Supporting Information for:

Acid-activation enhanced graphite additive manufactured polypropylene sensor for the detection of parathion in forensic and environmental samples

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Figure S1. XPS C 1s spectra for (A) the graphite powder and (B) Gr(HNO3) powder, and XPS O 1s spectra for (C) graphite powder and (D) Gr(HNO3) powder.

Table S1. The atomic concentration of the species in each graphite powder

Material	%			
	C=C	C—C, C—H	C—O	O—C=O
Graphite	43.7	15.3	24.7	16.4
Gr(HNO3)	59.0	6.2	11.7	23.1

Figure S2. Scan rate study (5−500 mV s−1) (A) in [Ru(NH3)6]3+ (1 mM in 0.1 M KCl) and (B) in [Fe(CN)6]4−/3− (1 mM in 0.1 M KCl) performed with the CB-Graphite/PP as the WE and (C) scan rate study (5−500 mV s−1) in [Fe(CN)6]4−/3− with the CB-Gr(HNO3)/PP as the WE.

Figure S3. Cyclic Voltammograms in 100 µM parathion and 0.1 M BR buffer solution at different pHs (2.0 – 12.0) at CB-Gr(HNO3)/PP electrode. Scan rate: 50 mV s–1.

Figure S4. Cyclic voltammetry towards 100 µM parathion in 0.1 M BR buffer solution at different pHs: (A) 2.0, (B) 3.0, (C) 4.0, (D) 5.0, (E) 6.0, and (F) 7.0, at CB-Gr(HNO3)/PP electrode. Scan rate: 50 mV s–1. In the graphs: O1: quasi-reversible oxidation process and R1:irreversible reduction process

Figure S5. Plots of (A) Ep vs pH and (B) Ip vs pH for 100 µM parathion in 0.1 M BR buffer solution at different pHs (2.0 – 7.0).

Table S2. Linear relationship between Ep and pH for parathion processes

Process	pH	Linear range	R^2
O1	2.0 – 7.0	Ep (V) = + 0.43 (±0.02) – 0.052 (±0.004) × pH	0.98
R1	2.0 – 4.0	Ep (V) = – 0.52 (±0.02) – 0.038 (±0.007) × pH	0.97

Figure S6. (A) Cyclic voltammetry for the supporting electrolyte study using H2SO4 (black line), HNO3 (blue line), HCl (red line), and BR buffer (magenta line) all at 0.1 M with 100 µM parathion performed at CB-Gr (HNO3)/PP electrode. (B) Cyclic voltammetry for the ionic strength study using HNO3 as the supporting electrolyte: 0.05 (black line), 0.1 (blue line), and 0.2 (red line) M. Scan rate: 50 mV s–1.

Figure S7. (A) Cyclic voltammetry for different scan rates (5 – 500 mV s−1) with 100 µM parathion in 0.1 M HNO3 at CB-Gr(HNO3)/PP. Plots (B) Ip vs v1/2, (C) log Ip vs log v, and (D) Ip vs v.

Scheme S1. Proposed electrochemical redox mechanism of the parathion using a CB-Gr(HNO3)/PP -Gr electrode in 0.1 M HNO3.

Figure S8. SWAdSV voltammograms obtained for 0.1 M HNO3 with 100 µM parathion using at CB-Gr(HNO3)/PP electrodes as WE. All measurements were performed using the optimised conditions. The pre-accumulation time ranged from 0 to 1 min. The inset shows a plot of Ip vs. pre-accumulation times.

Figure S9. SWAdSV voltammograms obtained for 0.1 M HNO_3 before (black line) and after addition of 30 to 90 µM parathion at CB-Graphite/PP. The inset shows linear regression. All measurements were performed in triplicate using the optimised conditions.

Table S3. Linear regression equations and R2 values of the plots of Ip vs. [parathion]

Electrode	Linear range (µM)	Linear regression equation	R2
CB-Graphite/PP	40 – 90	Ip (µA) = 2.10 (±0.06) + 0.008 (±0.001) × [parathion] (µM)	0.947
CB-Gr(HNO_3)/PP	20 – 100	Ip (µA) = 6.18 (±0.07) + 0.023 (±0.001) × [parathion] (µM)	0.993

Table S4. Comparison between the CB-Gr(HNO_3)/PP additive manufactured electrodes developed in this work and previously reported sensors for parathion detection

Electrode	Technique	Sample	Linear range (µM)	LOD (nM)	Ref
FeV/RGO@GCE	Amperometry	Green beans and river samples	0.001–260	0.7	1
MoC/SPCE	DPV	Water samples	0.02–43	4	2
Ag@GNRs/SPCE	Amperometry	Vegetables and fruits	0.005–2780	0.5	3
Nd-UiO-66@MWCNT/GCE	DPV	Water, fruit and vegetable samples	0.001–0.120	0.07	4
SnS_2/NS–RGO	Amperometry	River water and black grape samples	0.001–176	0.17	5

Additive manufactured CB/PLA	SWV	Honey and tap water samples	0.85–19.6	200	6
Au NPs/Nafion/GCE	SW-Ads CSV	Environmental water samples	0.00199–0.9 and 1.07–10.7	0.606	7
FT@CNT	DPV	Tomatoes, apples and soil samples	0.02–6.50	5.3	8
AgNPs@GO/IL@SPCE	SWV	Groundwater and surface water samples	0.025–200	9	9
GCE/ZnOHS/MIP	DPV	Fresh green beans, strawberry, tomato, and cabbage	5–10000	0.5	10
GDY-CNTs/GCE	DPV	Tap water and food samples	0.09–64.6	50	11
CB-Gr(HNO3)/PP additive manufactured electrodes	SWAdSV	River water and synthetic biological fluids	20–100	0.17	This work

Key: FeV/RGO@GCE: glassy carbon electrode modified with FeVO4/reduced graphene oxide; MoC/SPCE: screen-printed carbon electrode based on molybdenum carbide; Ag@GNRs/SPCE: silver particles supported graphene nanoribbons modified screen-printed carbon electrode; Nd-UiO-66@MWCNT/GCE: glassy carbon electrode modified with a composite comprising neodymium (Nd) incorporated into the UiO-66 metal–organic framework and further integrated with multi-walled carbon nanotubes (MWCNTs); SnS2/NS–RGO: SnS2 nanosheets supported in a N, S-co-doped reduced graphene oxide nanocomposite; Au NPs/Nafion/GCE: gold nanoparticles (AuNPs) functionalised Nafion nanocomposite modified glassy carbon electrode; SW-Ads CSV: square wave- adsorptive cathodic stripping voltammetry; FT@CNT: hybrid ferrocene-thiophene modified by carbon nanotube; AgNPs@GO/IL@SPCE: silver nanoparticles (AgNPs) in conjunction with graphene oxide/ionic liquid (GO/IL) on screen printed electrodes. GCE/ZnOHS/MIP: glassy carbon electrode functionalized with zinc oxide (ZnO) hollow spheres (ZnOHS) and a molecularly imprinted polymer (MIP); GDY-CNTs/GCE: glassy carbon electrode modified with graphdiyne (GDY)-carbon nanotubes (CNTs) nanocomposite.

Estimation of real surface area of the CB-Graphite/PP and CB-Gr(HNO3)/PP

The adsorption of parathion at CB-Graphite/PP and CB-Gr(HNO3)/PP electrodes was characterised by applying the Langmuir isothermal to the data in Figures 5 and S9, according to Equation (1):

$$\theta = (K \times [C])/(1+K \times [C]) \qquad (1)$$

Where θ is the fractional occupancy of the adsorption sites, Kis the equilibrium constant for adsorption, and [C] is the concentration of parathion. The Langmuir plot is shown in Figure S10, where a linear regression of 1/Q (μC−1) = 0.827 (±0.02) + 8.085(±0.1) × 1/[parathion] (μM) −1 was obtained with R2 of 0.967 for CB-Graphite/PP and 1/Q (μC−1) = 0.325 (±0.05) + 1.665(±0.2) × 1/[parathion] (μM) −1 (R2 = 0.968) for CB-Gr(HNO3)/PP.

Figure S10. Langmuir plot of 20 – 100 μM parathion obtained from peak area shown in Figures 6 and S6.

The rectangular box model illustrated in Scheme S1 was employed to estimate the surface area available for parathion adsorption on the working electrode, composed of graphite and carbon black. The side lengths were calculated using trigonometric methods based on bond lengths, bond angles, and Van der Waals radii of terminal atoms, determined with ChemSketch software. Scheme 1 presents possible adsorption orientations for parathion on the electrode surface, shown in plane view (A), edge view (B), and end view (C).

Scheme S1. Rectangular box model of parathion molecule for (A) flat, (B) edgewise and (C) endwise view. An empty rectangular section was included for layout symmetry of rectangular box.

Based on these calculations, the areas of the three sides of the rectangular box were determined to be 8.315×10¯15, 5.932×10¯15, and 5.778×10¯15 cm2, corresponding to 1.203×1014, 1.686×1014, and 1.731×1014 molecules per cm2 for the plane, edge, and end views, respectively. Using the fundamental electron charge of 1.602×10¯19 C and the Qmax values obtained (1.21 μC for CB-Graphite/PP and 3.08 μC for CB-Gr(HNO3)/PP), the number of molecules adsorbed on the electrode was calculated to be 3.02×1013 for CB-Graphite/PP and 7.69×1013 for CB-Gr(HNO3)/PP. Assuming a monolayer with close packing, the real surface area available for adsorption on the carbon black and graphite layers of the electrodes was estimated to be between 0.445 and 0.639 cm2 for CB-Gr(HNO3)/PP. This value is significantly larger than the area estimated for CB-Graphite/PP, between 0.175 and 0.251 cm2, corroborating the higher sensitivity of CB-Gr(HNO3)/PP for parathion detection.

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