Gold Nanoparticles Modified Cheap Sandpaper Electrode for Advanced Electroanalytical Applications: An Exploratory Approach

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The synergistic effect of the SiC and Graphite led to the fabrication of the paper electrode. The sandpaper with the average particle diameter of 25.8µm was used as the substrate for the study of ferricyanide solution. The Graphite bar was abraded against the sandpaper containing SiC leading to the SiC/Graphite (Gp) electrode creating a cheap and easily fabricated sensor for the electrochemical measurement with high sensitivity. Characterization of the paper electrode and the electrochemical activity was investigated using cyclic voltammetry and the results obtained indicated that LOD and LOQ of ferricyanide by the electrode was found to be 13.23µM and 40.09µM respectively. The linearity at different concentration explained the process to be diffusion controlled. Moreover, the electrodepositon of the gold nanoparticles onto the electrode was performed at -200mV for the duration of 120 s using chloroauric acid which lead to the enhancement of the current values explaining the presence and effect of the gold nanoparticles. Therefore, sandpaper electrode may hold great promise for fast, simple and sensitive detection in the complex matrices.

1. INTRODUCTION

SiC is an important interesting material for the power electronics. The large band gap energy of SiC which is 2.3-3.3eV results in high breakdown voltage with high thermal conductivity and drift velocity for electrons[1, 2].The Graphite (Gp)/SiC Composites are been prepared extensively using electrode graphite powder and the SiC powders creating a range of application with properties of high friction coefficient, toughness, biocompatibility property and mechanical strength [3,4].Scientific research papers have reported use of SiC surfaces for effective growth of graphene for studying their microstructure and properties [5-10].

The graphitization of SiC surfaces is known from a long time. Investigations have been reported for the graphite-SiC surfaces interface formation by the surface science techniques such as X-ray Photoelectron Spectroscopy(XPS) [11], inverse photoelectron Spectroscopy(IPES) [12], Raman Spectroscopy[13], and scanning tunnelling microscopy(STM) [14,15]. Moreover, monocrystalline graphite multilayers have been reported to grow by the sublimation of Si from SiC surfaces [16].The SiC is thought to act as a template to encourage the formation of sp^2 bonded C [17]. In cases the surface roughness is an important parameter since it heavily influences the electron mobility in the graphene epitaxial layer through strain and misorientation of graphene crystal structure [18]. Graphene/graphite-coated SiC nanowires have been reported to fabricate from diethylsilane or divinyldimethylsilane by Fe-assisted metal–organic chemical vapour deposition. When diethylsilane is used, a few layers of graphene are formed, while 30–40-nm-thick graphite is formed from divinyldimethylsilane [19].

The use of SiC coating on a glassy carbon electrode has been reported to resolve the overlapping voltammetric responses of ascorbic acid, dopamine, and uric acid which is been used for the selective determination of dopamine in the presence of ascorbic acid and uric acid. [20] Therefore, the SiC electrode behaves as an ordinary oxidation and reduction indicator like platinum and gold as mentioned in the literature. [21]

In this paper we tried to obtain the electrochemical results using Sandpaper electrode where the SiC/Gp synergism helped in the quantification of the ferricyanide solution. The low cost electrode was easy to prepare and the design was appropriate for study of electrochemical system. The fabricated electrode was used as the working electrode in the three electrode system with Ag/AgCl as reference and Pt wire as Counter electrode.

2. EXPERIMENTAL

2.1 Apparatus

Electrochemical measurements were carried out at AUTOLAB PGSTAT 302N (Eco- Chemie B.V., Utrecht, The Netherlands) potentiostat-galvanostat with IME 663 and NOVA 1.7 software. All measurements were carried out at room temperature. Experiments were performed in a standard three-electrode assembly incorporating the sandpaper Electrode as the working, Pt wire as auxiliary and Ag/AgCl/saturated KCl as reference electrode.

2.2 Reagents and chemicals

Potassium Ferricyanide and Potassium chloride was purchased from Merck (Mumbai, India) and chloroauric acid from Sigma-Aldrich. Graphite Bar (98.9% purity) and sandpaper (SiC as abrasive material with average particle diameter 25.8μm) was commercially available and was purchased from local market. The Ultra pure water, obtained from ELGA purification system (U.K) was used. All other chemicals used were of analytical grade and used without further purification.
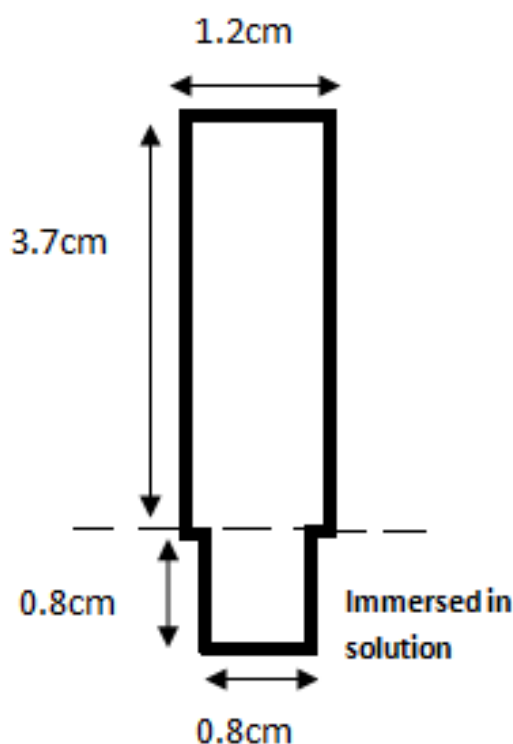
2.3 Preparation of solution system

The stock of potassium ferricyanide solution of 0.1M was prepared with KCl as supporting electrolyte. The test solutions were prepared and the concentration of the potassium ferricyanide was varied from 10×10^{-5}M to 50×10^{-5}M. For electrodeposition of gold nanoparticles, the stock of $HAuCl_4$ of conc. 167mg/L was prepared.

2.4 Fabrication of paper electrode

The electrode was prepared by cutting a strip of sandpaper (average particle diameter of 25.8µm) with a dimension of 4.5cm x1.2cm and the surface area of the part of the strip, which was immersed in solution for electrochemical measurement, was 0.8cm x 0.8cm (Fig-1).The above area left, other than submerged portion was used for the connection.

The electrode substrate was abraded via pure graphite bar making the electrode conducting and appropriate for the electrochemical study of solution system.


Figure 1. The design of the paper electrode illustrating the dimensions of the electrode for the study of solution system.

2.5 Electrodeposition of gold (Au) nanoparticles

The Chloroauric acid solution of conc. 167mg/L was used for the Au nanodeposition on the sandpaper electrode. The Amperometric technique with the three electrode assembly was employed for

the Au nanocoating onto the surface of working electrode (Fig-2).The time span for providing the potential was 120s at -200mV.
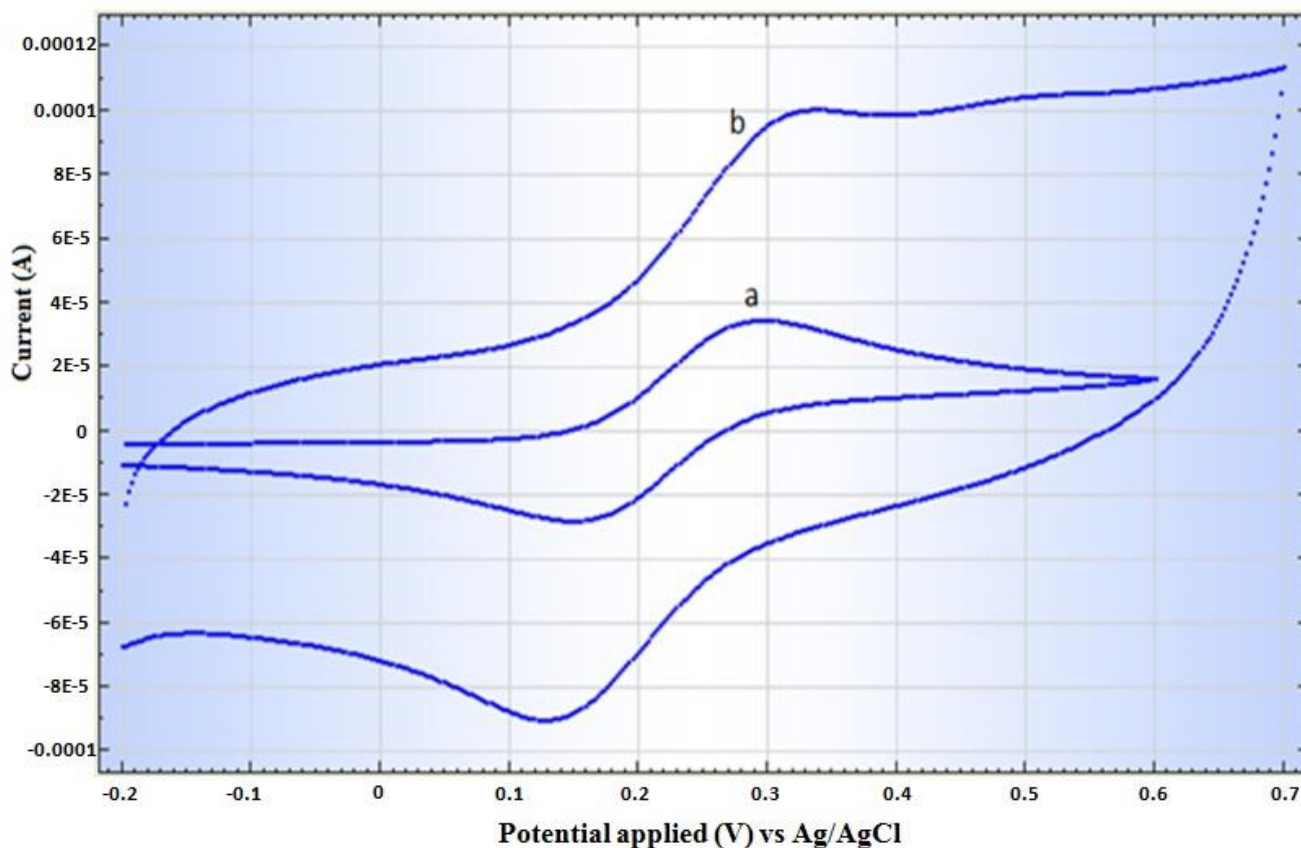
Figure 2. Comparison of the cyclic voltammograms obtained at a) Gp/SiC paper electrode b) Au/Gp/SiC paper electrode in 10 x 10^{-5}M ferricyanide solution.

3. RESULT AND DISCUSSIONS

3.1 Characterization of sandpaper electrode

The morphology and the topology of the sandpaper electrode were studied using the XRD pattern (Fig-3) showing the SiC and the Graphite peaks. The particle size of the graphite C at the sandpaper electrode which was abraded by the graphite bar came out to be 32 nm after applying the Scherrer equation.

$$t= 0.9 \lambda / B \cos \theta \qquad (1)$$

Where, B is full width at half wave length, t grain size, λ the wavelength of X ray used.

The abrasion of the graphite Carbon led to the formation of layers onto the surface of the sandpaper making it conductive and appropriate for the study of electron transfer of the ferricyanide solution. The SEM image of the Au modified sandpaper electrode clearly shows the white particles

adhered at the surface of the sandpaper electrode (Fig.4). Thereby, Au nanodeposition is responsible for the increase in the rate of electron transfer and led to the current enhancement.
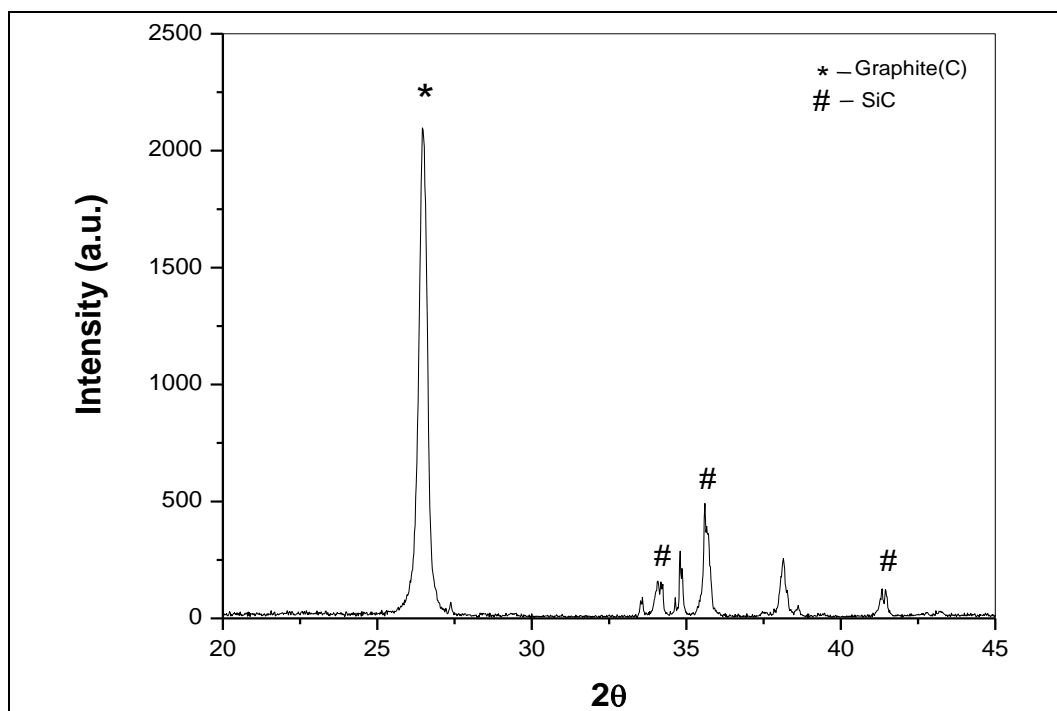
Figure 3. XRD pattern of the fabricated sandpaper electrode depicting the Graphite C and SiC on the electrode surface.
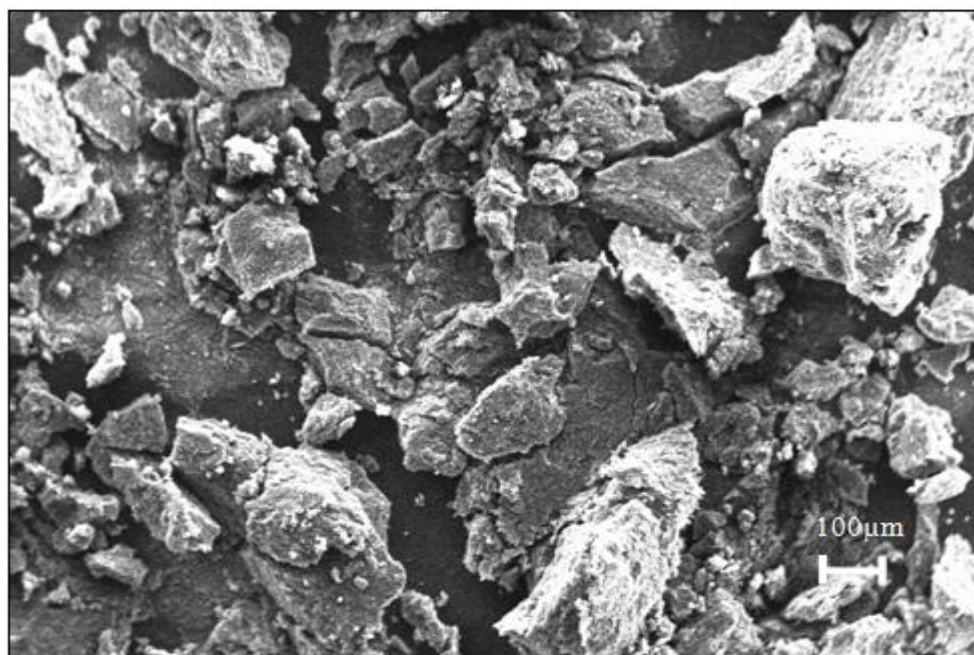
Figure 4. SEM image of the sandpaper electrode showing deposition of the Au nanoparticles at the paper electrode.

*3.2. Optimization of experimental conditions*

3.2.1. Effect of scan rate

To study the effect of scan rate on the redox potential of Potassium ferricyanide solution at sandpaper electrode, cyclic voltammograms were recorded for different scan rate (10, 20,30,40,50 and 100mV/sec respectively) at a fix concentration of ferricyanide solution. The anodic peak currents were increased linearly with the increase in scan rate. A graph of anodic peak currents (I_p) versus square root of scan rate (v) was plotted (Fig-5). The graph shows linear relationship b/w anodic peak currents and square root of scan rate which can be expressed by the equation:

$$I_p = 0.979 \, (v)^{1/2} - 0.642; \, R^2 = 0.999 \qquad\qquad (2)$$

This reveals that the electrode process was diffusion controlled and confirms that the CV of the ferricyanide is close to an ideal quasi-reversible system with paper electrode (Fig.6).
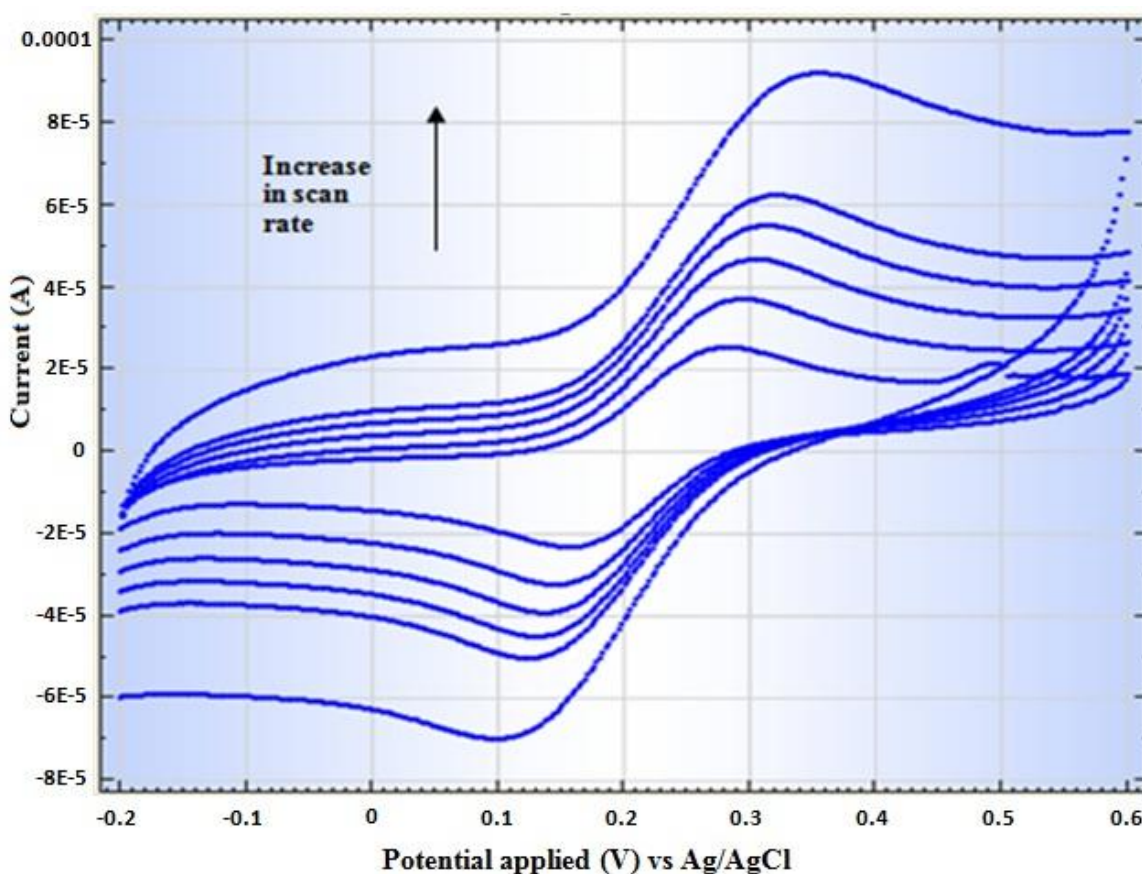
Figure 5. Figure represents the overlapped cyclic voltammograms of potassium ferricyanide solution at concentration of 10 x10^{-5}M with sweep rates (10, 20, 30, 40,50and 100mV/s respectively).
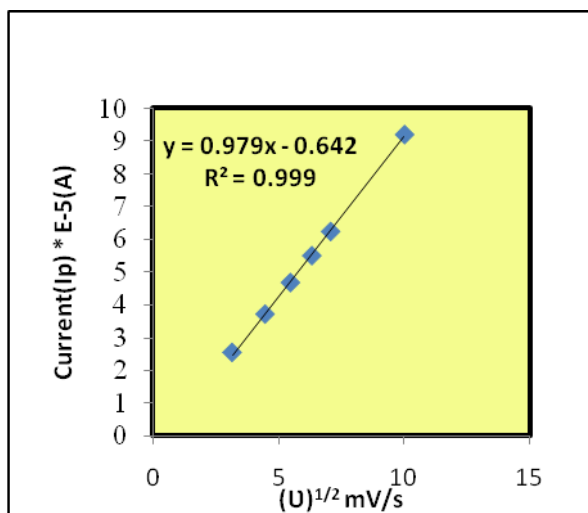
Figure 6. Calibration curve represents enhancement of anodic peak current I_p (A) at different sweep rates (10, 20, 30, 40,50and 100mV/s respectively).

3.2.2. Effect of concentration

Cyclic voltammograms obtained with increasing amounts of ferricyanide solution showed that peak current increased linearly with increasing concentration (Fig-7). Since the fabricated electrode greatly improves the sensitivity for the determination of the solution system, it signifies the electrocatalytic activity of the Gp/SiC electrode for the redox reaction of the Potassium ferricyanide under optimized conditions. Linear calibration curve (Fig-8) is obtained over the concentration of 10×10^{-5}M-50 $\times10^{-5}$M which can be expressed by the following equation:

$$I_p/A = (0.032) \, (\mu M) + 0.707; \, R^2 = 0.998 \qquad (3)$$

LOD and LOQ estimated as 3S/m and 10S/m respectively are 13.23 and 40.09 µM respectively where "S" is the standard deviation and "m" is the slope of the calibration curve (Table 1).

Table 1. Cyclic voltammetric method validation parameters for standard linearity.

Linearity Parameters	Results
Slope	0.0322
Intercept	0.7070
Standard deviation	0.1292
Correlation coefficient (R^2)	0.998
Limit of detection(µM)	13.23
Limit of quantification(µM)	40.09
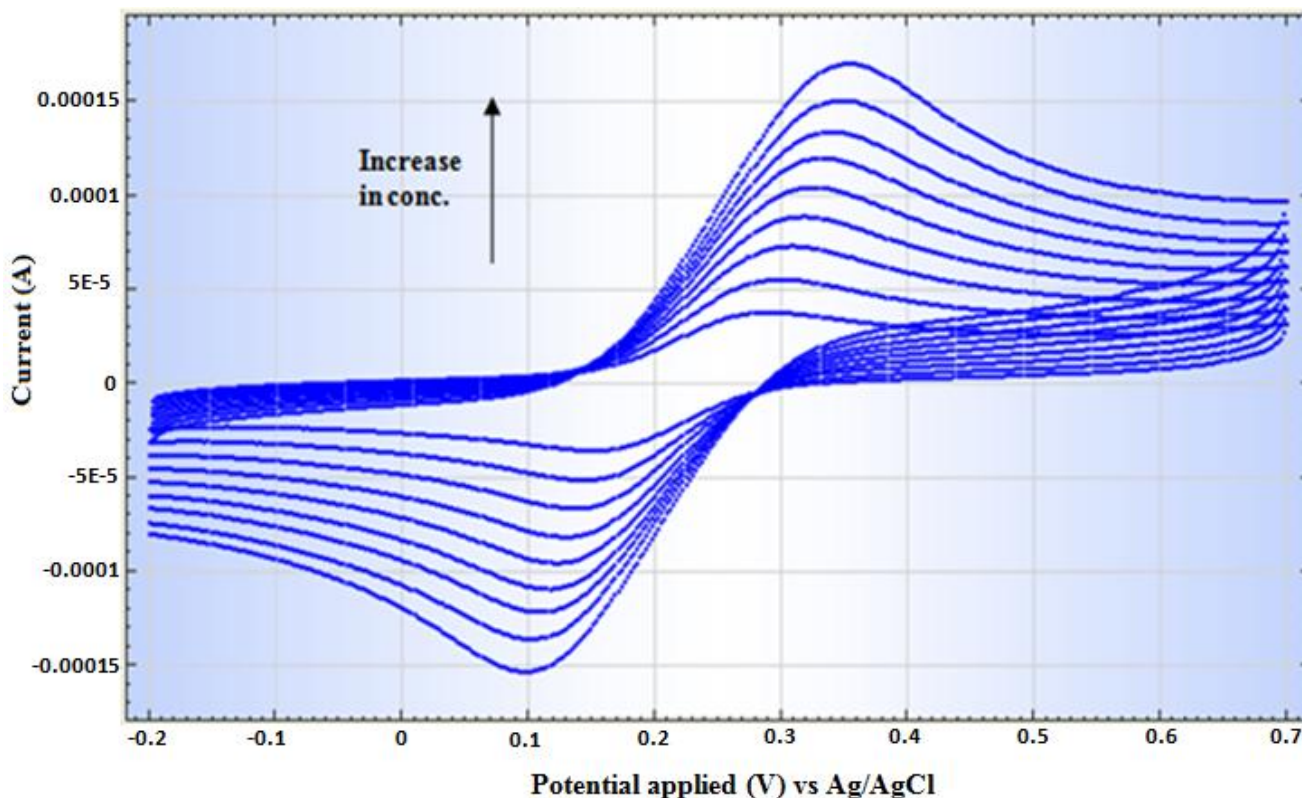
Figure 7. Figure represents overlapped cyclic voltammograms of potassium ferricyanide solution at different concentration levels varying from 10 x10^{-5}M to 50 x 10^{-5}M.
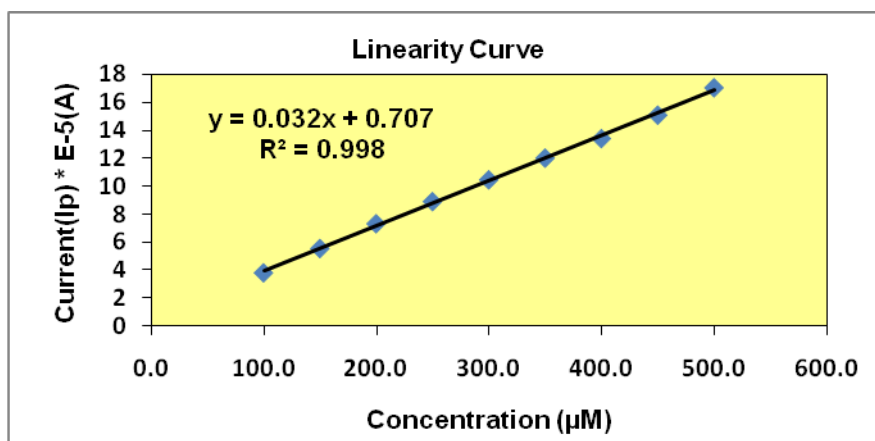
Figure 8. Calibration curve represents linearity of solution system at different concentrations from 10 x10^{-5}M to 50 x10^{-5}M.

4. CONCLUSION

Conclusively, the paper represents an exploratory approach towards the fabrication of cheap paper electrode which can be used as advanced carbon-based electrode material for the study of electrochemical solutions as seen in the case of ferricyanide system. Au deposited paper electrode showed current enhancements when compared with the bare Gp/SiC electrode. Variation of scan rate

study shows that the electrode process is diffusion controlled. Calibration plot reveals linearity within the conc. of 10 x10^{-5}M-50 x10^{-5}M with correlation coefficient of 0.998. LOD and LOQ are 13.23μM and 40.09μM as respectively.

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