

SUPPORTING INFORMATION

Solvent effects on the structure-property relationship of redox-active self-assembled nanoparticle-polyelectrolyte-surfactant composite thin films: Implications for the generation of bioelectrocatalytic signals in enzyme-containing assemblies

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Quartz crystal microbalance characterization - Protein adsorption

The QCM-D experiments were performed using a Q-Sense instrument (QCM-D, Q-Sense E1, Sweden) equipped with a Q-Sense Flow Module (QFM 401). The sensor was an AT-cut piezoelectric quartz crystal covered with two gold electrodes, and for all measurements QSX 301 Gold sensors were used. Samples were perfused using a peristaltic microflow system (ISMATEC, ISM 596D, Switzerland). All experiments were performed in a 0.1 M Tris-HCl, 0.1 M NaCl buffer solution at pH 7.4, in flow mode; the flow rate used in the experiments was 150 $\mu\text{L}/\text{min}$, and at temperature of 27 °C. The modified crystal was equilibrated in buffer and when a stable frequency baseline was achieved, a 1mg/mL GOx solution (in carrier buffer) was allowed to flow through the system (see Fig. S1). Once the GOx adsorption achieves a constant value, the flow was changed to the carrier buffer to rinse the unbound sample; in both cases, negligible changes were observed. All QCM-D experiments were processed using the acquisition software QSoft 401. The average coverage of GOx on modified surfaces is $2.8 \pm 0.4 \mu\text{g cm}^{-2}$, as estimated from microgravimetric measurements

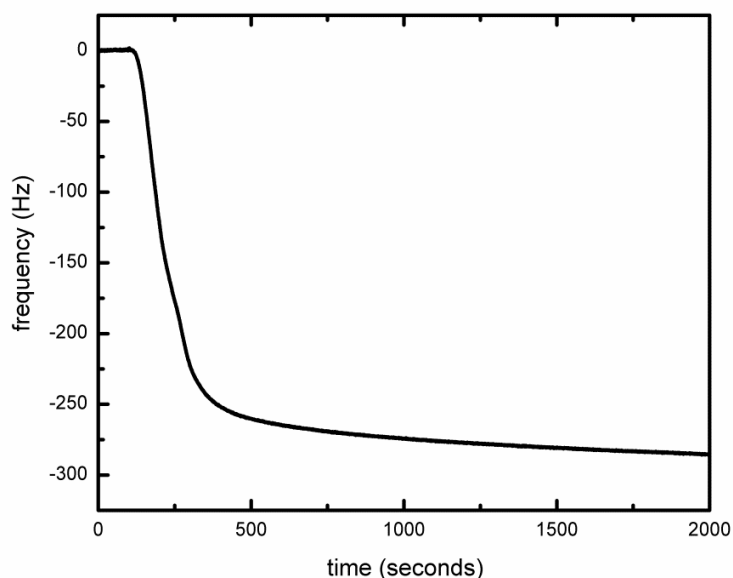


Figure S1. Quartz crystal microbalance response on frequency at the overtone number $n=3$ (15 MHz) when the OsPA-DS-AuNP(o) -coated quartz crystal is placed in 1 mg/mL GOx solution in 0.1 M Tris buffer, pH 7.4 and 0.1 M NaCl

X-ray photoelectron spectroscopy characterization.

XPS measurements were performed at D04A-SXS beamline of LNLS, using photon incident energy $h\nu = 1840$ eV with a 45° detection angle. Binding energies were referenced to the adventitious C 1s emission at 285 eV. Si (100) wafers were used as support substrates and were pretreated before coating. They were rinsed with acetone and dried with argon blowing before coating. Thin polymer films were prepared by spin-coating a 50 μ L portion of OsPA-DS dispersion using a commercial spin coater (Laurell WS-400B). XPS confirmed the presence of OsPA-DS complexes (Fig. S2a,b) as well as the presence of Au in the case of nanocomposite films (Fig. S2c). Supramolecular thin films were analyzed by XPS showing a ratio close to 1:1 between allylamine monomer and dodecylsulfate (N:S ratio).

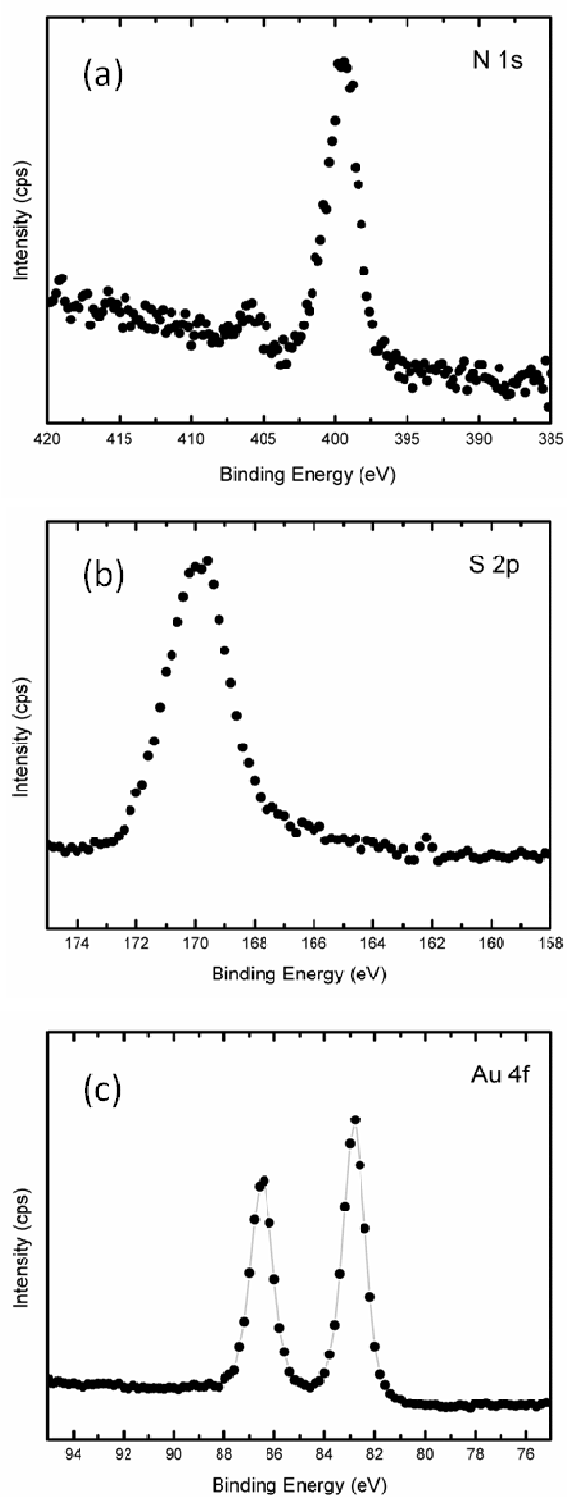


Figure S2. High-resolution XPS spectra of OsPA-DS-AuNP(o) films corresponding to: (a) N 1s, (b) S 2p, and (c) Au 4f.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) (TA Instruments).was employed to access the relative composition of polymer:surfactant within the OsPA-DS-AuNP composite material. Samples were identically subjected to TGA at a heating rate of 10 °C/min under N₂ environ-ment (Fig. S3). As shown in the TGA curve, the nanocomposite material shows a mass loss of 60 % upon heating to 500 °C, which is attributed to the thermal decomposition of the polymeric/organic material contained in the OsPA-DS-AuNP composite.

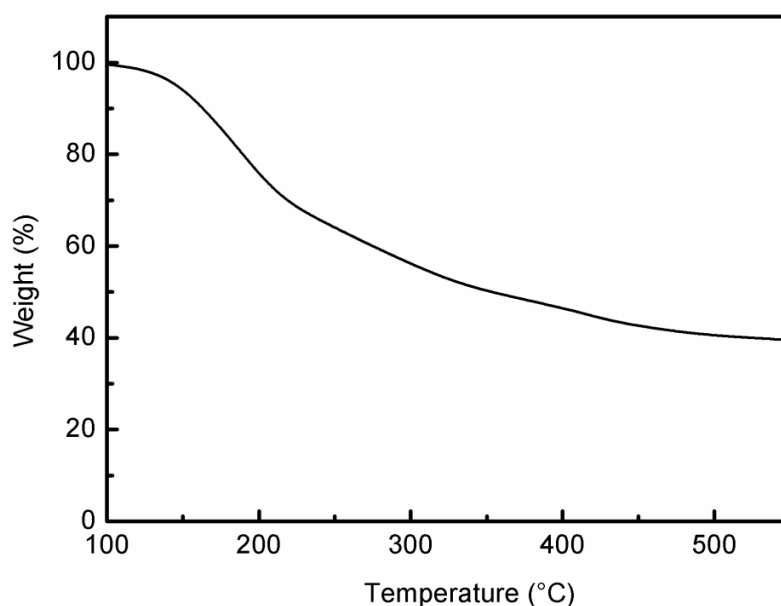


Figure S3. TGA thermogram of OsPA-DS-AuNP (o).

Atomic force microscopy (AFM)

Tapping mode atomic force microscopy (AFM) was performed by using a Nanoscope IIIa- Quadrex Multimode AFM (Bruker, Santa Barbara, CA, USA) equipped with a vertical J-scanner, having a maximal lateral range of approximately 150 mm. Topographic (height) and phase imaging were recorded simultaneously under dry nitrogen by using silicon probes. The scan rate was 1 Hz and each sample was imaged several times at different locations on the substrate to ensure reproducibility.

The topography images displayed in Figure S4 are dominated by a nanometer scale, low frequency height undulation that evolves to a more ordered structure for the assemblies containing gold

nanoparticles. Comparison of the AFM images of OsPA-DS and OsPA-DS-AuNP nanocomposites reveals differences with respect to topography and organization. In the case of OsPA-DS films, topographic imaging revealed the presence of aggregates with a roughness of 4.3 nm. Conversely, OsPA-DS-AuNP nanocomposites exhibited a homogeneous distribution of nanoscale bundles all over the substrate. In the case of nanocomposite architectures, the roughness of the film was 1.3 nm. It is evident that the presence of the metal nanoparticles plays a role in defining the morphological characteristics of the spin-coated films (Fig. S4). In addition, phase imaging also showed sharp changes in the appearance of the films, providing us with information complementary to the information drawn from topographic imaging. It revealed fine features that were much less apparent in the topographic image (Fig. S4). For instance, the presence of the nanoparticles on the composite surface was readily detected during phase imaging. Whereas phase imaging of OsPA-DS films is featureless, similar experiments performed on OsPA-DS-AuNP nanocomposites revealed the presence of nanoparticles in the polymer film (Fig. S4).

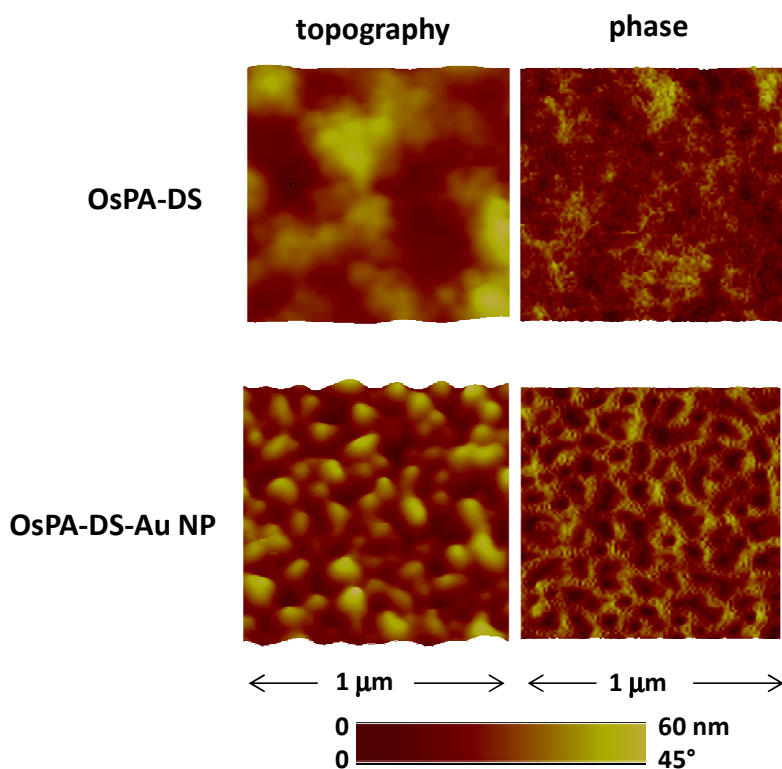


Figure S4. Topography and phase images of (top) OsPA-DS and (bottom) OsPA-DS-AuNP. Images were presented as surface plots to emphasize features: rotation 08 and pitch 90°. Scan size 1x1 μm^2 . Color scale represents a total range of 60 nm in the height image and 45° in the phase image.