Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

First principles of hydrazine electrooxidation at oxides-free and oxides-based palladium electrodes in complex media

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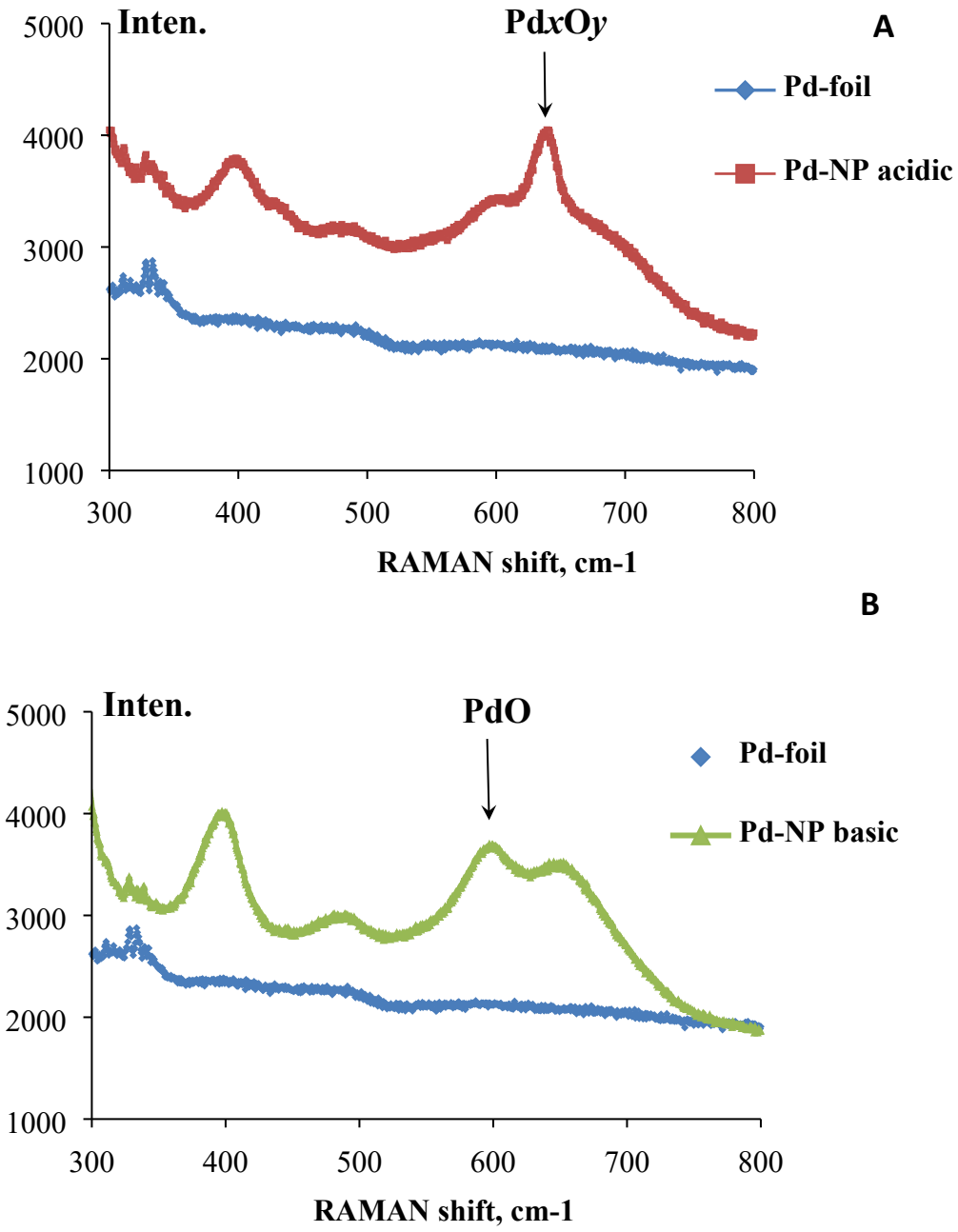

Fig. S1 – RAMAN spectra recorded from sputtered Pd-foil (*blue lines*) and Pd-NPs-modified electrode synthesized at -2.5 mA for 30 s (*red and olive lines*): **A** – Pd-NPs were synthesized from the acidic electrolyte, pH = 2; **B** – Pd-NPs were synthesized from the basic electrolyte, pH = 9.3. *Note:* to avoid the interference caused by oxides and oxygen species present on the surface of screen printed electrodes (SPE) covered by graphene oxide (GO), for this set of experiments Pd-NPs were deposited on steel templates at the same electroplating conditions as shown in Experimental part for SPE/GO.

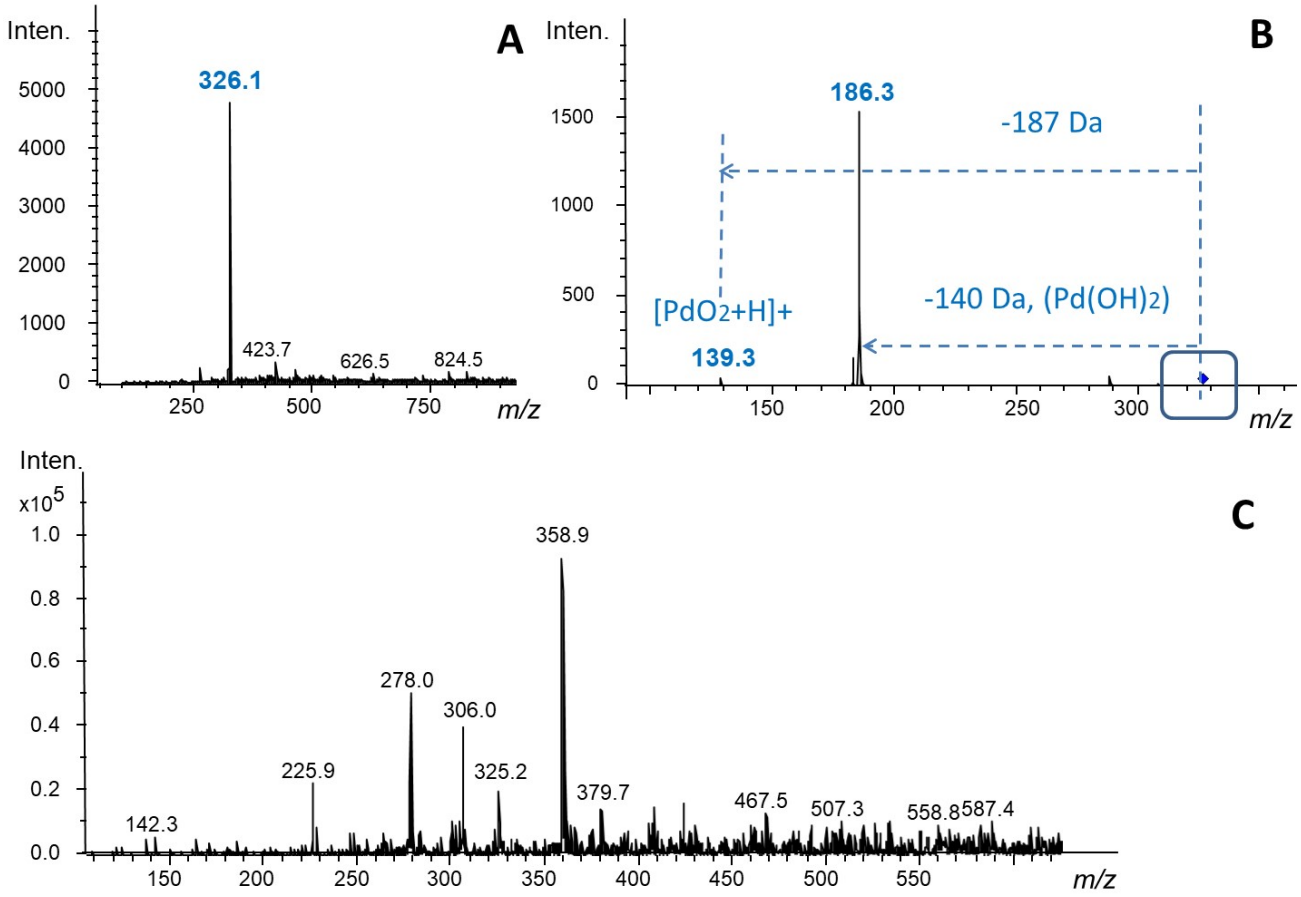

Fig. S2 – LDI-MS spectra recorded in positive detection mode from the surface of SPE/GO modified by: basic Pd-NPs (**A** – full scan, **B** – MS/MS of peak at *m/z* 326, CID 1 eV) and acidic Pd-NPs (C). Laser fluence 40%.

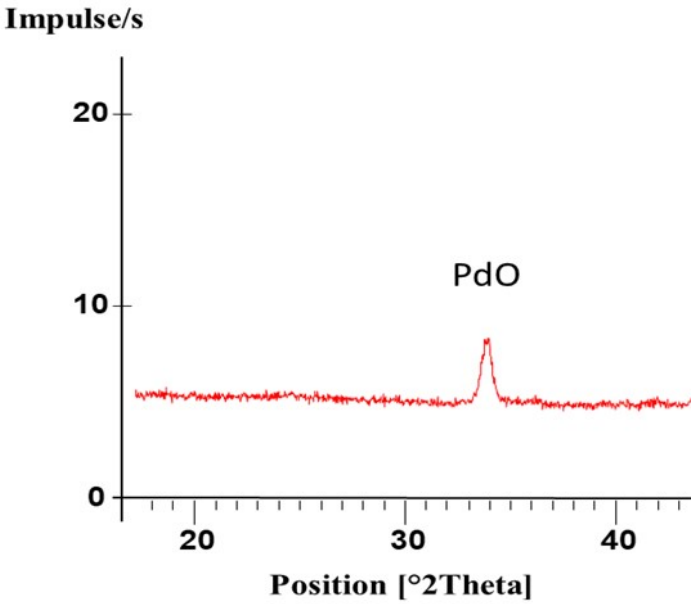

Fig. S3 – XRD diffractogram focused on PdO peak recorded from the basic Pd-NPs (**sample 2**). *Note:* Contrary to Raman spectroscopy, XRD analysis allows characterizing only the largest particles.

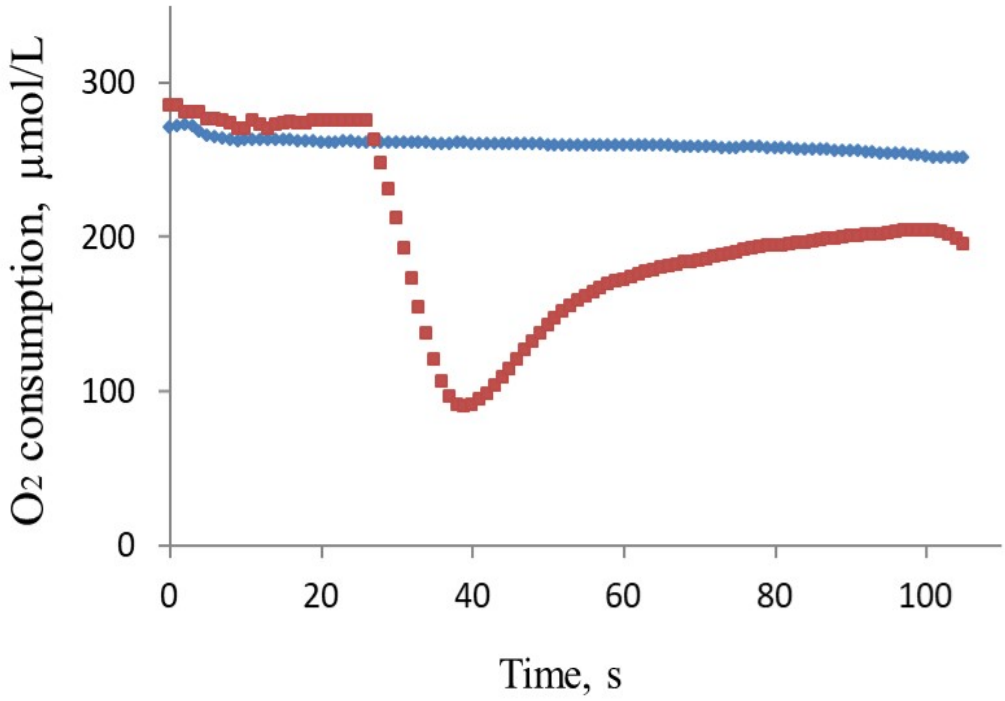

Fig. S4 – Dynamic responses of the oxygen minisensor (oxygen consumption, µmol/L) recorded in HC medium from electrodes modified by: Pd-sputtered foil (blue line); basic Pd-NPs (red line), sample 4. *Note:* Pd-modified electrodes during oxygen minisensor studies were operated in CV mode during first 100 s, the experiments were performed at room temperature, 20±2 °C.

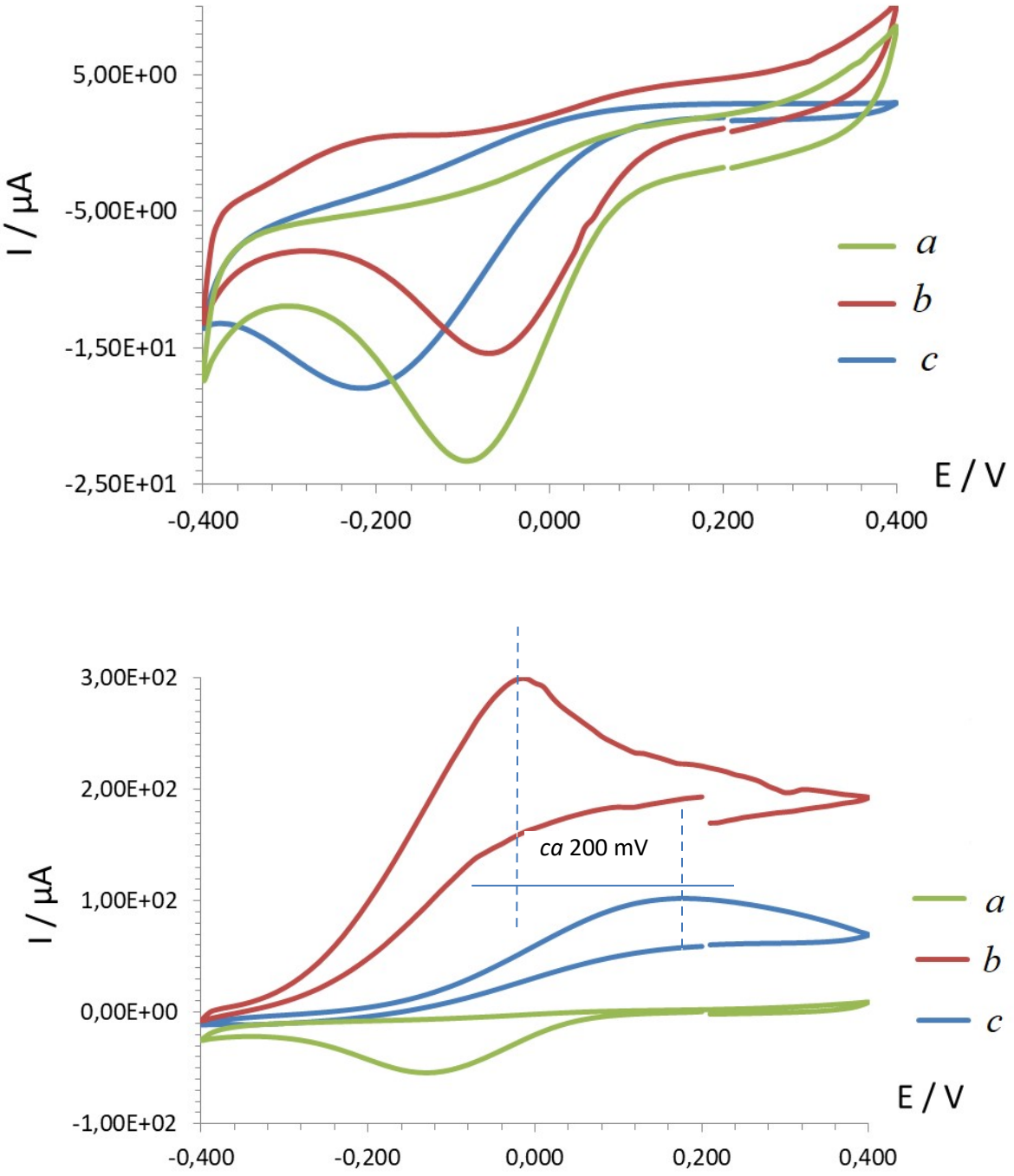

Fig. S5 – CV plots (*vs* Ag/AgCI, second scans shown) obtained at 20 mV/s from Pd-NPs-modified electrode produced from the basic electrolyte (basic Pd-NPs) in 200 µM (*top*) and 10 mM (*bottom*) of hydrazine solutions: *a* – CV plots recorded in acetate buffer; *b* – in a droplet of hydrazine solutions prepared in acetate buffer and dropped on the intact electrode surface; *c* – in a droplet of hydrazine solution dropped on the electrode surface after its heating at 200 °C for 20 min.

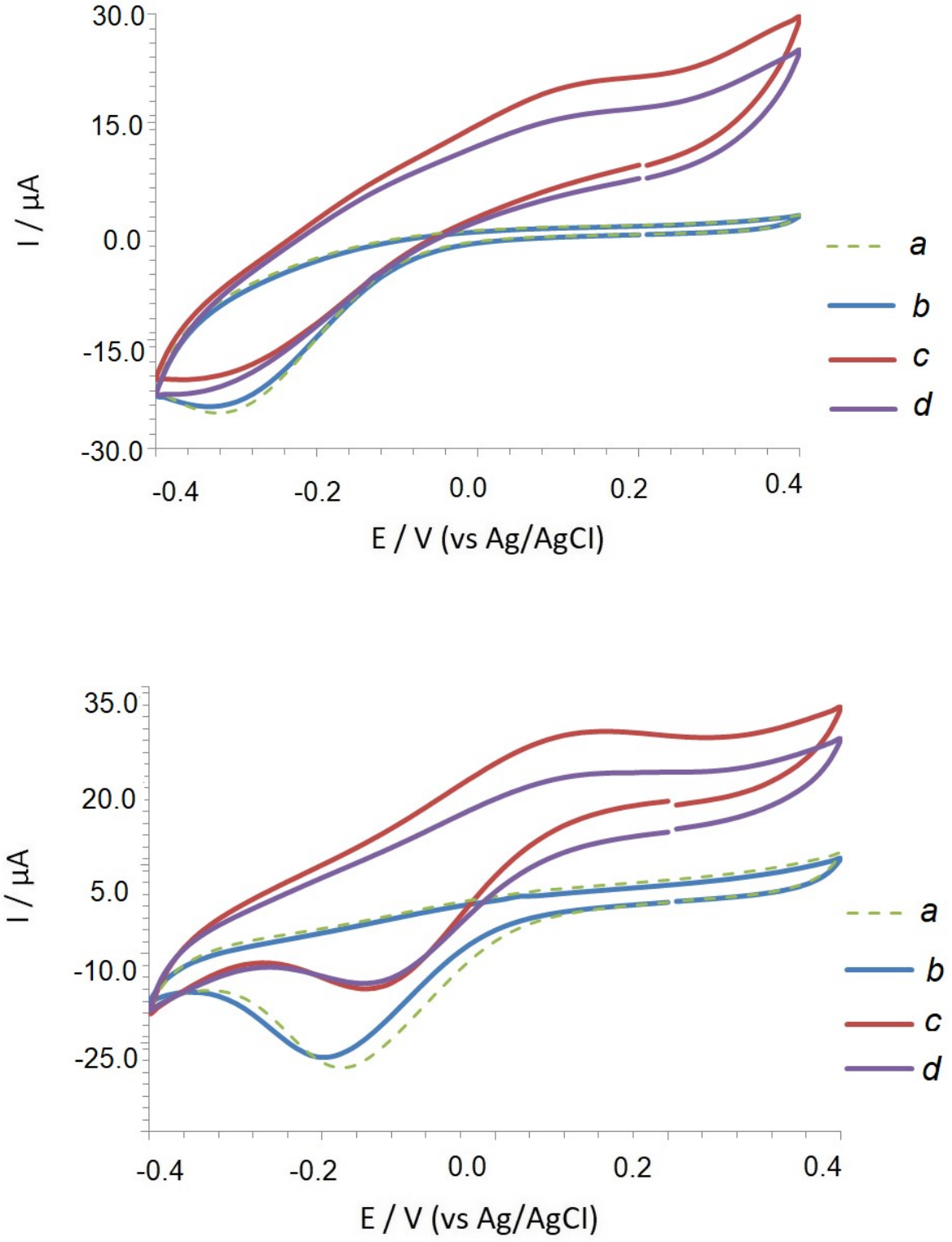

Fig. S6 – Representative CV plots (second scans shown) recorded at 20 mV/s from Pd-NPs-based electrodes produced from the basic, **sample 2** (**A**) and acidic, **sample 1** (**B**) electrolytes: *a* – in HC medium; *b* – 1 mM of H_2O_2 in HC medium (pH 4); *c* – 1 mM of N_2H_4 in HC medium; *d* – mixture of 1 mM of H_2O_2 +1 mM of N_2H_4 in HC medium.

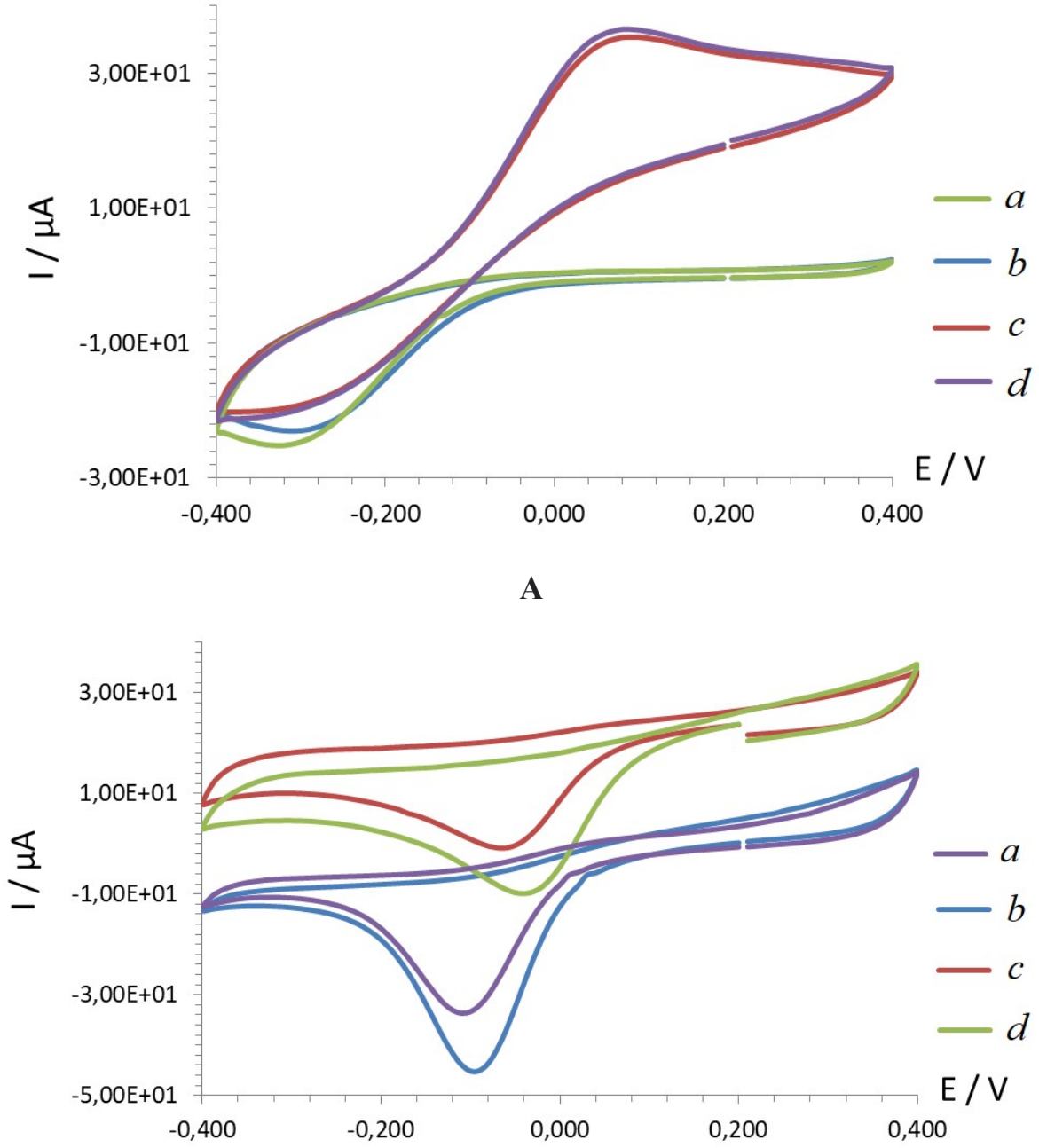

Fig. S7 – Representative CV plots (*vs* Ag/AgCI, second scans shown) recorded at 20 mV/s from Pd-NPs-modified electrodes (**sample 2**) in (**A**) acetate and (**B**) phosphate buffer solution spiked with target analytes: *a* – buffer; *b* – 1 mM of individual hydrogen peroxide; *c* – 1 mM of individual hydrazine; *d* – mixture of 1 mM of hydrazine + 1 mM of hydrogen peroxide. *Note:* Pd-NPs were produced from the basic electrolyte (oxides-based surface of electrodes).