Electronic supplementary information (ESI)

Bimetallic Nanowires as Electrocatalyst for Nonenzymatic Real Time Impedancimetric Detection of Glucose

Carmen C. Mayorga-Martinez[a,b], Maria Guix[a,c], Rossana E. Madrid[b], and Arben Merkoçi*[a,d]

---

[a] Nanobioelectronics & Biosensors Group, Catalan Institute of Nanotechnology, Campus UAB, 08193 Bellaterra, Barcelona, Catalonia, Spain.
b Laboratorio de Medios e Interfaces (LAMEIN), Departamento de Bioingeniería (DBI), (FACET), (UNT)/Instituto Superior de Investigaciones Biológicas (INSIBIO), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). CC 327 – Correo Central (4000) Tucumán, Argentina.
[c] Autonomous University of Barcelona, UAB Campus, 08193 Bellaterra, Spain
[d] ICREA, Barcelona, Catalonia, Spain. E-mail: arben.merkoci.icn@uab.es, Tel: +34935868014; Fax number: +34935868020.

Non-modified surfaces and IrOx or IrOx/Au-PtNWs modified SPEs were firstly evaluated in a PBS (pH=7.0) by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), so as to confirm the Au-PtNW immobilization. Fig. S1A shows CVs of the unmodified SPE, IrOx modified SPE and IrOx/Au-PtNW modified SPE. CV corresponding to the unmodified SPE does not show any peak. However, the CV of the SPE/IrOx and SPE/IrOx/Au-PtNW present characteristic peaks around 300 and 600mV.[1] When NWs are immobilized onto the electrode surface through entrapment within glutaraldehyde the obtained current slightly decreases.

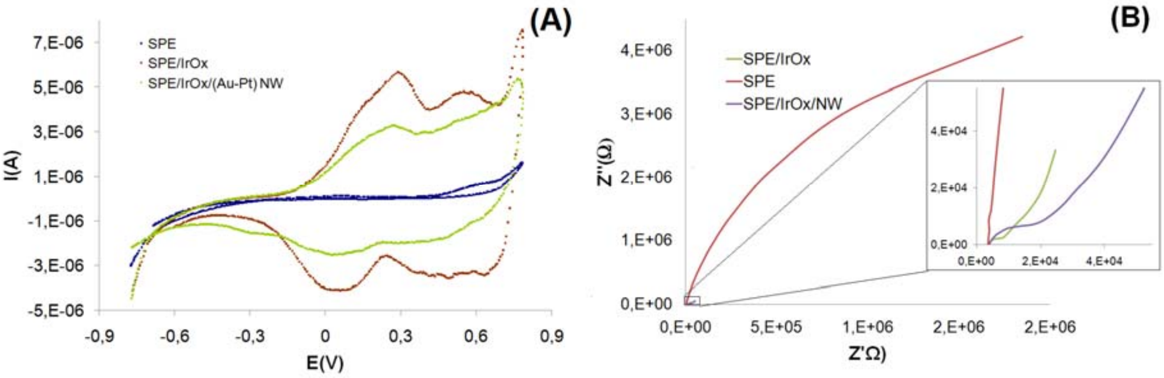

Fig. S1 Estimation of electroactive surface area by cyclic voltamperograms (CVs) at 50mV/s (A) and EIS characterization (B) of the bare, IrOX andIrOx/Au-PtNW modified SPE electrodes in phosphate buffer solution at pH 7.

EIS is a well known method used to study the surface features of modified electrodes.[2] It is employed to analyze the detailed electrochemical response of the modified electrodes by using individual or mixed components Argand diagram (Z' versus Z'') for the bare, SPE/IrOx and SPE/IrOx/Au-PtNW modified SPE, respectively shown in Fig. S1B. Bare SPE exhibits high electrode–electrolyte interface impedance (EEIZ), whereas IrOx modified electrode shows a reduction of two orders of magnitude in the EEIZ, similar to the one reported in the literature. NWs deposited through glutaraldehyde onto the electrode surface showed a slight EEIZ increase. The presence of glutaraldehyde, being an insulator, should have affected the EEIZ by increasing it.

In order to determine the working frequency, the percentage normalized modulus (PNM), defined in our previous work[7,8], was calculated by using equation inset in Fig. S2. The measured modules without ($Z_{0\mu M}$) and with 150µM of glucose ($Z_{150\mu M}$) in the range of 0.1–100 Hz are used to calculate the PNM, which indicates the rate of impedance variation per mole of glucose added to the system as a function of frequency. The PNM curve obtained (Fig. S2) presents a maximum value of 0.21%/µM, measured at 0.1 Hz. As frequency increases, the PNM curve continuously decreases down to approximately 0.03%/ µM for frequencies higher than 10 Hz.

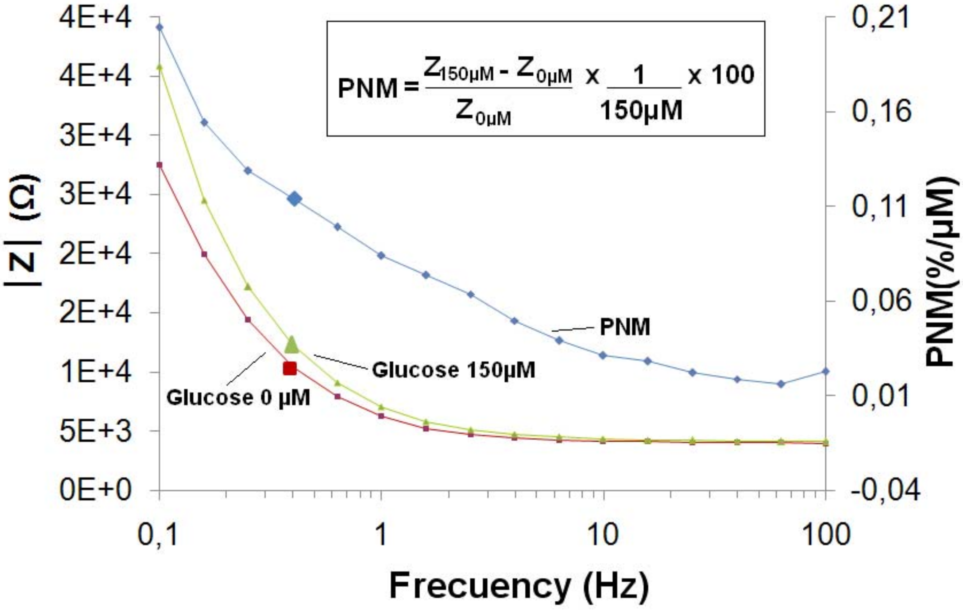

Fig. S2 Impedance magnitude in the absence and presence of 150 mM of glucose. Percentage Normalized Modulus (PNM) of the SPE/IrOx/Au–Pt NW sensor. $Z_{150\mu M}$ and $Z_{0\mu M}$ impedance modulus measured at 0 and 150 µM of glucose concentration.

MATERIALS AND METHODS

Apparatus and Reagents

Electrochemical measurements were performed with a Solartron 12508W impedance analyzer composed by a Solartron 1287 Electrochemical Analyzer and a Solartron 1250 Frequency Response Analyzer, commanded by the corresponding software provided by the manufacturer (ZPlot ®, Scribner Associates Incorporated). Magnetic stirrer was used to provide the convective transport during the impedancimetric measurements. Statistical computations were carried out by means of GraphPadPism version 3.00 Software. Scanning electron microscope (SEM) analysis was performed by using an EVO (Carl Zeiss NTS GmbH. Germany). Transmission electron microscope (TEM) images were taken with a JEM-2011 (Jeol, Ltd., Japan).

Track-etched porous aluminum oxide (0.02 µm) membranes were provided by Whatman (Anodisc 13mm, 0.02 µm). Glutaraldehyde (25%) was purchased from Sigma Aldrich. D-glucose anhydrous, potassium dihydrogen phosphate, sodium monohydrogen phosphate dehydrate and potassium chloride were purchased from Laboratories Cicarelli. All electrochemical experiments were carried out at room temperature (22ºC) in 0.07M phosphate buffer solution (PBS) pH 7 with 0.1M KCl. All solutions were prepared with single distilled water with conductivity lower than 5µS/m.

Synthesis of Platinum/Gold Nanowires (Au-Pt NW)

Pt-AuNW were prepared by using a three-step electrochemical deposition process, slightly adapted to the previously described setup.[3,4] Prior to Pt/AuNW synthesis, an ultrathin Au film was firstly sputtered by using a conventional ion sputtering method onto one side of the anodic alumina as to make the template conductive to be used as the working electrode contact. A platinum wire (0.3 mm diameter) was used as counter electrode and an Ag/AgCl wire was used as reference electrode. A cooper layer was previously electrodeposited so as to seal the aluminum oxide membrane porous.[5] Platinum had been electrodeposited at -2mA for 30 minutes and gold was electrodeposited at -0.9V for 40 minutes (see schematic of the setup, Figure S3). After electroplating, gold sputtered layer and copper layers are dissolved by mechanical polishing by using nitric acid 35%. As to release the NW from the alumina template, the membrane was dissolved by immersing it in NaOH 3M solution at room temperature for 1 hour. Then the Nanowires were centrifuged and rinsed in deionized water up to six times to remove the remaining NaOH. After template removal, NWs were resuspended and stored in acetone.

Preparation of Screen Printed Electrode (SPE) and Modification with Au-Pt NWs.

Screen printing electrodes fabrication is based on the sequential deposition of a graphite ink, Ag/AgCl ink and insulating ink on a polyester substrate. After the deposition of each layer a drying process is followed by keeping the polyester substrate at 90 ◦C for 15 min. The SPE working surface area was modified by electrodepositing an IrOx thin film, as previously reported.1,[6] A 10μL Au-PtNW solution drop was deposited onto the working SPE/IrOx electrode surface and allowed to dry at room temperature for 20min. Finally, 7 μl of glutaraldehyde (Glu) solution at 5% were cast onto the SPE/IrOx/Pt-AuNW electrode surface and let to dry at room temperature for 4 hours. The prepared SPE/IrOx/Pt-AuNW sensor was kept at room temperature.

Electrochemical Experiments

All electrochemical experiments were carried out at room temperature. The electrocatalytic detection of glucose by using SPE/IrOx/Au-PtNw was evaluated in 50mM NaOH solution in absence and in presence of different glucose concentrations (50, 100 and 150 μM). CV measurements were carried out at the potential range of -0.8 to 0.8 V vs. Ag/AgCl . In order to determine the working conditions for CIT implementation and study the characteristics of the modified electrodes surface, electrochemical impedance spectroscopy (EIS) studies were performed. The AC frequency range was 0.1 Hz to 100Hz logarithmic scale with 10 points per decade (in this frequency range it is possible to evaluate the impedance of the interface and the medium) in absence and in presence of 150μM glucose by applying 50mV of AC (optimization of AC value is previously reported[7,8]). CTI measurement was performed by stimulating the system with a composed signal from a 100mVDC potential superimposed with a 50mV AC potential to a single frequency of 0.4 Hz.

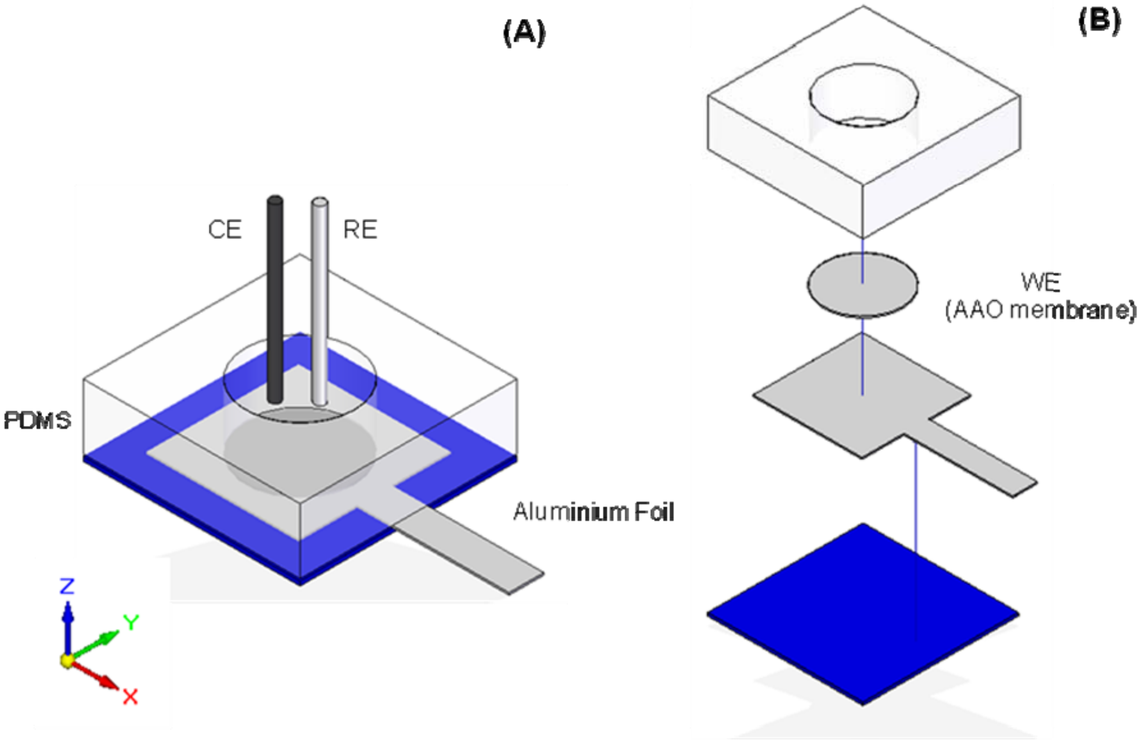

Fig. S3 Schematic of electrodeposition cell.

Notes and references

---

1 R. Meyer, S. Cogan, T. Nguyen, R. Rauh, *IEEE Trans. Neural. Sys. Rehabil. Eng.* **2001**, 9, 2.

2 G. Alarcón, M. Guix, A. Ambrosi, M. T. Ramirez Silva, M. E. Palomar Pardave, A. Merkoçi, *Nanotechnology* **2010**, 21, 245502 .

3 D. Kagan, P. Calvo-Marzal, S. Balasubramanian, S. Sattayasamitsathit, K. ManianManesh, G.-U. Flechsig, J. Wang, *J. Am. Chem. Soc.* **2009**, 131, 12082.

4 R. Laocharoensuk, J. Burdick, J. Wang, *ACS Nano*, **2009**, 2 (5), 1069.

5 J. Wang, J. Dai, T. Yarlagadda, *Langmuir* **2005**, 21(1), 9.

6 C. C. Mayorga Martinez, R. E.Madrid, C. J. Felice, Sens.Actuatiors B: Chem. 2008, 133, 682.

7 C. C. Mayorga Martinez; E. F. Treo, R. E. Madrid, C. J. Felice, *Biosens. Bioelectron.* **2010**, 26, 1239.

8 C. C. Mayorga Martinez, E. F. Treo, R. E. Madrid, C. J. Felice, Biosens. Bioelectron. 2011, 29, 200.