

Supplementary Materials

Electrochemical Operational Principles and Analytical Performance of Pd-based Amperometric Nanobiosensors

Y.E. Silina^{1}, N. Apushkinskaya¹,
N.V. Talagaeva², M.G. Levchenko², E.V. Zolotukhina^{2,3*}*

*¹Institute for Biochemistry, Zentrum für Human und Molekularbiologie (ZHMB),
Campus B 2.2, University of Saarland, 66123, Saarbrücken, Germany*

*²Institute of Problems of Chemical Physics RAS, 1 Ac. Semenov avenue, Chernogolovka,
142432, Moscow region, Russia*

*³Moscow Institute of Physics and Technology, 9 Institutskiy per., Dolgoprudny,
141700, Moscow region, Russia*

*To whom the correspondence
should be addressed/*authors with equal contribution

E-mail address 1: yuliya.silina@uni-saarland.de; yuliya.silina@gmx.de (Y.E. Silina)

E-mail address 2: zolek@icp.ac.ru (E.V. Zolotukhina)

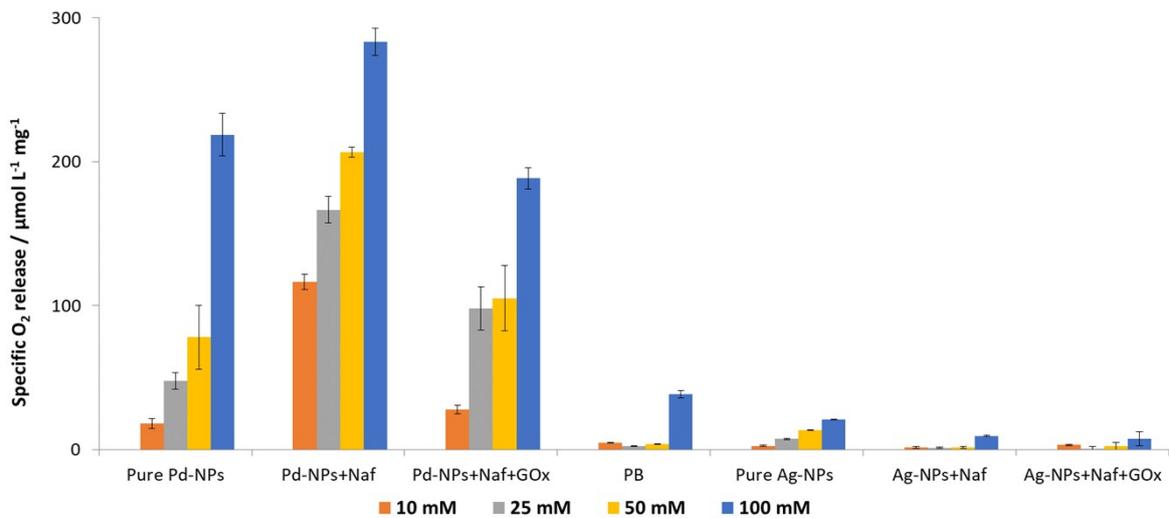


Figure S1. The effective response of the optical oxygen microsensor (dissolved oxygen, DO, $\mu\text{mol/L}$ divided into functional layer weight, mg) during the reaction between hydrogen peroxide (in phosphate buffer, pH = 6.98), pure/intact Pd-NPs, PB, Ag-NPs, and their hybrids (shown for GOx and Nafion as a case study). *Note:* the experiments were performed at room temperature, 20 ± 2 °C and signal was recorded by minisensor at 100 s ones the CV measurements were started. The experiments were performed in a triplicate as results were estimated as \pm SD. Amount of co-deposits/functional layer measured by QCM-sense system.

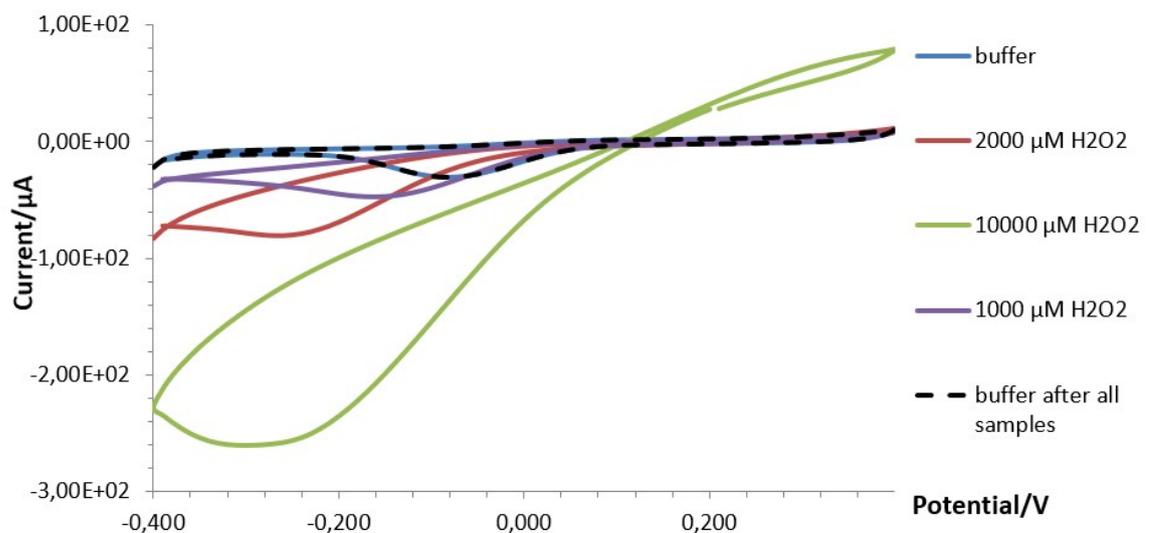


Figure S2. CV curves recorded on SPE/GO modified by pure Pd-NPs (-2.5 mA for 30 s) in the presence of hydrogen peroxide at the scan rate of 20 mV/s and pH 7 vs Ag/AgCl/sat.KCl. *Note:* the provided curves indicate that no irreversible changes occur on the surface of SPE/GO modified by Pd-NPs after H₂O₂ decomposition.

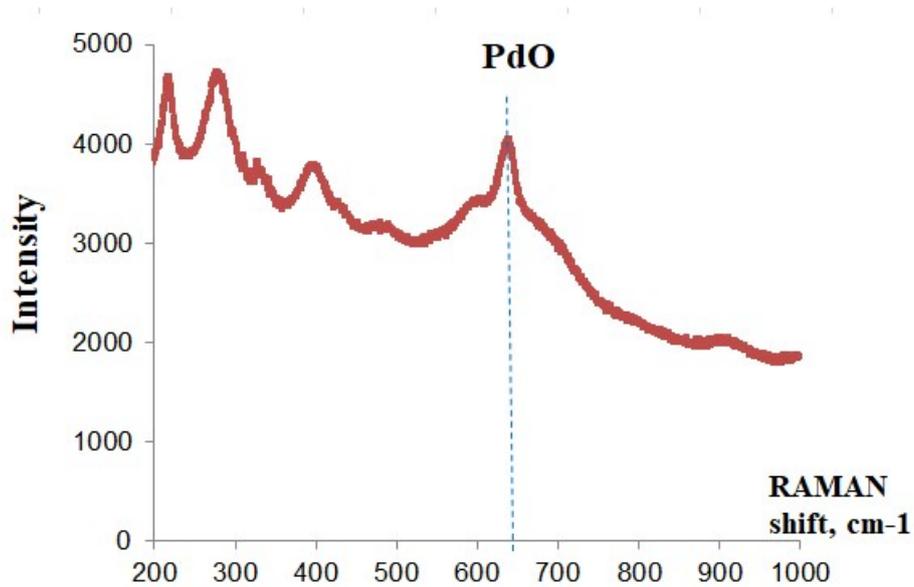


Figure S3. Raman spectra recorded from Pd-NPs-based nanobiosensor indicating presence of PdO at 640 cm^{-1} . *Note:* the peak at 640 cm^{-1} was approved as PdO according to (A. Baylet, P. Marécot, D. Duprez, P. Castellazzi, G. Groppi, *Phys. Chem. Chem. Phys.*, 2011, 13, 4607-4613. <https://doi.org/10.1039/C0CP01331E>)

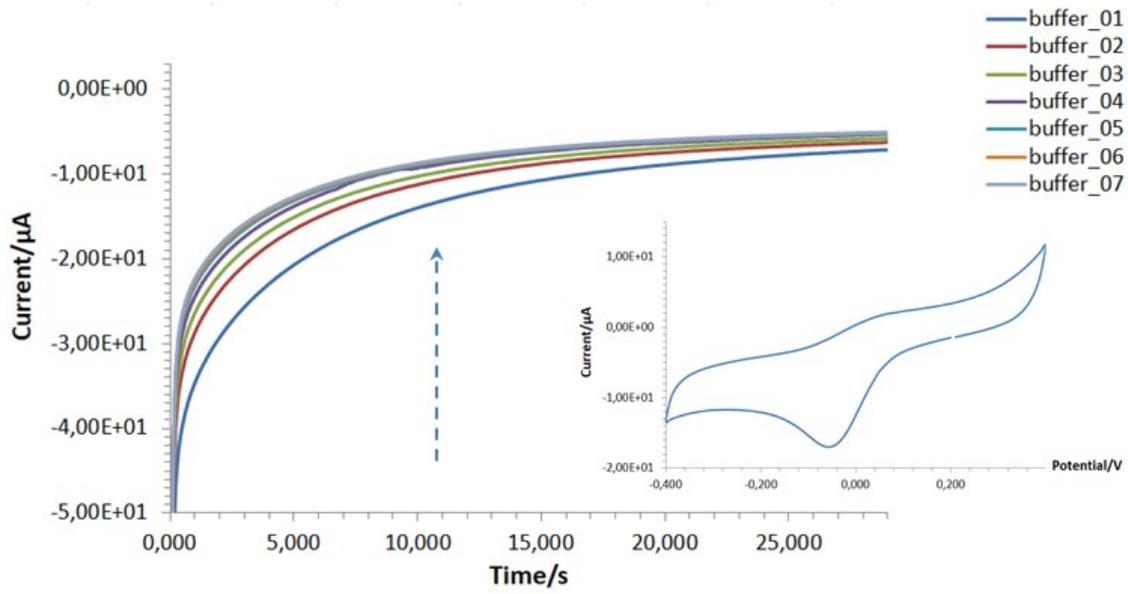


Figure S4. Chronoamperometric curves recorded from one-step produced AOx/Nafion/Pd-NPs hybrid in phosphate buffer with a new droplet at the applied potential of -0.05 V. The insert (CV curve) was obtained at 20 mV/s, pH = 7.

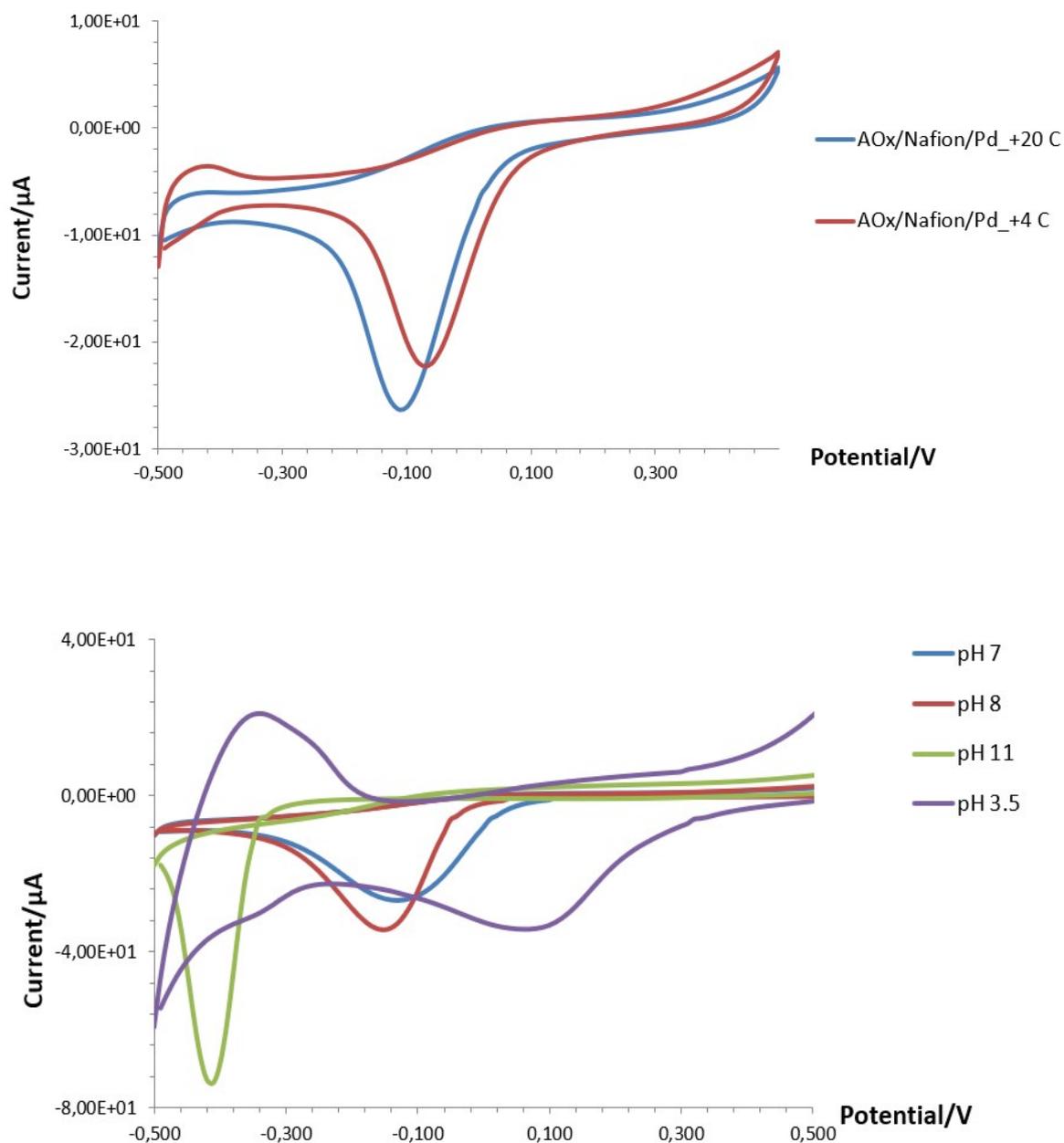


Figure S5. CV curves recorded in phosphate buffer at scan rate 20 mV/s from:
(top) – AOx/Naf/Pd nanobiosensors dried/stored at +4 °C and at +20 °C, pH 7;
(bottom) – GOx/Naf/Pd nanobiosensor (dried/stored at +4 °C) and tested in phosphate buffer at various pH.

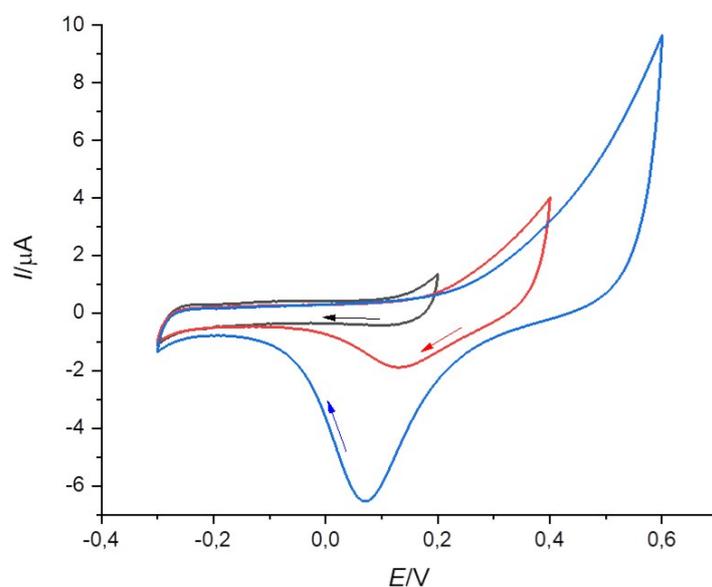


Figure S6. CV curves recorded in phosphate buffer on Pd-NPs-modified GCE (Ar-atmosphere, in the absence of O_2 , black line) at scan rate of 10 mV/sec, pH 7.5. *Note:* Red and blue lines were obtained in the presence of oxygen. Anodic scan limit was set as follows: 0.2, 0.4 and 0.6 V vs Ag/AgCl/sat.KCl.

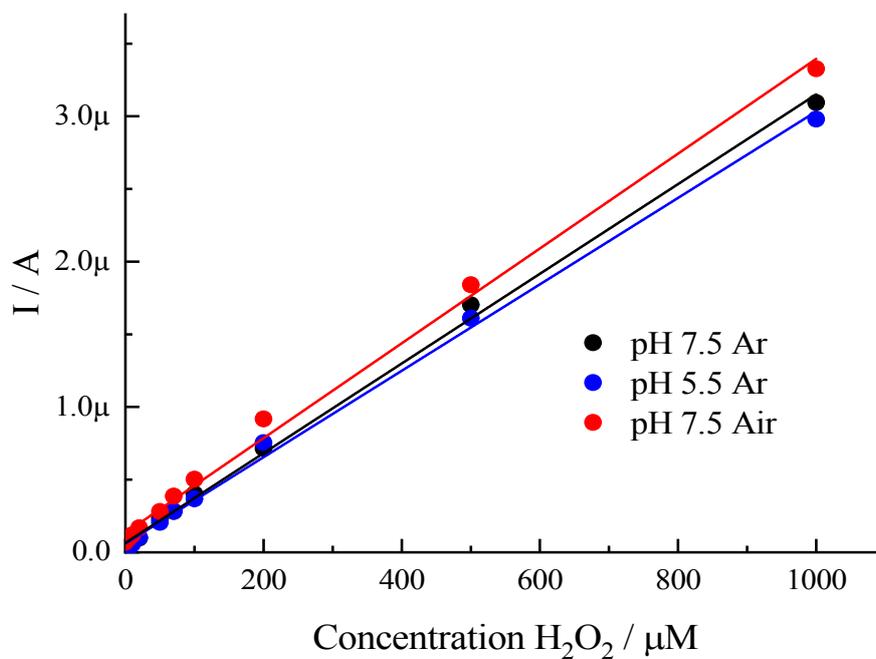


Figure S7. Steady-state current responses recorded at different pH on GCE modified by Pd-NPs in phosphate buffer with various concentrations of H_2O_2 at potential 0.4 V.

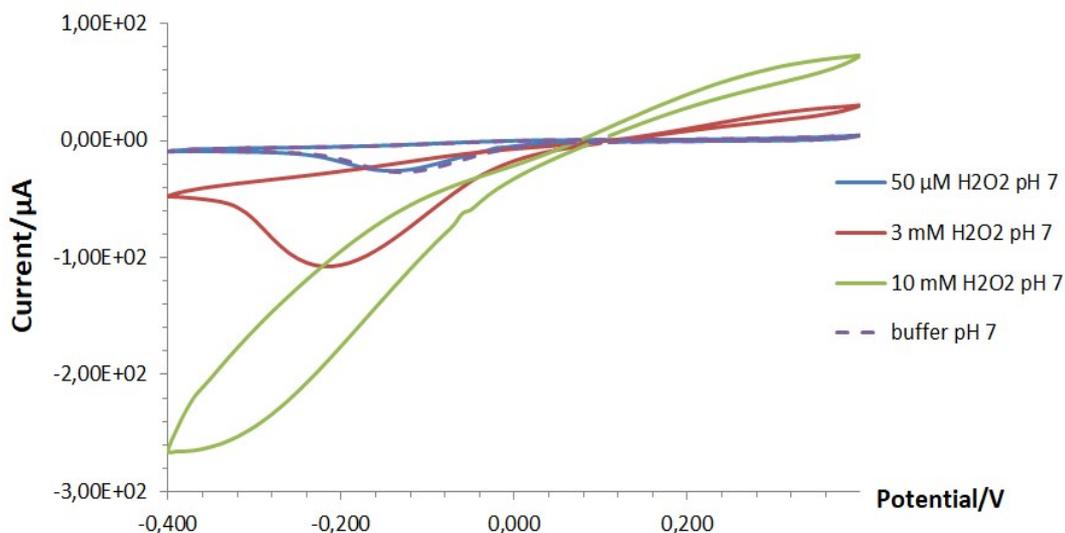


Figure S8. CV curves recorded on SPE/GO modified by Pd-NPs at 20 mV/s in phosphate buffer and H₂O₂ solutions (pH = 6.98) in the range from -0.4 V to 0.4 V.

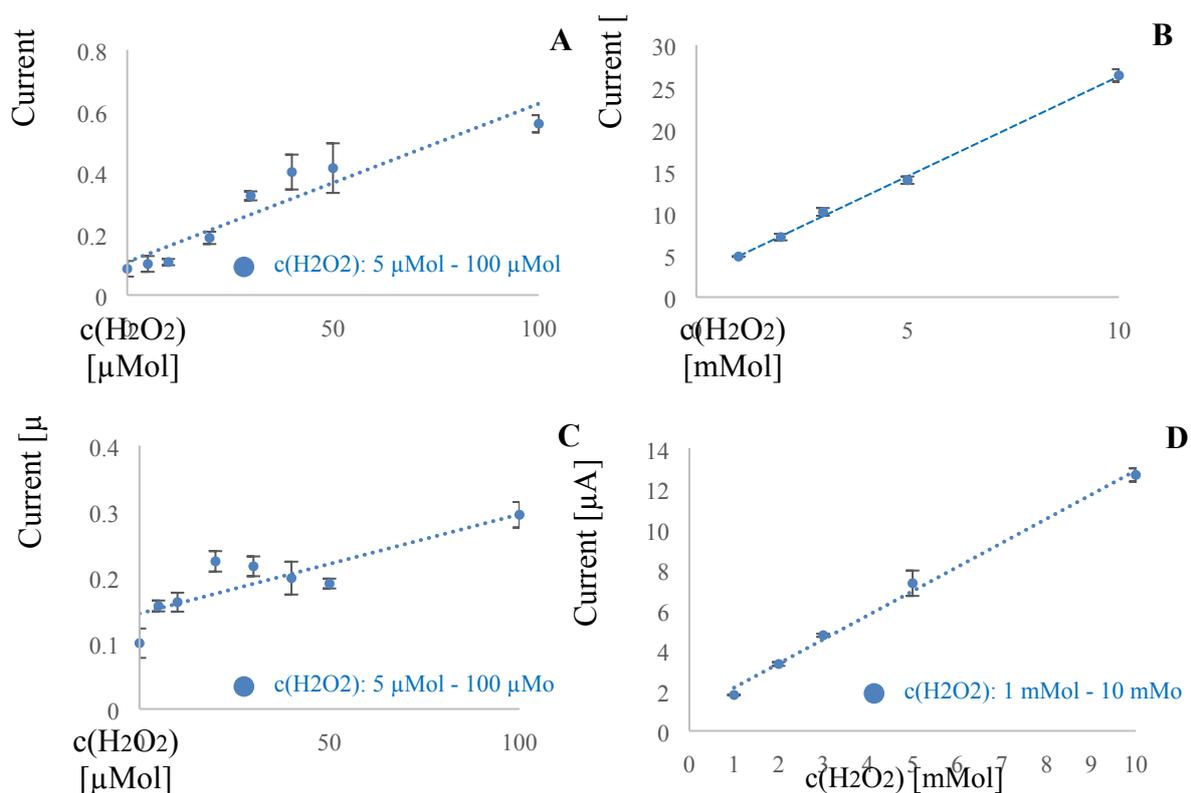


Figure S9. The calibration curves obtained for H₂O₂ in analytically relevant concentration range in multi-step amperometry mode (MAM): -0.08 V polarization voltage for 30 s (*step 1*) followed by 0.2 V for 60 s (*step 2*) from Pd-NPs synthesized at 30 s (**A,B**); 60 s (**C,D**). *Note:* the experiments were performed at pH = 6.98, n = 3.

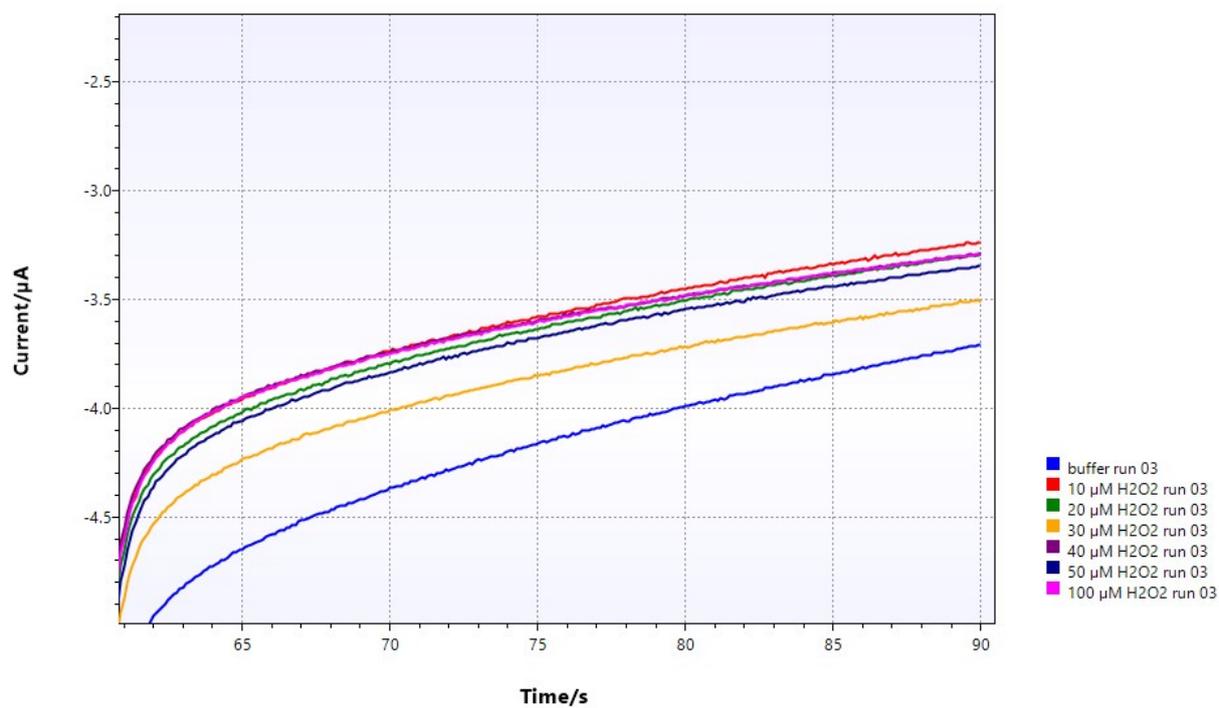
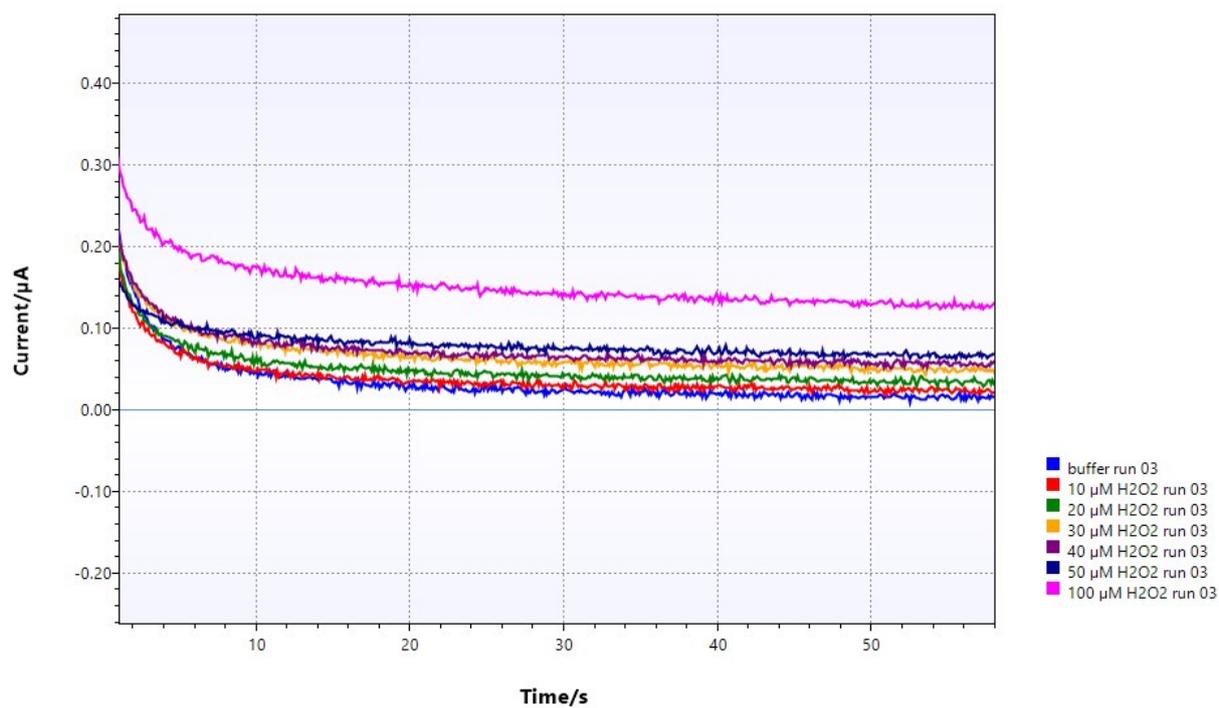


Figure S10. The analytical performance of SPE/GO modified by Pd-NPs in phosphate buffer towards peroxide decomposition recorded in multistep amperometric mode at the potential of 0.2 V (*top*) and -0.08 V (*bottom*).

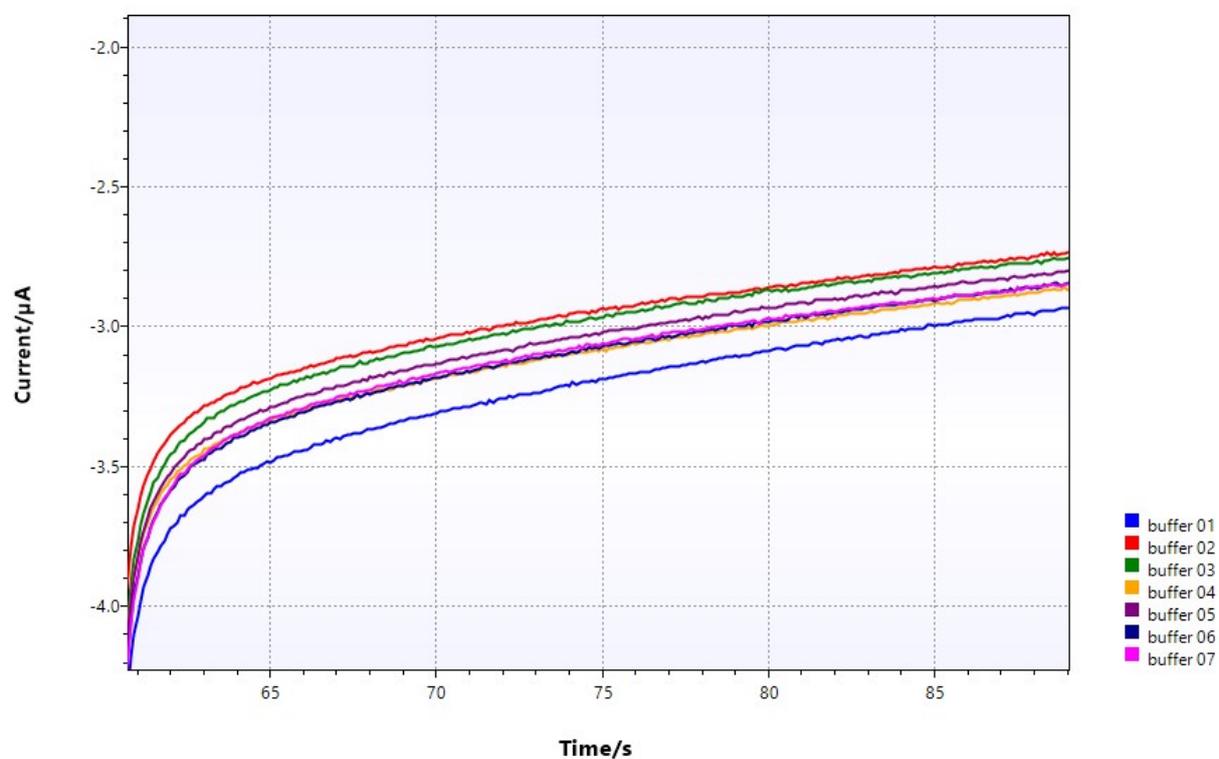
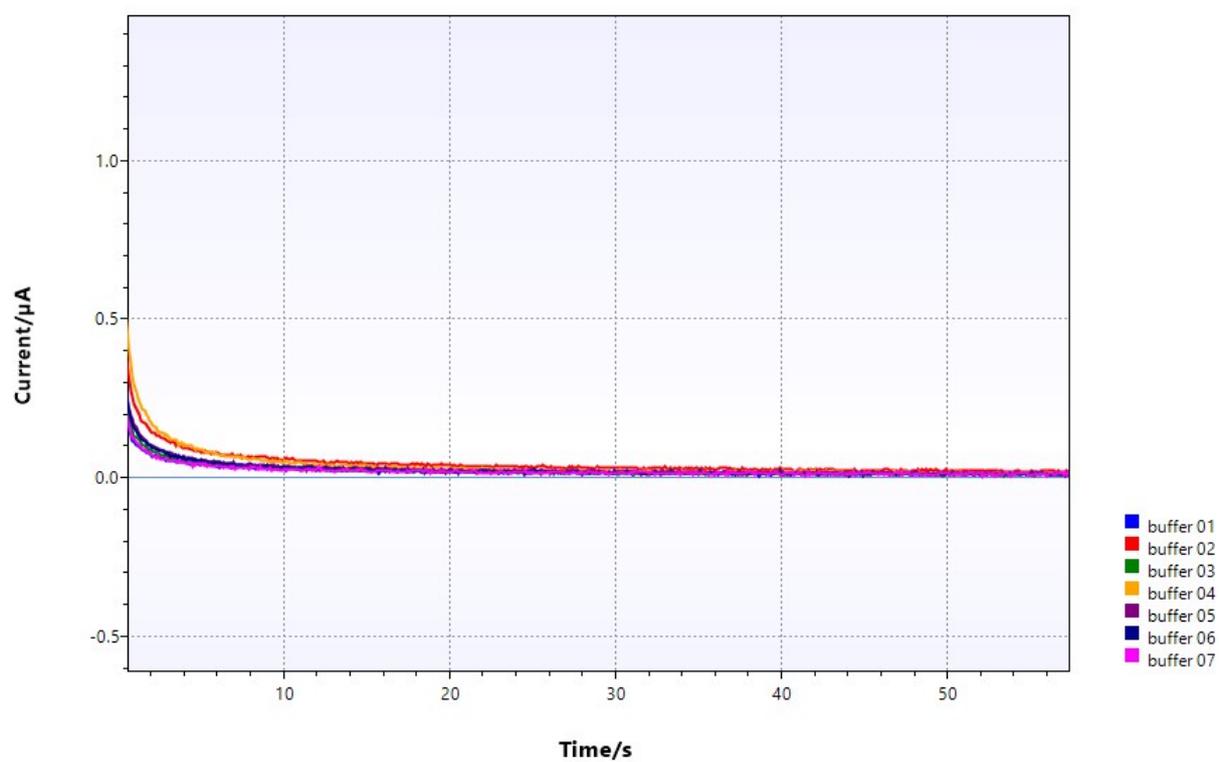


Figure S11. Validation of analytical performance/basic lines (blank experiments) of SPE/GO modified by Pd-NPs: responses obtained from Pd-NPs in phosphate buffer in multistep amperometric mode at the potential of 0.2 V (*top*) and -0.08 V (*bottom*).

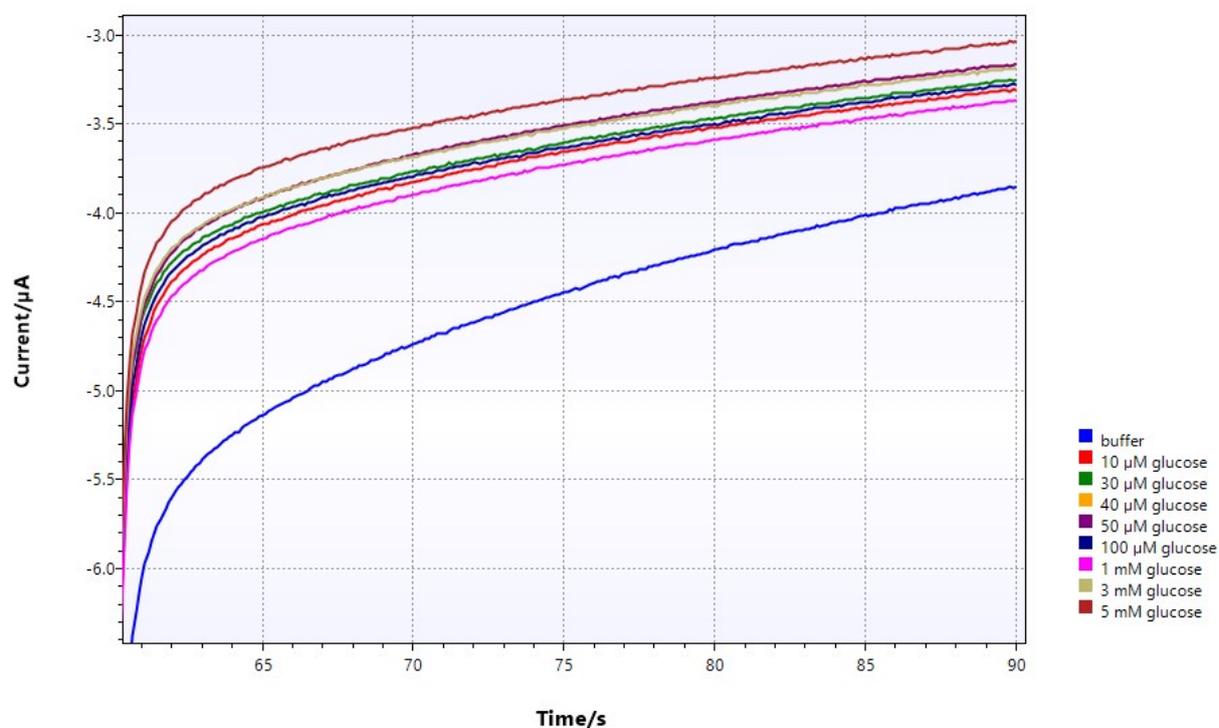
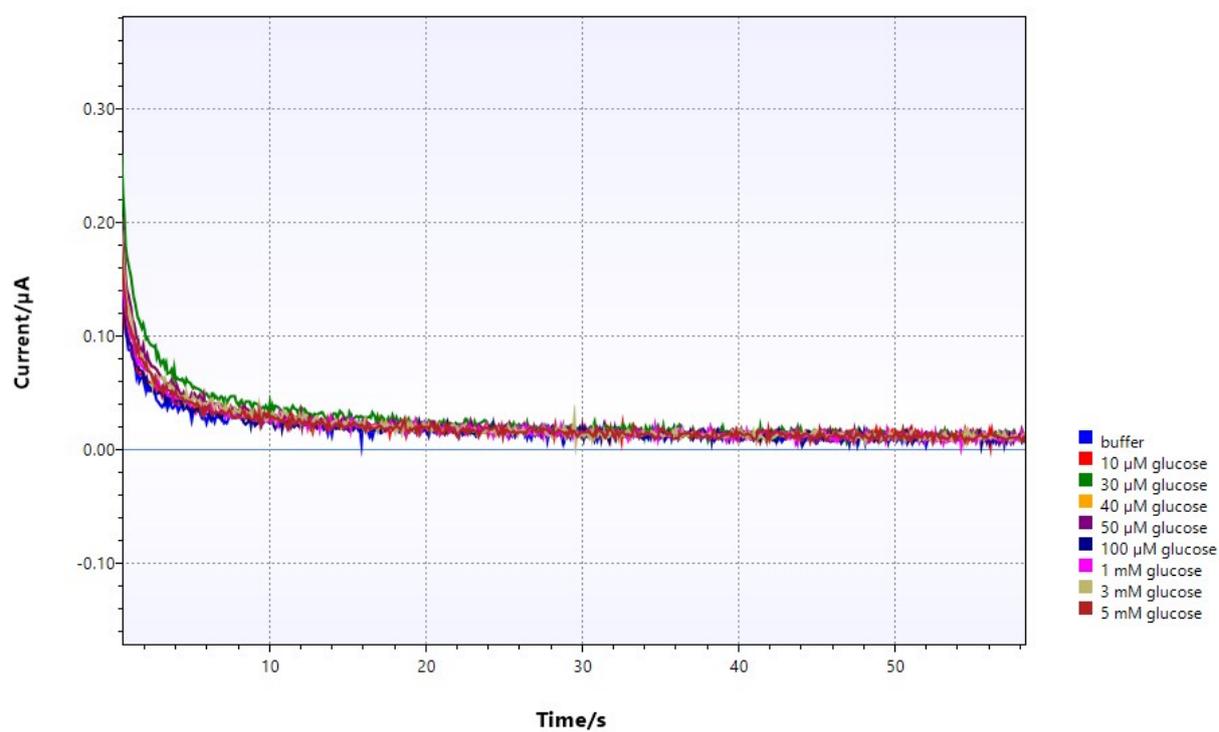


Figure S12. Validation of analytical performance/impact of interfering ionic species of SPE/GO modified by Pd-NPs: responses obtained from Pd-NPs in glucose solutions (as a case study) in multistep amperometric mode at the potential of 0.2 V (*top*) and -0.08 V (*bottom*).