Supplementary Material

Differential Pulse Voltammetric Detection of Acetaminophen Using Nickel Phthalocyanine/CeO_2 Modified ITO Electrodes

Emiliano C. Gomes[1], Camila L. Ribeiro[1], Vianney O. Santos Jr[2], and Leonardo G. Paterno[1*]

[1]Laboratório de Pesquisa em Polímeros e Nanomateriais, Instituto de Química, Universidade de Brasília, Brasília-DF, 70910-900, Brazil

[2]Centro de Pesquisas e Análises Tecnológicas (CPT), Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP), 70830-902, Brasília-DF, Brazil

*corresponding author: lpaterno@unb.br

Summary

Structural characterization of CeO_2 nanoparticles

Figure S1 reports the structural features of CeO_2 nanoparticles assessed by a set of characterization methods. The X-ray diffractogram (Figure S1a) is composed by the main peaks expected for CeO_2 FCC crystal (Fm3m space group) at 2θ: 28.7º (111), 33.1º (200), 47.5º (220), and 56.4º (311). The interplanar distance is calculated with the Bragg equation using the diffraction angle of the most intense peak (111). After that, the lattice parameter is estimated as 5.375 angstroms, which agrees with values reported for ceria in the literature [1]. The crystallite size determined after applying the Scherrer equation to the full width at half maximum (FWHM) of the most intense diffraction peak (111) is 3.1 nm. The Raman spectrum shown in Figure S1b confirms the CeO_2 structure with a single vibration mode at 459 cm^{-1}, which is ascribed to the symmetric stretching of Ce-O bonds (symmetry F_{2g}) [2]. The crystallite size can be determined from this peak using equation 1, in which β is the FWHM of that peak. Accordingly, the value found is 2.8 nm.

$$D = \frac{124.7}{(\beta(cm^{-1}) - 10)} \qquad (1)$$

The TEM micrograph (Figure S1c) shows nearly spherical particles, whereas the insert shows a high-resolution micrograph where it is possible to observe the regular spacing of atomic planes. The distance between them (determined with the Image J software) is highlighted in yellow and corresponds to 0.33 nm. Using this value and assuming it corresponds to the (111) plane, the estimated lattice parameter is 5.715 angstroms, which agrees even better with values reported in the literature and that estimated with the X-ray diffractogram shown in Figure S1a. Finally, Figure S1d displays the size distribution built after counting and measuring the diameter of 300 particles using the Image J software. After performing a log normal fit, the mean size of these particles is 2.93 ± 0.02 nm, which is very close to those determined from the X-ray diffractogram and the Raman spectrum.

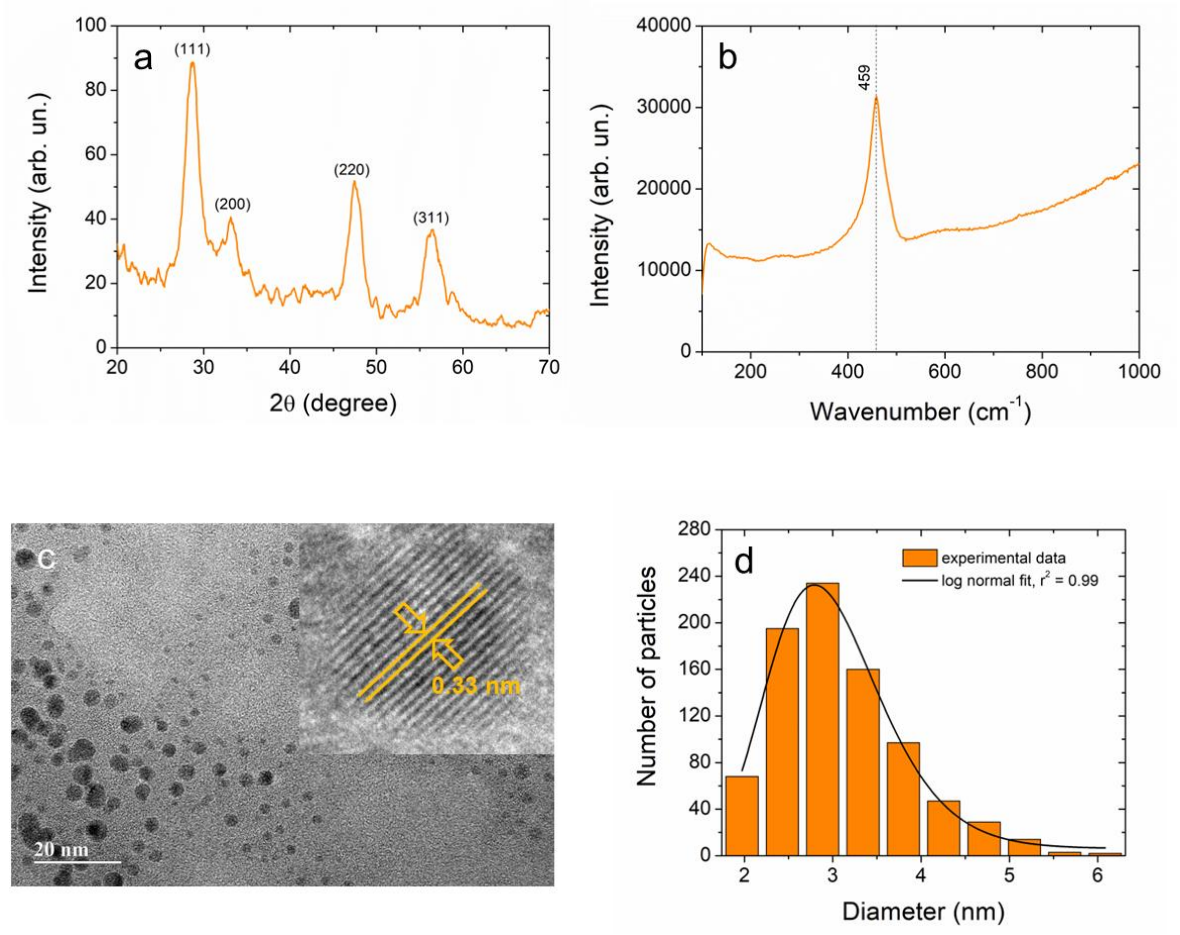

Figure S1. Structural features of CeO_2 nanoparticles: (a) X-ray diffractogram, (b) Raman spectrum, (c) TEM micrograph, and (d) histogram of size distribution.

References

1. Babitha, K.K.; Sreedevi, A.; Priyanka, K.P.; Sabu, B.; Varghese, T. Structural Characterization and Optical Studies of CeO_2 Nanoparticles Synthesized by Chemical Precipitation. *Indian J. Pure Appl. Phys*. **2015**, *53*, 596-603.

2. Spanier, J.E.; Robinson, R.D.; Zhang, F.; Chan, S.-W.; Herman, I.P. Size-Dependent Properties of CeO_2 Nanoparticles as Studied by Raman Scattering. *Phys. Rev. B* **2001**, *64*, 245407.

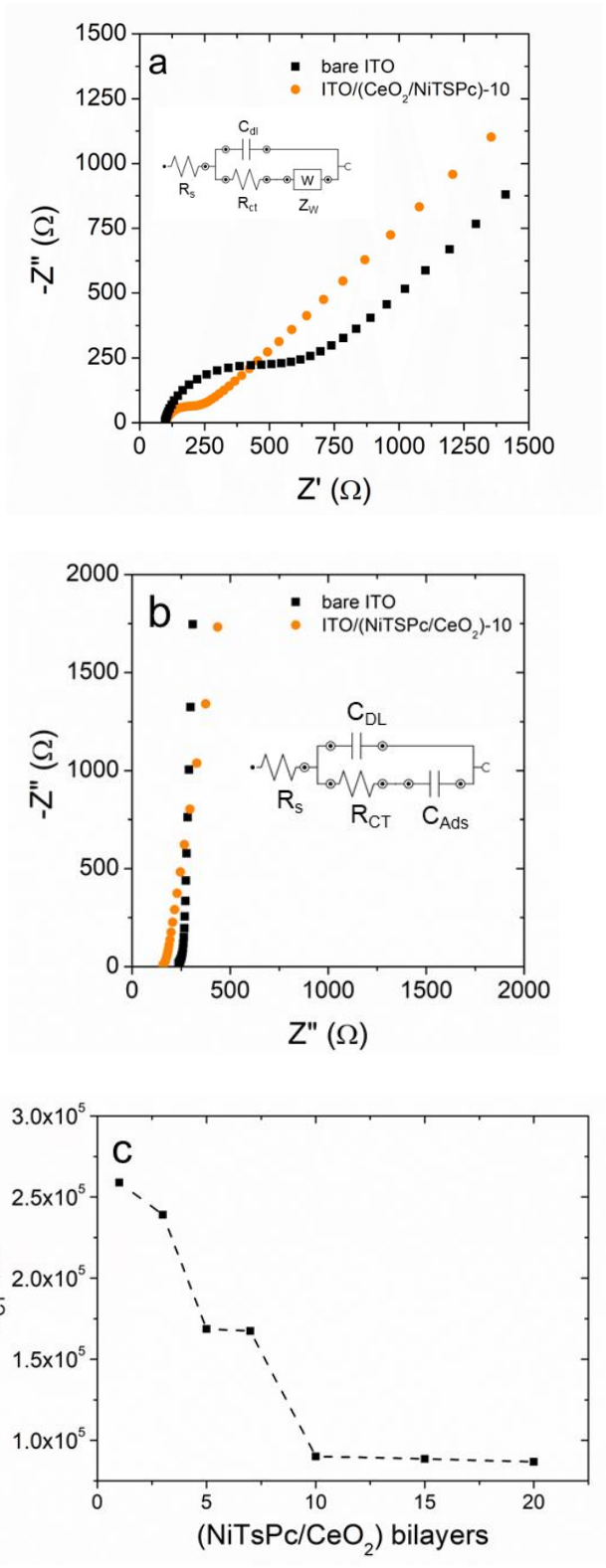

Figure S2. EIS spectra of (a) ferri/ferrocyanide (1 mM) and (b) acetaminophen (20 µM), using bare ITO and ITO/(NiTsPc/CeO_2)-10. Cell potential in (a) is +0.3 V, whereas in (b) is +0.65 V. amplitude: 25 mV. (c) Dependence of the charge-transfer resistance (R_{CT}) on the number of (NiTsPc/CeO_2) bilayers for acetaminophen. All experiments carried out in sodium acetate buffer (0.1 M, pH 3). Insets in parts a and b: Randles circuit and modified Randles circuit.

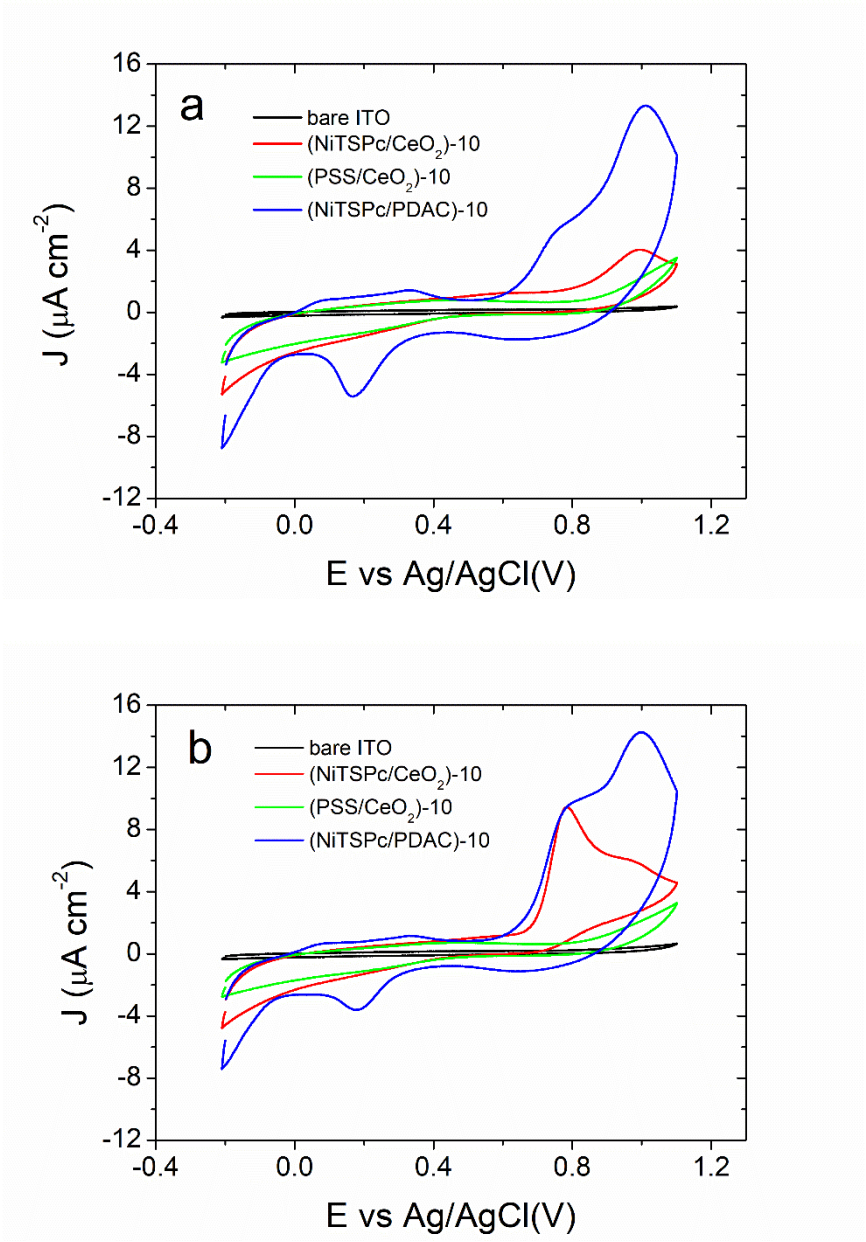

Figure S3. Cyclic voltammograms of acetaminophen registered with different electrode nanoarchitectures in (a) plain sodium acetate buffer (0.1 M, pH 3) and (b) acetaminophen (20 μM) in sodium acetate buffer (0.1 M, pH 3). Scan rate: 25 mV s^1.

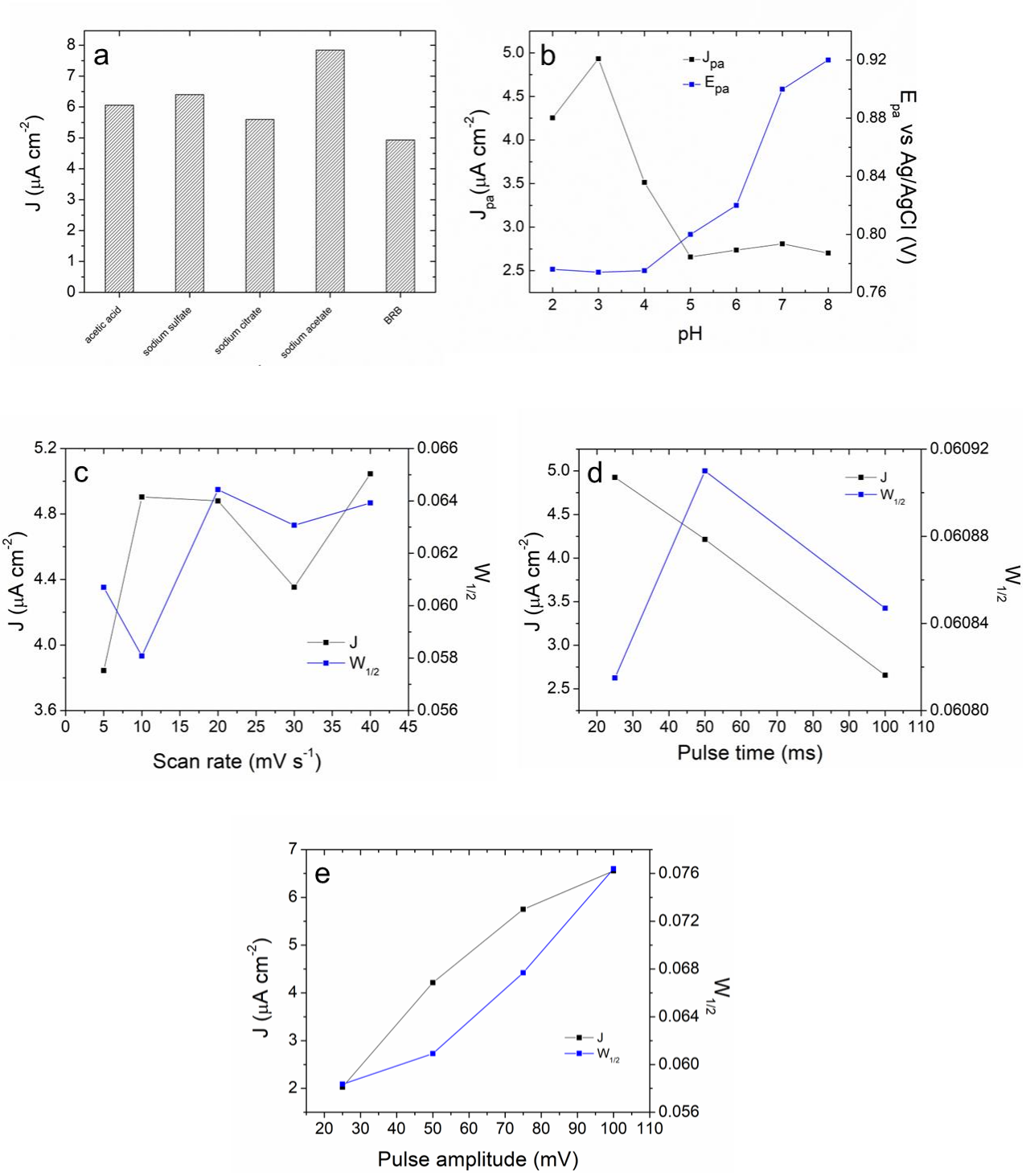

Figure S4. DPV experiments for optimization of the measurement conditions for determination of acetaminophen using the ITO/(NiTsPc/CeO_2)-10 electrode. (a) different supporting electrolytes at pH 3; (b) J_{pa} and E_{pa} versus pH in BR buffer; J and $W_{1/2}$ versus (c) scan rate, (d) pulse time, and (e) pulse amplitude. In all experiments, acetaminophen concentration was 20 µM. Curves in c-e registered with sodium acetate buffer (0.1 M, pH 3).

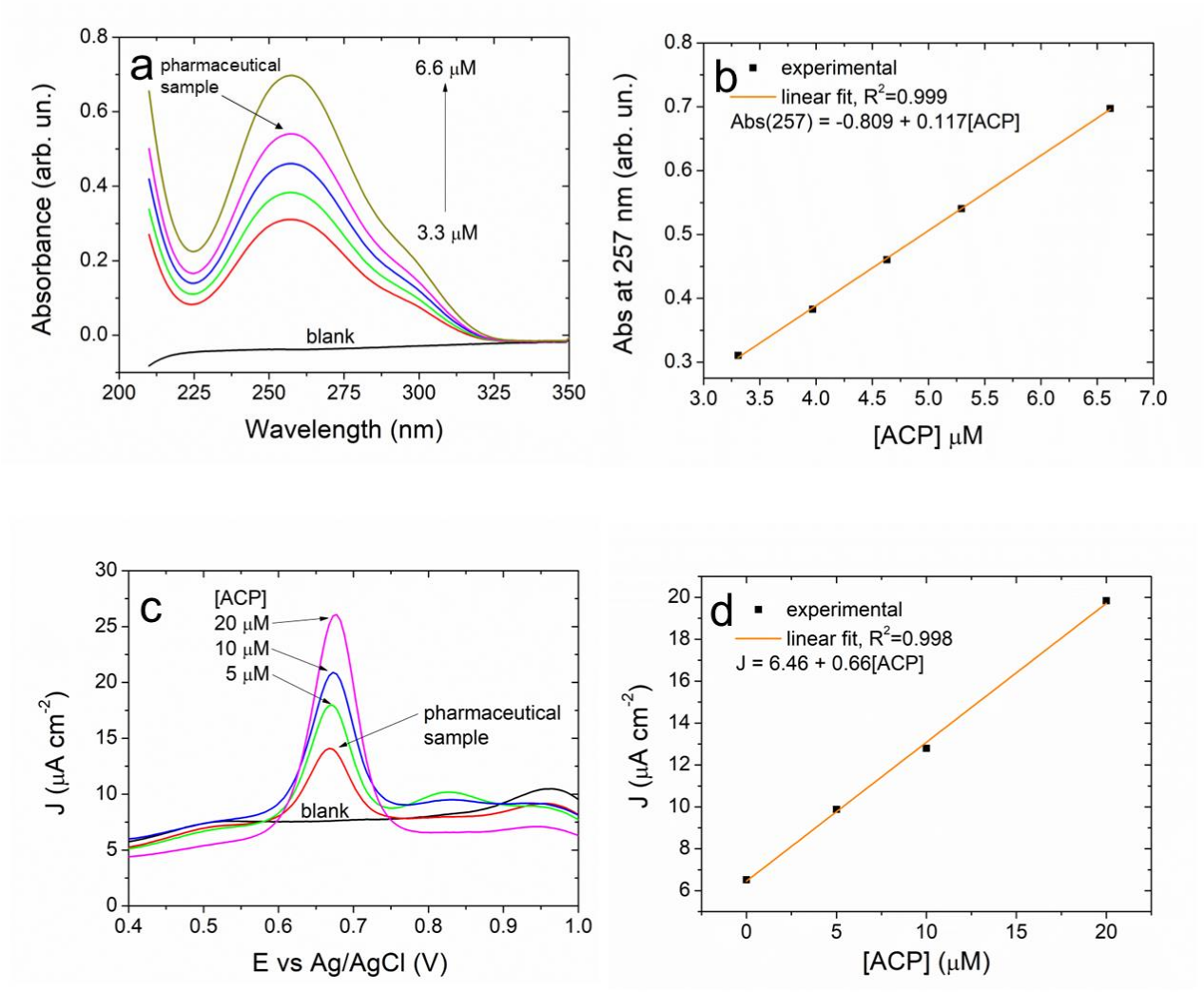

Figure S5. Determination of acetaminophen in pharmaceutical tablet using UV-Vis spectroscopy: (a) UV-Vis spectra and (b) calibration plot; and DPV with ITO/(NiTsPc/CeO_2)-10 electrode: (c) DPV curves and (d) calibration plot. DPV conditions: scan rate, 10 mV s^{-1}; pulse amplitude, 50 mV; pulse time: 25 ms.

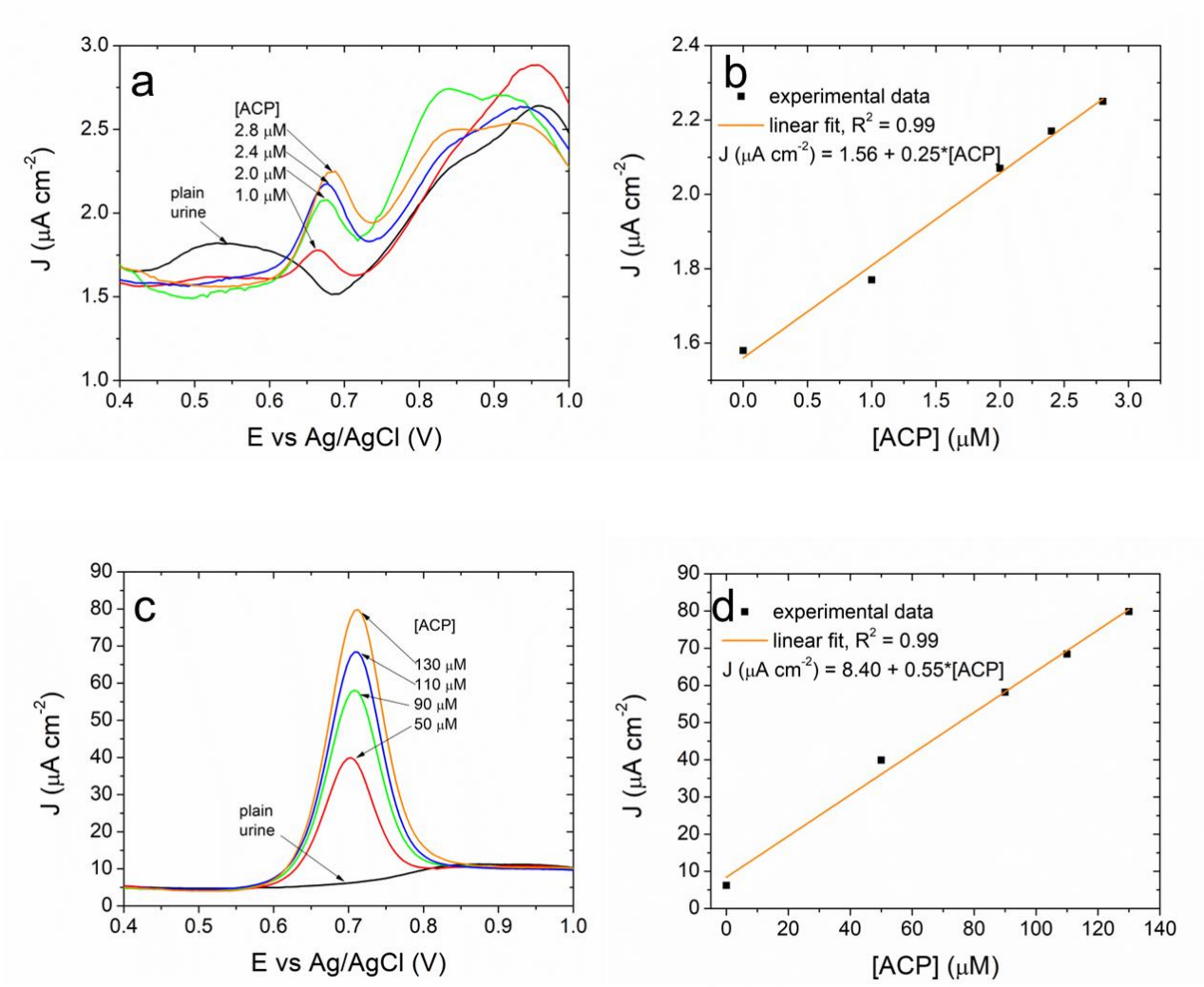

Figure S6. DPV determination of acetaminophen in synthetic urine using the ITO/(NiTsPc/CeO_2)-10 electrode: (a) DPV curves and (b) calibration plot for [ACP] = 1.0 – 2.8 μM; (c) DPV curves and (d) calibration plot for [ACP] = 50 – 130 μM. DPV conditions: scan rate, 10 mV s^{-1}; pulse amplitude, 50 mV; pulse time: 25 ms.

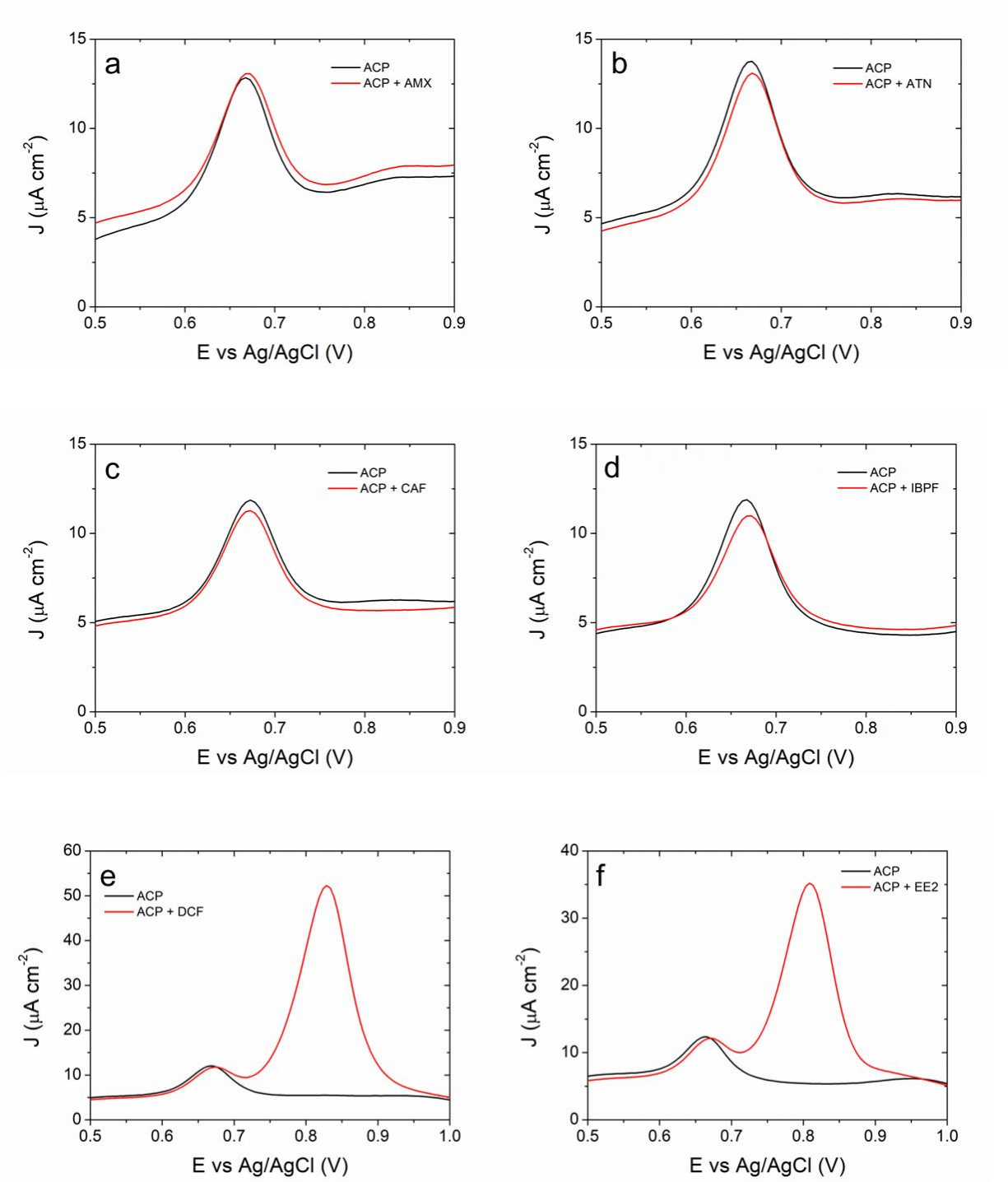

Figure S7. Study of interfering species at equimolar acetaminophen:interfering concentration (10 µM): (a) amoxicillin-AMX, (b) atenolol-ATN, (c) caffeine-CAF, (d) ibuprofen-IBPF, (d) diclofenac-DCF, and (e) ethinyl estradiol-EE2. All measurements performed in sodium acetate buffer (0.1 M, pH 3). DPV conditions: scan rate, 10 mV s^{-1}; pulse amplitude, 50 mV; pulse time: 25 ms.

Table S1. Fitting parameters for EIS spectra of acetaminophen registered with ITO//(NiTsPc/CeO_2)-n, with n = 1 to 20.

n	R_S (Ω)	C_{DL} (μF)	R_{CT} (MΩ)	C_{Ads} (μF)	χ^2
1	197.8	4.8	0.26	2.7	0.54
3	166.7	3.8	0.24	3.8	0.63
5	188.8	3.7	0.17	5.3	0.71
7	177.8	4.4	0.16	5.3	0.66
10	178.4	4.5	0.12	6.1	0.65
15	182.7	4.7	0.09	6.8	0.97
20	179.7	5.3	0.08	7.6	1.08

Table S2. Relative error of electrochemical signal for acetaminophen in the presence of interfering species.

Interfering species	Signal relative error (%)
Amoxicillin	-3.5
Atenolol	-1.15
Caffeine	-2.33
Diclofenac	-
Ethinyl estradiol	-
Ibuprofen	-12.70