

# **Supporting Information**

Yuanzhe Wang, Archana Kaliyaraj Selva Kumar and Richard G. Compton\*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford

University, South Parks Road, Oxford OX1 3QZ, UK

## **Section 1 Optimisation of Accumulation time of Fipronil at MWCNT Modified GC**

### **Electrodes**

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## Section 1 Optimisation of Accumulation time of Fipronil at MWCNT Modified GC

### Electrodes

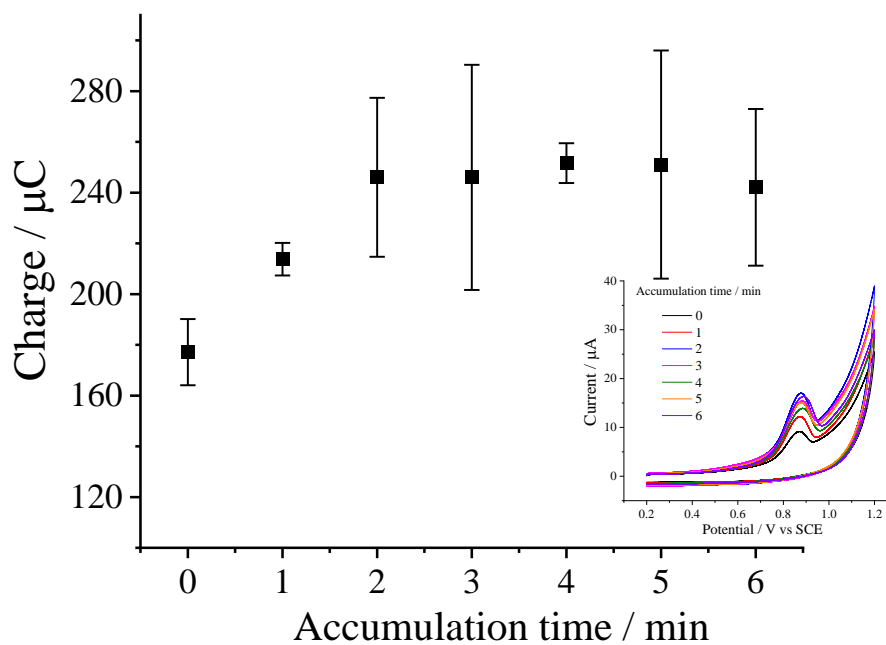


Figure S1. The plot of charge (error bar attained from three independent dropcasts) against accumulation time of 0-6 minutes under open circuit condition. The charges were obtained from the integration of peaks that were analysed by subtracting an 8<sup>th</sup> order polynomial fitted baseline from the voltammograms shown in the inset. Inset: The adsorptive stripping voltammetric responses recorded for MWCNT (10  $\mu\text{g}$ ) modified GC electrode immersing in 0.1 mM FIP solution at a scan rate of 5  $\text{mVs}^{-1}$

## Section 2 Scan Rate Study for the Oxidation of Fipronil

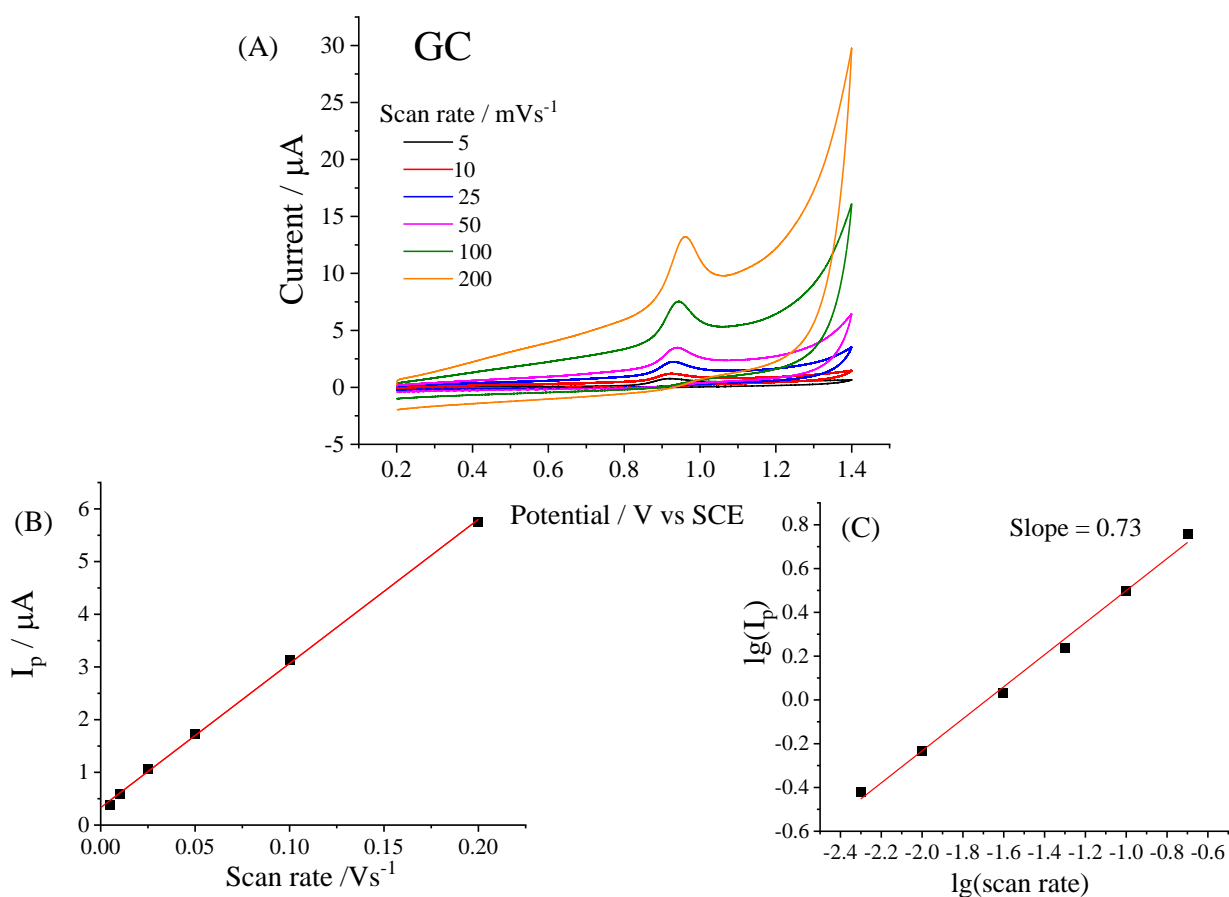


Figure S2. (A) Adsorptive stripping voltammetric responses 0.1 mM FIP at GC electrode recorded at varying scan rates of 5-200  $\text{mVs}^{-1}$  (B) plot of peak current versus scan rate (C) log-log plot in scan rate range of 5-200  $\text{mVs}^{-1}$

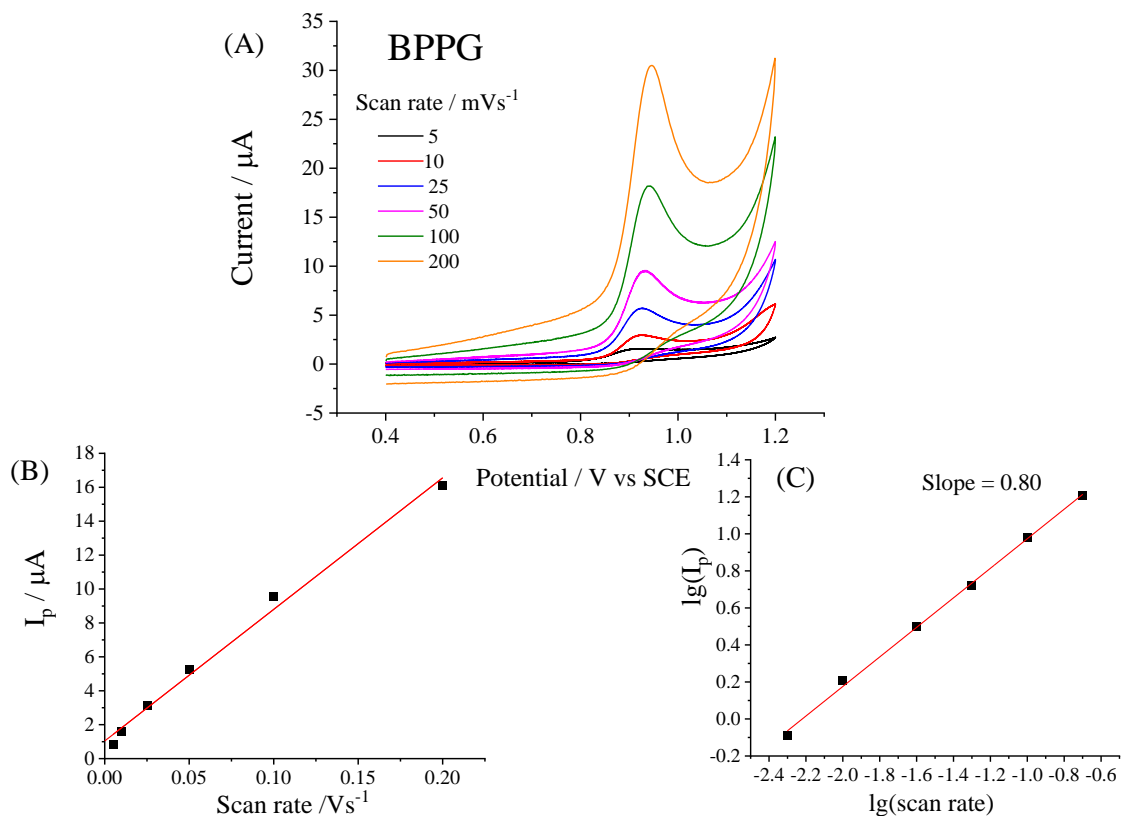


Figure S3. (A) Adsorptive stripping voltammetric responses 0.1 mM FIP at BPPG electrode recorded at varying scan rates of 5-200  $\text{mVs}^{-1}$  (B) plot of peak current versus scan rate (C) log-log plot in scan rate range of 5-200  $\text{mVs}^{-1}$

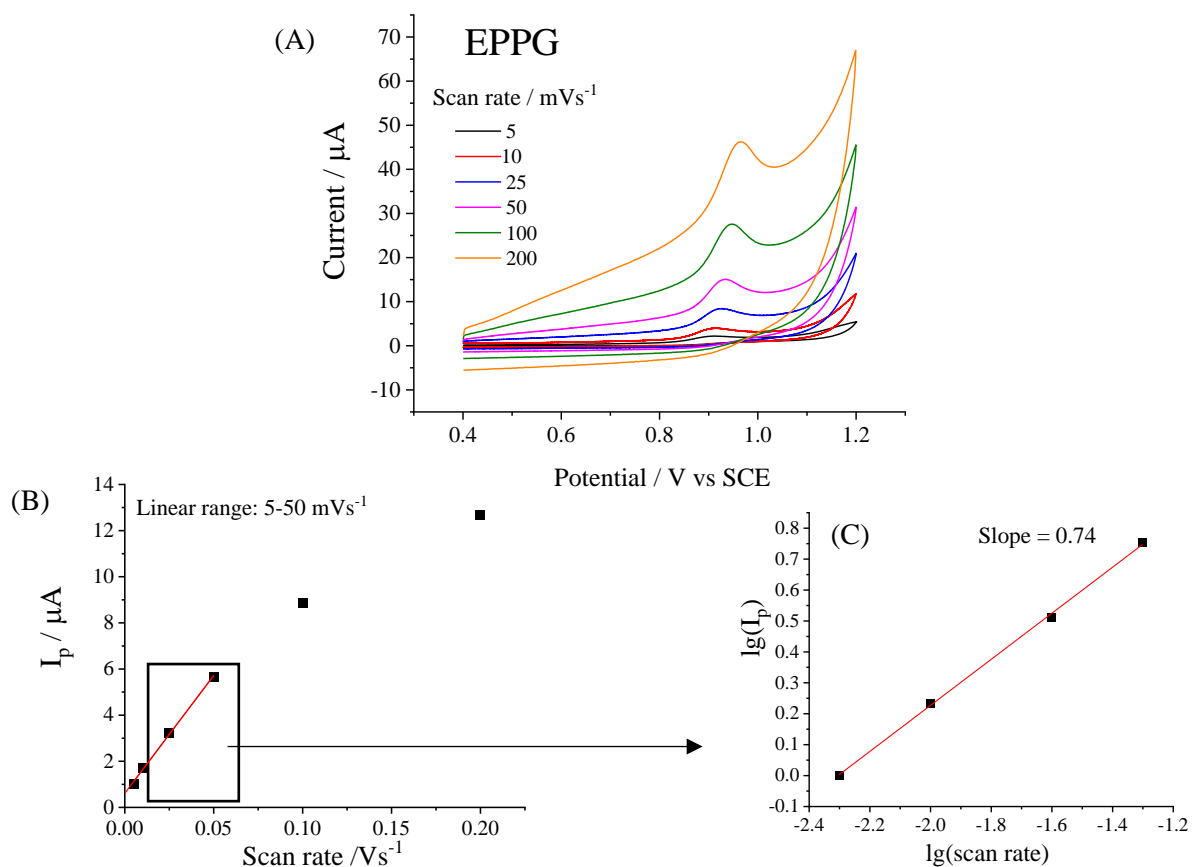


Figure S4. (A) Adsorptive stripping voltammetric responses 0.1 mM FIP at EPPG electrode recorded at varying scan rates of 5-200  $\text{mVs}^{-1}$  (B) plot of peak current versus scan rate (C) log-log plot in scan rate range of 5-50  $\text{mVs}^{-1}$

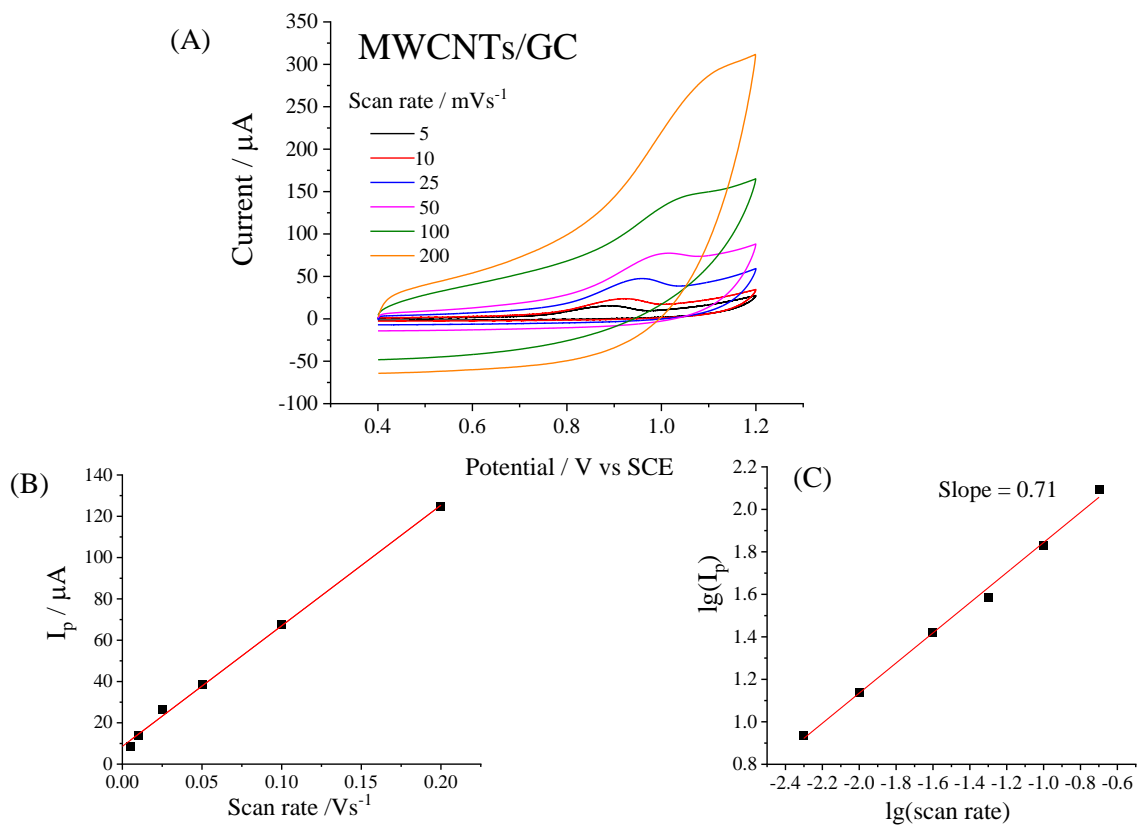


Figure S5. (A) Adsorptive stripping voltammetric responses 0.1 mM FIP at MWCNTs modified GC electrode (MWCNTs/GC) recorded at varying scan rates of 5-200  $\text{mVs}^{-1}$  (B) plot of peak current versus scan rate (C) log-log plot in scan rate range of 5-200  $\text{mVs}^{-1}$

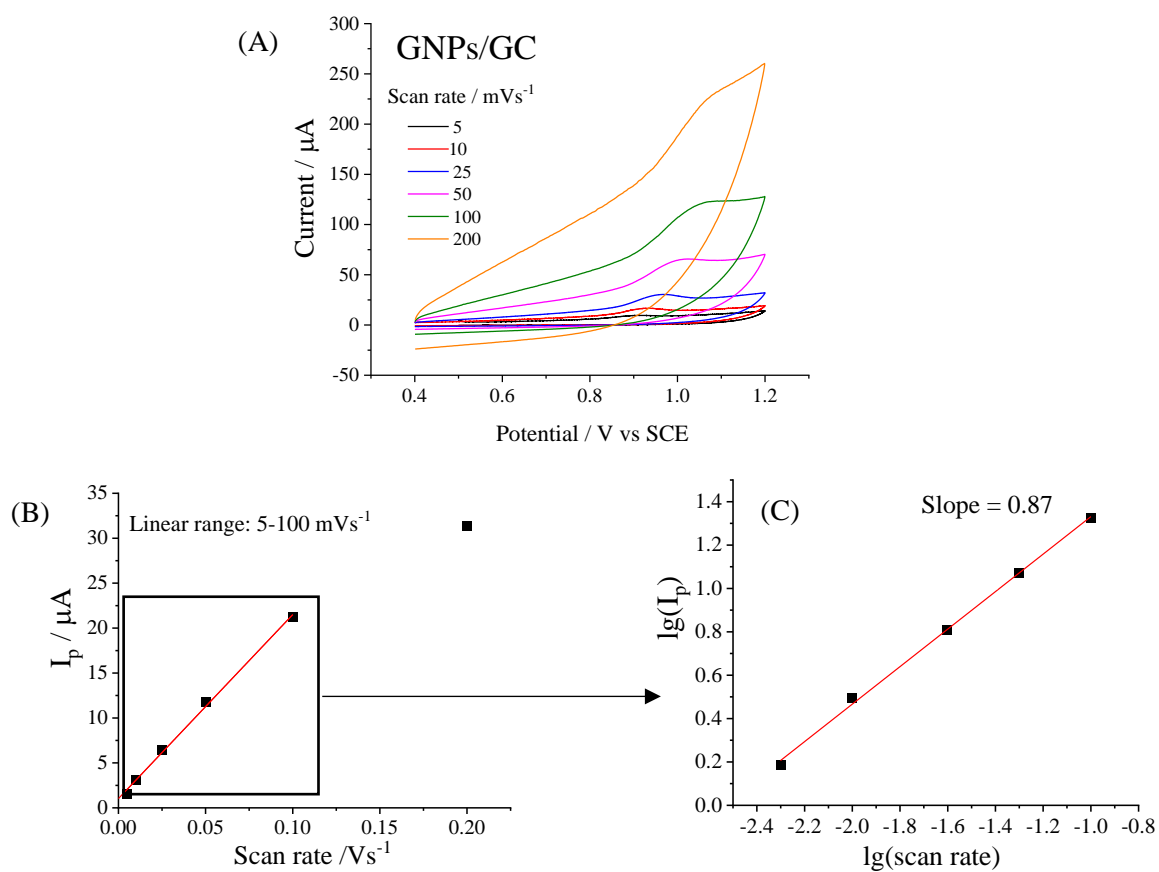
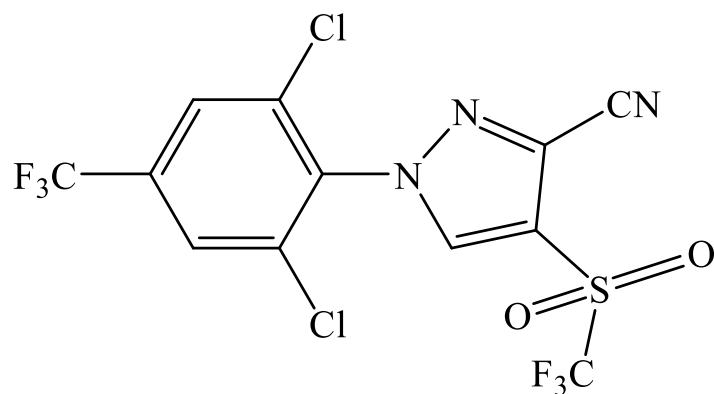


Figure S6. (A) Adsorptive stripping voltammetric responses  $0.1 \text{ mM}$  FIP at GNPs modified GC electrode (GNPs/GC) recorded at varying scan rates of  $5\text{-}200 \text{ mVs}^{-1}$  (B) plot of peak current versus scan rate (C) log-log plot in scan rate range of  $5\text{-}100 \text{ mVs}^{-1}$

### Section 3 Possible Oxidation Product of Fipronil



Fipronil Sulfone

Figure S7. The structure of the possible product of fipronil oxidation, fipronil sulfone<sup>[1]</sup>.

## Section 4 Langmuir Plots Measured at GC, BPPG, EPPG and GNP Surfaces

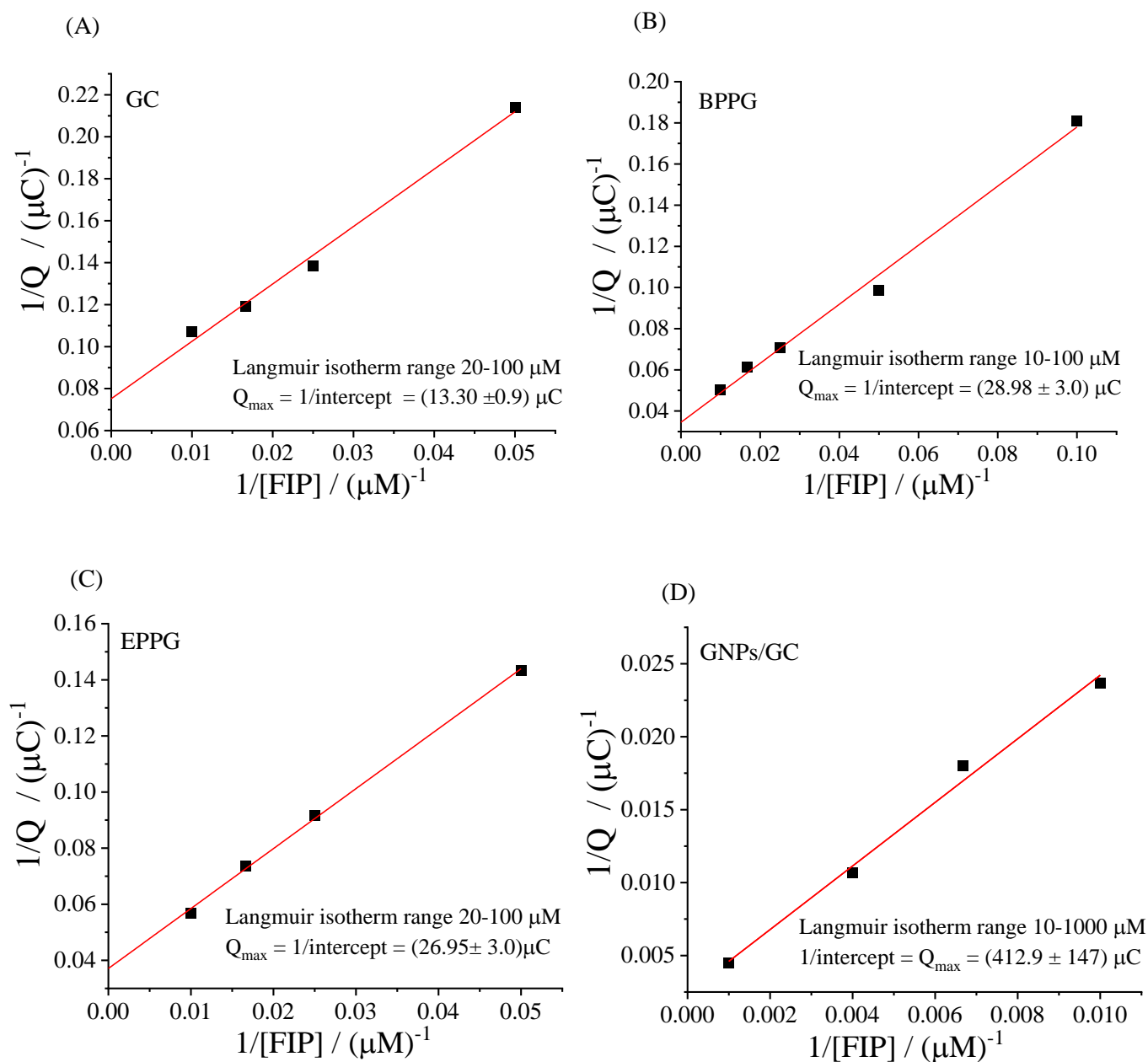


Figure S8. The Langmuir plots obtained from the adsorptive stripping voltammograms of 5-200  $\mu\text{M}$  FIP at (A) GC (B) BPPG (C) EPPG (D) GNPs modified GC.

## Section 5 Calculations of Geometric Electrode, MWCNTs and GNPs Surface Areas

GC, BPPG and EPPG electrodes:

The geometric electrode surface area of GC, BPPG, and EPPG electrode can be calculated from:  $A = \pi(d/2)^2$ , where  $A$  is the geometric surface area and  $d$  is the diameter of GC, BPPG and EPPG electrode which is 3 mm, 4.9mm and 4.3mm, respectively.

The obtained geometric surface area is 0.0707, 0.189 and 0.145 for GC, BPPG and EPPG electrode, respectively.

MWCNTs:

The surface areas of MWCNTs were calculated using the specific surface area (SSA) provided by the supplier, Nanolab (Brighton, MA, USA) as 200-400 m<sup>2</sup>/g

The total area of the given amount of MWCNTs dropcasted on electrode,  $S_{dropcast}$  can be calculated by  $A_{MWCNTs} = S_{SSA} m_{dropcast}$ , where  $m_{dropcast}$  is the mass of the MWCNTs dropcasted and  $S_{SSA}$ .

For 5, 7.5, 10, 20 and 30 µg MWCNT, the total surface area  $A_{MWCNTs}$  was calculated as 10 – 20, 15 – 30, 20 – 40, 40 – 80, 60 – 120 cm<sup>2</sup>, respectively.

The volume of a single MWCNT  $V_{MWCNT}$  was calculated by:

$$V_{MWCNT} = \pi r^2 h = (15 \times 10^{-9})^2 \times 2 \times 10^{-5} \times \pi m^3 = 1.4 \times 10^{20} m^3$$

The number of MWCNTs in 1g,  $N_{1g}$  can be calculated using a density of 1.54 g/cm<sup>2</sup> [2] by:

$$N_{1g} = \frac{V_{1g}}{V_{MWCNTs}} = \frac{\frac{1g}{1.54 g/cm^2}}{1.4 \times 10^{-14} cm^3} = 4.59 \times 10^{13}$$

The average surface area of each MWCNT,  $A_{single-MWCNT}$  was calculated by:

$$A_{single-MWCNT} = \frac{1 \times S_{SSA}}{N_{1g}} = \frac{200 \sim 400}{4.59 \times 10^{13}} m^2 = 4 \sim 9 \mu m^2$$

GNPs:

The surface area and the thickness of a single GNP was characterised to be 297±152 µm<sup>2</sup> and 7.1 ± 2 nm respectively from a previous SEM study<sup>[3]</sup>

Therefore the volume of a single GNP can be estimated as  $(2.11 \pm 1.08) \times 10^{-18} m^3$ . For ‘loose’ powders, the density of a single GNPs is assumed to be the same as graphite,  $2.3 \times 10^6 g/m^3$  [4]. Hence the mass of a single GNPs can be estimated as  $(4.8 \pm 2.4) \times 10^{-9} mg$ .

For 10  $\mu\text{g}$  GNPs, the total surface area can be calculated by:

$$A_{GNPs} = \frac{10 \times 10^{-3} \text{ mg}}{(4.77 \pm 2.44) \times 10^{-9}} \times (2.97 \pm 1.52) \times 10^{-6} \text{ cm}^2 = 6.2 \pm 3.2 \text{ cm}^2$$

Similarly the total surface area of 2.5, 5, 15, 20 mg GNPs was calculated as  $(1.6 \pm 0.8)$ ,  $(3.1 \pm 1.6)$ ,  $(9.3 \pm 4.8)$  and  $(18.7 \pm 9.6) \text{ cm}^2$ , respectively.

## Section 6 Nano-impact Study

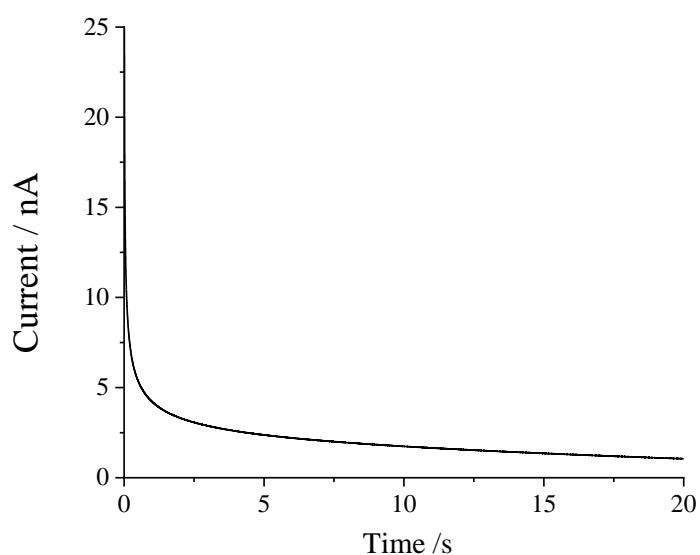
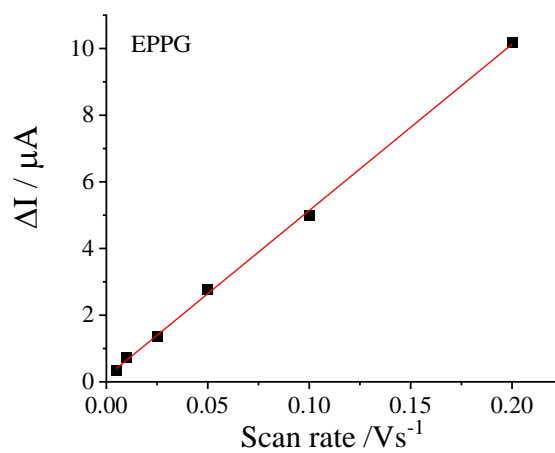
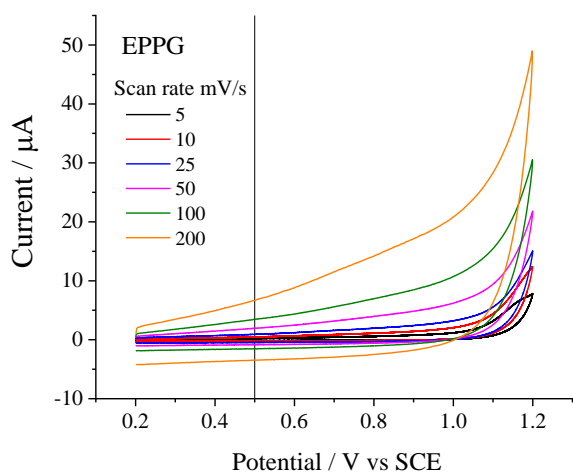
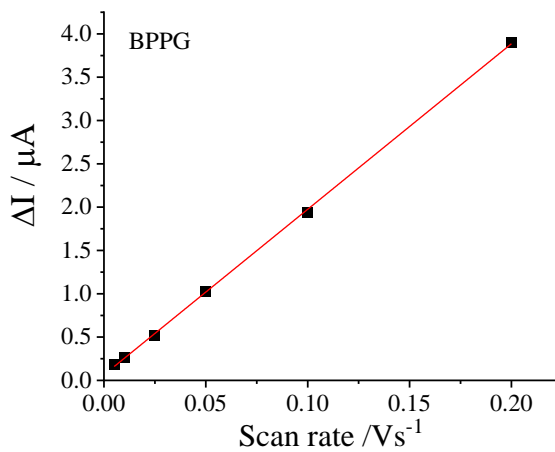
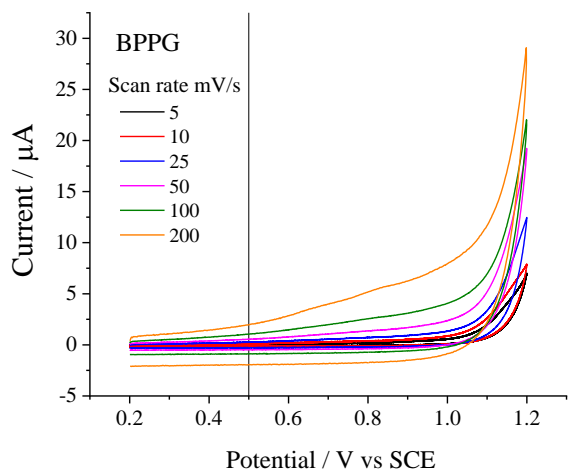
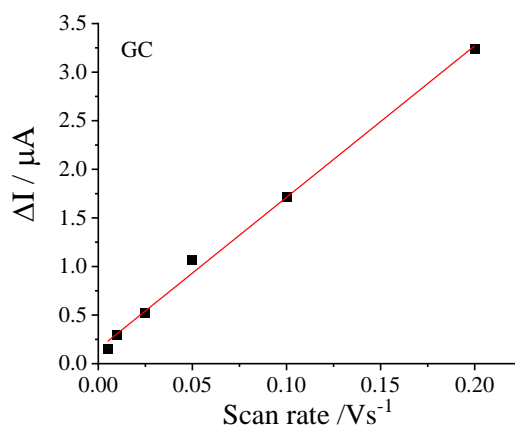
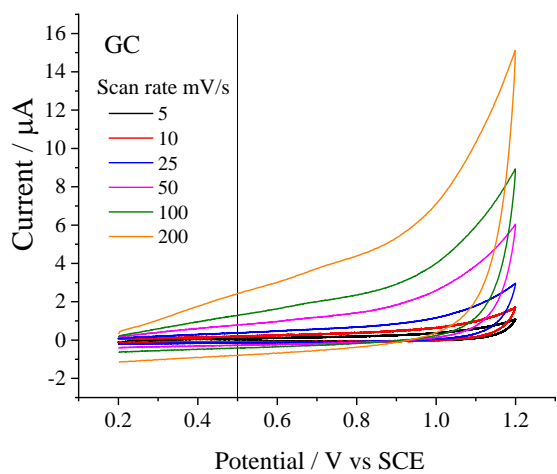


Figure S9. Representative chronoamperometric profile of 0.1 M FIP in a mixture of 60% pH 8 B-R buffer solution and 40% methanol without the addition of MWCNT suspension at 1.6 V vs. SCE.

## Section 7 Capacitance Measurements



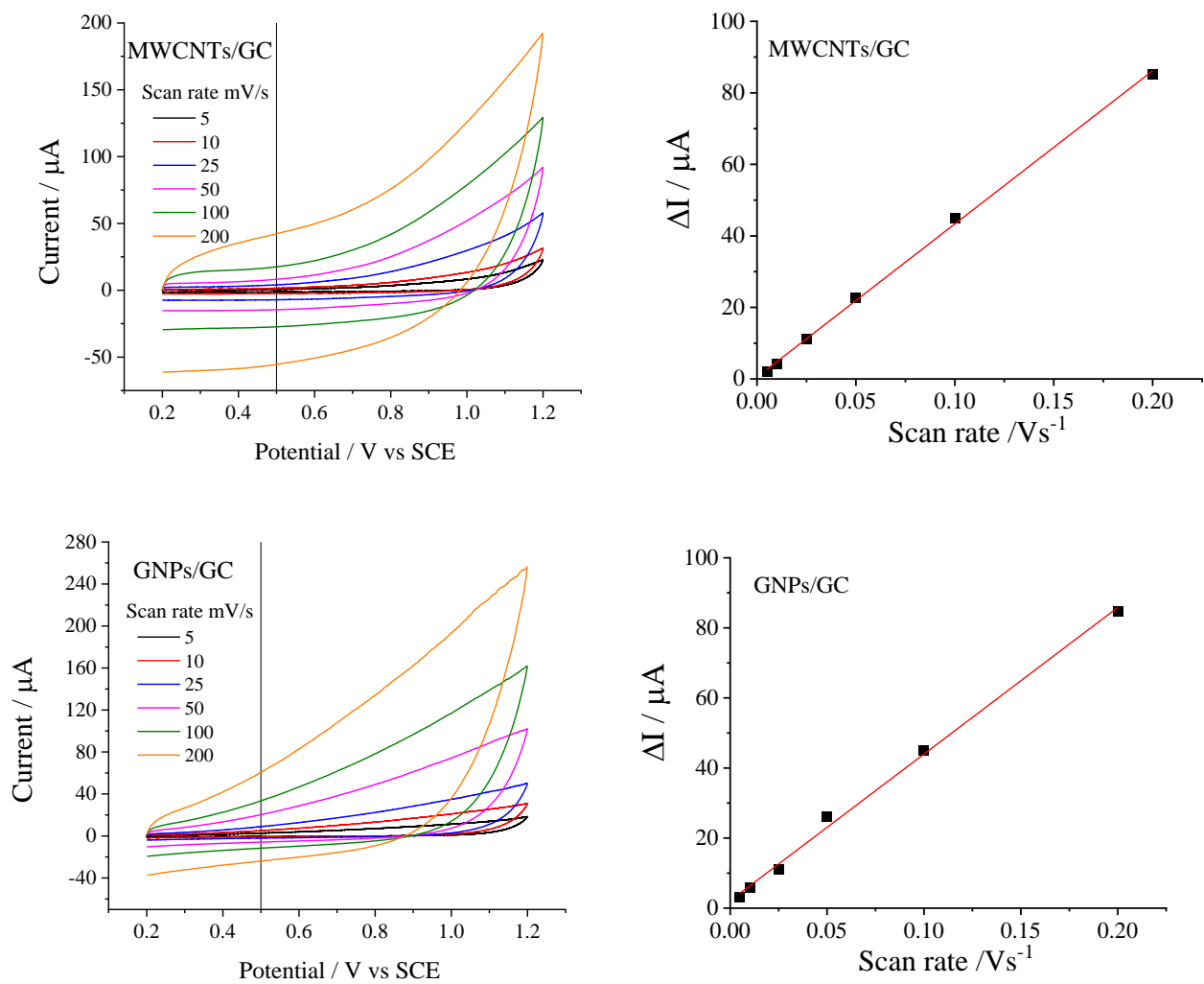


Figure S10. Cyclic voltammograms of the mixture of 60% pH 8.0 B-R buffer and 40% methanol blank solution recorded at varying scan rates at the studied electrode surfaces and the corresponding plots of the difference between the forward and backward current measured at 0.5 V vs SCE as a function of scan rate.

## Section 8 Capacitance Currents at MWCNTs and GNPs modified GC Electrodes

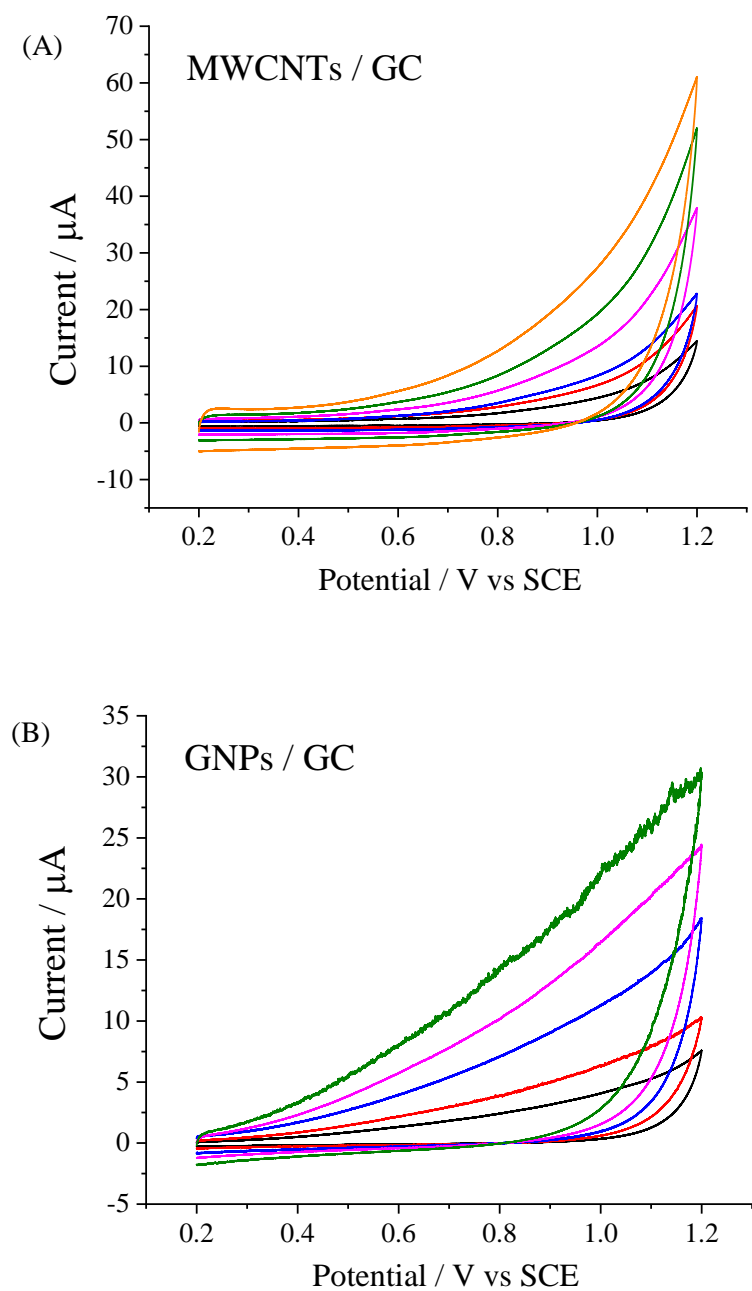


Figure S11. The background-subtracted adsorptive stripping voltammetric responses of the blank solution at (A) 5, 7.5, 10, 15, 20 and 30  $\mu\text{g}$  MWCNTs modified GC and (B) 2.5, 5, 10, 15 and 20  $\mu\text{g}$  GNPs modified GC electrode.

## Section 8 Adsorptive Square Wave and Adsorptive Semi-circular Voltammograms

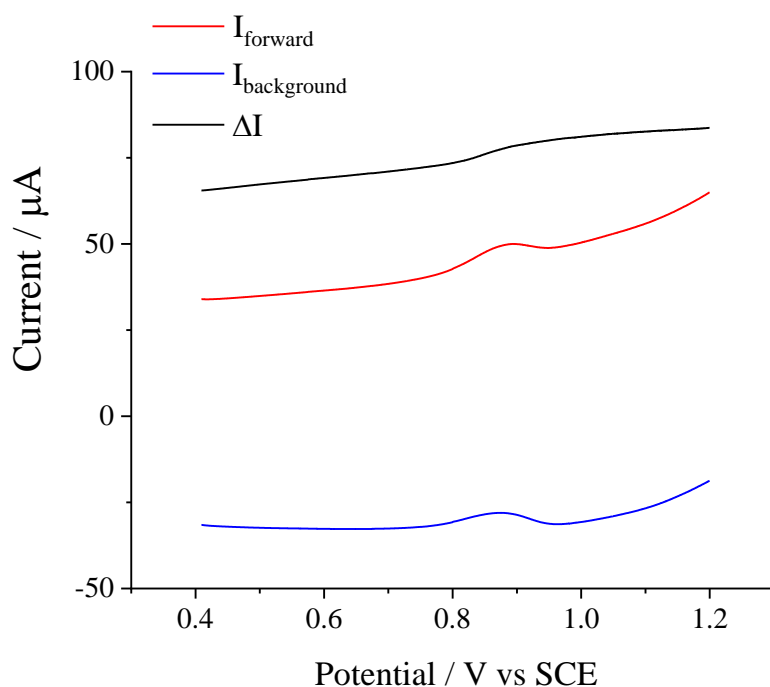


Figure 12. The adsorptive square wave voltammetric response of 0.1 mM FIP at the MWCNTs modified GC electrode in a mixture of 40% methanol and 60% PH 8 B-R buffer. The voltammograms were recorded after a 2-minute open circuit accumulation. The frequency was 10 Hz, the step potential was 0.5 mV, the amplitude was 50 mV and the scan rate was 5 mVs<sup>-1</sup>.

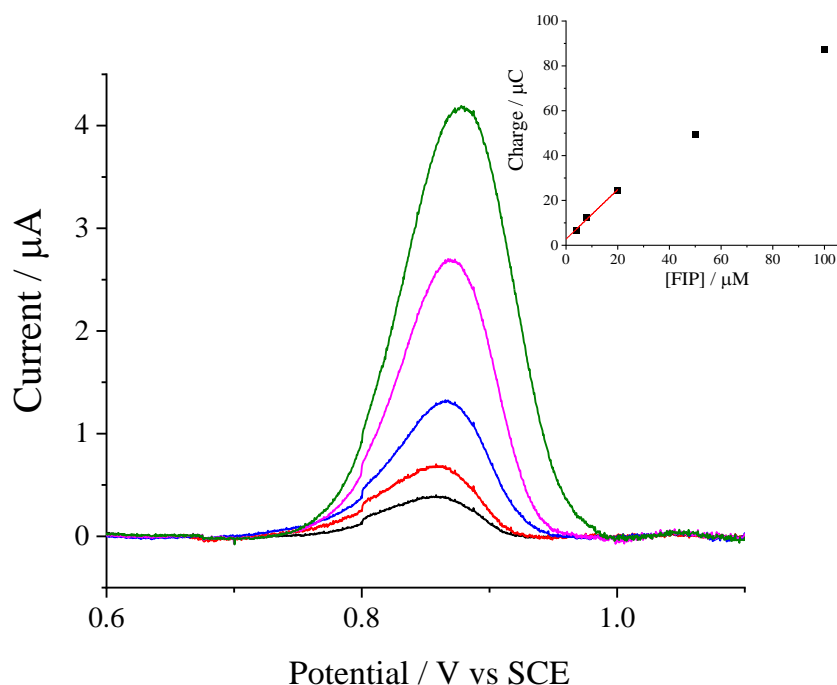


Figure 13. The forward scans of adsorptive square wave voltammograms of varying concentrations of FIP recorded after a 2-minute open circuit accumulation at the MWCNTs modified electrode. Inset; the plots of charge obtained from the voltammograms versus concentration.

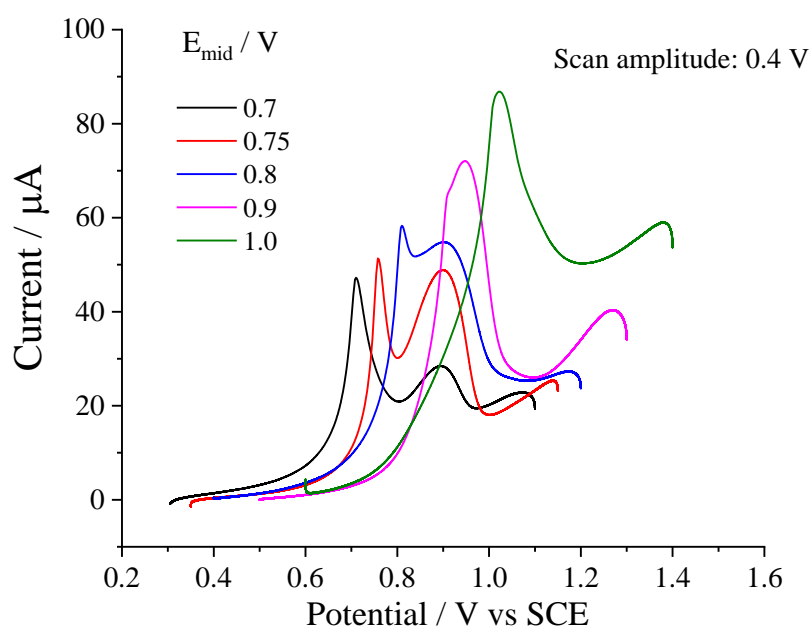


Figure 14. The adsorptive semi-circular sweep voltammetric responses of 0.1 mM FIP at the MWCNTs modified GC electrode using varying potential window with  $E_{mid}$  of 0.7-1.0 V vs SCE. The voltammograms were recorded after a 2-minute open circuit accumulation. The scan amplitude was 0.4 V and the average scan rate was 5 mV/s.

## References

- [1] a) M. Li, P. Li, L. Wang, M. Feng, L. Han, *J. Agric. Food Chem.* **2015**, *63*, 4435-4443; b) R. H. O. Montes, R. M. Dornellas, L. A. J. Silva, A. L. Squissato, E. M. Richter, R. A. A. Munoz, *J. Solid State Electrochem.* **2016**, *20*, 2453-2459.
- [2] T. W. B. Lo, L. Aldous, R. G. Compton, *Sensors Actuators B: Chem.* **2012**, *162*, 361-368.
- [3] J. Poon, C. Batchelor-McAuley, K. Tschulik, R. G. Compton, *Chem. Sci.* **2015**, *6*, 2869-2876.
- [4] E. Inc., Entegris Inc., Billerica, MA, **2013**.