Supplementary Material:

Comparison of activation processes for 3D printed PLA-graphene electrodes: electrochemical properties and application for sensing of dopamine

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SUMMARY:

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S1 – Comparison between references electrodes

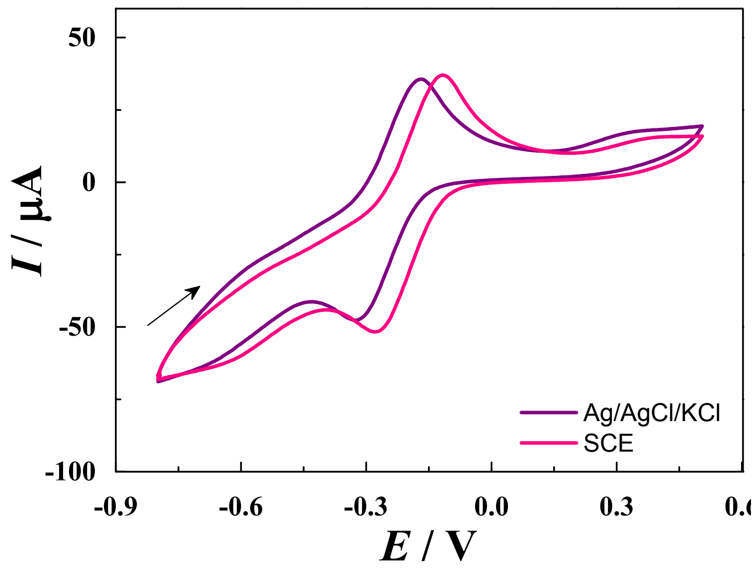

Fig. S1. Cyclic voltammograms obtained for PLA-G electrodes in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$, using SCE and Ag/AgCl/KCl as reference electrodes. ν = 50 mV s^{-1}.

SCE and Ag/AgCl/KCl, 3.5 mol L^{-1} references electrodes (RE) were used for the voltammetric performance evaluation using $[Ru(NH_3)_6]Cl_3$ as electrochemical probe. A conventional cell of three electrodes was used with PLA-G (without previous activations treatment) as working electrode, platinum as auxiliary electrode and two evaluated RE. **Fig. S1** shows the cyclic voltammograms correspondent to $[Ru(NH_3)_6]^{3+/4+}$ redox reaction. Similar signals were observed for both electrodes, however a slight baseline variation with the peak potentials shifting of around 40 mV was observed with SCE RE. In this sense, the variations of anodic and cathodic peaks ($\Delta Ep \approx 200$ mV) recorded for SCE and Ag/AgCl were similar to other reported works for 3D printed electrodes by using SCE[1] or Ag/AgCl RE[2, 3]. Considering the obtained information, the SCE was choice as reference electrode for further measurements.

S2 – Electrochemical characterization

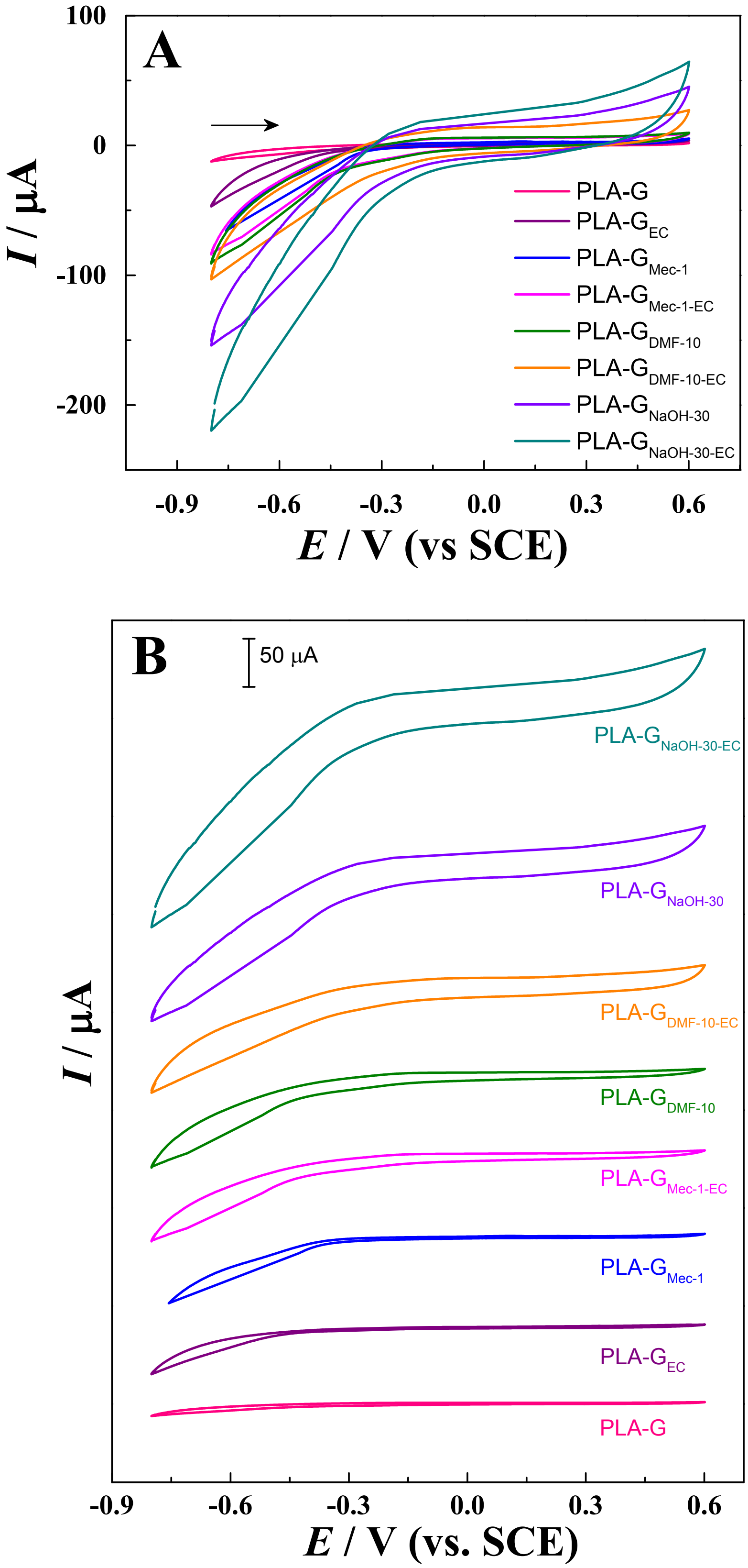

Fig. S2. Cyclic voltammograms obtained for PLA-G electrodes in the presence of 0.10 mol L^{-1} KCl (supporting electrolyte). $\nu = 50$ mV s^{-1}.

S3 – Electrochemical activation (EC)

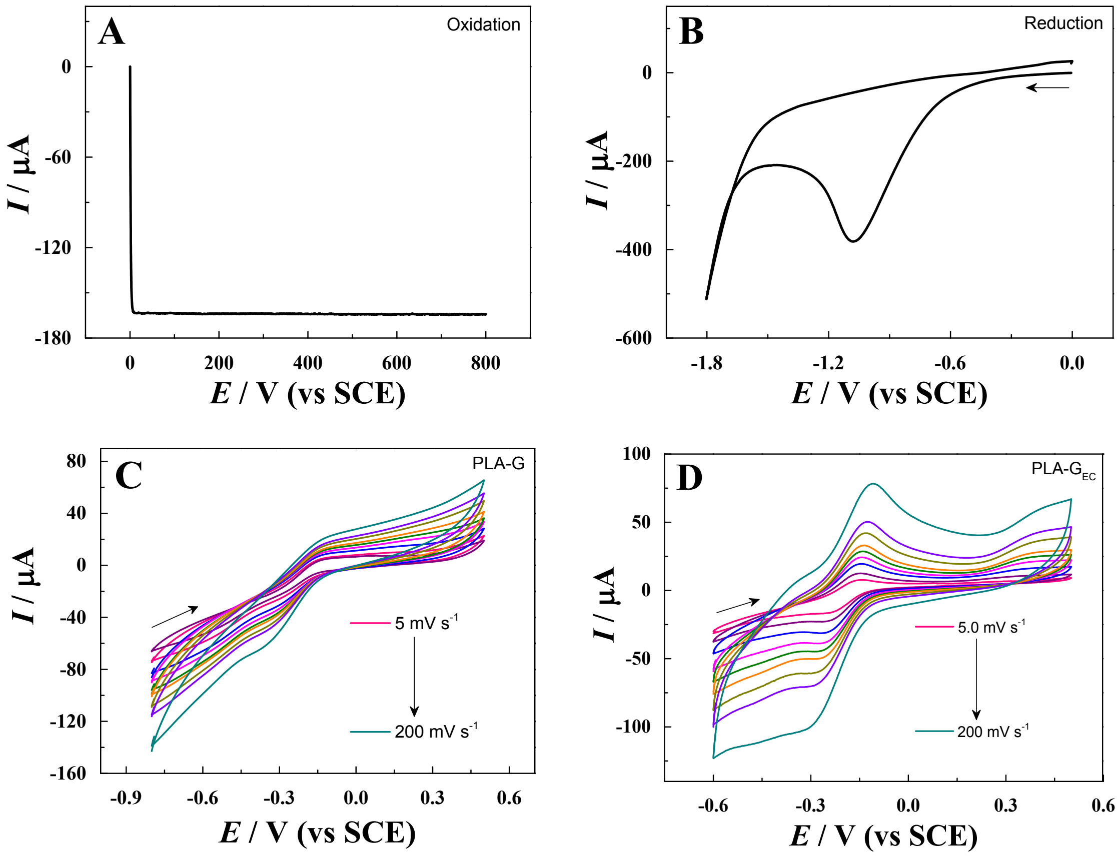

Fig. S3. Oxidation (A) and reduction (B) of PLA-G electrode in 0.10 mol L^{-1} phosphate buffer solution (pH 7.4). Cyclic voltammograms obtained at different scan rates (5.0–200 mV s^{-1}) in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$ for PLA-G (C) and PLA-G_{EC} electrodes (D).

S4 – Mechanical Activation (polishing)

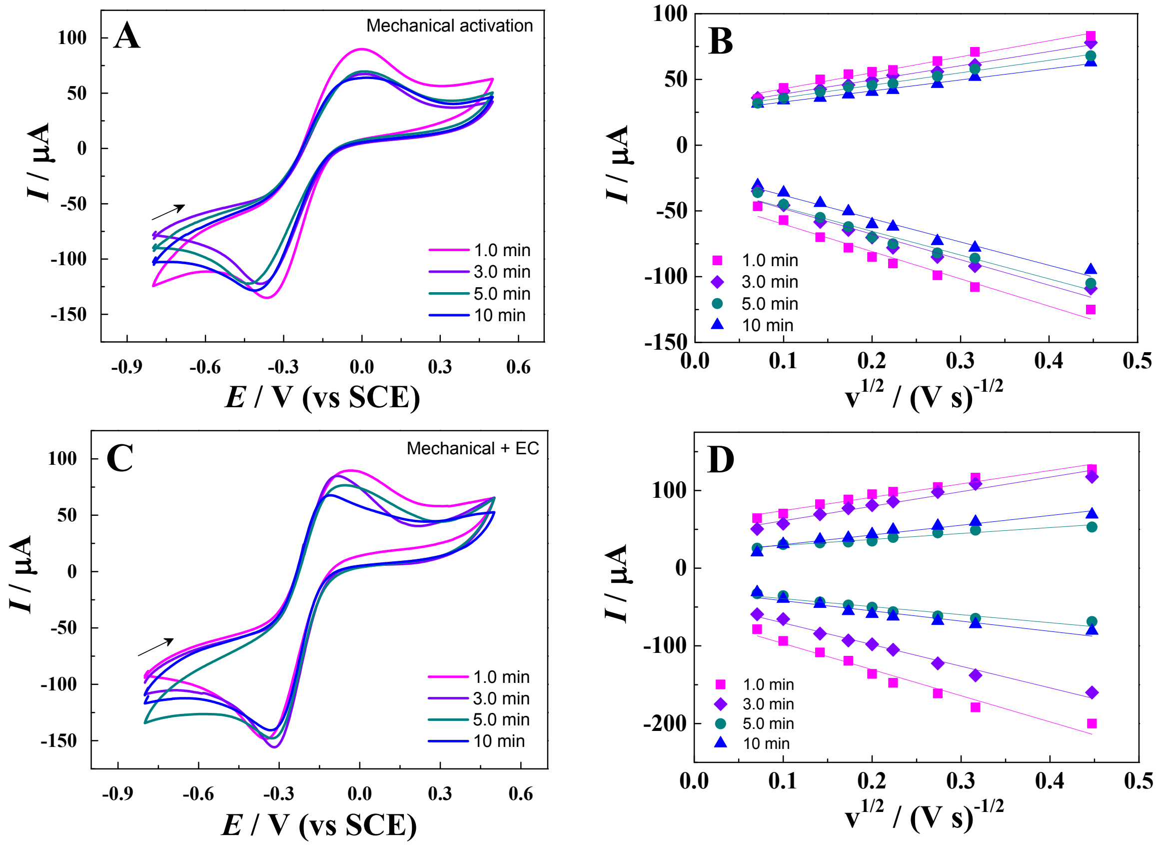

Fig. S4. Cyclic voltammograms obtained at 25 mV s^{-1} and correlation between peak currents and $v^{1/2}$ (5.0–200 mV s^{-1}) obtained for PLA-G electrodes after mechanical (A, B), mechanical + EC (C, D), in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$.

S5 – Solvent activation (DMF)

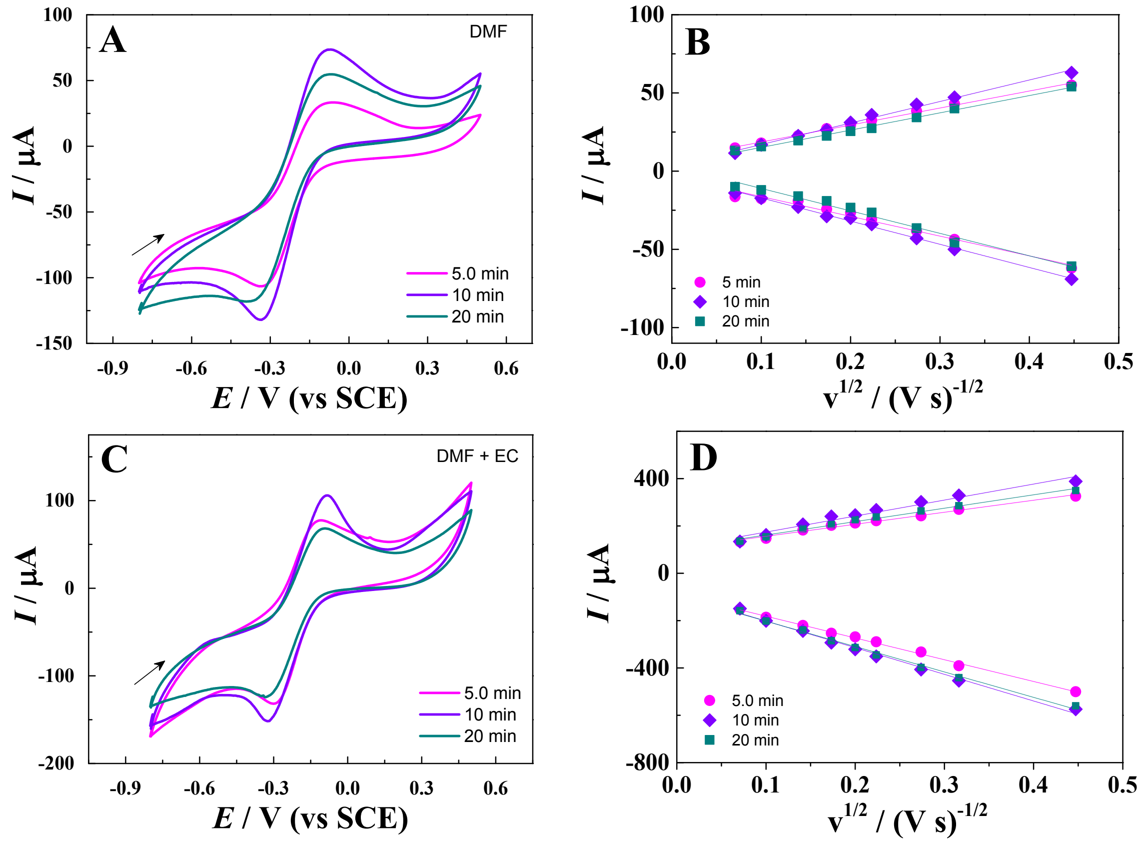

Fig. S5. Cyclic voltammograms obtained at 25 mV s^{-1} and correlation between peak currents and v$^{1/2}$ (5.0–200 mV s^{-1}) obtained for PLA-G electrodes after DMF (A, B) and DMF + EC activations (C, D), in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$.

S6 – Basic activation (NaOH)

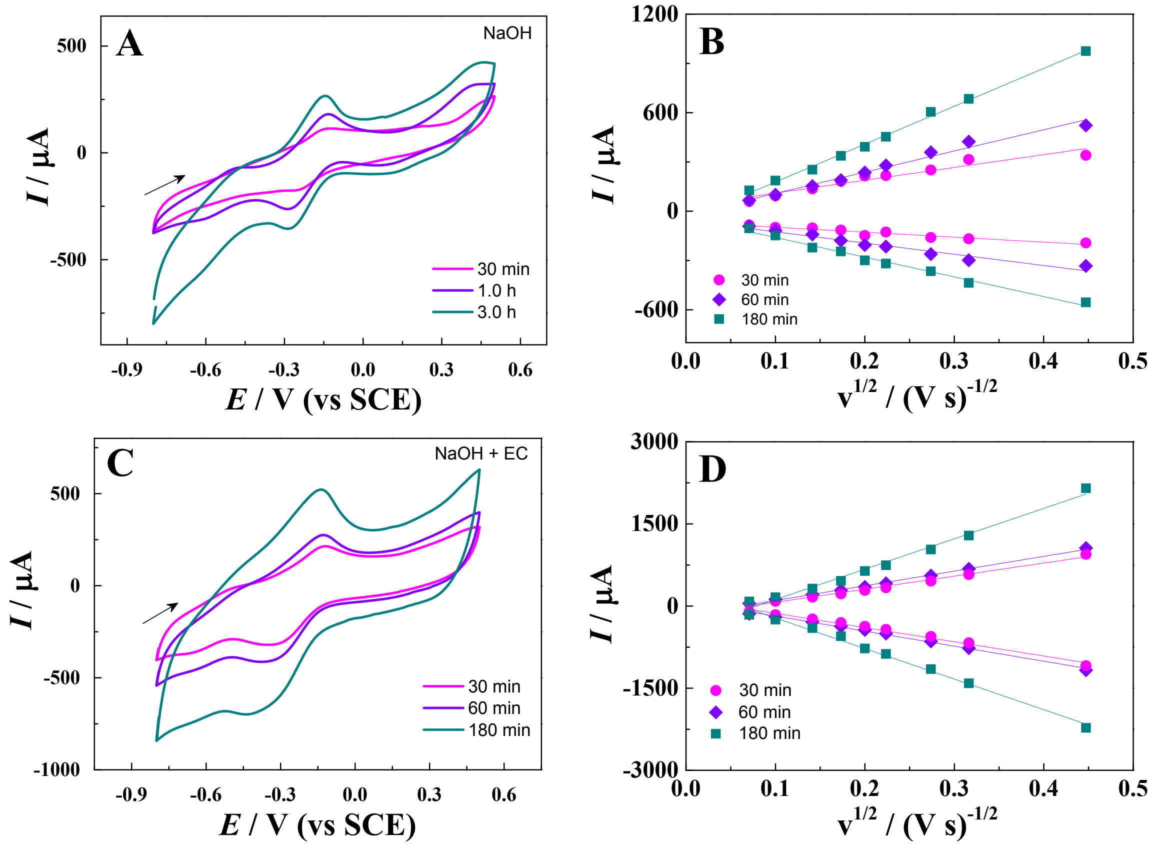

Fig. S6. Cyclic voltammograms obtained at 25 mV s^{-1} and correlation between peak currents and $v^{1/2}$ (5.0–200 mV s^{-1}) obtained for PLA-G electrodes after NaOH (A, B) and NaOH + EC activations (C, D), in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$.

S7 – Acid activation (HNO_3)

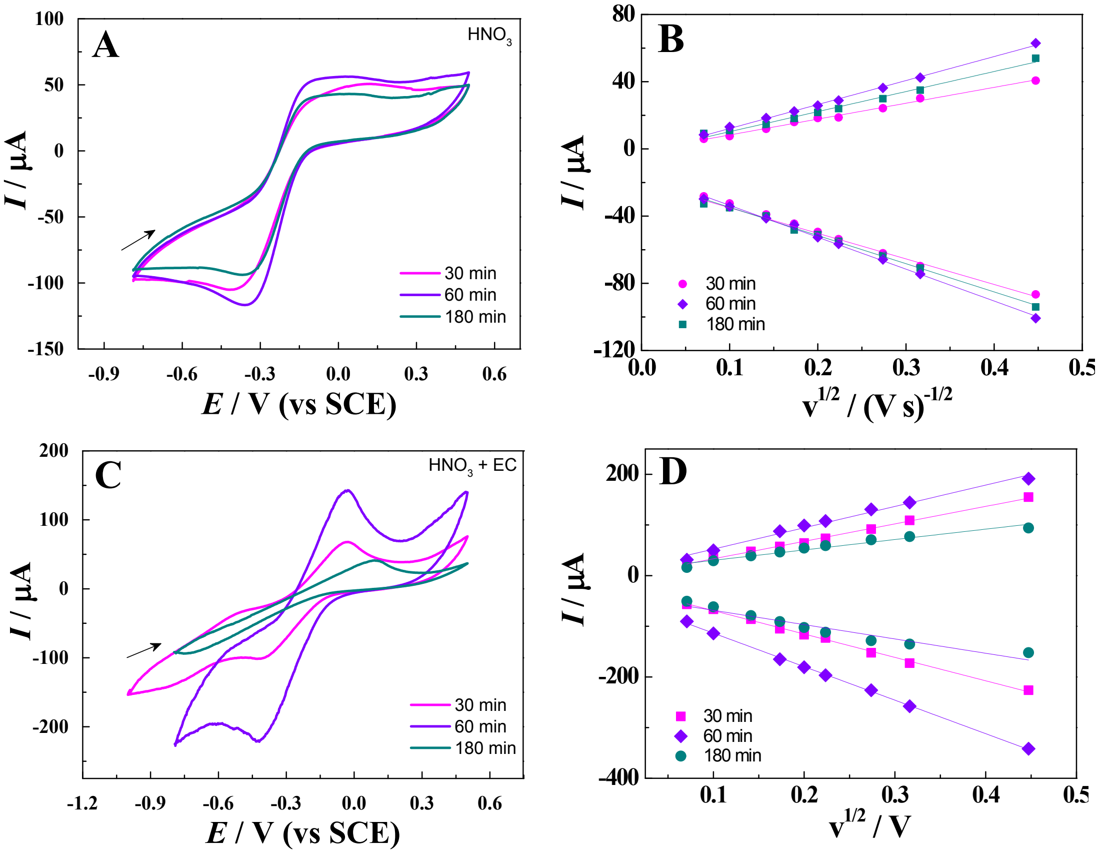

Fig. S7. Cyclic voltammograms obtained at 25 mV s^{-1} and correlation between peak currents and $v^{1/2}$ (5.0–200 mV s^{-1}) obtained for PLA-G electrodes after HNO_3 (A, B) and HNO_3 + EC activations (C, D), in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$.

S8 – Acid activation (H_2SO_4)

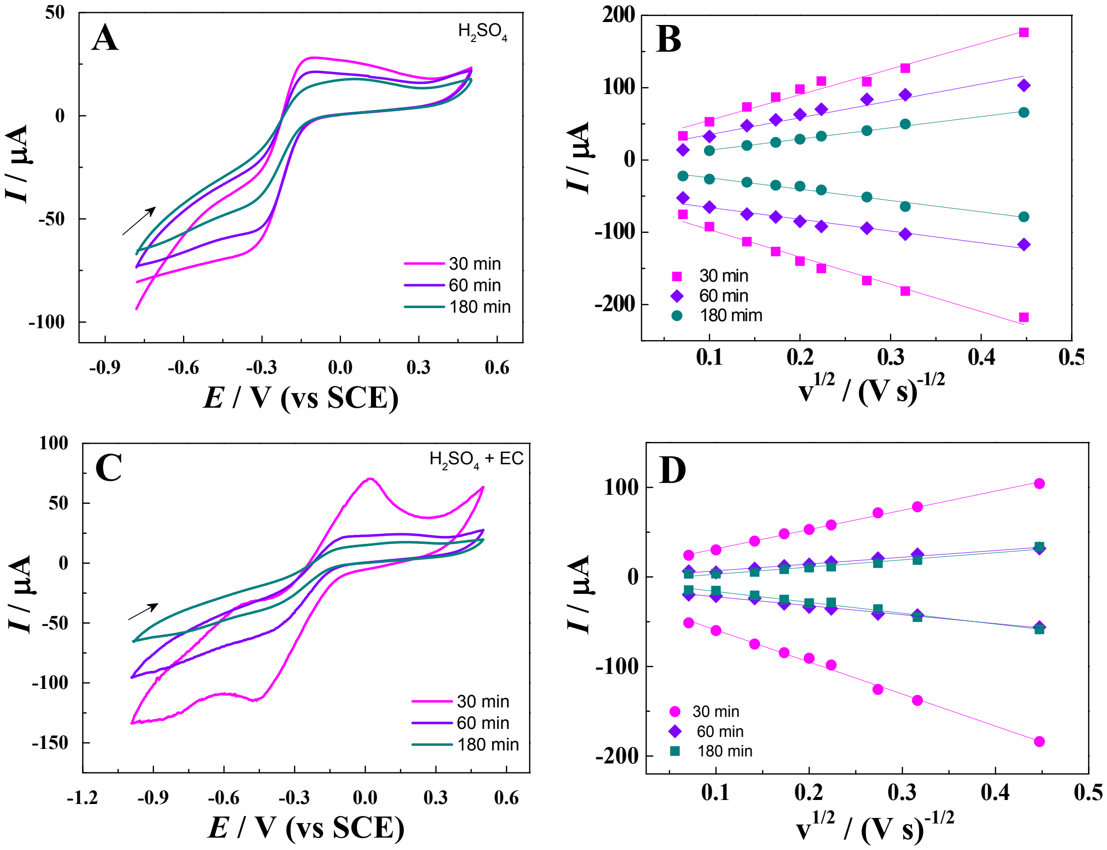

Fig. S8. Cyclic voltammograms obtained at 25 mV s^{-1} and correlation between peak currents and v$^{1/2}$ (5.0–200 mV s^{-1}) obtained for PLA-G electrodes after. H_2SO_4 (A, B) and H_2SO_4 + EC activations (C, D), in the presence of 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$.

S9 – Comparison between 3D PLA-G activation

Table S1. Comparison between the Raman and electroactive characteristics of 3D PLA-G before and after activation treatments (n=3).

3D Electrode	I_D/I_G	k^o_{obs} (cm s^{-1})	θ_{edge}	A_e (cm²)
PLA-G	0.634±0.002	2.73 x 10^{-4}±0.43 x 10^{-4}	0.07±0.01	0.020±0.006
PLA-G_{EC}	0.668±0.001	1.53 x 10^{-3}±0.11 x 10^{-3}	0.38±0.03	0.095±0.009
PLA-G_{Mec-1}	0.631±0.003	1.20 x 10^{-4}±0.28 x 10^{-4}	0.04±0.01	0.20±0.08
PLA-G_{Mec-3}	0.540±0.004	9.56 x 10^{-5}±2.63 x 10^{-5}	0.024±0.007	0.19±0.07
PLA-G_{Mec-5}	0.517±0.001	9.60 x 10^{-5}±1.97 x 10^{-5}	0.024±0.005	0.17±0.03
PLA-G_{Mec-10}	0.571±0.002	1.03 x 10^{-4}±0.14 x 10^{-4}	0.026±0.004	0.16±0.06
PLA-$G_{Mec-1-EC}$	0.730±0.006	1.53 x 10^{-4}±0.32 x 10^{-4}	0.038±0.008	0.31±0.09
PLA-$G_{Mec-3-EC}$	0.612±0.003	1.15 x 10^{-4}±0.24 x 10^{-4}	0.029±0.006	0.29±0.08
PLA-$G_{Mec-5-EC}$	0.634±0.002	1.20 x 10^{-4}±0.08 x 10^{-4}	0.030±0.002	0.11±0.02
PLA-$G_{Mec-10-EC}$	0.624±0.003	1.25 x 10^{-4}±0.35 x 10^{-4}	0.031±0.009	0.159±0.005
PLA-G_{DMF-5}	0.549±0.002	2.26 x 10^{-4}±0.97 x 10^{-4}	0.06±0.02	0.15±0.01
PLA-G_{DMF-10}	0.622±0.008	3.85 x 10^{-4}±0.86 x 10^{-4}	0.10±0.02	0.18±0.01
PLA-G_{DMF-20}	0.556±0.003	2.92 x 10^{-4}±4.45 x 10^{-4}	0.07±0.01	0.15±0.03
PLA-$G_{DMF-5-EC}$	0.649±0.008	3.47 x 10^{-4}±0.43 x 10^{-4}	0.09±0.01	0.88±0.04
PLA-$G_{DMF-10-EC}$	0.889±0.009	5.01 x 10^{-4}±0.13 x 10^{-4}	0.125±0.003	1.11±0.09
PLA-$G_{DMF-20-EC}$	0.567±0.002	4.69 x 10^{-4}±0.44 x 10^{-4}	0.18±0.01	1.02±0.04
PLA-$G_{NaOH-30}$	0.489±0.003	9.34 x 10^{-4}±1.08 x 10^{-4}	0.23±0.03	0.88±0.09
PLA-$G_{NaOH-60}$	0.500±0.001	1.10 x 10^{-3}±0.59 x 10^{-3}	0.28±0.01	1.23±0.05
PLA-$G_{NaOH-180}$	0.544±0.004	1.15 x 10^{-3}±0.20 x 10^{-3}	0.29±0.05	2.35±0.07
PLA-$G_{NaOH-30-EC}$	0.852±0.06	1.11 x 10^{-3}±0.28 x 10^{-3}	0.28±0.02	3.19±0.02
PLA-$G_{NaOH-60-EC}$	0.522±0.001	1.13 x 10^{-3}±0.04 x 10^{-3}	0.28±0.01	3.13±0.09
PLA-$G_{NaOH-180-EC}$	0.578±0.003	9.11 x 10^{-4}±1.27 x 10^{-4}	0.23±0.03	6.87± 0.03
PLA-$G_{HNO3-30}$	0.624±0.003	1.02 x 10^{-4}±0.06 x 10^{-4}	0.03±0.01	0.15±0.05
PLA-$G_{HNO3-60}$	0.522±0.001	1.53 x 10^{-4}±0.31 x 10^{-4}	0.04±0.02	0.20±0.04
PLA-$G_{HNO3-180}$	0.544±0.008	2.11 x 10^{-4}±0.41 x 10^{-4}	0.05±0.01	0.18±0.04
PLA-$G_{HNO3-30-EC}$	0.656±0.002	1.60 x 10^{-4}±0.14 x 10^{-4}	0.040±0.004	0.49±0.09
PLA-$G_{HNO3-60-EC}$	0.578±0.001	2.50 x 10^{-4}±0.71 x 10^{-4}	0.063±0.008	0.67±0.02
PLA-$G_{HNO3-180-EC}$	0.611±0.002	9.02 x 10^{-5}±8.46 x 10^{-5}	0.02±0.02	0.31±0.06
PLA-$G_{H2SO4-30}$	0.523±0.005	3.25 x 10^{-4}±1.06 x 10^{-4}	0.08±0.03	0.45±0.03
PLA-$G_{H2SO4-60}$	0.518±0.001	4.31 x 10^{-4}±1.14 x 10^{-4}	0.11±0.03	0.24±0.06
PLA-$G_{H2SO4-180}$	0.511±0.001	3.00 x 10^{-4}±0.71 x 10^{-4}	0.08±0.02	0.199±0.002
PLA-$G_{H2SO4-30-EC}$	0.591±0.004	6.76 x 10^{-4}±0.22 x 10^{-4}	0.169±0.005	0.36±0.09
PLA-$G_{H2SO4-60-EC}$	0.586±0.002	7.00 x 10^{-4}±0.28 x 10^{-4}	0.175±0.007	0.11±0.02
PLA-$G_{H2SO4-180-EC}$	0.575±0.002	2.90 x 10^{-4}±0.14 x 10^{-4}	0.073±0.004	0.12±0.04

I_D/I_G: G and D bands ratio; k^o_{obs}: heterogeneous rate constant; θ_{edge}: amount of edge sites; A_e: electroactive area.

S10 – Dopamine Determination

Table S2. Results obtained (%) for interference study using ascorbic acid (AA) and uric acid (UA) for DA determination. Supporting electrolyte: 0.10 mol L^{-1} PBS pH 6.0. $C_{DA:}$ 30 µmol L^{-1}.

Specie	**Concentration**		
	3.0 µmol L^{-1}	**30 µmol L^{-1}**	**300 µmol L^{-1}**
AA	−0.99	+3.43	+6.45
UA	+0.54	+1.91	+5.66
AA + UA	+1.57	+2.63	+6.89

References

1. P. L. dos Santos, V. Katic, H. C. Loureiro, M. F. dos Santos, D. P. dos Santos, A. L. Formiga and J. A. Bonacin, *Sensors and Actuators B: Chemical*, 2018, **281**, 837-848.
2. R. M. Cardoso, D. M. H. Mendonça, W. P. Silva, M. N. T. Silva, E. Nossol, R. A. B. da Silva, E. M. Richter and R. A. A. Muñoz, *Analytica chimica acta*, 2018, **1033**, 49-57.
3. C. L. Manzanares Palenzuela, F. Novotný, P. Krupička, Z. Sofer and M. Pumera, *Analytical Chemistry*, 2018, **90**, 5753-5757.