

Supporting Information

# Do carbon nanotubes catalyse bromine/bromide redox chemistry?

Archana Kaliyaraj Selva Kumar, Ruiyang Miao, Danlei Li, Richard G Compton\*

*Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*

## Contents

**Section 1** Experimental

**Section 2** Calculations of Transfer Coefficients from Tafel Analyses

**Section 3** Calculations of Diffusion Coefficients

**Section 4** Characterising Mass Transport at MWCNTs Modified Electrodes

**Section 5** Chronoamperograms in the absence of MWCNTs

**Section 6** Mass transport corrected Tafel analyses for impact voltammogram

**Section 7** Calculation of MWCNT length distributions

**Section 8** DIGSIM simulation of BOR and BRR

**Section 9:** Calculation for predicting the number of monolayers of MWCNTs drop casted at GC electrode

**Section 10:** Chronoamperograms in 0.1 M HNO<sub>3</sub> and 100 µg of MWCNTs

**Section 11:** Chronoamperograms observed at different potentials for BOR and BRR

\* Corresponding author.

E-mail: [richard.compton@chem.ox.ac.uk](mailto:richard.compton@chem.ox.ac.uk) (Richard Compton)

## Section 1: Experimental

### Materials

All materials were purchased commercially and used without any further purification. These were sodium bromide (NaBr, 99.0%, Sigma Aldrich, USA), Bamboo like multi-walled carbon nanotubes, MWCNTs, Nano Lab, diameter  $30 \pm 10$  nm, length of 5 - 20  $\mu\text{m}$ , Laboratory grade acetone (Merck, UK), bromine (Merck, UK) bromine water (HACH, UK) and nitric acid ( $\text{HNO}_3$ , 70.0%, Fisher Scientific, UK). All the solutions were prepared using Millipore water with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  at 298 K.

### A) Cyclic voltammetry studies

The cyclic voltammetry studies were conducted using a  $\mu\text{Autolab II}$  potentiostat (Metrohm-Autolab BV, Netherlands), using a three-electrode configuration comprising a working electrode, a saturated calomel reference electrode (SCE) and a graphite rod counter electrode in a Faraday cage at 298 K. The voltammetry was controlled through GPES software.

#### i) Pristine GC working electrode

Electro-oxidation of bromide (BOR) and reduction of bromine (BRR) were conducted in solutions of either  $5.00 \pm 0.05$  mM NaBr in 0.10 M  $\text{HNO}_3$  or  $5.00 \pm 0.06$  mM bromine in 0.10 M  $\text{HNO}_3$ . A pristine glassy carbon (GC) electrode of diameter 0.30 cm and area  $0.07 \text{ cm}^2$  was used as the working electrode after thorough cleaning using alumina powder (Buehler, Micropolish II) of sizes 1  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$  in an descending order on lapping pads. The electrode was further sonicated (Fisher Scientific FB15050 ultrasonic) in ultrapure water for 10 s to remove any residual alumina powder. The electrode was then dried under  $\text{N}_2$  before experiments.

#### ii) MWCNTs modified GC working electrode

1 mg of MWCNTs in 1 mL of acetone was dispersed by sonicating it for 10 mins. 30  $\mu\text{L}$  (30  $\mu\text{g}$  of MWCNTs) from the dispersed solution was dropcasted on a clean pristine GC and dried under constant  $\text{N}_2$  flow. Voltammetry was then conducted to study both BOR and BRR at the MWCNTs dropcasted GC.

### B) MWCNTs impact experiments at carbon micro wire electrodes – Chronoamperometry studies

A carbon micro wire electrode (diameter 7  $\mu\text{m}$ , length 1 mm from Goodfellow, Cambridge Ltd.) was used as the working electrode in a three-electrode cell as above. The electrode fabrication is reported in the literature.<sup>1</sup> In brief, the carbon wire is attached to a conducting wire using a silver epoxy adhesive. After drying the wire was adhered into a plastic pipette such that the carbon fibre is protuded out of the tip. The pipette tip was then sealed using cyanoacrylate adhesive, dried and used for experiments. For both BOR and BRR, the dispersed MWCNTs solution was obtained by adding 1 mg of MWCNTs in 1 mL of ultrapure water and then sonicated for 15 mins. In a chronoamperometry experiment, 50  $\mu\text{L}$  each of the dispersed MWCNTs solution was added to  $5.00 \pm 0.05$  mM of NaBr in 0.10 M  $\text{HNO}_3$  for observing impacts corresponding to BOR and  $5.00 \pm 0.06$  mM of bromine in 0.10 M  $\text{HNO}_3$  to observe impacts for BRR ( $1.10 \times 10^{-15}$  M of dispersed MWCNTs). The experiments were controlled using NOVA software in a Faraday cage at 298 K.

## Section 2: Calculations of Transfer coefficients from Tafel Analyses

This section elaborates on the use of Tafel analysis for obtaining the transfer coefficients  $\beta$  and  $\alpha$  for the BOR and BRR respectively. The transfer coefficients  $\beta$  and  $\alpha$  can be calculated from the following expressions 1 and 2.<sup>2</sup>

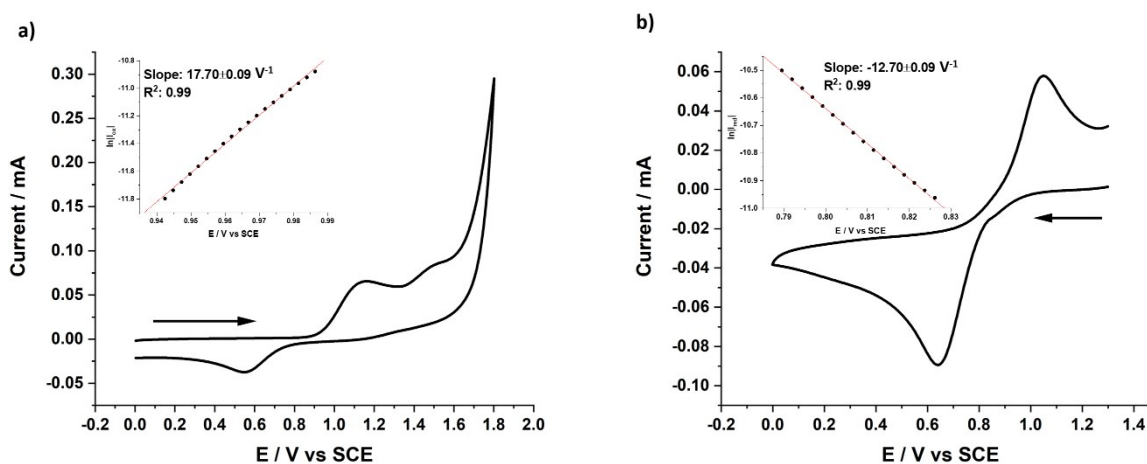
$$\beta = \frac{RT}{F} \frac{\partial \ln |I_{ox}|}{\partial E} \quad (1)$$

$$\alpha = \frac{RT}{F} \frac{\partial \ln |I_{red}|}{\partial E} \quad (2)$$

where  $I_{ox}$  is the oxidative current,  $I_{red}$  is the reductive current.

Considering the BOR at pristine GC in 5.00 ( $\pm$  0.05) mM NaBr supported by 0.10 M a Tafel slope of 17.70 ( $\pm$  0.09)  $V^{-1}$  was obtained from a plot of  $\ln |I_{ox}|$  vs potential (E vs SCE), shown in the inlay of Figure S1a, inferred from the voltammetric response recorded at 0.05  $Vs^{-1}$  (Figure S1a). Further,  $\beta$  was calculated to be 0.45 ( $\pm$  0.01) for BOR.

Similarly, the Tafel slope and  $\alpha$  for BRR were found to be -12.70 ( $\pm$  0.09)  $V^{-1}$  and 0.33 ( $\pm$  0.01) respectively. The voltammetry for BRR at pristine GC in 5.00 ( $\pm$  0.06) mM bromine supported by 0.10 M  $HNO_3$  at 0.05  $V s^{-1}$  is given in Figure S1b, the inset shows the Tafel analyses. In both the cases a current range of 10% - 30% of the peak current was used for analysis to avoid the influence of mass



transport.<sup>3</sup>

**Figure S1.** Cyclic voltammogram at pristine GC electrode a) for BOR in 5.00 ( $\pm$  0.05) mM NaBr in 0.10 M  $HNO_3$  at a scan rate of 0.05  $Vs^{-1}$ ; Inset shows the Tafel plot with a slope of 17.70 ( $\pm$  0.09)  $V^{-1}$  giving  $\beta$  of 0.45 ( $\pm$  0.01), b) for BRR 5.00 ( $\pm$  0.06) mM Bromine in 0.10 M  $HNO_3$  at a scan rate of 0.05  $V s^{-1}$ ; Inset shows Tafel plot with a slope of -12.70 ( $\pm$  0.09)  $V^{-1}$  giving  $\alpha$  of 0.33 ( $\pm$  0.01). In both the cases 10% - 30% of the current range of the forward wave was used.

### Section 3: Calculation of Diffusion Coefficients

This section explains the calculation of the diffusion coefficients,  $D$ , for  $\text{Br}^-$  and  $\text{Br}_2$  from the voltammograms obtained as a function of scan rate for BOR and BRR respectively.

The Randles–Ševčík equation for an irreversible electrode reaction under conditions of semi-infinite diffusion was used to calculate the  $D$  for  $\text{Br}^-$  and  $\text{Br}_2$  and is given below in the equations 3 and 4 which assume that the first electron transfer is rate determining<sup>2</sup>;

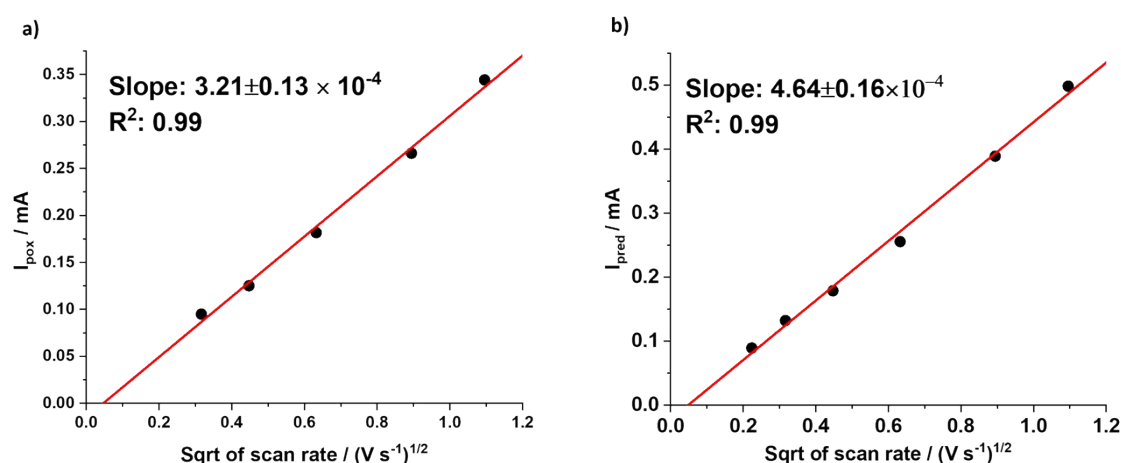
$$I_{\text{pox}} = 2.99 \times 10^5 n \sqrt{\beta} [C]_{\text{bulk}} D^{1/2} A v^{1/2}; n = 1 \quad (3)$$

$$I_{\text{pred}} = 2.99 \times 10^5 n \sqrt{\alpha} [C]_{\text{bulk}} D^{1/2} A v^{1/2}; n = 2 \quad (4)$$

where  $I_{\text{pox}}$  is the oxidative peak current,  $I_{\text{pred}}$  is the reductive peak current,  $n$  is the total number of electrons transferred,  $\beta/\alpha$  are the transfer coefficients calculated from the Tafel analyses discussed in the previous section,  $A$  is the area of the pristine GC electrode ( $7.07 \times 10^{-2} \text{ cm}^2$ ).  $[C]_{\text{bulk}}$  is the bulk concentration of the analyte. For the BOR and BRR  $5.00 (\pm 0.05) \text{ mM}$  of  $\text{NaBr}$  and  $5.00 (\pm 0.06) \text{ mM}$  bromine water were used respectively and the working electrode was an unmodified Glassy Carbon (pristine GC) electrode.

The peak currents are linearly proportional to the square root of scan rate and are shown in Figure S2. During the BRR two electrons are transferred in subsequent steps and the first electron transferred is considered to be the rate determining step.

The diffusion coefficient  $D_{\text{Br}^-}$  was calculated to be  $2.05 (\pm 0.04) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (literature value  $2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )<sup>4</sup> for BOR where  $n$  is 1 and  $D_{\text{Br}_2}$  was found to be  $1.50 (\pm 0.04) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (literature value  $1.20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )<sup>4</sup> for BRR where  $n$  is 2. The obtained values agree well with the literature values.



**Figure S2.** a) Plot of oxidative peak current ( $I_{\text{pox}}$ ) vs square root of scan rate for  $5.00 (\pm 0.05) \text{ mM}$   $\text{NaBr}$  in  $0.10 \text{ M}$   $\text{HNO}_3$  and  $D_{\text{Br}^-} 2.05 (\pm 0.04) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  b) plot of  $I_{\text{pred}}$  vs square root of scan rate for  $5.00 (\pm 0.06) \text{ mM}$  Bromine in  $0.10 \text{ M}$   $\text{HNO}_3$  and  $D_{\text{Br}_2} 1.50 (\pm 0.04) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

## Section 4: Characterising Mass Transport at CNT Modified Electrodes

MWCNTs on the surface of a GC electrode form a porous layer containing trapped electrolyte. Since the CNTs are conductive allowing electrolysis at their surfaces the diffusion of the trapped species under electrolysis resembles a thin layer cell of large electrode area imitating the surface area of the CNTs. If, on the timescale of the voltammetry  $t$ , the thickness of the solution zones (pores) is small compared to the distance diffused on this timescale,  $(Dt)^{0.5}$ , then the peak current in a voltammetric scan  $I_p$  is directly proportional to  $v$  and is given by equation 5.

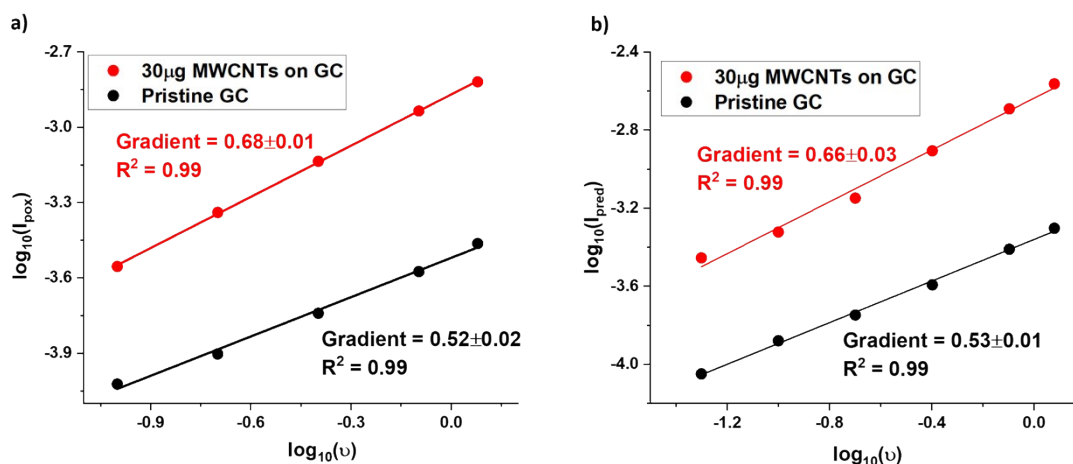
$$I_p = \frac{F^2}{4RT} v C V \quad (5)$$

where  $C$  is the analyte concentration and  $V$  is the volume of solution trapped in the MWCNTs pores.

Equation 5 contrasts with the Randles–Ševčík equation given in equations 3 and 4 in that  $I_p$  in equation 5 the peak current scales directly with scan rate whereas under semi-infinite diffusion it is directly proportional to square root of  $v$ . Since, the peak current ( $I_p$ ) is proportional to scan rate ( $v$ ) to different powers,  $v^N$ , the different regimes of mass transport can be distinguished by means of a log-log plot of peak current versus scan rate with a slope of unity corresponding to thin layer electrolysis and a slope of 0.5 to semi-infinite diffusion. An intermediate value of  $N$  often indicates a mixed regime as is thought to operate for CNT modified electrodes.<sup>5,6</sup>

The comparative plots of  $\log I_p$  vs  $\log v$  for BOR and BRR at a MWCNT modified GC electrode (made using 30  $\mu\text{g}$  of CNTs, corresponding to at least ca. 125 monolayers) and at a pristine GC electrode are shown in Figure S3. For the BOR shown in Figure S3a, a gradient value of 0.68 ( $\pm 0.01$ ) was obtained at the modified GC and 0.52 ( $\pm 0.02$ ) at the pristine GC in a solution of 5.00 ( $\pm 0.05$ ) mM NaBr supported by 0.10 M  $\text{HNO}_3$ .

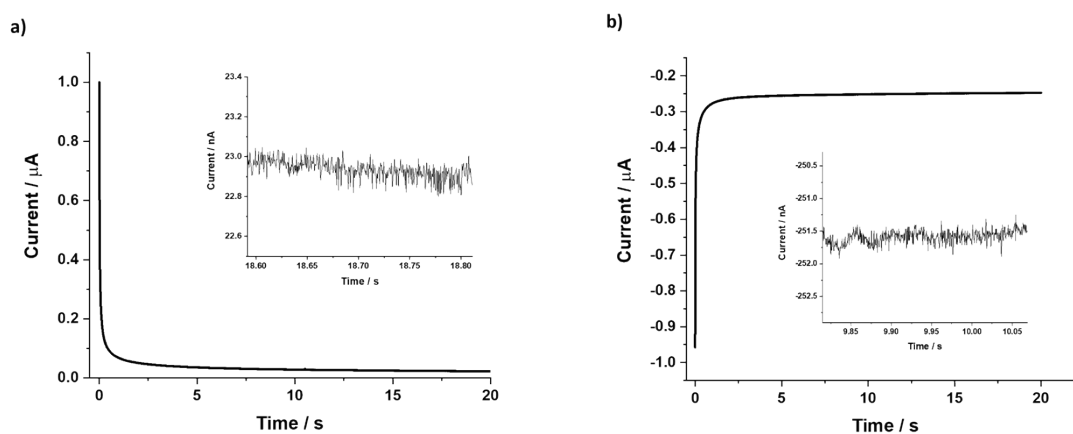
For, BRR (Figure S3b), a gradient value of 0.66 ( $\pm 0.03$ ) was obtained at the MWCNTs modified GC and 0.53 ( $\pm 0.01$ ) at the pristine GC in a solution of 5.00 ( $\pm 0.06$ ) mM bromine supported by 0.10 M  $\text{HNO}_3$ .



**Figure S3.** Plot of  $\log I_p$  vs  $\log v$  a) for BOR at a GC modified with 30  $\mu\text{g}$  of CNTs (red line) with a gradient value of  $0.68 (\pm 0.01)$ ; and at a pristine GC (black line with a gradient value of  $0.52 (\pm 0.02)$ , b) for BRR at the MWCNT modified GC (red line) with a gradient value of  $0.66 (\pm 0.03)$  and at a pristine GC (black line with gradient value of  $0.53 (\pm 0.01)$ ).

## Section 5: Chronoamperograms in the absence of MWCNTs

Chronoamperograms were recorded in the absence of MWCNTs for BOR and BRR at 1.3 V vs SCE and 0.2 V vs SCE respectively. No Faradaic currents were observed.



**Figure S4.** Chronoamperograms in the absence of MWCNTs a) BOR at 1.3 V vs SCE, b) BRR at 0.2 V vs SCE.

## Section 6: Mass transport corrected Tafel analyses for impact voltammogram

The transfer coefficients  $\beta$  and  $\alpha$  were calculated for the BOR and BRR occurring at the MWCNT from the impact – potential plot given in figure 4. Mass transport corrected Tafel analysis was conducted using the following equations<sup>7</sup>,

$$\beta = \frac{RT}{F} \frac{\partial \ln \left| \frac{1}{I_{ox}} - \frac{1}{I_{lim}} \right|}{\partial E} \quad (7)$$

$$\alpha = \frac{RT}{F} \frac{\partial \ln \left| \frac{1}{I_{red}} - \frac{1}{I_{lim}} \right|}{\partial E} \quad (8)$$

where,  $I_{lim}$  is the limiting current.

A Tafel slope of  $-16.32 (\pm 1.50) \text{ V}^{-1}$  was obtained for the BOR giving  $\beta$  equal to  $0.42 (\pm 0.03)$ . For the BRR slope of  $7.10 (\pm 0.34) \text{ V}^{-1}$  was obtained yielding  $\alpha$  of  $0.20 (\pm 0.01)$  (Figure 4a and b inset).

## Section 7: Calculation of MWCNT length distributions

The length of the MWCNTs were calculated from the impact current obtained for both the BOR and the BRR.

For this calculation, the MWCNT is considered to resemble a cylindrical electrode with length  $l$  and radius  $r$ , the current for time  $t$  is given by equation 6.<sup>1</sup>

$$I_p = 2\pi nFDClf(\tau) \quad (6)$$

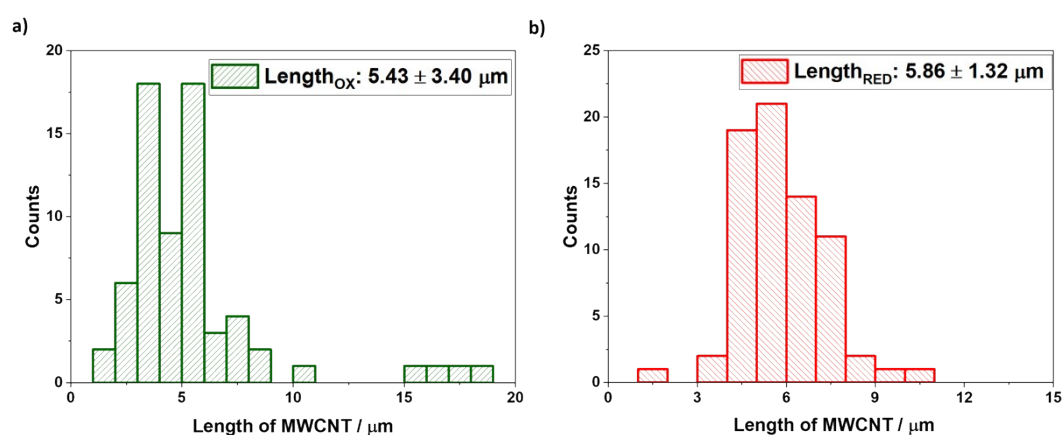
with,

$$f(\tau) = \frac{e^{-\sqrt{\pi\tau}/20}}{\sqrt{\pi\tau}} + \frac{1}{\ln[(2e^{-\gamma\tau})^{1/2} + e^{-5/3}]}$$

$$\tau = \frac{4Dt}{r^2}$$

where  $D$  is the diffusion coefficient (given in Section 3),  $c$  is the analyte concentration,  $n$  is the number of electrons and  $t$  impact duration ( $t = 0.10$  s).

For BOR, the length of the MWCNTs was calculated to be  $5.43 (\pm 3.40) \mu\text{m}$  from the impact currents obtained at 1.3 V and for BRR it was calculated to be  $5.86 (\pm 1.32) \mu\text{m}$  from the impact currents obtained at 0.2 V and is given in Figure S5 a and b respectively.



**Figure S5.** Histogram showing the length of MWCNTs calculated from observed impacts a) for BOR at 1.30 V vs SCE to be  $5.43 (\pm 3.40) \mu\text{m}$ , b) for BRR at 0.20 V vs SCE to be  $5.86 (\pm 1.32) \mu\text{m}$ .

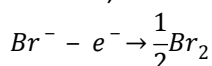


## Section 8: DIGISIM simulation of BOR and BRR

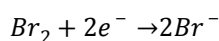
### i) For impacts observed from MWCNTs

The commercial software DIGISIM was used for the simulations.<sup>8,9</sup> Voltammograms were simulated using Butler – Volmer kinetics and a cylindrical electrode geometry. The CNT radius of  $15 \pm 5$  nm was used as provided by the supplier and the length obtained from the impacts were employed (SI, Section 7). The formal potential of 0.82 V vs SCE was obtained from the CV at the pristine GC was used at 298.15 K. The transfer coefficients  $\beta$  and  $\alpha$  of 0.42 and 0.20 were used calculated from the mass transport corrected Tafel analyses of the impacts (SI, Section 6). Diffusion coefficients  $D_{Br^-}$  ( $2.05 \times 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ ) and  $D_{Br_2}$  ( $1.50 \times 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ ) were used as calculated from the CV at pristine GC (SI, Section 3).

For BOR, a one electron transfer process was considered as given below,



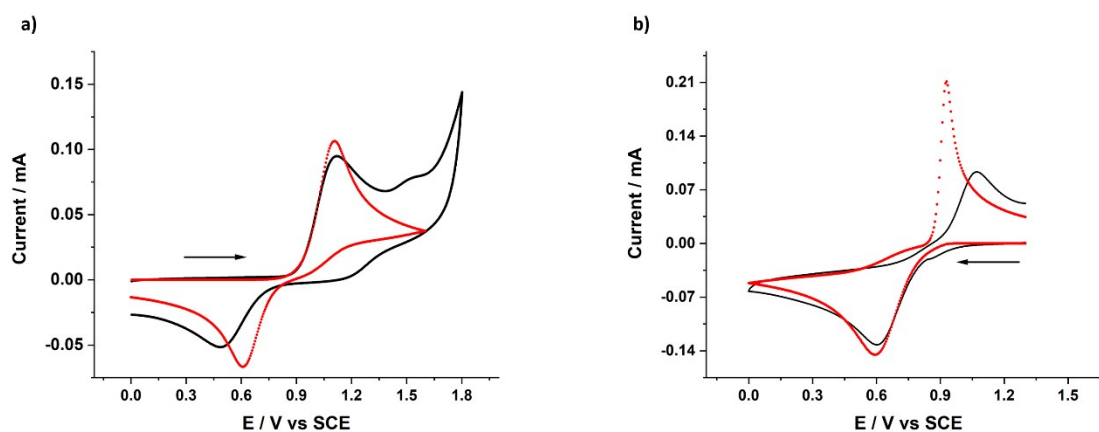
And for BRR the a two electron transfer process was modelled,



The bulk concentrations of both  $Br^-$  and  $Br_2$  were 5 mM with other bulk concentrations set to zero at the beginning of the simulation. With all the parameters fixed, the rate constants for both the BOR and the BRR were optimised to get the best fit for the voltammogram as shown in figure 6. The standard electrochemical rate constants for each process,  $k_{BOR}$  and  $k_{BRR}$  were found to be  $1.0 (\pm 0.1) \times 10^{-3} \text{cm s}^{-1}$  and  $5.0 (\pm 0.1) \times 10^{-4} \text{cm s}^{-1}$  respectively.

### ii) For voltammograms at pristine GC

To simulate the voltammograms at pristine GC the electrode geometry was considered to be planar with area of the electrode to be  $7.07 \times 10^{-2} \text{cm}^2$ . The transfer coefficients  $\beta$  and  $\alpha$  were 0.45 and 0.33 for BOR and BRR respectively as discussed in SI, Section 2. All the other parameters were as used for impact voltammogram. In this way the rate constants at pristine GC for BOR and BRR were calculated to be  $9.5 (\pm 0.1) \times 10^{-5} \text{cm s}^{-1}$  and  $2.0 (\pm 0.1) \times 10^{-5} \text{cm s}^{-1}$  respectively (figure S6) again referenced to the standard potential for the bromide/bromine couple of 0.82 V vs SCE.



**Figure S6.** Overlay of DIGISIM simulated curves (red line) and experimental voltammograms at pristine GC (black line) a) for BOR with the standard electrochemical rate constant ( $k_{BOR}$ )  $9.5 (\pm 0.1) \times 10^{-5} \text{ cm s}^{-1}$ , b) for BRR with standard electrochemical rate constant ( $k_{BRR}$ )  $2.0 (\pm 0.1) \times 10^{-5} \text{ cm s}^{-1}$ .

## Section 9: Calculation for predicting the number of monolayers of MWCNTs drop casted at GC electrode

To estimate the number of monolayers at the glassy carbon (GC) electrode for 30  $\mu\text{g}$  of drop cast we assume a closed pack arrangement of the MWCNTs laid uniformly across the whole GC surface (area of GC electrode is  $7.07 \times 10^{-2} \text{ cm}^2$ ). The diameter of the MWCNTs is 30 nm, length is 6 – 20  $\mu\text{m}$  and density is  $1.4 \text{ g cm}^{-3}$  (these values were sourced from the manufacturer).

Volume of single MWCNT (cylindrical geometry);

$$Volume = \pi r^2 l$$

Where  $r$  is the radius of the MWCNT and  $l$  is the length of the MWCNT. Hence volume of single MWCNT is calculated to be  $4.24 \times 10^{-15} \text{ cm}^3$ .

To find out the mass of single MWCNTs

$$Mass = Density \times Volume \text{ of single MWCNT}$$

Thus, the mass of single MWCNT is  $5.94 \times 10^{-15} \text{ g}$ .

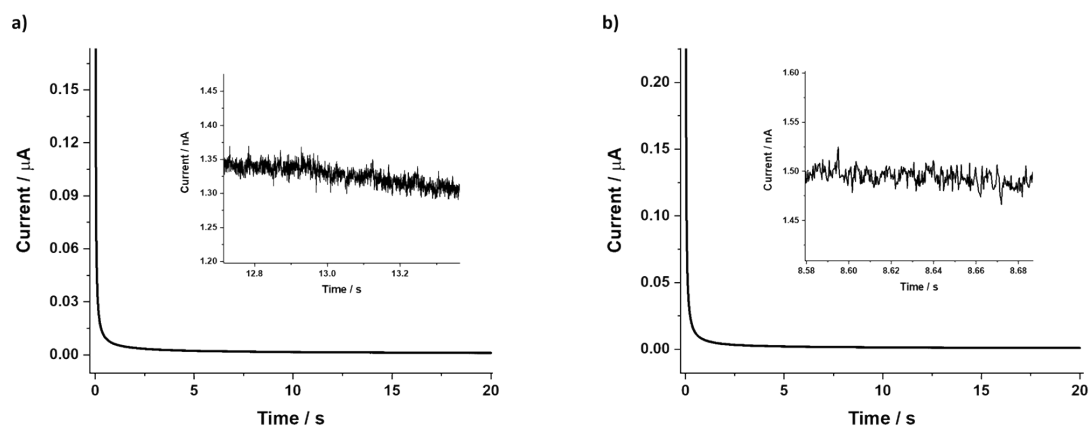
1 mg of MWCNTs was dispersed in 1 mL of acetone for the drop cast experiment, hence 30  $\mu\text{L}$  of drop cast will contain  $3.00 \times 10^{-5} \text{ g}$  of MWCNTs. Therefore, number of MWCNTs present in 30  $\mu\text{L}$  drop cast is found to be  $5.00 \times 10^9$ .

Assuming the MWCNTs contact at the GC surface to be rectangular when arranged in a closed pack manner, the area covered by unit MWCNT is  $1.80 \times 10^{-9} \text{ cm}^2$ . Hence, area covered by  $5.00 \times 10^9$  MWCNTs is  $9.09 \text{ cm}^2$ . Now that we know the total area of both GC electrode and that of MWCNTs number of layers can be calculated as follows;

$$\text{No. of monolayers of MWCNTs for } 30 \mu\text{L drop cast} = \frac{\text{Total area covered by MWCNTs}}{\text{Total surface area of GC electrode}}$$

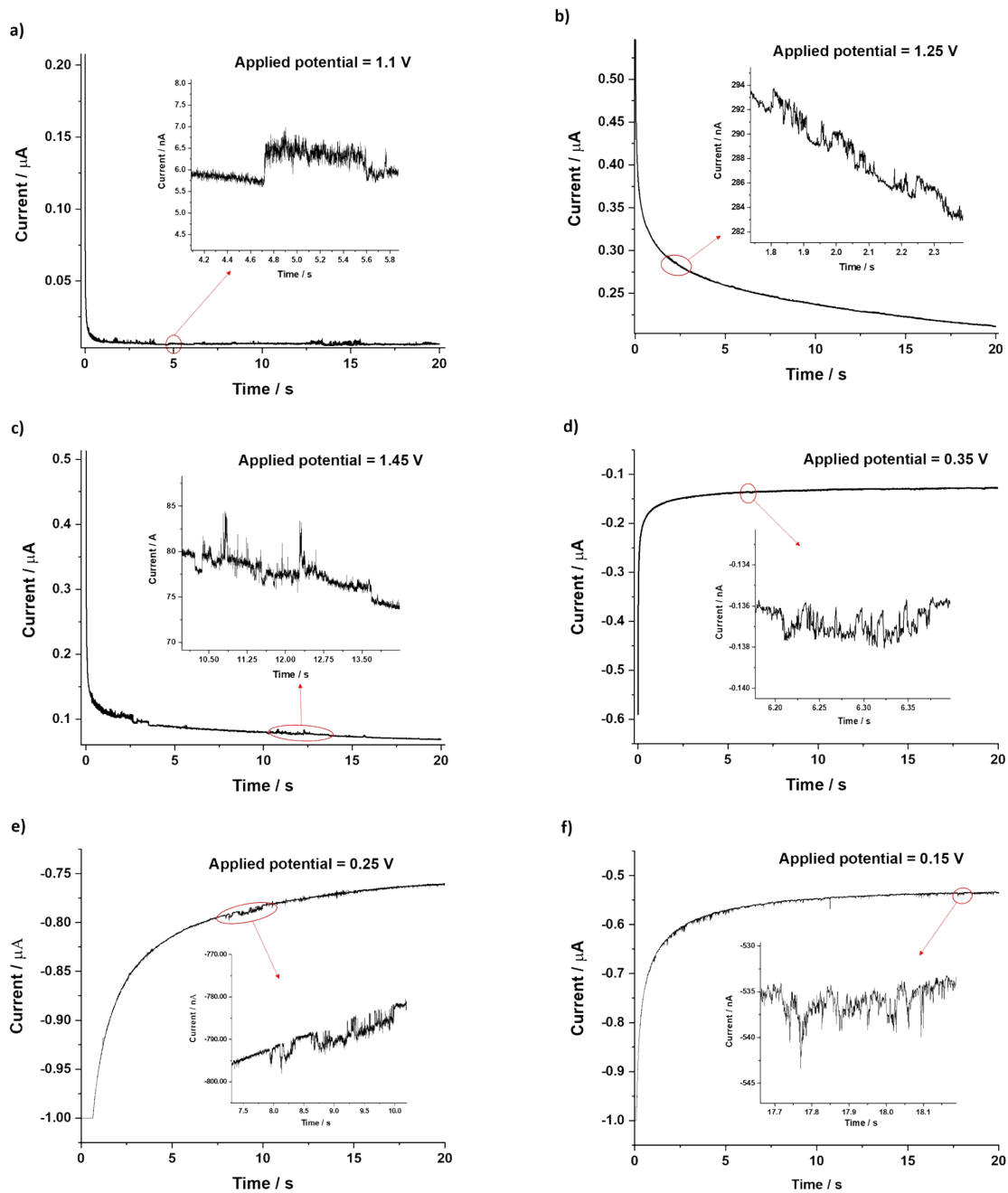
Thus, number of layers for 30  $\mu\text{L}$  drop cast on GC electrode is found to be  $125 \pm 5$  monolayers.

## Section 10: Chronoamperograms in 0.1 M HNO<sub>3</sub> and 100 μg of MWCNTs



**Figure S7.** Chronoamperograms in 0.1 M HNO<sub>3</sub> a) at 1.3 V vs SCE in the absence of MWCNTs b) at 1.3 V vs SCE in 100 μg of dispersed MWCNTs.

## Section 11: Chronoamperograms observed at different potentials for BOR



and BRR

**Figure S8.** Chronoamperograms showing the impact step current for BOR in 5.0 mM NaBr in 0.1 M  $\text{HNO}_3$  at a) 1.0V , b) 1.25 V and c) 1.45 V and for BRR in 5.0 mM Bromine in 0.1 M  $\text{HNO}_3$  at d) 0.35 V, e) 0.25 V and f) 0.15 V.

## References

1. J. Ellison, C. Batchelor-McAuley, K. Tschulik and R. G. Compton, *Sensor Actuat B-Chem*, 2014, **200**, 47-52.
2. R. G. Compton and C. E. Banks, *Understanding Voltammetry, 3rd Edition*, 2018, 1-439.
3. D. L. Li, C. H. Lin, C. Batchelor-McAuley, L. F. Chen and R. G. Compton, *J Electroanal Chem*, 2018, **826**, 117-124.
4. R. E. White and S. E. Lorimer, *J Electrochem Soc*, 1983, **130**, 1096-1103.
5. I. Streeter, G. G. Wildgoose, L. D. Shao and R. G. Compton, *Sensor Actuat B-Chem*, 2008, **133**, 462-466.
6. G. P. Keeley and M. E. G. Lyons, *Int J Electrochem Sc*, 2009, **4**, 794-809.
7. W. J. Albery, *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 1981, **302**, 221-235.
8. A. W. Bott, S. W. Feldberg and M. J. C. S. Rudolph, 1996, **15**, 67-71.
9. BASi research products, Digisim® Simulation Software For Cyclic Voltammetry, <https://www.basinc.com/products/ec/digisim>).