04	0.0016

4	1.60	–0.16	0.0256
5	1.90	+0.14	0.0196
Sum, $\sum x_i$ (μA)	8.80	—	—
Mean, $\bar{x}$ (μA)	1.76	—	—
σ (μA), $\sigma = \frac{\sum(xi - \bar{x})^2}{n - 1}$	0.20	—	—

From the table, the standard deviation of the blank signal, σ = 0.20

Hence, LOD = 3.3σ/S = 0.097 nM

LOQ = 10σ/S = 0.294 nM

3. RSD & Stability Calculations

3.1. Repeatability Test – RSD Calculation

The repeatability of the sensor was evaluated by performing five consecutive measurements of rGO–MnO_2 modified GCE in presence of 10 μM Hg^{2+} under same condition. The stripping peak currents obtained from these trials exhibited minimal variation, with a relative standard deviation (RSD) of just 1.03%.

Table S3. Calculation of RSD (Repeatability Test)

Measurement No.	Response, xi (μA)	Deviation from Mean, (xi-$\bar{x}$) (μA)	(Deviation)² (μA²)
1	151	–2	4
2	153	0	0
3	154	+1	1
4	152	–1	1
5	155	+2	4
Sum	**765**	—	**10**
Mean ($\bar{x}$)	**153**	—	—

Variance, $s2 = \frac{\sum(xi - \bar{x})2}{n - 1}$ = 2.5

Standard Deviation (SD), $s = \sqrt{2.5}$ = 1.58

Relative Standard Deviation, RSD(%) $= \frac{s}{\bar{x}} \times 100$ = 1.03 %

3.2. Reproducibility Test – RSD Calculation

To examine the reproducibility of the fabrication process, three independently prepared rGO–MnO_2 modified GCEs were employed to detect 10 µM Hg^{2+} under identical conditions. Both electrodes yielded highly comparable stripping responses, with an RSD of 1.02%. These results affirm the reliability and uniformity of the electrode modification protocol, indicating that the method can consistently produce functionally equivalent sensors.

Table S4. Calculation of RSD (Reproducibility Test)

Measurement No.	Response, xi (µA)	Deviation from Mean, (xi-x̄) (µA)	(Deviation)², ∑(xi-x̄)², (µA²)
1	233.4	+2.27	5.15
2	231.3	+0.17	0.03
3	228.7	–2.43	5.90
Sum	**693.4**	—	**11.08**
Mean ($\bar{x}$)	**231.13**	—	—

Variance, $s2 = \frac{\sum(xi - \bar{x})2}{n-1}$ = 5.54

Standard Deviation (SD), $s = \sqrt{5.54}$ = 2.35

Relative Standard Deviation, RSD(%) $= \frac{s}{\bar{x}} \times 100$ = 1.02 %

3.3. Calculation of % stability

The long-term operational stability of the modified electrode was assessed over a 30-day period. Stripping voltammetry measurements were taken at three-day intervals while the electrodes were stored under ambient laboratory conditions. The sensor retained 96.23% of its initial response after 12 days and 92.34% even after 30 days, confirming outstanding long-term stability.

$$\text{Stability at day t, } S(\%) = \frac{Current\ Response,\ \ I}{Peak\ Current} \times 100\ \%$$

Table S5. Calculation of % stability at different days

Day	Current Response, I (µA)	Stability (%)
1	233.27	100.00
3	231.12	99.08
6	229.46	98.37
9	227.14	97.37
12	224.48	96.23
15	222.15	95.23
18	220.65	94.58
21	218.82	93.80
24	217.06	93.06
27	216.67	92.88
30	215.4	92.34