Electrochemical Oxidation of Ammonia Borane on Au-Ag nanoparticles Modified Poly (p-aminophenol) film Glassy Carbon Electrode

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ABSTRACT

An Au-Ag nanoparticles modified poly(p-aminophenol) film electrode (Au-Ag/PPAP/GCE) was prepared by cyclic voltammetry. The electrochemical behaviour of ammonia borane (NH_3BH_3, AB) was studied in alkaline media at Au-Ag/PPAP/GCE. The surface morphology and chemistry were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and CV techniques. There was no any oxidation reaction occurs on bare GCE and PPAP/GCE in the presence of AB. Among the five electrodes which were Au disk, Ag/PPAP/GCE, Au/PPAP/GCE and Au-Ag/PAP/GCE. The comparative studies were revealed that Au-Ag/PPAP/GCE yield the best results due to the highest peak current and shifting the oxidation potential to more negative values for AB oxidation.

Keywords: metal nanoparticles, polymer film, ammonia borane, fuel cell, composite electrodes

1 INTRODUCTION

Environmental friendly, cost effective and efficient alternative energy sources have been searched intensively in recent years due to the world energy demand is growing parallel to the population increase and fuel consumption produce pollutants beside the harmful emissions. Fuel cells have emerged as promising alternatives and produce energy as long as fuel is supplied [1-2]. Fuel cells usually directly convert the chemical energy of the reactants, a fuel and oxidant, into electrical power, ensuring continuity of operation for as long as externally stored reactants are supplied. The fuel cells are working quietly and do not produce environmental pollution [3]. At present, hydrogen remains as the only practical fuel available. Use of hydrogen as fuel is accompanied by severe storage and transportation concerns [2], and therefore alternative fuels such as methanol [4], ethanol [5] etc. have been employed as a substitute to hydrogen for low-temperature fuel cells. However, these liquid fuels are all toxic, electrochemically sluggish, leading to a large anodic polarization and voltage loss. On this background, boron based fuels such as boron hydride and ammonia borane, which is a safe, non-toxic, chemically stable, easy to transport in its dry state and is highly soluble in water, their high hydrogen density, higher energy capacity and density aside from very negative equilibrium potential and faster anodic kinetics compared to organic based fuels is emerging as a potential fuel for fuel cells [6]. Ammonia borane fuel cell possesses high capacity (5.2 Ahg1) and energy density (8.4Wh g1 at 1.62 V) according to the following total cell reaction:

$$\mathrm{NH_3BH_3} + 3/2\,\mathrm{O_2} \rightarrow BO_2^- + \mathrm{H_2}O + \mathrm{NH_4^+} \qquad (1)$$

The electrochemical oxidation of NH_3BH_3 is supposed to be as follows:

$$\mathrm{NH_3BH_3} + 6\,\mathrm{OH^-} \rightarrow BO_2^- + 4\mathrm{H_2}O + \mathrm{NH_4^+} + 6e^-$$

E^0=-1.216 V (2)

Hydrolysis as a main unwanted reaction, occurring to some extent in NH_3BH_3 solutions, generates hydrogen gas:

$$\mathrm{NH_3BH_3} + 2\mathrm{H_2}O \rightarrow BO_2^- + \mathrm{NH_4^+} + 3H_2 \qquad (3)$$

Competition between NH_3BH_3 oxidation and hydrogen evolutions is a function of electrode material, electrolyte composition and applied potential. To subpress formation of H_2 gas, the electrolyte solution pH can be increased and choose suitable electrode materials [7-9].

The efficiency of energy conversion mostly depends on the catalytic activity of the electrode surface. Developing more selective catalysts is very important for the development of fuel cells technology. By this means, the fuel can be oxidized at more negative potentials at the anode while the oxygen reduces at more positive region. Nanometer-sized metal particles are objects of great interest in modern chemical research due to their unique electrical, magnetic, optical and other properties, which are distinct from both those of the bulk metal and those of isolated atoms and molecules. The development of polymer-stabilized metallic or bimetallic nanoparticles is one of the most promising solutions to their stability problem. Besides, electrochemical synthesis of such particles in the porous layer of polymeric film is free from chemical contamination and can be more controlled in respect to the chemical synthesis [10, 11].

In this study, the electrochemical oxidation of AB on Au-Ag/PPAP/GCE was investigated using electrochemical techniques. The surface morphology and chemistry were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and CV techniques.

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.).The electrochemical experiments were performed Autolab 4.9 interface Electrochemical Analyzer. A conventional three-electrode system was used. Ag/AgCl was used as the reference electrode and a platinum wire electrode as auxiliary electrode,while various modified electrodes were used as the working electrode. All experiments were carried out at room temperature. SEM and EDX analysis was carried out Phillips XL-30S FEG instrument. Bandelin Sonorex model ultrasonic bath was used for cleaning of electrodes.

2.2 Preparation of Modified Electrodes

Prior to preparation of the Au-Ag/PAP/GCE, the glassy carbon electrode was cleaned by polishing with different grades of alumina slurry (0.05-3µm) on a synthetic cloth and rinsed with doubly distilled water. Subsequently, it was ultrasonicated with ethanol (1:1, v/v), and ultra pure water respectively. The electrochemical deposition of poly(p-aminophenol) (PAP) on 18 GCE was performed using cyclic voltammetry in a 5 mM SDS + 5 mM p-aminophenol + 0.5 M HClO4 solution by cyclic voltammetry between −0.50 V and +2.00 V with 0.10 V.s^{-1} scan rate for various cycle numbers. 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 were incorporated in the PPAP film from the metal aqueous solution of with cyclic voltammetry between various potential range with 10 cycles. Firstly, The electrochemical deposition of nanoparticles of Ag was performed using the electrochemical reduction of 1 mM $AgNO_3$ on PPAP/GCE in 0.1 M HNO_3 solution using cyclic voltammetry. Then, Au nanoparticles were covered on Ag/PPAP/GC surface using the electrochemical reduction of 1 mM $HAuCl_4$ in 0.1 M HCl solution. A 1.0 mM $HAuCl_4$ was prepared by diluting the concentrated Au solution with 0.1 M HCl after dissolving the Au wire (99.999% in purity) in HNO_3:HCl (1:3).

3 RESULTS AND DISCUSSION

3.1 Preparation of Au and Ag nanoparticles modified PPAP/GC electrodes

Figure 1 shows the multi sweep cyclic voltammograms of p-aminophenol electropolymerization During the CV scan an irreversible oxidation peak was observed at 1.60 V for p-AP without the corresponding cathodic processes in the reverse scan. Also, a single cathodic peak at -0.1 V and reversible oxidation and reduction peaks were seen at around +0.60 and +0.55 V respectively. The generation of the peaks might be attributed to the intermediate species during the oxidation process of the AP. The peak current increasing with repetitive CV cycles shows an increasing of polymer content on the surface of the electrode. [13].

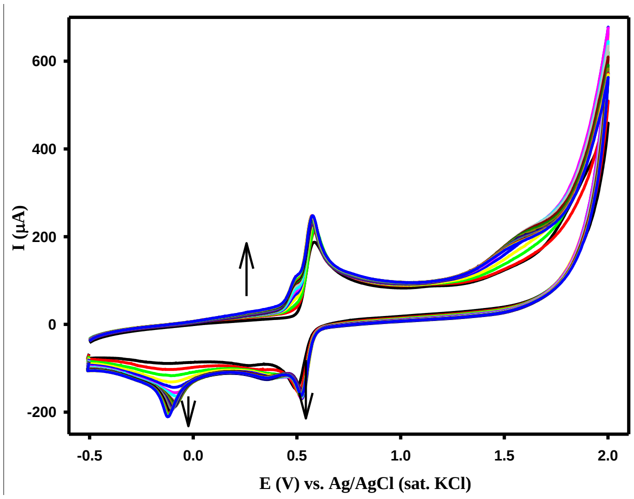


Figure 1: Successive 40 cyclic voltammograms of PAP electropolymerization on GCE at a scan rate of 0.1 V.s^{-1}.

Figure 2A displays the continuous CVs for the preparation of Ag nanoparticles in 1.0 mM $AgNO_3$ + 0.1 M HNO_3 on the PPAP/GCE in the potential range of 0.3 V to -0.9 V at 0.05 V/s for 10 cycles. There is a cathodic peak at about -0.40 V corresponding to the reduction of Ag$^+$ ions. The Au nanoparticles modified electrode was prepared in 1 mM $HAuCl_4$ + 0.1 M HCl on the electrode surface by applying the same method in the potential range of 0.1 V to -1.20 V at 0.05 V/s for 10 cycles. It is clearly seen from Figure 2B that there is a cathodic peak at about -0.45 V corresponding to the reduction of Au^{3+} ions. Finally Au-Ag/PPAP/GC electrodes were obtained by respectively applying the procedure as mentioned above (Figure 2b). The CV results confirmed that the deposition of nano Au and Ag formed on the PPAP/GCE surface during the current–potential cycles.

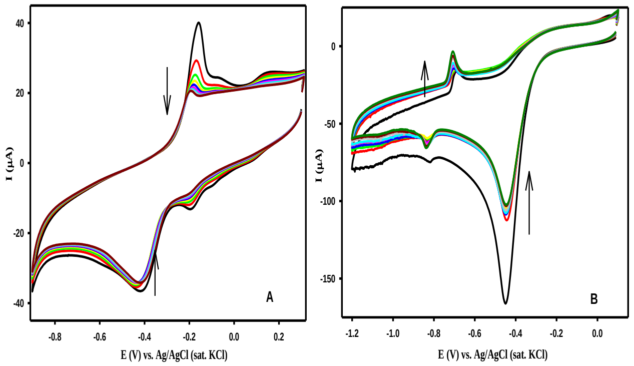
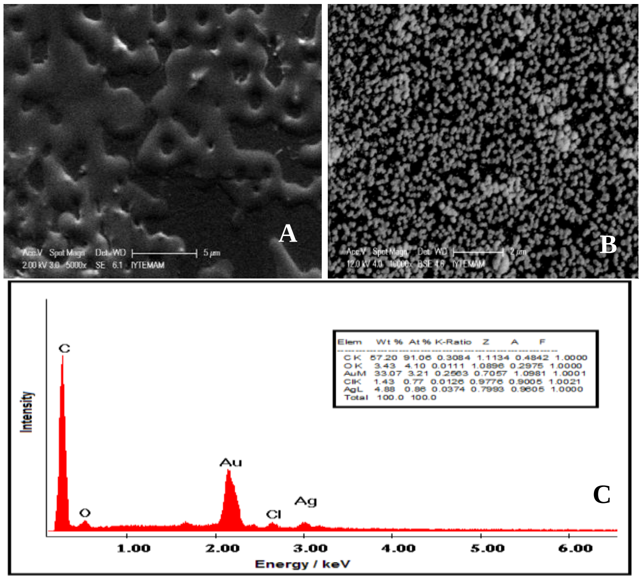


Figure 2: The PPAP/GCE modified with (A) Ag nanoparticles in 1mM $AgNO_3$, (b) Ag/PPAP/GCE modified with Au nanoparticles in 1 mM $HAuCl_4$ by repeating the potential scan at 0.05 $V.s^{-1}$ for 10 cycles.

3.2 Characterization of modified electrodes

Figure 3 shows the SEM images of PPAP/GCE and Au-Ag/PPAP/GC electrodes. The SEM image polymer film (Figure 3A) revealed that the distribution of polymer on the GCE surface was rather uniform with a smooth surface. The top SEM view of nanostructures of Au-Ag in Figure 3B on the PPAP/GCE shows that there was nano Au and Ag formation as bright, round-shaped, homogeneously dispersed particles covered to the electrode surface. The average particle size of Au and Ag on PPAP/GCE were calculated as 100-150 nm and 80-120 nm, respectively. The energy dispersive X-ray spectroscopy (EDX) measurements which showed in figure 3C confirmed that Au-Ag nanoparticles were successfully electrodeposited on PPAP/GCE. The weight gain of the PPAP due to the Au and Ag loading was about 33.07% and 4.88%, respectively.



Elem	Wt %	At %	K-Ratio	Z	A	F
C K	57.20	91.06	0.3084	1.1134	0.4842	1.0000
O K	3.43	4.10	0.0111	1.0896	0.2975	1.0000
AuM	33.07	3.21	0.2563	0.7057	1.0981	1.0001
ClK	1.43	0.77	0.0126	0.9776	0.9005	1.0021
AgL	4.88	0.86	0.0374	0.7993	0.9605	1.0000
Total	100.0	100.0				

Figure 3: SEM images of (A) PPAP/GCE, (B) Au–Ag /PPAP/GCE and (C) EDX image of Au-Ag/PPAP/GCE.

3.3 Electrooxidation of Ammonia borane on modified electrodes

The electrochemical behaviour of 1.0 mM AB was studied in 2.0 M NaOH at various electrodes (Fig. 4 A-B). As can be clearly seen, there was no any oxidation reaction take place on bare GCE and PPAP/GCE in the presence of AB (Fig.2A). On the other hand, a well defined oxidation peak of 1.00 mM AB in 2.0 M NaOH solution was observed at ca. -0.91 V on Au disk, -0.92 V on Au_{10cyc}/PPAP, -0.87 V on Ag_{10cyc}/PPAP, -0.94 V on Ag_{10cyc}-Au_{10cyc}/PPAP and -0.98 V on Au_{10cyc}-Ag_{10cyc} /PPAP modified GC electrodes. Among the five electrodes Au-Ag/PPAP/GC electrode has the highest peak current and the shifting the oxidation potential to more negative values and thus represents the highest electrocatalytic activity of Au-Ag/PPAP/GC electrocatalyst for AB electrooxidation. It can be attributed to the synergistic effect of Au-Ag bimetallic nanoparticles, which jointly improves the electrocatalytic oxidation of AB.

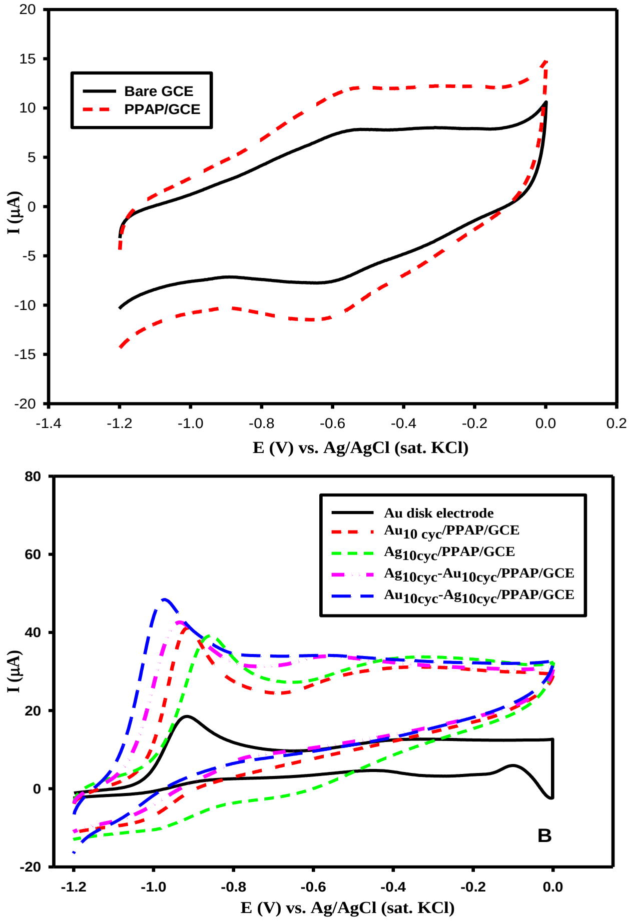


Figure 4: Cyclic voltammetric behavior of 1.0 mM AB in 2.0 M NaOH on A) bare GCE and PPAP/GCE, B) Au disk electrode and different metal nanoparticle modified MWCNT/GC electrodes

To obtain the optimum parameters of AB oxidation on Au-Ag/PPAP/GC electrode, the major factors that should be considered were p-aminophenol concentration, polymerization cycle numbers of monomer, concentration of $AgNO_3$ and $HAuCl_4$ solutions, cycle number effect on electrodeposition of Ag and Au nanoparticles and the concentration of NaOH solution. The optimum conditions for electrochemical oxidation of AB were obtained by measuring the peak currents while varying each parameter which mentioned above. Thus, the optimum parameters that were chosen for subsequent studies are as follows, 5.0 mM p-aminophenol, 40 cycles for electropolymerization of PAP, 1.0 mM and 5.0 mM concentration of $AgNO_3$ and $HAuCl_4$ solutions, respectively, 10 cycles for electrodeposition of Ag nano particles, 10 cycles for electrodeposition of Au nano particles and 2.0 M NaOH solution for supporting electrolyte medium.

Fig. 5 shows cyclic voltammograms recorded at Au_{10cyc}-Ag_{10cyc}/PPAP/GC electrode in the absence and in the presence of 1.0 mM AB solution in different concentration of NaOH (0.01, 0.10, 0.50, 1.00, 2.00, 3.00 and 4.00 M). The voltammograms which were recorded in the absence of AB show that there is no oxidation or reduction peaks at interesting potential range. On the other hand, oxidation peak of AB was observed at all NaOH concentration. The peak characteristics such as peak potential and peak current were improved with increase in NaOH concentration. The oxidation peak potential was shifted from -0.66 V to -1.01 V by increasing NaOH concentration. The peak potential for borohydride oxidation in 2.0 M NaOH solution was much negative than other examined NaOH concentrations. Therefore, 2.0 M NaOH solution was chosen as supporting electrolyte for future studies.

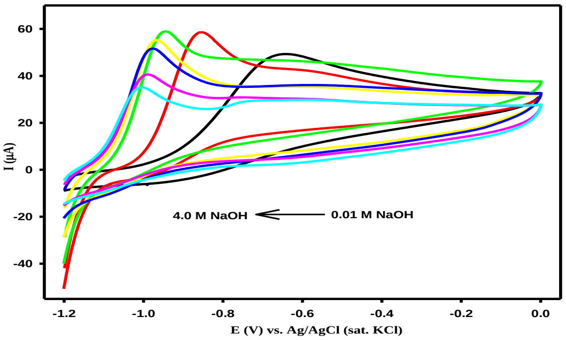


Figure 5: CVs recorded for presence of 1.0 mM AB in different NaOH concentrations at Au_{10cyc}-Ag_{10cyc}/PPAP/GC at 0.05 V.s^{-1} scan rate.

Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current or potential and scan rate. The effect of scan rate on the anodic peak current of ammonia borane was investigated in 2.0 M NaOH at Au_{10cyc}-Ag_{10cyc} /PPAP/GC electrode. The results indicated that the peak current was linearly changed with the square root of scan rate over the range of 0.003–1.000V. The linear regression equation was $ip\ (\mu A) = 5.2285v^{1/2}\ (V/s) + 0.7569$ with a correlation coefficient of $R^2 = 0.9989$, therefore, the anodic peak current was controlled by 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.

4 CONCLUSION

In the present study, a purely bimetallic electrode surface was prepared by electrochemically deposited Au and Ag on PPAP/GC electrode. Electrocatalytic oxidation of ammonia borane was studied at electrochemically deposited Au-Ag modified polymer film electrode and the results were compared with Au disk, Au/PPAP and Ag/PPAP electrodes in 2.0 M NaOH solution. CVs results revealed that the peak potential of AB shifted at Au-Ag/PPAP/GC electrode about 0.08 V, 0.07 V and 0.12 V in negative directions compared to the Au disk, Au/PPAP and Ag/PPAP respectively. The relatively higher electrocatalytic activity of Au-Ag/PPAP/GC electrode compared to bare and other modified electrodes can be attributed to a synergistic effect of bimetallic surface.

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