

# Supplementary Information

## Nano-Assembled Supramolecular Films from Chitosan-Stabilized Gold Nanoparticles and Cobalt(II) Phthalocyanine

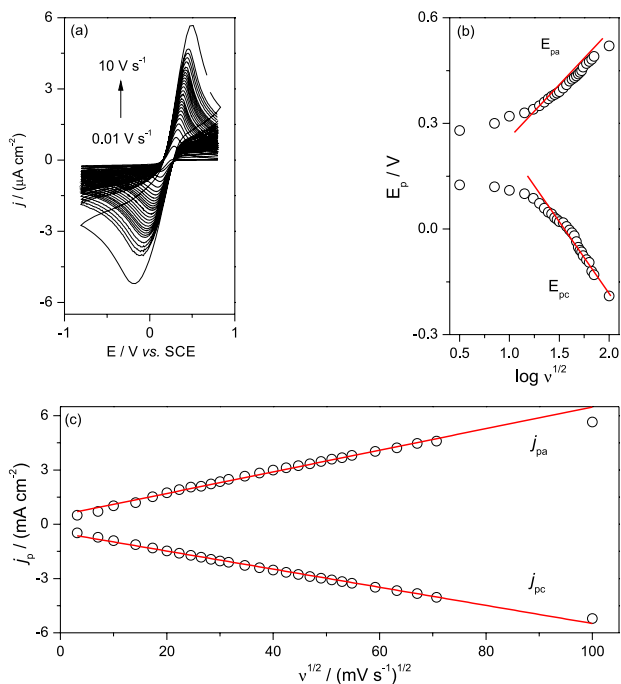
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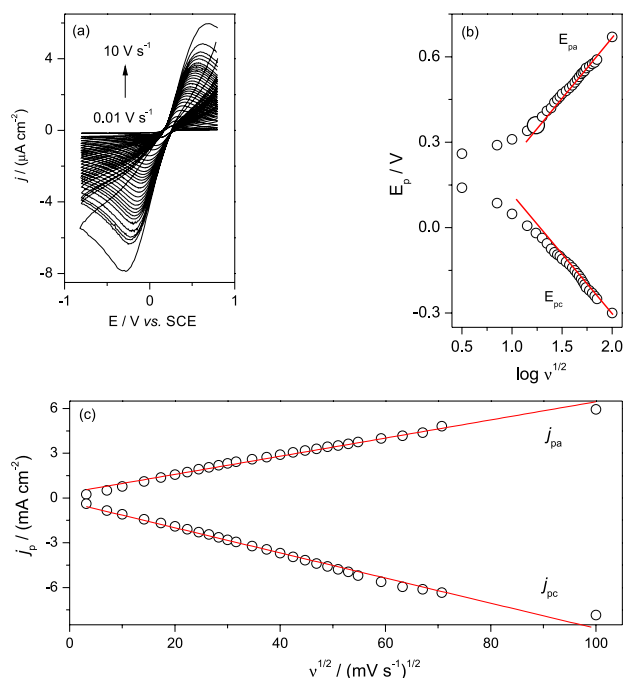
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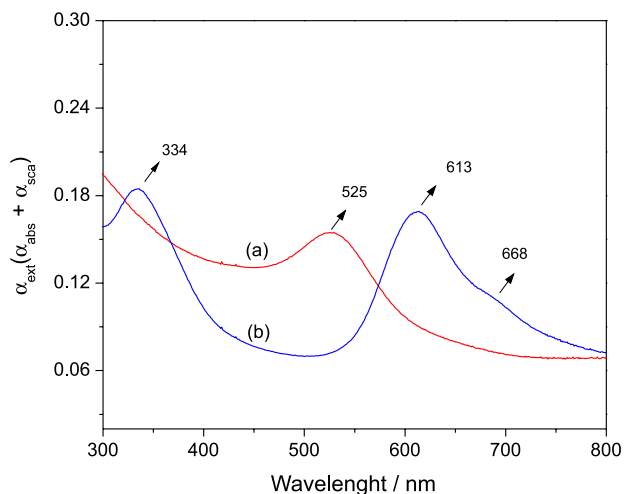


**Figure S1.** (a) Cyclic voltammograms of bare ITO with increasing scan rate from 0.01 to 10  $\text{V s}^{-1}$ . (b) Variation of peak potential ( $E_{pa}$  and  $E_{pc}$ ) vs.  $\log v^{1/2}$  of ITO. (c) Plot of the cathodic ( $j_{pc}$ ) and anodic ( $j_{pa}$ ) peak currents vs.  $v^{1/2}$ . Electrolyte:  $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$  in 0.1  $\text{mol L}^{-1}$  KCl solution,  $T = 25^\circ\text{C}$ .

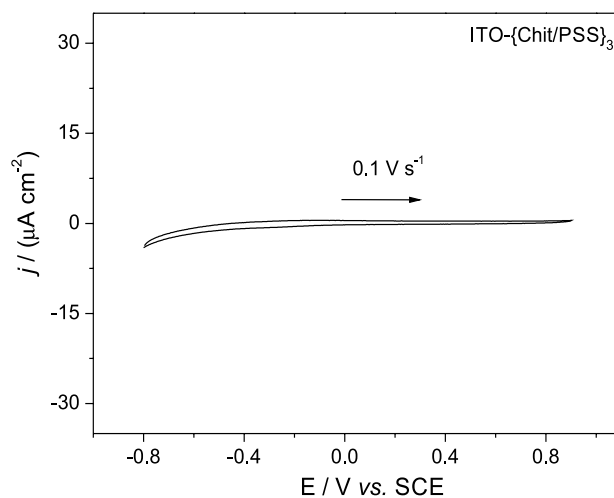


**Figure S2.** (a) Cyclic voltammograms of the ITO-Chit modified electrode with increasing scan rate from 0.01 to 10  $\text{V s}^{-1}$ . (b) Variation of peak potential ( $E_{pa}$  and  $E_{pc}$ ) vs.  $\log v^{1/2}$  for ITO-Chit. (c) Plot of the cathodic ( $j_{pc}$ ) and anodic ( $j_{pa}$ ) peak currents vs.  $v^{1/2}$ . Electrolyte:  $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$  in 0.1  $\text{mol L}^{-1}$  KCl solution,  $T = 25^\circ\text{C}$ .

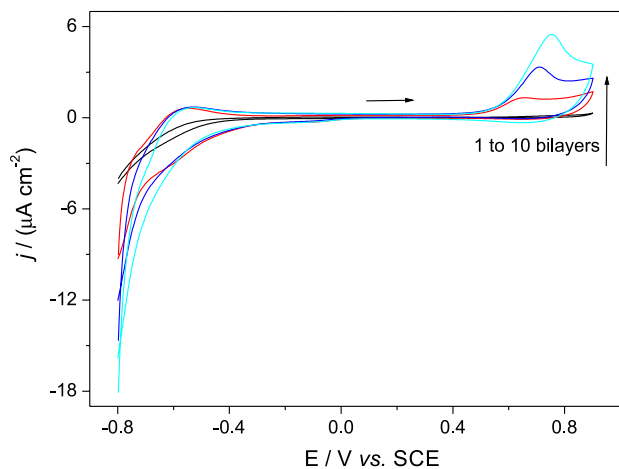
\*e-mail: welter@ufpi.edu.br



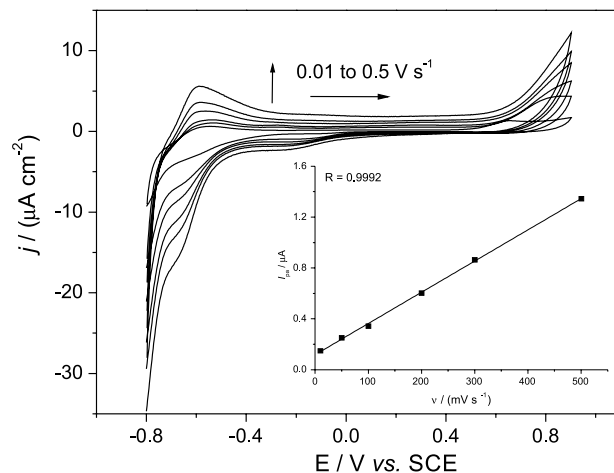
**Figure S3.** Comparison between the UV-Vis spectra of the cast films: (a) Chit-AuNPs and (b) CoTsPc.



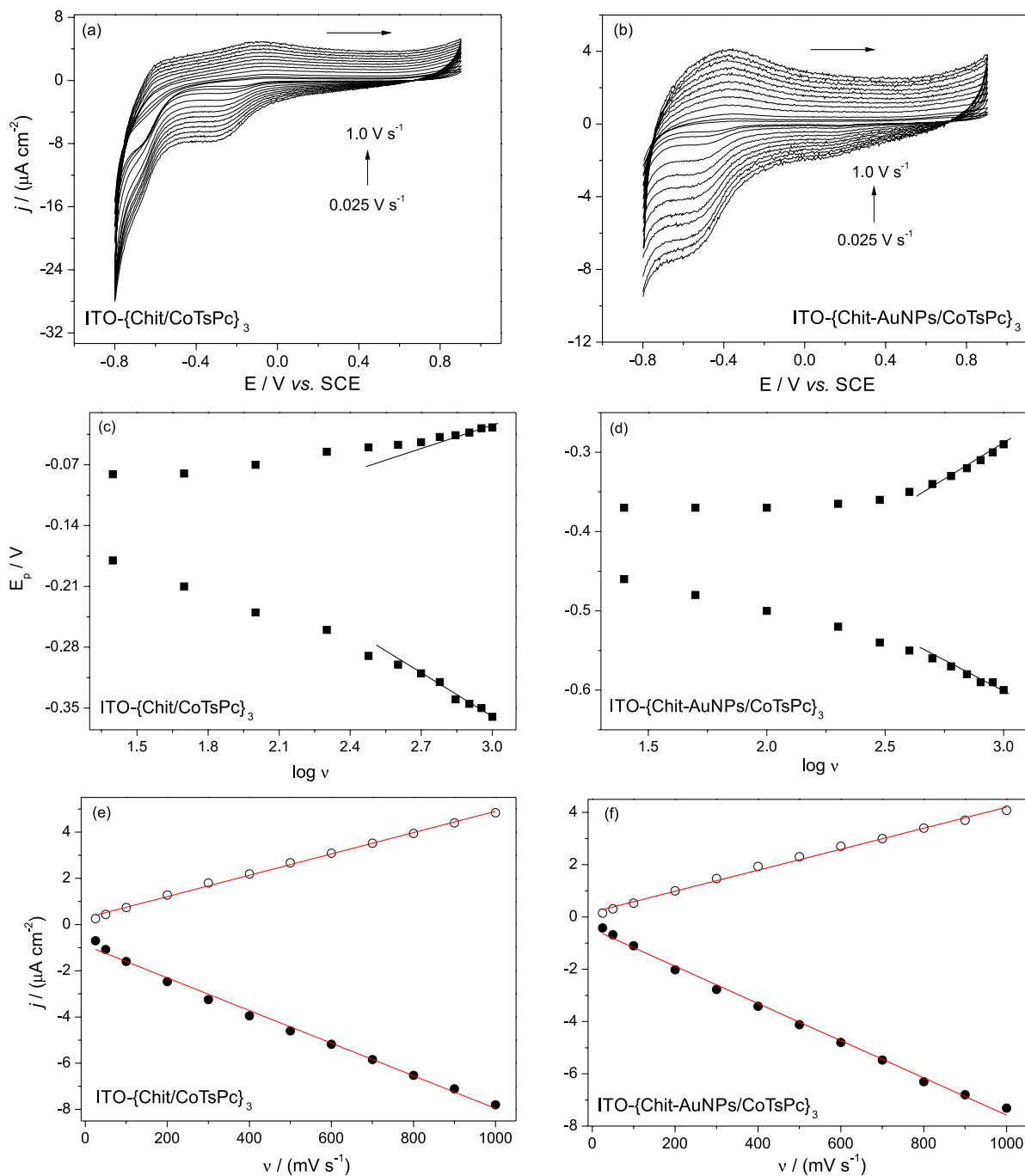
**Figure S5.** Cyclic voltammogram for the ITO-{Chit/PSS}<sub>3</sub> film in 0.1 mol L<sup>-1</sup> PBS electrolyte (pH 7.2), scan rate of 0.1 V s<sup>-1</sup>.



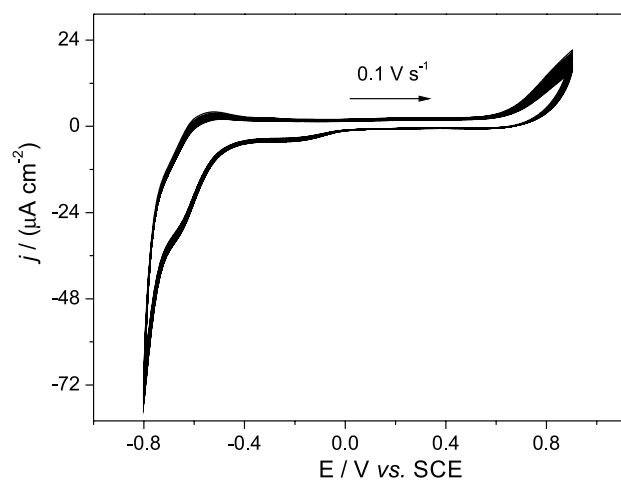
**Figure S4.** Cyclic voltammograms of the LbL ITO-{Chit-AuNPs/CoTsPc}<sub>n</sub> films, where n = 1, 3, 7 and 10 bilayers, in 0.1 mol L<sup>-1</sup> PBS electrolyte (pH 7.2), scan rate of 0.01 V s<sup>-1</sup>.



**Figure S6.** Cyclic voltammograms for the ITO-{Chit-AuNPs/CoTsPc}<sub>3</sub> electrode. The inset contains the plot of the anodic peak current ( $I_{pa} = -0.59 \text{ V}$ ) vs. scan rate (0.01 to 0.5 V s<sup>-1</sup>). Electrolyte: 0.1 mol L<sup>-1</sup> PBS solution (pH 7.2), T = 25 °C.



**Figure S7.** Variation of the scan rate (0.025, 0.050, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0  $\text{V s}^{-1}$ ) for (a) ITO-{Chit/CoTsPc}<sub>3</sub> and (b) ITO-{Chit-AuNPs/CoTsPc}<sub>3</sub>. Laviron plots for (c) ITO-{Chit/CoTsPc}<sub>3</sub> and (d) ITO-{Chit-AuNPs/CoTsPc}<sub>3</sub> systems. Dependence of cathodic and anodic peak potentials with scan rates for (e) ITO-{Chit/CoTsPc}<sub>3</sub> and (f) ITO-{Chit-AuNPs/CoTsPc}<sub>3</sub>. Electrolyte: 0.1 mol L<sup>-1</sup> PBS solution (pH 7.2), T = 25 °C.



**Figure S8.** Cyclic voltammograms for the ITO- $\{\text{Chit-AuNPs/CoTsPc}\}_3$  electrode with 20 cycles in 0.1 mol L<sup>-1</sup> PBS solution (pH 7.2), scan rate of 0.1 V s<sup>-1</sup>.

**Table S1.**  $I_{613}/I_{668}$  values from UV-Vis spectra for the  $\{\text{Chit-AuNPs/CoTsPc}\}_n$  system

Number of bilayers	$I_{613}$	$I_{681}$	$I_{613}/I_{668}$
1	0.02958	0.01664	1.78
2	0.06774	0.03515	1.93
3	0.10011	0.05195	1.93
5	0.15332	0.08226	1.86
7	0.20652	0.10995	1.88
10	0.27804	0.15036	1.85

**Table S2.** Average square roughness ( $R_{ms}$ ) and maximum roughness for the  $\{\text{Chit/CoTsPc}\}_n$  and  $\{\text{Chit-AuNPs/CoTsPc}\}_n$  films with 1, 3 and 5 bilayers

System	Number of bilayers	Average square roughness / nm	Maximum roughness / nm
$\{\text{Chit/CoTsPc}\}_n$	1	4.40	34.0
	3	8.80	68.0
	5	14.20	108.0
$\{\text{Chit-AuNPs/CoTsPc}\}_n$	1	5.10	45.0
	3	9.60	79.0
	5	14.60	98.0

**Table S3.** Kinetic parameters for LbL modified electrodes

Electrode	$\alpha$	$k_{ET} / \text{s}^{-1}$
ITO- $\{\text{Chit/CoTsPc}\}_3$	0.025	0.39
ITO- $\{\text{Chit-AuNPs/CoTsPc}\}_3$	0.08	0.93

$\alpha$ : electrochemical transfer coefficient;  $k_{ET}$ : constant of heterogeneous electron transfer.