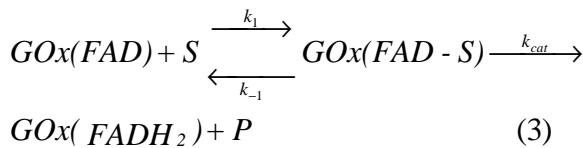
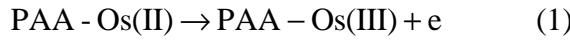


# Wiring Efficiency in Layer-by-Layer (PAA-Os)<sub>n</sub>(GOx)<sub>n</sub> Self-assembled Glucose Biosensors

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The oxidation of  $\beta$ -D-glucose catalyzed by GOx and mediated by the redox polymer PAA-Os in organized self-assembled layer-by-layer bioelectrodes is given by<sup>1-5</sup>:



where GOx(FADH<sub>2</sub>) and GOx(FAD) are the reduced and oxidized forms of the enzyme, PAA-Os(II/III) the reduced and oxidized forms of the osmium modified poly(allylamine), (PAA-Os), and S and P are the substrate and product,  $\beta$ -D-glucose and glucono-D-lactone, respectively. The Michaelis constants for substrate and redox co-substrate are  $K_{MS} = (k_{-1} + k_{cat})/k_1$  and  $K_{MO} = k_{cat}/k$  respectively. Neglecting diffusion of the substrate in the thin layers, the catalytic oxidation current density is<sup>1</sup>:

$$i_{cat} = \frac{2F k_{cat} \Gamma_E}{1 + \frac{k_{cat}}{k [Os(III)]} + \frac{K_{MS}}{[S]}} \quad (4)$$

where  $\Gamma_E$  is the surface concentration of the total active enzyme wired by the Os polymer and  $[S]$  is the soluble substrate concentration.

By combining ellipsometry and quartz crystal microbalance (Fig. 1) with electrocatalytic measurements of glucose oxidation (Fig. 2) we can assess the wiring efficiency of different multilayer structures.

From the best fit lines to eqn. (4) in Fig. 2 we evaluate the pseudo first order rate constant  $k[Os]$  and the concentration of wired enzyme,  $\Gamma_E^{1-4}$ .

With the redox surface concentration,  $\Gamma_{Os}$ , obtained from the integrated voltammetric charge in the absence of glucose and the ellipsometric thickness  $d_f$  we assess the electrochemically active osmium volume concentration  $[Os]_{elec}$  in each one of the structures studied.

With this value we obtain the second order rate constant for the oxidation of FADH<sub>2</sub> by the redox polymer  $k$ , which results an order of magnitude lower than the value

reported for the soluble Os complex and enzyme due to the limitations of backbone segmental motion in the redox polymer layers.

The surface concentration of enzyme electrically wired by the Os polymer,  $\Gamma_E$ , is larger when PAA-Os layers can wire the enzyme from below and above the GOx layer.

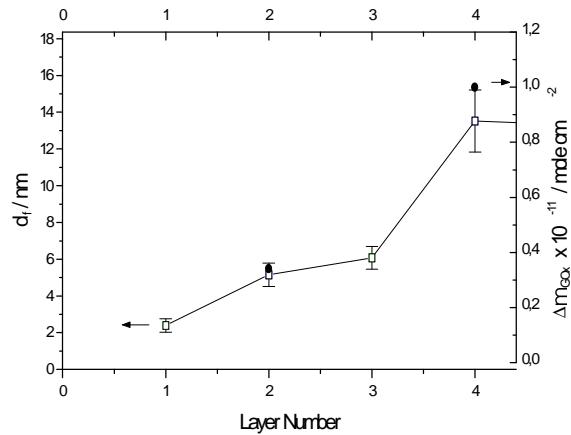


Fig. 1 Ellipsometric thickness ( ) for each layer: (PAA-Os), (PAA-Os)(GOx), (PAA-Os)<sub>2</sub>(GOx), and (PAA-Os)<sub>2</sub>(GOx)<sub>2</sub> and QCM mass for GOx layers (●)

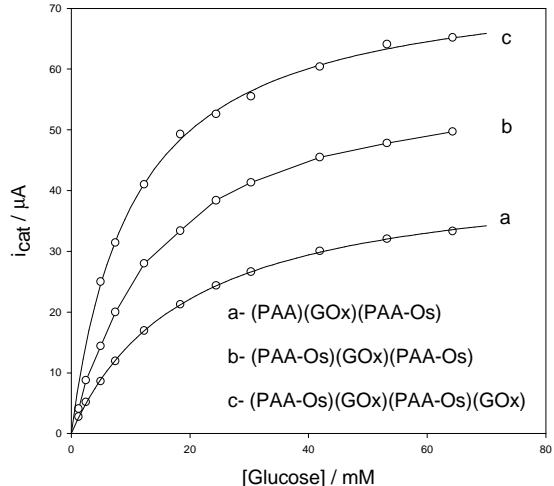


Fig. 2: Catalytic current dependence on glucose concentration for different multilayer architectures at 0.5 V.

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