ENHANCED GOLD-TO-POLYMER ADHESION FOR INTEGRATED ELECTROCHEMICAL BIOSENSING ON COST-EFFICIENT LAB-ON-A-CHIP CARTRIDGES

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ABSTRACT

Adhesion of gold electrodes to polymers for electrochemical biosensing is typically achieved by depositing Ti- and Cr-based adhesion layers. In this work, we describe for the first time the patterning of gold electrodes on polymeric substrates mediated by a plasma-polymerized organic coupling agent L-cysteine. The enhanced adhesion was confirmed by mechanical abrasion tests. The modified surface chemistry was investigated by surface energy, Raman and FTIR spectroscopy measurements. Electrochemical characterization by cyclic voltammetry was consistent with commercial electrodes. Finally, this inexpensive technique was demonstrated for electrochemical biosensing on a polymeric lab-on-a-chip system.

KEYWORDS: Gold adhesion, biosensor, lab on a disc

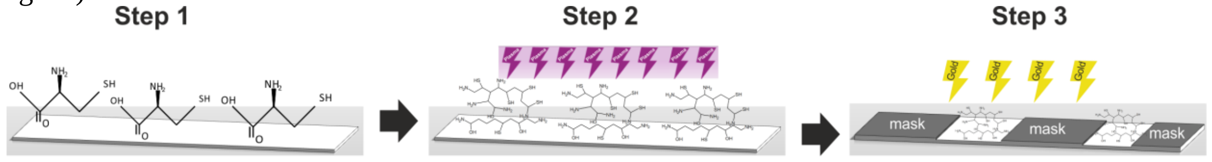
INTRODUCTION

Label-free electrochemical biosensors offer better sensitivity (femto-molar concentrations), significantly reduced cost and simplified instrumentation [1, 2]. However, integration of gold electrodes in common plastic microfluidic cartridges remains a significant challenge due to their poor adhesion. Traditionally, Ti- or Cr-based adhesion layers are employed which tend to raise production costs beyond the limits tolerable for the typically disposable bioanalytical lab-on-a-chip systems [3].

In this work we plasma-polymerize an organic L-cysteine layer to strengthen the adhesion of patterned gold electrodes on a polymeric substrate. This method harnesses the molecular structure of thiol- and carboxyl-group containing L-cysteine ($HO_2CCH(NH_2)CH_2SH$) molecule – with a covalent bond of the -COOH group to the plasma-activated substrate, and the -SH functional group strongly attaching to gold electrode layer to a sturdy 'lock-and-key' link between the two layers.

EXPERIMENTAL

Following UV plasma activation, L-cysteine is self-assembled and plasma-polymerized on the plastic substrate (Fig. 1a & b); next the gold electrodes are patterned by mask-based vapor-phase deposition (Fig. 1c).



Surface coating of the polymer substrate with L-cystein chemistry following UV activation

Plasma polymerisation of the L-cysteine chemistry to form a stable polymeric chain on the polymer substrate

Sputtering of gold onto the L-cysteine plasma polymer. Patterned mask is used to isolate the electrode region.

Figure 1: (a) UV-activation and self-assembly of L-cysteine monomer, (b) Plasma polymerization forming a dense and highly cross-linked organic polymer, and (c) Patterning of gold to the treated plastic substrate.

Mechanical characterization of the deposited coating was carried out by peel, rubbing and scratch tests [4]. Surface chemistry was characterized by contact angle measurements and surface energy calculations, as well as Fourier transform infra-red (FTIR) and Raman spectroscopy measurements [5]. Electrochemical characterization of the coated substrate was carried out using cyclic voltammogram. We also optically examination the deposited coating by Scanning Electron microscopy (SEM) and microscope imaging.

RESULTS AND DISCUSSION

The enhanced adhesion of the coated substrate was corroborated by peel, rubbing and scratch tests. Figure 2 demonstrates the enhanced gold-plastic adhesion and mechanical superiority of this plasma polymerized thin film (Fig. 2a-i), when compared with non-treated (Fig. -2a-ii) or plasma activated (Fig. -2a-iii) plastic substrate. The scratch tests in Fig. 2b depicts no coating delamination on the plasma polymerized coated substrate (Fig. 2a-iii) when compared with other substrates.

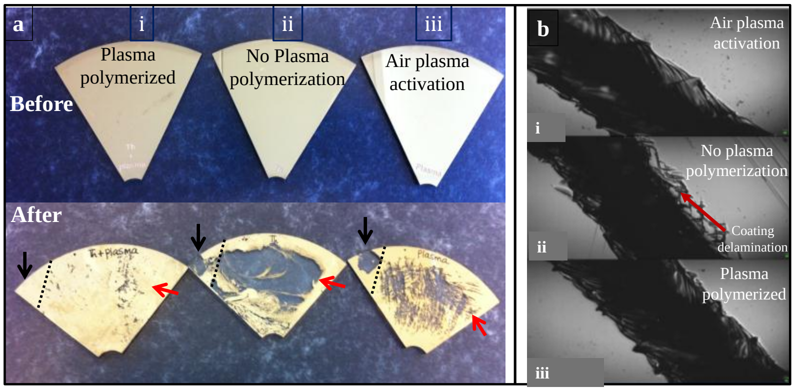


Figure 2: Adhesion and mechanical resilience of the new technique was evaluated a) i-iii Peel and mechanical rubbing tests; and b) i-iii Scratch tests. Tests clearly corroborate that the cysteine chemistry significantly enhances adhesion of gold to the polymer substrate.

Water contact angle and surface energy of the treated substrate prior to gold deposition further shows stability of the new chemistry (Fig. 3a).

Presence of –SH and –COOH functional groups on the plasma polymerized substrate surface which mediates the enhanced adhesion was confirmed by Fourier Transform Infra-Red Spectroscopy (FTIR, Fig. 3b). Raman spectra of treated and untreated gold-deposited PMMA substrates are shown in Fig. 4.

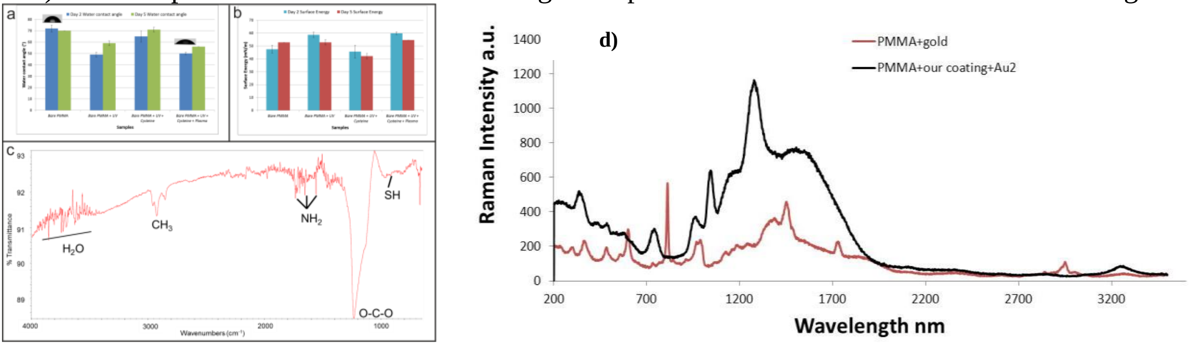


Figure 3: a) Water contact angle, and b) surface energy of the modified surface after 2nd and 5th days – providing evidence for the high stability of the coatings. (c) FTIR spectrum confirms presence of key functional groups critical for enhanced adhesion. (d) Raman spectra of gold-coated PMMA substrates showing treated (black line) and untreated (red line) surfaces. These spectra add to the body of evidence indicating uniqueness of our technique.

To benchmark our new technique, electrochemical characterization using cyclic voltammetry of our electrodes (Fig. 4a) was compared with standard commercial electrodes (Fig. 4b). The results demonstrate consistency with the more expensive, commercial electrodes.

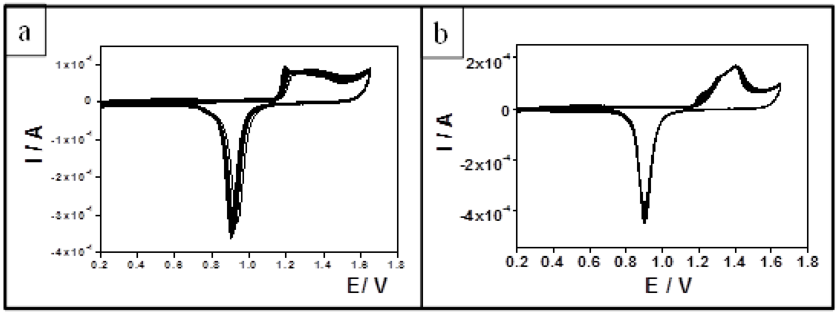


Figure 4: Cyclic voltammograms of a) gold working electrode manufactured using our technique and b) commercially available, gold-coated silicon wafer indicating electrochemical consistency.

Scanning Electron Microscope (SEM), cyclic voltammogram and photo of working electrode taken after electro-deposition of platinum nanoparticles by nucleation and growth cycles further demonstrate stability of the gold layer (Fig. 5a & b).

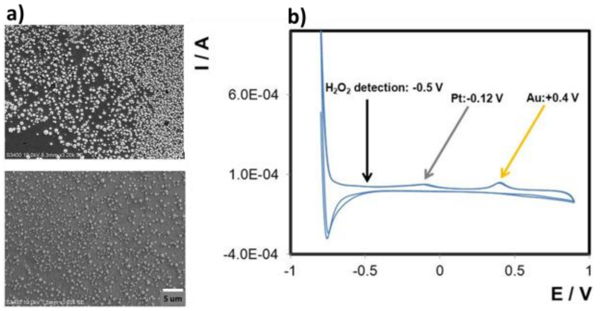


Figure 5: a) SEM images of gold-coated electrodes following platinum nanoparticle electro deposition, using the nucleation and growth cycles; (b) Cyclic voltammogram showing the platinum nanoparticle peak.

CONCLUSION

We have developed and characterized a cost-efficient technique for depositing stable gold electrodes on plastic lab-on-a-chip substrates for sample-to-answer automated electrochemical detection of bio samples.

ACKNOWLEDGEMENTS

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