Supplementary Information

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

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Figure S1. (a) Cyclic voltammograms of bare ITO with increasing scan rate from 0.01 to 10 V s⁻¹. (b) Variation of peak potential (Eₚa and Eₚc) vs. log ν₁/² of ITO. (c) Plot of the cathodic (jₚc) and anodic (jₚa) peak currents vs. ν₁/². Electrolyte: 5.0 × 10⁻³ mol L⁻¹ K₃[Fe(CN)₆] in 0.1 mol L⁻¹ KCl solution, T = 25 °C.

Figure S2. (a) Cyclic voltammograms of the ITO-Chit modified electrode with increasing scan rate from 0.01 to 10 V s⁻¹. (b) Variation of peak potential (Eₚa and Eₚc) vs. log ν₁/² for ITO-Chit. (c) Plot of the cathodic (jₚc) and anodic (jₚa) peak currents vs. ν₁/². Electrolyte: 5.0 × 10⁻³ mol L⁻¹ K₃[Fe(CN)₆] in 0.1 mol L⁻¹ KCl solution, T = 25 °C.

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

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

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

Figure S6. Cyclic voltammograms for the ITO-{Chit-AuNPs/CoTsPc}^{3} electrode. The inset contains the plot of the anodic peak current (I_{p1} = -0.59 V) vs. scan rate (0.01 to 0.5 V s^{-1}). Electrolyte: 0.1 mol L^{-1} 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 V s\(^{-1}\)) for (a) ITO-{Chit/CoTsPc}\(_3\) and (b) ITO-{Chit-AuNPs/CoTsPc}\(_3\). Laviron plots for (c) ITO-{Chit/CoTsPc}\(_3\) and (d) ITO-{Chit-AuNPs/CoTsPc}\(_3\) systems. Dependence of cathodic and anodic peak potentials with scan rates for (e) ITO-{Chit/CoTsPc}\(_3\) and (f) ITO-{Chit-AuNPs/CoTsPc}\(_3\). Electrolyte: 0.1 mol L\(^{-1}\) PBS solution (pH 7.2), T = 25 °C.
Figure S8. Cyclic voltammograms for the ITO-{Chit-AuNPs/CoTsPc} electrode with 20 cycles in 0.1 mol L\(^{-1}\) PBS solution (pH 7.2), scan rate of 0.1 V s\(^{-1}\).

Table S1. \(I_{613}/I_{668}\) values from UV-Vis spectra for the [Chit-AuNPs/CoTsPc] system

| Number of bilayers | \(I_{613}\)     | \(I_{668}\)   | \(I_{613}/I_{668}\) |
|--------------------|----------------|--------------|---------------------|
| 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 (\(R_{sq}\)) and maximum roughness for the [Chit/CoTsPc] and [Chit-AuNPs/CoTsPc] films with 1, 3 and 5 bilayers

| System              | Number of bilayers | Average square roughness / nm | Maximum roughness / nm |
|---------------------|--------------------|-------------------------------|------------------------|
| [Chit/CoTsPc]       |                    |                               |                        |
| 1                   | 1                  | 4.40                          | 34.0                   |
| 3                   | 3                  | 8.80                          | 68.0                   |
| 5                   | 5                  | 14.20                         | 108.0                  |
| [Chit-AuNPs/CoTsPc] |                    |                               |                        |
| 1                   | 1                  | 5.10                          | 45.0                   |
| 3                   | 3                  | 9.60                          | 79.0                   |
| 5                   | 5                  | 14.60                         | 98.0                   |

Table S3. Kinetic parameters for LbL modified electrodes

| Electrode            | \(a\) | \(k_{et}/s^{-1}\) |
|----------------------|-------|------------------|
| ITO-{Chit/CoTsPc}    | 0.025 | 0.39             |
| ITO-{Chit-AuNPs/CoTsPc} | 0.08  | 0.93             |

\(a\): electrochemical transfer coefficient; \(k_{et}\): constant of heterogeneous electron transfer.