Electronic Supplementary Material (ESI) for Analyst.

Evaluation of the electroanalytical performance of carbon-on-gold films prepared by electron-beam evaporation

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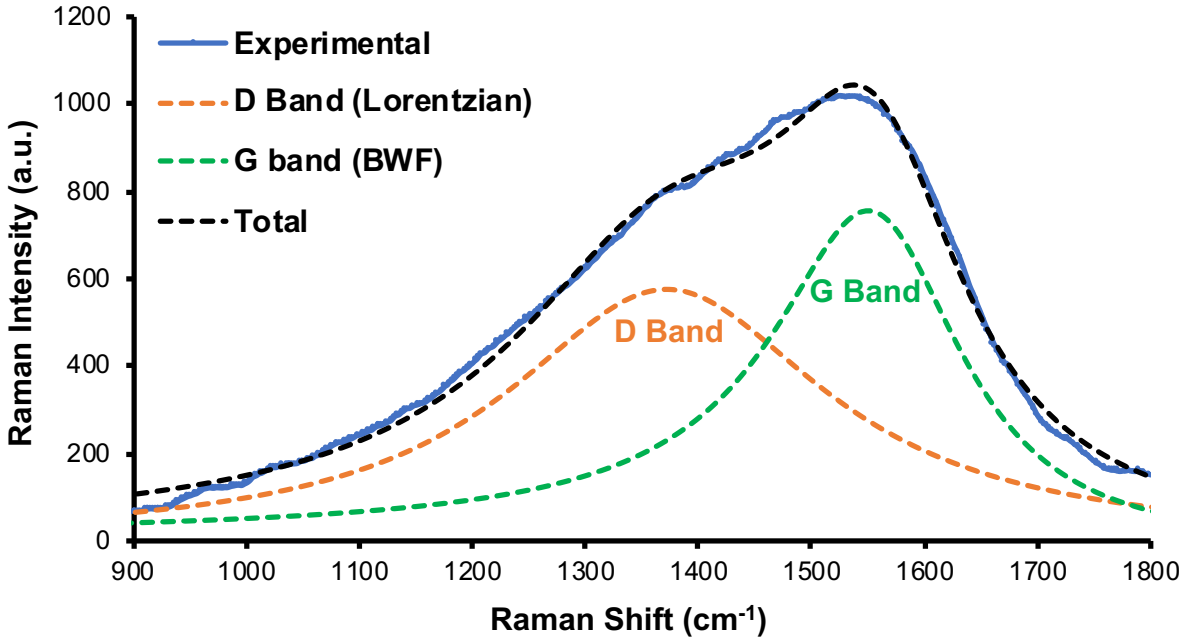

Figure S1. Raman spectrum of eC/Au (514.5 nm, 30 mW, 100 s, 50x). Breit-Wigner-Fano (BWF) and Lorentzian fittings for D and G bands respectively results in excellent deconvolution with low residuals as suggested by Ferrari and Robertson.[1] The relative positions of D (1372 cm^{-1}) and G (1559 cm^{-1}) bands were used to estimate sp^3 content. [1]

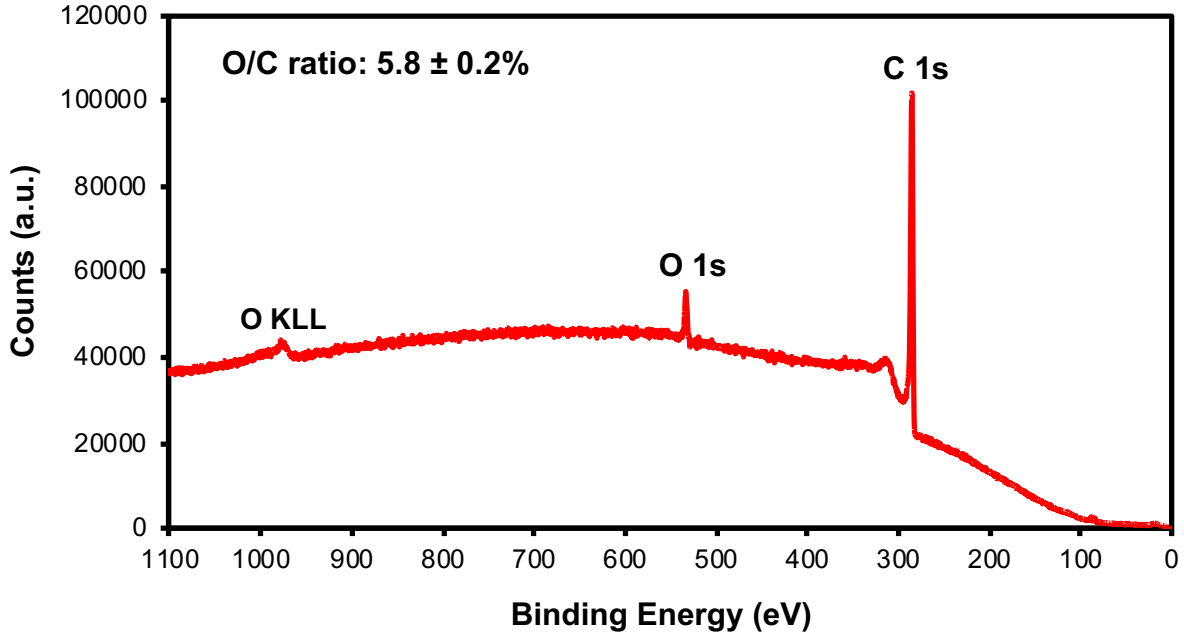

Figure S2. XPS survey spectrum of freshly prepared eC/Au.

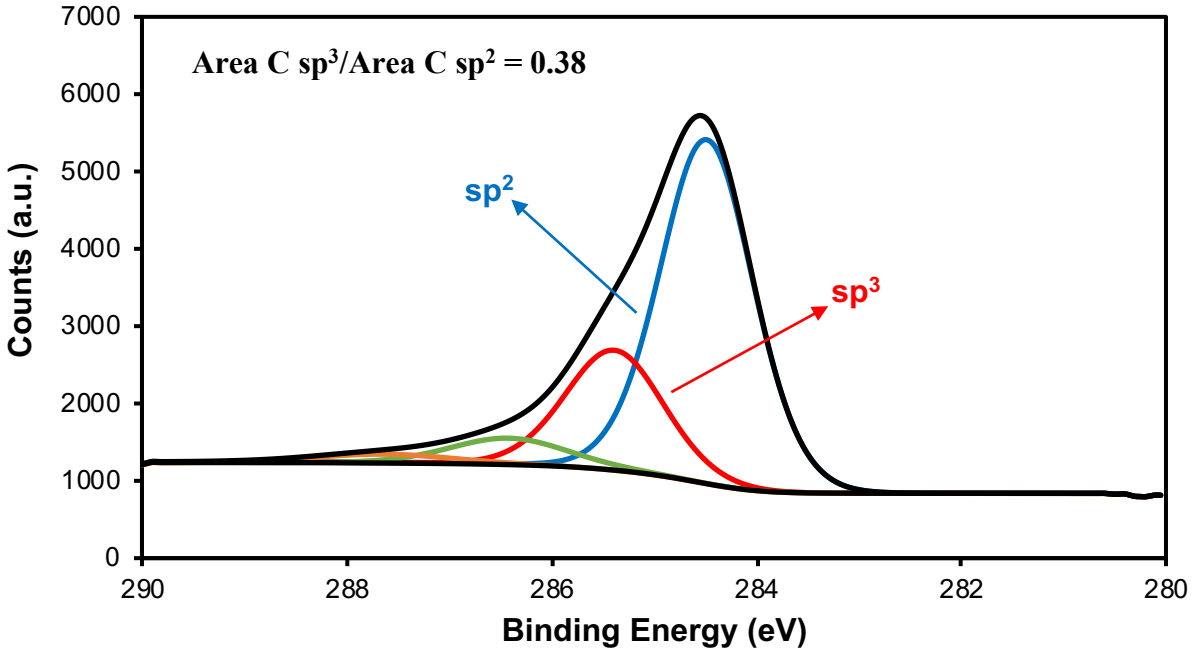

Figure S3. XPS C1s high resolution spectrum of freshly prepared eC/Au. The C1s peak can be decomposed into 4 components. The peaks at 284.3 eV and 285.3 eV are assigned to sp^2 and sp^3 hybrids, respectively.[2]

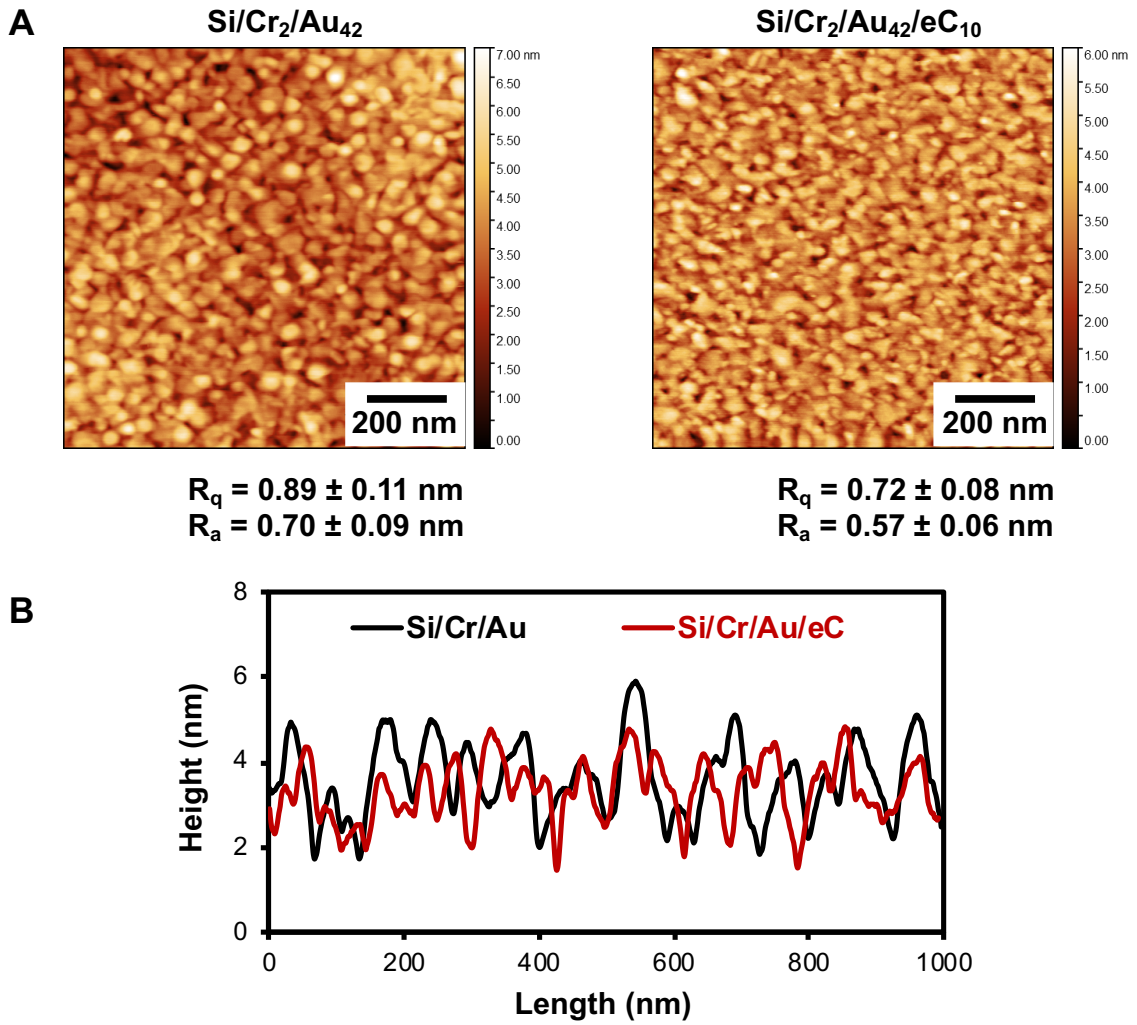

Figure S4. (A) AFM images of $Si/Cr_2/Au_{42}$ (Au) and $Si/Cr_2/Au_{42}/eC_{10}$ (eC/Au) films (the subscripts indicate thicknesses in nm). (B) AFM line scan profiles of the surfaces shown in panel A.

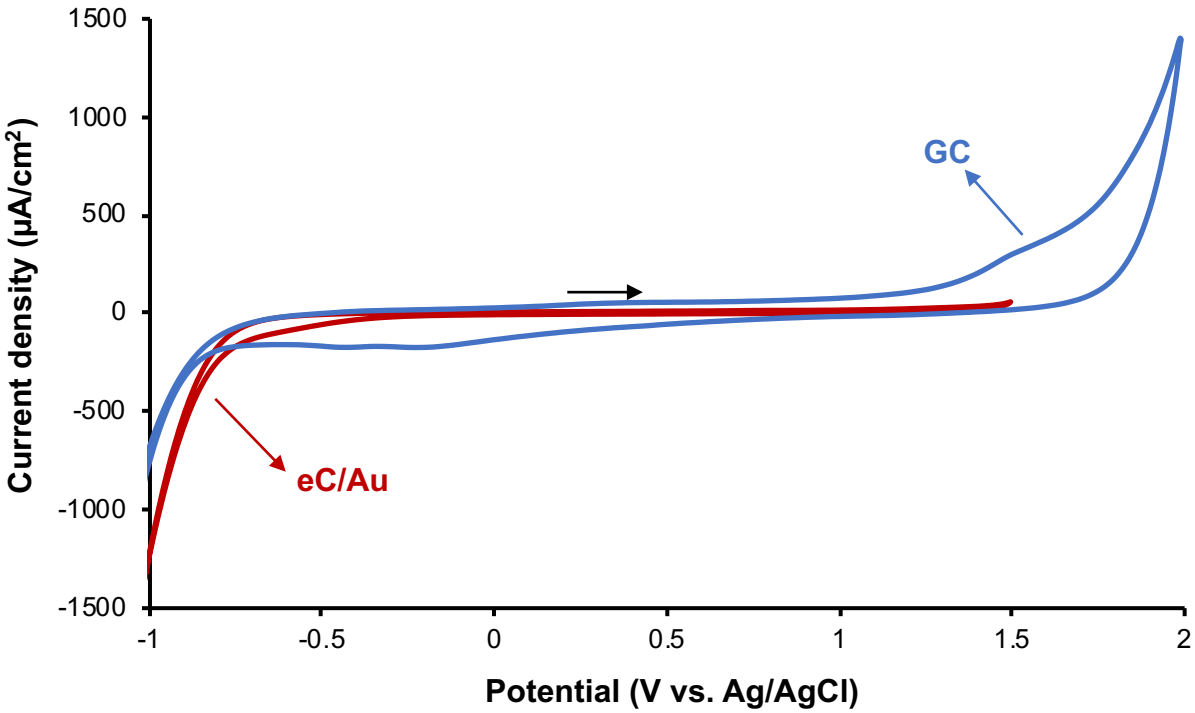

Figure S5. Background voltammograms of eC/Au and polished GC in H_2SO_4 0.05 M, $\nu = 0.1$ V/s. The current is normalized to the electrode area to give current density. The black arrow indicates the scan direction.

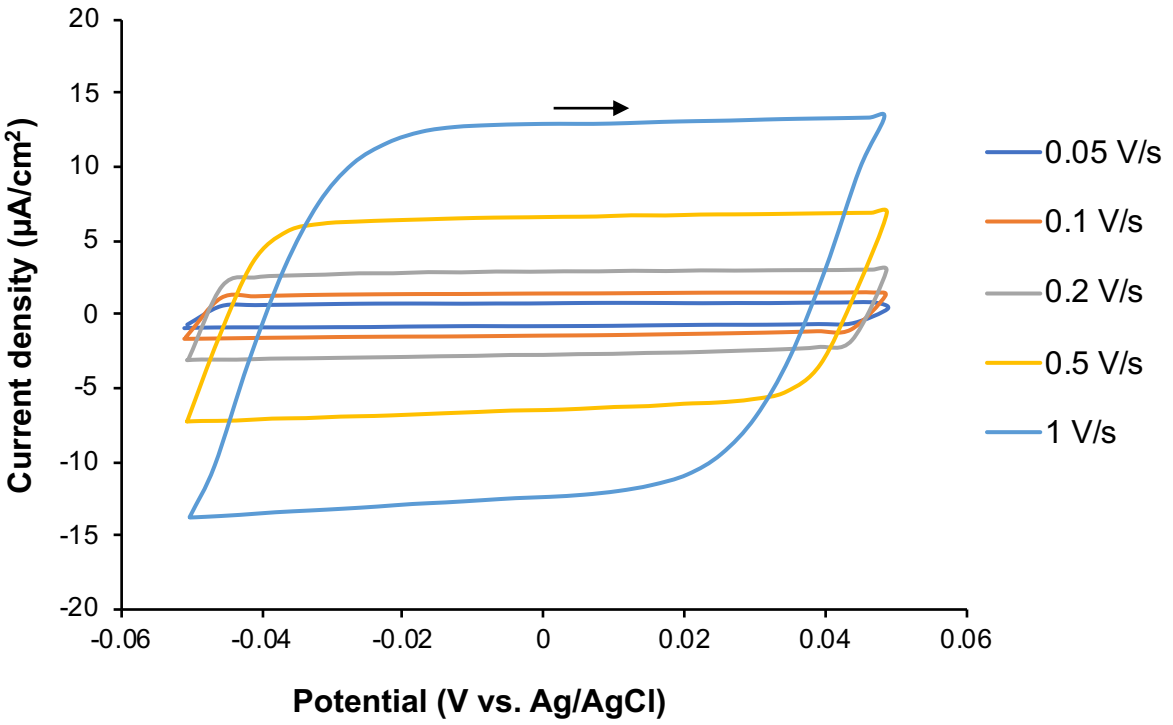

Figure S6. Scan rate dependent background current for eC/Au in 1 M KCl. The black arrow indicates the scan direction.

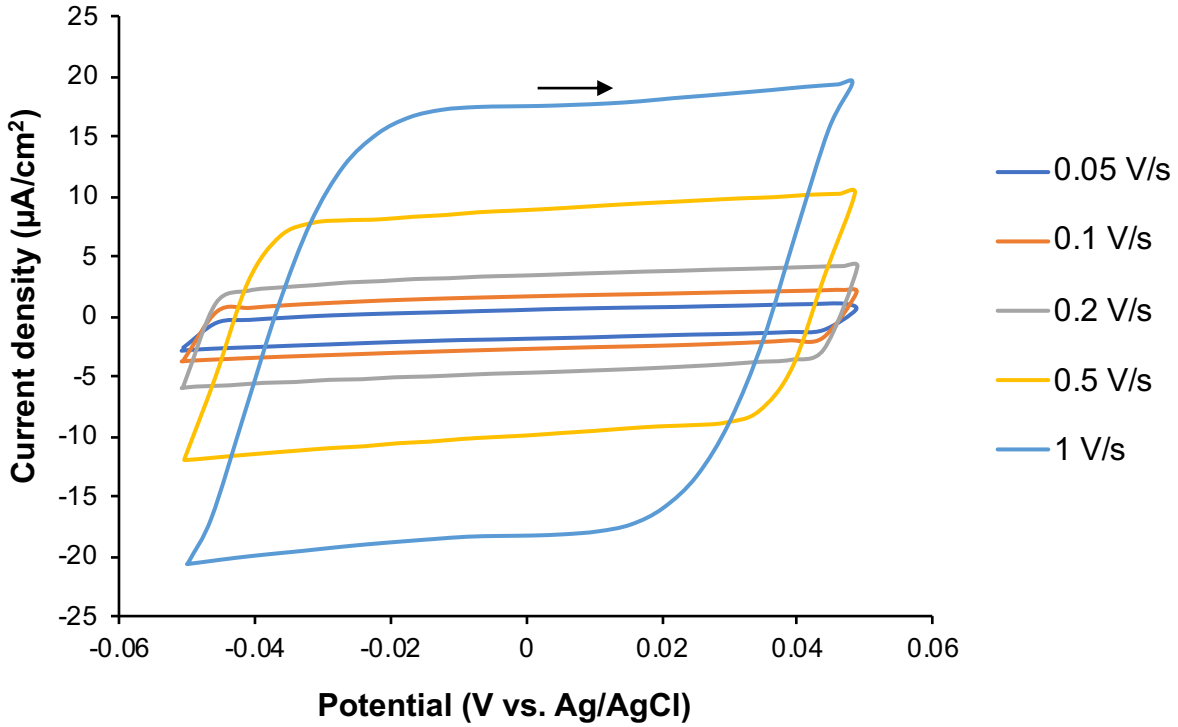

Figure S7. Scan rate dependent background current for eC/Au in 1 M $HClO_4$. The black arrow indicates the scan direction.

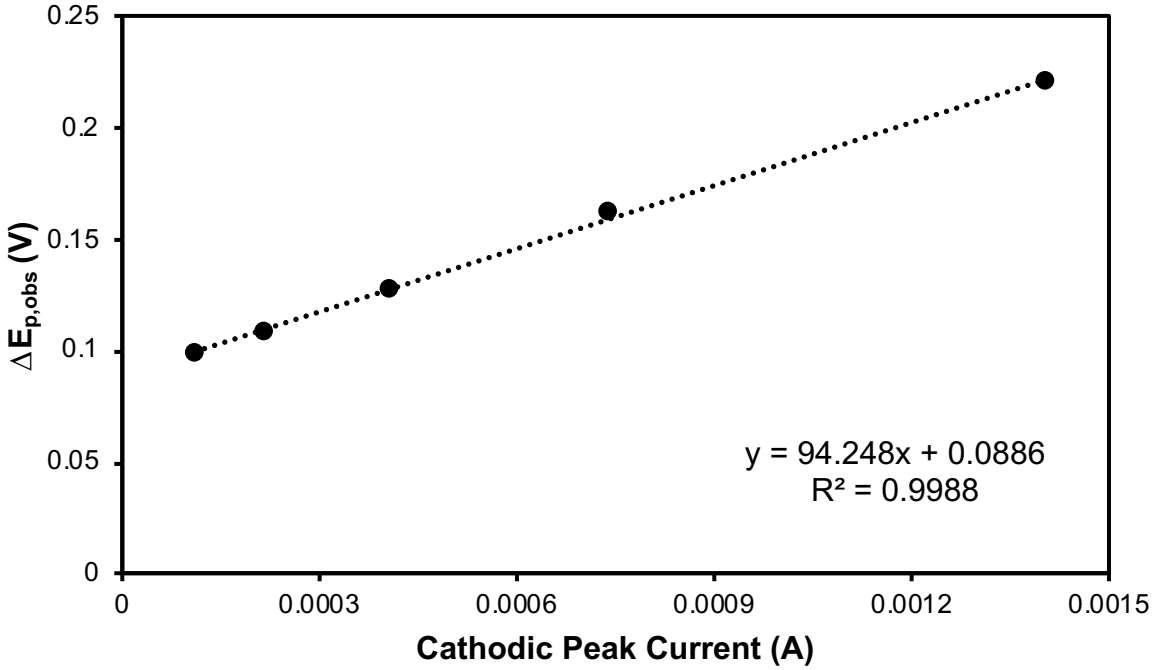

Figure S8. Representative plot of $\Delta E_{p,obs}$ vs. cathodic peak current from cyclic voltammetry of $Fe(CN)_6^{3-}$ (1 M KCl, $\nu = 0.1$ V/s) at an eC/Au film. The concentration of $Fe(CN)_6^{3-}$ was varied from 1 to 16 mM to affect the different peak currents. The slope of each least-squares, linear fit yields $2R_u$.

The effects of electrode resistance on electron transfer kinetics at pyrolyzed photoresist films (PPF) were observed in a report by Ranganathan et al.[3] Specifically, ΔE_p of $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$ increased with higher concentrations, implying a significant contribution from the iR drop in the PPF electrode due to its thinness. In a later report,[4] they noted that the resistance within the PPF increases the observed peak separation according to

$$\Delta E_{p,corrected} = \Delta E_{p,observed} - 2 \mid i \mid R_u \qquad (1)$$

where i the peak current in amperes, R_u is the uncompensated cell resistance in ohms, $\Delta E_{p,observed}$ is the observed ΔE_p in the presence of the uncompensated cell resistance in volts, and $\Delta E_{p,corrected}$ is the corrected ΔE_p in volts.

Rearranging eq. (1), we obtain

$$\Delta E_{p,observed} = 2 \left| i \right| R_u + \Delta E_{p,corrected}$$

In our previous work,[5] we reported that a plot of $\Delta E_{p,observed}$ vs. i from voltammograms at a common scan rate would yield a linear relationship, in which the slope of the fit equals to $2R_u$. The concentrations of $Fe(CN)_6^{3-}$ can be varied to affect the different peak currents. Since $i_{pc}/i_{pa} \sim 1$ for $Fe(CN)_6^{3-}$ at eC/Au electrodes, either i_{pc} or i_{pa} can be used in the calculations.

References

(1) Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. *Phys. Rev. B* **2000**, *61* (20), 14095–14107. https://doi.org/10.1103/PhysRevB.61.14095.

(2) Díaz, J.; Paolicelli, G.; Ferrer, S.; Comin, F. Separation of the Sp 3 and Sp 2 Components in the C1 *s* Photoemission Spectra of Amorphous Carbon Films. *Phys. Rev. B* **1996**, *54* (11), 8064–8069. https://doi.org/10.1103/PhysRevB.54.8064.

(3) Ranganathan, S.; McCreery, R.; Majji, S. M.; Madou, M. Photoresist-Derived Carbon for Microelectromechanical Systems and Electrochemical Applications. *J. Electrochem. Soc.* **2000**, *147* (1), 277. https://doi.org/10.1149/1.1393188.

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(5) Blackstock, J. J.; Rostami, A. A.; Nowak, A. M.; McCreery, R. L.; Freeman, M. R.; McDermott, M. T. Ultraflat Carbon Film Electrodes Prepared by Electron Beam Evaporation. *Anal. Chem.* **2004**, *76* (9), 2544–2552. https://doi.org/10.1021/ac035003j.