Supporting Information

Distance-Dependent Electron Transfer at Passivated Electrodes Decorated by Gold Nanoparticles

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Figure S-1: SEM image of a representative GC/poly(ethylenediamine)/NP surface, showing the nanoparticles have a diameter of $27.5 (\pm 5)$ nm.

Figure S-2: Representative SEM images of the GC/poly(ethylenediamine)/NP surfaces at different magnification. They show the nanoparticles are distributed uniformly throughout the surface of the sample.

Figure S-3: AFM topographic images of a) the bare GC and b) GC/poly(ethylenediamine) surfaces acquired in Tapping Mode.

Figure S-4: Variation in the rate of electron transfer to ruthenium (III) hexamine with the thickness of the organic film for GC/poly(ethylenediamine) surfaces.

Figure S-5: Simulated cyclic voltammograms of GC/poly(ethylenediamine)/NP surfaces as a function of the thickness of the organic film. To be consistent with the Fig. 3b, the number of applied CV cycles in order to deposit ethylenediamine is presented in the curve. The system parameters are k_{et} values in the Table 1, and all other similar experimental conditions.

Figure S-6: Representative SEM images of the GC/poly(ethylenediamine)/NP surfaces as a function of AuNP deposition time. a) 2 min b) 10 min c) 30 min d) 180 min and e) 360 min deposition time.

Figure S-7: Cyclic voltammograms and Nyquist plots recorded in phosphate buffer solution containing 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ for GC/poly(ethylenediamine)/NP surfaces as a function of the AuNPs deposition time including 2, 10, 30, 60, 180 and 360 min at a scan rate of 100 mV.s^{-1} for the polymer thicknesses a) $24.1 \text{ \AA}$ and b) $27.7 \text{ \AA}$. The response from bare GC is also displayed for comparison (dotted line in the voltammogram). The figure legends indicate the AuNPs deposition time. In the impedance spectra, dots are the experimental data and lines are the fitted data. The Randles equivalent circuit used to fit the data is shown in the insert in Figure 4b.

Table S-1. Electrochemical impedance spectroscopy and SEM data for GC/poly(ethylenediamine)/NP surfaces as a function of the AuNPs deposition time.

<i>AuNP Deposition Time / min</i>	2	10	30	60	180	360
<i>AuNP Surface Coverage / cm⁻²</i>	$1.1 (\pm 0.2) \times 10^8$	$3.8 (\pm 0.4) \times 10^8$	$6.7 (\pm 0.3) \times 10^8$	$2.2 (\pm 0.3) \times 10^9$	$2.4 (\pm 0.4) \times 10^9$	$2.5 (\pm 0.3) \times 10^9$
$k_{et} / \text{cm.s}^{-1}$ (Thickness 24.1 Å)	$8.3 (\pm 0.9) \times 10^{-2}$	$8.3 (\pm 1.1) \times 10^{-2}$	$8.3 (\pm 0.8) \times 10^{-2}$	$8.4 (\pm 1.2) \times 10^{-2}$	$8.3 (\pm 0.9) \times 10^{-2}$	$8.4 (\pm 0.7) \times 10^{-2}$
$k_{et} / \text{cm.s}^{-1}$ (Thickness 27.7 Å)	$1.6 (\pm 0.6) \times 10^{-2}$	$1.6 (\pm 0.8) \times 10^{-2}$	$1.6 (\pm 0.8) \times 10^{-2}$	$1.6 (\pm 0.7) \times 10^{-2}$	$1.6 (\pm 0.4) \times 10^{-2}$	$1.6 (\pm 0.5) \times 10^{-2}$