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# Rough Gold Electrodes for Decreasing Impedance at the Electrolyte/Electrode Interface

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ABSTRACT

Electrode polarization at the electrolyte/electrode interface is often undesirable for bio-sensing applications, where charge accumulated over an electrode at constant potential causes large potential drop at the interface and low measurement sensitivity. In this study, novel rough electrodes were developed for decreasing electrical impedance at the interface. The electrodes were fabricated using electrochemical deposition of gold and sintering of gold nanoparticles. The performances of the gold electrodes were compared with platinum black electrodes. A constant phase element model was used to describe the interfacial impedance. Hundred folds of decrease in interfacial impedance were observed for fractal gold electrodes and platinum black. Biotoxicity, contact angle, and surface morphology of the electrodes were investigated. Relatively low toxicity and hydrophilic nature of the fractal and granulated gold electrodes make them suitable for bioimpedance and cell electromanipulation studies compared to platinum black electrodes which are both hydrophobic and toxic.



## 1. Introduction

Application of a constant electric potential to electrodes causes charge accumulation on electrodes that are in contact with an electrolyte solution. As a consequence of the accumulation, a large impedance forms at the electrode/electrolyte interface, and causes large electric potential to drop at the interface. This adverse effect is identified as electrode polarization (EP). Specifically, the sensitivity of dielectric spectroscopy (DS) is limited in sub-MHz range due to the EP effect. DS is a noninvasive and a label free technique to characterize biological samples. It was successfully used to investigate dielectric properties of cells, tissues and bacteria [1–7]. DS involves application of a small test voltage to the sample under study. Various types of approaches were used to reduce EP in DS. These include electrode separation distance variation technique [8], substitution technique [8], increasing effective surface area of electrodes [9–11] and four electrode techniques [12–16]. However, there is no single accepted method for the EP correction due to the complexity of the phenomenon. One of the most efficient techniques to minimize EP effect is to maximize the electrode/electrolyte interfacial area to produce rough, recessed and complex conductive structures on flat electrode surfaces. This technique is especially more suitable for microfluidic systems, where micro-electrodes are present, as portability and device size are important considerations.

Platinum black (PB) is widely used to create rough electrodes and to enable DS in sub-MHz range [17], and also in many distinct areas such as neural signal sensor [17–22], tissue sensor for orbicularis oculi muscle [23], gas sensor [24,25], drug screening and thermal infrared detection [26] due to its unique contribution to reduction of EP. However, the fragility of electrodeposited PB under mechanical contact, poor reproducibility of deposition, its hydrophobic behavior and bio-toxicity [27] have limited its use in physiological measurements. Different electrode materials and fabrication techniques, including IrOX [9,28,29], TiN [9], Pedot-Nanotubes [22], conductive polymers [9,22,30–32] and activated carbon [33], were sought to reduce EP. However, the common disadvantage of these materials is their electrical stability under mechanical contact.

The gold based rough electrodes can reduce EP, since they can preserve its recessive structure under mechanical contact and its electrical behavior for long term electrical measurements. Plain gold electrodes have already been used extensively in impedance measurements owing to its biologically inert nature [34]. Recently, gold electrodes with fractal nanostructures were utilized in novel antennas [35], solar cells [36], and ultrasensitive biosensors [37–40]. Also the hydrophilic nature of the rough gold surface compared to PB surface offers a major advantage for microfluidic

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systems. Therefore, rough gold electrodes can be a favorable alternative to PB and other materials to reduce EP owing to its dendritic and recursively constructed shape to maximize effective surface area [41].

In this study, we developed two different kinds of gold nanostructured electrodes that have increased effective surface area compared to that of plain gold electrodes. While one of the techniques uses electrochemical deposition of gold to generate nanostructures, the other method depends on sintering of gold nanoparticles on plain gold electrodes. Electrochemical deposition requires expensive equipment, costly reagents, and can result in poor reproducibility, whereas nanoparticle sintering depends on a relatively simple procedure. In order to measure electrical impedance at the electrode/electrolyte interface a microfluidic channel was fabricated and filled with phosphate buffer saline (PBS), where the electrodes were at parallel plate configuration. Measuring PBS is relevant for physiological measurements, as PBS with physiological concentrations of ions cause strong EP. A constant phase element (CPE) model was used to model the impedance response at the interface. The parameters in the CPE model were used to characterize the electrodes. Surface topographies of each electrode were investigated with scanning electron microscopy (SEM) and a profilometer. Hydrophobicity of electrodes was measured using contact angles. Furthermore, the toxicity of the electrodes on a T-cell leukemia cell line was measured using Trypan Blue exclusion assay.

## 2. Materials and Methods

### 2.1. Electrode Fabrication

Glass slides were cut into $2.5 \times 2.5\,cm^2$ pieces using diamond cutter. The glass pieces were cleaned in an ultrasonic bath (FB11201, Fisher Scientific) at 37 kHz-at 25 °C sequentially in DI (deionized) water, 1 M KOH, and acetone for 10 min, followed by a rinse with DI water. The substrates were dried with nitrogen gas following the cleaning steps. The glass slides were then put into 150 °C oven to fully evaporate water. A masking tape was used as a negative mask to generate electrode patterns. The tape was cut with a craft cutter (Silver Bullet) to obtain 4 mm diameter circular shapes as negative masks. After the tape was stuck on the glass substrates, the slides were sequentially sputter-coated (EMS300TD, Emitech) with chromium (120mA-60s) and gold (120mA-150s) or platinum (120mA-150s). Chromium layer was used as a seeding layer to provide a fine adhesion between Au/Pt and glass. Sputtering generated thin layers of metals, where the thickness was on the order of nanometers. Following the sputtering process, the tape was removed and electrodes were rinsed using DI water. Copper tapes (3M) were used as terminal leads. The tapes were bond using silver conductive epoxy. Following this step, the electrodes were ready to be modified using electrochemical deposition.

### 2.2. Electrode Modification

A three-electrode potentiostat/galvanostat system was used for electrochemical deposition (EZstatPro, Nuvant). In the setup, electric current flows between a platinum counter electrode (MW-4130, BASI) and working electrodes (Au/Pt sputtered electrodes), where the potential at the working electrode is controlled with reference to a Ag/AgCl electrode (MF-2052, BASI). All solutions for electrochemical deposition were prepared in ultrapure DI water (EMD Millipore, electrical conductivity $5 \times 10^{-6}$ S/m at 25 °C). Only circular part of electrodes was immersed in the solution in order to have a fixed area of deposition. The following modifications were made on electrodes:

#### 2.2.1. Platinum Black Electrodes (PBEs)

The PB electroplating solution contains 1% Chloroplatinic acid (Sigma Aldrich) and 0.08% Lead Acetate (Sigma Aldrich). The electrodeposition setup was used in galvanostatic mode, where the electrodes were coated with PB at different current densities (mA/$cm^2$) and varying time periods. PB is coated on Platinum electrodes.

#### 2.2.2. Gold Nanostructured Electrodes (GNEs)

Gold electrodes were electrochemically coated in 1 mg/ml Sodium Tetrachloroaurate (III) ($AuCl_4$ Na $2H_2O$) (Sigma Aldrich) solution using the deposition setup in the potentiostatic mode. Depositions were conducted at varying durations and electric potentials.

#### 2.2.3. Gold Granulated Electrodes (GGEs)

Gold nanoparticles that are in 10 nm diameter (nominal) and made using tannic acid and citrate were purchased from Sigma Aldrich. In order to have gold granulated electrodes, gold sputtered electrodes were placed on a hot plate (Isotherm, Fisher Scientific) that is kept at a constant temperature. Gold nanoparticle suspension droplets of ~80 μl, which was in 0.1 mM PBS solution at a concentration of $6 \times 10^{12}$ particles/ml, was slowly pipetted on the electrodes sequentially as water of a previous droplet evaporated at the surface.

Following all the deposition processes, modified electrodes were kept in an oven at 100 °C for 10 min for dehydration.

### 2.3. Device Assembly

Microfluidic channels were utilized to measure low amounts of liquids. The channels were fabricated using double sided tapes and glass substrates that bear electrodes (Fig. 1). Inlets and outlets were perforated with a diamond drill bit on glass substrates. Double sided tape was cut with a craft cutter (Silver Bullet) into the shape of a microfluidic channel. Double sided tape was stuck on one substrate. A second substrate was aligned so that the two electrodes were aligned on top of each other in the middle region of the microfluidic channel. The thickness of the microfluidic channels was 500 μm.

### 2.4. Characterization Studies

A high precision impedance analyzer (4194A, Agilent) was used to measure the impedance of the microfluidic channel that was

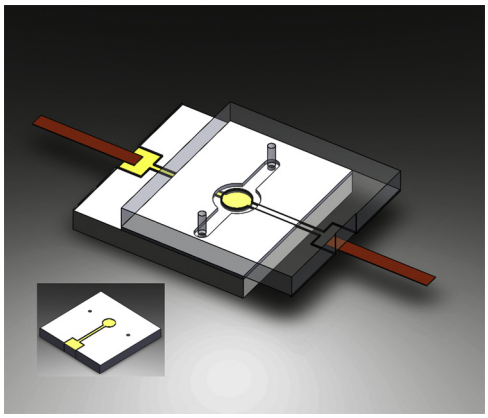

**Fig. 1.** A schematic of the microfluidic channel. Two electrodes (4 mm diameter) were aligned on top of each other. A double sided tape formed the microfluidic channel. The solutions were fed using a pipette through the inlet. Inset figure shows a glass substrate with an electrode.