Electro-Oxidation of Amino-Functionalized Multiwalled Carbon Nanotubes

-Supplementary Information-

Yuanyuan Lu[1], Xiuting Li[2], Richard G. Compton[1*]

[1] Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, Great Britain

[2] Institute for Advanced Study, Shenzhen University, Shenzhen, Guangdong 518060, China

*Corresponding author： Richard G. Compton (Email: richard.compton@chem.ox.ac.uk)

Table of Contents:

Section 1: Fourier-transform infrared spectroscopy (FTIR) characterization of MWCNTs

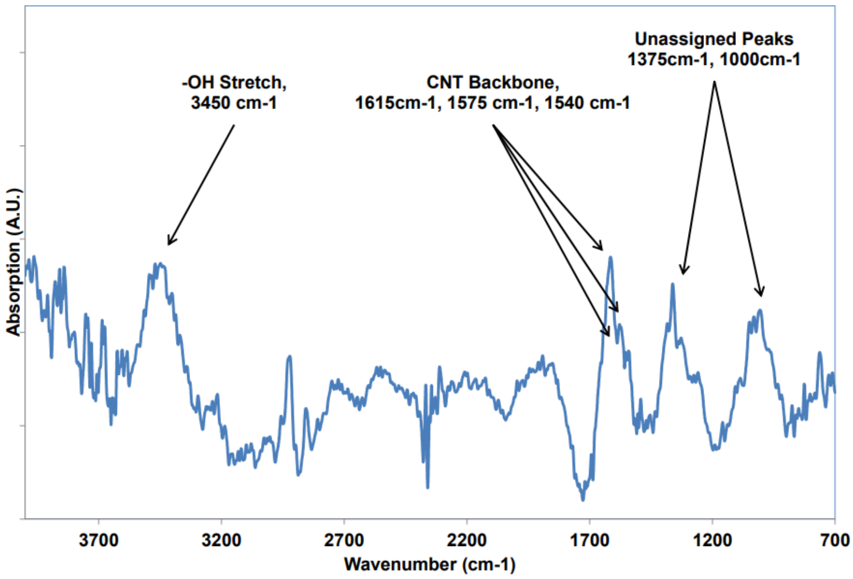

Figure.S1 Fourier-transform infrared spectroscopy (FTIR) of MWCNTs from Nanolab [1].

Section 2: Chronoamperograms of a carbon micro-disc electrode at lower potentials

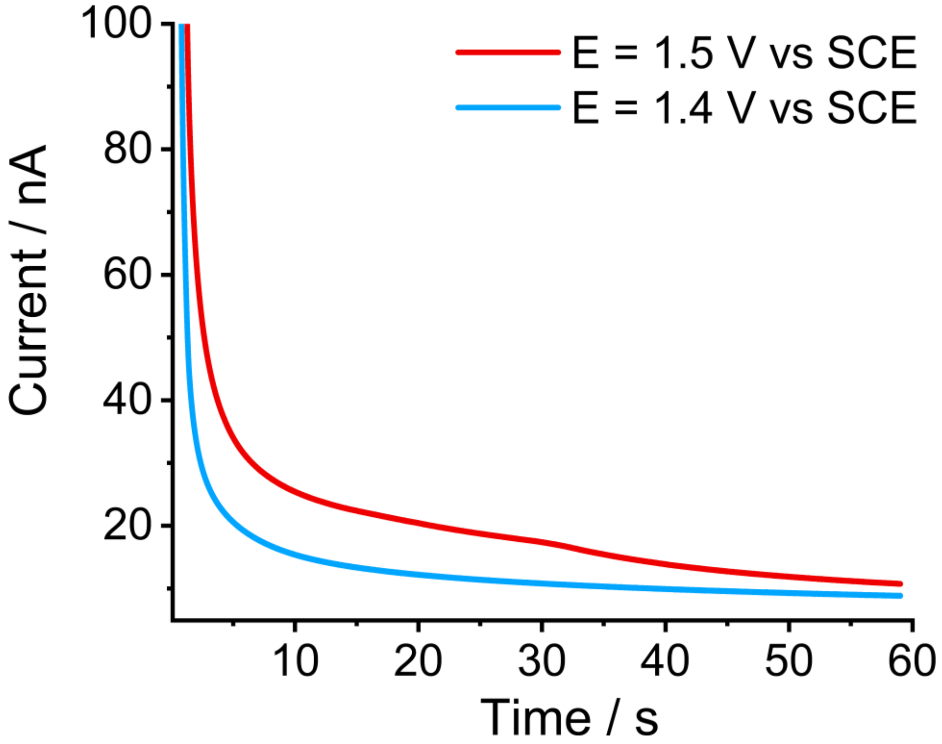

Figure.S2 Chronoamperograms of a carbon micro-disc electrode at 1.5 and 1.4 V vs SCE in a suspension of 0.01 gL^{-1} MWCNTs particle containing 0.1 M KNO_3 (pH=6.4).

Section 3: Potential variation of impact frequency and the average spike duration time in the presence of MWCNTs

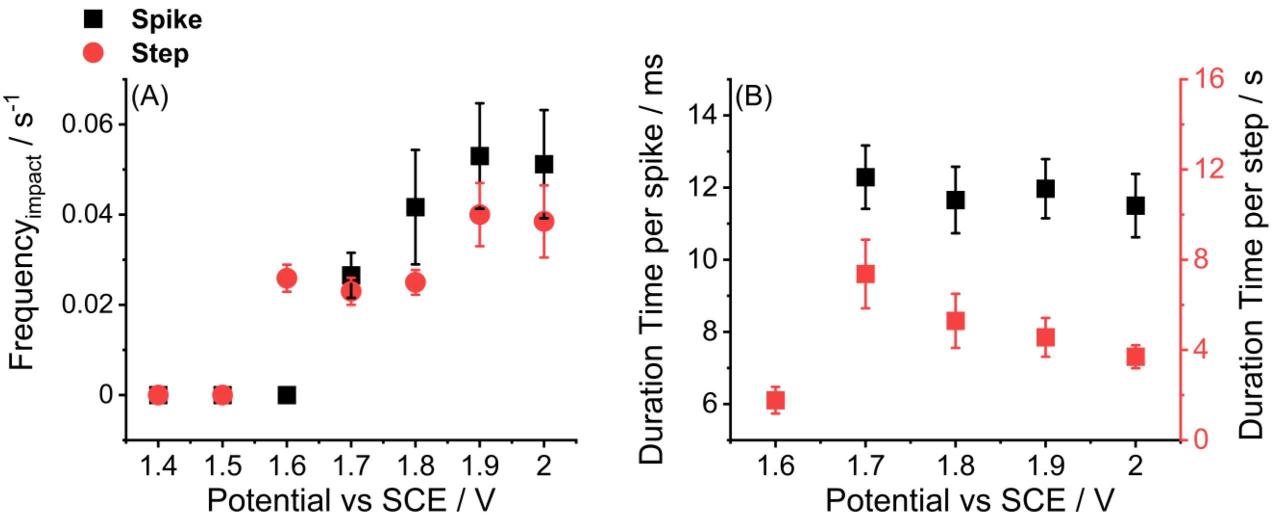

Figure.S3 (A) Impact frequency plot as a function of applied potentials from 1.4 V to 2.0 V vs SCE in the presence of 0.01 g L^{-1} MWCNTs; (B) Impact spike and step average duration time as a function of applied potentials from 1.6 V to 2.0 V in the presence of 0.01 g L^{-1} MWCNTs.

Section 4: The charge distribution of spikes in the presence of MWCNTs

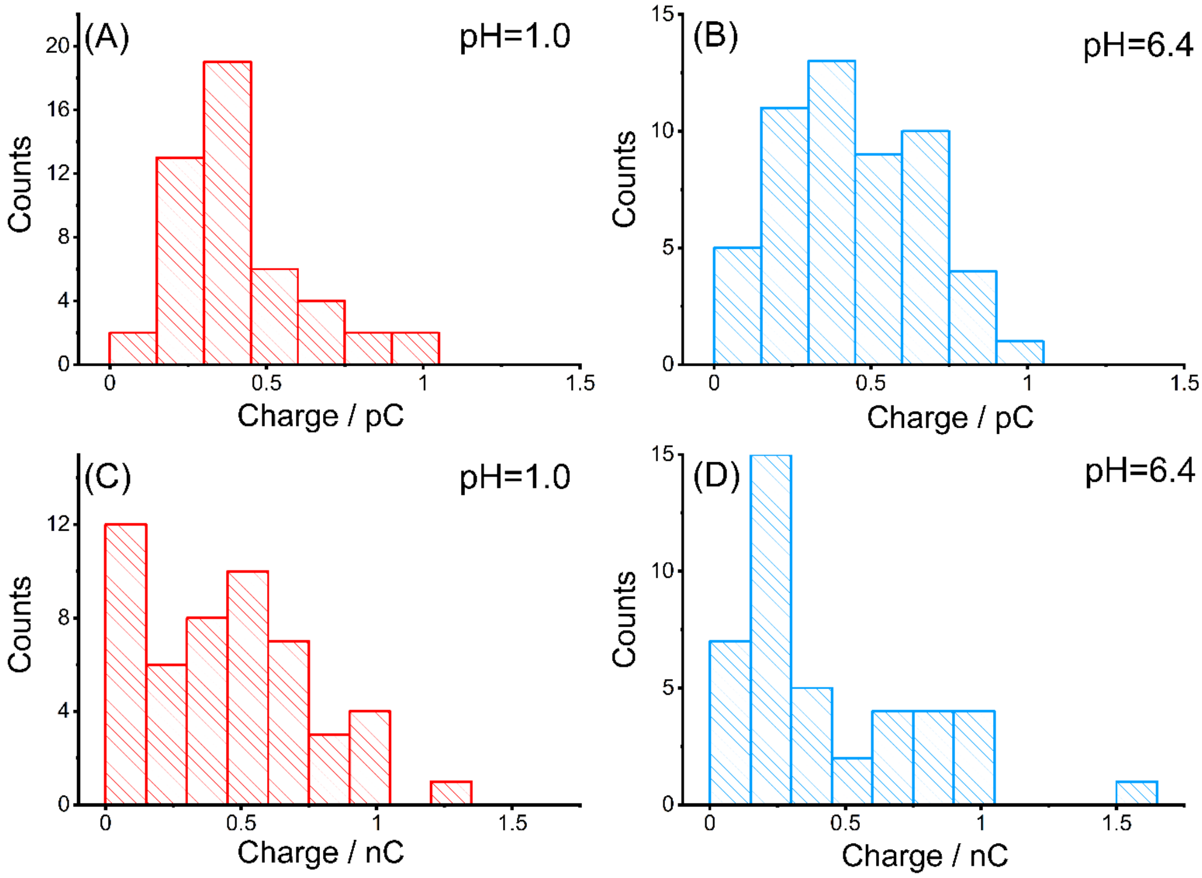

Figure.S4 The charge distribution of 48 and 53 current spikes from the oxidation of MWCNTs in pH=1.0 (A) and pH=6.4 (B) solution respectively; The charge distribution of 52 and 43 current steps in the presence of 0.01 gL^{-1} MWCNTs in pH=1.0 (C) and pH=6.4 (D) solution respectively.

Section 5: The average functional group coverage on a single MWCNT based on ensemble electrochemistry

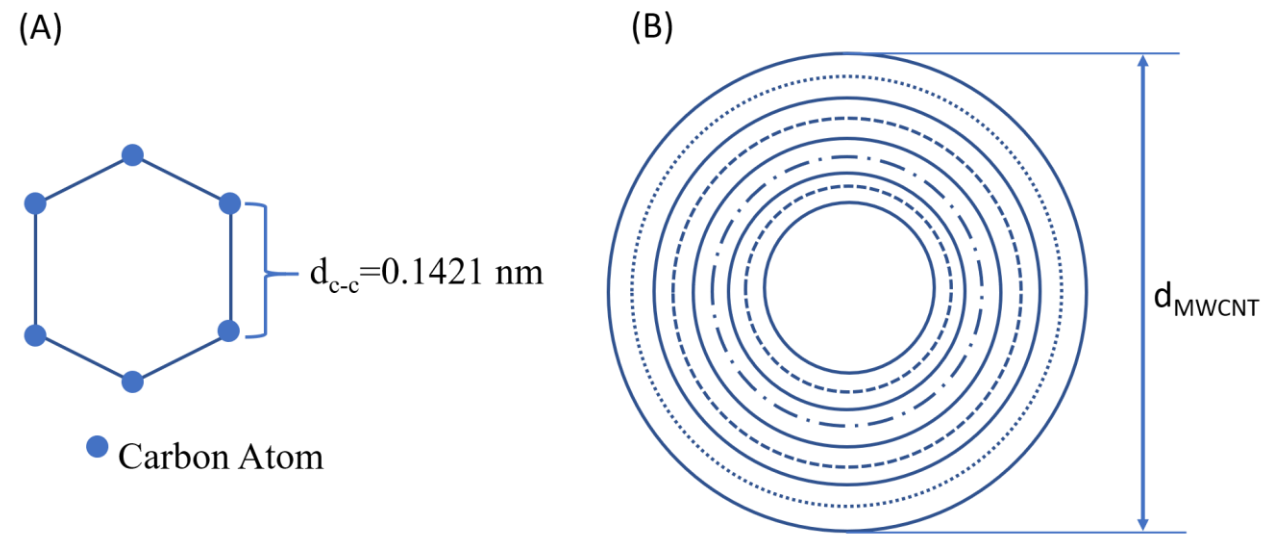

Figure.S5.1 Schematic representation of the arrangement of carbon atoms within the carbon nanotube layer (A) and an end on view of a multi-walled carbon nanotube made up of nine concentric shells (B)

The area (S_h) of one hexagon composed of six carbon atoms (Fig.S5.1(A)) is

$S_h=3\ d_{c\text{-}c}^2 \times \frac{\sqrt{3}}{2} = 5.2 \times 10^{-20}\ m^2$,

where $d_{c\text{-}c}$ (= 0.1421 nm) is the length of the C-C bond

The area (S_{mw}) of all the concentric tubes in one single MWCNT

$S_{mw}= l \times \pi d_{MWCNT} \times L = 9 \times \pi \times 3\times10^{-8}\ m \times 2.0\times10^{-5}\ m = 1.7\times10^{-11}\ m^2$,

where l (=9) is the number of concentric tubes within each MWCNT (Fig.S5.1(B), supplied by NanoLab[1]), d_{MWCNT} (=30 nm) is the diameter of a carbon tube and L (=20 μm) is the length of each tube.

The number of carbon atoms per tube $N_c = 2\times S_{mw} / S_h = 2\times1.7\times10^{-11}\ m^2 / 5.2\times10^{-20}\ m^2 = 6.6\times10^8$

The mass per carbon tube $w_{mw} = 6.6\times10^8 \times 2\times10^{-23}\ g = 1.3\times10^{-14}\ g$

(one Carbon atom mass $w_c = 2\times10^{-23}$ g)

Therefore, the number of carbon tubes present on the surface of a modified GCE (N_{MWCNT}) is

$N_{MWCNT} = 2\times10^{-7}\ g / 1.3\times10^{-14}\ g = 1.5\times10^7$

The cyclic voltammograms at different scan rates in the range of 25–400 mVs^{-1} in 0.1M KNO_3 (pH=6.4) (Fig.S5.2) were recorded, the peak shape gradually became better defined as the scan rate was decreased. The charge was estimated as a function of scan rate with an increased charge being observed at lower scan rates corresponding to a greater proportion of the drop cast layer being oxidized. Extrapolation of the reciprocal charge against scan rate to zero scan rate gave a charge $Q_{MWCNT\text{-}ensemble}$ of 7 mC averaged over five measurements.

The charge of oxidized groups (q_1) on each MWCNTs particle via electro-oxidation can be estimated to be $q_1 = Q_{MWCNT\text{-}ensemble} / N_{MWCNT} = 7\times10^{-3}$ C / $1.5\times10^{7} = 4.6\times10^{-10}$ C,

where $Q_{MWCNT\text{-}ensemble}$ is the average charge passed at MWCNTs modified GCE from CV in 0.1 M KNO_3 (pH=6.4) based on the polynomial fitting curve shown in Fig S5.2

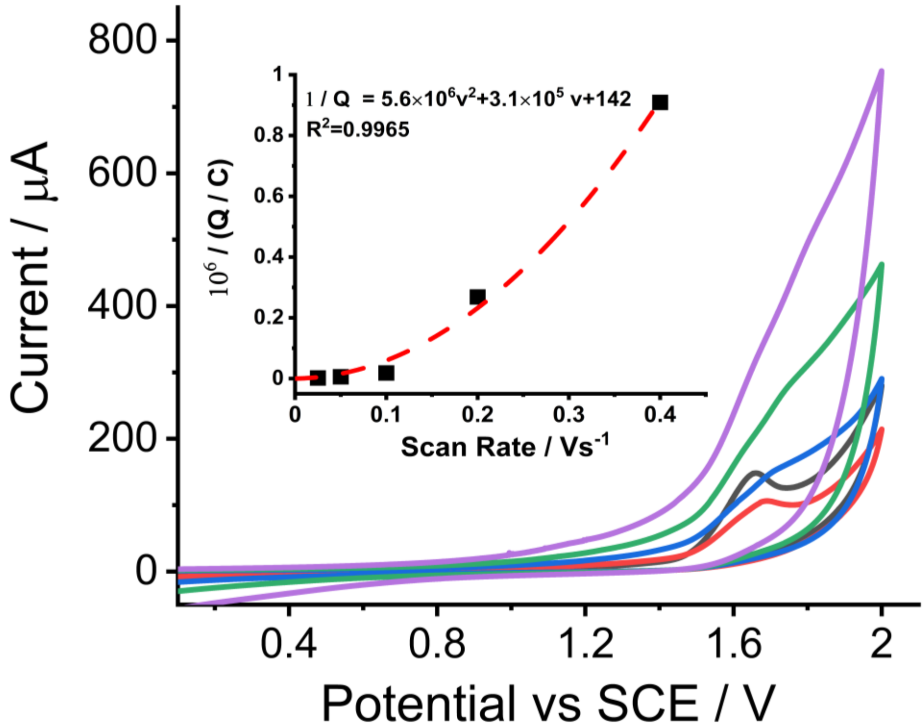

Figure.S5.2 Cyclic voltammograms of a MWCNTs modified GCE in 0.1 M KNO_3 (pH = 6.4) at varying scan rates of 25 mVs^{-1}, 50 mVs^{-1}, 100 mVs^{-1}, 200 mVs^{-1} and 400 mVs^{-1} (Inlay: Plot of 1/Q versus scan rate from 25 mVs^{-1} to 50 mVs^{-1}, 100 mVs^{-1}, 200 mVs^{-1} and 400 mVs^{-1} where Q is the average charge passed at MWCNTs modified GCE).

Section 6: Estimation of the number of layers of MWCNTs drop-casted on the GC electrodes

To estimate a minimum number of MWCNT monolayers on the bare GC electrode, we assume a closed pack arrangement of the MWCNT is laid uniformly across the whole GC surface. This gives a lower limit estimate for the number of layers.

The diameter and length of the bamboo-like multiwalled carbon nanotubes (purchased from NanoLab, USA) is ca. 30 nm and ca. 20 μm respectively.

Assuming the MWCNTs contact at the GC surface to be rectangular when arranged in a closed pack manner, the area covered by one MWCNT is 6×10^{-8} cm^2.

2 μL 0.1 gL^{-1} MWCNTs was drop cast on the bare GC electro, the number of MWCNTs modified on the surface of modified GCE (N_{MWCNT}) (calculated in SI Section 5) is $N_{MWCNT}=1.5\times10^7$

Hence, the total area covered by 1.5×10^7 MWCNTs is 0.9 cm^2

The diameter of GC electrode is 3.02 +/- 0.005 mm, the area is $A = (\pi D^2) / 4 = 7.07\times10^{-2}$ cm^2

The number of monolayers of MWCNTs for 2 μL 0.1 gL^{-1} MWCNTs drop cast

$$N_{layer} = \frac{Total\ area\ covered\ by\ MWCNTs}{Total\ surface\ area\ of\ GC\ electrode} = 0.9\ cm^2 / 0.07\ cm^2 \approx 13$$

Section 7: Estimation of the number of functional groups possibly created by electro-oxidation on a single MWCNT

The number of functional groups (N_{ox}) introduced into a single MWCNTs particle via electro-oxidation can be estimated from nano-impact experiments to be

$N_{ox}=Q_{MWCNT\text{-}single}/n_1e=4.3\times10^{-13}$ C / ($4\times1.6\times10^{-19}$ C) $=6.7\times10^{5}$

where $Q_{MWCNT\text{-}single}$ is the average charge from the oxidative spike current, n_1 is the number of electrons transferred, which is estimated to be equal to four corresponding to hypothetical quinone formation.

The circumferences of the one end of a single MWCNT has a total length of

$l_{end} = \pi d_{MWCNT} = \pi\times3\times10^{-8}$ m $= 9.5\times10^{-8}$ m

where d_{MWCNT} (=30 nm) is the diameter of carbon tube

The distance between each functional group oxidized at the end of carbon nanotube (d_1)

$d_1 = l_{end} / N_2 = 9.5\times10^{-8}$ m / (6.7×10^{5}) $= 1.4\times10^{-13}$ m $=1.4\times10^{-3}$ Å

This extremely low value suggests that far more functionality is introduced than can possibly be accommodated on a single tube end. Hence the likely interpretation of the short timescale of the spikes lies in the dynamics of the collision rather than the finite extent of the part of the CNT available for oxidation to quinones.

Section 8: The calculation of the average charge passed at a MWCNT-NH$_2$ modified GCE

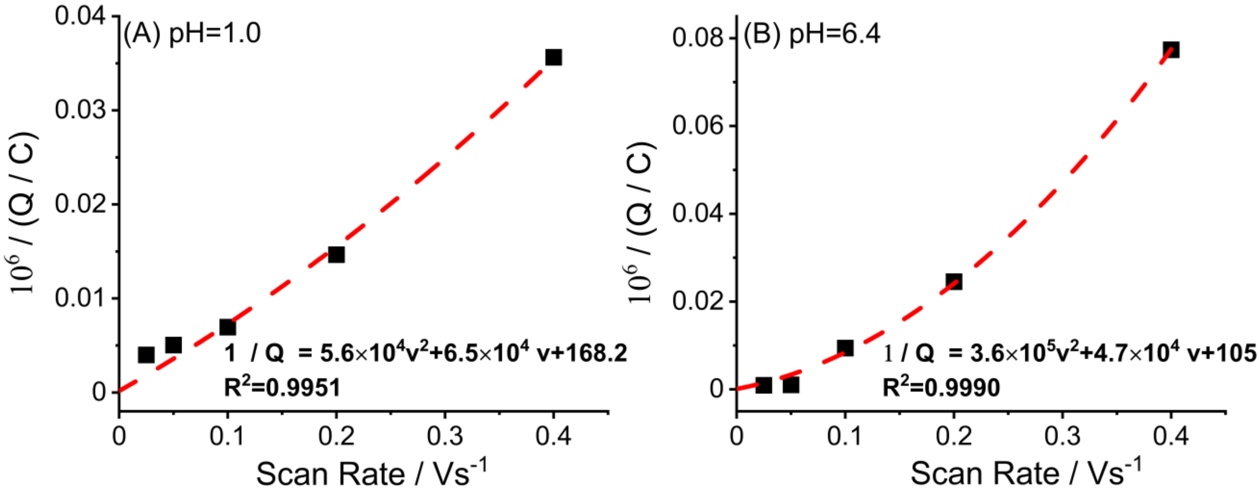

Figure. S6 Plot of 1/Q versus scan rate from 0.025 Vs^{-1} to 0.05, 0.1, 0.2 and 0.4 Vs^{-1} where Q is the average charge passed at MWCNTs-NH$_2$ modified GCE in pH=1.0 (A) and pH=6.4 (B) solution.

Section 9: Representative chronoamperograms showing impacts of $MWCNTs\text{-}NH_2$

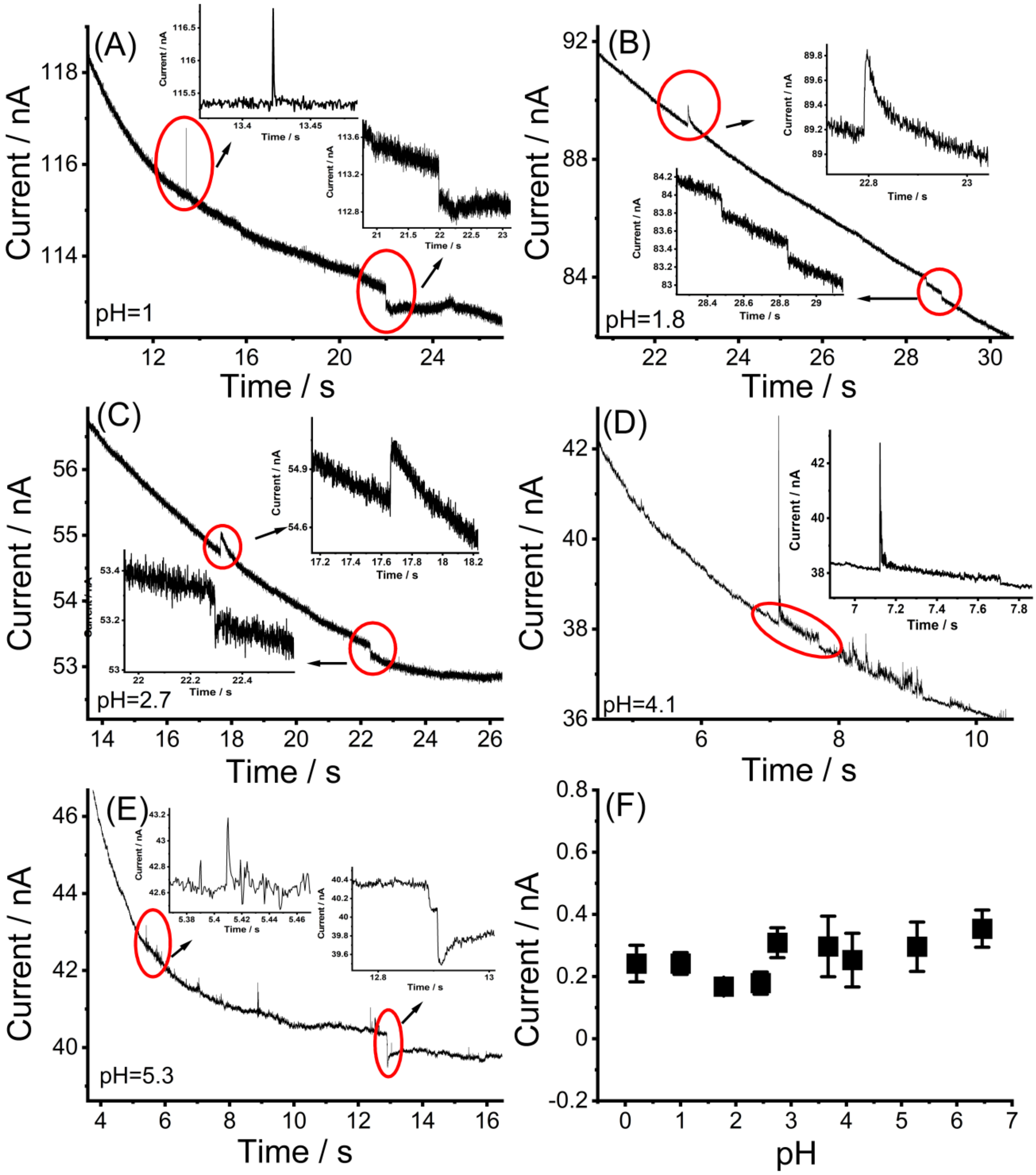

Figure.S7 (A)-(E) Representative chronoamperograms of a carbon micro-disc electrode immersed in a 0.1 M HNO_3 (pH=1.0) and 0.1 M KNO_3 solutions at different pH values of 1.8, 2.7, 4.1 and 5.3 containing 0.01 gL^{-1} $MWCNTs\text{-}NH_2$ at a potential of 1.90 V vs SCE; (F) The plot of average step current as a function of solution pH.

Section 10: pH variation of impact frequency and average duration time of spikes and steps in impacts of MWCNTs-NH$_2$

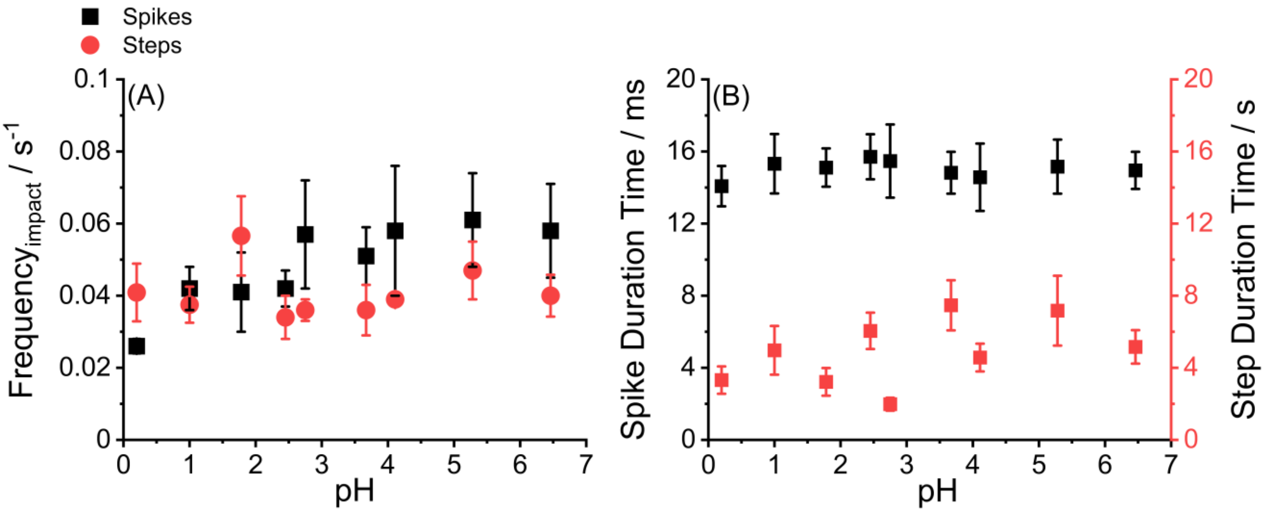

Figure.S8 (A) Impact frequency plot as a function of pH from 0.3 to 6.4 in the presence of 0.01 g L^{-1} MWCNTs-NH$_2$; (B) Impact spike and step average duration time as a function of pH from 0.3 to 6.4 in the presence of 0.01 g L^{-1} MWCNTs-NH$_2$.

Section 11: The charge distribution of spikes from impacts of $MWCNTs-NH_2$

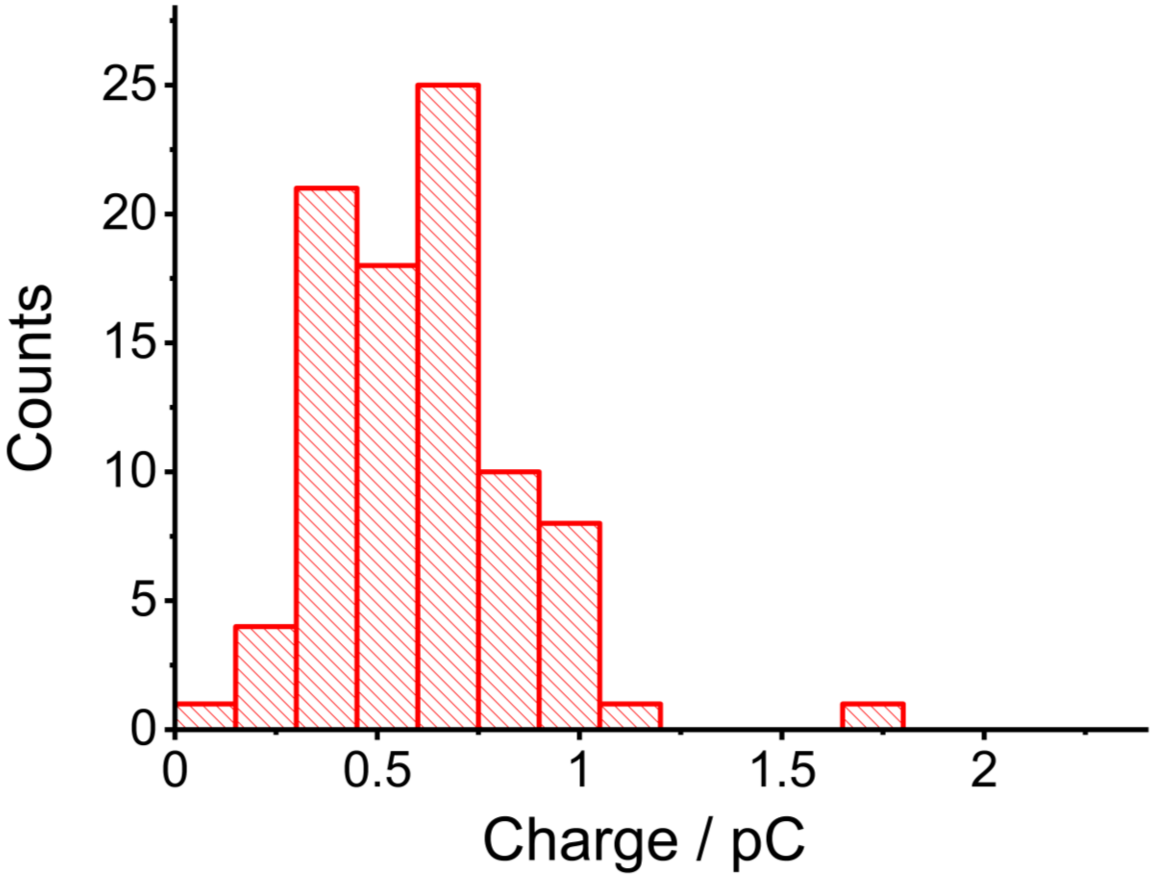

Figure.S9 The charge distribution of 89 current spikes from the oxidation of $MWCNTs-NH_2$ particle in 0.1 M KNO_3 (pH=6.4) solution.

Section 12: The non-linear fitting of the relationship between average charge of oxidative spikes and pH value

The oxidative spike average charge (q) is given by:

$q = q_{-NH_2}[MWCNTs\text{-}NH_2] + q_{-NH_3^+}[MWCNTs\text{-}NH_3^+]$ (1)

where q_{-NH_2} and $q_{-NH_3^+}$ can be determined from the average spike charge at high pH >4 (0.61 nC) and low pH <2 (0.40 nC) where the difference between the two charges represents q-NH_2 and the value at low pH gives q-NH_3^+

Combined with $pH = pK_a + \log_{10}\left[\frac{[MWCNTs-NH_2]}{[MWCNTs-NH_3^+]}\right]$ (2)

And assuming the sum [MWCNTs-NH_2] + [MWCNTs-NH_3^+] is a constant, the following equation can be obtained (3):

$pK_a = pH - \log_{10}\left(\frac{q_{-NH_3^+} - q_{-NH_2}}{q - q_{-NH_2}} - 1\right)$ (3)

Using the Origin Pro2020 non-linear fitting function, the Fitting Function Formula is input by simplifying the equation (3) as:

$q = 0.61 - \frac{0.21}{10^{pH - pKa + 1}}$ (4)

Setting the initial value of pKa to be around 2.5, the fitting curve was then generated automatically (R^2 = 0.9656).

Section 13: Background subtraction of original cyclic voltammograms

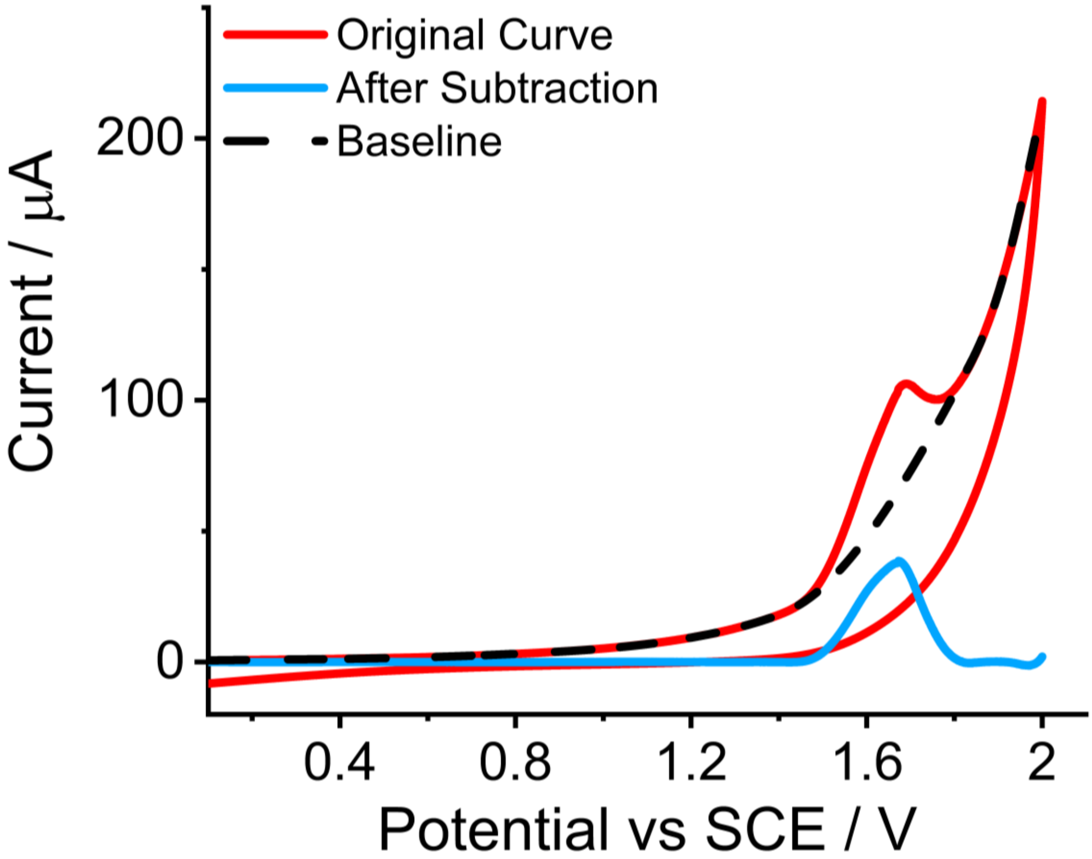

Figure.S10 Subtraction scheme for obtaining the peak height in cyclic voltammograms recorded at a MWCNTs modified GCEs in 0.1 M KNO_3 (pH 6.4) at a scan rate of 50 mVs^{-1} via background correction to the original cyclic voltammogram: the original curve (red line), the baseline (black line) and subtracted curve (blue line).

References

1. Inc., N., Multipul Carbon Nanotubes, Bamboo Structure.