Electronic Supplementary Material (ESI) for Analytical Methods.
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Sensitive determination of 4,6-Dinitro-o-cresol based on Glassy Carbon Electrode modified with Zr-UiO-66 metal-organic framework entrapped FMWCNT

Ranjit Hazarika [a], Gullit Deffo [a, b], Honore Nogholesso Wamba [b, c], Nayab Hussain [a], Shyamali Kalita [a], Mwina Basumatary [a], Evangéline Njanja [b], Soumen Dasgupta [c], Panchanan Puzari [a] *.

[a] *Department of Chemical Sciences, Tezpur University, Tezpur, Assam 784028, India.*

[b]*Electrochemistry and Chemistry of Materials, Department of Chemistry, Faculty of Science, University of Dschang, P.O. Box 67, Dschang, Cameroon.*

[c]*CSIR-Indian Institute of Petroleum, Dehradun, 248005, Uttarakhand, India.*

* Corresponding author. *E-mail address:* pancha@tezu.ernet.in (P. Puzari)

Supporting information

SI-1: BET analysis of Zr-UiO-66and EDX analysis.

Brunauer-Emmett-Teller (BET) characterization shown in Figure SI-1 has been used to determine the geometric surface area of synthesized MOF which is 927 m^2/g, the Langmuir surface is 1365 m^2/g, and the micropore volume is 0.24 cm^3/g.

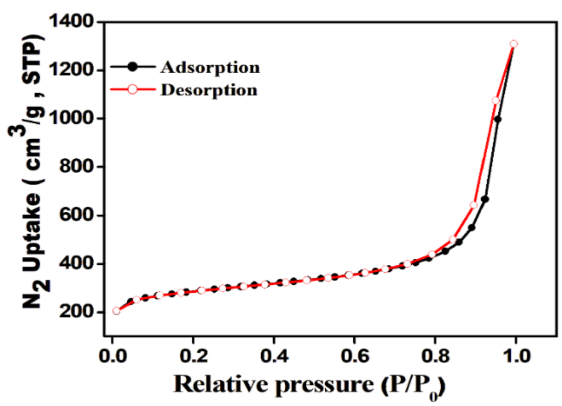


Figure SI-1. Nitrogen isotherms of Zr-UiO-66

EDX analysis

Table SI-1 EDX of Zr-UiO-66, MWCNT, FMWCNT, and Zr-UiO-66/FMWCNT

Film	% C	% N	% O	% Zr	% Cl
Zr-UiO-66	34.36	17.53	5.63	7.07	36.62
MWCNT	94.18	/	5.60	/	0.12
FMWCNT	89.15	/	10.69	/	0.07
Zr-UiO-66/FMWCNT	50.76	/	6.24	4.65	/

SI-2 Determination of Active Surfaces

Figure SI-2A, B show the cyclic voltammograms of 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl, pH 5 recorded at different scan rates from 50 to 300 mV/s on bare GCE (A) and Zr-UiO-66/FMWCNT/GCE (B). The plotting of the peak current against the square root of the scan rate for GCE (Figure SI-2C) and Zr-UiO-66/FMWCNT/GCE (Figure SI-2D), was used to determine the real surface. The real surface of electrodes was calculated using the Randles Sevick equation ($Ipc = K n^{3/2} A D^{1/2} C V^{1/2}$), with the constant $K = 2.09 \times 10^5$, the number of electrons exchanged n = 1, the concentration of the analyte C = 5 mM, the real surface (cm^2) A, the scan rate v, the diffusion coefficient $D = 7.6 \times 10^{-6}\ cm^2\ s^{-1}$ [1]. From the Randles Sevick equation, the active surface area obtained with bare GCE is 0.004 cm^2 whereas for Zr-UiO-66/FMWCNT/GCE is 0.009 cm^2, showing that the active surface of the modified electrode is 2.25 times higher than the one of bare GCE.

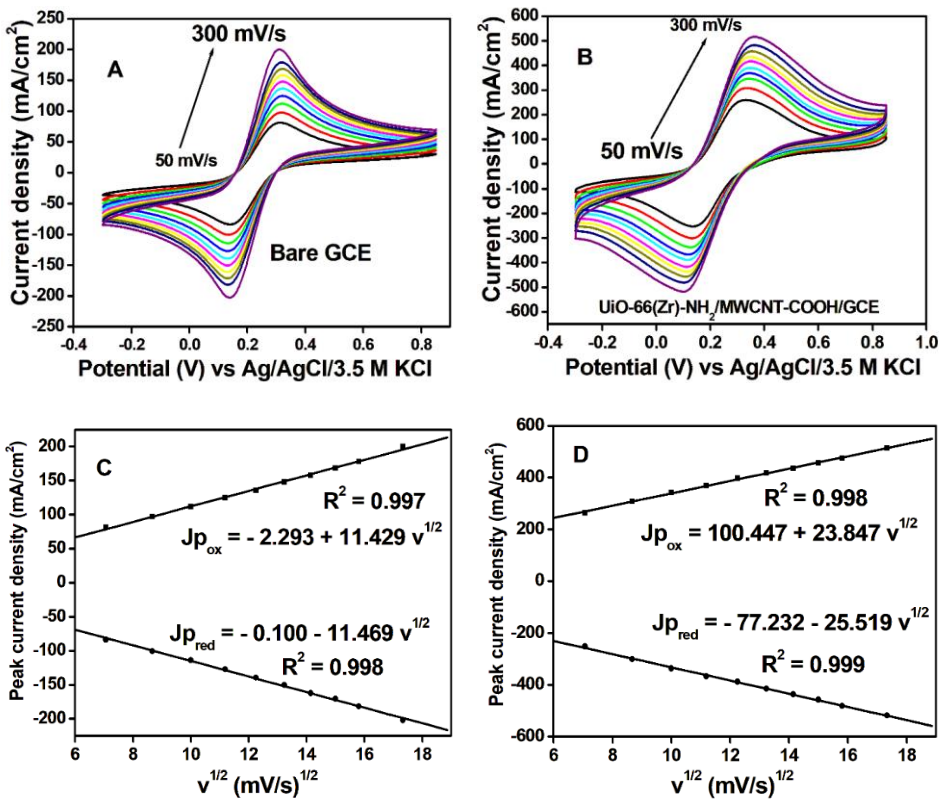


Figure SI-2. Multisweep cyclic voltammograms (A and B) and the corresponding peak current versus the root square of the scan rate (C and D) respectively for bare GCE and Zr-UiO-66/FMWCNT/GCE recorded in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{3-/4-}$ at pH 5. The scan rate was 50; 75; 100; 125; 150; 175; 200; 225; 250 and 300 mV s^{-1}.

SI-3: Determination of heterogeneous rate constant of the various electrode modifications using EIS with 5 Mm $[Fe(CN)_6]^{3-/4-}$.

The apparent heterogeneous rate constant k_{app} and the real heterogeneous rate constants k_0 were calculated by using equation (1) and (2).[2-4]

$$k_{app} = \frac{RT}{F^2C}\frac{1}{R_{CT}} \quad cms^{-1} \qquad (1)$$

$$k_0 = \frac{RT}{n^2F^2CA}\frac{1}{R_{CT}} cms^{-1} \qquad (2)$$

Electrode	R_{CT} Ohm	$k_{app} = \frac{RT}{F^2C}\frac{1}{R_{CT}} \quad cms^{-1}$	$k_0 = \frac{RT}{n^2F^2CA}\frac{1}{R_{CT}} cms^{-1}$
GC	316.40	1.7 X 10-4	0.0425
MOF-GC	280.20	1.9X 10-4	0.0502
FMWCNT-GC	146.80	3.7 X 10-4	0.0591
FMWCNT-MOF-GC	95.24	5.7X 10-4	0.0753

With R= 8.314 JK-1mol^{-1}; T= 305K; F= 96485 Cmol^{-1}; and C= 0.005 molL-1

$$\frac{RT}{F^2C} = 5.447x\ 10^{-5}$$

$$k_{app} = (5.447x10^{-5})\frac{1}{R_{CT}} \text{ x } 10^3 \text{ cm s}^{-1}$$

k_0 values obtained by plotting R_{CT} vs 1/C.

SI-4: Influence of buffer and the ratio of the composite material

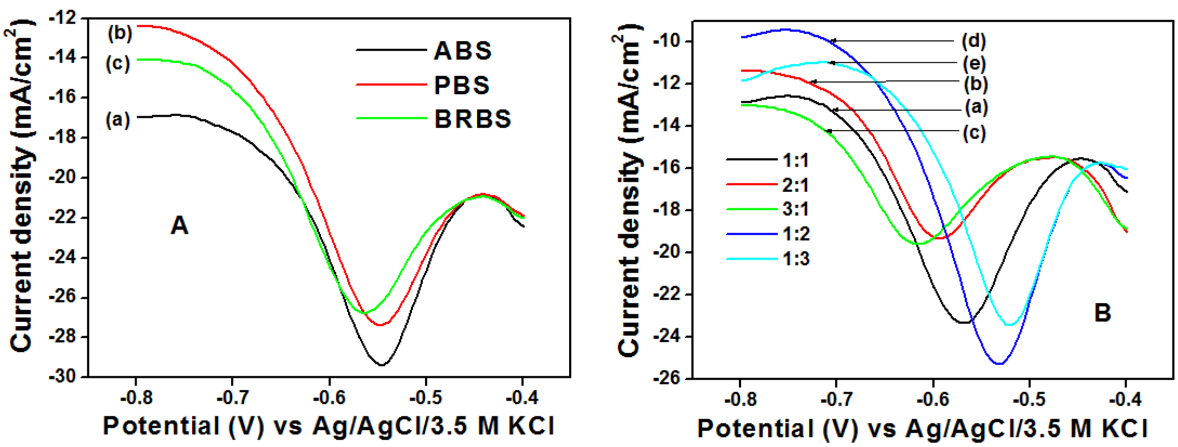


Figure SI-4. DPV curve of 50 µM DNOC measured on (A) Zr-UiO-66/FMWCNT/GCE in media (a) acetate buffer, (b) phosphate buffer, and (c) Britton Robinson buffer at pH 5, (B) GCE modified by Zr-UiO-66 and FMWCNT/GCE in the following ratios. (a) 1.1, (b) 2.1, (c) 3.1, (d) 1.2, and (e) 1.3.

SI 5: Sensitivity

Sensitivity = slope of the calibration curve

=1.249 mA/μM

=1249 mA/mM.

SI-6: Repeatability, Reproducibility and Storage stability

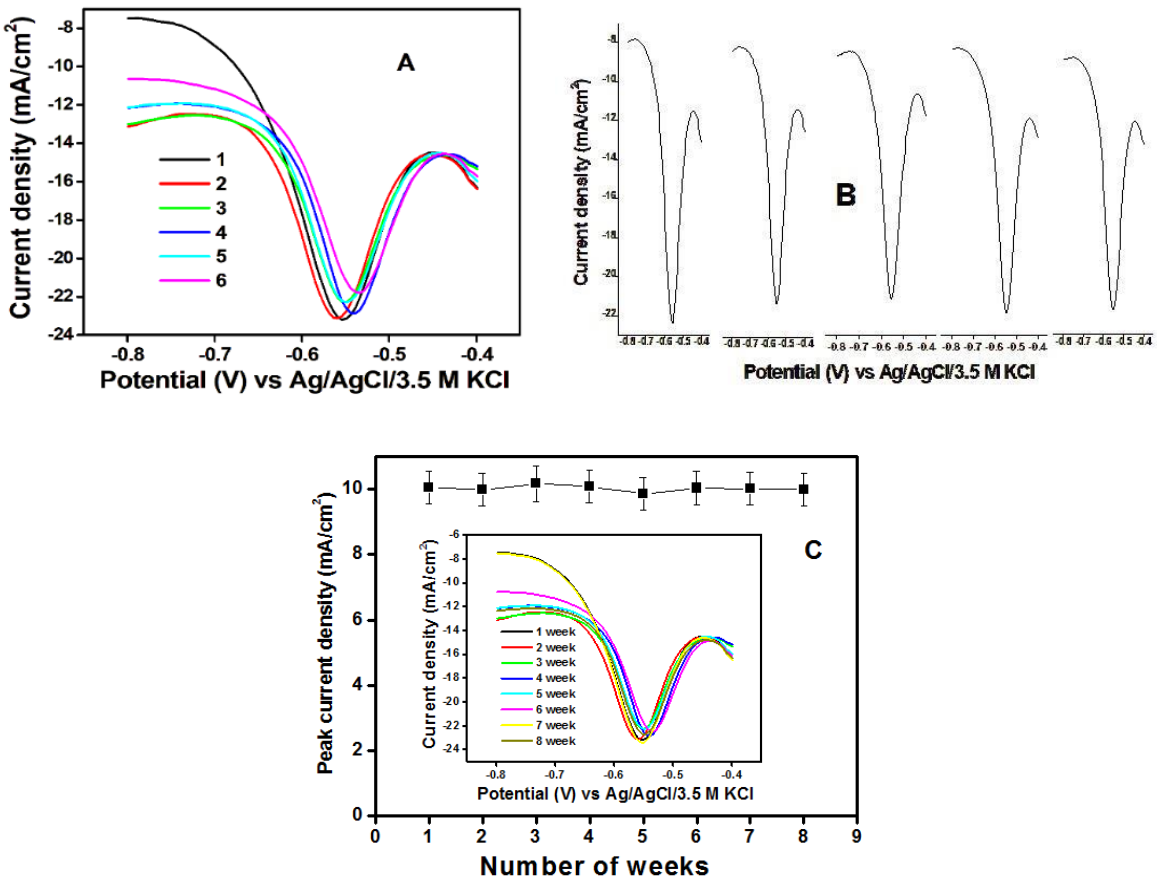
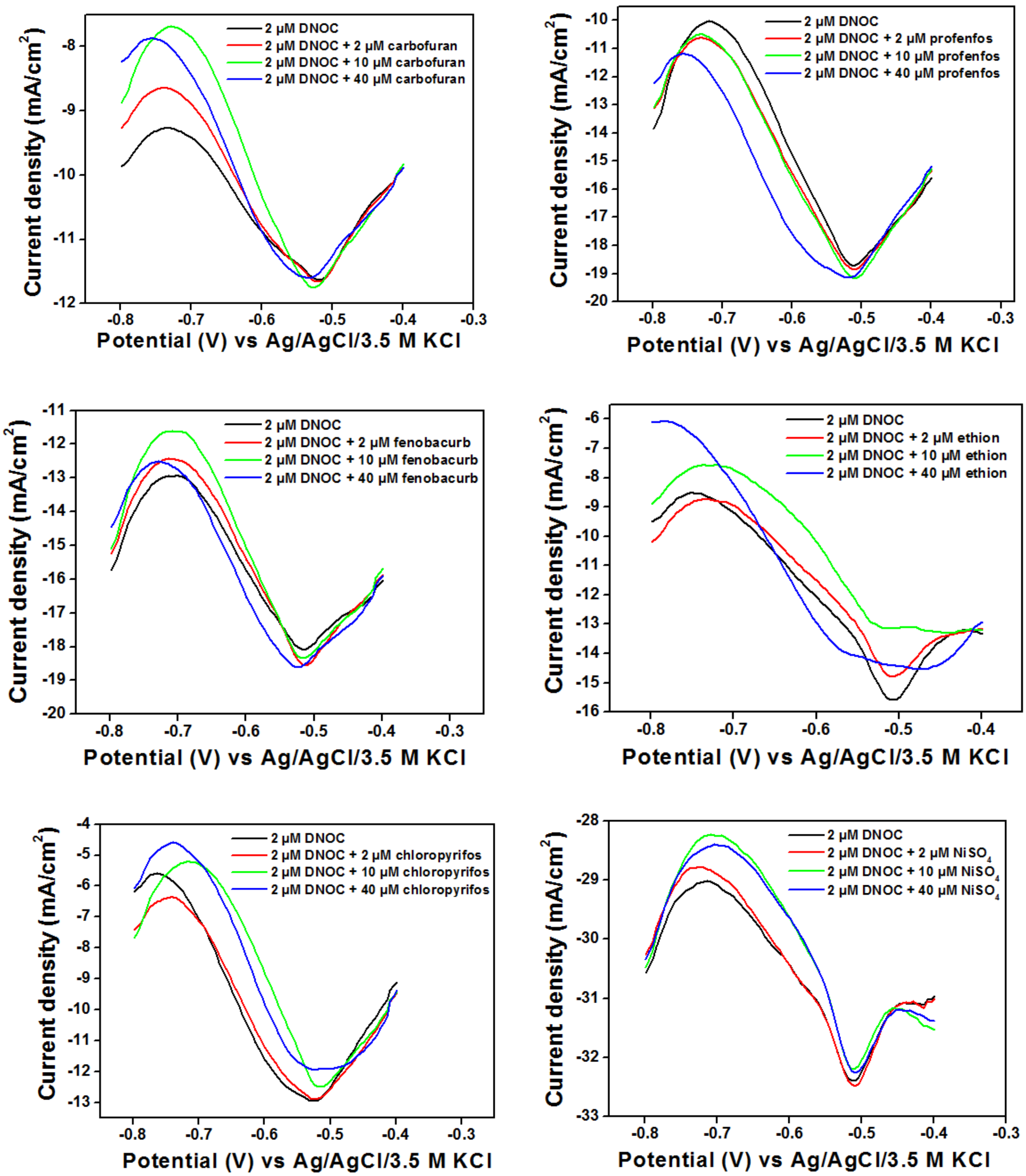


Figure SI-6. DPV curve of 50 μM DNOC in ABS (0.1 M, pH 5) for repeatability (A), reproducibility (B), and stability (C) recorded with Zr-UiO-66/MWCNT-COOH/GCE.

SI-7. Interferences study



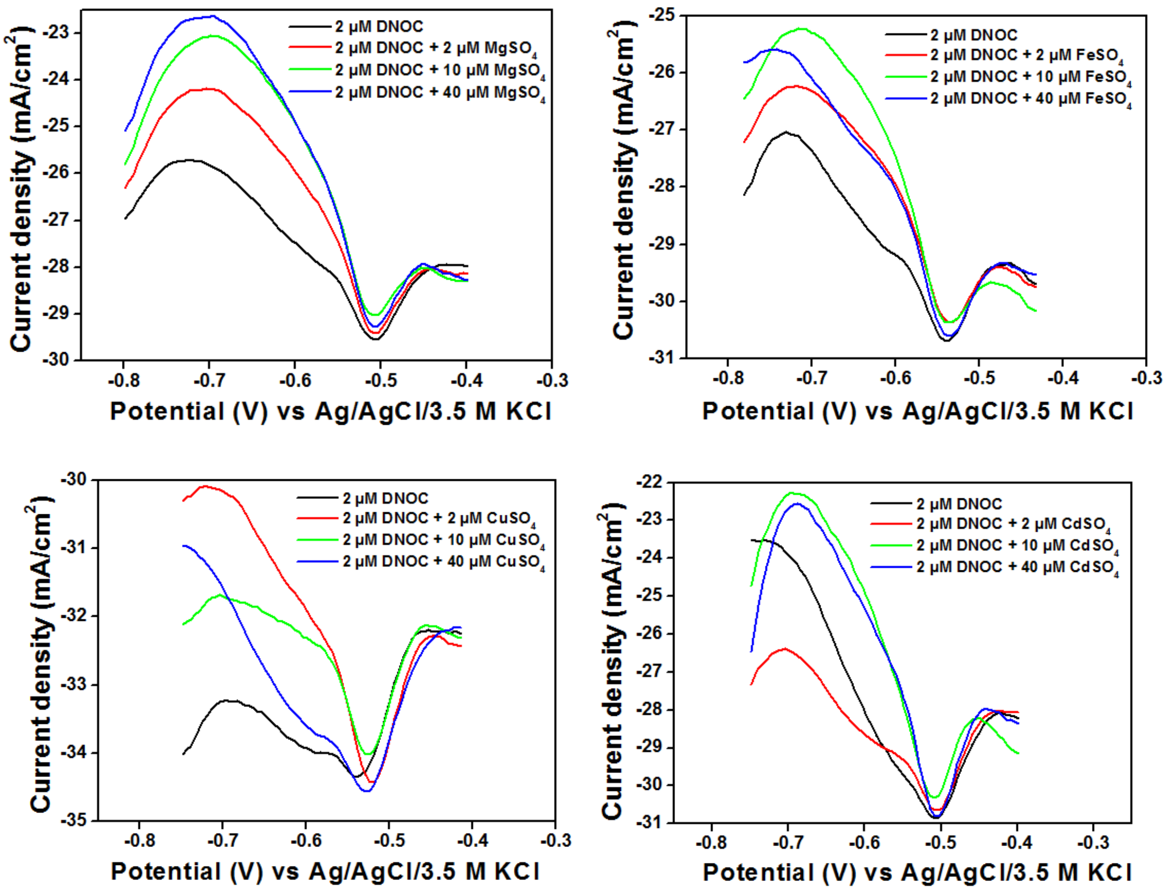


Figure SI-7. DPV curves of 2 µM DNOC in ABS pH 5 recorded on Zr-UiO-66/MWCNT-COOH/GCE in the presence of a different concentration of interferences.

Table SI-2. Comparison of interfering effects of different pesticides.

Interference species	Added amount of interference(µM) over DNOC concentration of 2 µM	Recovery (%)
Carbofuran	2	98.18
	10	95.9
	40	99.94
Profenofos	2	97.98
	10	95.93
	40	96.56
Fenobacurb	2	104.41
	10	106.43
	40	107.44
Ethion	2	67.04
	10	15.29
	40	No peak found
Chloropyrifos	2	100.29

	10	92
	40	81.48
Nickel Sulphate	2	102.75
	10	96.33
	40	96.10
Magnesium Sulphate	2	95.95
	10	92.24
	40	91.07
Iron Sulphate	2	97.71
	10	97.63
	40	89.91
Copper Sulphate	2	100.61
	10	103.43
	40	103.46
Cadmium Sulphate	2	96.06
	10	101.62
	40	92.12

SI-8. Real medium study and validation of the methods

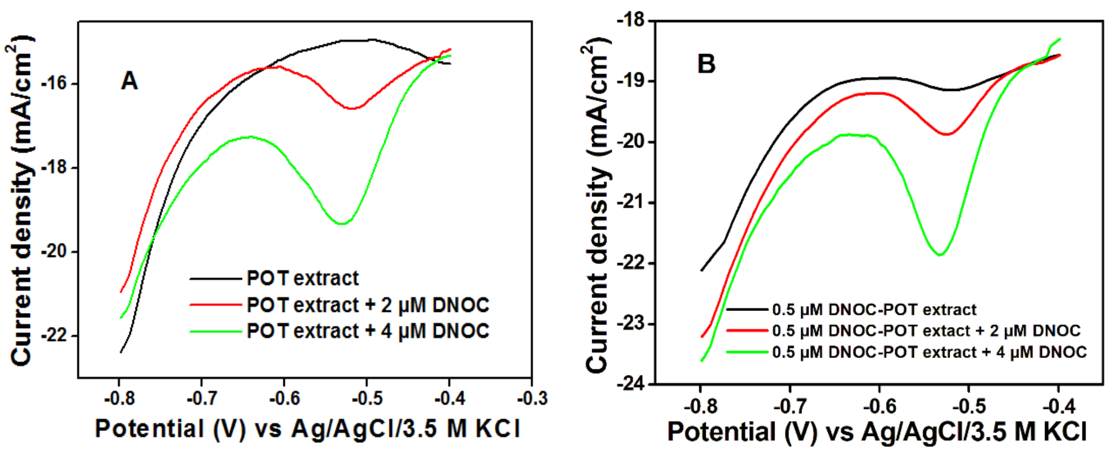


Figure SI-8. DPV curves were obtained from pure potato extract with single step spiking (A) and multiple spiking (B).

References

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