Supplementary Material

Improving the direct electron transfer in monolithic bioelectrodes prepared by immobilization of FDH enzyme on carbon-coated anodic aluminum oxide films

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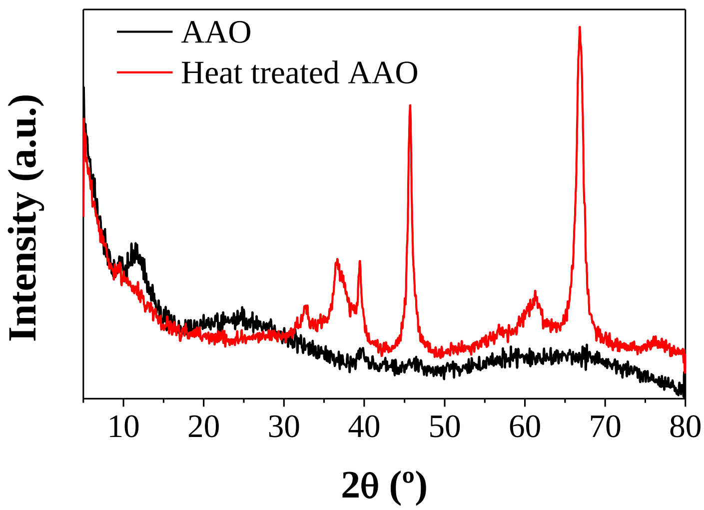
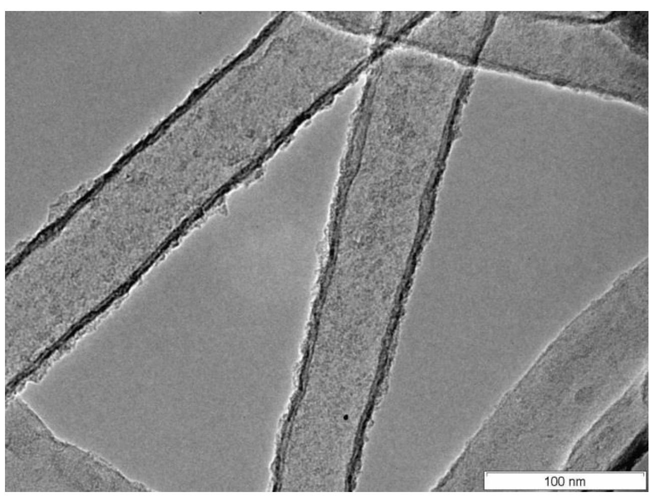
AAO preparation

The crystalline structure of the as obtained AAO films is amorphous (see Supplementary Figure 1) but the structure undergoes several phase transitions with increasing the temperature (Mardilovich et al., 1995;Mata-Zamora and Saniger, 2005). The transition from amorphous to δ-alumina occurs at temperatures around 850 °C and a slight change of the pore volume takes place due to a change in the atomic packing. This change in the volume may impede a homogeneous coating of the AAO films surface. To avoid this problem, the films were annealed at 950 °C for 1 h in air. After the heat treatment, the structure is changed to δ-alumina (see Supplementary Figure 1) and this phase transition is irreversible, i.e. after cooling down to room temperature, the films show the δ-alumina structure. The pretreatment also serves to clean up the surface of the AAO films from any organic impurities that might remain after the AAO films preparation process.



Supplementary Figure 1: XRD patterns of as-prepared and heat-treated AAO films.



Supplementary Figure 2: TEM micrograph of the nanotubes obtained after dissolving the AAO of CAAO films.

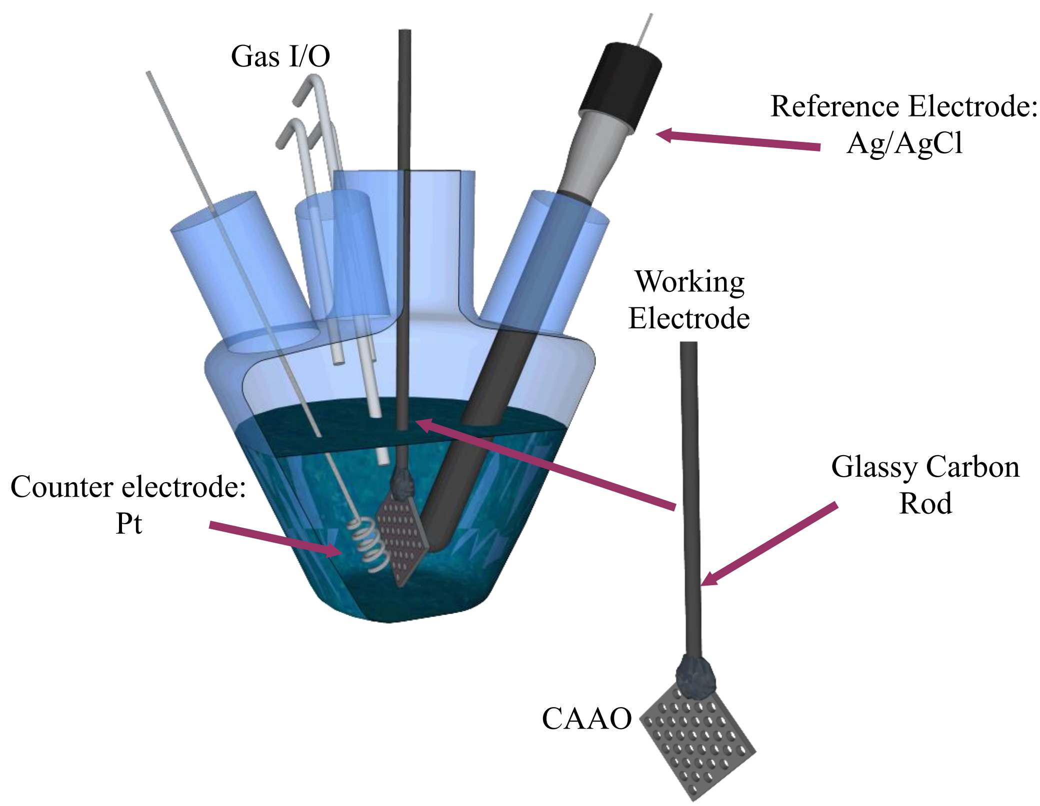
Surface energy

The surface free energy, γ, was calculated by measuring the contact angles between the films and water and CH_2I_2 and applying them to the Owens formula (Hoshikawa et al., 2012):

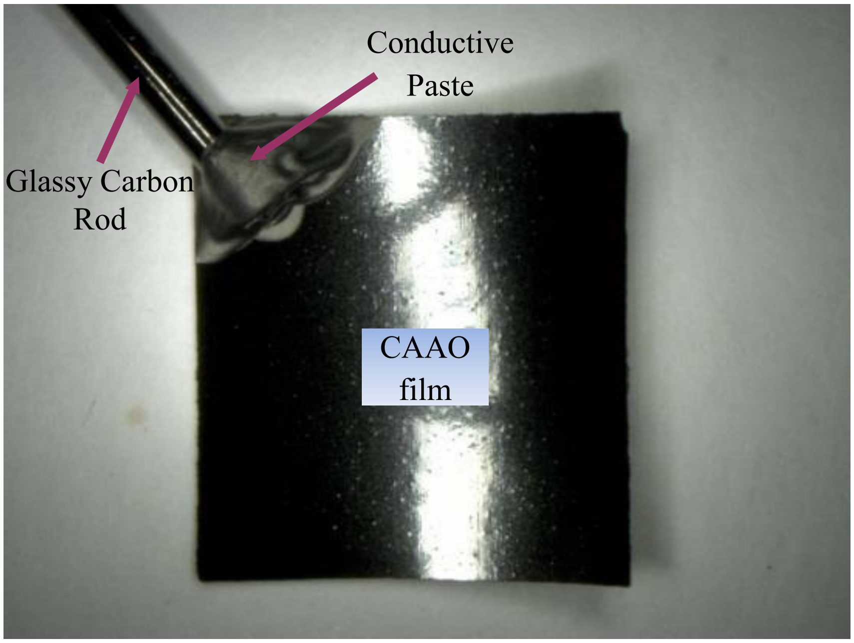
$$1 + cos\theta = 2\left[\frac{\sqrt{\gamma_s^d \gamma_l^d}}{\gamma_l} + \frac{\sqrt{\gamma_s^p \gamma_l^p}}{\gamma_l}\right] \tag{S1}$$

Where γ^d is the mean dispersion force, γ^p the dipole hydrogen force and $\gamma = \gamma^d + \gamma^p$ is the total surface energy. The subscript l indicates the values corresponding to the water (γ_l^d, γ_l^p =29.1 and 43.7 mJ/m^2) and CH_2I_2 (γ_l^d , γ_l^p = 46.8 and 4.0 mJ/m^2). The subscript s stands for the values corresponding to the sample.

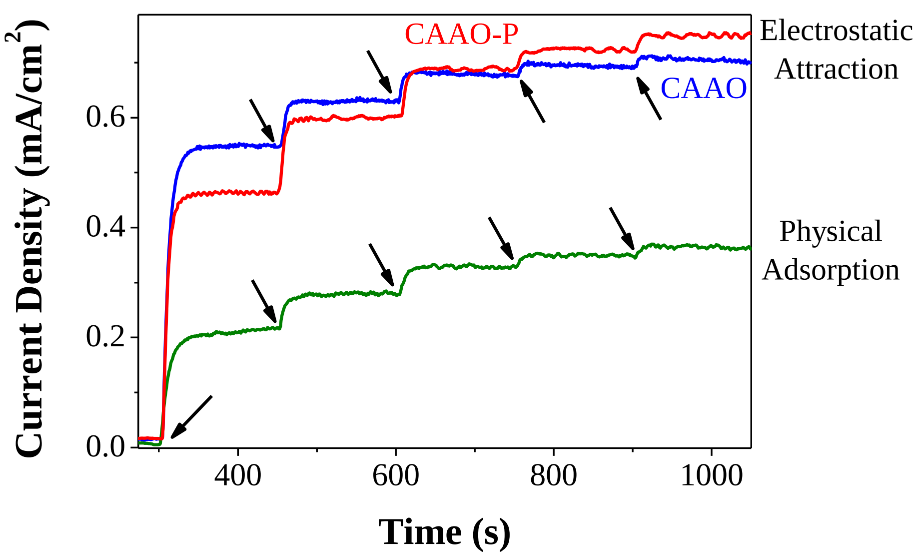
Electrochemical performance



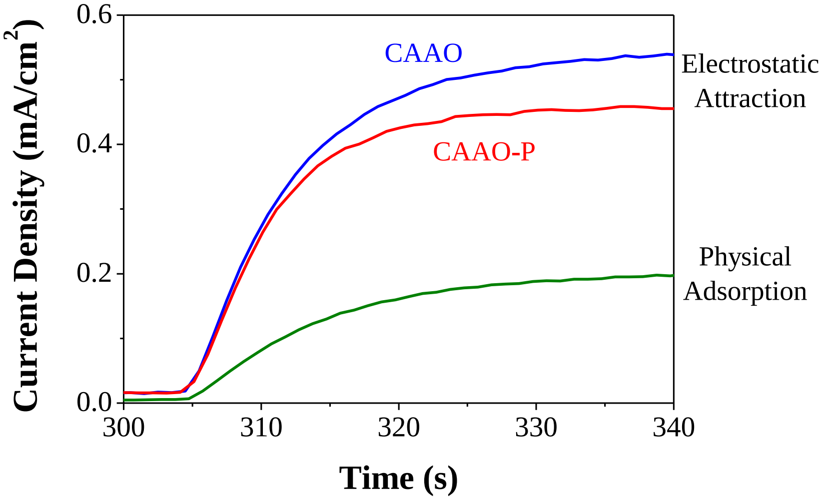
Supplementary Figure 3: Scheme of the three-electrode cell used in the electrochemical performance tests.



Supplementary Figure 4: Image of a CAAO film attached to a glassy carbon rod by the conductive paste.



Supplementary Figure 5: Chronoamperometry at 0.6 V vs. Ag/AgCl of the CAAO electrodes in McIlvaine buffer solution pH 5. The arrows indicate the time points when the fructose aliquots were added.



Supplementary Figure 6: Detail of the first fructose aliquot addition in the chronoamperometry of Supplementary Figure 5.

References

Mardilovich, P.P., Govyadinov, A.N., Mukhurov, N.I., Rzhevskii, A.M., and Paterson, R. (1995). New and modified anodic alumina membranes part I. Thermotreatment of anodic alumina membranes. *Journal of Membrane Science* 98**,** 131-142. doi: 10.1016/0376-7388(94)00184-z.

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