

# Comparison of Electrocatalytic Activity of poly(p-aminophenol) Film Supported Au-M (M= Pt, Cu and Ag) Bimetallic Nanoparticles for Oxidation of Sodium Borohydride

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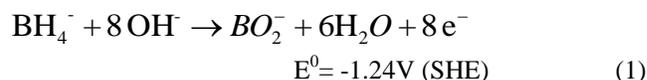
## ABSTRACT

A poly (p-aminophenol) film (PPAP) and bimetallic nanoparticles modified polymer film galssy carbon electrodes (GCE), Au-Pt/PPAP/GCE, Au-Ag/PPAP/GCE and Au-Cu/PPAP/GCE were prepared by electrochemical techniques. The modified electrode surfaces were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The electrocatalytic activities of modified PPAP/GC and bulk electrodes were investigated for borohydride oxidation in alkaline media and the response of electrodes were compared with each other from the corresponding voltammetric curves. There was no any oxidation take place on bare GCE, PPAP/GCE and Cu/PPAP/GCE in the presence of sodium borohydride. Au-Pt bimetallic modified PPAP/GGCE showed higher catalytic activity toward sodium borohydride in terms of the manner of both peak potential and peak current.

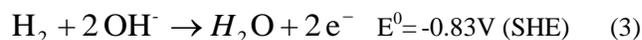
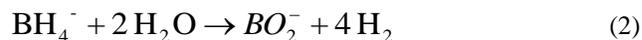
**Keywords:** borohydride electrooxidation, metal nanoparticles, polymer film

## 1 INTRODUCTION

Fuel cells, convert chemical energy into electrical energy based on redox reactions occurring at electrode-electrolyte interfaces, have an important role to play in the future world energy scenario. Fuel cells have some advantages such as efficiency, reliability, economy, cleanliness [1]. There are remaining serious problems relating to safety and efficiency during storage at the fuel cells which using hydrogen as a fuel. The hydrogen storage problem has caused a search for alternative fuels that should be safety and easily transported, rapidly oxidized at a negative potential. The organic liquid fuels such as methanol, ethanol etc. can be considered as alternative fuel to hydrogen. However, these liquid fuels are all toxic, electrochemically sluggish, leading to a large anodic polarization and voltage loss [2]. An alternative fuel borohydride has attracted considerable interest not only as a hydrogen-storage material but also as a fuel for direct borohydride fuel cells (DBFCs) and as an electrochemical H<sub>2</sub> generator due to its high energy density. BH<sub>4</sub><sup>-</sup> ideally undergoes 8 electron oxidation [3, 4]:



Although BH<sub>4</sub><sup>-</sup> is a promising fuel there are significant problems with the electrochemical oxidation of BH<sub>4</sub><sup>-</sup>. Hydrogen is released through a hydrolysis reaction which is unwanted reaction using heterogeneous catalyst (e.g. ruthenium, platinum, nickel and palladium):



Alkaline solutions (pH > 12) hinder the borohydride hydrolysis reaction and the BH<sub>4</sub><sup>-</sup> can be oxidized directly with 8 electrons. Eight electrons oxidation was observed on the Au and Au-M electrodes because gold is effective catalyst for BH<sub>4</sub><sup>-</sup> oxidation but not for BH<sub>4</sub><sup>-</sup> hydrolysis and only four electron oxidation occurred on the Pt, Ni and Ni alloys due to borohydride hydrolysis and/or hydrogen evolution [5, 6].

In the present work, Au-M (Pt, Cu or Ag) bimetallic poly (p-aminophenol) electrodes were prepared by cyclic voltammetry and the electrocatalytic activities of were investigated in alkaline media and catalytic activities. Voltammetric curves at different modified electrodes were compared with each other. The modified electrode surfaces were characterized using SEM and EDX.

## 2 EXPERIMENTAL

### 2.1 Chemicals and Instrumentations

All the chemicals were purchased from Aldrich as analytical grades and were used without any further purification. All solutions were prepared using ultra pure water (Milli-Q 18.2 MΩ cm, Millipore System Inc.). Bandelin Sonorex model ultrasonic bath was used for cleaning of electrodes. Voltammetric measurements were carried out using Autolab 4.9 interface Electrochemical Analyzer with a three electrode system consisting of a working electrode (bare GCE, PAP/GCE and various metal/bimetallic modified PPAP/GCE), a platinum wire

counter electrode and an Ag/AgCl (sat. KCl) reference electrode, respectively. All experiments were carried out at room temperature. SEM and EDX analysis was carried out Phillips XL-30S FEG instrument.

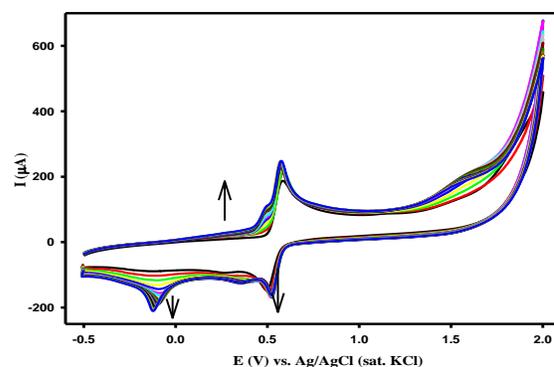
## 2.2 Preparation of Modified Electrodes

Before modification, the GCE was polished with 0.05  $\mu\text{m}$  alumina slurries, thoroughly rinsed with water and sonicated in ultrapure water, ethanol and ultrapure water for 3 min each. To preparing poly (p-aminophenol) film on the GCE, it was placed in 0.5 M aqueous  $\text{HClO}_4$  solution containing 5.00 mM PAP in the presence of 5.00 mM sodium dodecyl sulphate (SDS). The potential was scan between  $-0.50$  V and  $+2.00$  V with  $0.10 \text{ V}\cdot\text{s}^{-1}$  by using cyclic voltammetry. The obtained PPAP/GCE was rinsed with distilled water several times to remove the remaining PAP adsorbed on the surface of the electrode. Electrodeposition of metal nanoparticles was incorporated in the PPAP film through electrochemical deposition from the metal aqueous solution of with cyclic voltammetry between various potential range 10 cycles. Firstly, The electrochemical deposition of nanoparticles of metals (Pt, Ag and Cu) on PPAP/GCE was performed using the electrochemical reduction of related solution which are 1.0 mM  $\text{K}_2\text{PtCl}_6$ , 1.0 mM  $\text{AgNO}_3$  and 1.0 mM  $\text{CuSO}_4$ . Then, Au nanoparticle was covered on Ag/PPAP/GC surface using the electrochemical reduction of 1 mM  $\text{HAuCl}_4$  on 0.1 M HCl solution. A 1.0 mM  $\text{HAuCl}_4$  was prepared by diluting the concentrated Au solution with 0.1 M HCl after dissolving the Au wire (99.999% in purity) in  $\text{HNO}_3:\text{HCl}$  (1:3). The other method for preparing Au-Pt bimetallic modified polymer film electrode, GCE covered with PPAP immersed into solution containing 3.0 mM  $\text{HAuCl}_4$  and 2.0 mM  $\text{H}_2\text{PtCl}_6$ .

## 3.RESULTS AND DISCUSSION

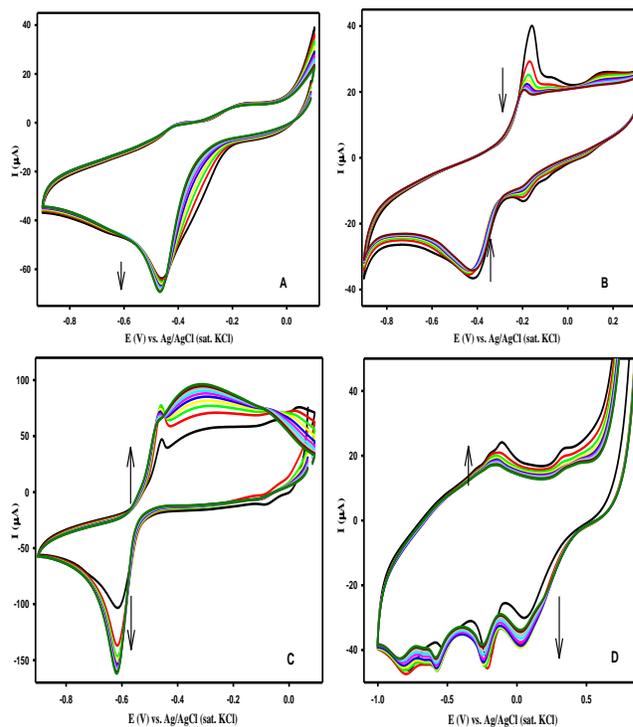
### 2.3 Preparation of Au-M (Pt, Ag and Cu) Modified PPAP/GC Electrodes

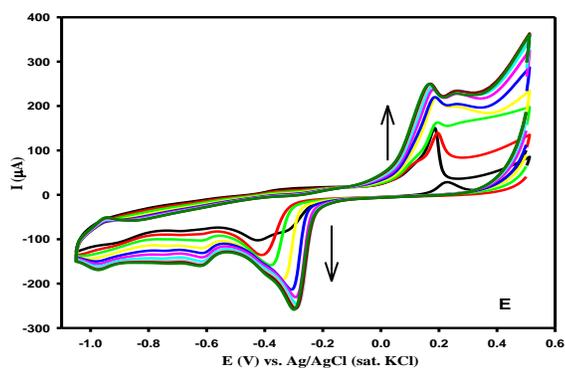
Fig. 1 shows the multi sweep cyclic voltammograms of p-aminophenol electropolymerization. SDS, as an anionic dopant of the polymer increased the conductivity of PPAP [7]. The arrows in the figure indicate the trends of current during CVs. During the forty CV scans, an irreversible oxidation peak was observed at 1.55 V for PAP without the corresponding cathodic processes in the reverse scan. Also, a single cathodic peak was observed at  $-0.1$  V and reversible oxidation and reduction peaks were seen at around  $+0.55$  and  $+0.50$  V respectively. The generation of the peaks might be attributed to the intermediate species during the oxidation process of the AP [8].



**Figure 1:** Successive 40 cyclic voltammograms of PAP electropolymerization on GCE at a scan rate of  $0.1 \text{ V}\cdot\text{s}^{-1}$ .

Electrochemically deposition of various metal nano particles on different polymer film GCE surface were carried out by cyclic voltammetry with  $0.05 \text{ V/s}$  between various potential range for Au, Ag, Cu and Pt metal particles in related metal solution (Fig. 2A-D). Stable peak currents were observed for both reduction and oxidation reaction after the 10 CV cycles. An alternative method was also used for preparing Au-Pt bimetallic modified polymer film electrode by immersing of PPA/GCE into 3.0 mM  $\text{HAuCl}_4$  and 2.0 mM  $\text{H}_2\text{PtCl}_6$  containing solution and then the cyclic voltammograms were recorded (Figure 2-D).

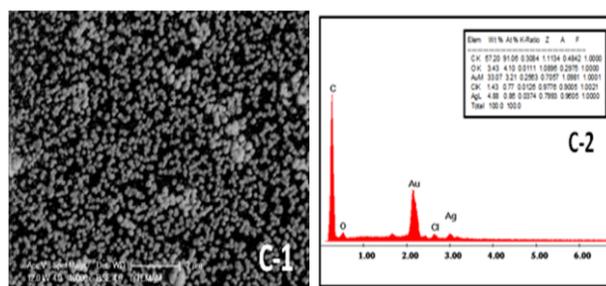
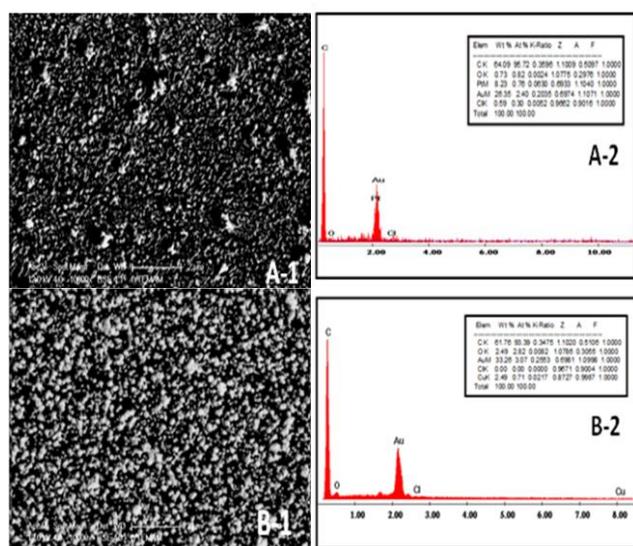




**Figure 2:** Cyclic voltammograms for (A) deposition of Au nanoparticles from 1mM  $\text{HAuCl}_4$ , (B) deposition of Ag nanoparticles from  $\text{AgNO}_3$ , (C) Cu nanoparticles covered from 1.0 mM  $\text{CuSO}_4$  solution, (D) deposition of Pt nanoparticles from 1 mM  $\text{K}_2\text{PtCl}_6$  solution and (E) deposition of Au-Pt bimetallic nanoparticles from 1mM  $\text{HAuCl}_4$ + 1.0 mM  $\text{K}_2\text{PtCl}_6$  mix solution.

## 2.4 Characterization of Various Au-M (Pt, Cu and Ag) Bimetallic Nanoparticles Modified poly (P-Aminophenol) Film Electrodes

The physical characterization and the dispersion degree of the Au-M (Pt, Cu and Ag) nanoparticles on PPAP/GC electrode surface were obtained through SEM images, EDX analysis provided the chemical composition. In Fig. 3A-C, SEM micrographs and EDX results are presented for the Au-Pt, Au-Cu and Au-Ag deposits formed by applying CV scan. The SEM image shows that the catalytic nanoparticles are dispersed uniformly with a smooth surface. The EDX measurements confirmed that Au-Pt, Au-Ag and Au-Cu nanoparticles were successfully electrodeposited on PPAP/GCE. These results were obtained from all the EDX spectra which showed the characteristic peaks Au, Pt, Ag and Cu elements.

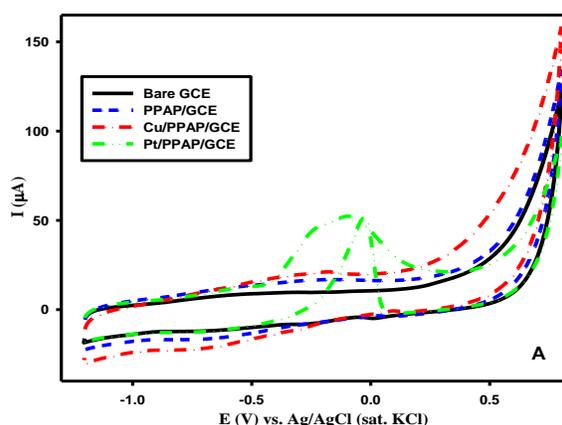


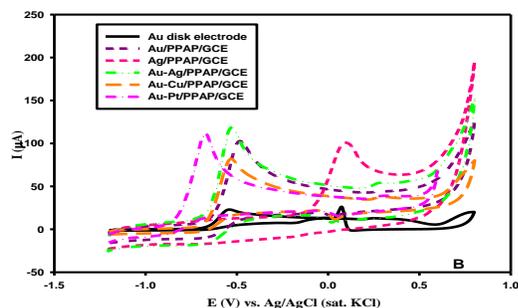
**Figure 3:** SEM images(A-1, B-1, C-1) and EDX images (A-2, B-2, C-2) of the A) Au-Pt/PPAP/GCE, B-1) Au-Cu/PPAP/GCE and C-1) Au-Ag/PPAP/GC electrodes.

## 2.5 Electrocatalytic oxidation of Borohydride on modified electrodes

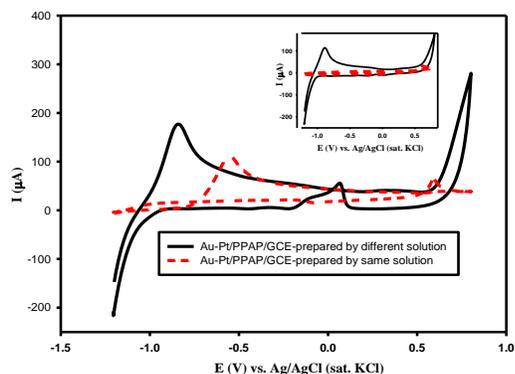
Fig. 4 displays a comparative cyclic voltammograms of 1.0 mM  $\text{NaBH}_4$  which were recorded at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$  in the potential range of -1.2 V to 0.8 V vs. Ag/AgCl (sat. KCl) in 2.0 M NaOH alkaline media for bare GCE, PPAP/GCE, Cu/PPAP/GCE, Pt/PPAP/GCE, Ag/PPAP/GCE, Au/PPAP/GCE, Au-Ag/PPAP, Au-Pt/PPAP, Au-Cu/PPAP, and Au disk electrodes (Fig. 3). There was no any oxidation reaction takes place on bare GCE, PPAP/GCE and Cu/PPAP/GCE in the presence of  $\text{BH}_4^-$  (Fig.4A). It can be seen clearly in Fig. 4B, an irreversible electrochemical behavior with an anodic peak potential of about -0.54 V, -0.48 V, 0.087 V, -0.67 V, -0.52 V and -0.53 V at Au disk, Au/PPAP, Ag/PPAP, Au-Pt/PPAP, Au-Ag/PPAP and Au-Cu/PPAP, respectively. The Au-Pt/PPAP/GCE showed excellent electrocatalytic activity towards on sodium borohydride than that other modified electrodes.

Au-Pt bimetallic surface which showed electrocatalytical effect on  $\text{BH}_4^-$  electrooxidation was prepared from solution containing 1mM  $\text{HAuCl}_4$ + 1.0 mM  $\text{K}_2\text{PtCl}_6$ . When the Au-Pt/PPAP/GC electrode is prepared separately solutions of  $\text{HAuCl}_4$  and 1.0 mM  $\text{K}_2\text{PtCl}_6$ , hydrogen gas evolution occurred during the electrooxidation of borohydride. This comparison is shown in the Fig.5.





**Figure 4:** Cyclic voltammograms of 1 mM NaBH<sub>4</sub> in 2M NaOH at various working electrode. Scan rate: 50 mV/s.



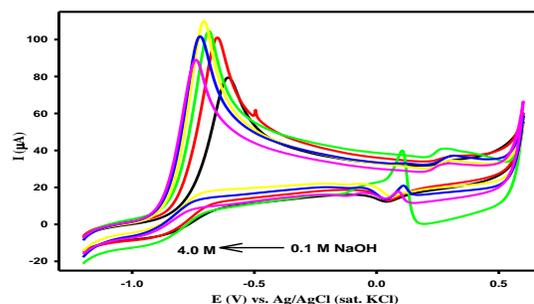
**Figure 5:** Cyclic voltammograms of electrooxidation presence of 1 mM borohydride on Au-Pt/PPAP/GCE prepared in same solution and different solution. inset: voltammetric behaviour of 2.0 M NaOH supporting electrolyte on different prepared Au-Pt/PPAP/GCE.

## 2.6 Influence of the Sodium Hydroxide Concentration on Borohydride Oxidation at Au-Pt/PPAP/GC Electrode

Fig. 6 shows cyclic voltammograms recorded at Au-Pt/PPAP/GC electrode in the presence of 1.0 mM borohydride solution in different concentration of NaOH (0.10, 0.50, 1.00, 2.0, 3.0 and 4.00M). A single well defined oxidation peak was observed for borohydride at all NaOH concentration. The peak characteristics such as peak potential and peak current were improved with increasing NaOH concentration. The oxidation peak potential was shifted from -0.61 V to -0.74 V by increasing NaOH concentration. The current density for borohydride oxidation in 2.0 M NaOH solution was much higher than other studied NaOH concentrations. Therefore, 2.0 M NaOH solution was chosen as supporting electrolyte for future studies.

The effect of scan rate on the anodic peak current of 1.0 mM borohydride was investigated in 2.0 M NaOH at Au-Pt/PPAP/GC electrode. The results indicated that the  $i_{p_a}$  was linearly changed with the square root of scan rate over the range of 0.003–1.000V. The linear regression equation was

$i_p (\mu A) = 13.337 v^{1/2} (mV/s) + 6.3676$  with a correlation coefficient of  $R^2 = 0.9986$ , therefore, the anodic peak current was controlled by the mass diffusion, showing a diffusion-controlled process in the solution. The peak potential shifted to more positive values with increasing the scan rates. The linear relation between peak potential and logarithm of scan rate indicated that an irreversible electrode process.



**Figure 6:** CVs recorded for presence of 1.0 mM BH<sub>4</sub><sup>-</sup> in different NaOH concentrations at Au-Pt/PPAP/GC at 0.05 V.s<sup>-1</sup> scan rate.

## 3 CONCLUSION

In the present study, a purely bimetallic electrode surface was prepared by electrochemically deposited Pt, Ag and Cu on Au/PPAP/GC electrodes. Electrocatalytic oxidation of borohydride was studied at electrochemically deposited metal nanoparticles modified polymer film electrodes and the results were compared with bulk electrodes in 2.0 M NaOH solution. CVs display that the peak potential of borohydride shifted at Au-Pt modified PPAP/GC electrodes about 0.13 V in negative directions compared to the Au disk electrodes. The relatively higher electrocatalytic activity of Au-Pt modified PPAP/GC electrode compared to other Au-M (Ag and Cu) bimetallic surface.

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