Electronic Supplementary Material (ESI) for Chemical Science.

# Supporting Information

# Impact Electrochemistry Reveals that Graphene Nanoplatelets Catalyse the Oxidation of Dopamine via Adsorption

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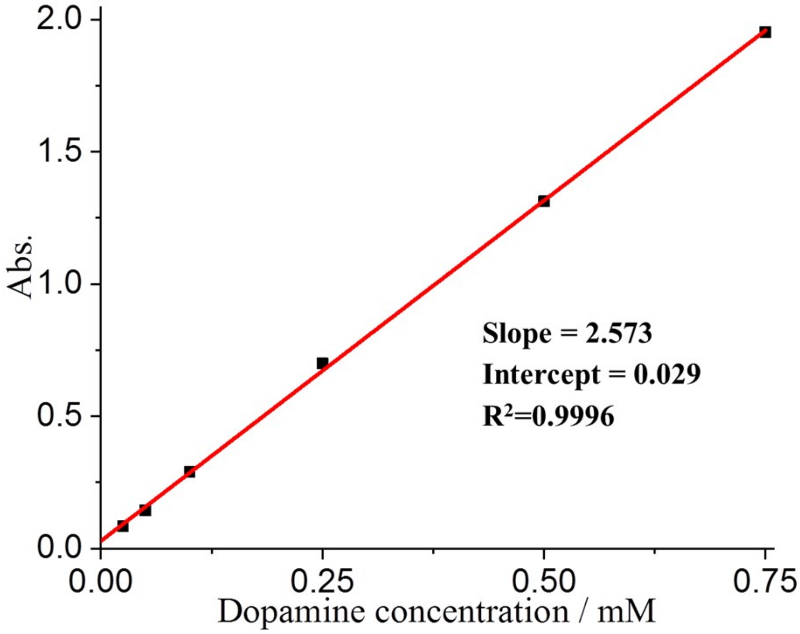

**Figure S1.** Beer–Lambert plot of dopamine in buffer (pH=0)

The linear relationship between absorbance and absorber concentration can be examined by the Beer-Lambert law.

$$A = \varepsilon\, l\, c$$

Where $A$ is the measured absorbance, $\varepsilon$ is the extinction coefficient, $l$ is the path length, and $c$ is the absorber concentration.

$$Slope = \frac{A}{c} = \varepsilon\, l = 2.574\ mM^{-1}$$

$$\varepsilon = \frac{2.574\ mM^{-1}}{l} = \frac{2.574\ mM^{-1}}{10\ mm} = 0.257\ M^{-1}m^{-1}$$

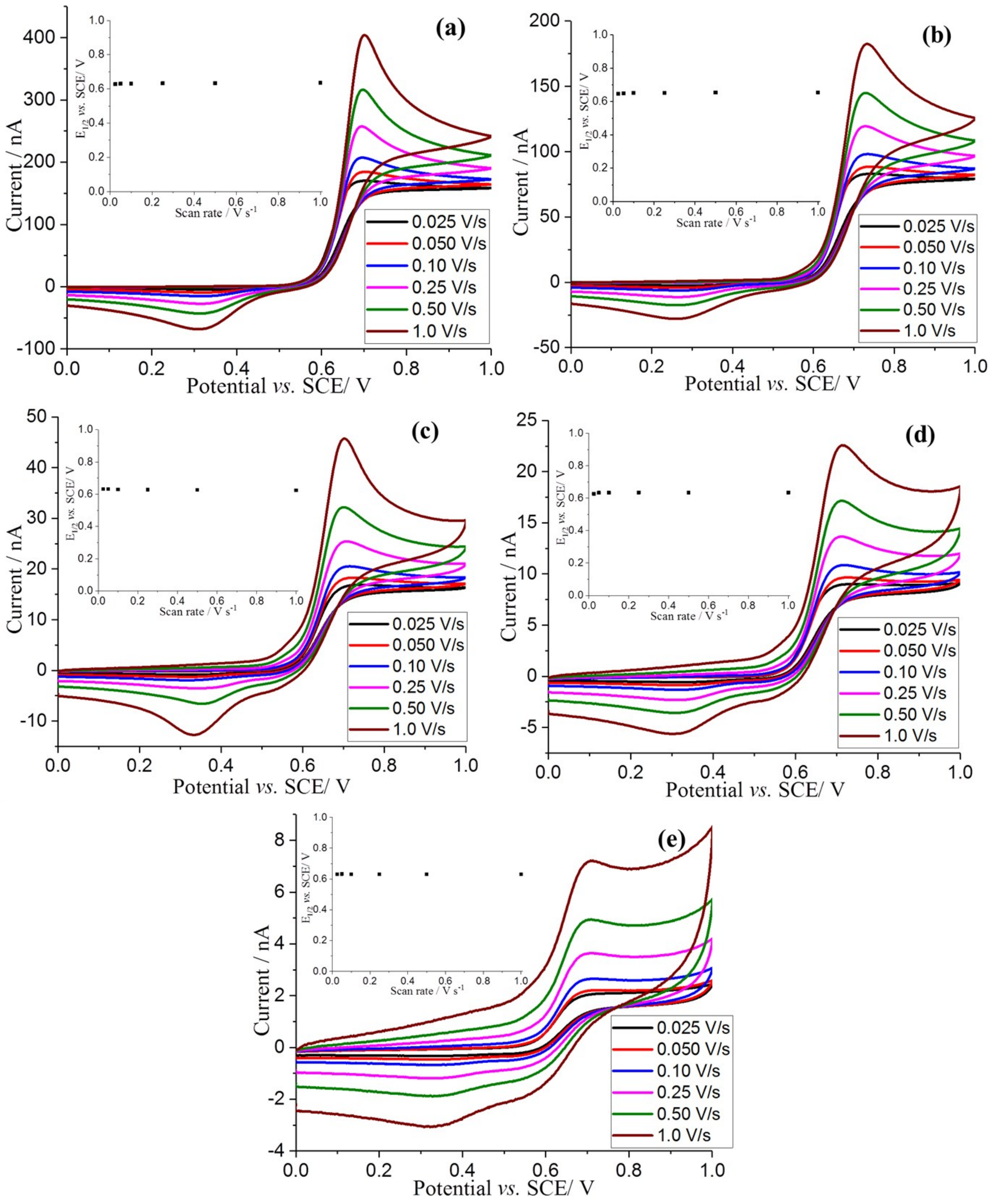

**Figure S2** Cyclic voltammograms of a bare microdisc carbon electrode in pH 0 buffered solution containing variable concentrations of dopamine recorded as a function of scan rate from 25 mV s$^{-1}$ to 1000 mV s$^{-1}$. Inset: the plot of half-wave potential as a function of the scan rate. (a) 10 mM DA, (b) 5 mM DA, (c) 1 mM DA, (d) 0.5 mM DA and (e) 0.1 mM DA.

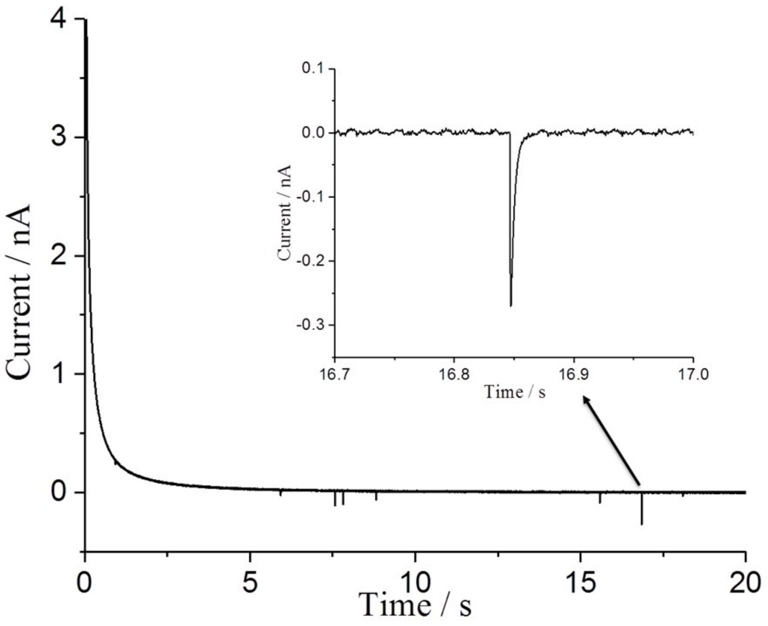

**Figure S3.** Representative chronoamperometric profiles of nano-impacts at +0.40 V versus SCE in pH 0 buffer containing GNPs only

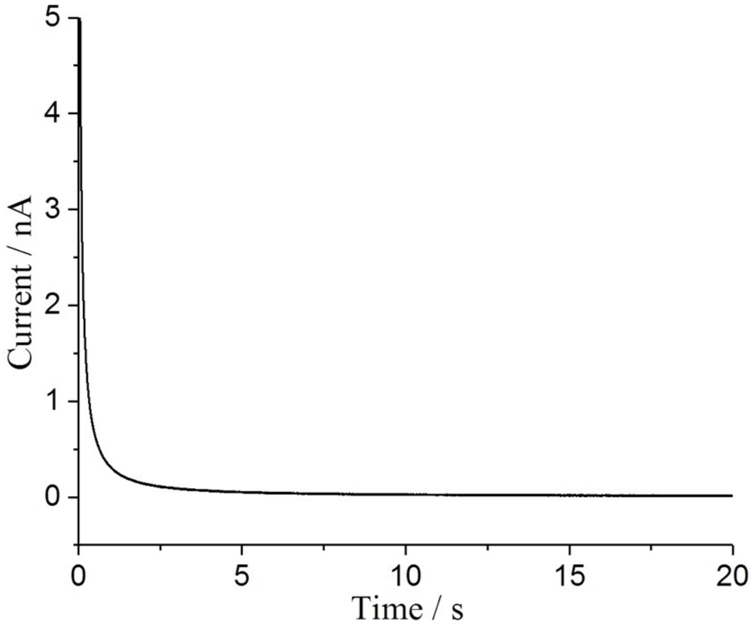

**Figure S4.** Representative chronoamperometric profiles of nano-impacts at +0.55 V versus SCE in pH 0 buffer without addition of GNPs suspensions

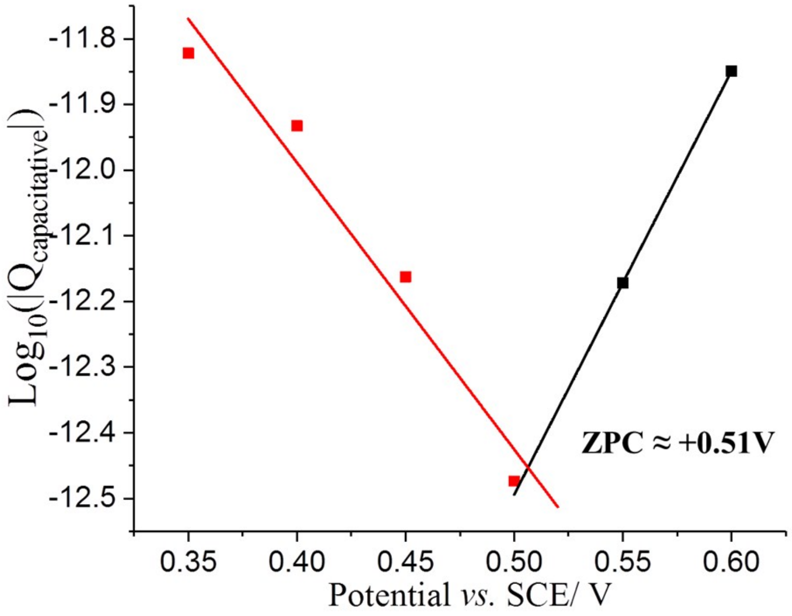

**Figure S5.** Capacitative impacts with absolute charge in logarithmic ($\log_{10}$) scale plotted against applied potential (vs. SCE). Red squares: values with negative charge; black squares: values with positive charge. The intersection potential of the two lines is used to estimate the PZC value of GNPs at pH 0 environment, where PZC is determined to be +0.51 V (vs. SCE) in pH 0 condition.

| Potentials | +0.35V | +0.40V | +0.45V | +0.50V | +0.55V | +0.60V |
|---|---|---|---|---|---|---|
| NOT Sharp | 7 | 6 | 6 | 4 | 3 | 1 |
| Total | 248 | 146 | 170 | 213 | 193 | 112 |
| % of Sharp | 97% | 96% | 97% | 98% | 99% | 99% |

**Table S1.** Statistics of spike shape of DA-saturated GNPs (modified via sonication) in 10mM of DA at different potentials

| Potential (V) | Γ from UV-Vis of 10mM DA-GNPs (mol / mg of GNP) | Γ from Impact at (mol / mg of GNP) | Percentage of oxidation (%) |
|---|---|---|---|
| +0.35 | $11.4 \times 10^{-8}$ | $(3.30 \pm 1.60) \times 10^{-11}$ | $0.03 \pm 0.01$ |
| +0.40 | $11.4 \times 10^{-8}$ | $(9.17 \pm 0.27) \times 10^{-10}$ | $0.80 \pm 0.02$ |
| +0.45 | $11.4 \times 10^{-8}$ | $(2.02 \pm 0.11) \times 10^{-9}$ | $1.8 \pm 0.1$ |
| +0.50 | $11.4 \times 10^{-8}$ | $(3.82 \pm 0.46) \times 10^{-9}$ | $3.4 \pm 0.4$ |
| +0.55 | $11.4 \times 10^{-8}$ | $(5.99 \pm 0.56) \times 10^{-9}$ | $5.3 \pm 0.5$ |
| +0.60 | $11.4 \times 10^{-8}$ | $(1.50 \pm 0.12) \times 10^{-8}$ | $13.1 \pm 1.0$ |

**Table S2.** Summary percentage of adsorbed dopamine during the impact as a function of potential

| DA Concentration (mM) | Γ from UV-Vis (mol / mg of GNP) | Γ from Impact at E= 0.55V (mol / mg of GNP) | Percentage of oxidation (%) |
|---|---|---|---|
| 5 | $8.84 \times 10^{-8}$ | $(4.96 \pm 0.56) \times 10^{-9}$ | $5.6 \pm 0.6$ |
| 10 | $11.4 \times 10^{-8}$ | $(5.99 \pm 0.56) \times 10^{-9}$ | $5.3 \pm 0.5$ |
| 20 | $13.0\times 10^{-8}$ | $(7.73 \pm 0.65) \times 10^{-9}$ | $5.9 \pm 0.5$ |

**Table S3.** Summary percentage of adsorbed dopamine during the impact at +0.55 V.

| Potentials | +0.35V | +0.40V | +0.45V | +0.50V | +0.55V | +0.60V |
|---|---|---|---|---|---|---|
| Impact time (ms) | 25.1 | 23.2 | 25.7 | 23.9 | 24.8 | 24.3 |
| Error of mean | 1.5 | 1.9 | 1.9 | 1.9 | 1.3 | 1.6 |

**Table S4.** Summary of average impact times spike shape at different potentials

**Adsorption isotherm calculation:**

We present an example based on the addition of GNPs to a 5 mM solution of dopamine.

$A_1$ (absorbance of original 5 mM dopamine solution before GNPs adsorption) = 1.3123

$A_2$ (absorbance of supernatant after GNPs adsorption) = 1.0655

$D$ (Dilution factor) = 10

The actual concentration of original dopamine solution before GNPs adsorption, $c_1$, is

$$c_1 = \frac{A_1}{\varepsilon\, l} \times D = \frac{1.3123}{0.257\ M^{-1}m^{-1} \times 10\ mm} \times 10 = 5.10\ mM$$

Similarly, the concentration of supernatant after GNPs adsorption, $c_2 = 4.14\ mM$

10.9 mg of GNPs was used to mix with 1 ml of 5 mM dopamine solution during experiment, hence the amount of DA ($n$) adsorbed onto 1 mg of GNPs can be determined as

$$n = \frac{(5.10\ mM - 4.14\ mM) \times 1\ ml}{10.9\ mg\ of\ GNPs} = 8.81 \times 10^{-8}\ mol\ of\ DA\ /\ mg\ of\ GNPs$$

Similar calculations are conducted at different dopamine concentrations and consequently the dopamine adsorption isotherm for GNPs in pH 0 buffer is constructed as shown in Figure 1b.

**Concentration driven phase transition calculation:**

For single GNP particle, average surface area of GNP is 297 ± 152 μm$^2$ and the thickness is 7.1 ± 2 nm (estimated from scanning electron microscopy[1]). Hence the volume (V) of a single GNP can be estimated as (2.11 ± 1.08) × 10$^{-18}$ m$^3$. The bulk density of the GNPs is 1 × 10$^5$ g m$^{-3}$ reported by the supplier.[2] For loose powders, the density of a single GNP is assumed to be the same as graphite, 2.26 × 10$^6$ g m$^{-3}$. [3] Therefore, the mass for single GNP can be estimated as (4.77 ± 2.44) × 10$^{-9}$ mg.

The amount of DA ($n$) adsorbed onto 1 mg of GNPs reaches the first plateau at $n_{\text{max}} = 1.7 \times 10^{-7}$ mol mg$^{-1}$. For 1 mg of GNP, the total surface area is:

$$\frac{1}{(4.77 \pm 2.44) \times 10^{-9}\, mg} \times (2.97 \pm 1.52) \times 10^{-6}\, cm^2 = (6.23 \pm 3.19) \times 10^{2}\, cm^2\, mg^{-1}$$

Therefore, the maximum surface coverage ($\Gamma_{\text{max}}$) at the first plateau can be determined as:

$$\Gamma_{max} = \frac{1.7 \times 10^{-7}\, mol\, mg^{-1}}{(6.23 \pm 3.19) \times 10^{2}\, cm^2\, mg^{-1}} = (2.6 \pm 0.8) \times 10^{-10}\, mol\, cm^{-2}$$

The average area occupied by each individual molecule ($S_{\text{R-DA}}$) can be then determined as:

$$S_{R-DA} = \frac{1}{N_A \Gamma_{max}} = \frac{1}{6.022 \times 10^{23}\, mol^{-1} \times (2.6 \pm 0.8) \times 10^{-10}\, mol\, cm^{-2}} = (\quad cm^2$$

A similar calculation is conducted to obtain $S'_{\text{R-DA}}$ at the second plateau.