

Supporting Information for the paper:

Switchable Photochemical/Electrochemical Wiring of Glucose Oxidase and Electrodes

Omer Yehezkeli,^a Michal Moshe,^a Ran Tel-Vered,^a Yanli Feng,^b Yang Li,^b
He Tian,^b Itamar Willner^a

^a*Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

^b*Laboratory for Advanced Materials, Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, 200237, P.R. China.*

Modification of the electrodes: Clean Au wires (d=0.5 mm), were reacted with an aqueous solution of cysteamine, 50 mM, for 24 hours. The cysteamine monolayer-modified electrodes were, then, introduced into a HEPES buffer solution, 10 mM (pH=7.2) containing 1 mg ml⁻¹ of 1,2-bis[2-methyl-5(4-pyridinium)-3-thienyl]cyclopentene N,N'-biacetic acid, (**1**), for 2 hours, in the presence of 10 mM of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysulfosuccinimide sodium salt (NHS). The resulting electrodes were further reacted with 2-amino-ethyl flavin adenine dinucleotide, (**2**), 1 mg ml⁻¹, in a HEPES solution (pH=7.4). To reconstitute the GOx, the (**1**)/(**2**) monolayer-modified electrodes were immersed in an apo-GOx solution, 6 mg ml⁻¹, for 24 hours at 4°C.

Determination of the catalytically active reconstituted GOx on the electrode: The catalytically active reconstituted GOx was determined by the analysis of the O₂-mediated oxidation of glucose, which formed gluconic acid and H₂O₂, and the subsequent quantitative colorimetric analysis of the resulting H₂O₂ by horseradish peroxidase (HRP)-mediated oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), ABTS²⁻, to ABTS⁻ (at λ =414 nm). A calibration curve corresponding to the amount of GOx introduced (and the resulting H₂O₂ generated), was derived, Figure S1.

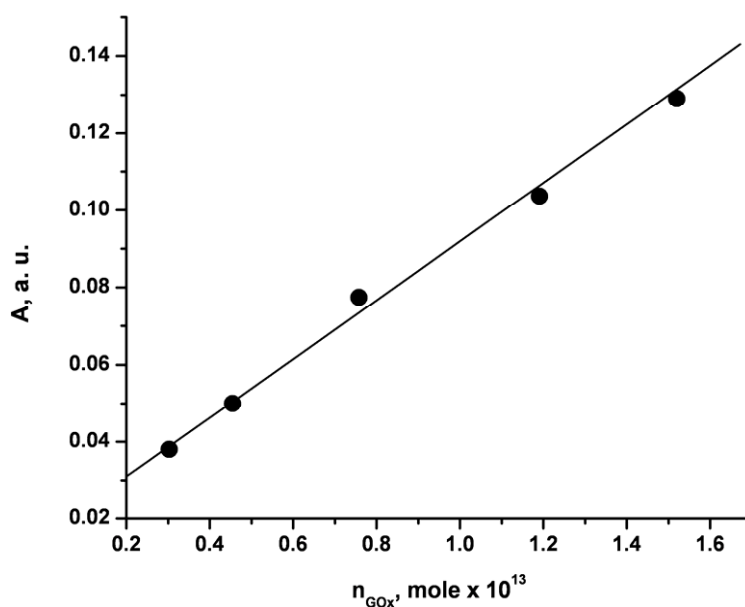


Figure S1. Calibration curve, corresponding to ABTS^{•−} absorption (at $\lambda=414$ nm), recorded after 2.5 minutes of reaction, for a 412 μL phosphate buffer solution (pH 7.4, 0.1 M) containing 130 μM ABTS^{2−}, 100 nM HRP, 24 mM glucose, and different concentrations of GOx.

The GOx-reconstituted electrode was, then, activated towards the biocatalyzed oxidation of glucose, and the resulting H_2O_2 was quantitatively analyzed by the HRP-mediated oxidation of ABTS^{2−}. Assuming that the activity of the GOx on the electrode surface was similar to that in solution, and using the calibration curve, we estimated the surface coverage of the catalytically active GOx to be $2.0 \times 10^{-13} \text{ mole} \cdot \text{cm}^{-2}$.

Cyclic voltammetry of the (1a)/(2a) monolayer-modified electrode.

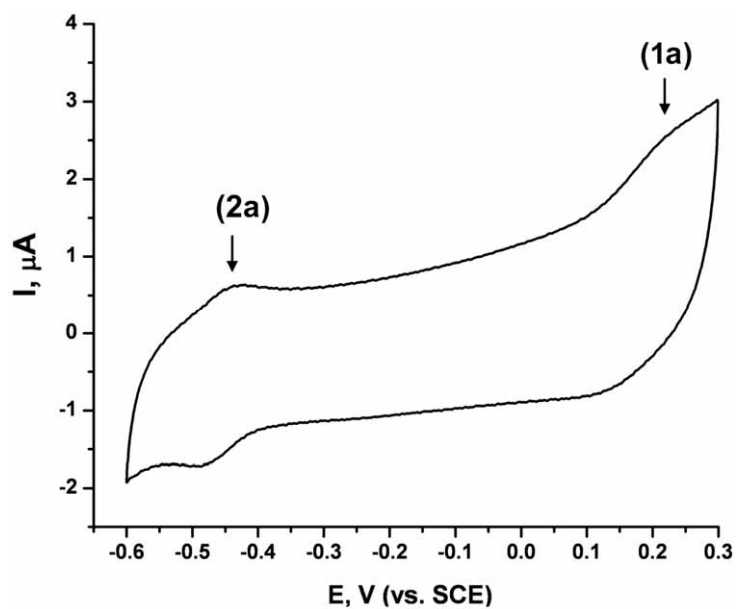


Figure S2. Differential pulse voltammogram of the (1a)/(2a) monolayer-modified Au electrode. Scan rate: 100 mV s^{-1} .

Control experiment – The non-directed GOx linked to the (1a)-modified Au electrode. The (1)-monolayer-modified Au electrode was reacted with HEPES buffer solution, 10 mM (pH=7.2), containing GOx, 1 mg ml⁻¹, for 2 hours in the presence of 10 mM of EDC/NHS. The resulting bioelectrocatalytic anodic currents associated with this electrode are depicted in Figure S2.

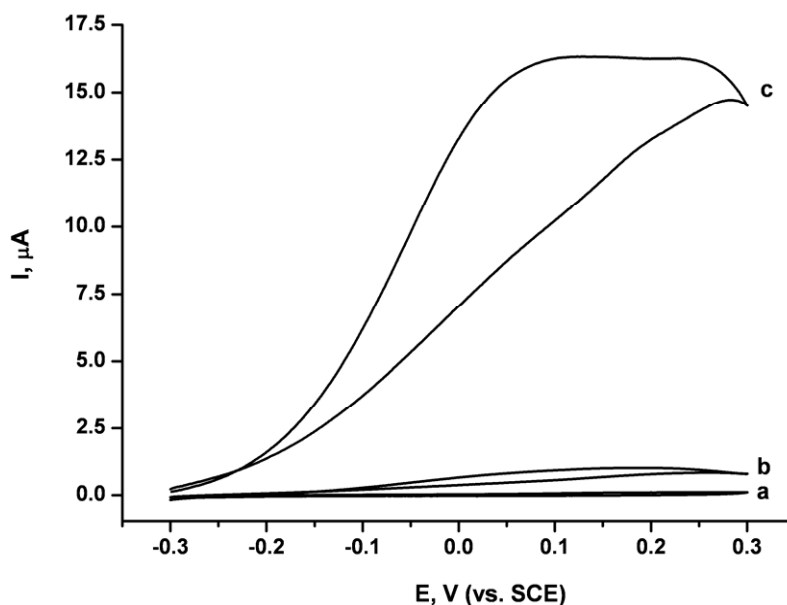


Figure S3. Electrocatalytic anodic currents, generated by: (a) The non-directed GOx linked to the (1a)-modified Au electrode in the absence of glucose, (b) The electrode in (a) in the presence of glucose, 120 mM. (c) Electrocatalytic anodic current generated by the GOx-reconstituted (1a)-modified Au electrode in the presence of glucose, 120 mM. Scan rate 5 mV s⁻¹. All data were recorded in a 0.1 M phosphate buffer solution, pH=7.4, under Ar.