

**Redox and Electron Charge Transfer Characteristics of Glassy Carbon Electrode Modified with Polyvinylpyrrolidone and Biosynthesized Silver Nanoparticles**S. Sandeep¹, A. S. Santhosh¹, N. Kumara Swamy^{1*}, N. A. Chamaraja², K. S. Nitin³

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Received: 12th June 2017; Revised 28th July 2017; Accepted 03rd August 2017**ABSTRACT**

In the present work, we have developed a metal nanoparticle and polymer framework (MNPPF) on glassy carbon electrode (GCE) using biosynthesized silver nanoparticles (AgNPs) and polyvinyl pyrrolidone (PVP), and investigated its redox and electron charge transfer behavior. The MNPPF is prepared on bare GCE by drop casting a layer of PVP on bare GCE electrode followed by deposition of biosynthesized AgNPs over PVP layer. The resulting GCE/PVP/AgNPs electrode is characterized using scanning electron microscopy and cyclic voltammetry (CV). Further, the redox behavior of bare and modified GCE electrode is studied by CV technique using 5 mM Fe(CN)₆^{3-/4-} as electrochemical probe in phosphate buffered saline (pH 7.0). The modified electrode showed better redox behavior compared to bare GCE electrode. The charge transfer process is studied by electrochemical impedance spectroscopy (EIS) measurements. The EIS results indicate lower charge transfer resistance (R_{ct}) for the GCE/PVP/AgNPs electrode compared to bare GCE electrode which is attributed to good conductive behavior of PVP and Ag. From this study, we conclude that the AgNPs and PVP-based MNPPF developed on bare GCE exhibit excellent redox and electron transfer characteristics; hence, it can find potential applications in sensors and electroanalytical instrumentation.

Key words: Biosynthesis, Modified glassy carbon electrode, Redox behavior.**1. INTRODUCTION**

Metal nanoparticle and polymer frameworks (MNPPFs) have attracted tremendous research interest as emerging porous materials, due to their structural diversity, flexibility, and tenability as well as high porosity. The conducting polymers serve as excellent electrode fabrication materials for electrochemical sensors because of their unique characteristics such as good compatibility, conductivity, electron promotion, and low cost [1,2]. However, not many single material modified electrodes are commercialized till date due to problems such as low sensitivity, poor selectivity, surface poisoning, and the interference from other species [3]. MNPPFs modified electrodes avoid some of these problems by providing some advantages such as efficient surface for the interaction between recognizing element and host matrix. MNPPFs are also very suitable to achieve the adequate sensitivity and stability because metal nanoparticles act as redox mediator of biomolecules, and polymer acts as selective adsorbate for biomolecules [2,4].

The research interest in metal nanoparticles such as silver nanoparticles (AgNPs) is motivated by their small size (1-100 nm), unique chemical, physical, and electronic properties and flexibility to construct novel and improved sensing devices [5]. In general, excellent conductivity and catalytic properties of metal nanoparticles make them suitable electrochemical catalysts to enhance the electron transfer between redox centers in target molecules and electrode surfaces. Formation of metal nanoparticle in a polymer matrix is a popular tool for design of new MNPPFs and the properties of polymer can be greatly altered by incorporating metal nanoparticles [1].

Polyvinylpyrrolidone is a water-soluble and long-chain polymer which has C=O, C-N, and CH₂ functional groups. It can be used as a surface stabilizer in nanoparticle synthesis. It has advantages such as nontoxicity, biocompatibility, high surface, and strong adsorption ability to the analyte which makes it a potential candidate for sensor application [6].

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The AgNPs are reasonably low-cost materials with good conductivity, catalytic property, and excellent antimicrobial and antifouling properties which make it a suitable metal nanoparticle for the electrode matrix. The biosynthesized nanoparticles provide additional safety due to their biocompatibility and environment-friendly attributes [5]. Motivated by these facts, the biosynthesized AgNPs and polyvinylpyrrolidone-based MNPPF is developed on bare glassy carbon electrode (GCE) electrode surface, and its charge transfer characteristics and redox behavior are investigated in the present study.

2. EXPERIMENTAL METHODS

2.1. Reagents and Instruments

The chemicals used in our experiments are purchased from Sigma Aldrich and Fischer Scientific. The ultraviolet (UV)-visible spectral studies are carried out using Shimadzu – 1800 UV-visible spectrometer. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies are performed using Biologic Science Instrument SP-150. The morphological characteristics of electrode surface is studied using ZEISS EV040EP (Germany) scanning electron microscope.

2.2. Biosynthesis of AgNPs

The AgNPs used in our experiments are biosynthesized using a procedure previously reported by our group [7]. For the synthesis of Ag nanoparticles, 10 ml of leaf extract of *Euphorbia geniculata* plant is added to 50 ml aqueous solution of 0.05 M AgNO₃ and the mixture is incubated at room temperature until the solution color changed from pale yellow-to-dark brown. The formation of Ag is monitored and confirmed through UV-visible spectroscopy by diluting a small aliquot of the reaction mixture with distilled water and measuring absorbance.

2.3. Modification and Surface Characterization of GCE Electrode

The GCE electrode surface is polished using PK-3 electrode polishing kit using diamond (1 μm) and alumina (0.05 μm) slurry and it is sonicated several times and dried with nitrogen gas.

The polyvinylpyrrolidone (PVP) polymer (2 mg/ml) is dissolved in deionized water, and then, uniformly dispersed on electrode by ultrasonication for 10-15 min. 5 μl of above PVP solution is later drop casted onto GCE electrode and it is dried at room temperature to get modified GCE/PVP electrode. Further, a suspension of biosynthesized AgNPs is prepared in by mixing 10 mg of AgNPs in 1 ml deionized water and 10 μl of this suspension is directly drop cast over the GCE/PVP electrode surface. The electrode is dried and stored at 4°C until it is used for further studies.

2.4. Electrochemical Studies

The electrochemical studies are carried out using a three electrode electrochemical cell with modified GCE as working electrode, saturated calomel electrode, and platinum wire are, respectively, used as reference and counter electrodes. The electrochemical properties of bare and modified GCE electrode are investigated by cyclic voltammetric method in phosphate buffered saline (PBS) of pH 7.0 while the redox behavior is studied in PBS (pH 7.0) using 5 mM Fe(CN)₆^{3-/4-} as electrochemical probe. The charge transfer process at electrode/electrolyte interface of modified electrode is studied using EIS technique in the frequency range of 100 MHz to 10 KHz.

3. RESULTS AND DISCUSSIONS

3.1. Biosynthesis of AgNPs

During the biosynthesis of Ag nanoparticles, the mixture of aqueous solution of AgNO₃ and leaf extract of *E. geniculata* plant gradually changed its color from pale yellow-to-dark brown. This visible color change indicates the formation of Ag nanoparticles through reduction of Ag⁺ ions to Ag⁰ in presence of leaf extract. The formation of Ag nanoparticles is further confirmed using UV-visible spectral measurements of reaction mixture. UV-visible spectrum showed a strong and broad peak in the wavelength range of 415-420 nm which suggests the formation of AgNPs (Figure 1).

3.2. Morphological Characteristics of Bare and Modified GCE

The GCE electrode is modified in successive steps by drop casting PVP and AgNPs. The surface morphology of modified electrode is studied using scanning electron microscopy (SEM) as an effective tool. Figure 2 shows the SEM images of GCE/PVP/AgNPs modified electrode. The SEM image indicates very bright powdery deposits correspond to AgNPs embedded in PVP matrix.

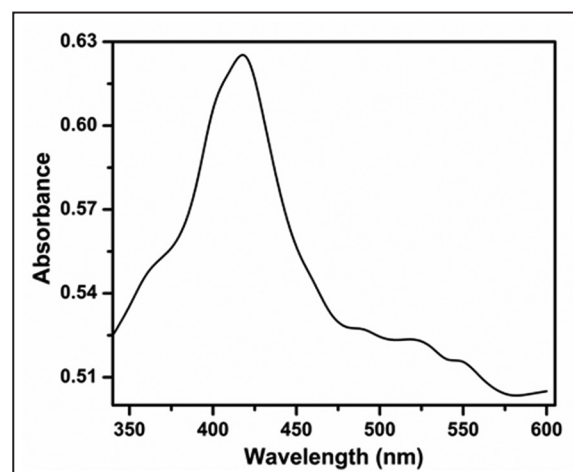


Figure 1: Ultraviolet-visible spectra of biosynthesized silver nanoparticles.

3.3. Redox Behavior of Bare and Modified GCE

The conductive behavior of bare GCE and modified electrodes is examined in PBS (pH 7.0) by CV and the CV results are shown in Figure 3. The CV plot shows that the conductivity of GCE electrode (Figure 3a) increased on the deposition of PVP (Figure 3b) due to the conductive character of PVP. The deposition of AgNPs further enhances the conductivity (Figure 3c) indicating that the modified GCE/PVP/AgNPs electrode provides excellent conductive surface compared to bare GCE and GCE/PVP electrodes.

The redox behavior of bare and modified GCE electrode is investigated in PBS (pH 7.0) by cyclic voltammetric method using 5 mM $\text{Fe}(\text{CN})_6^{-3/4}$ as a electrochemical probe. The cyclic voltammograms of Gr electrode obtained after each modification step are shown in Figure 4. The CV of GCE (Figure 4a) in 5 mM $\text{Fe}(\text{CN})_6^{-3/4}$ showed a pair of well-defined quasi-reversible redox peaks with a peak separation (ΔE_p) of

307 mV. The CV of GCE/PVP showed an increase in both oxidation and reduction current (Figure 4b) which is possibly due to good conducting properties of the polymer PVP. On further modification of GCE/PVP electrode with Ag nanoparticles, the resulting electrode (GCE/PVP/AgNPs) showed a further enhancement in enhanced oxidation and reduction current with decreased ΔE_p value of 107 mV (Figure 4c). This indicate that the GCE/PVP/AgNPs electrode surface provide easier penetration of $\text{Fe}(\text{CN})_6^{-3/4}$ ion toward its surface which help in its enhanced redox behavior.

3.4. Impedance and Charge Transfer Characteristics

The impedance and charge transfer characteristics of modified electrodes are studied by carrying out EIS measurements in a frequency range of 100 MHz to 10 KHz with amplitude of 5 mV. The Nyquist plot developed from EIS experimental data are shown in Figure 5. The Nyquist plot indicate a larger semicircle for the bare GCE electrode (a) while the successive modifications with PVP, (b) resulted in

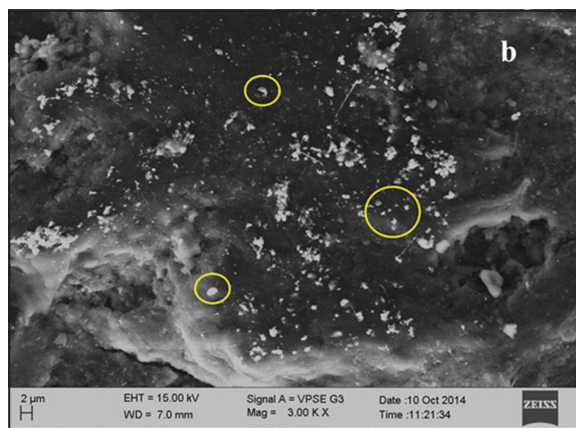


Figure 2: Scanning electron microscopy image of glassy carbon electrode/polyvinylpyrrolidone/silver nanoparticles electrode surface.

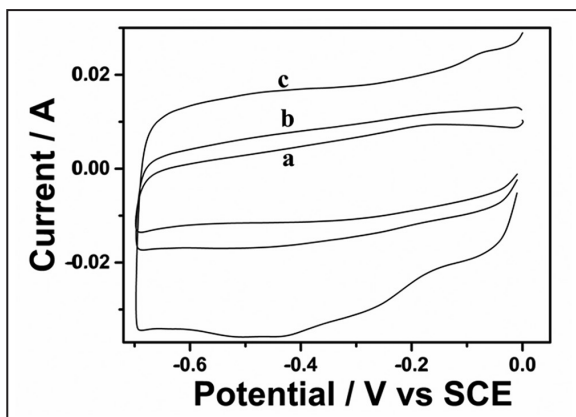


Figure 3: Cyclic voltammeters of phosphate buffered saline solution (pH 7.0) obtained at (a) bare glassy carbon electrode (GCE), (b) GCE/polyvinylpyrrolidone (PVP), (c) GCE/PVP/silver nanoparticles.

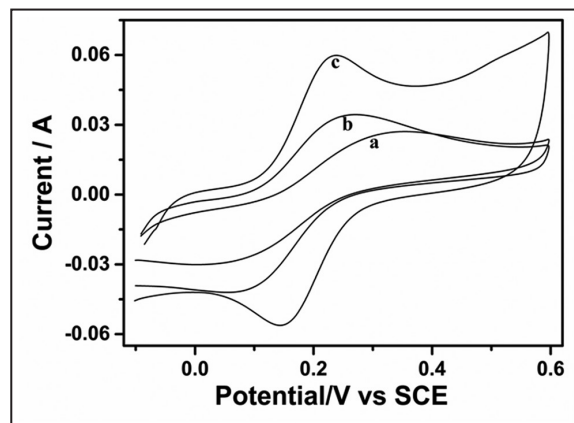


Figure 4: Cyclic voltammeters of 5 mM $\text{Fe}(\text{CN})_6^{-3/4}$ solution obtained at (a) bare glassy carbon electrode (GCE), (b) GCE/polyvinylpyrrolidone (PVP), (c) GCE/PVP/silver nanoparticles.

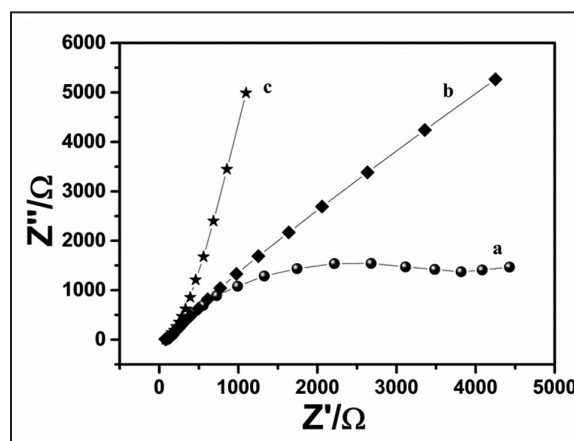


Figure 5: Impedance spectrum of (a) bare glassy carbon electrode (GCE), (b) GCE/polyvinylpyrrolidone (PVP), (c) GCE/PVP/silver nanoparticles.

Table 1: EIS data of bare GCE, GCE/PVP, GCE/PVP/AgNPs.

Electrode	Rs (Ω)	n	Rct (Ω)	Cf/F
Bare GCE	32.06	0.5	804	8.03×10^{-5}
GCE/PVP	35	0.5	709.2	3.65×10^{-5}
GCE/PVP/AgNPs	34.5	0.7	351.1	4.45×10^{-5}

GCE=Glassy carbon electrode,
PVP=Polyvinylpyrrolidone, AgNP=Silver nanoparticles,
EIS=Electrochemical impedance spectroscopy

reduced semicircle and modification with AgNPs, and (c) revealed almost straight line, implying reduced R_{ct} due to the superior conductivity of AgNPs. This indicates that modification enhanced the electrical conductance of the electrode surface.

Various parameters such as charge transfer resistance (R_{ct}), solution resistance (R_s), number of electrons transferred (n), and Faradaic capacitance (C_f) calculated by fitting Randles equivalent circuit are shown in Table 1. The calculated charge transfer resistance of bare GCE is much higher compared to that of GCE/PVP electrode. The reduced R_{ct} value for GCE/PVP may be attributed to increased surface area of electrode due to deposition of polymer. The modified GCE/PVP/AgNPs showed a further decrease in R_{ct} value indicating that the rate of electron transfer is increased due to incorporation of Ag to electrode surface. In other words, the developed MNPPF on GCE is stable and it immensely contributed to the enhanced electron transfer and redox behavior of modified GCE electrode.

4. CONCLUSIONS

In the present work, we have developed a MNPPF on GCE using biosynthesized AgNPs and PVP and investigated its electron charge transfer and redox behavior. The results of the study indicated that the MNPPF development on GCE electrode has immensely enhanced the conductive and electron transfer properties of the electrode. These properties are possibly due to conductive nature of both PVP and AgNPs. Further, the modified electrode (GCE/PVP/

AgNPs) showed excellent stability and redox behavior with a very high electron transfer rate as apparent from the increased peak currents and reduced peak separation. Based on these results, we claim that the developed (GCE/PVP/AgNPs) electrode exhibited all the characteristics of an efficient electrode and it can find potential applications in sensor development.

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