

Fabrication of Electroless Plated Nano Porous Gold Film For Trace Heavy Metal Ion Detection In Sensor Applications

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ABSTRACT

Nano porous gold film (NPGF) was fabricated by electroless plating with Potassium Gold Cyanide (PGC) as plating solution and E-beam deposited Cu substrates. The pore size of NPGF was found to be 100 ± 20 nm from SEM characterization. The roughness average of both NPGF and Au-E-beam samples were studied using AFM analysis. Electrochemical active surface areas (EASA) of E-beam deposited Au and fabricated NPGF gold electrodes were determined through CV with 2 mm and 25 μ m gold disc electrodes as the standards for comparison. A 10-fold increase in EASA was found with NPGF than that of the E-beam Au thin film. CVs were also conducted in PBS buffer to characterize NPGF as an electrochemical sensor for heavy metal ion detection. The thin film and NPGF were modified with L-Cysteine SAM and characterized using CV and LSSV proving NPGF to be an effective gateway for fabricating nanosensors by surface modification.

Keywords: electroless plating, nano porous gold film, SAM modified electrode, heavy metal ion detection, sensor

1 INTRODUCTION

Nano porous gold is highly coveted for development of electrodes due to its high electrical conductivity and specific surface area and ease of Self Assembled Monolayer (SAM) modification [1,2]. It provides suitable microenvironment for immobilization of biomolecules by maintaining their biological activity and facilitates electron transfer between the immobilized proteins and electrode surfaces, leading to its intensive usage in electrochemical biosensors with enhanced analytical performance compared to other biosensor designs. The ability of Au nano porous film to decrease proteins metal inter-particulate distance, and its functioning as electron conducting pathway between prosthetic groups and the electrode surface, facilitate electron transfer between redox proteins and electrode surfaces. Thus, Nano Porous Gold Film provide the foundation for fabricating electrochemical nanosensors.

In this study, Nano Porous Gold Film (NPGF) was synthesized employing a template-free and cost effective Electroless Plating method. Conventional lithography although suitable for fabrication of nano-meter sized structures, is often expensive with high capital and running costs. As a result, alternative and unconventional techniques have been developed in recent years to fulfill the needs for use in research environments where rapid prototyping and versatility are crucial. Electroless plating is characterized by the selective reduction of metal ions only at the surface of a catalytic substrate immersed into an aqueous solution of metal ions to be deposited. The deposit catalyzes the reduction reaction and that makes the whole process autocatalytic and substrate catalyzed. Hence, external current is not required and both conductive and nonconductive substrates, such as glass and plastic can be plated. Here, Potassium Gold Cyanide (PGC) was the plating solution and E-beam deposited Cu substrates were chosen for plating.

The structural morphology of NPGF was investigated using SEM, AFM and XRD characterization. The film was transformed into a working electrode and Cyclic Voltammetry (CV) was performed to study the electrode behavior. Electrochemical active surface areas (EASA) of E-beam and fabricated NPGF gold electrodes were determined using Potassium Ferricyanide as the electrolyte. And for comparison gold disc electrodes (2 mm and 25 μ m) were used as standards proving NPGF to be an effective gateway for fabricating nanosensors. The NPGF and Au E-beam thin film were surface modified with L-Cysteine SAM and characterized by using Cyclic Voltammetry in the presence of Cu^{+2} ions to study the sensing capability of the electrodes.

2 EXPERIMENTAL

Crystalline p-type Si wafers were cleaned by standard RCA method and deposited with adhesive Ti layer (10nm) and seed metal Cu layer (100 nm) using an e-beam

evaporator (Ultech). After metal deposition, the substrate was immersed into the Potassium Gold Cyanide. Fig. 1 shows the schematic for fabrication of NPGF. Electroless plating was carried out for different time periods (2 min, 6 h, 9 h, 18 h) by maintaining double layered system of heating and constant initial temperature (70°C). The experimental set up is shown in Fig. 2. The duration and temperature of electroless plating are critical criteria to test a sample for mono layers of gold onto a metal substrate.

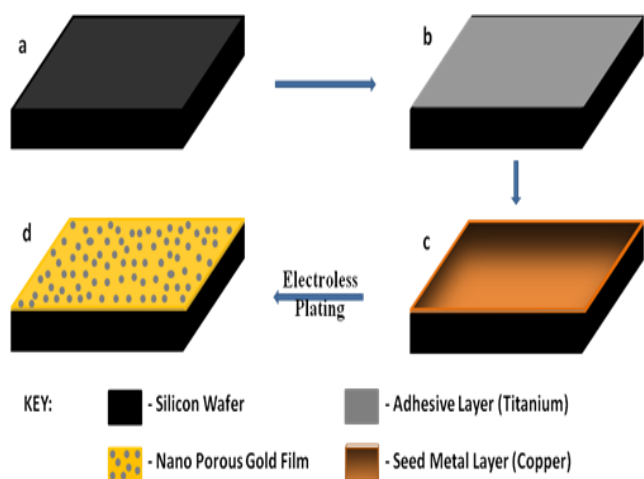


Figure 1: Schematic for fabrication of NPGF using electroless plating



Figure 2: Electroless plating experimental setup

The electroless plated samples were characterized using XRD with Rigaku Miniflex II Desktop X-ray Diffractometer.

SEM characterization of both pure E-beam Au thin film and electroless plated Au [9 h, 70°C] was performed using Carl Zeiss EVO 18 Special Edition (Fig. 3). The NPGF was transformed into a working electrode and connected to the electrochemical analyzer/workstation (CH Instrument Model 700E series) with Ag/AgCl as the reference

electrode and Pt wire as the counter electrode, in a 3-electrode cell setup as shown in Fig. 4.

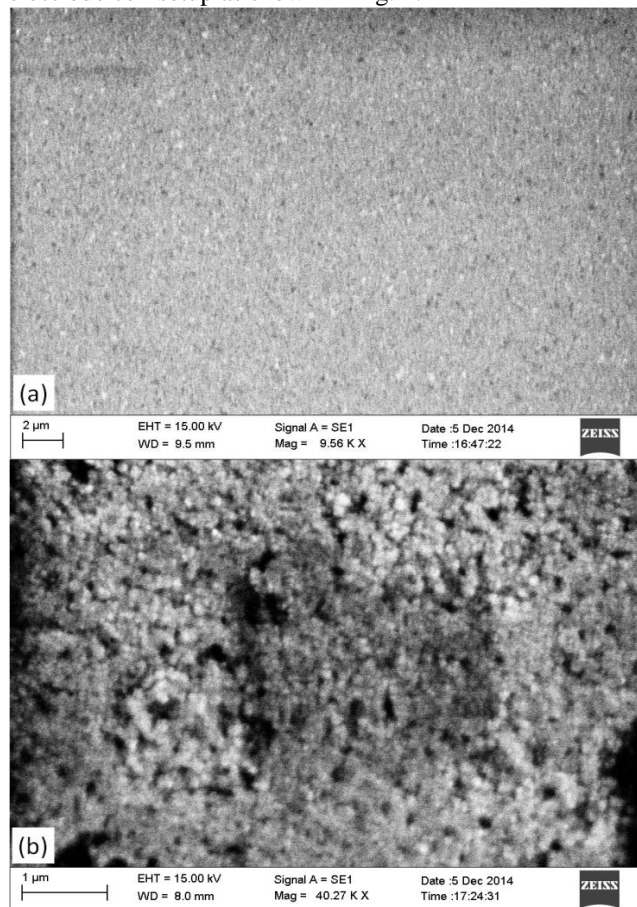


Figure 3: SEM images of- (a) E-beam deposited Au thin film and (b) Electroless plated Au [9 h, 70°C]

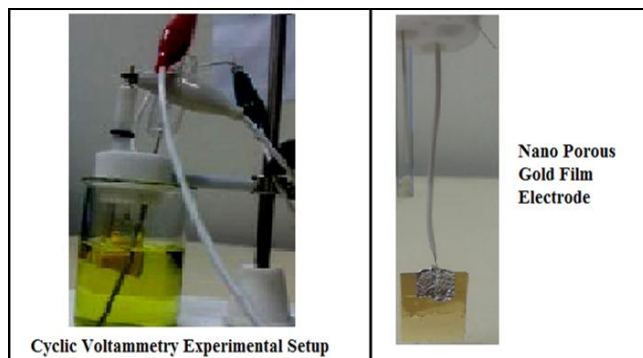


Figure 4: NPGF Working Electrode employed for Cyclic Voltammetry

A 10mM Potassium Ferricyanide in 0.1M Potassium Chloride (aq.) solution was used as an electrolyte. The Cyclic Voltammetry was conducted with 2mm and 25µm gold disc electrodes and e-beam deposited Au thin film as standards (Fig. 5) for comparison.

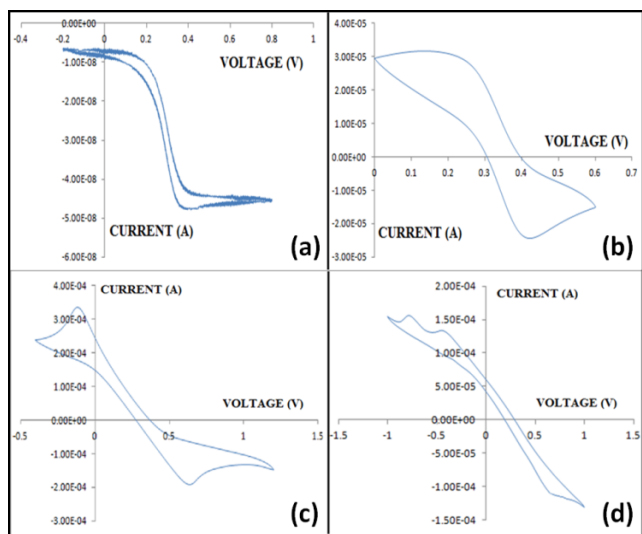


Figure 5: CV graphs of- (a) 25µm Au disc, (b) 2mm Au disc, (c) E-beam deposited Au thin film [Scan rate=0.1V/s] and (d) 2min Electroless plated Au electrodes in 10mM $K_3Fe(CN)_6$ in 0.1M KCl [Scan rate=0.01V/s]

In order to study further usage of the film in fabricating a nano-sensor for detection of heavy metal ions [3], Cyclic Voltammetry was conducted using 0.1M Sodium Perchlorate ($NaClO_4$) in Phosphate Buffer solution (pH 7). The results are as shown in Fig. 6.

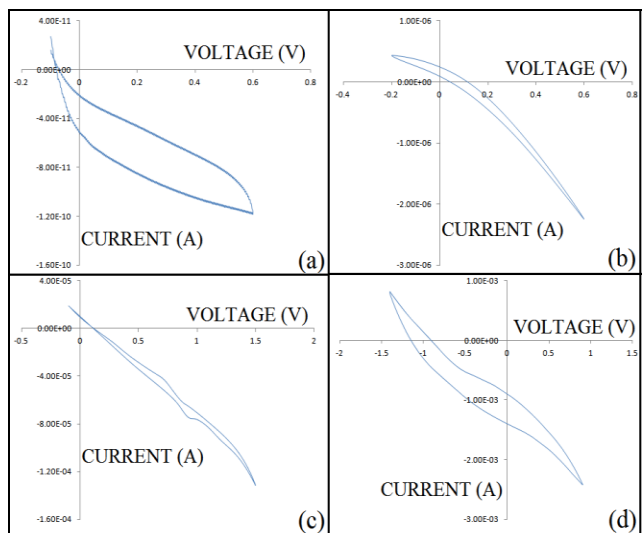


Figure 6: CV graphs of- (a) 25µm Au disc, (b) 2mm Au disc, (c) E-beam deposited Au thin film, and (d) 9 h Electroless plated Au electrodes in 0.1M $NaClO_4$ in PBS

The 9 h electroless plated NPGF and e-beam deposited Au thin film were surface modified by placing them in an 8mM L-Cysteine solution in 0.2M Phosphate Buffer (pH 5) for 1 h to form the L-Cysteine SAM. The E-beam deposited Au thin film and NPGF [9 h, 70 °C] were characterized before

and after L-Cysteine SAM modification using AFM (Model: Nanosurf Easy Scan 2) and the following images were obtained as shown in Fig. 7.

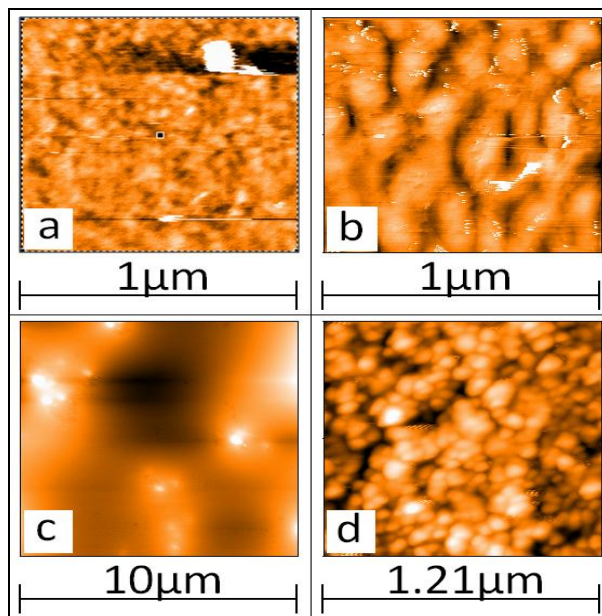


Figure 7: AFM images of- (a) Au thin film, (b) L-Cysteine SAM modified Au thin film, (c) NPGF and (d) L-Cysteine SAM modified NPGF

3 RESULTS AND DISCUSSION

The XRD characterization of electroless plated Au gave intensity peaks [$Au(1,1,1)$, $Au(2,0,0)$, $Au(2,2,0)$ and $Au(3,1,1)$] at 9 h duration, 70°C and a highly porous gold film was expected to be seen on the sample. SEM characterization of pure E-beam Au thin film and NPGF [9 h, 70°C] revealed the pore size of NPGF to be 100 ± 20 nm. From AFM characterization, the Roughness Average of NPGF [9 h, 70°C] was found to be 27 times that of E-beam deposited Au thin film.

The Peak Current (I_p) values from the Cyclic Voltammetry graphs of the Au electrodes (electrolyte: 10mM $K_3Fe(CN)_6$ in 0.1M KCl) were used to determine electrochemical active surface areas (EASA) of electrodes using Randles-Sevcik equation:

$$I_p = 2.69E05n^{1.5}AD^{0.5}Cv^{0.5} \quad (1)$$

The Roughness Factors (ratio of EASA to Geometric Surface Area) of electrodes were also calculated. The roughness factor (RF) of 18h plated NPGF was found to be nearly 100 times greater than that of e-beam gold thin film and in comparison to commercial electrodes (twice the RF of 2mm disc and one-third the RF of 25µm disc) and nearly 30 times that of 2min plated sample, which establishes the

high surface area of NPGF, and hence its high surface energy and electrochemical activity.

Electrode	Geometric Surface Area (cm ²)	Electrochemically Active Surface Area (cm ²)	Scan Rate (V/s)	Peak Current (A)	Roughness Factor
2mm Φ	3.14E-02	9.63E-03	0.1	2.26E-05	3.07E-01
25 μ m Φ	4.91E-06	9.01E-06	0.1	2.11E-08	1.83E+00
Pure Au E-Beam	2	1.20E-02	0.1	2.82E-05	6.01E-03
2min NPGF	2	3.42E-02	0.01	2.53E-05	1.71E-02
18h NPGF	2	1.17E+00	0.01	8.69E-04	5.87E-01

Table 1: EASA and Roughness Factors of Gold Electrodes

The attachment to gold via sulfur linkages has been of particular interest for fabricating biosensors, because the sulfur-containing peptides may be directly adsorbed on the gold surface. Once at the surface, the possibility for using the attached peptide as a sensor for metal ions becomes realized. Hence, surface modification of the Au electrodes was conducted using a thiol group containing amino acid, L-Cysteine (HO₂C-CHNH₂-CH₂SH) to develop a sensor.

Cyclic Voltammetry was conducted using Au thin film and NPGF as the working electrodes after L-Cysteine SAM modification. The electrolyte used was 0.1M NaClO₄ solution in 0.2M Phosphate Buffer (pH=5 for Au thin film and pH=7 for NPGF) and Pt gauze and Calomel electrode were the counter and reference electrodes respectively. The experiment was repeated after pre-concentration of the working electrodes in Cu⁺² solution for 10 minutes (Fig. 8).

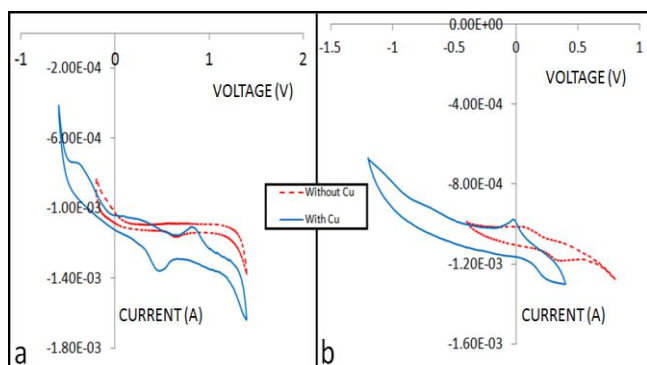


Figure 8: CV graphs of L-Cysteine SAM modified- (a) Au thin film [electrolyte: pH=5] and (b) NPGF electrode [electrolyte: pH=7] in 0.2M Phosphate Solution with 0.1M NaClO₄ before (red) and after (blue) pre-concentration in Cu⁺² solution

The SAM modified electrodes showed a considerable increase in peak current values after Cu⁺² pre-concentration indicating that the Cu⁺² binded electrode was still accessible to the redox couple in the electrolyte and the interfacial electron transfer had increased. The peak potential values were also significantly affected. Further research is in

progress for nano-sensing applications with reference to a variety of SAM modifications of NPGF.

Stripping voltammetry is a highly effective method for the detection and analysis of electroactive species in solution which are in trace concentrations extending upto sub-ppb levels. Hence, Linear Sweep Stripping Voltammetry was conducted employing SAM modified NPGF as the working electrode, Pt wire as the counter electrode and saturated Calomel Electrode as the reference electrode, using 1 μ M Copper Sulphate in 0.1M Phosphate Buffer solution (pH 7) as the electrolyte, and the role of L-Cysteine SAM in detection of trace amounts of Cu(II) ions (Fig. 9) was verified.

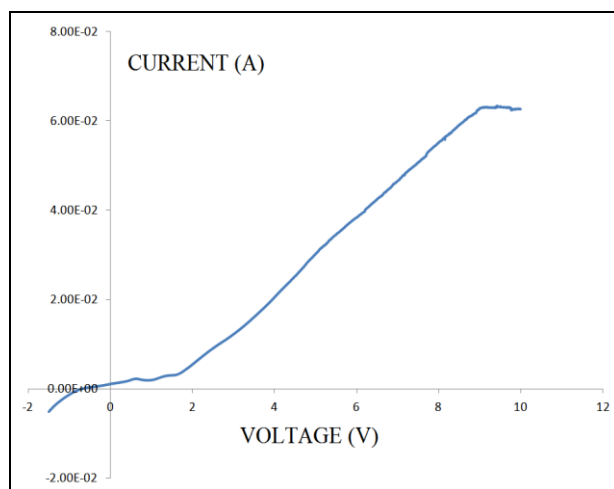


Figure 9: Linear Sweep Stripping Voltammetry of SAM modified NPGF in 1 μ M CuSO₄ in 0.1M PBS (pH 7)

4 ACKNOWLEDGEMENTS

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