

Supporting Information for:

**Oxidized/reduced graphene nanoribbons facilitate charge transfer to the
 $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple and towards oxygen reduction**

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Table S1. ECSA values for bare and modified GC electrodes obtained in an N₂-saturated 0.1 M KCl aqueous solution containing a total 2 mM concentration of K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1 molar ratio) [1].

Electrode	ECSA (cm ²)
Bare GC	0.33
GC/MWCNT2 (80 µg cm ⁻²)	0.37
GC/MWCNT2 (32 µg cm ⁻²)	0.23
GC/MWCNT2 (8 µg cm ⁻²)	0.08
GC/MWCNT2 (2 µg cm ⁻²)	0.14
GC/MWCNT1 (80 µg cm ⁻²)	0.50
GC/MWCNT1 (32 µg cm ⁻²)	0.42
GC/MWCNT1 (8 µg cm ⁻²)	0.22
GC/MWCNT1 (2 µg cm ⁻²)	0.24
GC/GONR2 (80 µg cm ⁻²)	0.64
GC/GONR2 (32 µg cm ⁻²)	0.54
GC/GONR2 (8 µg cm ⁻²)	0.37
GC/GONR2 (2 µg cm ⁻²)	0.36
GC/GONR1 (80 µg cm ⁻²)	0.30
GC/GONR1 (32 µg cm ⁻²)	0.25
GC/GONR1 (8 µg cm ⁻²)	0.38
GC/GONR1 (2 µg cm ⁻²)	0.22
GC/GNR2 (80 µg cm ⁻²)	0.77
GC/GNR2 (32 µg cm ⁻²)	0.43
GC/GNR2 (8 µg cm ⁻²)	0.39
GC/GNR2 (2 µg cm ⁻²)	0.38
GC/GNR1 (80 µg cm ⁻²)	0.51
GC/GNR1 (32 µg cm ⁻²)	0.47
GC/GNR1 (8 µg cm ⁻²)	0.38
GC/GNR1 (2 µg cm ⁻²)	0.36

S1. CV Responses from Bare GC, GC/MWCNT1, GC/MWCNT2, GC/GONR1, GC/GONR2, GC/GNR1, and GC/GNR2 Electrodes in an N₂-Saturated 0.1 M KCl Solution Containing a Total 2 mM Concentration of K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1 Molar Ratio)

The principal features of an electrochemically reversible (Nernstian) system observed during cyclic voltammetric experiments (reversible wave) are peak potential separation close to 60/*n* mV (25 °C), regardless of scan rate; chemical stability of the reduced form, demonstrated by a peak current ratio of 1, and *I*_p (as well as the current at any other point on the wave) proportional to $\nu^{1/2}$, intercepting the origin by extrapolation—a characteristic feature of Nernstian waves of diffusing species [1]. As we initially used K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (total 2 mM concentration, 1:1 molar ratio) as the redox probe—an expected Nernstian system—we examined in closer detail

the influence of electrode surface on the expected Nernstian behavior. In the case of a Nernstian system [1]:

$$I_p = (2.69 \times 10^5) n^{2/3} A D_R^{1/2} C_R^* \nu^{1/2} \quad (\text{S1})$$

where n is the number of transferred electrons, A is the electrochemically active surface area ($ECSA$), D_R is the diffusion coefficient of reduced species, and C_R^* is the bulk reduced-species concentration (for oxidized species, the terms diffusion coefficient of oxidized species and bulk oxidized-species concentration apply, respectively). Thus, if n , D_R and C_R^* are known, the slopes of I_p vs. $\nu^{1/2}$ (see insets A to Figures S1-S7), which are linear and intercept the origin by extrapolation, allow us to determine $ECSA$. In the present case, for $K_4[Fe(CN)_6]$ (cathodic branch), for example, n equaled 1, D_R was assumed equal to $6.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [2], and C_R^* was 1 mM.

Cyclic voltammogram curves normalized by $ECSA$ (Table S1) are shown in Figures S1-S7. The redox peaks are centered at around 0.19 V for bare GC (Figure S1), GC/MWCNT2, and GC/MWCNT1 electrodes (Figures S2 and S3, respectively), and 0.17 V for GC/GONR2, GC/GONR1, GC/GNR2, and GC/GNR1 electrodes (Figures S4-S7), with an $I_{p \text{ anodic}}/I_{p \text{ cathodic}}$ ratio approaching 1 when the potential scan rate is increased (see insets A to Figures S1-S7). However, peak potential separation approaches 76, 86, 63, 59, 84, 74, and 74 mV only at a low potential scan rate (insets B to Figures S1-S7). These responses enhance the surface effect of GC/MWCNT2, GC/MWCNT1, GC/GONR2, GC/GONR1, GC/GNR2, and GC/GNR1 electrodes on $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox behavior, since the only difference between the results obtained with GC/MWCNT2, GC/MWCNT1, GC/GONR2, GC/GONR1, GC/GNR2, and GC/GNR1 (Figures S2-S7) and bare GC (Figure S1) are the presence of a MWCNT2, MWCNT1, GONR2, GONR1, GNR2, or GNR1 film containing $80 \mu\text{g cm}^{-2}$ of the respective compound on the GC surface.

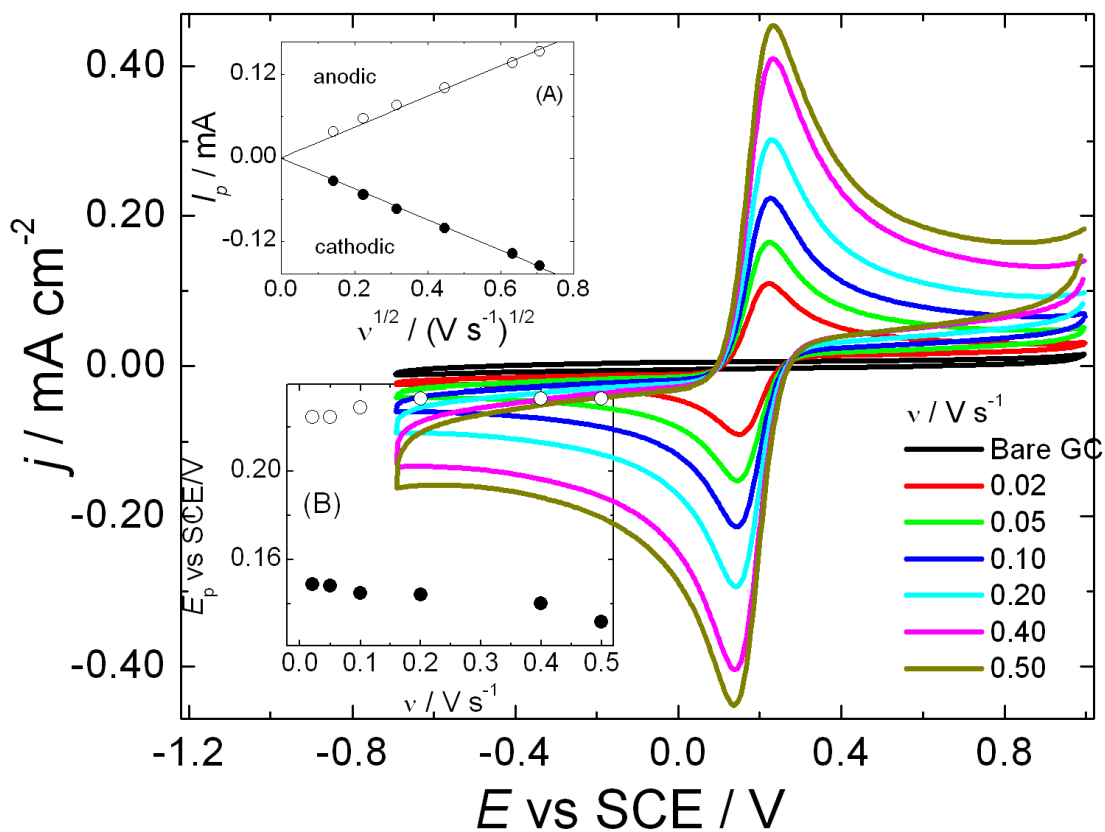


Figure S1. Cyclic voltammograms for a bare GC electrode in N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1 molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V.

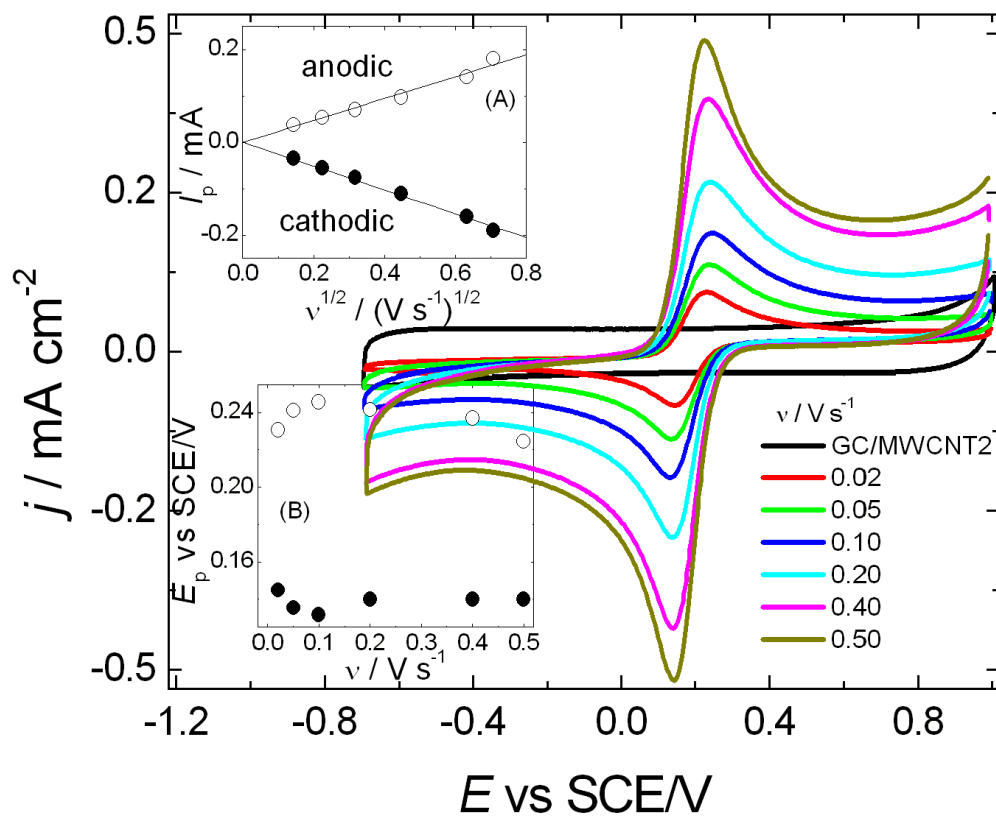


Figure S2. Cyclic voltammograms for a GC/MWCNT2 electrode ($80 \mu\text{g cm}^{-2}$ of MWCNT2 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ ($1:1$ molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V .

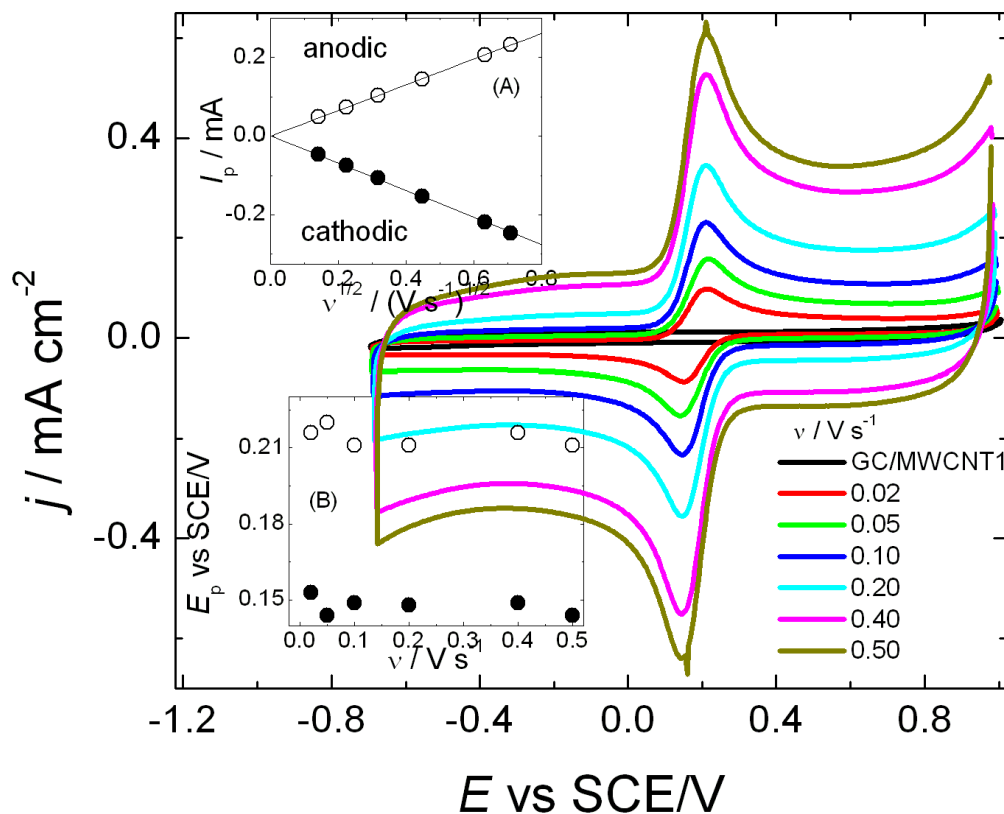


Figure S3. Cyclic voltammograms for a GC/MWCNT1 electrode (80 $\mu\text{g cm}^{-2}$ of MWCNT1 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1 molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V.

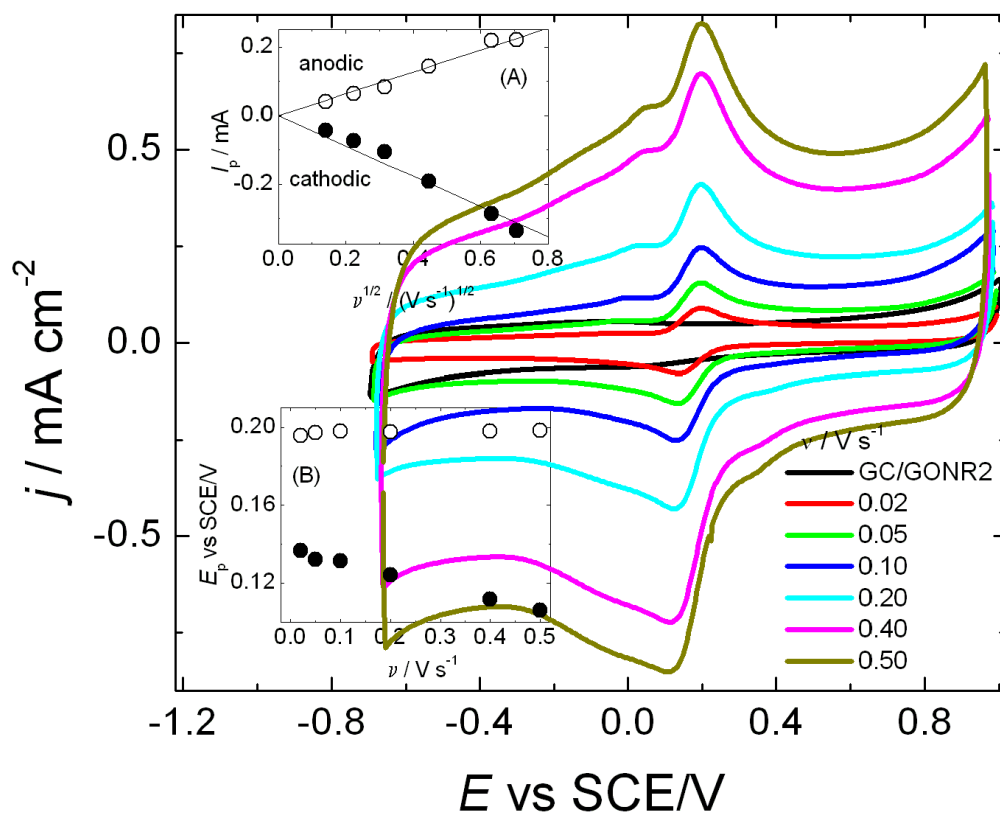


Figure S4. Cyclic voltammograms for a GC/GONR2 electrode ($80 \mu\text{g cm}^{-2}$ of GONR2 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1 molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V.

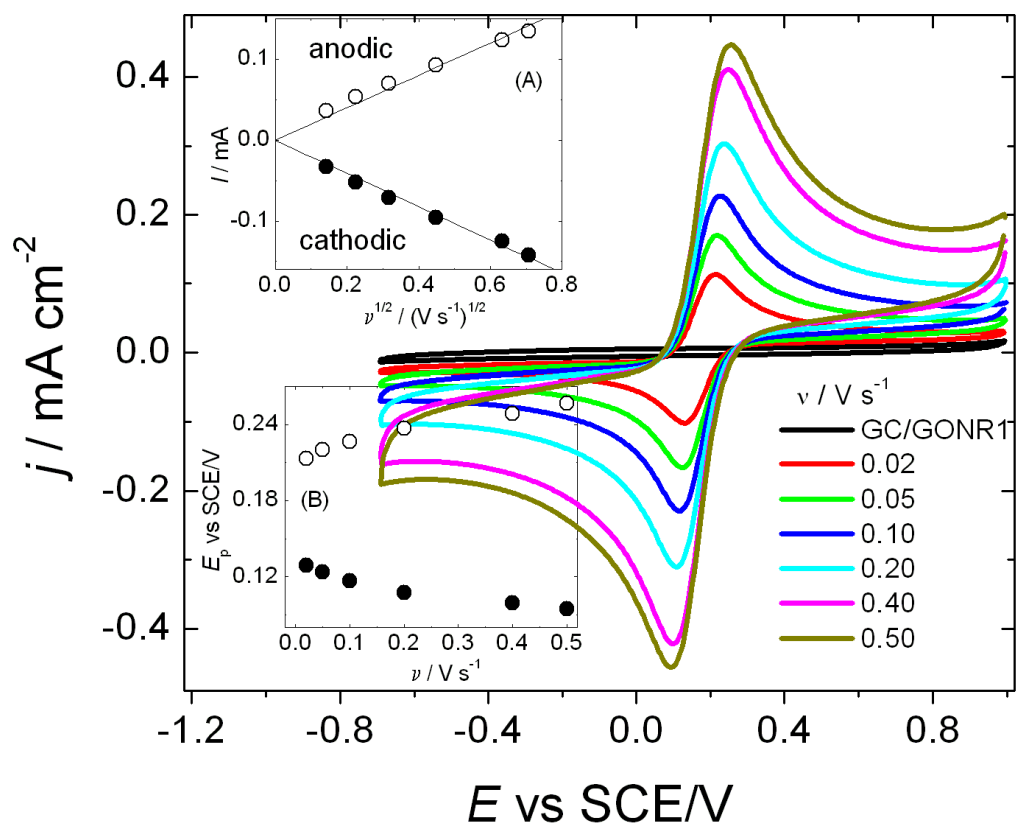


Figure S5. Cyclic voltammograms for a GC/GONR1 electrode (80 $\mu\text{g cm}^{-2}$ of GONR1 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1 molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V.

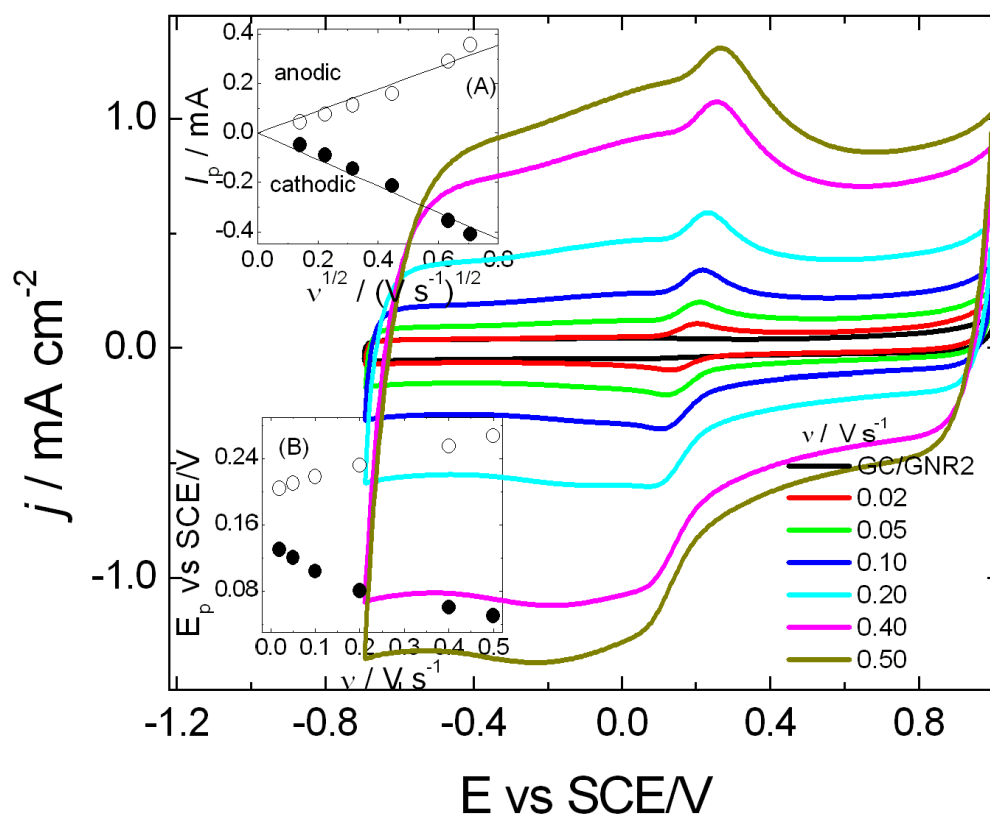


Figure S6. Cyclic voltammograms for a GC/GNR2 electrode ($80 \mu\text{g cm}^{-2}$ of GNR2 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ ($1:1$ molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate plot (B) for the same electrode and conditions. Scans started at 1.0 V .

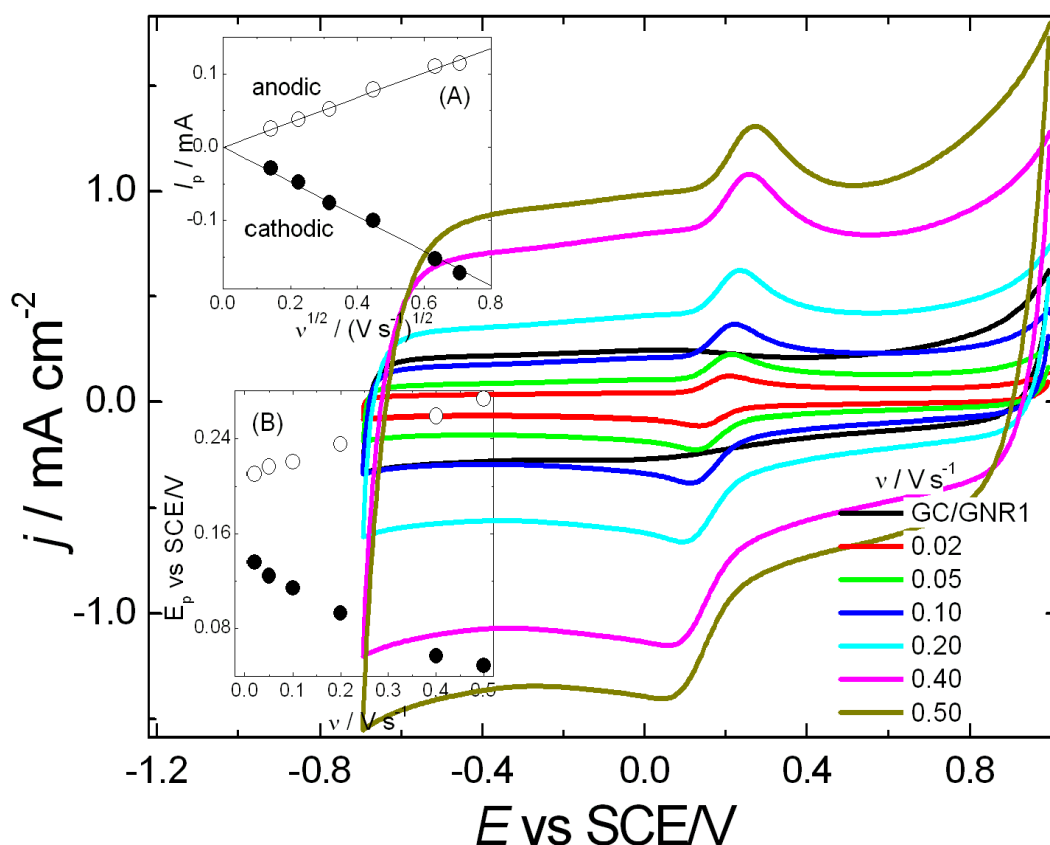


Figure S7. Cyclic voltammograms for a GC/GNR1 electrode ($80 \mu\text{g cm}^{-2}$ of GNR1 on the GC surface) in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ ($1:1$ molar ratio). Insets: Anodic and cathodic peak currents vs. square-root potential scan rate (A) and anodic and cathodic peak potentials vs. potential scan rate (B) for the same electrode and conditions. Scans started at 1.0 V .

When the loadings of MWCNT2, MWCNT1, GONR2, GONR1, GNR2, or GNR1 on the GC surface are decreased, redox peaks remain centered at around 0.20 V for GC/MWCNT2 and GC/MWCNT1, and at 0.17 V for GC/GONR2, GC/GONR1, GC/GNR2, and GC/GNR1, with $I_{\text{p anodic}}/I_{\text{p cathodic}}$ ratios approaching 1 when the potential scan rate is increased. For GC/MWCNT2, GC/MWCNT1, GC/GONR2, and GC/GONR1 electrodes, I_{p} intercepting the origin by extrapolation is not as proportional to $v^{1/2}$ at low loadings ($2 \mu\text{g cm}^{-2}$). In addition, peak potential separation approaches $570\text{--}170 \text{ mV}$ only at a low potential scan rate for GC/MWCNT2, GC/MWCNT1, and GC/GONR1 electrodes, making the surface effect of GC/MWCNT2, GC/MWCNT1, GC/GONR2, GC/GONR1, GC/GNR2, and GC/GNR1 electrodes on $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox behavior differ from that exerted by bare GC (results not shown). Also, ECSA decreases substantially when the MWCNT2,

MWCNT1, GONR2, GONR1, GNR2, or GNR1 loadings on the GC surface are lowered (Table S1).

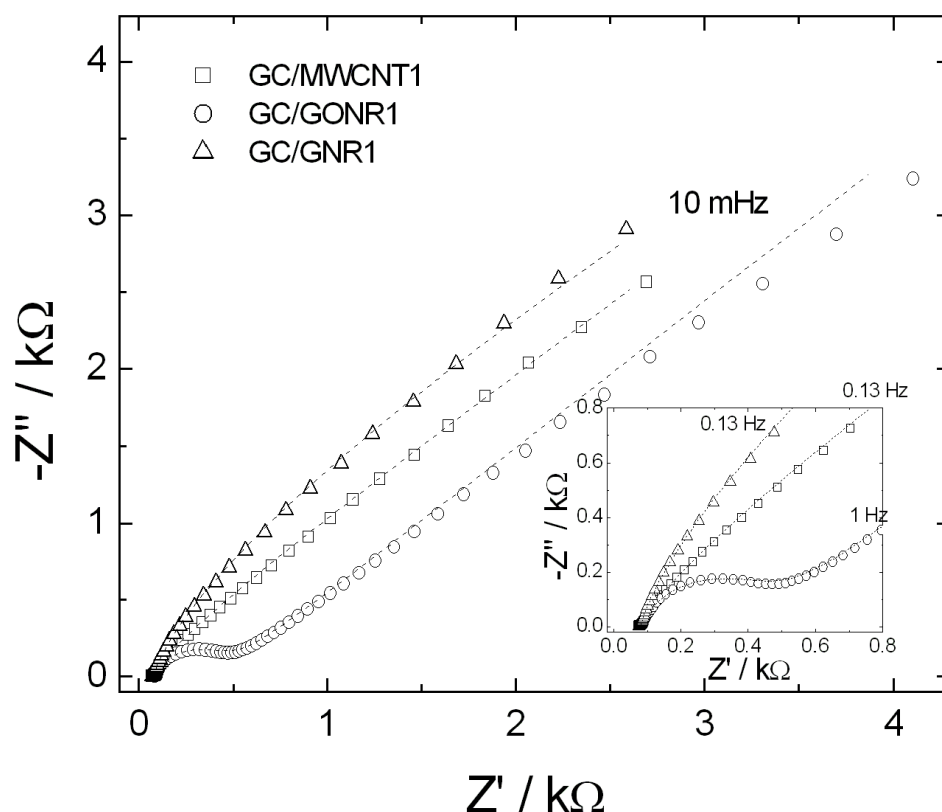


Figure S8. Impedance plane plots obtained in an N_2 -saturated 0.1 M KCl solution containing a total 2 mM concentration of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1 molar ratio) for GC electrodes surface-modified with $80 \mu g cm^{-2}$ of MWCNT1 ($\square$), GONR1 ($\circ$), or GNR1 ($\triangle$). Potential perturbation: 25 mV (rms). Frequency range: 100 kHz–10 mHz. Constant potential for EIS acquisition: OCP (0.18 V vs. SCE on average). Lines represent spectra (adjusted) calculated using a non-linear least-squares program, conforming to the equivalent circuit $R_s[Q_{dl}(R_{ct}W_{lf})]$, or $R_s[Q_{dl}(R_{ct}Q_{lf})]$. Calculated average values: $R_s = 70 \Omega$, $Q_{dl} = 0.80 mF s^{n-1}$, $n = 0.60$, $W_{lf} = 0.70 mF$. Inset: Impedance plane plots restricted to 0.8 k Ω in the main graph.

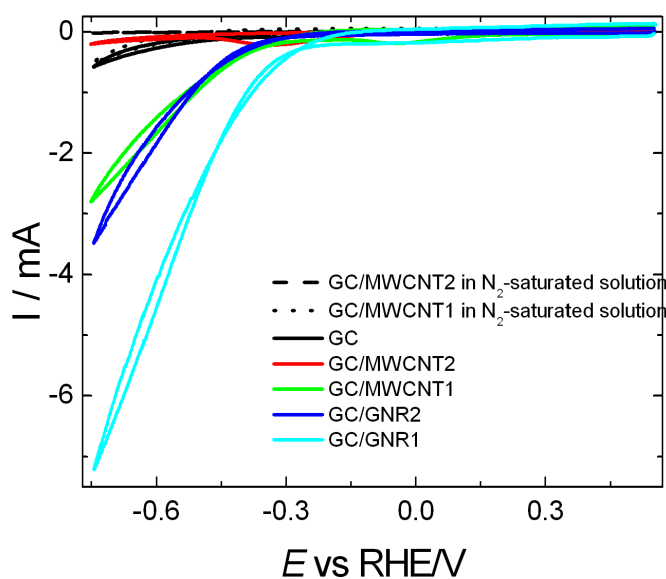


Figure S9. Cyclic voltammograms obtained in N₂- or O₂-saturated 0.1 M HClO₄ for a bare GC electrode and GC electrodes surface-modified with 80 $\mu\text{g cm}^{-2}$ of MWCNT1, MWCNT2, GNR1, or GNR2. $\nu = 50 \text{ mV s}^{-1}$. Scans started at 0.55 V.

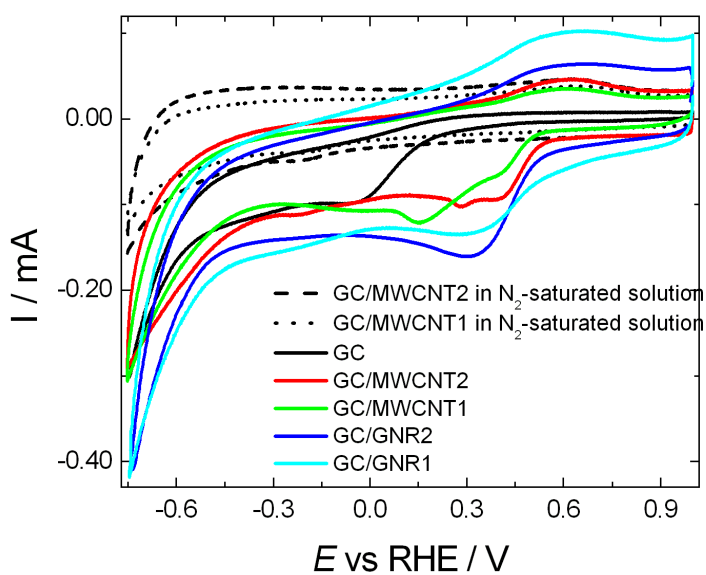


Figure S10. Cyclic voltammograms obtained in N₂- or O₂-saturated 0.1 M KH₂PO₄ (pH 7.0) for a bare GC electrode and GC electrodes surface-modified with 80 $\mu\text{g cm}^{-2}$ of MWCNT1, MWCNT2, GNR1, or GNR2. $\nu = 50 \text{ mV s}^{-1}$. Scans started at 1.00 V.

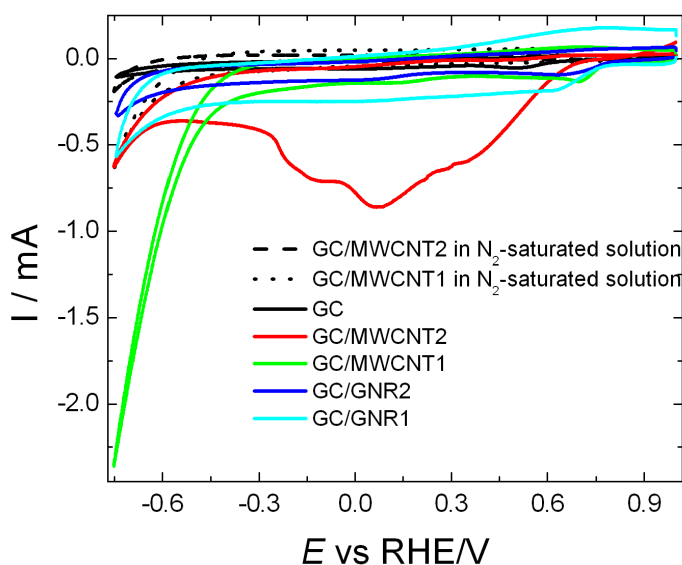


Figure S11. Cyclic voltammograms obtained in N_2 - or O_2 -saturated 0.1 M KOH for a bare GC electrode and GC electrodes surface-modified with $80 \mu\text{g cm}^{-2}$ of MWCNT1, MWCNT2, GNR1, or GNR2. $\nu = 50 \text{ mV s}^{-1}$. Scans started at 1.00 V.

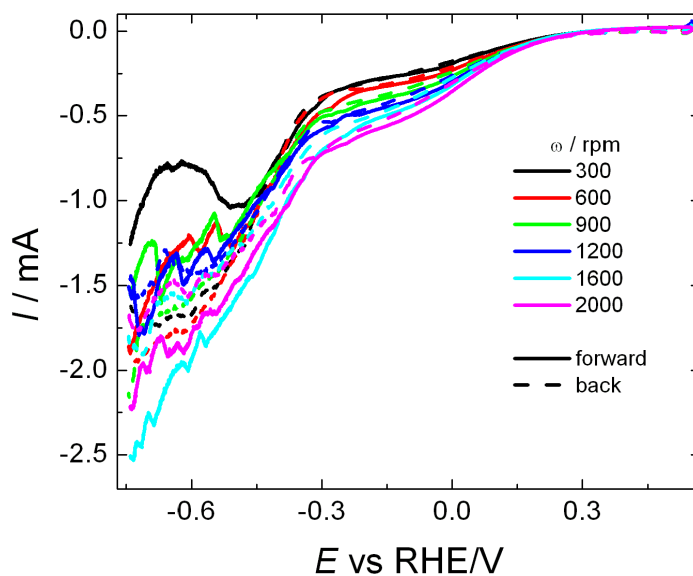


Figure S12. Hydrodynamic voltammetry curves obtained in O_2 -saturated 0.1 M HClO_4 for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1, subtracted from their respective hydrodynamic voltammetry curves obtained in N_2 -saturated 0.1 M HClO_4 . $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

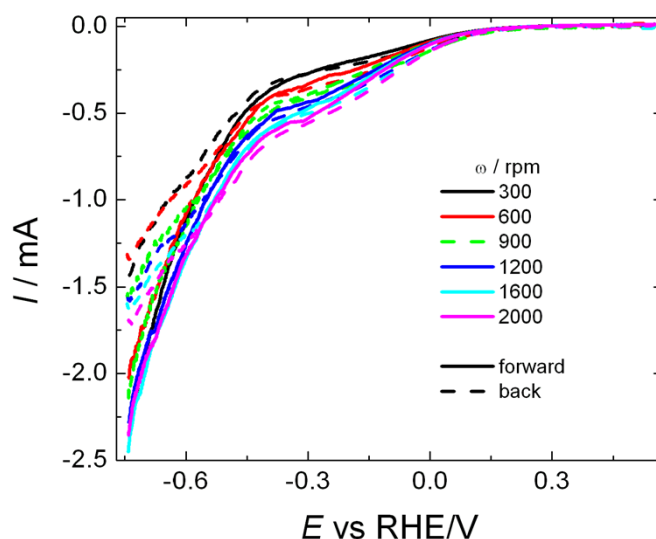


Figure S13. Hydrodynamic voltammetry curves obtained in O_2 -saturated 0.1 M HClO_4 for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR2, subtracted from their respective hydrodynamic voltammetry curves obtained in N_2 -saturated 0.1 M HClO_4 . $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

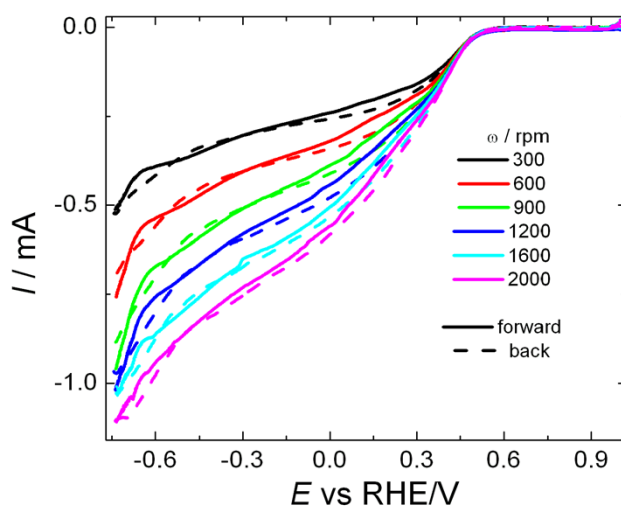


Figure S14. Hydrodynamic voltammetry curves obtained in O_2 -saturated 0.1 M KH_2PO_4 (pH 7.0) for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1, subtracted from their respective hydrodynamic voltammetry curves obtained in N_2 -saturated 0.1 M KH_2PO_4 (pH 7.0). $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

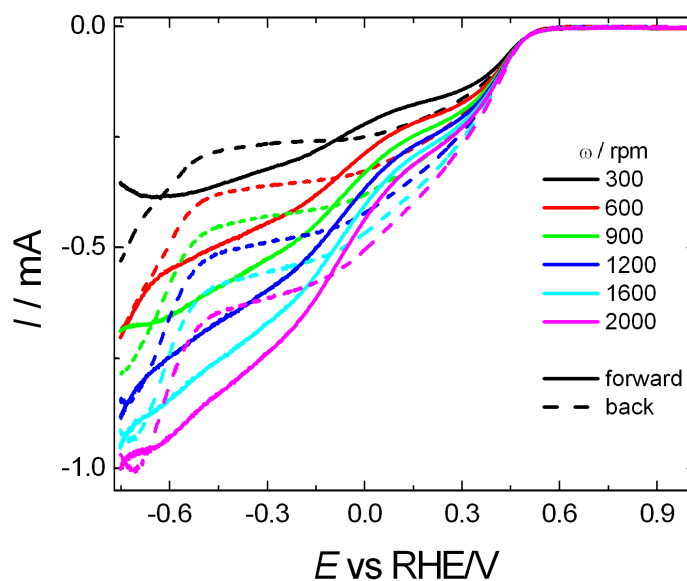


Figure S15. Hydrodynamic voltammetry curves obtained in O_2 -saturated 0.1 M KH_2PO_4 (pH 7.0) for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR2, subtracted from their respective hydrodynamic voltammetry curves obtained in N_2 -saturated 0.1 M KH_2PO_4 (pH 7.0). $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

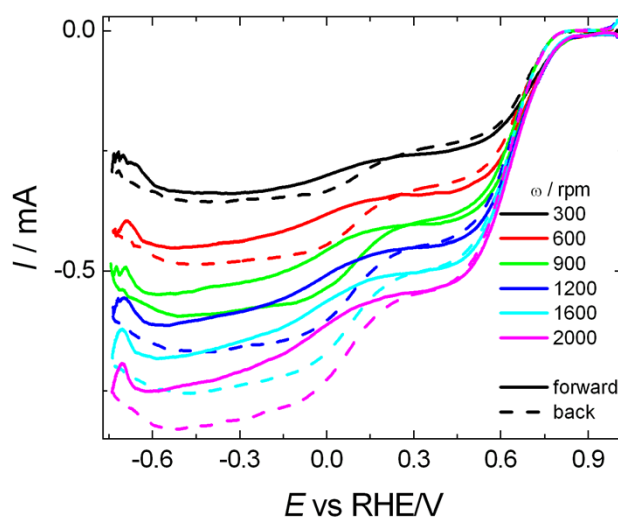


Figure S16. Hydrodynamic voltammetry curves obtained in O_2 -saturated 0.1 M KOH for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1, subtracted from their respective hydrodynamic voltammetry curves obtained in N_2 -saturated 0.1 M KOH . $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

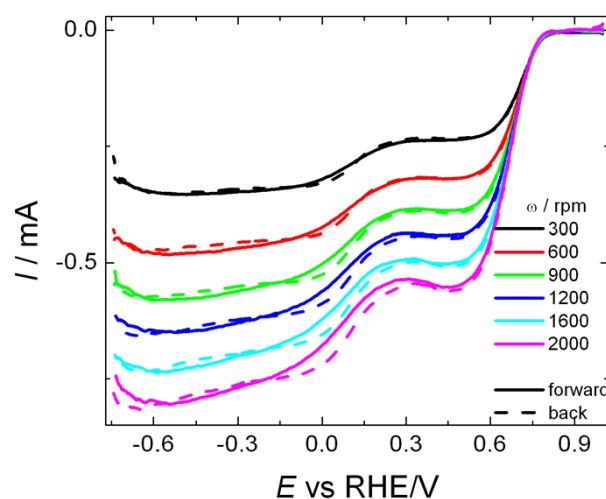


Figure S17. Hydrodynamic voltammograms obtained in O_2 -saturated 0.1 M KOH for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR2, subtracted from their respective hydrodynamic voltammograms obtained in N_2 -saturated 0.1 M KOH. $\nu = 10 \text{ mV s}^{-1}$. Scans started at -0.75 V .

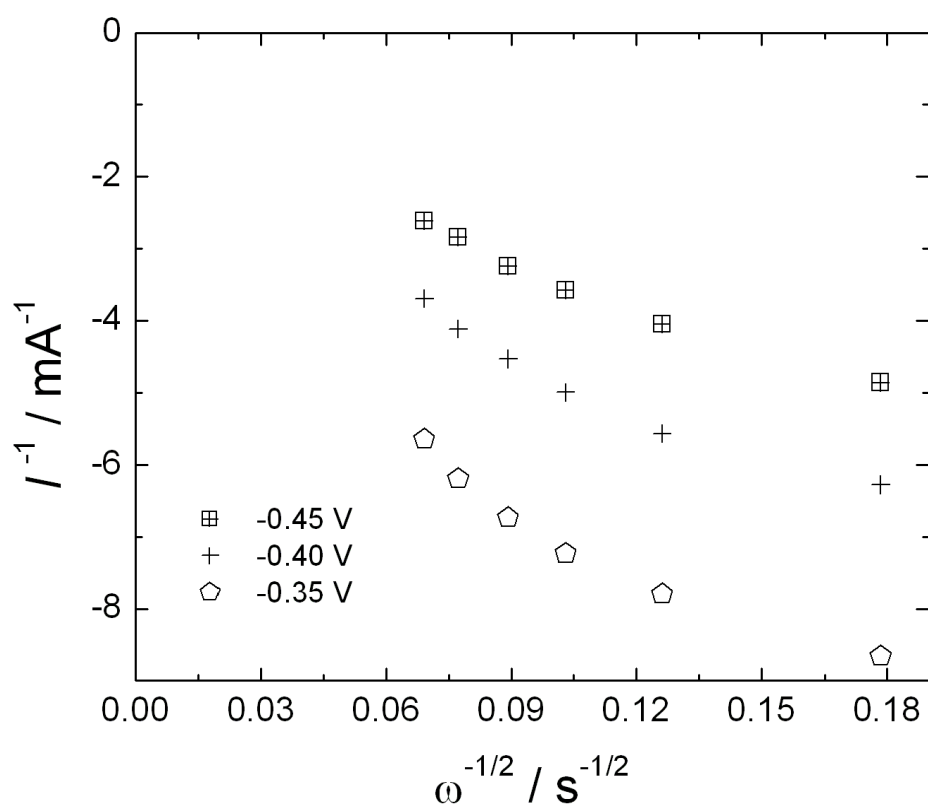


Figure S18. Koutecký–Levich plots based on negative-going potential scans for O_2 reduction on a bare GC electrode in O_2 -saturated 0.1 M HClO_4 .

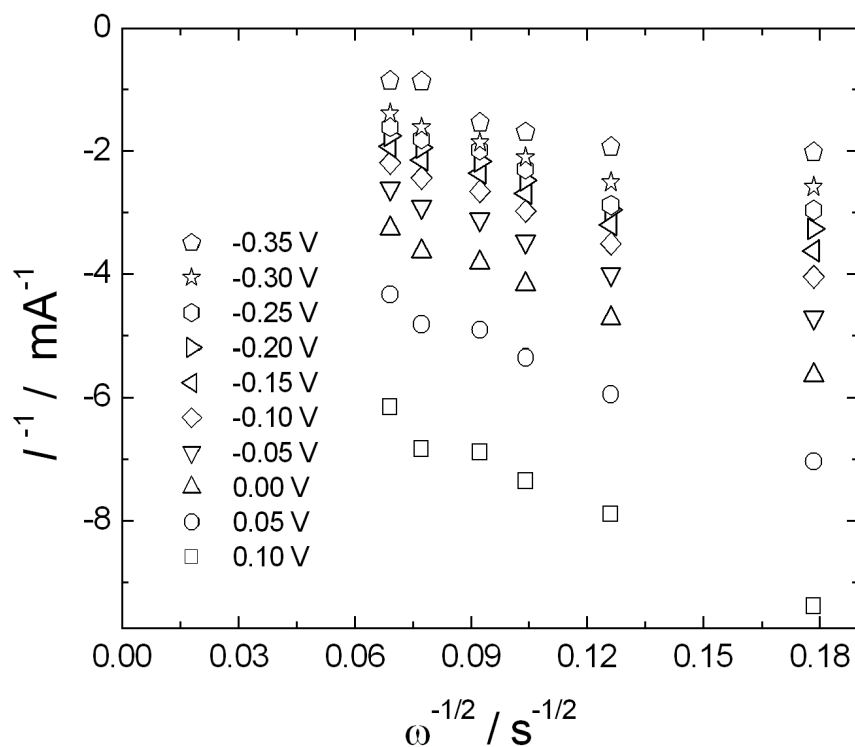


Figure S19. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated 0.1 M HClO_4 for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1 (data from Figure S12).

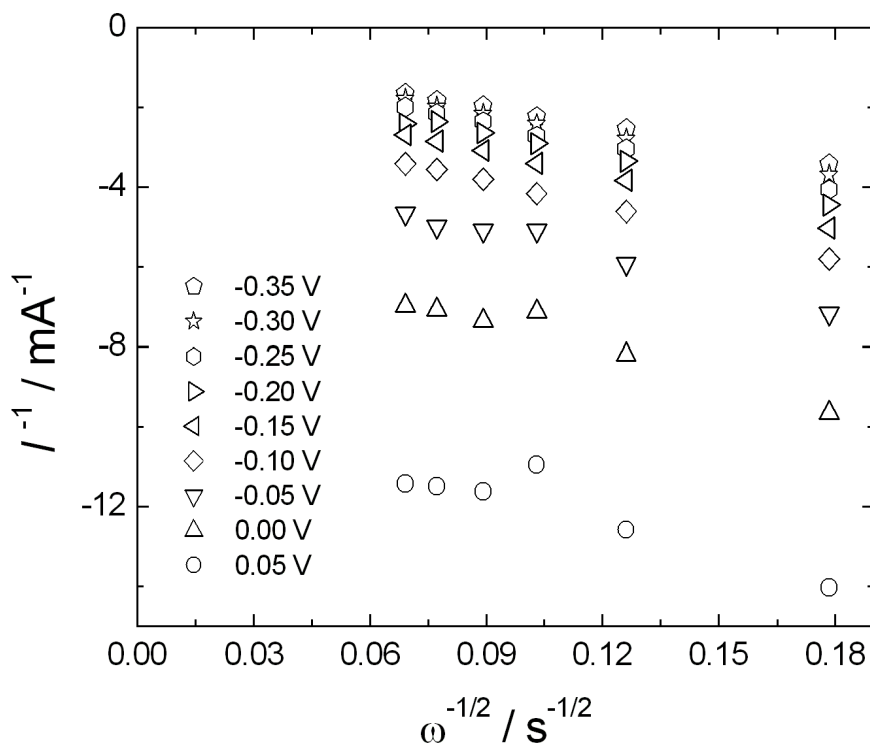


Figure S20. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated 0.1 M HClO_4 for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR2 (data from Figure S13).

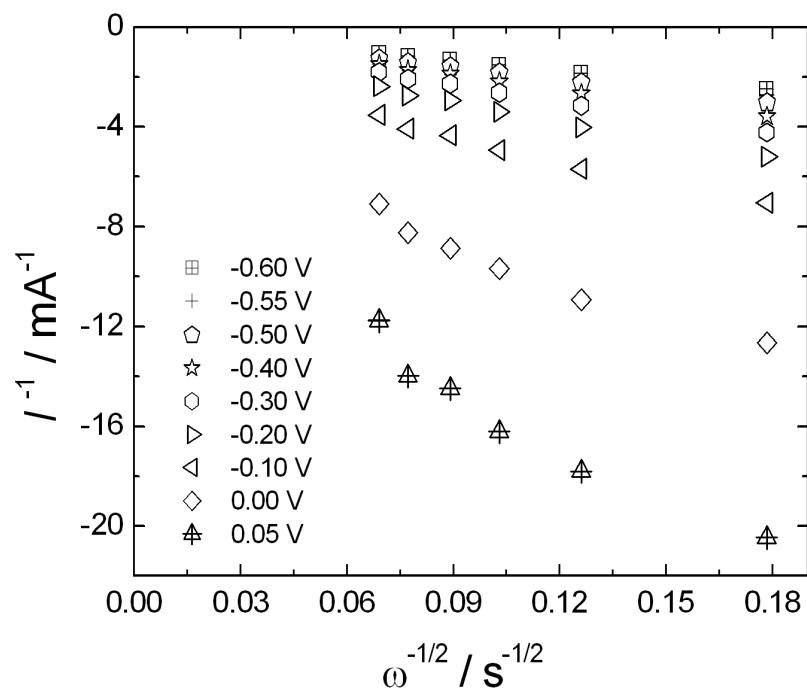


Figure S21. Koutecký–Levich plots based on negative-going potential scans for O_2 reduction on a bare GC electrode in O_2 -saturated 0.1 M KH_2PO_4 (pH 7.0).

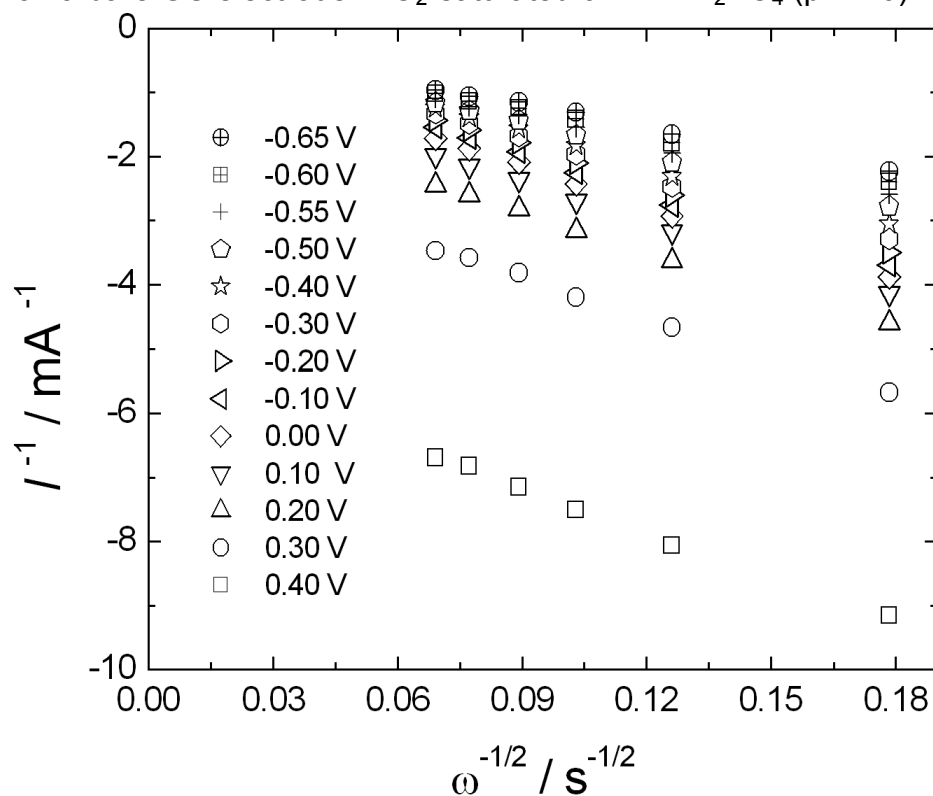


Figure S22. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated 0.1 M KH_2PO_4 (pH 7.0) for O_2 reduction on a GC electrode surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1 (data from Figure S14).

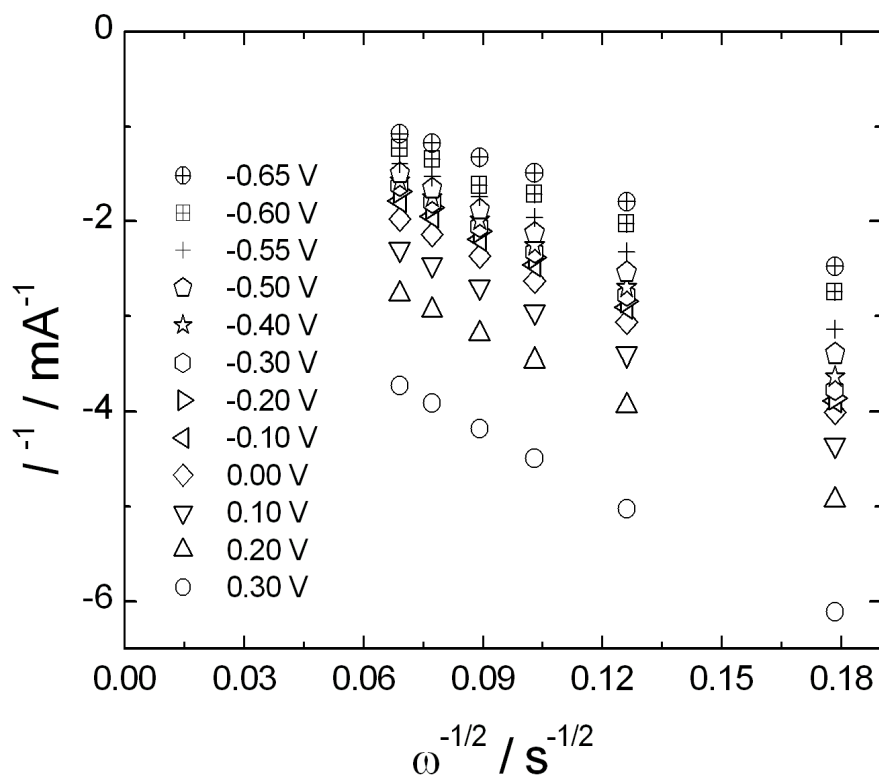


Figure S23. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated $0.1 \text{ M KH}_2\text{PO}_4$ (pH 7.0) for O_2 reduction on a GC electrode surface modified with $80 \mu\text{g cm}^{-2}$ of GNR2 (data from Figure S15).

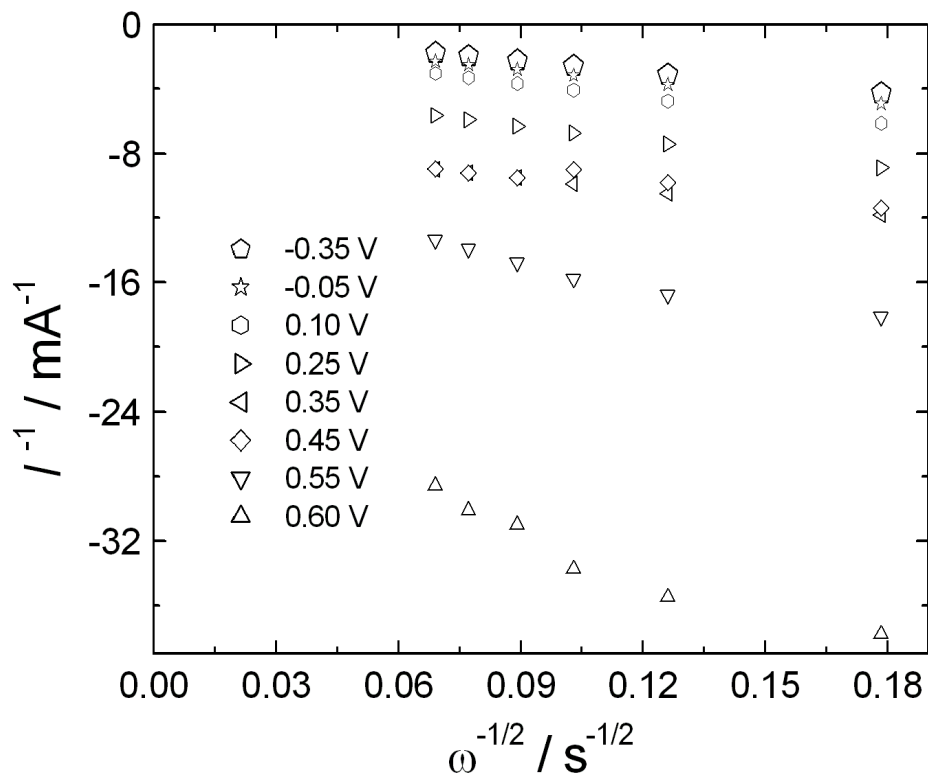


Figure S24. Koutecký–Levich plots based on negative-going potential scans for O_2 reduction on a bare GC electrode in O_2 -saturated 0.1 M KOH .

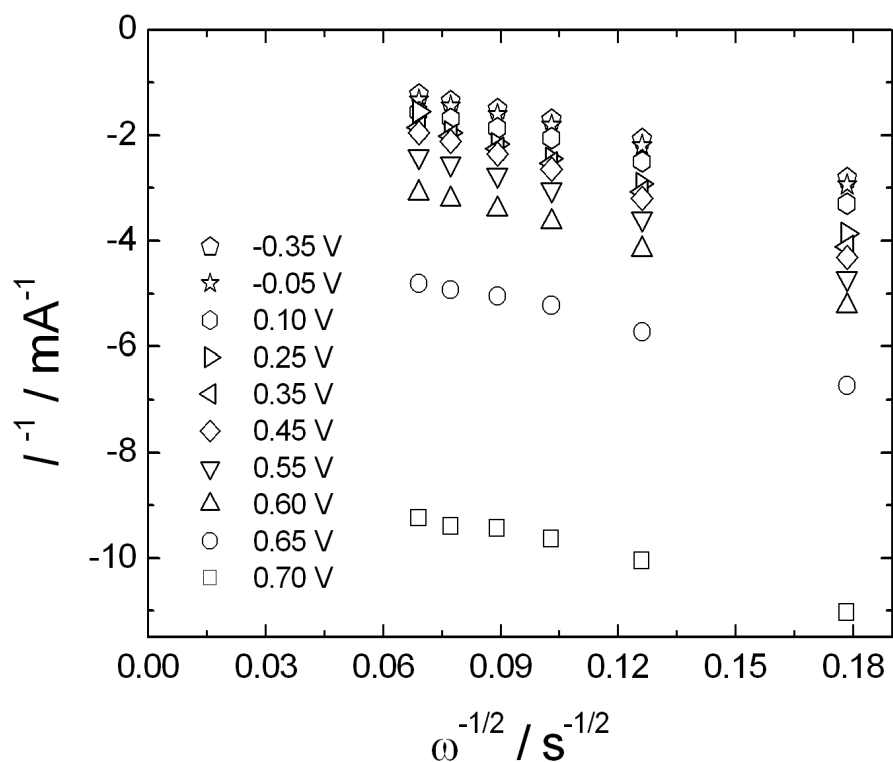


Figure S25. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated 0.1 M KOH for O_2 reduction on a GC electrode surface-modified with 80 $\mu\text{g cm}^{-2}$ of GNR1 (data from Figure S16).

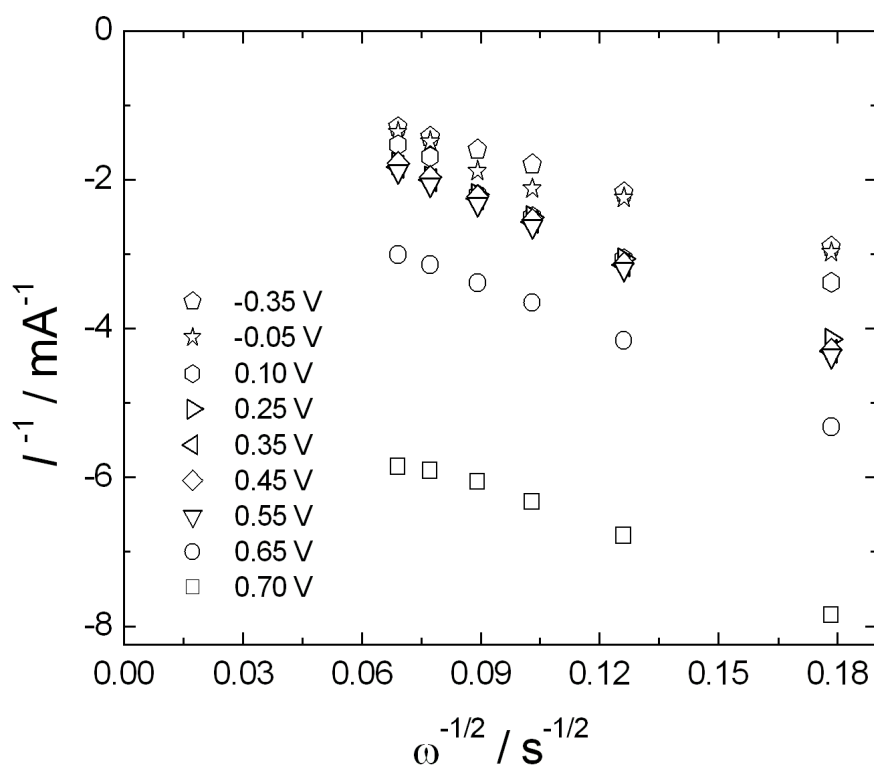


Figure S26. Koutecký–Levich plots based on negative-going potential scans in O_2 -saturated 0.1 M KOH for O_2 reduction on a GC electrode surface-modified with 80 $\mu\text{g cm}^{-2}$ of GNR2 (data from Figure S17).

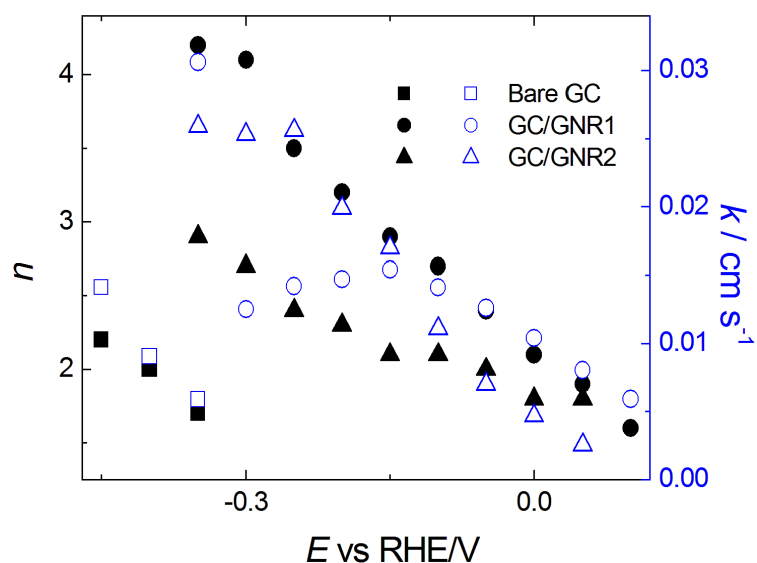


Figure S27. n and k vs. E plots obtained from data in Figures S18-S20 for O_2 reduction on a bare GC electrode and GC electrodes surface-modified with $80 \mu\text{g cm}^{-2}$ of GNR1 or GNR2, in O_2 -saturated 0.1 M HClO_4 .

Table S2. Percentages of H_2O_2 formation, calculated using Equations S2 and S3.

Solution	Electrode (and loading of modifier)	Positive-direction potential (V) scan				Negative-direction potential (V) scan			
		0.45	-0.15	-0.30	-0.35	0.45	-0.15	-0.30	-0.35
0.1 M $HClO_4$	Bare GC	-	0.06	-	-	-	0.03	-	-
	GC/GNR1 ($80 \mu\text{g cm}^{-2}$)	-	0.08	-	-	-	0.13	-	-
	GC/GNR2 ($80 \mu\text{g cm}^{-2}$)	-	0.05	-	-	-	0.06	-	-
0.1 M KH_2PO_4 (pH 7.0)	Bare GC	-	-	0.25	-	-	-	0.60	-
	GC/GNR1 ($80 \mu\text{g cm}^{-2}$)	-	-	2.05	-	-	-	1.45	-
	GC/GNR2 ($80 \mu\text{g cm}^{-2}$)	-	-	0.43	-	-	-	0.60	-
0.1 M KOH	Bare GC	39.5			14.5	33.6			8.5
	GC/GNR1 ($80 \mu\text{g cm}^{-2}$)	20.4			25.3	15.9			7.2
	GC/GNR2 ($80 \mu\text{g cm}^{-2}$)	49.2			37.4	34.1			14.1

The fraction (percentage) of H_2O_2 formation, $X_{\text{H}_2\text{O}_2}$, can be calculated from the molar flux rates of O_2 , $\dot{n}_{\text{O}_2(4e^-)}$, and H_2O_2 , $\dot{n}_{\text{O}_2(2e^-)}$, according to Equations S2 and S3 [3-5]:

$$\dot{n}_{\text{O}_2(4e^-)} = \frac{I_{\text{H}_2\text{O}}}{4F} \quad \text{and} \quad \dot{n}_{\text{O}_2(2e^-)} = \frac{I_{\text{H}_2\text{O}_2}}{2F} \quad (\text{S2})$$

$$X_{\text{H}_2\text{O}_2} = \frac{\dot{n}_{\text{O}_2(2e^-)}}{\dot{n}_{\text{O}_2(2e^-)} + \dot{n}_{\text{O}_2(4e^-)}} = \frac{\frac{2}{N} \frac{I_R}{I_D}}{1 + \frac{I_R}{I_D}} \quad (\text{S3})$$

where $I_{\text{H}_2\text{O}} = I_D - I_{\text{H}_2\text{O}_2}$, $I_{\text{H}_2\text{O}_2} = I_R N^{-1}$, and $N = -\frac{I_R}{I_D}$, such that $I_{\text{H}_2\text{O}}$ and $I_{\text{H}_2\text{O}_2}$ are the currents for O_2 reduction to water and H_2O_2 , respectively, F is the Faraday constant ($96\,485 \text{ C mol}^{-1}$), I_R and I_D are the ring and disk currents, respectively, and N is the collection efficiency (0.26).

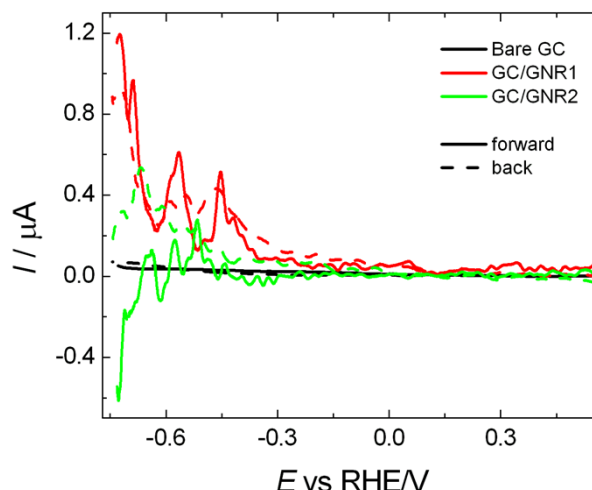


Figure S28. Hydrodynamic voltammetric curves for a Au ring electrode maintained at 1.0 V during potential scan (scan rate: 10 mV s^{-1}) using a bare GC electrode and a GC disk electrode modified with $80 \mu\text{g cm}^{-2}$ of GNR1 or GNR2 in O_2 -saturated 0.1 M HClO_4 . $\omega = 1600 \text{ rpm}$.

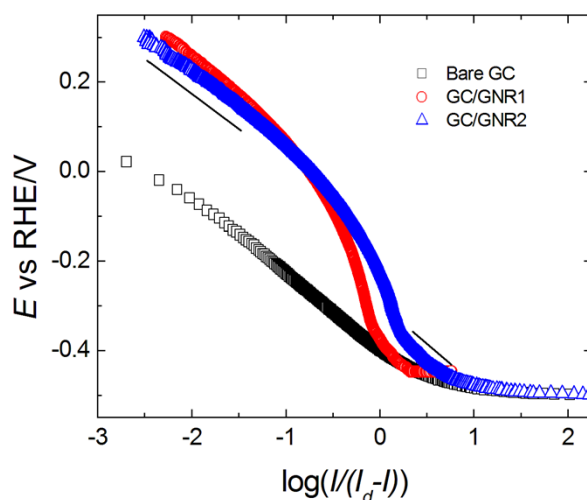


Figure S29. Tafel curves drawn from data in Figures S12-S13 for hydrodynamic voltammetric curves obtained at 1600 rpm. Lines indicate the regions selected to determine Tafel inclinations at low and high polarizations (currents).

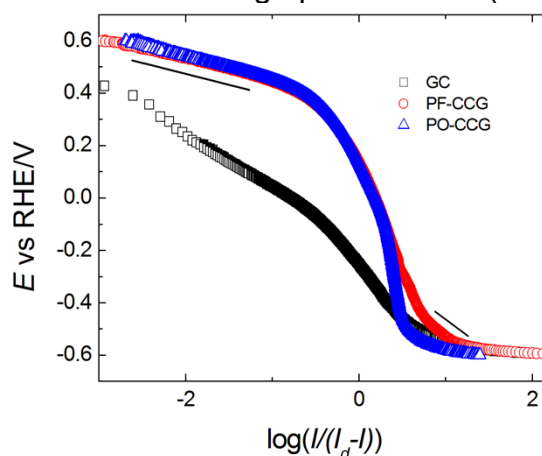


Figure S30. Tafel curves drawn from data in Figures S14-S15 for hydrodynamic voltammetric curves obtained at 1600 rpm. Lines indicate the regions selected to determine Tafel inclinations at low and high polarizations (currents).

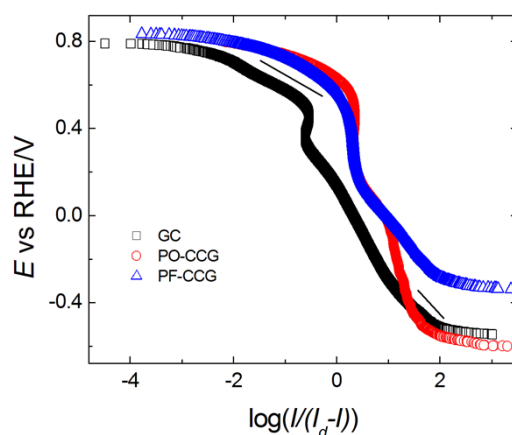


Figure S31. Tafel curves drawn from data in Figures S16-S17 for hydrodynamic voltammetric curves obtained at 1600 rpm. Lines indicate the regions selected to determine Tafel inclinations at low and high polarizations (currents).

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