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COUPLING OF THERMOELECTRIC AND ELECTROCHEMICAL MEASUREMENTS FOR SINGLE STRANDED DNA FUNCTIONALIZATION ON GOLD ELECTRODES

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ABSTRACT

Microfluidics enable to perform multiple experiments by using minimal sample volumes, leading to higher sensitivities and a highly detailed investigation of biochemical processes respect to traditional laboratory methods. Here we present an original and novel DNA biosensor able to perform both electrochemical and thermoelectric measurements thanks to the integration of a thermopile and an electrochemical cell into a microfluidic device.

KEYWORDS: DNA Biosensor, Thermopile, Electrochemical Detection, Microfluidic Device

INTRODUCTION

Self-assembled monolayers (SAMs) are often employed in miniaturized biosensors for biochemical and clinical applications. Calorimetry is the most direct technique to measure heat released during chemical reactions [1], while electrochemical detectors offer good sensibility and selectivity [2]. The integration of a thermopile into an electrochemical microfluidic device could lead to a direct and real time information about SAM formation, which today remains a challenge.

THEORY

Thiol SAM on gold assures a relative stability thanks to van der Waals interactions, when the S-Au bond is formed the released energy is on the order of 50 kcal mol^{-1} [3]. The energy released modifies the local temperature of the solution. This temperature change is converted into a voltage difference by a thin film thermopile having the electrodes close to the reaction point. This permits to monitor the ssDNA functionalization as a function of time. In addition, the cyclic voltammetry (CV) measurement provides a direct electronic signal transduction thanks to the electrons transfer between the electrolyte and the electrode [4]. When the functionalization takes place the current decreases due to the reduction of redox reactions at the working electrode.

EXPERIMENTAL

Our microfluidic chip is composed by a glass substrate and a polydimethylsiloxane (PDMS) cover fabricated by a SU8 mold which contains the channel pattern. These two parts are bound together by air plasma. The substrate carries 50 gold-nickel thermocouples in series and the electrochemical cell composed by a working (WE) and a counter (CE) gold electrodes (**Figure 1A**). The fabrication process requires two steps of photolithography, evaporation and lift-off for the gold (100 nm) and the nickel (150 nm) depositions.

We characterized the thermopile by inserting in the active junction side 0.1 mL of water, heated at different temperatures. The voltage across the thermopile was measured as a function of time by a voltmeter. The area under curve (AUC) of the thermopile response was calculated and plotted as a function of the water temperature (**Figure 1B**), this represents the released heat. The bare gold electrodes were characterized by a CV measurement by using $[\text{Fe}(\text{III})(\text{CN})_6]^{3-} / [\text{Fe}(\text{II})(\text{CN})_6]^{4-}$ solution. Then we introduced into the channel a 23-base thiol modifier C6 ssDNA at 10^{-4} mol/L in NaCl 0.5 mol/L. During the functionalization time the thermoelectric measurement was performed. Finally we executed again the CV measurement to prove the SAM formation.

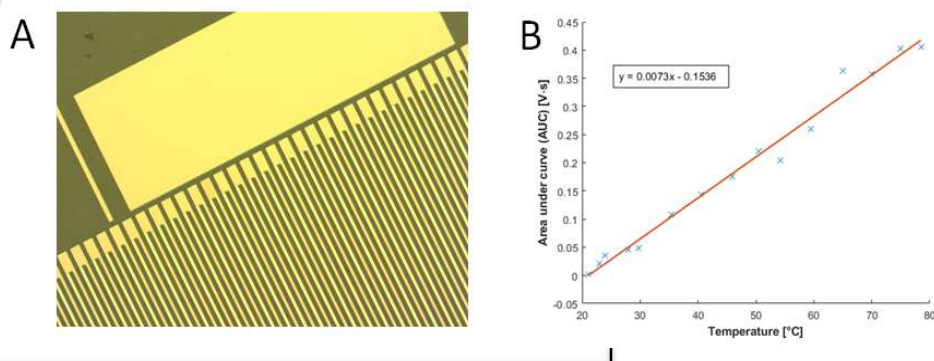


Figure 1: *A.* Thin film thermopile and WE (30x300µm) and CE (2000x300µm). The thermopile junctions next to the electrode correspond to the active junction side, separated by 6.65mm respect to the reference junction side. *B.* AUC as a function of different temperatures.

RESULTS AND DISCUSSION

Figure 2A shows the thermopile response after the NaCl injection inside the channel, it is possible to see that

after injection the temperature immediately stabilized. On the other hand, after the injection of ssDNA sample (Figure 2B), we measured a small temperature gradient for the first 30 minutes, caused by the heat released during the SAM.

To prove that the functionalization took place, the CV measurement is also performed after the introduction of the ssDNA in $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrolyte (Figure 2C) the current at the electrode was visibly reduced by about 60nA.

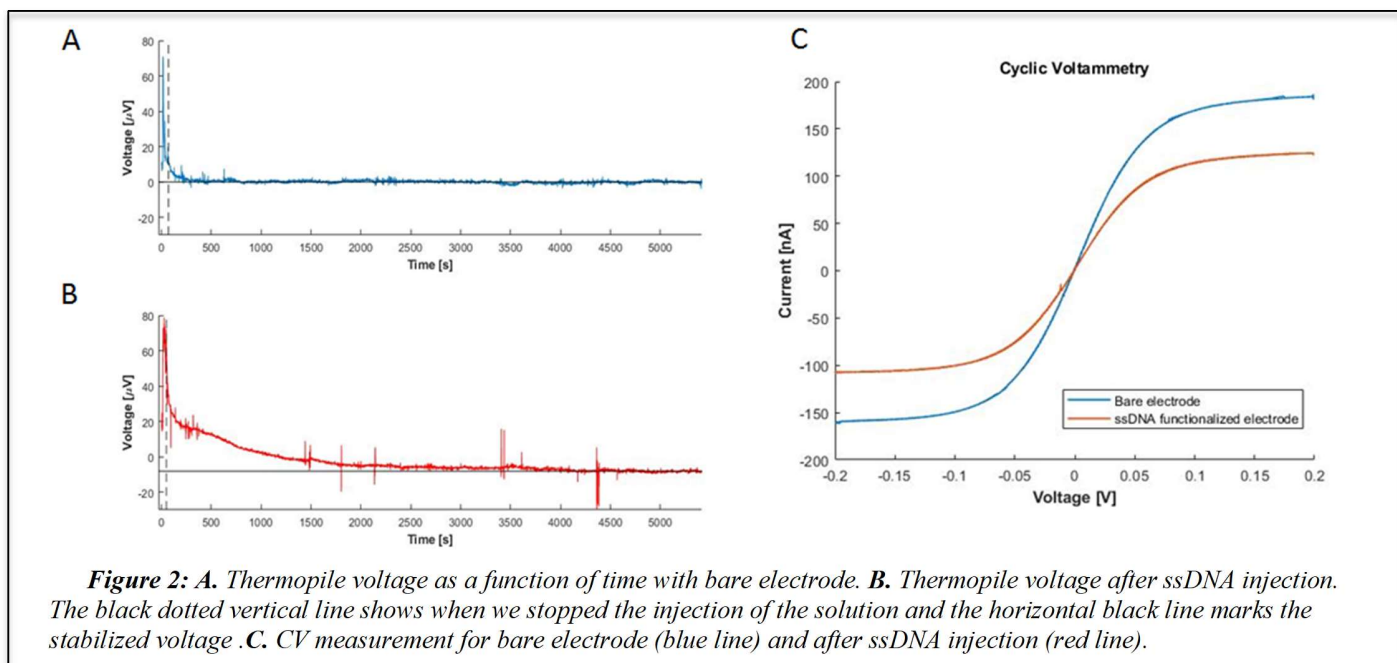


Figure 2: *A.* Thermopile voltage as a function of time with bare electrode. *B.* Thermopile voltage after ssDNA injection. The black dotted vertical line shows when we stopped the injection of the solution and the horizontal black line marks the stabilized voltage. *C.* CV measurement for bare electrode (blue line) and after ssDNA injection (red line).

CONCLUSION

In our work we coupled electrochemical and thermoelectric measurements in a microfluidic device. The characterization we performed shows that our biosensor is able to detect the SAM formation thanks to a thermoelectric measurement, which can give information about what is happening at the electrodes in real time, giving hints about the time dynamics of the functionalization, which takes about 30 minutes. In addition, our electrochemical measurement shows a current decrease, specific to the SAM formation. In the future, the hybridization with a complementary target in different concentrations will also be analyzed.

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