Supplementary Materials

Synthesis of Phosphorus-Containing Polyanilines by Electrochemical Copolymerization

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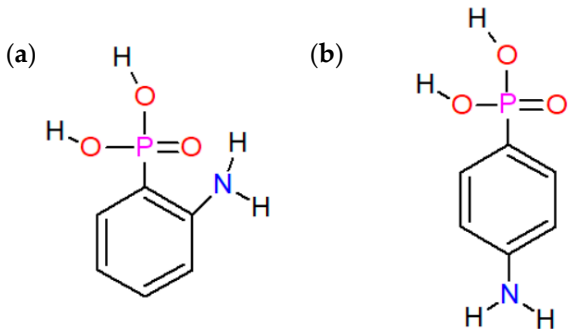

Figure S1. Chemical structure of phosphonated monomers: (**a**) 2-APPA and (**b**) 4-APPA.

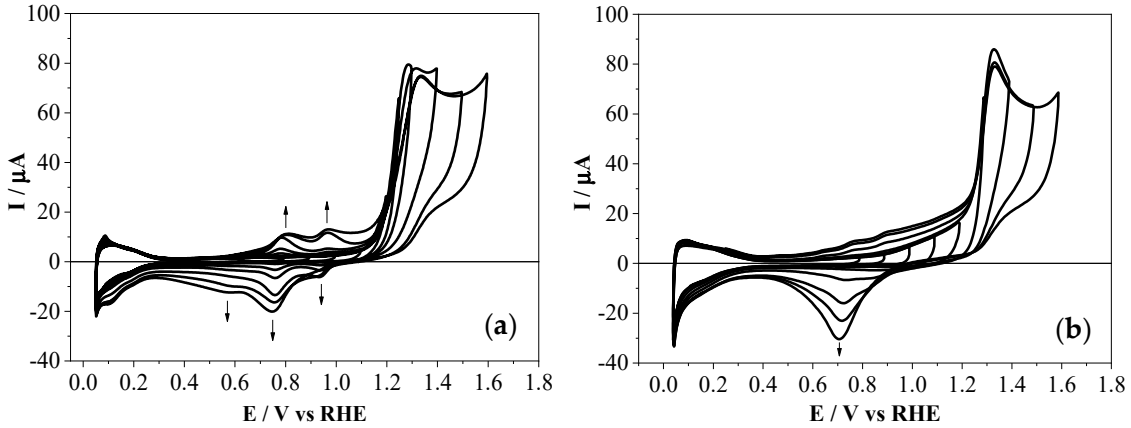

Figure S2. Cyclic voltammograms of the open stepwise upper potential limit for the polycrystalline Pt electrode in presence of: (**a**) 1 mM 2-APPA and (**b**) 1 mM 4-APPA, in 1 M $HClO_4$ at 50 $mV \cdot s^{-1}$ under N_2 atmosphere.

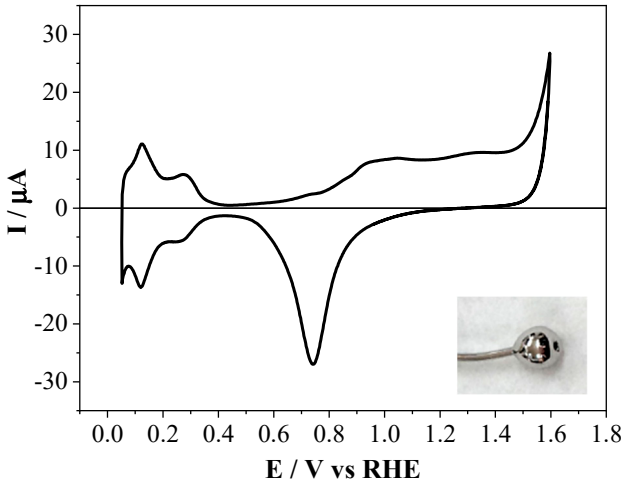

Figure S3. Stable cyclic voltammogram for a platinum electrode in 1 M $HClO_4$ at 50 $mV \cdot s^{-1}$. Inset: Picture of clean platinum electrode.

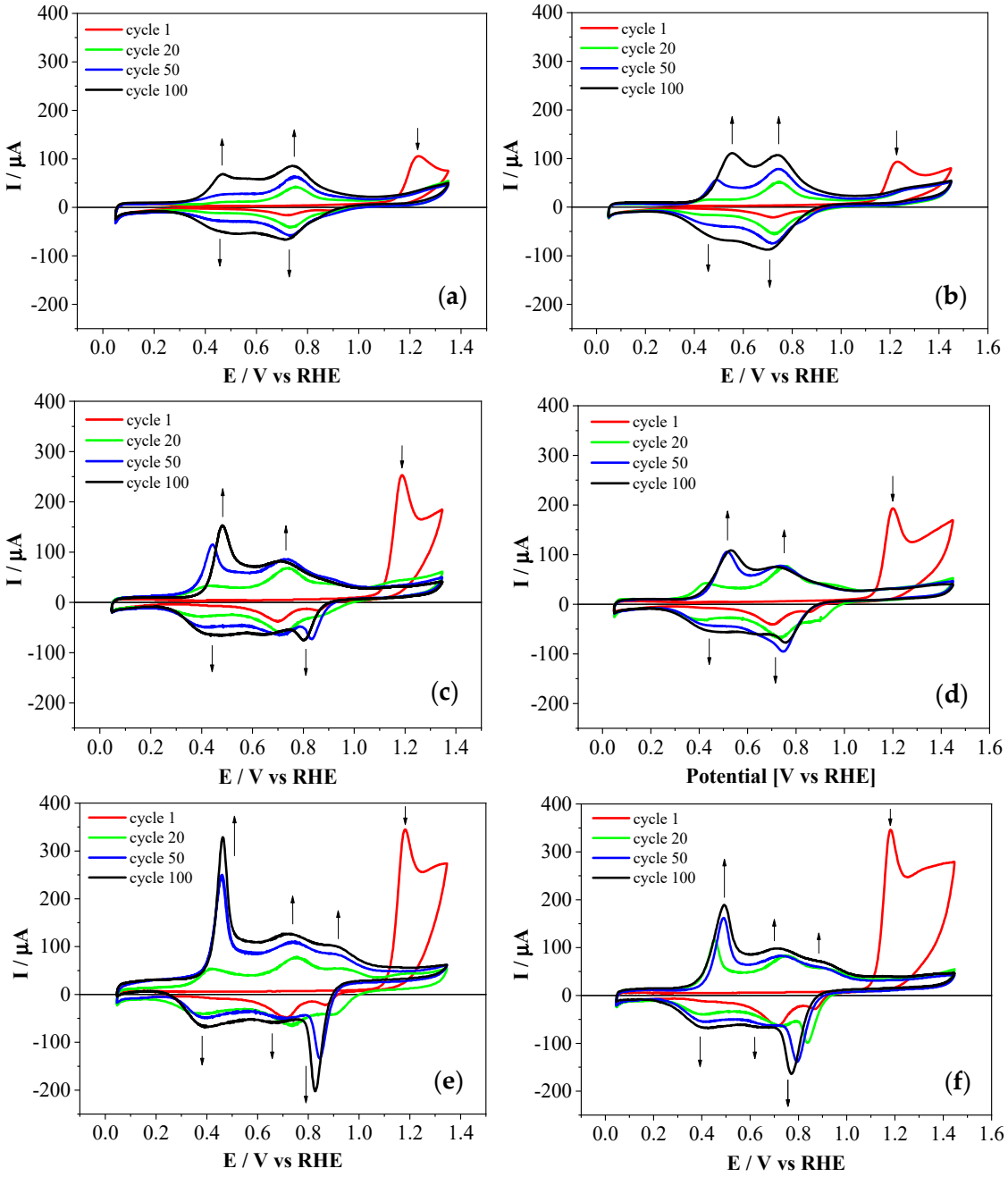

Figure S4. Cyclic voltammograms for synthesis of PANI, obtained during 100 cycles in 1 M $HClO_4$ on the polycrystalline Pt electrode at 50 $mV \cdot s^{-1}$ under N_2 atmosphere at 1.35 V (left) and 1.45 V (right), in presence of different concentrations of aniline: (**a, b**) 1 mM, (**c, d**) 3 mM and (**e, f**) 10 mM.

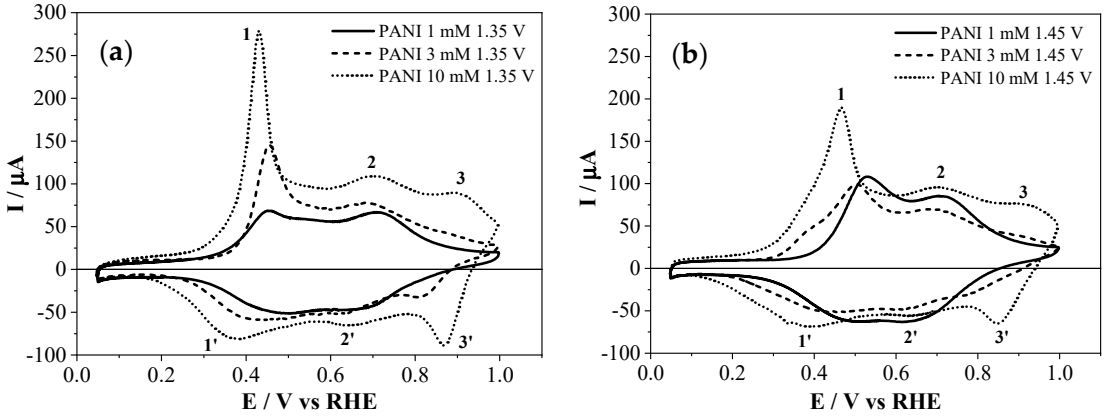

Figure S5. Stable cyclic voltammograms of characterization in 1 M $HClO_4$ at 50 $mV \cdot s^{-1}$ of PANI previously obtained at different concentrations of aniline during 100 cycles under N_2 atmosphere at different potentials: (**a**) 1.35 V and (**b**) 1.45 V.

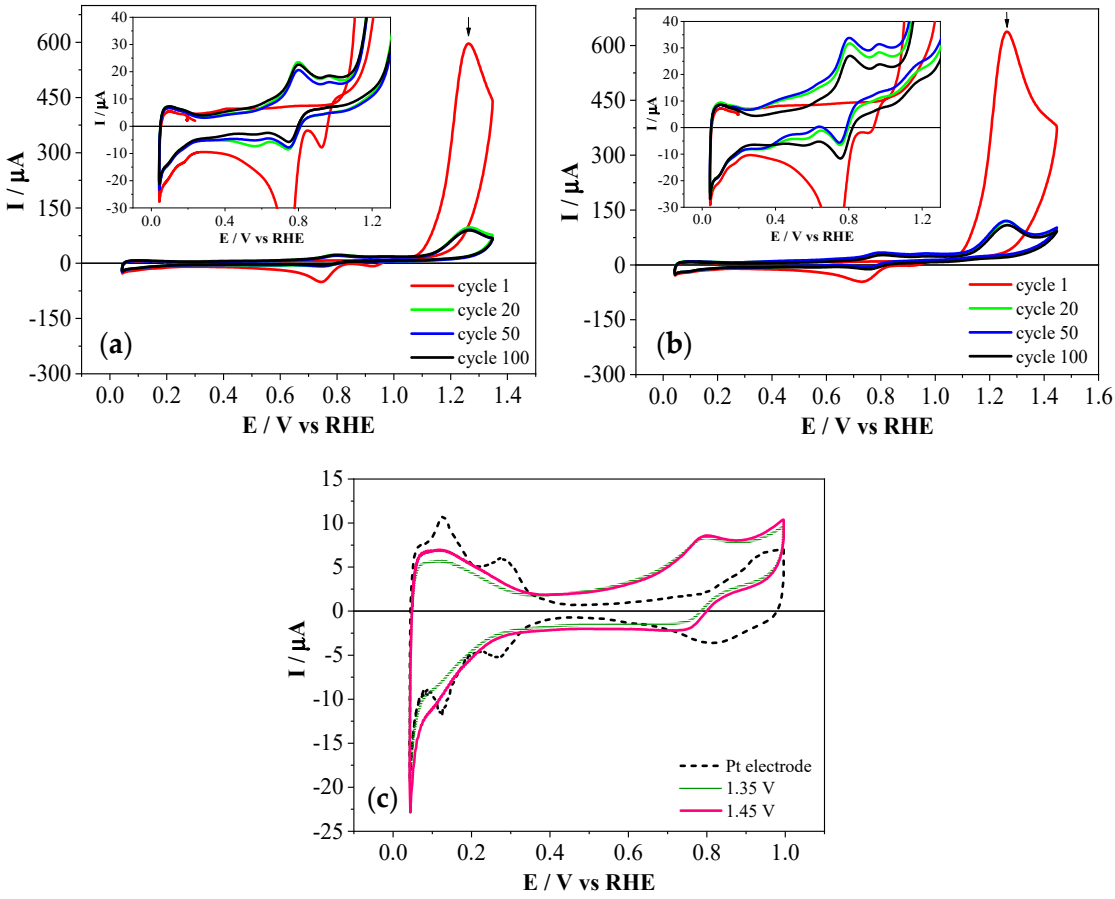

Figure S6. Cyclic voltammograms of the electrooxidation during 100 cycles in 1 M $HClO_4$ on the polycrystalline Pt electrode in presence of 10 mM 2-APPA at 50 $mV \cdot s^{-1}$ under N_2 at different potentials: (**a**) 1.35 V and (**b**) 1.45 V. Inset: Magnification of the redox processes that occur on the electrode surface during the electrooxidation. (**c**) Stable voltammograms of the modified electrode in acid media in absence of the monomer in the solution.

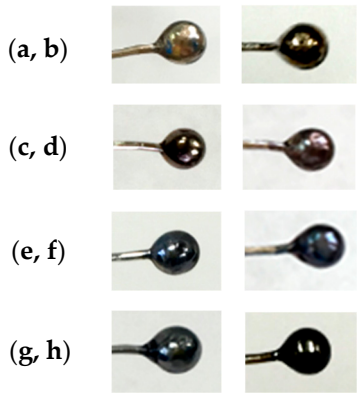

Figure S7. Pictures of the modified polycrystalline platinum electrode with the polymeric film of PANI-2APPA (left) and PANI-4APPA (right) deposited onto the surface after 100 cycles at different upper potential limits: (**a, b**) 1.25 V, (**c, d**) 1.35 V, (**e, f**) 1.45 V and (**g, h**) 1.60 V.

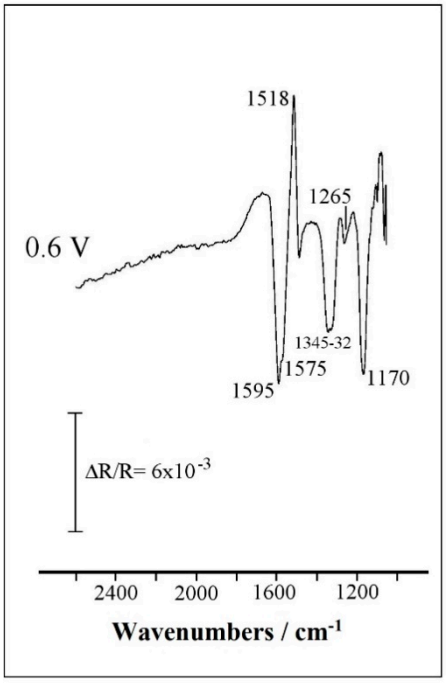

Figure S8. In situ FTIR spectra obtained in 0.1 M H_2SO_4 solution of the polycrystalline Pt electrode modified with polyaniline (PANI). Reference spectra acquired at 0.1 V and sample spectra at 0.6 V, 100 interferograms recorded at each potential. 8 cm^{-1} resolution.

Table S1. Vibrational frequencies and assignments proposed for the reduced and oxidized form of PANI in acidic medium at 0.6 V.

Oxidation State	Frequency / cm^{-1}	Assignments	References
Reduced	1518	Benzenoid aromatic ring (C–C) stretching	[41–43]
	1300–1310	Secondary aromatic amines (N–H) stretching	[42]
Oxidized	1595	Imine (N-H) bending (>C=N–H) and/or (C=N) stretching	[40,41]
	1575, 1595	Quinoid ring (C-C) stretching	[42,43]
	1332–1345	Intermediate order (C=N) stretching	[42]
	1265	($C–N^{\bullet+}$) stretching	[42]
	1170	(C–H) bending and/or quinoid ring (C–N–C) stretching	[40,44]

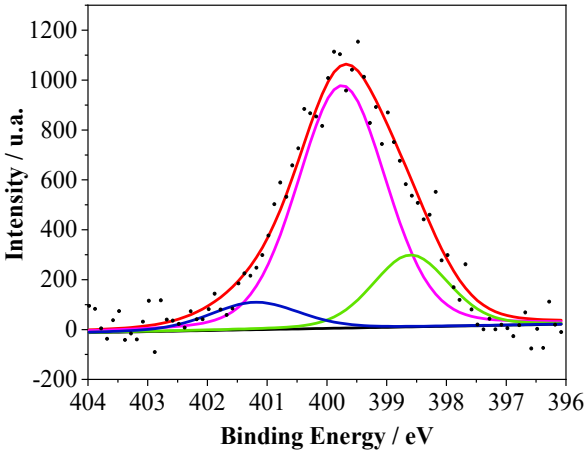

Figure S9. XPS spectra for N1s signals for PANI synthesized at 1.35 V.

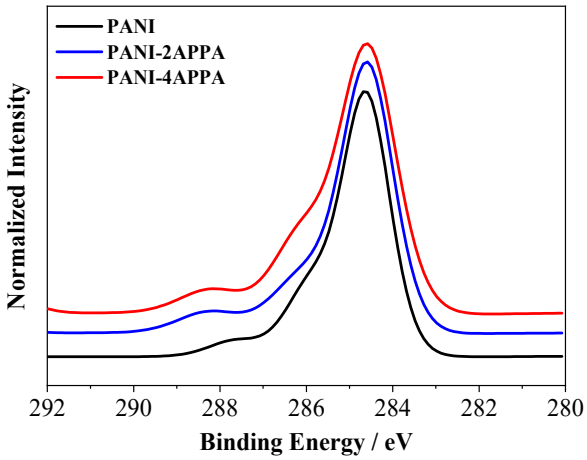

Figure S10. XPS spectras for C1s signals for PANI, PANI-2APPA and PANI-4APPA, respectively, synthesized at 1.35 V.