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

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Dear Editor,

Re: ID CC-COM-10-2011-016380

It is a pleasure for me to send you the manuscript entitled "Bimetallic Nanowires as Electrocatalyst for Nonenzymatic Real Time Impedancimetric Detection of Glucose" to be considered for publication at Chemical Communications. We sent it before for mistake in a full article format (ID CC-COM-10-2011-016380) but now it is adapted accordingly following the communication format.

This manuscript is related to the use of a bimetallic gold / platinum based nanowires as electrocatalysts in a real time nonenzymatic impedancimetric detection of glucose. This biosensor uses a very low DC potential, decreasing this way the effect of inferences such as uric acid, ascorbic acid and citric acid. The obtained results show that the use of the chronoimpedance technique as a novel transduction platform coupled to bimetallic nanowires can bring advantages in the design of nonenzymatic sensor achieving improved analytical performance beside the robustness and stability of the biosensing system with interest for applications in various fields.

Please find also at the end of this letter a list of suggested referees for the evaluation of this manuscript.

With the best regards,

Arben Merkoçi

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Bellaterra (Barcelona), October 24th, 2011

COMMUNICATION

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]

Gold-platinum nanowires are proposed as electrocatalysts in a real time nonenzymatic impedancimetric detection of
10 **glucose. The most important aspects for obtaining the bimetallic gold and platinum nanowires are described. The electrochemical behavior of the obtained platform toward electrocatalytic oxidation of glucose, including a proposal for the detection mechanism, are shown.**

15
Development and improvement of glucose biosensors has been an important subject of interest during the last fifty years.[1] Most of the known amperometric glucose biosensors are based on glucose oxidase (GOx) or glucose dehydrogenase (GDH)
20 immobilizations.[2,3] Moreover, in some applications, it is necessary to have sensors which are stable when exposed to high temperatures or other aggressive environment.[4] Most of these nonenzymatic electrochemical glucose sensors rely on measuring the current response during the direct glucose
25 oxidation on the electrode surface. The use of noble metals such as Pt and Au as to develop nonenzymatic sensors has been reported.[2] However, in presence of glucose these electrodes quickly lose their activity due to accumulation of chemisorbed intermediates, which block the electrocatalytic surface.[2]
30 In the other hand Chronoimpedance technique (CIT) for real time determination of glucose concentration in a first and second generation glucose oxidase/carbon paste electrodes have been implemented. This technique allows continuous and rapid time response measurements is only limited by the
35 transient response of the biosensor. This new method is supposed to be applicable to any other biosensor system. [5,6] It has been reported that the nanostructured electrodes possess

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Electronic supplementary information (ESI) available: additional characterization data for SPE/IrOX/Au-PtNW Fig. S1and experimental section and (Fig. S2).

40

45 avery large surface to area activation ratio, favoring kinetically controlled reactions like electrocatalytic oxidation of glucose more than diffusion controlled reactions expecting a high sensitivity toward glucose detection.[7] For this reason we propose the combination of both materials and consequently
50 the use of a bimetallic platinum/gold nanowire (Au-Pt NW) as a free-enzyme electrocatalyst for glucose. This is achieved through Au-Pt NW integration on the working electrode of a screen printed electrode (SPE) followed by CIT measurements performed for the first time in an integrated and miniaturized
55 three electrode system. The use of an iridium oxide (IrOx) thin layer electrodeposited onto the working electrode surface was necessary to reduce the electrode-electrolyte interface impedance (EEIZ) for CIT measurements, as previously described.[8] Au-Pt NWs were immobilized onto the SPE
60 working electrode surface by using the IrOx thin layer and the cross-linking agent glutaraldehyde.
Morphological and structural studies of bimetallic nanowires were performed by Transmission Electron Microscope (TEM). Highly regular and uniform average diameter Au-Pt NW of
65 about 140nm (Fig. 1) can be observed. X-ray microanalysis of nanowires was performed by TEM, showing an Au and Pt alloy at different proportions along the nanowire. Compositions in terms of Pt and Au percentages at different sections of the Au-Pt NW are given on the inset table at Fig. 1(A). A
70 homogeneous distribution of the nanowires on the electrodes surface can be observed by Scanning Electron Microscopy (SEM) image (Fig. 1B). The Fig. 1C shows the effect of glutaraldehyde as a binding matrix is also observed, showing a good entrapment of the wires within the mentioned matrix.
75 Electrocatalytic effect of Au-PtNWs toward glucose detection was evaluated (see ESI for experimental condition). By increasing glucose concentration a current decrease was observed, indicating that Au-PtNWs are exhibiting electrocatalytic activity toward glucose presence. For all the
80 glucose concentrations it can be clearly observed the catalytic effect of NWs at the range from 0 to 0.1V(data not show).
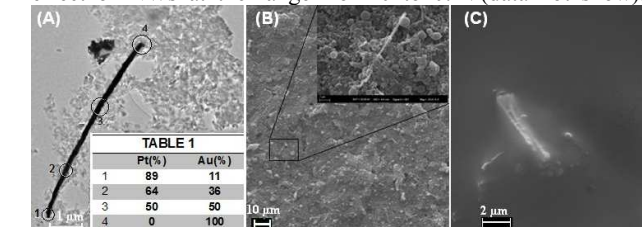

TABLE 1	Pt(%)	Au(%)
1	89	11
2	64	36
3	50	50
4	0	100

Fig.1 TEM image of a single (Au/Pt)NW(A). SEM micrographs of modified SPE with (Au/Pt)NW (B). Effect of glutaraldehyde as a
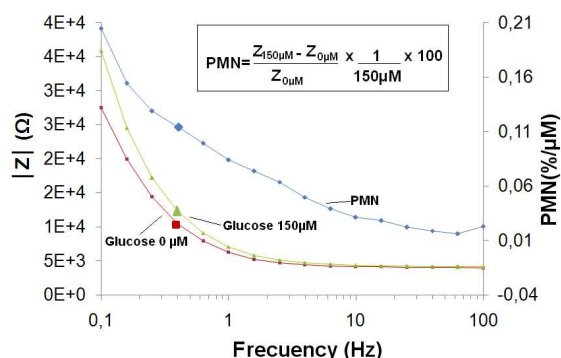85 binding matrix for NWs entrapment (C).

Fig.2 Impedance magnitude in absence and in presence of 150 μM of glucose. Right: Percent Normalized Module (PNM) of the SPE/IrOx/Au-PtNW sensor. $Z_{150μM}$ and $Z_{0μM}$ impedance modulus
5 measured at 0 and 150μM of glucose concentration.

Bode diagram was determined using electrochemical impedance spectroscopy (EIS) (Fig. 2). After testing different DC potentials in the range of -0.1 V to 0.1 V (data not shown), the highest activity of this sensor was observed at 0.1V. The
10 EIS data were used to calculate the Percentage Normalized Modulus (PNM), which indicates the rate of impedance variation per mole of glucose added to the system as a function of frequency. PNM is calculated in the range of 0.1–100 Hz. This value was corrected before, by applying the equation
15 presents in Fig. 2. The PMN curve obtained (Fig.2), presents a maximum value of 0.21%/μM, measured at 0.1 Hz. As frequency increases, PNM curve continuously decreases down to approximately 0.03%/μM for frequencies higher than 10 Hz. Higher PMN values were observed at the low-frequency range
20 (0.1–10 Hz).

It is possible to conclude from the PMN evaluation that the most important impedancimetric response is observed at the low frequencies range, being this phenomenon similar to the one reported in the previous work.[5,6] Therefore for CIT
25 implementation 0.4 Hz was used, because at this frequency the response obtained appreciably reflects |Z| change.

In an electrode electrolyte interface (EEI) the electric current flows due to the charge transfer occurring during the electrochemical reactions that take place between the electrode
30 surface and the electrolyte. In our specific case, the electrochemical reaction on the SPE/IrOx/Au-PtNW sensor surface can be described considering the different metallic surfaces present along the alloy (Fig. 3). The mentioned mechanism based on the glucose oxidation onto gold surface
35 and H_2O_2 reduction onto platinum surface, is the reason why this sensor presents such a high sensitivity and low linear range for glucose detection. It is well known that Au nanoclusters can behave as GOx mimicking units able to catalytically oxidize glucose and produce gluconates and H_2O_2.[9]
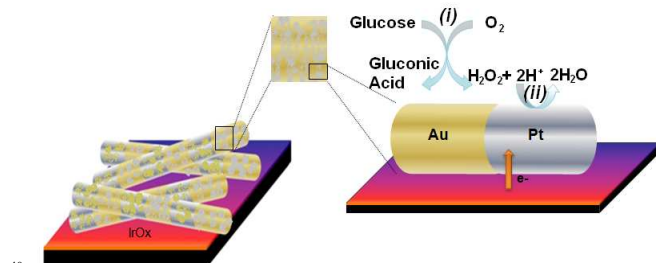

40 **Fig.3** Proposed mechanism for the glucose electrocatalytic detection using Au-PtNW. *(i)*Glucose is transported by convection to the gold surface, where is oxidized to glucoronic acid by reducing O_2 to H_2O_2. *(ii)* H_2O_2 decomposes into H_2O on the platinum surface.
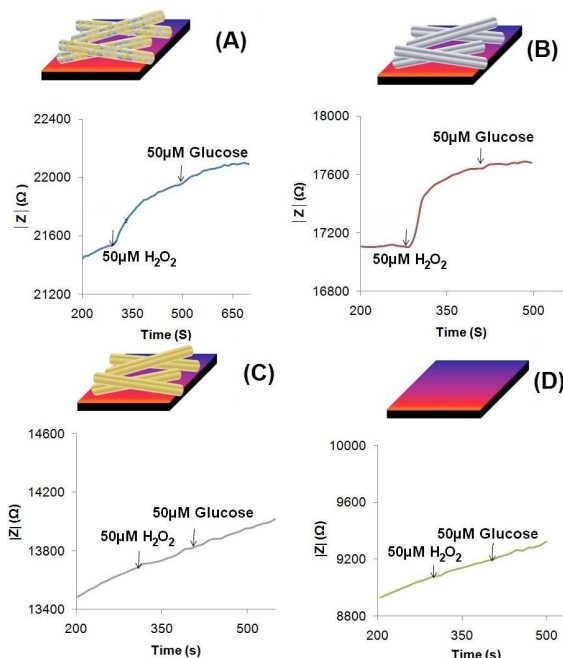

45 **Fig.4** Real time impedancimetric response of the SPE/IrOx/Au-PtNW (A), SPE/IrOx/PtNW (B), SPE/IrOx/AuNW (C) and SPE/IrOx (D) sensors upon successive additions of 50 μM H_2O_2 and 50 μM glucose.

This process, catalysed by AuNPs, is similar to the one
50 performed by the natural enzyme glucose oxidase, which also catalyzes the oxidation of glucose with the co-substrate O_2.
The recent implementation of an Au NW modified sensor for nonenzymatic glucose detection also has confirmed that nanostructured gold is able to act by mimicking the GOx
55 activity.[1] On the other hand, Pt is a widely used electrode material for H_2O_2 detection and biosensor fabrication. Most of the platinum based biosensors detect H_2O_2 at relatively high potential (around 0.6 V). However, Pt NW and Pt nanoparticles (NP) were recently reported for H_2O_2 detection at 0 mV.[10,11]
60 The use of bimetallic gold–platinum nanowire as a free-enzyme electrocatalyst for glucose is a very interesting application due to the non-competitive mechanism held on the electroactive surface.

For a better elucidation of the glucose detection mechanism
65 further impedance measurements were carried out. Measurements were performed under different experimental conditions. The first one (Fig. 4A) is carried out using a SPE/IrOx/Au-PtNW, while the second (Fig. 4B) and the third (Fig. 4C) case correspond to SPE/IrOx sensor modified only
70 with platinum and gold nanowires, respectively. Finally, a SPE/IrOx without NW was also checked (Fig. 4D). The impedance response (|Z|) of each electrode toward 50μM H_2O_2 and 50 μM glucose additions were recorded showing an appropriate impedance response to H_2O_2 (see Fig. 4 A and B).
75 An increase of |Z| of around 500 Ω and 300 Ω can be observed for SPE/IrOx/PtNW and SPE/IrOx/Au-PtNW sensors respectively. The higher SPE/IrOx/PtNW sensor response toward peroxide is due to the fact that more platinum area is available for the reduction of H_2O_2 than the Pt-AU NW sensor.
80 SPE/IrOx/AuNW (Fig. 4C) and SPE/IrOx (Fig. 4D) sensors don't show any response toward either H_2O_2 or glucose. Results are consistent with the sensors composition, as on the first configuration platinum is not present as to reduce H_2O_2 (product of glucose oxidation on the Au surface) and on the
85 second configuration H_2O_2 is not catalyzed by iridium oxide at this potential value.[12,13]
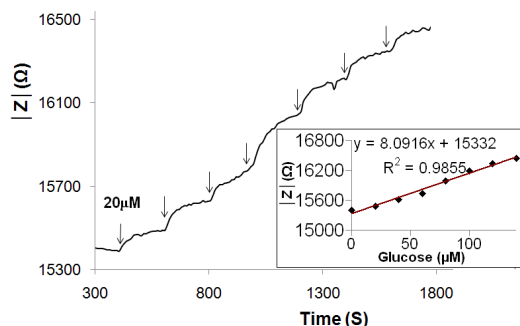
Fig.5 (A) Real time impedancimetric response of SPE/IrOx/Au-PtNW sensor. (B) Sensor calibration given as impedance magnitude versus glucose concentration at 0–140µM range.

SPE/IrOx/Au-PtNW sensor is the only one which exhibits response to glucose addition, showing an impedance change around 150 Ω (Fig. 4A). This sensor can detect glucose because both metals (Pt and Au) are present and both reactions can be coupled, the oxidation of glucose to gluconic acid (Au surface) and reduction of hydrogen peroxide (Pt surface).

Real time determination of impedance changes ($|Z|$) in NaOH 50mM solution during successive addition of glucose 20µM was carried out by using a composed signal of 100mV DC plus a 50mV AC of 0.4Hz (Fig. 5). Impedance response shows a linear range up to 140µm with $8557\Omega mM^{-1}$ of sensitivity, and 0.99 of correlation coefficient (inset Fig. 5). In order to compare the repeatability of 3 sensors, the normalized impedance (relative value to zero concentration of glucose) is evaluated. The results of triplicate sets, indicated by error bars, show the repeatability and reproducibility corresponding to the measurements with a relative standard deviation (RSD) less than 5% for a glucose concentration range of 20-140 µM.

The low detection range obtained by this glucose sensor may allow applications to non-invasive detection of glucose in other biological fluids (saliva, sweat and urine) where glucose is too low. Moreover this low detection range would allow the implementation of a miniaturized system for detection of glucose in diluted blood samples using just few µl of sample.

It is well known that for the systems based on electrochemical detection of the produced H_2O_2 at a potential range of about 0-200 mV vs. Ag/AgCl there is almost no effect of interferences. Working at these conditions would bring a high selectivity along with the high sensitivity and the fast response of the developed biosensor.[14] In our case working with a DC potential of 100 mV combined with the chronoimpedance technique are the main reasons for such improvements.

Selectivity is a very important parameter to be considered for nonenzymatic glucose sensors. To evaluate the selectivity of the sensor, impedancimetric response toward uric acid (UA) and ascorbic acid (AA) was measured. These interference species are normally present in real physiological samples and are usually examined in presence of glucose. It must be considered that the concentration of glucose studied is at least 30 times lower than the one in human blood,[15] and in addition for this experiments the glucose concentration is 20 times higher than the concentration of interference species. Citric acid (AC) is also evaluated due to its presence as a preservative in soft drinks and other foods. Fig. 6 presents experimental results obtained by adding 50µM of glucose in NaOH 50mM, followed by 2.5 µM UA, 2.5 µM AA and 10 µM CA. Good selectivity of the SPE/IrOx/Au-PtNW sensor is shown toward glucose oxidation, because interference species (such as AU,AA and CA) can be neglected.
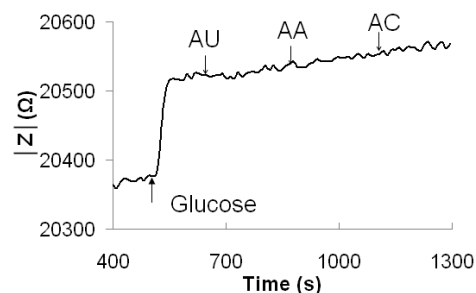

Fig.6 Evaluation of interfering species.

Au-PtNWs are obtained by an electrodeposition method and implemented on a glucose sensor based on SPE modified by IrOx and Au-Pt nanowires. Their electrochemical behavior toward glucose detection is evaluated by CIT. This sensor uses a very low DC potential, decreasing this way the effect of inferences such as UA, AA and CA. This sensor presents high repeatability and sensitivity. Glucose detection mechanism associated to the designed sensor is also determined. The obtained results show that the use of the CIT as a novel transduction platform coupled to bimetallic nanowires can bring advantages in the design of nonenzymatic sensor achieving improved analytical performance beside the robustness and stability of the biosensing system with interest for applications in various fields.

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Electronic supplementary information (ESI)

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

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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.
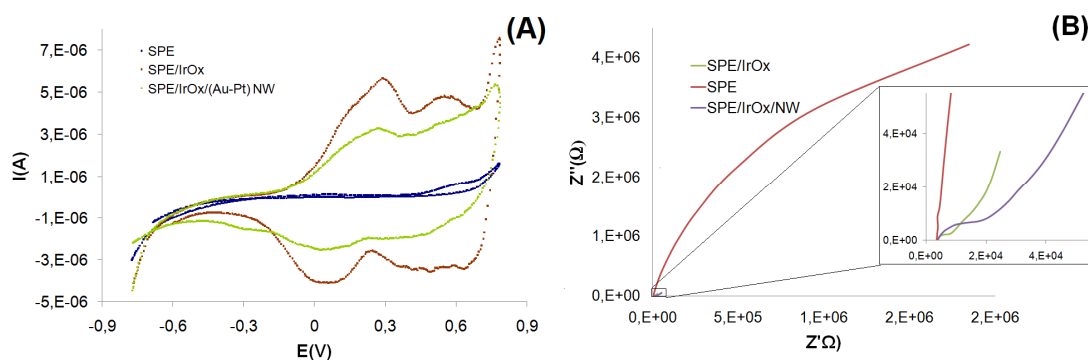

Figure S1. Estimation of electroactive surface area by cyclic voltamperograms (CVs) at 50mV/s (A) and EIS characterization (B) of the bare, IrOX andIrOx/Au-PtNW modified SPE electrodes in phosphate buffer solution at pH 7.

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.

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 S2). 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
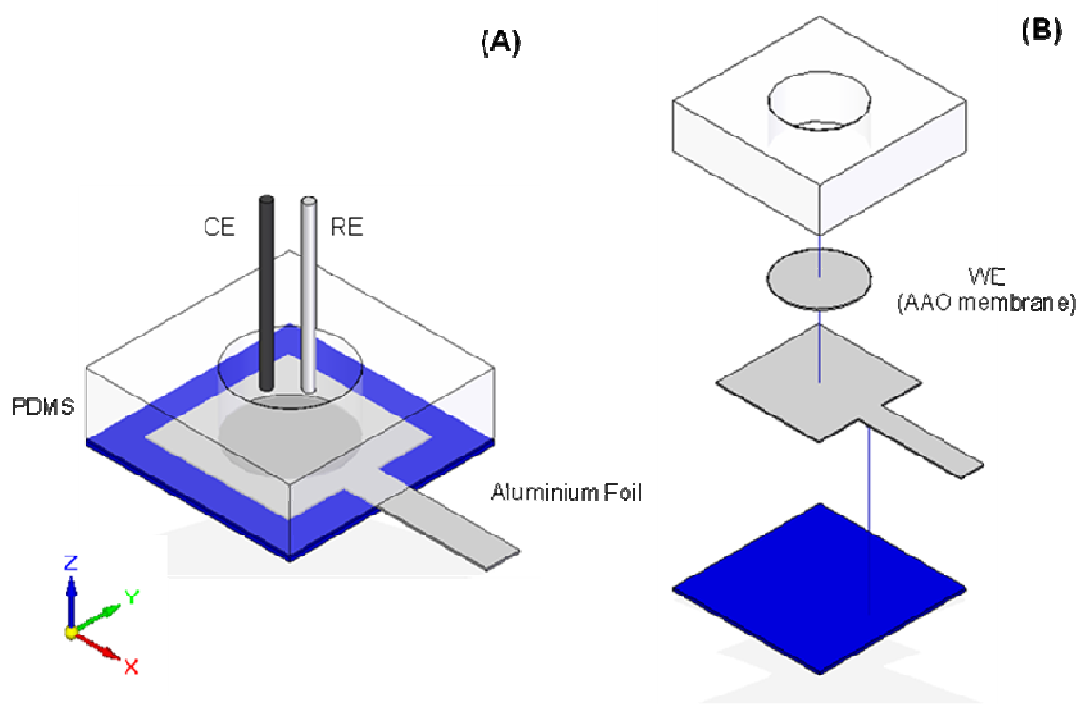
potential to a single frequency of 0.4 Hz.

Figure S2. Schematic of electrodeposition cell.

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