Electronic Supplementary Material (ESI) for RSC Advances.

Gold Nanoparticle-mediated Electron Transfer of Cytochrome c on a Self-Assembled Surface

Roberto Alves de Sousa Luz[a] *and Frank Nelson Crespilho*[a*]

[a]Instituto de Química de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil.

[*]frankcrespilho@iqsc.usp.br

Supporting Information

S1. Formation of gold nanoparticles

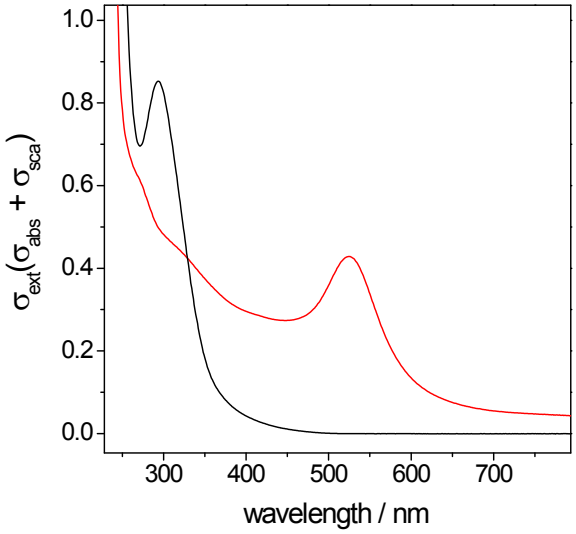

Fig. S1. UV-Vis spectra of the aqueous 1 mM $HAuCl_4$ solution (black line), and AuNP-PAH suspension (red line). Electronic spectra were recorded on Jasco V-670 spectrophotometer.

S2. Determination of average diameter of nanoparticles

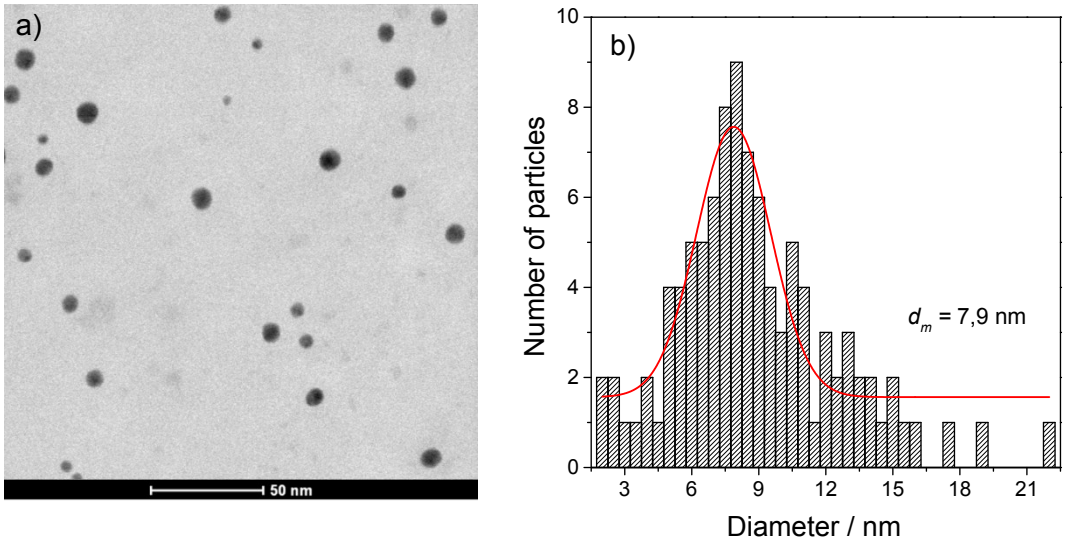

Figure S2. a) Transmission Electron Microscopy image of AuNPs-PAH; b) histogram of size distribution obtained by counting 100 particles. Images were recorded on FEI TECNAI G² F20 HRTEM.

S3. Biocatalytic properties of Cyt c in the presence of nanoparticles

The retention of electrocatalytic properties of Cyt c after immobilization was verified by analyzing the electrocatalytic activity of Cyt c towards electroreduction of hydrogen peroxide. Upon addition of H_2O_2, an increase in reduction current was observed with an onset at 0.20 V for Au/Cys/AuNP-PAH/Cys/Cytc (Figure S3a, red line). However, no electrocatalytic current was observed at the bare Au electrode within identical scanning potential range (Figure S3a, blue line), indicating that reduction of H_2O_2 was catalyzed by the Cyt c that was self-assembled on the modified electrode.

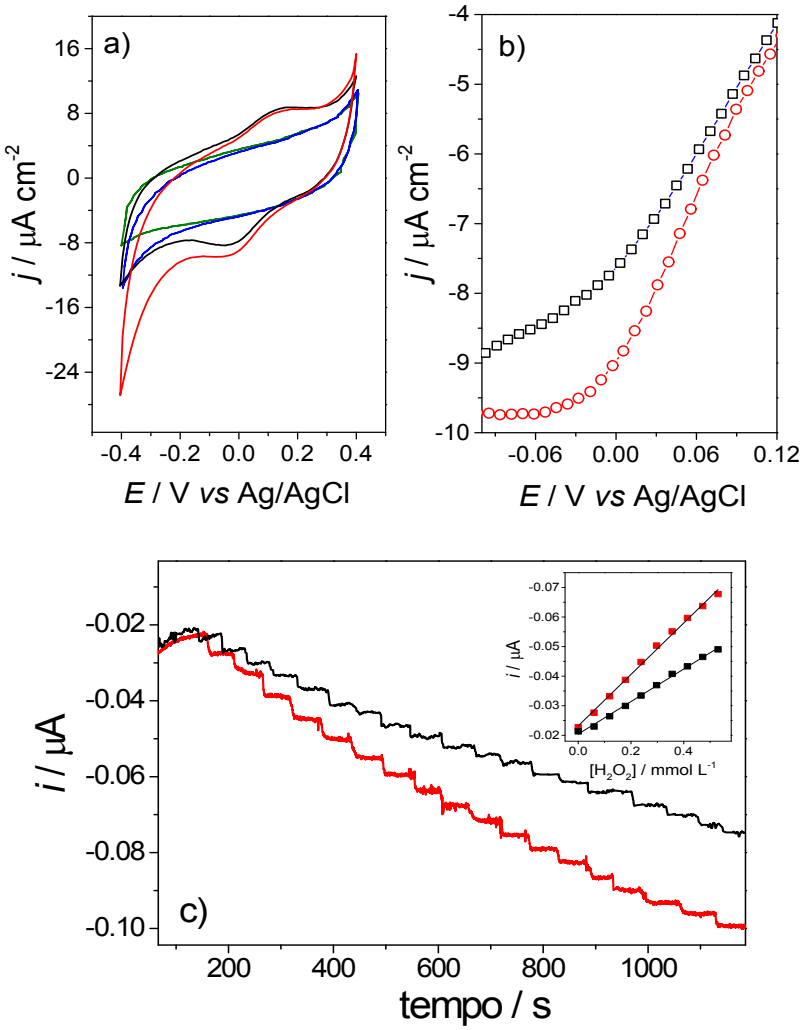

Figure S3. a) Cyclic voltammograms for Au/Cys/AuNP-PAH/Cys/Cytc (black line), and the bare Au electrode (green line) at a scanning rates of 50 mV s^{-1} in phosphate buffer without H_2O_2 and with 0.37 mM H_2O_2 (red and blue lines, respectively); b) Polarization curves for bioelectrodes Au/Cys/PAH/Cys/Cytc (black squares), and Au/Cys/AuNP-PAH/Cys/Cytc (red circles) in the presence of 0.37 mM H_2O_2; c) Amperometric responses of Au/Cys/AuNP-PAH/Cys/Cytc (red line), and Au/Cys/PAH/Cys/Cytc (black line) at 0.0 V upon successive additions of 50 µL 30 mM H_2O_2 solution to 25 mL phosphate buffer. A plot of current versus H_2O_2 concentrations is shown in the inset.

Higher currents were observed for Au/Cys/AuNP-PAH/Cys/Cytc when the bioelectrodes with and without AuNPs were compared (Figure S3b). The red line indicates the typical current-

time amperometric curves for Au/Cys/AuNP-PAH/Cys/Cytc recorded under conditions of continuous stirring and successive addition of 50 µL 30 mM H_2O_2 into phosphate buffer. Based on the optmization experiments, 0.0 V was selected as the applied potential for H_2O_2 reduction. The reduction current increased abruptly and reached a stable value after the addition of each aliquot. About 6 s were needed to reach the maximum current, indicating a fast response process. A chronoamperometric curve for Au/Cys/PAH/Cys/Cytc (Figure S3c, black line) was recorded under identical conditions, where a similar behavior albeit with a discrete increase in the catalytic currents was observed. Both bioelectrodes exhibited increasing amperometric responses to H_2O_2 with good linear ranges from 6.0×10^{-5} M to 5.3×10^{-4} M (inset Figure S3c, r = 0.998). This behavior indicated that H_2O_2 could be easily reduced at low concentrations by Au/Cys/AuNP-PAH/Cys/Cytc and Au/Cys/PAH/Cys/Cytc bioelectrodes, further implying retention in Cyt c activity after its immobilization on the modified electrode.