# Supporting Information

**Journal:** RSC Advances

**Title:** Electrochemical properties of silver nanoparticle-supported reduced graphene oxide in nitric oxide oxidation and detection

**Authors:** Nurul Izrini Ikhsan[a,b], Perumal Rameshkumar[a,*], and Nay Ming Huang[a,c*]

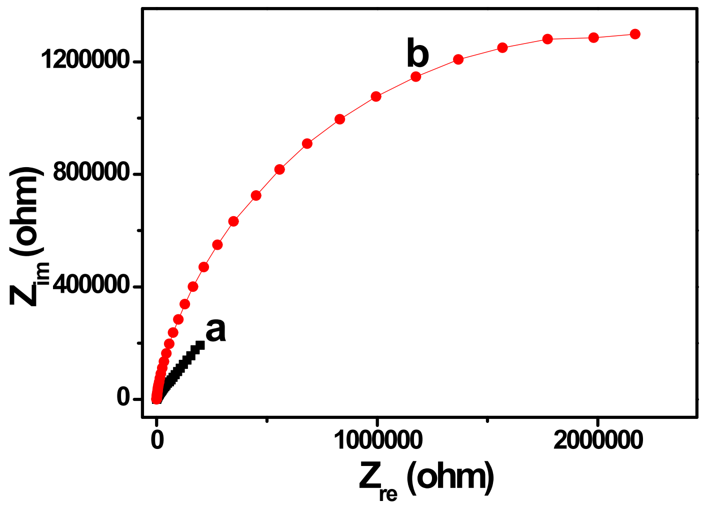
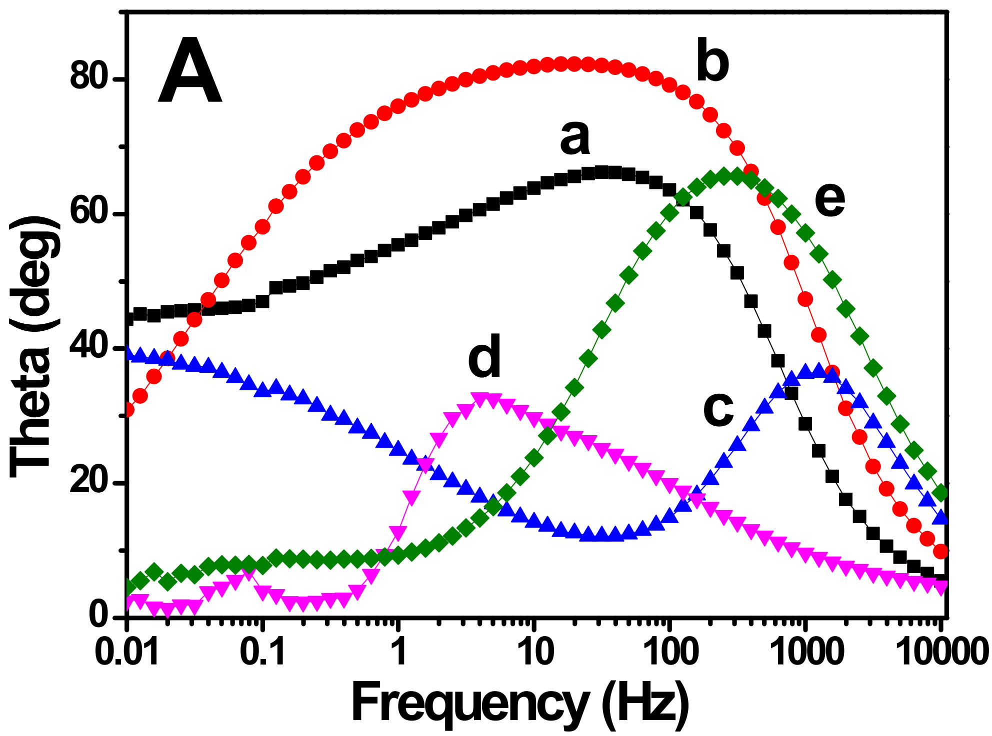



**Fig. S1** Nyquist plots obtained for bare GCE (a) and GO (b) for 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl.

**Bode phase and Bode impedance plots**

The phase peak shifts toward the low frequency region for the rGO-Ag nanocomposite modified electrodes indicated the fast electron-transfer process at the modified electrode surface (Fig. S2A). The phase angles of the rGO-Ag nanocomposite-modified electrodes were less than 90° at higher frequencies, which made it possible to assume that the electrode did not exhibit a capacitive behavior. The Bode impedance plots of the rGO-Ag nanocomposite-modified electrodes showed lower log Z values at a low frequency range of 1–100 Hz in the logarithm compared to the bare GCE and GO modified electrodes (Fig. S2B).



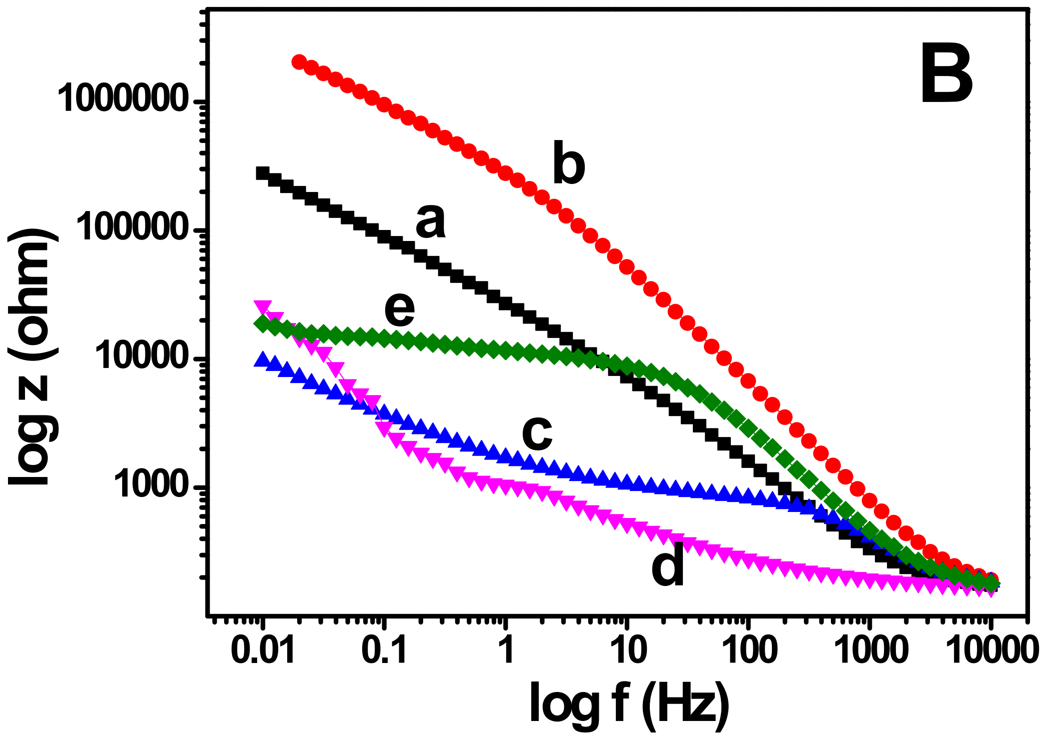



**Fig. S2 (A)** Bode phase plots obtained for bare GC (a) GO (b), rGO-Ag (0.5 M) (c), rGO-Ag (1.0 M) (d) and rGO-Ag (5.0 M) (e) modified GC electrodes for 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl. **(B)** Bode impedance plots (log Z *vs.* log f) obtained for bare GC (a) GO (b), rGO-Ag (0.5 M) (c), rGO-Ag (1.0 M) (d) and rGO-Ag (5.0 M) (e) modified GC electrodes for 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl.

**rGO-Ag nanocomposite modified GCE characterization and coverage of Ag NPs on GCE surface**

A cyclic voltammogram was recorded at the GC/rGO-Ag (5.0 M) nanocomposite-modified electrode in the 0.1 M phosphate buffer (pH 2.5) to confirm the existence of Ag on the GCE surface (Fig. S3b). The anodic peak current appearing in the positive scan region at +0.16 V proves the oxidation of Ag to $Ag_2O$, which confirms the presence of Ag NPs on the modified electrode surface[1] and reveals that the Ag NPs were in good electrical contact with the GCE electrode surface. Nevertheless, no typical redox peaks were observed for the GO-modified GCE (Fig. S3a). For a further examination, the surface coverage of the AgNPs on the electrode surface of the rGO-Ag (0.5 M, 1.0 M, and 5.0 M) nanocomposite-modified electrodes was also calculated using Lavirons' equation (eqn (1)).[2]

$$I_p = \frac{n^2 F^2 \upsilon A \Gamma}{4RT} \quad \text{-------- (1)}$$

where $I_p$ is the anodic peak current; n is the number of electrons transferred; ν is the scan rate; *Γ* is the surface coverage of the Ag NPs; A is the surface area of the electrode; and *T*, *F*, and *R* are absolute temperature, Faraday constant, and mol gas constant, respectively. Using eqn. (1), the surface coverage (Γ) values of the Ag NPs were calculated to be $1.678 \times 10^{-9}$ mol cm$^{-2}$, $1.968 \times 10^{-9}$ mol cm$^{-2}$, and $2.099 \times 10^{-9}$ mol cm$^{-2}$ using the slopes ($I_p$/ν) obtained from the cyclic voltammograms of the rGO-Ag (0.5 M), rGO-Ag (1.0 M), and rGO-Ag (5.0 M) nanocomposite-modified electrodes recorded in a 0.1 M phosphate buffer (pH 2.5) at different scan rates (Fig. S4(A–C)). Based on the calculation, it was confirmed that the rGO-Ag (5.0 M) nanocomposite-modified electrode received the highest coverage of AgNPs on its surface, which was beneficial for the electrocatalytic reactions.

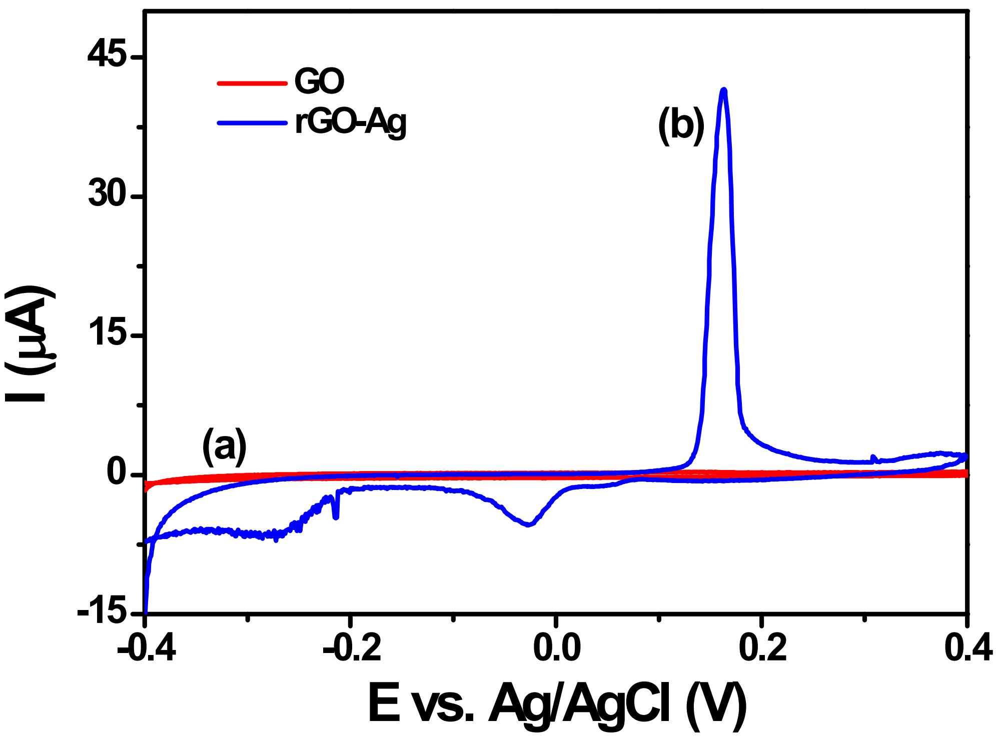
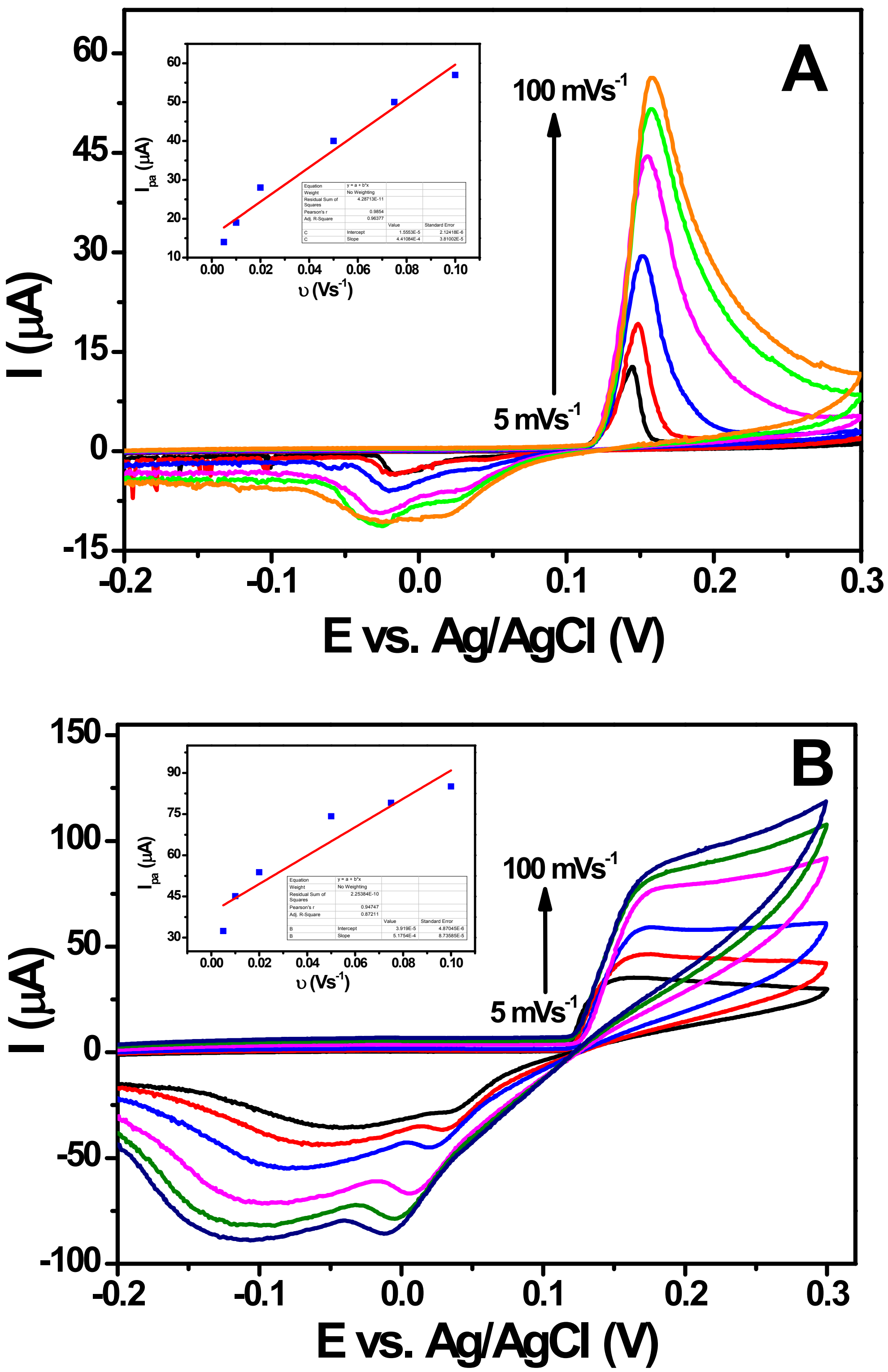



**Fig. S3** Cyclic voltammogram recorded at GO (a) and rGO-Ag (5.0 M) nanocomposite (b) modified electrode in 0.1 M phosphate buffer (pH 2.5) with scan rate of 50 mV $s^{-1}$.



A
100 mVs-1
5 mVs-1
I (μA)
E vs. Ag/AgCl (V)
Ipa (μA)
υ (Vs-1)
B
100 mVs-1
5 mVs-1
I (μA)
E vs. Ag/AgCl (V)
Ipa (μA)
υ (Vs-1)

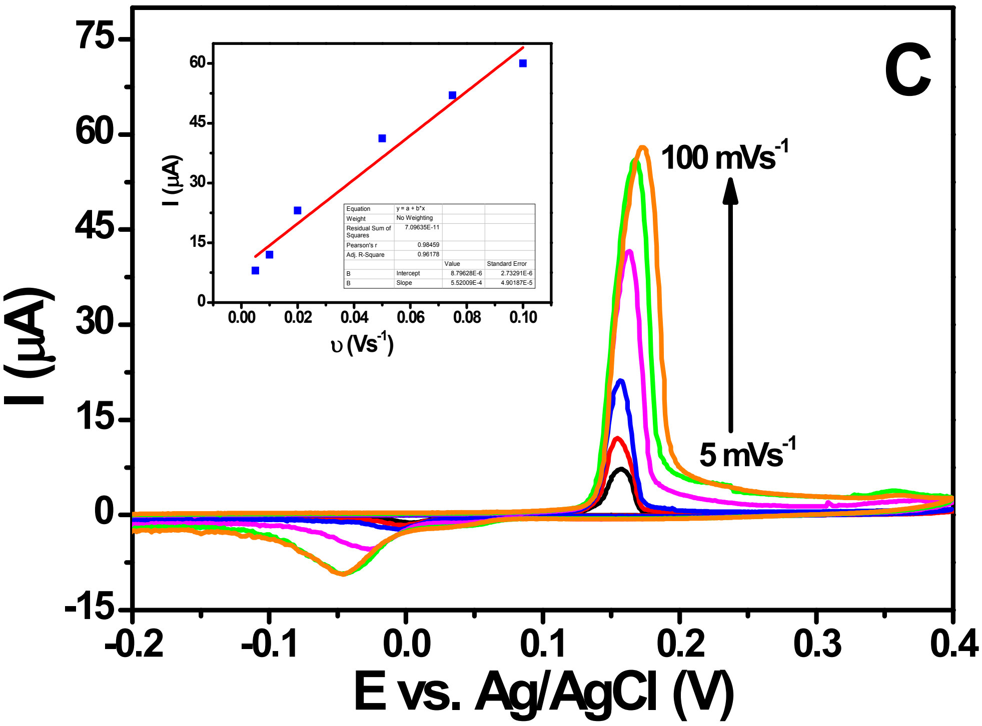



**Fig. S4** Cyclic voltammograms recorded at rGO-Ag (A: 0.5 M, B: 1.0 M and C: 5.0 M) nanocomposite modified electrodes in $N_2$-saturated 0.1 M phosphate buffer (pH 2.5) with different scan rates (5-100 mV $s^{-1}$) and inset shows the plot of anodic peak current versus scan rate.

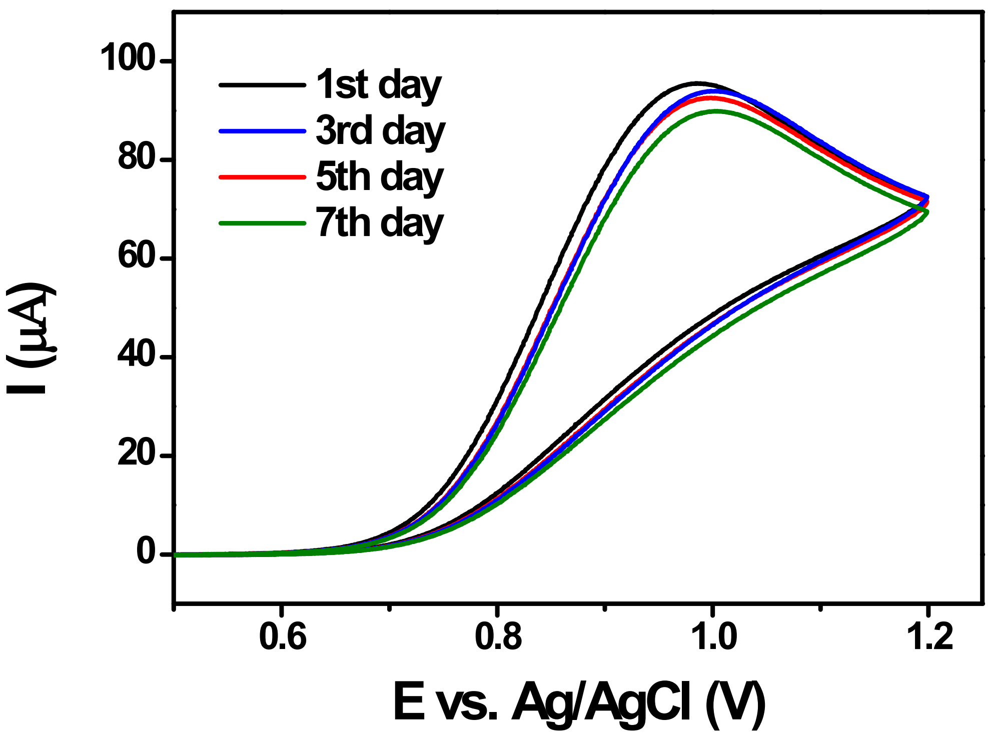



**Fig. S5** Cyclic voltammograms recorded for 1 mM $NO_2^-$ at the GC/rGO-Ag (5.0 M) nanocomposite modified electrode during different days in 0.1 M PBS (pH 2.5) with a scan rate of 50 mV $s^{-1}$.

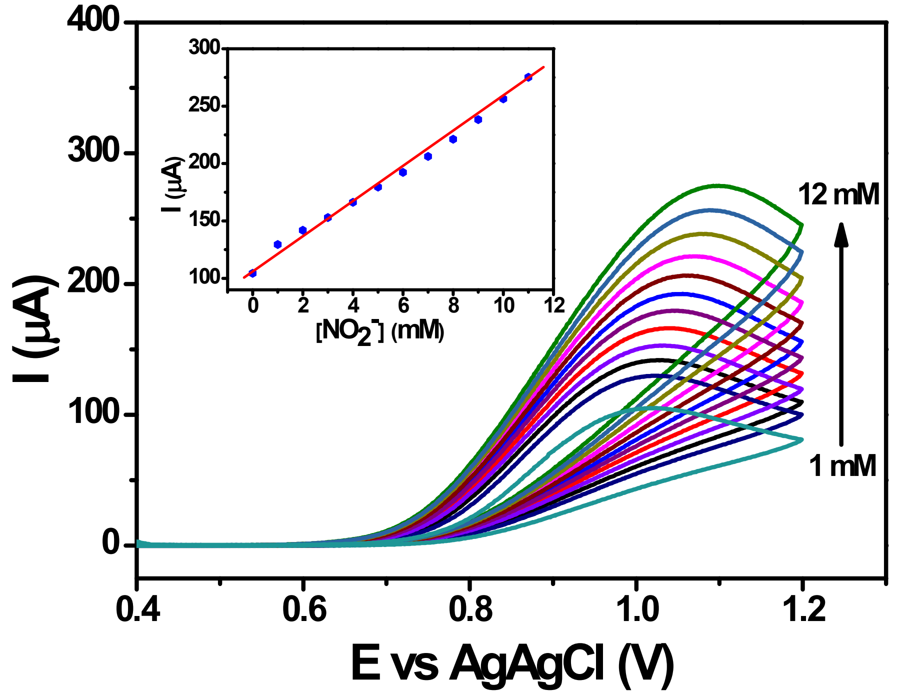



**Fig. S6** Cyclic voltammograms obtained at the rGO-Ag (5.0 M) nanocomposite modified electrode for the successive addition of each 1 mM of $NO_2^-$ (1-12 mM) in 0.1 M phosphate buffer (pH 2.5) with a scan rate of 50 mV $s^{-1}$. Inset: Plot of peak current versus concentration of $NO_2^-$.

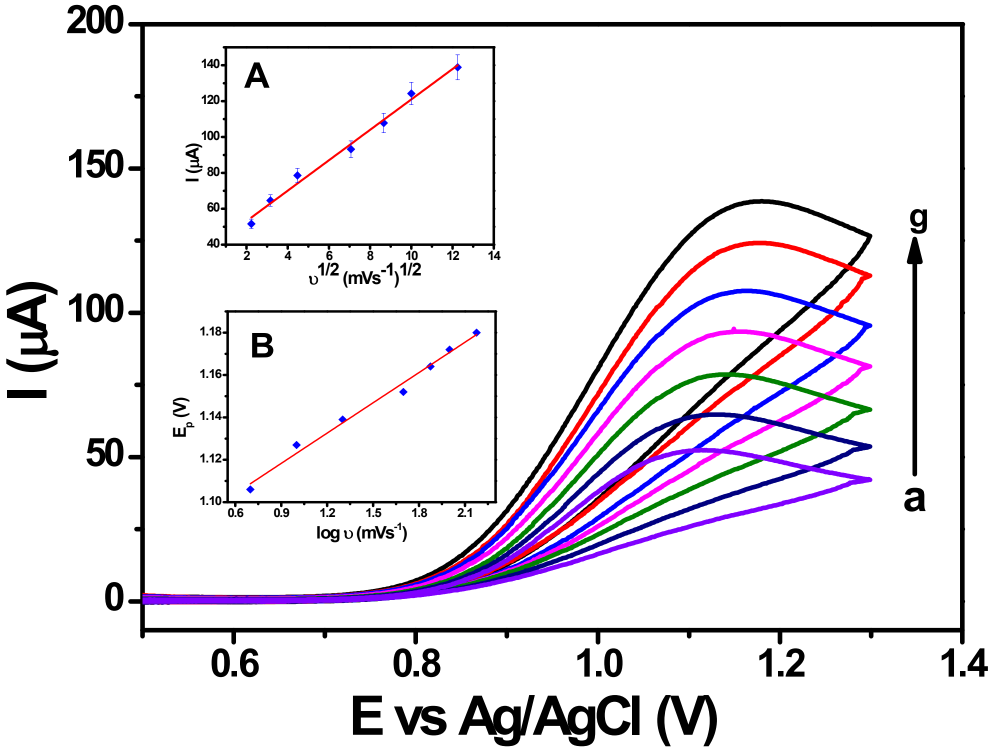



**Fig. S7** Cyclic voltammograms recorded at rGO-Ag (5.0 M ascorbic acid) nanocomposite modified electrode for 5 mM of $NO_2^-$ in 0.1 M phosphate buffer (pH 2.5) with various scan rates (a: 5, b: 10, c: 20, d:50, e: 75, f: 100 and g: 150 mV $s^{-1}$). Inset: Plot of peak current versus square root of scan rate (A) and plot of peak potential versus log (scan rate) (B).

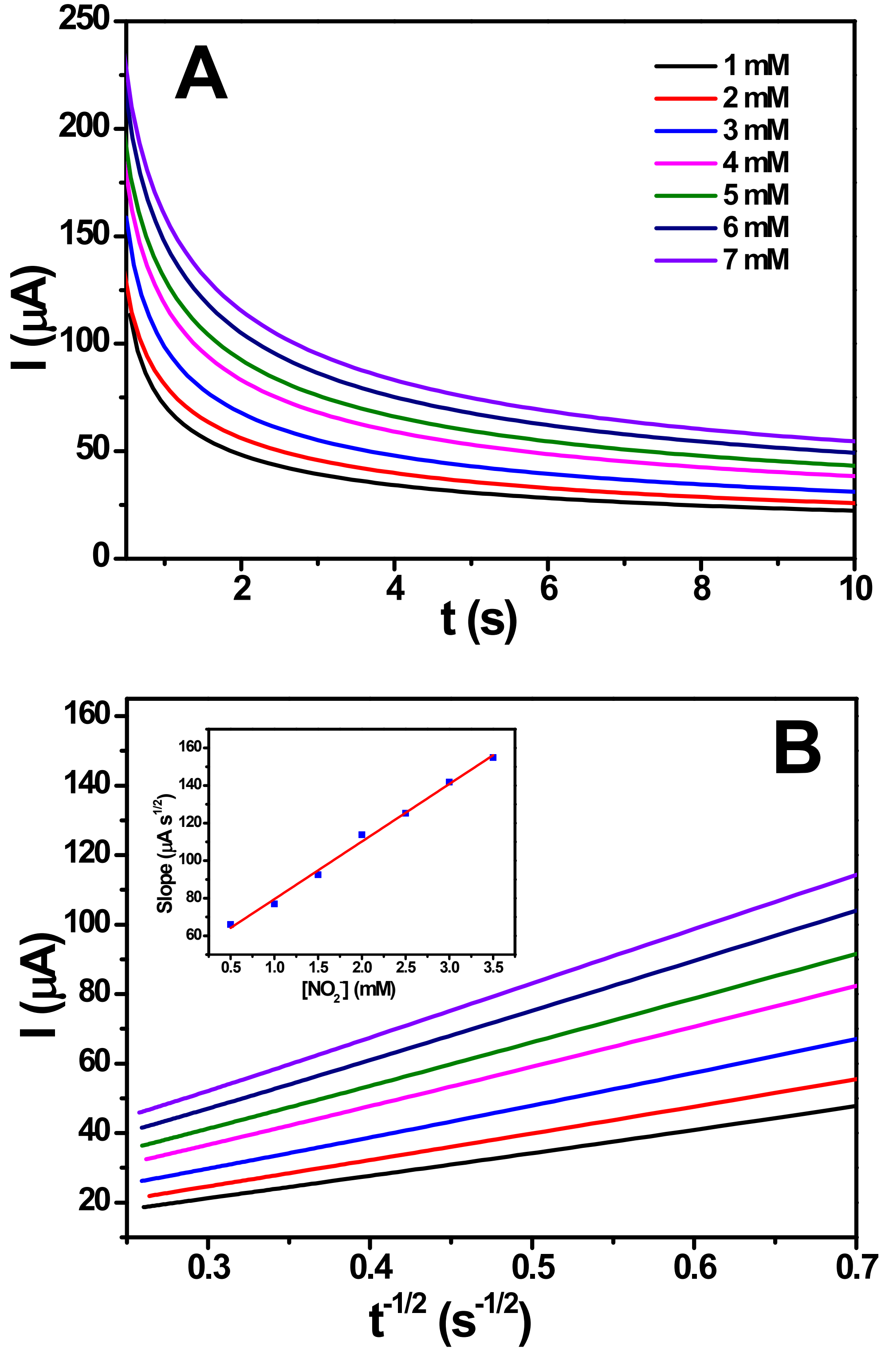
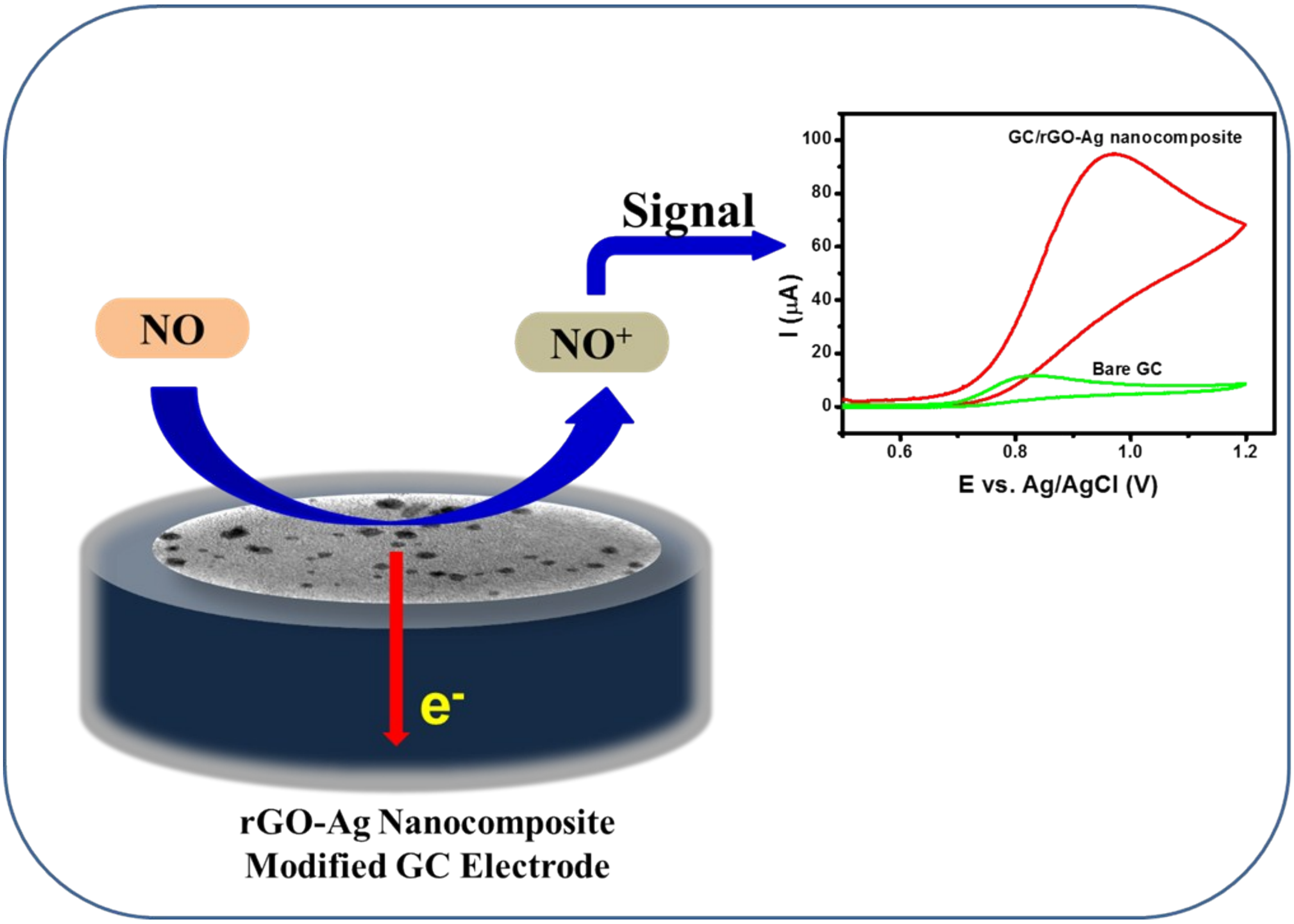



**Fig. S8** Chronoamperograms obtained at rGO-Ag (5.0 M) nanocomposite modified electrode with different concentrations of $NO_2^-$ in 0.1 M phosphate buffer (pH 2.5). Applied potential was +0.96 V (A) and plot of current versus $t^{-1/2}$ (B). Inset: Plot of slopes obtained from straight lines of 'B' versus concentration of $NO_2^-$.

**Table S1** Impedance values obtained from the fitted impedance spectrum of rGO-Ag (5.0 M) nanocomposite.

| **Parameters** | **Impedance Values** | **Relative standard error (%)** |
|---|---|---|
| Solution resistance ($R_s$) | 178.8 Ω | 2.177 |
| Double layer capacitance ($C_{dl}$) | 5.228E-7 F | 3.106 |
| Charge transfer resistance ($R_{ct}$) | 613.8 Ω | 1.76 |
| Warburg impedance ($Z_W$) | 0.000404 | 1.399 |




**Scheme S1.** Graphical illustration of NO electrooxidation at the rGO-Ag (5.0 M) nanocomposite modified GC electrode.

**Reference**

[1] P. Rameshkumar, R. Ramaraj, J. Electroanal. Chem. 731 (2014) 72.

[2] E. Laviron, J. Electroanal. Chem. Interfacial Electrochem. 100 (1979) 263.