Electrochemical and imaging evaluations of electrochemically activated screen-printed gold electrodes

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Equations for calculating the roughness factor (ρ)

$$Charge\ (Q_{real}) = \frac{Intergarted\ area\ under\ reduction\ peak}{Scan\ rate\ of\ CV}$$

Eq.1

$$Real\ electroactive\ surface\ (A_{real}) = \frac{Q_{real}}{Q_{theoretical}}$$

Eq.2

$Q_{theoretical}$ = Theoretical charge density of Au as 390 μC cm^{-2}.

$$Roughnes\ factor\ (\rho) = \frac{A_{Real}}{A_{Geo}}$$

Eq.3

A_{geo} = Geometric surface area of the SPGE (0.11 cm^2)

Parameter	Value	Fitting error / %
R_u	34.04 Ω	0.56
R_{ct1}	111.17 Ω	10.15
R_{ct2}	584.13 Ω	0.747

Table S1: Resistance, fitting error, and convergence fit values for the unactivated SPGE, obtained from the fitted Nyquist and Bode plots using an equivalent model circuit proposed in Figure 2D.

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Convergence fit value (x^2) = 0.0098

Parameter	Value	Fitting error / %
R_u	29.45 Ω	1.66
R_{ct1}	10.78 Ω	3.44
R_{ct2}	16.83 Ω	9.00

Table S2: Resistance, fitting error, and convergence fit values for the activated SPGE, obtained from the fitted Nyquist and Bode plots using an equivalent model circuit proposed in Figure 2D.

Convergence fit value (x^2) = 0.0026

Equations used for obtaining capacitance, A_{real}, and roughness factor values

$$C_{dl} = \frac{i_a - i_c}{2V} \quad \textbf{Eq. 4}$$

$$i_C = A_{Real} C_{dl} \frac{\delta_E}{\delta_t} = A_{real} C_{dl} v \qquad \textbf{Eq. 5}$$

$$\rho = \frac{A_{Real}}{A_{Geo}} \qquad \textbf{Eq. 6}$$

C_{dl} = Double layer capacitance
ia= Anodic capacitive current
ic= Cathodic capacitive current
v= CV scan rate
A_{real}= Real electrode surface area
A_{geo}= The geometric electrode surface area
ρ = Roughness factor

The equation used for calculating the heterogeneous electron-transfer rate constant

$$k^o = \frac{RT}{R_{ct} F^2 n A C} \qquad \textbf{Eq. 7}$$

k^o = Heterogeneous electron-transfer rate constant

R= Gas constant

T= Temperature in K at room temperature

R_{ct}= Charge transfer resistance obtained from the fitted Nyquist plot

F= Faradaic constant

C= $[Fe(CN)_6]^{3-/4-}$ solution in mol cm^{-3}

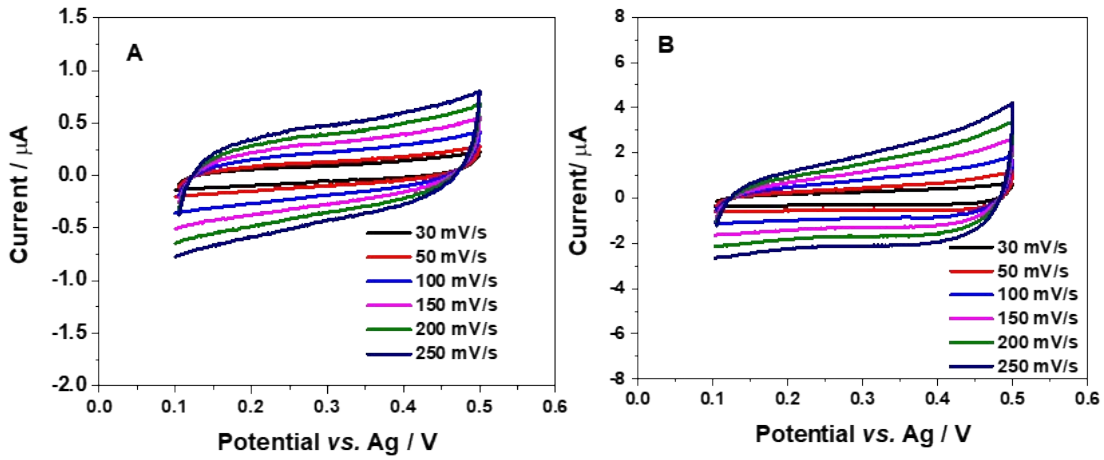


Figure S1: A and B) Cyclic voltammograms for unactivated SPGE and activated SPGE at scant rates of 0.03, 0.05, 0.1, 0.15, 0.2 and 0.25 Vs^{-1}, respectively. The CV measurements were carried out in a 0.1 M KCl solution.

Table S3: Capacitance, $A_{real,}$ and roughness factor values for unactivated and activated SPGEs, calculated from cyclic voltammetric measurements as shown in Figures S1A, S1B, and 3B.

Parameters	E8		E9		E14	
	Unactivated	Activated	Unactivated	Activated	Unactivated	Activated
Capacitance (slope)/ µF	1.75	8.06	1.64	8.50	1.59	5.32
A_{real}/ cm^2	1.19	1.20	1.20	1.12	1.12	1.20
Roughness factor	10.8	10.9	10.9	10.2	10.2	10.9

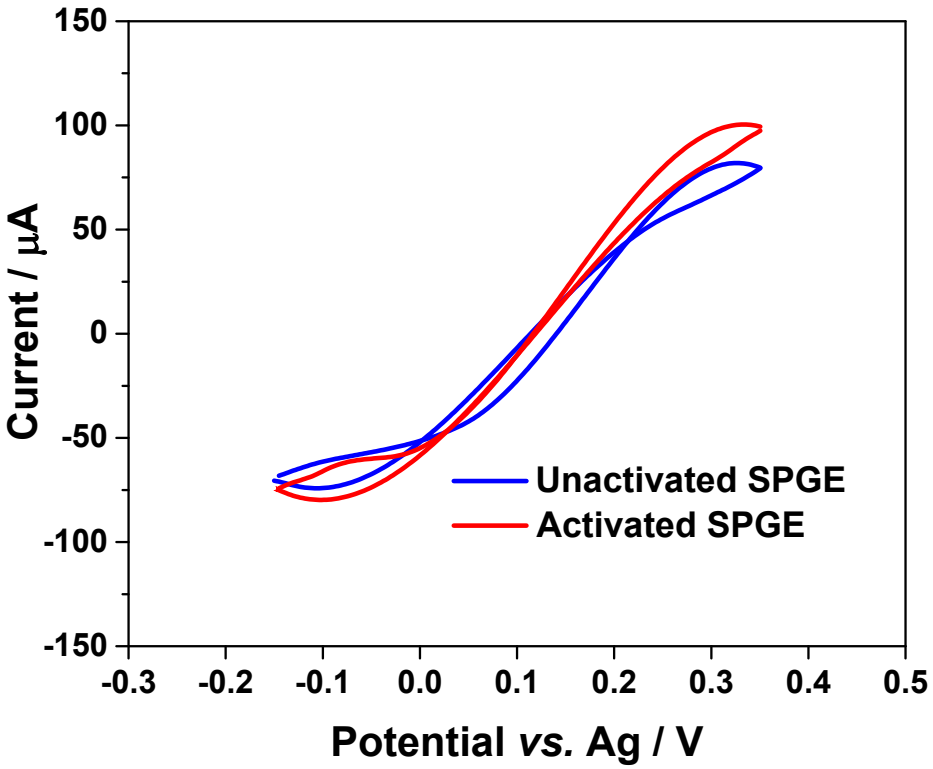
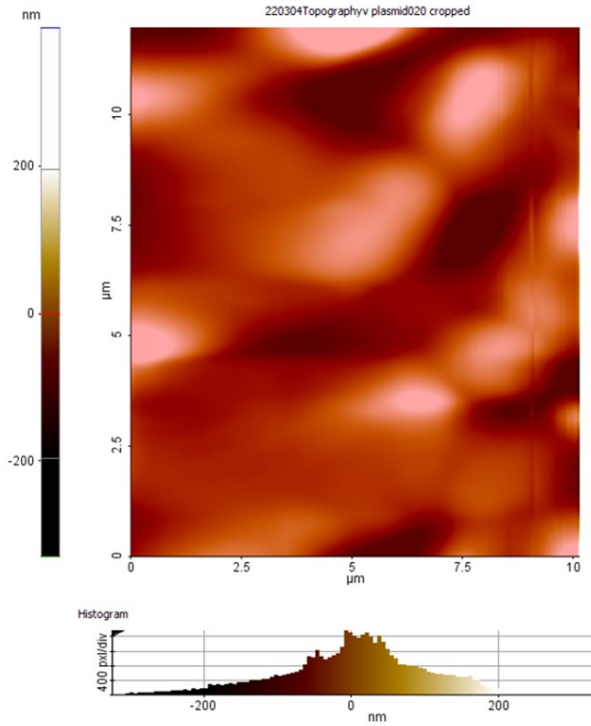
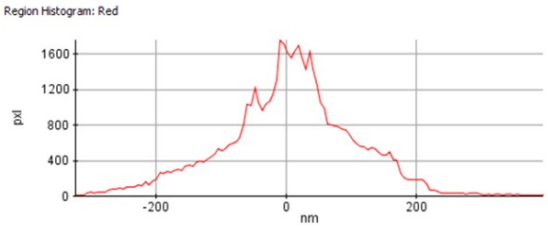


Figure S2: Created baseline for capacitive currents of unactivated SPGE and activated SPGE in a mixture of 10 mM ferrocyanide/ferricyanide at 100 mV/s. The crated baselines for both electrodes were obtained from CV responses shown in Figure 2A. The baselines were created using Origin software.

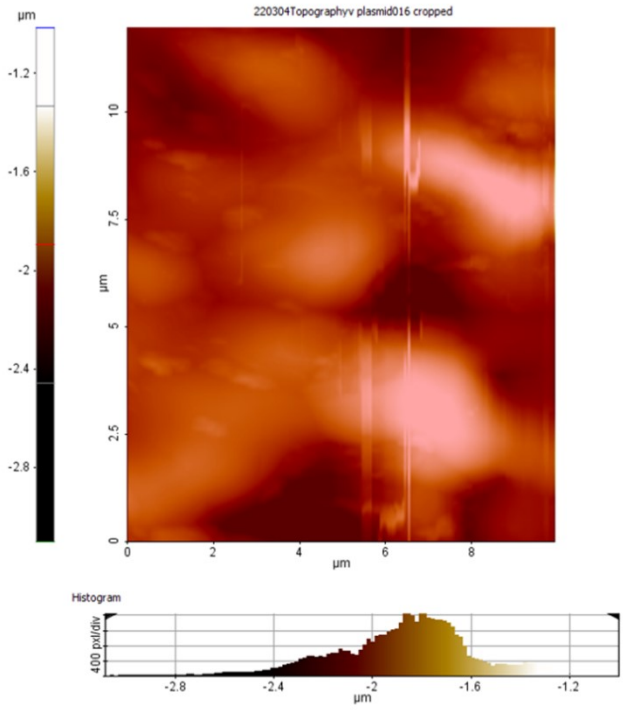




Statistics

Region	Min(µm)	Max(µm)	Mid(µm)	Mean(µm)	Rpv(µm)	Rq(µm)	Ra(µm)	Rz(µm)	Rsk	Rku
☑ Red	-0.330	0.387	0.029	0.000	0.717	0.100	0.076	0.690	0.140	3.447

Figure S3: AFM topographical analysis for unactivated SPGE. Analysis was made at 10 x 12 µM.



Statistics

Region	Min(µm)	Max(µm)	Mid(µm)	Mean(µm)	Rpv(µm)	Rq(µm)	Ra(µm)	Rz(µm)	Rsk	Rku
Red	-3.102	-1.016	-2.059	-1.896	2.087	0.286	0.218	2.066	0.497	3.799

Figure S4: AFM topographical analysis for activated SPGE. Analysis was made at 10 x 12 µM.

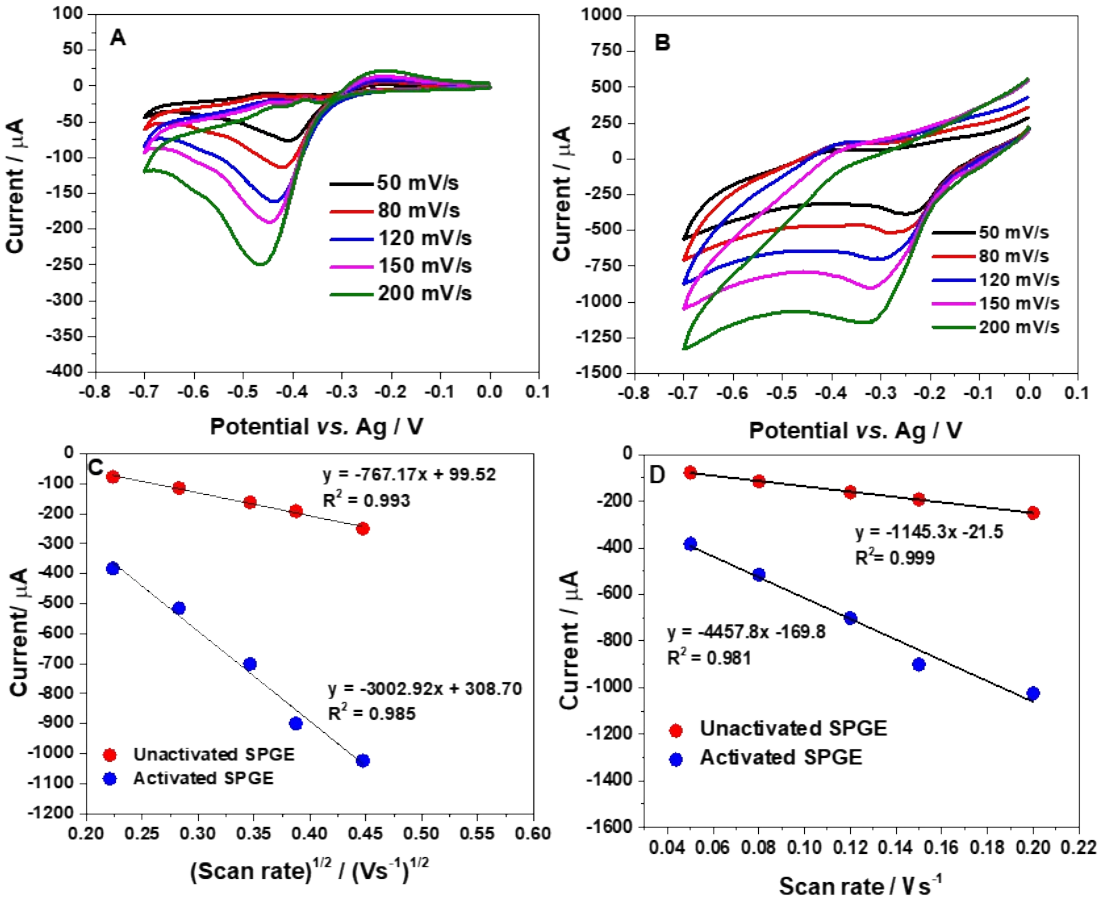


Figure S5: (A) Cyclic voltammograms of unactivated SPGE at different scan rates of 0.05, 0.08, 0.12, 0.15, and 0.2 Vs^{-1}, measured in 0.1 M KCl at saturated O_2. (B) Cyclic voltammograms of activated SPGE at different scan rates of 0.05, 0.08, 0.12, 0.15, and 0.2 Vs^{-1}, measured in 0.1 M KCl at saturated O_2. (C) plots of cathodic peak currents *versus* square root of scan rates ($v^{1/2}$) and (D) plots of cathodic peak currents *versus* different scan rates (v).