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# A regenerating self-assembled gold nanoparticle-containing electrochemical impedance sensor

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## ARTICLE INFO

## Article history:

Received 7 November 2013

Received in revised form

2 January 2014

Accepted 13 January 2014

Available online 23 January 2014

## Keywords:

Self-assembly

Electrochemical impedance spectroscopy

Cyclic voltammetry

Electrode regeneration

Gold nanoparticles modified electrodes

## ABSTRACT

We report on the development of an electrochemical reductive desorption protocol for repeated regeneration of gold electrodes modified with multi-layers of self-assembled surfaces for use in electrochemical sensing. The gold electrodes were first modified with 1,6-hexanedithiol to which gold nanoparticles were attached in a subsequent modification step. Attachment of thiolated single-stranded nucleic acid oligomers to the gold nanoparticles completed the electrochemical sensor. The changes of electrode behavior after each assembly and desorption processes were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy techniques. The self-assembled sensor showed a wide dynamic range (0.1–100 nM), a low detection limit (20 pM) and high reproducibility (4.4% RSD) for complementary nucleic acid target molecules, along with reusability. On a single gold electrode, the complete sensor–target structure could be assembled and disassembled at least four times with 90% of its original signal intact.

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## 1. Introduction

Electrochemical impedance spectroscopy (EIS) provides a powerful yet simple method for measuring changes in bulk or interfacial properties of materials on an electrode surface, including surfaces sensitive to molecular recognition events (Barsoukov and Macdonald, 2005; Wang et al., 2012; K'owino and Sadik, 2005; Drummond et al., 2003; Katz and Willner, 2003; Lisdat and Schafer, 2008; Chang and Park, 2010). A major advantage of EIS is that detection can be performed label-free; i.e., the changes in the electrical properties of the electrode surface arise from the interaction with the target molecule alone. However, electrode surfaces typically suffer degradation with use in complex samples that require cleaning procedures or electrode replacement. While these steps are convenient in a laboratory, they are less so in a standalone, field deployable unit. In this work, we develop a sequence of self-assembly steps designed to allow the sensor layer to be used once, cleaned from the electrode surface, and then reassembled for the subsequent measurement. A simple molecular recognition system, surface immobilized 20-mer polydeoxyadenine (dA<sub>20</sub>) with complementary 20-mer polydeoxythymine (dT<sub>20</sub>) as target, was employed for demonstration. Signal transduction

was obtained from the electron-transfer resistance of the redox couple, [Fe(CN)<sub>6</sub>]<sup>3−/4−</sup>, through the modified surface.

Surface modification of electrodes is a critical area for electrochemical sensor development (Lisdat and Schafer, 2008; Chang and Park, 2010; Matharu et al., 2012; Oliveria et al., 2011; Love et al., 2005; Ding et al., 2005; Canaria et al., 2006; Qu et al., 2009; Prashar, 2012). It imparts insulation and orientation to the surface architecture of the electrodes, and can enhance reproducibility in the presence of fouling agents in a sample. The modification process herein was initiated by a self-assembled monolayer (SAM) of 1,6-hexanedithiol (1,6-HDT) to which gold nanoparticles (Au NPs) were linked via the peripheral thiol group exposed to solution, followed by attachment of 3' thiol dA<sub>20</sub>. The Au NPs have the potential for enhancing the sensitivity of the sensor by increasing the surface area of an electrode (Wang et al., 2011; Zhang et al., 2008; Liu et al., 2010; Yamada et al., 2003; Jena and Raj, 2007).

Long term stability of SAMs on gold electrodes has been shown to be a challenge in sensor design (Yan et al., 2006; Nishida et al., 1996; Shadnam and Amirfazli, 2005; Lee et al., 2004; Schoenfish and Pemberton, 1998; Cooper and Legget, 1998; Cometto et al., 2012). For example, hexanethiol SAMs on Au surfaces were shown to be unstable above 30 °C (Cometto et al., 2012). Further, when molecular recognition via DNA hybridization is utilized for sensing on a SAM/Au assembly, the temperature required for melting the hybrid (~80 °C) to regenerate an active sensing surface has been shown to cause loss of ~20% of the SAM from the gold electrode (Cometto et al., 2012). In response to this problem, for many

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biochemical sensing applications the SAM modified electrode is discarded after use (Yan et al., 2006). In order to reuse the underlying electrode, a variety of SAM removal and surface cleaning methods have been employed. These include ion sputtering (Chenakin et al., 1999), UV–ozone cleaning (English et al., 2000), and chemical treatment (Schneider and Buttry, 1993) by either strong oxidant (e.g. piranha) or reducing agents (e.g.  $\text{NaBH}_4$ ). Electrochemical oxidation and reduction techniques have also been reported for removing SAMs from electrode surfaces (Canaria et al., 2006; Loglio et al., 2003; Bhalla et al., 2010; Jiang et al., 2003; Bullen et al., 1998; Sondag-Huethorst and Fokkink, 1995; Ferreira et al., 2009) and were selected here as they are well suited for cleaning electrodes embedded in microfluidic devices used for long term monitoring.

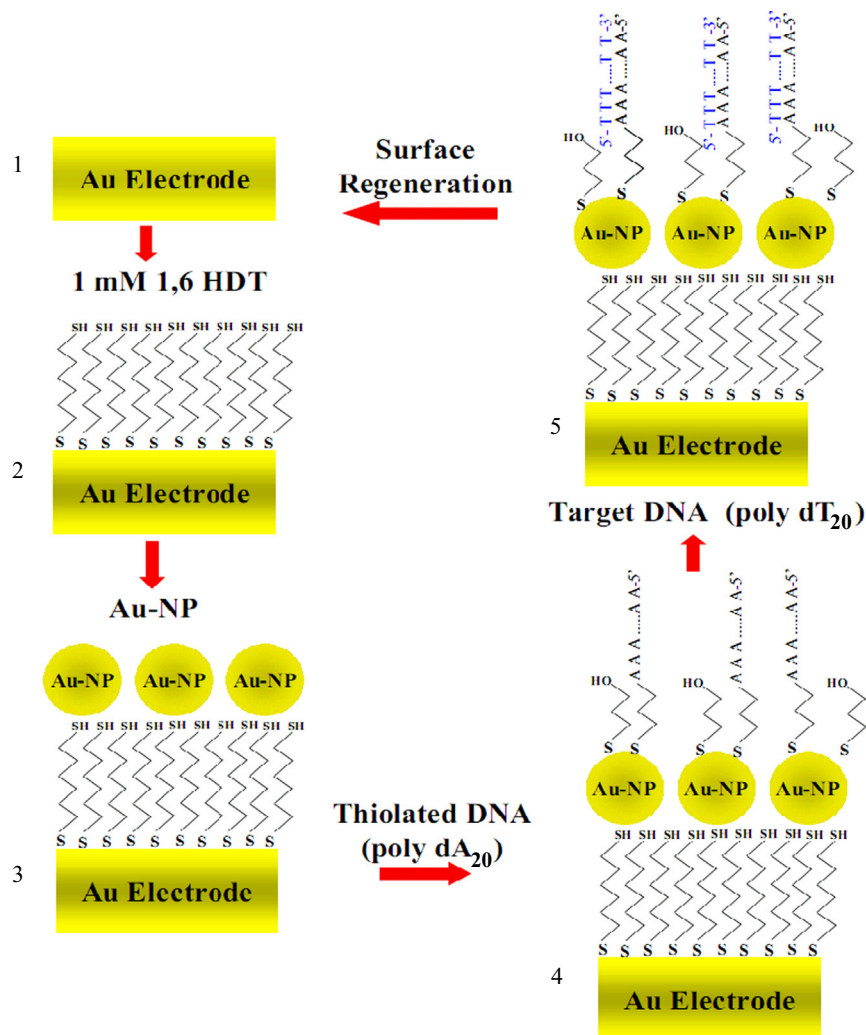
Two related self-assembled sensor designs have been developed elsewhere to increase the amount of immobilized DNA probe and enhance the sensitivity of the sensor (Zhang et al., 2008; Liu et al., 2010). One (Liu et al., 2010) used a thiol/Au NP/thiolated DNA structure as similarly employed here, with high temperature dehybridization leading to fairly rapid electrode performance loss. The other approach (Zhang et al., 2008) eliminated the first thiol layer, and used NaOH to dehybridize the probe–target duplex, but reproducibility of the regenerated sensor performance was not described. Here we have taken a maximal approach with removal of the deposited materials using electrochemical reductive desorption to restore a bare Au electrode, with subsequent reassembly

of the entire sensor architecture. The effectiveness of the regeneration was studied electrochemically through cyclic voltammetry (CV), EIS and by X-ray photoelectron spectroscopy. The work presented here employs a number of characteristics of good sensor design in a single system such as self-assembly of the sensor, label-free all-electronic signal transduction, miniaturized electrodes, electrochemical regeneration of the sensor surface and high reproducibility. To our knowledge this is the first report wherein all these characteristics have been executed together to produce a complete regenerating sensor device based on molecular self-assembly and electrochemical detection. The overall challenge in sensor development is in good design, drawing together the technologies that will permit seamless function in the analytical process.

## 2. Experimental

### 2.1. Chemicals, solvents and materials

$\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $\text{KNO}_3$ , 1,6-hexanedithiol (1,6-HDT), and gold nanoparticles (diameter 10 nm,  $\sim 0.75 \text{ A}_{520}$  units/ml) were purchased from Sigma-Aldrich Canada (Oakville, ON). Anhydrous ethyl alcohol was obtained from Commercial Alcohols Inc. (Brampton, ON). Deionized water having a resistivity of  $18 \text{ M}\Omega \text{ cm}$  (Milli-Q UV Plus Ultra-Pure Millipore System) was used for aqueous



**Scheme 1.** Schematic representation of the regenerable self-assembled sensor fabrication process.

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