

Electrochemical Modification Of Carbon Paste Electrode Using Polyaniline And Gold Particles For Signal Enhancement

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Abstract: The paper contains a detailed overview of recent advances relating to polyaniline (PANI) and gold particles as a transducer material for sensor applications. This conducting polymer provides enormous opportunities for binding metals, tuning their catalytic properties, rapid electron transfer and direct communication to produce a range of analytical signals and new analytical applications. Merging the specific nature of metal (gold particles) and the key properties of this modern conducting matrix, sensor designed using polymer (polyaniline) and metal (gold particles) and their sensing characteristics have been analysed which showed an increase in peak currents according to their modification (Bare, Polyaniline and Gold/Polyaniline Carbon Paste Electrode) as shown below with a diffusion co-efficiency of 1 using potassium ferrocyanide ($K_4Fe(CN)_6$) as the electro active specie. These modified electrodes exhibited an increase in surface area (Bare- $0.014cm^2$, Polyaniline- $0.019cm^2$ and Gold/Polyaniline- $0.026cm^2$). Efforts have been made to discuss and explore various characteristics of PANI responsible for direct electron transfer leading towards fabrication of mediator-less sensors.

Keywords: Electrochemical, Carbon Paste Electrode, Polyaniline, Gold particles and Potassium Ferrocyanide

I. INTRODUCTION

Electrochemical techniques are those that show a quantitative relationship between the magnitude of an electrical quantity and the bulk concentration of the analyte. The electrode in the solution is in many respects, a transducer between chemical and electrical entities. The role of the electrode is either to monitor species in the solution or to generate new species. Electroanalytical methods are categorized as either static or dynamic. Static method (e.g: potentiometry) that involves measurements of potential difference at zero current without changing Nernstian equilibrium at the electrode – solution interface. In dynamic techniques (e.g.: voltammetry and amperometry), the system is distributed by electrical excitation signal consisting of a variety of potential or current programmes, and the resulting response is measured [1]. For a molecule to be directly investigated electrochemically, it must have an electroactive group (electrophore) for reduction or oxidation. In certain cases, the molecule of interest (analyte) shows electroactivity beyond the available potential range of the working electrode, as a result of sluggish kinetics. The rate of electron transfer of such reactions can easily be increased by means of electrocatalysis, a process in which the introduction of a catalyst decreases the reduction (oxidation) potential of the analyte by decreasing the overpotential, or alternatively, increases the reduction (oxidation) current. Electrocatalysis can also be used to avoid interference from dissolved species [2]

Because of the simple preparation and easy renewal of the surface, carbon has been used extensively as a working electrode for a variety of electrochemical applications. Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes [3].

More interestingly, some electroactive modifiers provide an excellent electrocatalytic property, which makes the analyte electroactive at a lower potential enhancing the power of electrochemical detection. Electroactive modifiers, on the other hand, interact with analyte molecules and alter chemical reactions, or alternatively, they act as a new phase on the conducting phase of the electrode [4].

Likewise, metal nanoparticles exhibit unique optical, electrical, thermal and catalytic properties. Therefore, they have attracted considerable interest and have been employed for construction of various electrochemical sensors in this work. Metal nanoparticles exhibit unique electronic, optical, thermal and catalytic properties [5-9]. Au nanoparticles possess exceeding advantages over other nanomaterial's including

stability, conductivity, biocompatibility, low cytotoxicity and size-related electronic, magnetic and optical properties [5-10].

II. EXPERIMENTAL

2.1 Material

Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98% Sigma Aldrich), hydrochloric acid (HCl, 35%, Alpha), sulfuric acid (H_2SO_4 , 98%, Fisher chemicals), ammonium hydroxide (NH_4OH , 35%, PSPark), cyclohexane (99%, Fisher Chemicals), acetone (CH_3CO , 100%, Whitehouse Runcorn), ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$, 99%, Sigma Aldrich), potassium nitrite (KNO_2 , 99%, Qualikems), aniline ($\text{C}_6\text{H}_5\text{NH}_2$, 100%, Sigma Aldrich) were used as received without any other treatment. Aqueous solutions were prepared with deionized water. In this study, the chemicals were used as received without further purification.

For the preparation of the carbon paste electrode, graphite powder (100%, Sigma Aldrich) was mixed with Mineral oil (paraffin, 95%, Finkem) and the paste filled into the tip of plastic syringe (2.3 mm internal diameter, Shan Chuan) and connected with copper wire (99.9%, Finkem).

2.2 Preparation of bare carbon paste electrode

Bare carbon paste electrode will be prepared by mixing (800 mg) graphite powder with (100 μL) of paraffin oil and thoroughly hand mixed in a mortar and pestle. The paste was packed into electrode assemblies made from 3mL plastic syringe of 2.4mm outer diameter using spatula and smoothed on a glass slide surface. Electrical contact will be made with a copper wire through the syringe [11].

2.3 Electrodeposition of Polyaniline

Electropolymerisation was carried out by mixing 2.5 ml of 0.25 M of ammonium persulfate aqueous solution with 2.5 ml of 1M aniline hydrochloride in a vial. Cyclic voltammetry at potential between -0.2 and 1.0 V, on carbon paste electrode vs. Ag/AgCl electrode at a scan rate of 50 mV in 5 cycles was carried out, taking several successive scans [8]

2.4 Electrodeposition of Gold

Gold nanoparticles were electrodeposited on CPE according to the procedure in the literature [11]. 10 μL of 0.5 mol/L of KAuCl_4 was added in 5 mL of 0.5 mol/L H_2SO_4 in an electrochemical cell. Chronoamperometry (CA) was run with general parameters of initial potential of 1.1V stepped to 0 V for a 2 s at scan rate of 50mV/s.

2.5 Electrochemical Measurements

The Epsilon (BASI) was used to carry out all electrochemical measurements. A conventional three-electrode setup was used with the CPE electrode as the working electrode and a platinum wire as a counter electrode ((1 mm) mw 4130, an Ag/AgCl (Thermo Scientific Orion Model Number: 900011) served as a reference electrode. All potentials were reported with respect to this reference electrode. All gold depositions were performed from solutions containing 10 μL of $\text{KAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 0.5 mL H_2SO_4 .

III. RESULTS AND DISCUSSION

3.1 Characterization of electrodes

Cyclic voltammetry (CV) of redox species can provide information on redox behaviour of the chemicals and using a well know chemical it can also be used for characterization of the property of a working electrode. Three types of sensors were constructed which includes (a) Bare Carbon paste electrode (CPE), (b) Polyaniline modified carbon paste electrode (PANI modified CPE) and (c) electrochemical deposited gold on PANI modified CPE (Au / PANI modified CPE). Their electrochemical behaviors were studied in 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$

3.2 Characterization of bare CPE in 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$

The cyclic voltammogram of CPE in 1M KNO_3 containing 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$ at 50 mV/ is presented on Fig.1. Five carbon paste electrodes were prepared and CV response of the electrodes was compared. No significant difference was observed between the CPEs.

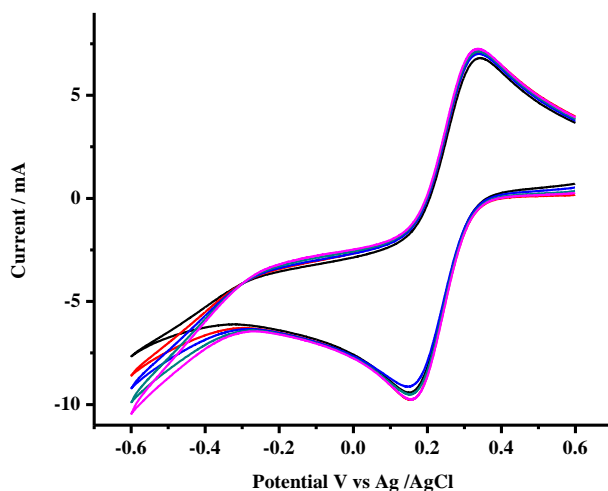


Figure 1. Cyclic Voltammogram of 0.1M $K_3Fe(CN)_6$ in a 1M supporting electrolyte of KNO_3 at 5 bare CPEs at a scan rate of 50 mVs^{-1}

The narrow redox potential difference (of $< 80\text{ mV}$) was obtained for all CPE which an indicator of the reversibility of the electrochemical process and the CVs showed good overlay owing to the good reproducibility of the preparation procedure for CPE. The CPE also showed low background current, renewal of surface and ease of modification.

3.3 Characterization of PANI modified electrode in 0.1 M $K_3Fe(CN)_6$

PANI-modified CPE was prepared using surface approaches PANI modification of CPE with PANI where the PANI was synthesized and incorporated to carbon paste. The electrode made from the modification approach was characterized by cyclic voltammetry in $0.5\text{ mM H}_2\text{SO}_4$ electrolyte solution. Fig 2 is the electropolymerized one with other. The voltammogram shows some basic information like the features of the PANI reduction and oxidation. The peaks potential of PANI electrodeposited at CPE were found to be at 0.3, 0.6 and 0.4 V respectively of which were in accordance with other [12]

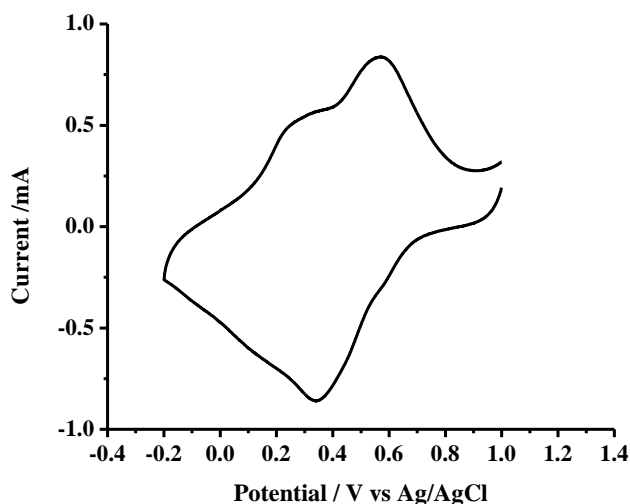


Figure 2. Cyclic voltammogram for surface PANI modified electrode in $0.5\text{ mM H}_2\text{SO}_4$ at scan rate 100 mVs^{-1} between potentials of -0.4 and 1.4 V .

The surface PANI modified CPE further run in $0.5\text{ mM H}_2\text{SO}_4$ including the potential range of atrazine. This was done to check whether reduction peak of PANI interferes the reduction potential range of atrazine or not. It was observed that there was no effect around the possible potential range of atrazine at -0.5 V [13].

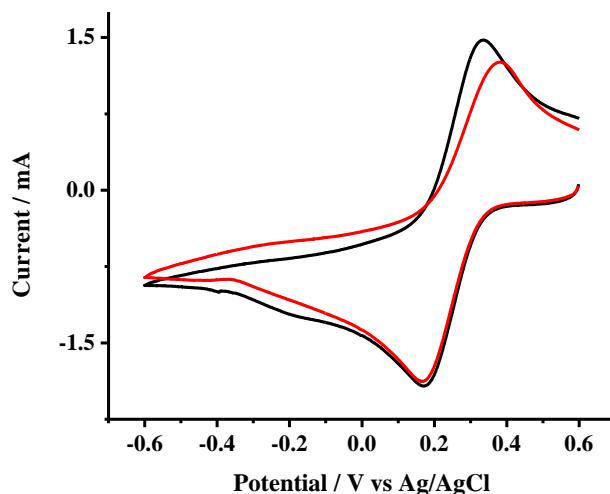


Figure 3: Cyclic Voltammogram of in 0.1M $K_3Fe(CN)_6$ in a 1M supporting electrolyte of KNO_3 at surface PANI modified CPE at a scan rate of 50 mVs^{-1}

3.4 Characterization of Au/PANI modified electrode in 0.1 M $K_3Fe(CN)_6$

The Analine Polymerised as shown on Fig 3 and Gold deposited Fig 4 on the CPE surface was meant to increase the surface area of the electrode. The modified electrode was characterized using 0.1 M $K_3Fe(CN)_6$. The cyclic voltammograms show a large background current at the Au/PANI modified electrode which shows that the modified electrode exhibit an increased in surface area as shown on Fig 4 and the current responds higher than observed with PANI modified CPE. This process was repeated with different electrodes and there was no significant difference at the electrode current response.

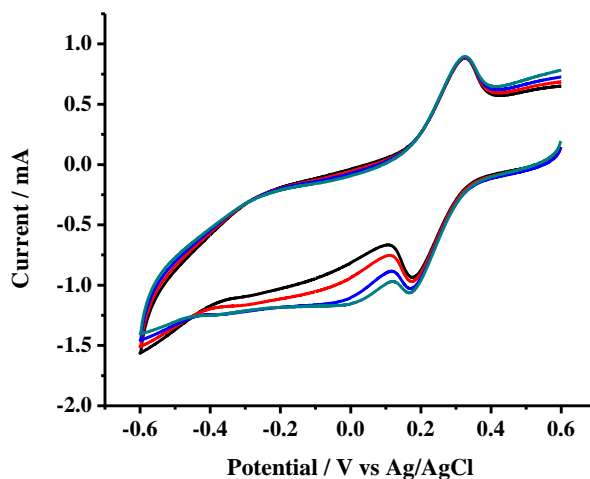


Figure 4: Cyclic Voltammogram of effect of deposition time of Au nanoparticles with 0.1M $K_3Fe(CN)_6$ in a 1M supporting electrolyte of KNO_3 at PANI modified CPE at a scan rate of 50 mVs^{-1}

3.4 Determination of the active surface area of the prepared electrode

The active surface area of the prepared CPE was determined by the Randle-Sevcik relationship that considers an electrode reaction in which the rate is governed by diffusion of the electroactive species to a planar electrode surface. The peak current, I_p , is related to area of the electrodes as:

$$I_p = k n^{3/2} A D^{1/2} C^b v^{1/2}$$

Where the constant $k = 2.7 \times 10^5$

n = number of moles of electrons transferred per mole of electroactive species

A = area of the electrode in cm^2

D = diffusion coefficient in cm^2/s

c = solution concentration in mole/L

ν = scan rate of the potential in volt/s.

I_p = linearly proportional to the bulk concentration c , of the electroactive species, and the square root of the scan rate, $\nu^{1/2}$.

Thus, a CV of scan rates at 25, 50, 75, 100, 125 and 150 m/Vs were run (Fig: 5) and a graph of the I_p vs. $\nu^{1/2}$ was plotted (Fig: 5) and the slope from the linear equation: $y = 2.58x - 0.1358$ (x in V/s), $r = 0.9999$ was used to calculate the area of the electrode used using the above equation. The calculated area was found to be 0.014 cm^2 . In the same manner the active surface area of PANI modified CPE, Au/PANI modified CPE were also determined.

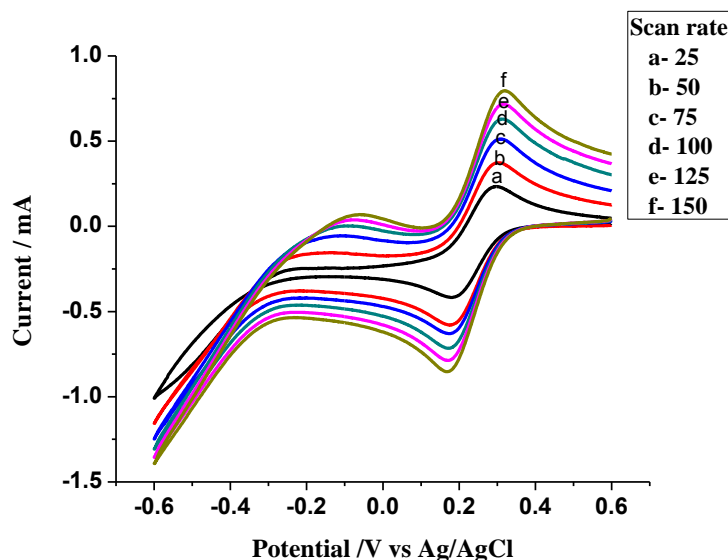


Figure 5: (a) Cyclic Voltammogram of scan rate run in $0.1 \text{ M K}_3\text{Fe}(\text{CN})_6$ in a 1 M supporting electrolyte of KNO_3 at bare CPE at scan rates of 25, 50, 75, 100, 125, 150 mVs^{-1}

Table 1. The surface area of the electrodes

Surface area of bare CPE (cm^2)	Surface area of PANI modified CPE (cm^2)	Surface area of Au/PANI modified CPE (cm^2)
0.014	0.019	0.026

3.5. Comparative working potentials of the three characterized electrodes with respect to $0.1 \text{ M K}_3\text{Fe}(\text{CN})_6$

The voltammetric response of $\text{K}_3\text{Fe}(\text{CN})_6$ on bare, PANI modified and Au/PANI modified CPEs was recorded and compared. Figure 6 demonstrates the overlay of the voltammograms of $0.1 \text{ M K}_3\text{Fe}(\text{CN})_6$ at the three electrodes.

A current response was observed for Au/ PANI modified CPE than PANI modified and bare CPE. Therefore, it is possible to claim that modifying the electrodes increase the surface area as such increase current responds has being achieved. With these characterizations further the analysis of the atrazine.

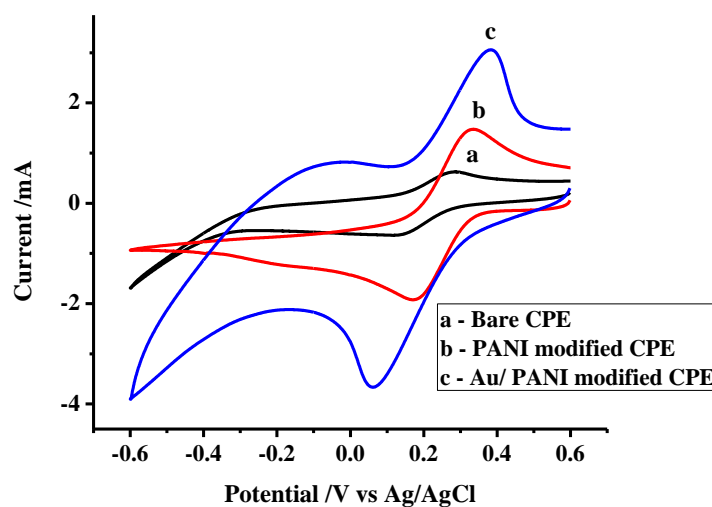


Figure 6. Cyclic voltammogram of current response of (a) bare (b) PANI (c) Au/PANI modified CPE in 0.1M $K_3Fe(CN)_6$ in a 1M supporting electrolyte of KNO_3 at a scan rate of 50 mVs^{-1}

IV. CONCLUSION

Monitoring the current levels analyte requires more specific, sensitive and accurate measurements. Existing analytical techniques have several drawback (CPE) and consequently, electroanalytical techniques attract chemist due to their desirable properties. Furthermore, the use of electrodes modified with polymer, and metals and other functionalities provides large surface area for detection of analyte given a sensitive promising research area.

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