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Supplementary Material

Aniline Electropolymerization on Indium-Tin Oxide Nanofilms with Different Surface Resistivity: A Comprehensive Study

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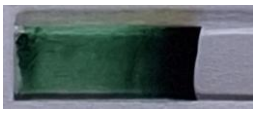
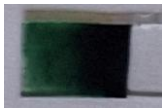
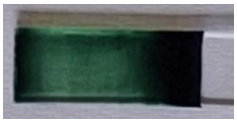
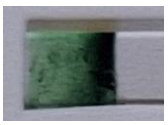
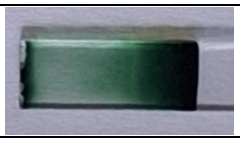
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Table S1. Photo of the obtained polyaniline layers.

Number of cycles / scan rate	Polyaniline, ITO with:		
	70-100 Ω/sq glass	80-100 Ω/sq glass	15-25 Ω/sq glass
7 / 50 mV·s^{-1}			
13 / 50 mV·s^{-1}			-
7 / 100 mV·s^{-1}			
13 / 100 mV·s^{-1}			-

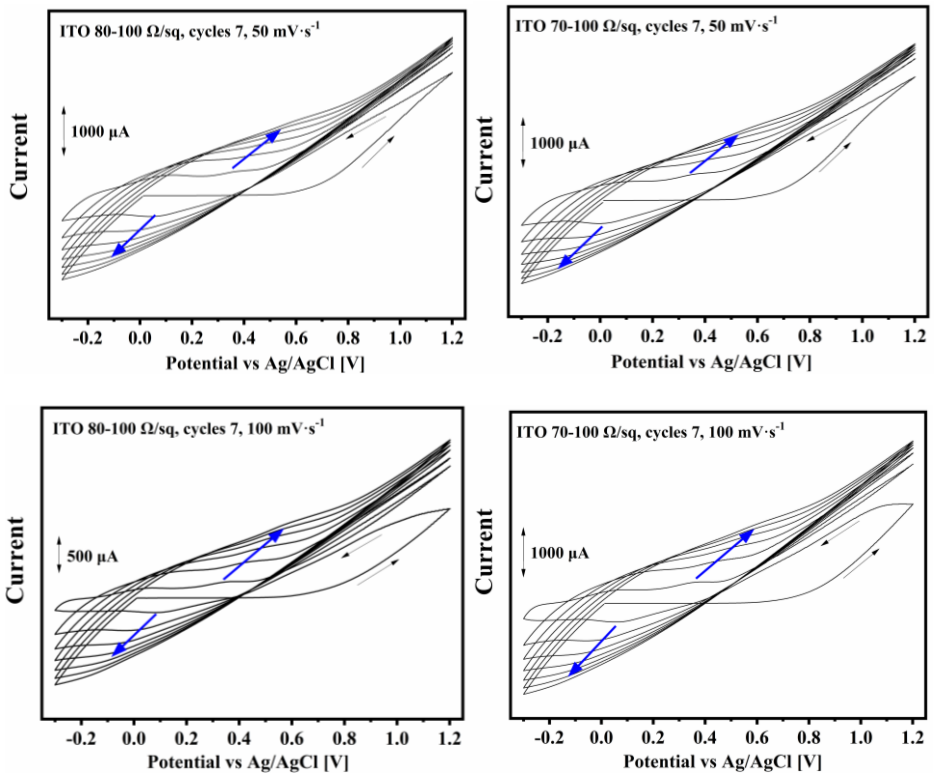


Figure S1. Cyclic voltammograms obtained during the electropolymerization. The process was conducted in 0.5 mol·dm^{-3} H_2SO_4/water solution with aniline, and the ITO working electrode with different surface resistivity. The scan rates were 50 mV·s^{-1} and 100 mV·s^{-1} and 7 or 13 cycles were performed.

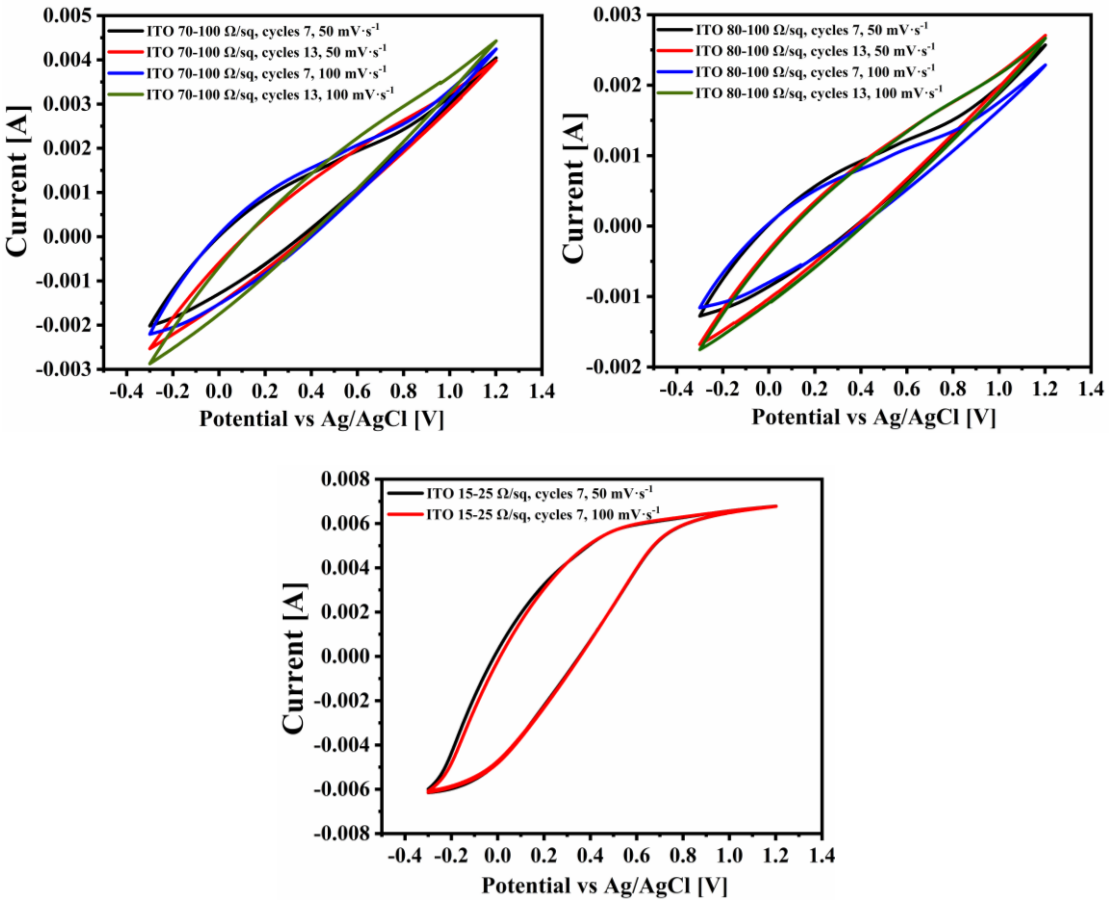
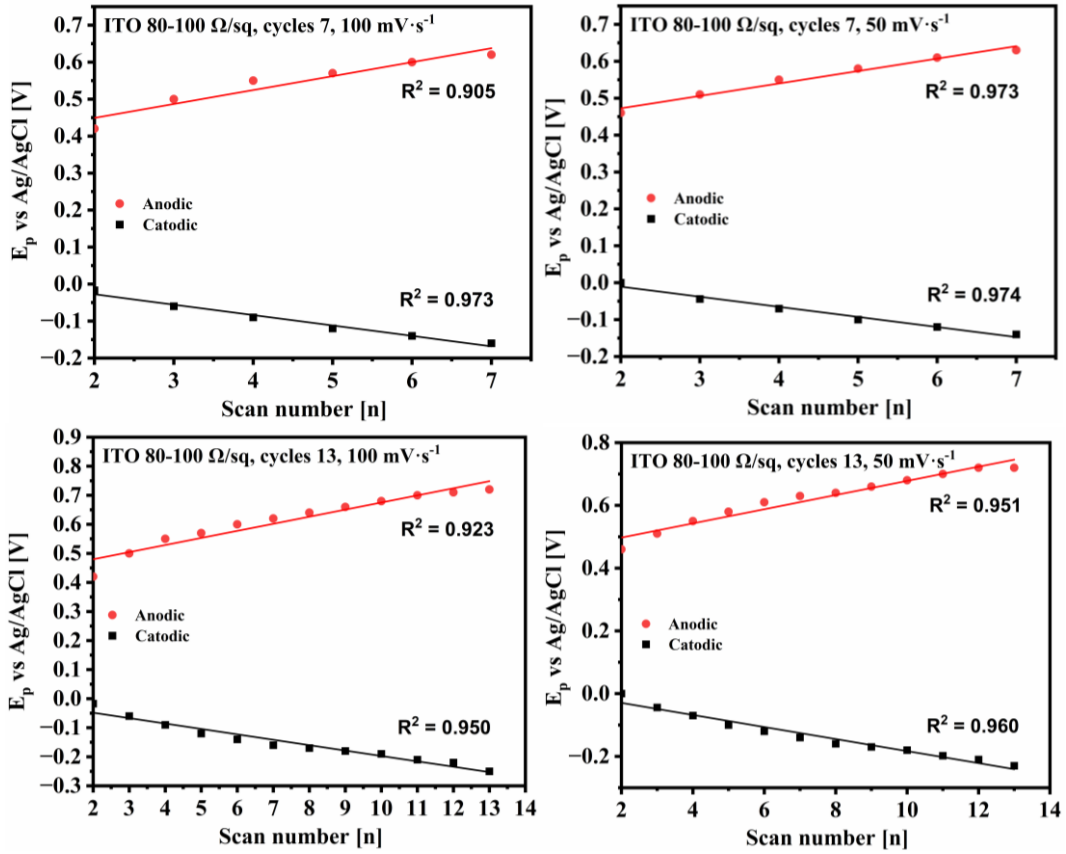


Figure S1. Continued. Cyclic voltammograms of the last cycle in 0.5 mol·dm^{-3} H_2SO_4/water solution.



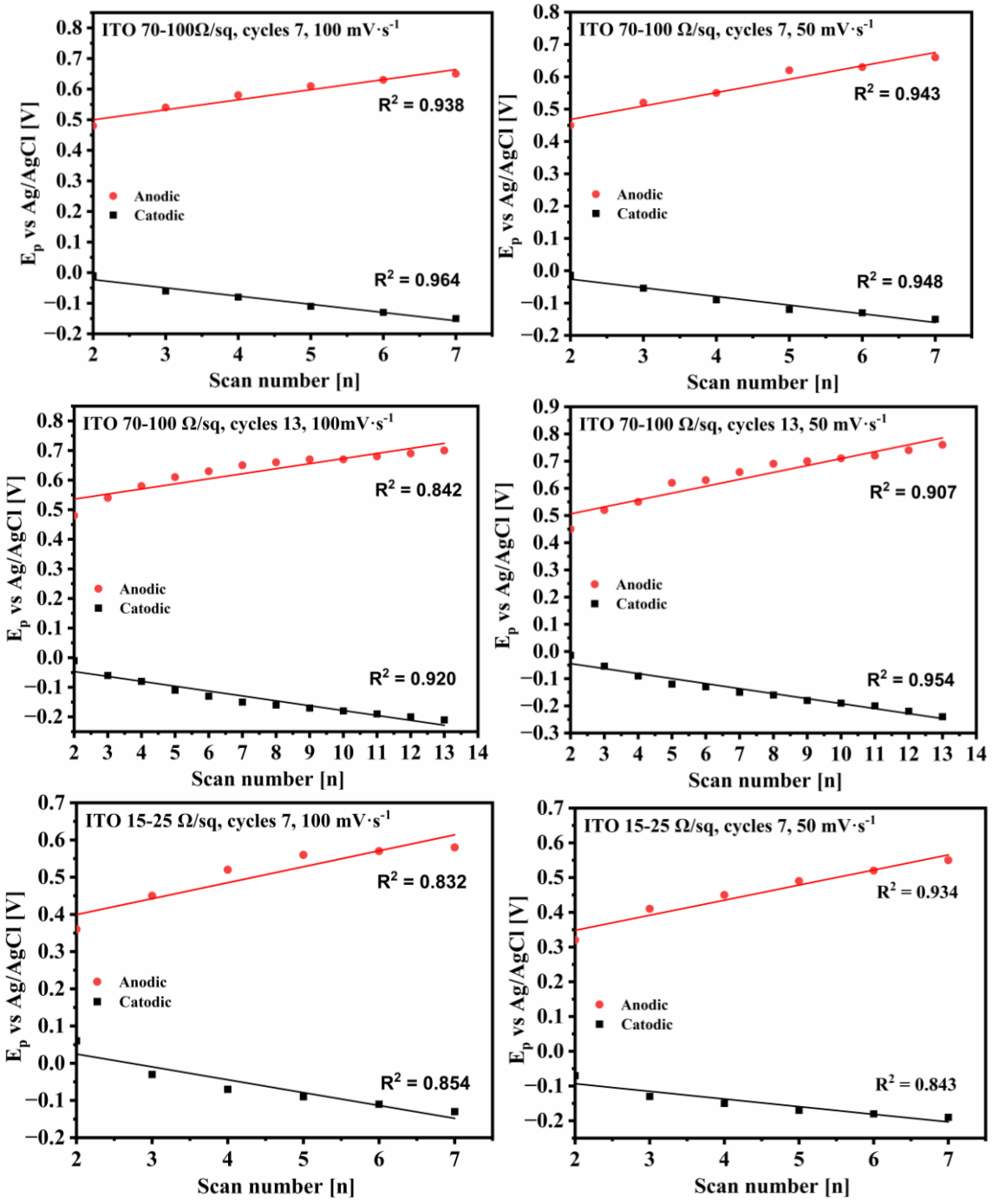


Figure S2. Plot of peak potential (E_p^{2a} anodic and E_p^{1c} cathodic [V]) vs voltametric cycles – scan number [n]. Linear regression fitting was performed and the coefficient of determination was calculated.

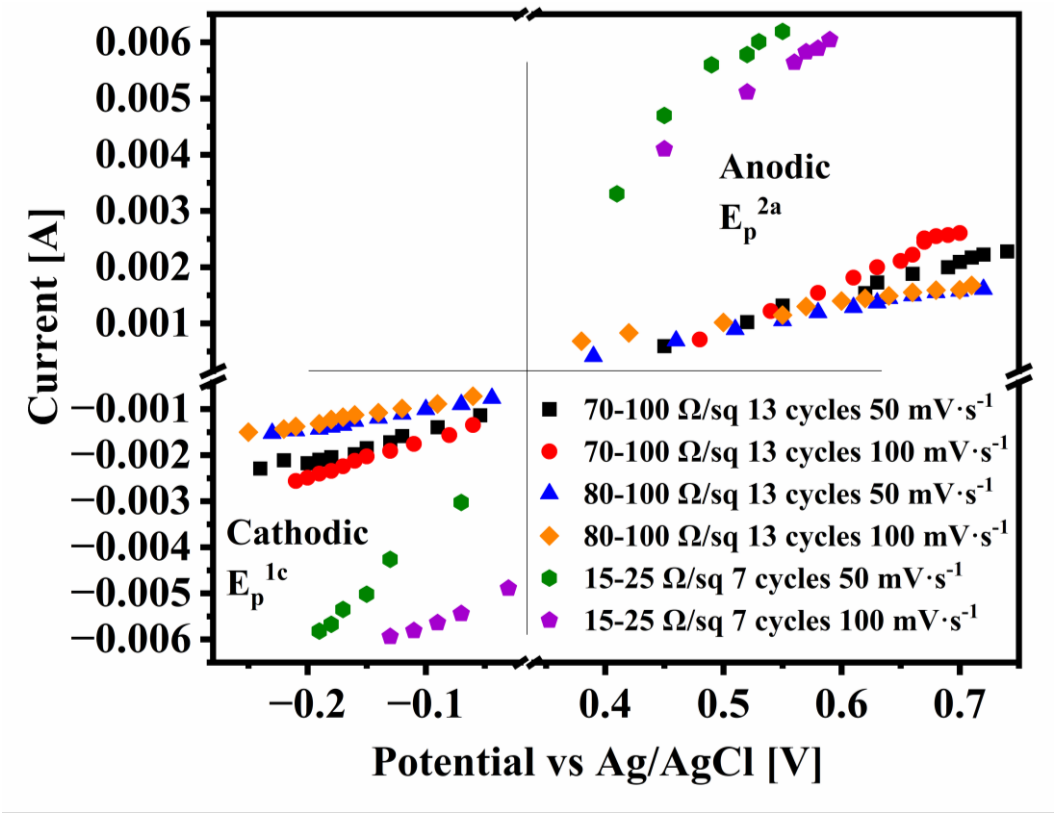
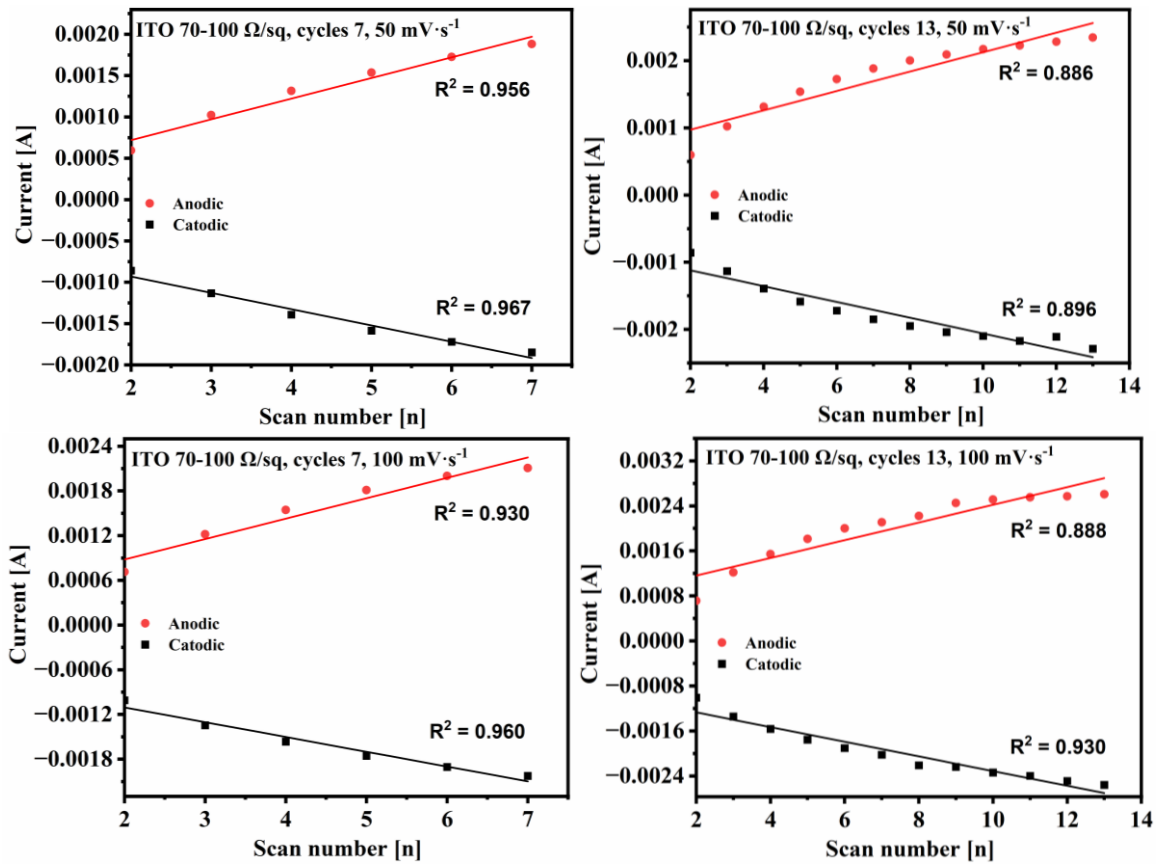


Figure S3. Plot of the current [A] read at anodic (E_p^a) and cathodic (E_p^c) peak potentials obtained from CV voltammograms at different scan rates as a function of potential (V vs Ag/AgCl).



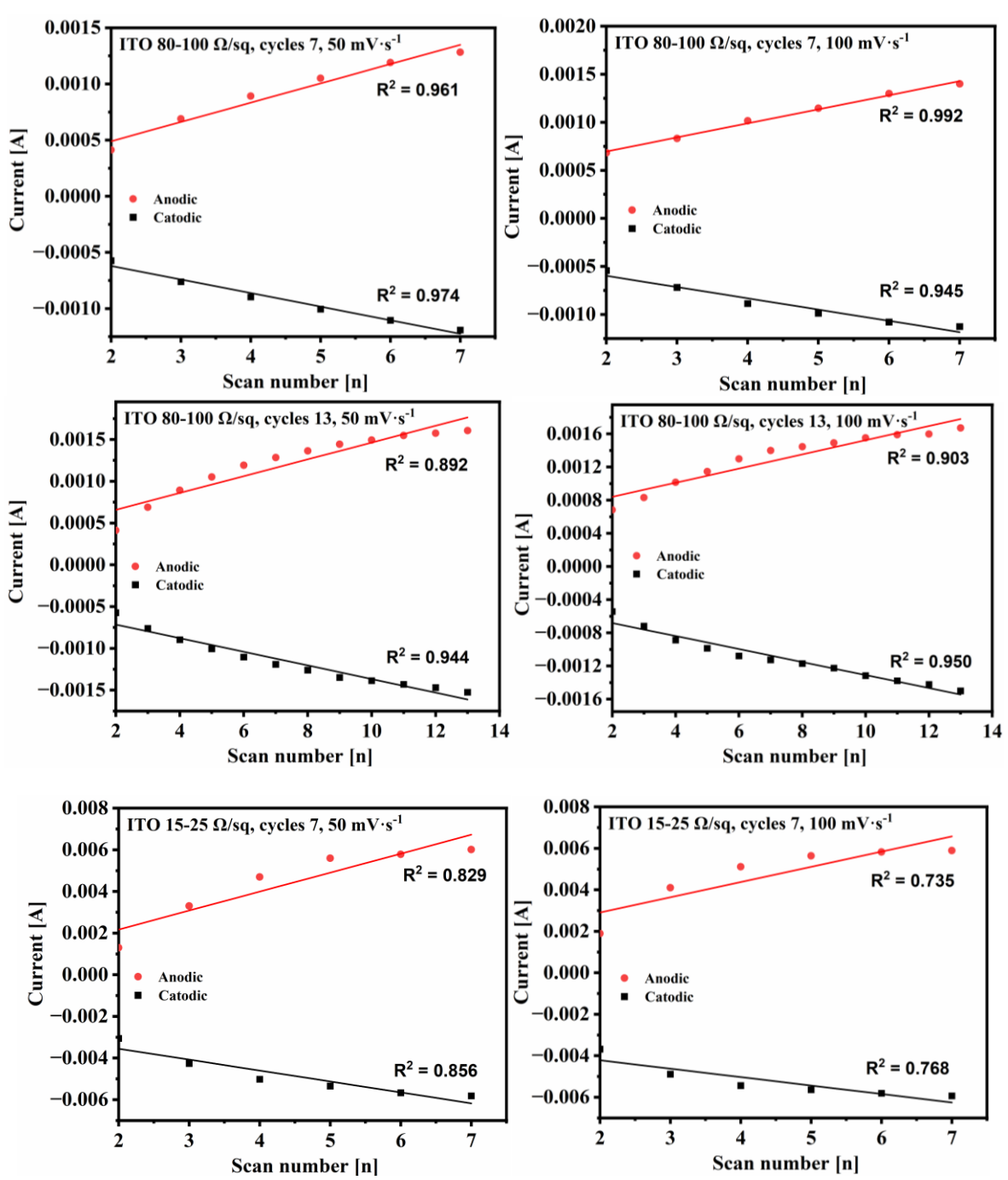


Figure S4. Plot of the current [A] read at anodic and cathodic peak potentials (current at E_p^{2a} and E_p^{1c}) vs voltametric cycles – scan number [n]. Linear regression fitting was performed and the coefficient of determination was calculated.

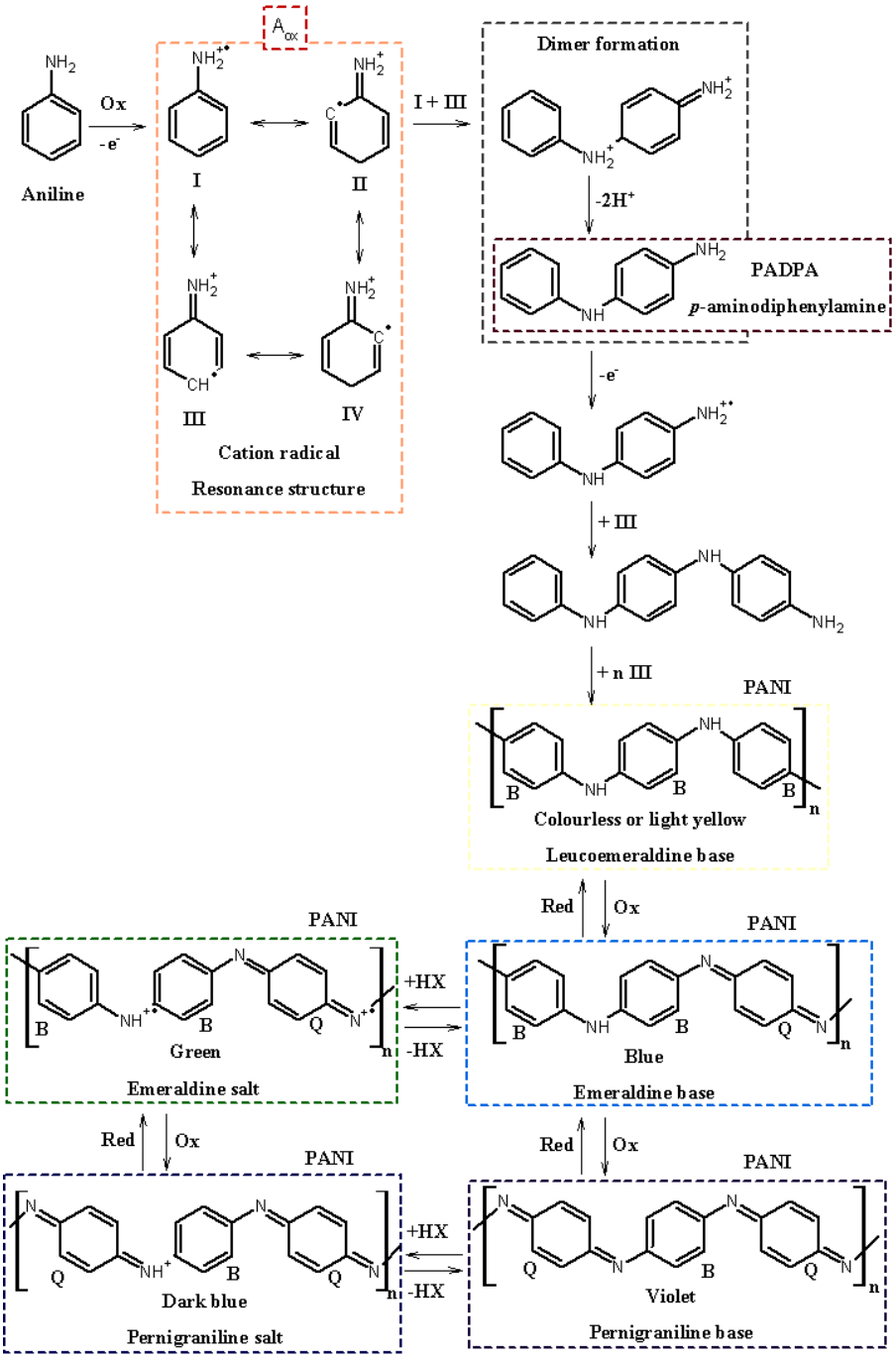


Figure S5. The proposed mechanism of the electrochemical synthesis of aniline on ITO based on [5,40-55].

Calculations for *3.1. Electropolymerization*:

- **Mass estimation based on Faraday's Law and [41]**

$$m = \frac{Q \cdot M}{z \cdot F}$$

where:

m	–	mass [μg],
Q	–	amount of charge calculated from the last cycle of CV [C],
M	–	molecular weight of the aniline monomer [g·mol^{-1}],
z	–	number of electrons,
F	–	Faraday's constants [C·mol^{-1}],

- **Thickness estimation based on [56;57;59;60]**

$$d = \frac{Q \cdot M}{z \cdot F \cdot S \cdot \rho}$$

where:

d – thickness [μm or nm],
S – working area of electrode [cm^2],
Q – amount of charge calculated from the last cycle of CV [C],
z – number of electrons,
F – Faraday's constants [C·mol^{-1}],
M – molecular weight of the aniline monomer [g·mol^{-1}],
ρ – specific density of aniline [g·cm^{-3}].

- **Specific capacitance [58;61]**

$$C_{sp} = \frac{\int IdV}{2 \cdot m \cdot \vartheta \cdot \Delta V}$$

where:

C_{sp} – specific capacitance [F·g^{-1}],
m – mass of the electroactive material [g],
$\int IdV$ – integrated area under the CV curve from the last cycle [W],
ϑ – scan rate [V·s^{-1}],
ΔV – potential window [V].

- **Areal capacitance [61]**

$$C_{ar} = \frac{\int IdV}{2 \cdot S \cdot \vartheta \cdot \Delta V}$$

where:

C_{ar} – areal capacitance [F·cm^{-2}],
S – working area of electrode [cm^2],
$\int IdV$ – integrated area under the CV curve from the last cycle [W],
ϑ – scan rate [V·s^{-1}],
ΔV – potential window [V].

Table S2. The mass, areal and specific capacitance calculated for the last CV scan.

Number of cycles / scan rate	**m [g], C_{ar} [F·cm^{-2}] and C_{sp} [F·g^{-1}]; Polyaniline on ITO with:**		
	70-100 Ω/sq glass	**80-100 Ω/sq glass**	**15-25 Ω/sq glass**
7 / 50 mV·s^{-1}	**m = 7.8 · 10^{-6} g C_{ar} = 16 mF·cm^{-2} C_{sp} = 575 F·g^{-1}**	**m = 8.3 · 10^{-6} g C_{ar} = 11 mF·cm^{-2} C_{sp} = 599 F·g^{-1}**	**m = 2.7 · 10^{-5} g C_{ar} = 33 mF·cm^{-2} C_{sp} = 997 F·g^{-1}**
13 / 50 mV·s^{-1}	**m = 7.9 · 10^{-6} g C_{ar} = 20 mF·cm^{-2} C_{sp} = 597 F·g^{-1}**	**m = 8.5 · 10^{-6} g C_{ar} = 12 mF·cm^{-2} C_{sp} = 605 F·g^{-1}**	-
7 / 100 mV·s^{-1}	**m = 8.5 · 10^{-6} g C_{ar} = 8 mF·cm^{-2} C_{sp} = 565 F·g^{-1}**	**m = 4.5 · 10^{-6} g C_{ar} = 5 mF·cm^{-2} C_{sp} = 515 F·g^{-1}**	**m = 1.9 · 10^{-5} g C_{ar} = 28 mF·cm^{-2} C_{sp} = 1000 F·g^{-1}**
13 / 100 mV·s^{-1}	**m = 8.7 · 10^{-6} g C_{ar} = 9 mF·cm^{-2} C_{sp} = 585 F·g^{-1}**	**m = 4.3 · 10^{-6} g C_{ar} = 6 mF·cm^{-2} C_{sp} = 568 F·g^{-1}**	-

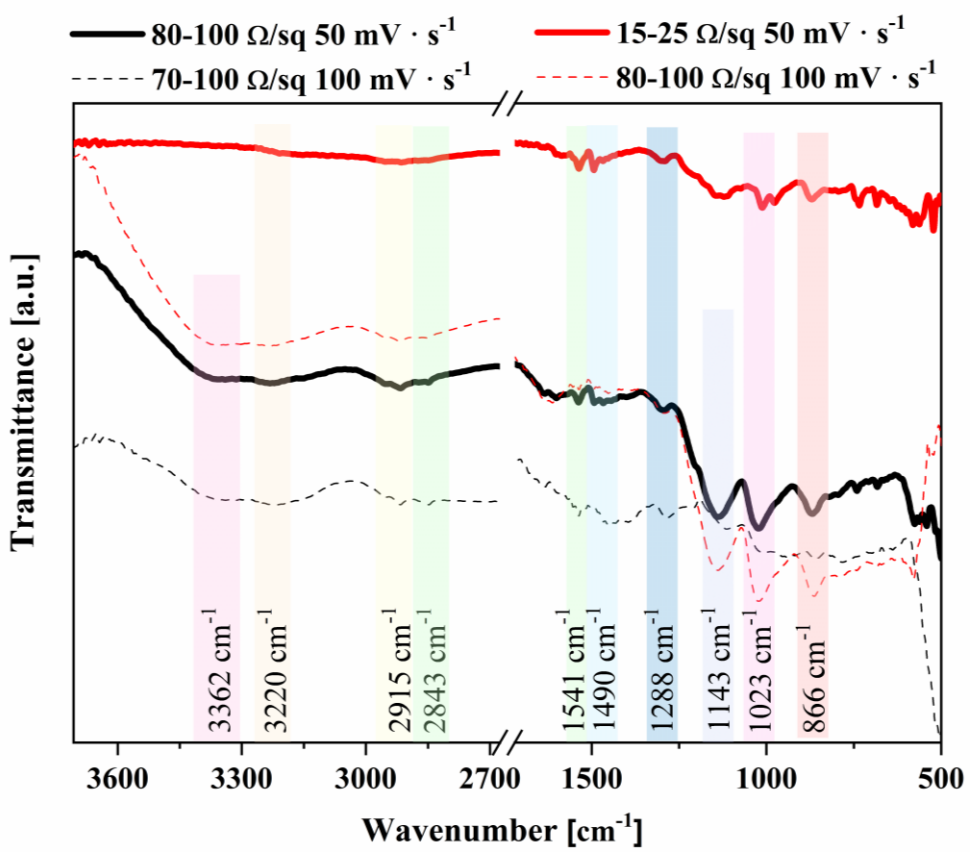
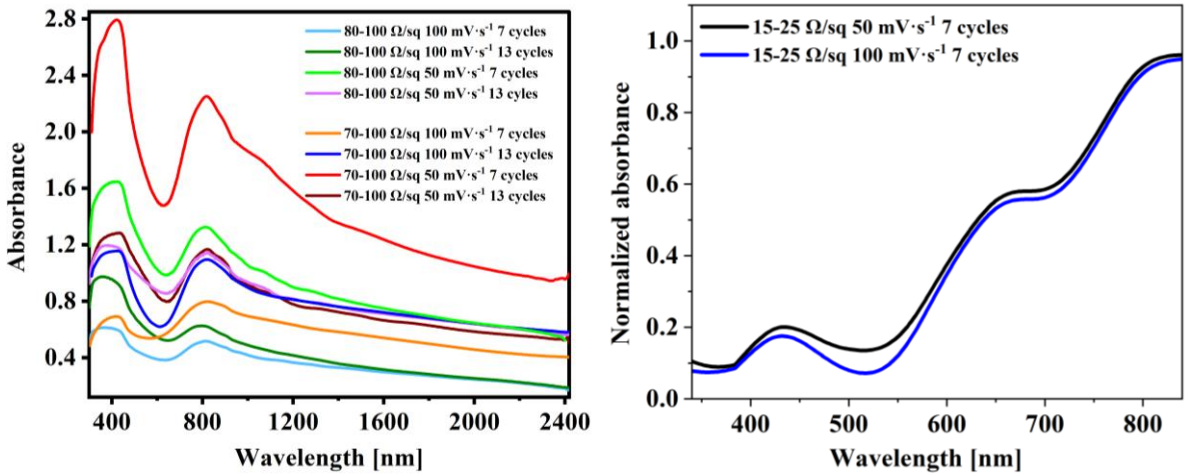


Figure S6. ATR IR spectra.



(a) (b)

Figure S7. (a) Absorption spectra of PANI films on ITO 70 - 100 Ω/sq and 80 - 100 Ω/sq, and (b) absorption spectra of PANI on ITO 15 - 25 Ω/sq.

Table S3. The maximum absorption bands (λ_{abs}) with the energy-band gaps (E_g).

Number of cycles/ scan rate	λ_{abs} [eV] and [nm]; Polyaniline on ITO with:		
	70-100 Ω/sq glass	80-100 Ω/sq glass	15-25 Ω/sq glass
7 / 50 mV·s^{-1}	3.01; 1.51 412; 819 E_g^{DT} = 2.24 eV	3.46; 1.56 362; 794 E_g^{DT} = 2.34 eV	1.51; 1.84; 2.84 821; 674; 436 E_g^{DT} = n
13 / 50 mV·s^{-1}	2.91; 1.52 426; 815 E_g^{DT} = 2.31 eV	3.52; 1.56 352; 794 E_g^{DT} = 2.31 eV	-
7 / 100 mV·s^{-1}	3.02; 1.51 410; 819 E_g^{DT} = 2.34 eV	2.93; 1.52 423; 815 E_g^{DT} = 2.31 eV	1.51; 1.84; 2.83 821; 674; 438 E_g^{DT} = n
13 / 100 mV·s^{-1}	2.88; 1.51 430; 819 E_g^{DT} = 2.11 eV	3.29; 1.51 376; 819 E_g^{DT} = 2.17 eV	-
E_g^{DT} – energy-band gap, direct transitions. n – couldn't get a proper fit.			

(a)



(b)

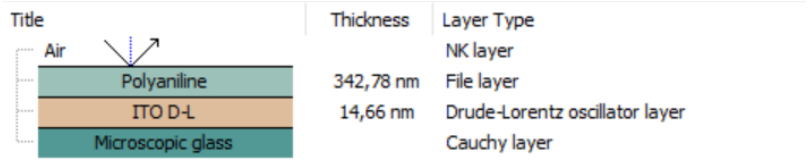


Figure S8. (a) The ellipsometric model applied for ITO substrates modelling, and (b) the ellipsometric model applied for polyaniline films.

Calculations for *3.3. Absorption study:*

➢ **Energy-band gap calculation based on the Tauc equation [78-81]:**

$$(\alpha h\nu)^{\frac{1}{n}} = A\,(h\nu - E_g)$$

where:

α – absorption coefficient,
h – Planck constant,
ν – frequency,
E_g – energy band gap,
A – proportionality constant,
n – Tauc exponent; n = $\frac{1}{2}$ direct transitions.

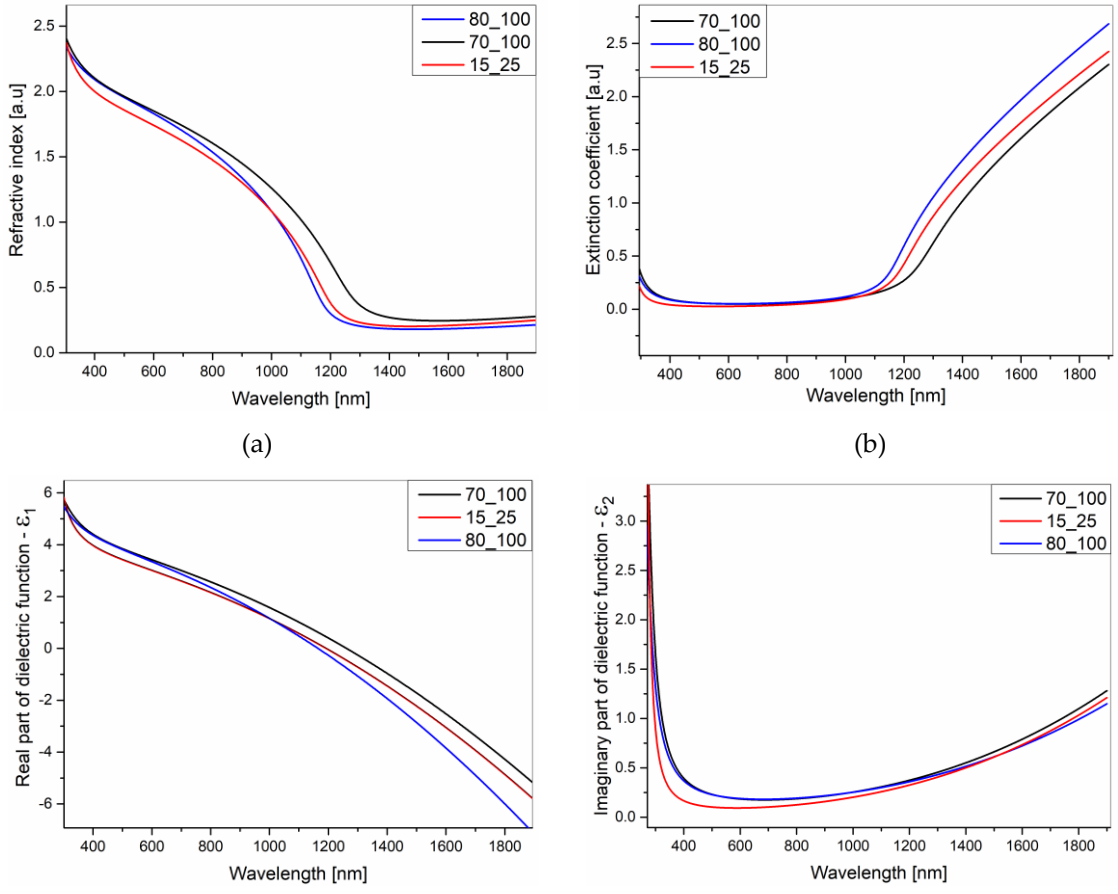


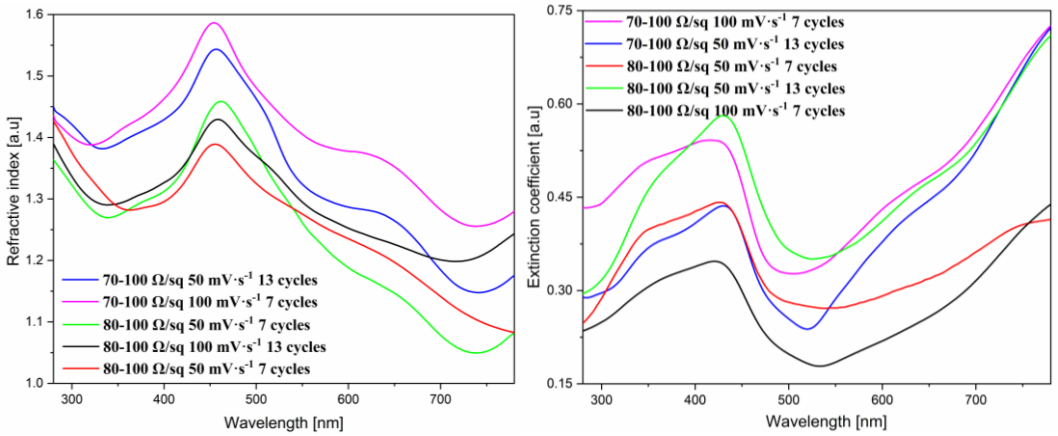
Figure S9. Optical and dielectrical coefficients obtained for the ITO substrates.

Table S4. The optical and dielectrical coefficient values taken for λ = 1900 nm.

Parameter	ITO type		
	70-100 Ω/sq	**80-100 Ω/sq**	**15-25 Ω/sq**
n [a.u.]	**0.28**	**0.22**	**0.25**
k [a.u.]	**2.30**	**2.69**	**2.42**

Table S5. Drude parameters for ITO, determined with ellipsometric model.

Parameter	ITO type		
	70-100 Ω/sq	80-100 Ω/sq	15-25 Ω/sq
Ω_p [1/cm]	15803	15810	16461
Ω_τ [1/cm]	724	819	655
d [nm]	17	15	73



(a) (b)

Figure S10. (a) Optical coefficients n and (b) extinction k determined for PANI, deposited on ITO substrates.

Calculations for *3.5. Surface and electrical study:*

➢ **Resistivity calculations for resistance measurement by four-point probe and s>d (s – distance between probes):**

$$\rho = \frac{U}{I} \cdot \frac{\pi \cdot d}{ln2}$$

where:

ρ – resistivity [Ω·cm],
d – thickness [cm],
$\frac{U}{I}$ – resistance [Ω].

➢ **Conductivity:**

$$\sigma = \frac{1}{\rho}$$

where:

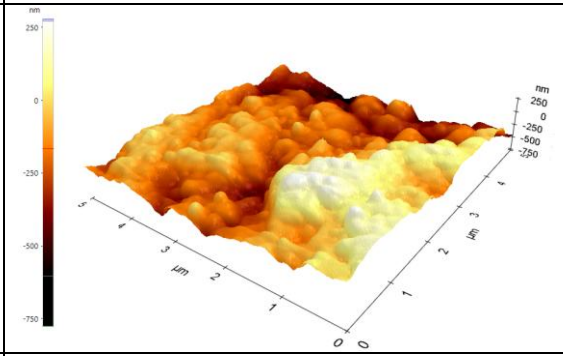
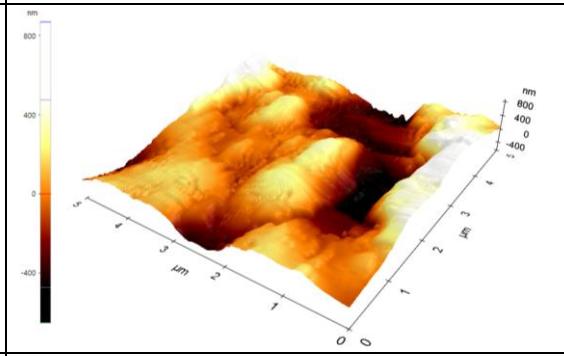
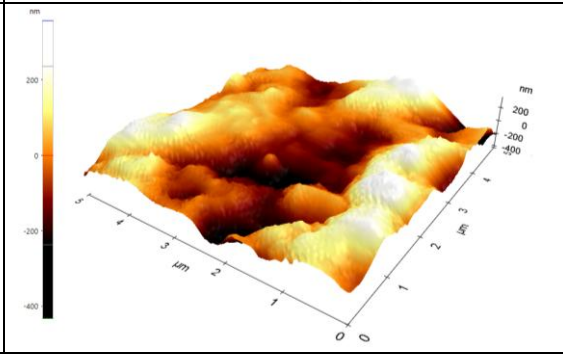
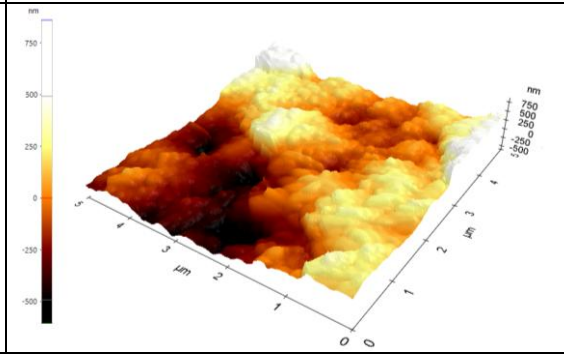
ρ – resistivity [Ω·cm],
σ – conductivity [S/cm].

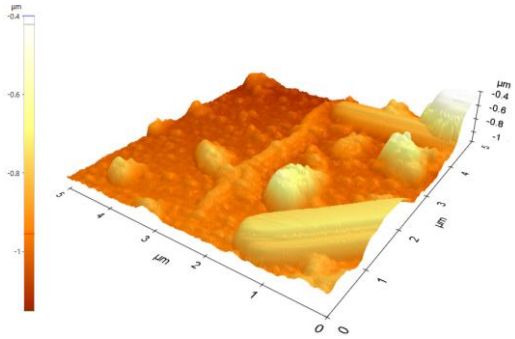
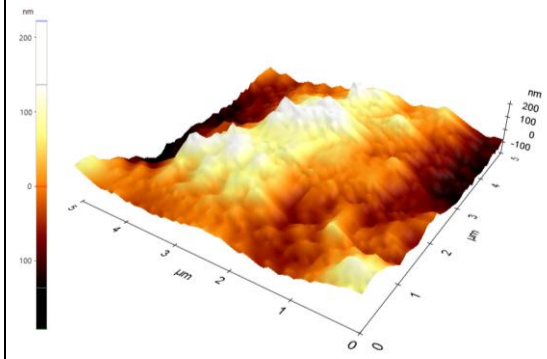
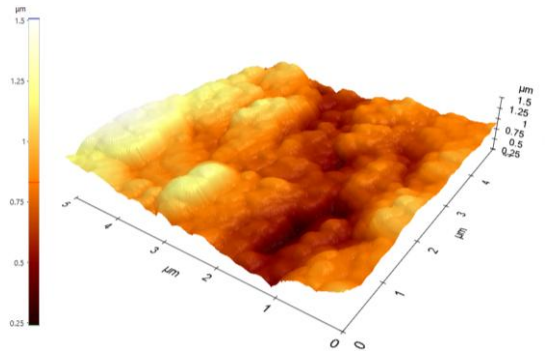
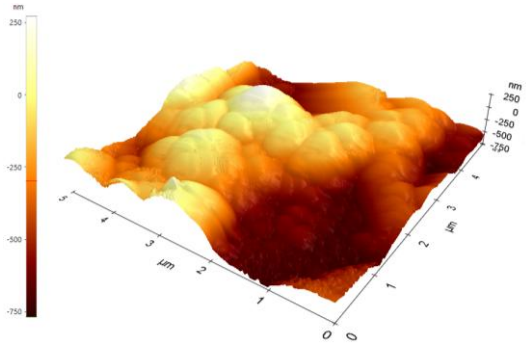
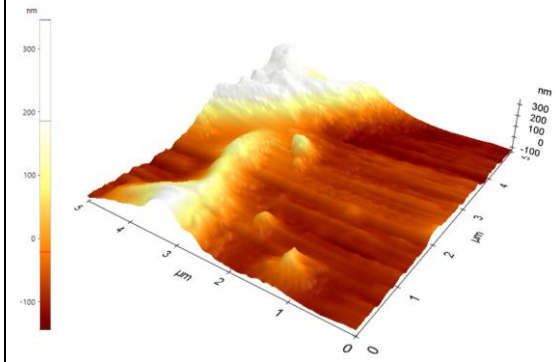
Table S6. The resistivity (ρ) and conductivity (σ) calculation results.

Number of cycles/ scan rate	ρ [Ω·cm], σ [S/cm]; Polyaniline on ITO with:		
	70-100 Ω/sq glass	80-100 Ω/sq glass	15-25 Ω/sq glass
7 / 50 mV·s^{-1}	$\rho_{elips.}$ = 0.077 ± 0.014 $\sigma_{elips.}$ = 12.924 ρ_{AFM} = 0.100 ± 0.014 σ_{AFM} = 9.995	$\rho_{elips.}$ = 0.698 ± 0.009 $\sigma_{elips.}$ = 1.432 ρ_{AFM} = 0.887 ± 0.009 σ_{AFM} = 1.127	$\rho_{cal.}$ = 19.624 ± 0.065 $\sigma_{cal.}$ = 0.0510
13 / 50 mV·s^{-1}	$\rho_{elips.}$ = 1.606 ± 0.015 $\sigma_{elips.}$ = 0.622 ρ_{AFM} = 1.768 ± 0.015 σ_{AFM} = 0.566	$\rho_{elips.}$ = 0.771 ± 0.023 $\sigma_{elips.}$ = 1.296 ρ_{AFM} = 0.898 ± 0.023 σ_{AFM} = 1.114	-
7 / 100 mV·s^{-1}	$\rho_{elips.}$ = 0.283 ± 0.012 $\sigma_{elips.}$ = 3.534 ρ_{AFM} = 0.278 ± 0.012 σ_{AFM} = 3.593	$\rho_{elips.}$ = 0.443 ± 0.046 $\sigma_{elips.}$ = 2.259 ρ_{AFM} = 0.516 ± 0.046 σ_{AFM} = 1.940	$\rho_{cal.}$ = 11.074 ± 0.075 $\sigma_{cal.}$ = 0.090 ρ_{AFM} = 6.102 ± 0.075 σ_{AFM} = 0.164
13 / 100 mV·s^{-1}	$\rho_{elips.}$ = 0.580 ± 0.031 $\sigma_{elips.}$ = 1.725 ρ_{AFM} = 0.464 ± 0.031 σ_{AFM} = 2.157	$\rho_{elips.}$ = 0.562 ± 0.054 $\sigma_{elips.}$ = 1.778 ρ_{AFM} = 0.598 ± 0.054 σ_{AFM} = 1.672	-

ρ – resistivity [Ω·cm], σ – conductivity [S/cm]. Measurement taken in the center part of the sample, positioning parallel to the four-point probe. Measurement performed three times. Elips. means calculation using thickness estimated by spectroscopic ellipsometry and AFM means calculation using thickness estimated by atomic force microscope. Cal. – resistivity and conductivity evaluated from the thickness calculations based on [56;57;59;60].

Table S7. AFM images (5 μm x 5 μm).

Number of cycles / scan rate	Polyaniline on ITO with:		
	70-100 Ω/sq glass	**80-100 Ω/sq glass**	**15-25 Ω/sq glass**
7 / 50 mV·s^{-1}			-
13 / 50 mV·s^{-1}			-

7 / 100 mV·s^{-1}			
13 / 100 mV·s^{-1}			**-**

201

202

203

204

Table S8. Thickness values of PANI, determined by AFM, with R_q and R_a.

Number of cycles / scan rate	Polyaniline on ITO with:		
	70-100 Ω/sq	80-100 Ω/sq	15-25 Ω/sq
7 / 50 mV·s^{-1}	d* = 1 μm d = 414 nm R_q = 189 nm R_a = 149 nm	d* = 1.72 μm d = 631 nm R_q = 718 nm R_a = 568 nm	-
13 / 50 mV·s^{-1}	d* = 1.75 μm d = 820 nm R_q = 206 nm R_a = 159 nm	d* = 1.98 μm d = 881 nm R_q = 318 nm R_a = 254 nm	-
7 / 100 mV·s^{-1}	d* = 1.14 μm d = 240 nm R_q = 164 nm R_a = 127 nm	d* = 0.50 μm d = 396 nm R_q = 94 nm R_a = 75 nm	d = 5.51 μm R_q = 625 nm R_a = 532 nm
13 / 100 mV·s^{-1}	d* = 1.25 μm d = 311 nm R_q = 389 nm R_a = 320 nm	d* = 0.98 μm d = 654 nm R_q = 290 nm R_a = 216 nm	-

R_q – Root Mean Square (RMS) Roughness [nm], R_a – Roughness average [nm], d – thickness from the middle of the sample, green, d* – thickness close to the solution-air interface, dark green (a little bit of blue).