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ELECTROCHEMICAL STUDY OF MODIFIED GLASSY CARBON ELECTRODE WITH POLYANILINE NANOPARTICLES USING CYCLIC VOLTAMMETRY

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ABSTRACT. The mechanical attachment method was used to modify the glass carbon electrode (GCE) with polyaniline nanoparticles (PANI NPs) to produce a new nanosensor (PAN NPs/GCE). Electrochemical properties was studied by a new nano working electrode using cyclic voltammetric (CV) technique to develop the oxidation – reduction reaction. $K_4[Fe(CN)_6]$ solution is one of the standard solutions for CV titration by redox peak current of FeII/FeIII in KCl solution as electrolyte, which can be used to study different concentrations, scan rates, pH, diffusion coefficient (Df) and reliability and stability PAN NPs/GCE modified electrode. The CV results of the new PANI NPs/GCE nanosensor have two peaks at 400 and 200 mV for oxidation-reduction FeII/FeIII, respectively. The current ratio value of the new PAN NPs/GCE was found to be $I_{pa}/I_{pc} \approx 1$ with a separation peak of $\Delta E_{pa\text{-}pc} = 200$ mV. From these results, the nanosensor acts as an irreversible and heterogeneous reaction. Other electrochemical properties of the new sensor have a low detection limit of $K_4[Fe(CN)_6]$. In addition to the highly enhancement of the redox peak current in acidic pH, it was obtained good stability of nanomaterial on the electrode.

KEY WORDS: Polyaniline nanoparticles, GCE, $K_4[Fe(CN)_6]$, Redox process, Cyclic voltammetry

INTRODUCTION

Cyclic voltammetry (CV) is one of the most effective and versatile electroanalytical tools and it has very popular for initial electrochemical studies. Because of measurement ease, CV was used in the fields of electrochemistry, inorganic chemistry, organic chemistry and biochemistry. CV is used for study of electrochemical reactions on an electrode surface. In this studied, CV is very popular for initial electrochemical studies of new systems and interference reactions. The determination of the mechanisms of oxidation - reduction reactions can be achieved through a different of electrochemical methods. Cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox reactions [1-5]. Polyaniline (PANI) is defined as one of the conductive polymers was used in energy storage and conversion devices in addition to carbon materials and metallic compounds. PANI was used in fabricating electrodes [6]. Poly(aniline) (PANI) is an important conducting polymer because of its good environmental, chemical and thermal stability and easy preparation. The conducting polymer that can be grown chemically or electrochemically from suitable oxidizable monomers have recently attracted much attention due to its many applications [7]. Polyaniline nanoparticles (PANI NPs) can be obtained from the solvent displacement method by using N-methylpyrrolidone (NMP) as good solvent and water as poor solvent. Different polymers was used as stabilizers such as polyvinyl pyrrolidone (PVP), chondroitin sulfate (ChS), polyvinyl alcohol (PVA), and polyacrylic acid (PAA) [8]. Polyaniline (PANI) with graphene oxide (GO) nanocomposites were prepared by

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hydrothermal method. GO was reduced to rGO under high temperature and high pressure and converted aniline to PANI in situ polymerization by using ammonium persulfate. Characterization of PANI/rGO was used SEM, FTIR. Grown PAN-NFs on rGO sheets, prevent aggregate of rGO. In this study, synthesis of PANI-NFs/rGO nanocomposites by using hydrothermal method. Go was reduced to rGO and act as substrate and PANI is formed and acts as spacer. PANI-NFs/rGO nanocomposites exhibited solid structure. High conductivity of rGO and high ion transport, the PANI/NFs/rGO nanocomposites exhibited electrochemical and capacitance properties [9]. The microstructure of PANI/G mixture was characterized by SEM, TEM, and EDX. Modification of glassy carbon electrodes was prepared by PANI/G nanocomposite to detect heavy metal ions. Polyaniline (PANI) can be used to modified GCE to detect heavy metal ions. But PANI has less sensitivity in detecting heavy metal ions than PANI/G. In this studied, detection of heavy metal ions in aqueous phase was studied by development of PANI/G and modified anodic stripping voltammetry. Situ polymerization was used to PANI/G synthesize and characterization of PANI/G microstructure. PANI improved the sensitivity of the graphene [10].

The aim of this work is to study the glassy carbon electrode modified with polyaniline nanoparticles (PANI NPS /GCE) by cyclic voltammetric technique as modified nanomaterials to find the electrochemical behavior of Fe(II)/Fe(III) in KCl as an electrolyte. The study was conducted at different concentrations, pH, scan rates and the reliability – stability of the nanoparticles on glassy carbon electrode.

EXPERIMENTAL

Chemicals

Polyaniline nanoparticles received from Panichem Co, Ltd, Korea, $K_4[Fe(CN)_6]$ and potassium chloride (KCl 98%) received from Sinopharm Chemical Reagent Co, Ltd. (SCRC) (China), NaOH, and 0.1 N HCl solution from BDH Company were used as received. Deionised water was used in this work.

Cyclic voltammetry cell

Cyclic voltammetry is a technique utilized for electrochemistry study of typical electrochemical reaction, an electrode surface. Voltammetric measurements were done by use of an electrochemical cell (size 15 mL) including three electrodes immersed in KCl solution. The cyclic voltammetric cell consisted of quartz container. Contain a cap with holes for the entry and outlet of nitrogen gas and three electrodes, working electrode, reference electrode, and auxiliary electrode.

Preparation of PAN NPs/GCE

GCE (working electrode) was modified with PANI NPs/GCE using mechanical attachment method. The clean GCE surface was polished by ultrasonic bath and dried with hair dryer at room temperature [10].

Apparatuses

Potentiostat type EZstat series Potentiostat/Galvanostat, NuVant Systems Inc. USA was used for all the experiments. Three electrodes (PANI NPs/GCE as a working electrode, silver/silver chloride as a reference electrode (Ag/ AgCl in 3 M KCl), and a platinum wire with the diameter of 1 mm as an auxiliary electrode) were connected to a potentiostat and with cell of CV also connected with personal computer. Before modification of the GCE, it must be cleaned with

polishing and treated with ultrasonic path water for 10 min. Mechanical attachment method was used to modify the GCE with PAN NPs [11].

Atomic force microscopy (AFM)

AFM is a technique which can be used to characterize materials on the nanometer scale and gain information about the surface morphology. AFM images were obtained from measurement of the force on sharp tip over surface of the sample generated on computer. AFM probe tip is very sharp, a pyramidal silicon nitride tip is used with a curvature radius on the order of 100 Å [12, 13]. The main objective of using AFM in this work is to determine the morphology of PANI.

AFM technique is good method for identified the diameter of nanoparticles. The diameter of polyaniline nanoparticles was determined by AFM which found as average dimension of 58 nm as shown in Figure 1.

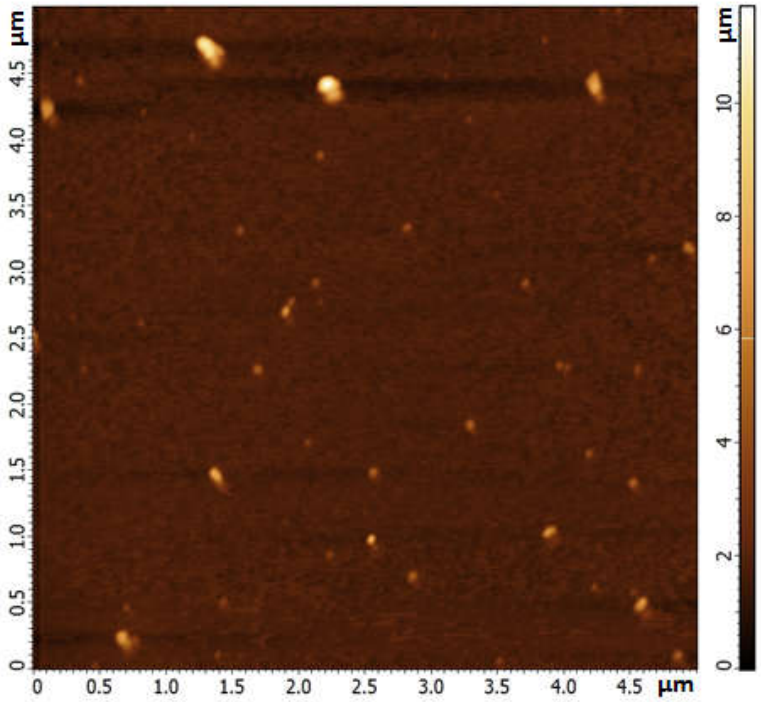

Figure 1. Atomic force microscopy (AFM) of the polyaniline nanoparticles (PAN NPs).

RESULTS AND DISCUSSION

Polyaniline nanoparticles (PANI NPs) as a modified nano-material on the glassy carbon electrode (GCE) was used as a new sensor and electrochemical characterize using $K_4[Fe(CN)_6]$ in an electrolyte (1 M KCl) at different concentrations, scan rates, pH, and stability study on the new sensor.

Calibration curve

The new nano-polymer sensor (PANI-NPs/GCE) was provided as a high sensitive working electrode by cyclic voltammetric technique, ferrous ions $K_4[Fe(CN)_6]$ was used for the determination of detection limit by the oxidation-reduction peak current as shown in Figure 2. The calibration curve of the oxidation-reduction peaks FeII/FeIII was found in Figures 3 and 4, respectively. The low detection limit of the reduction peak for different concentrations of Fe ions at 0.06 to 0.18 mM with equations of reduction peak:

$y = 131x + 4.84$, and $R^2 = 0.4853$

and for oxidation peak:

$y = 119.64\ x + 10.843$, and $R^2 = 6345$

The relationships of the redox current of Fe ions against to the different concentrations confirm that increasing the concentration enhanced the conductivity by the current of the sensor in the electrolyte (KCl) [14].

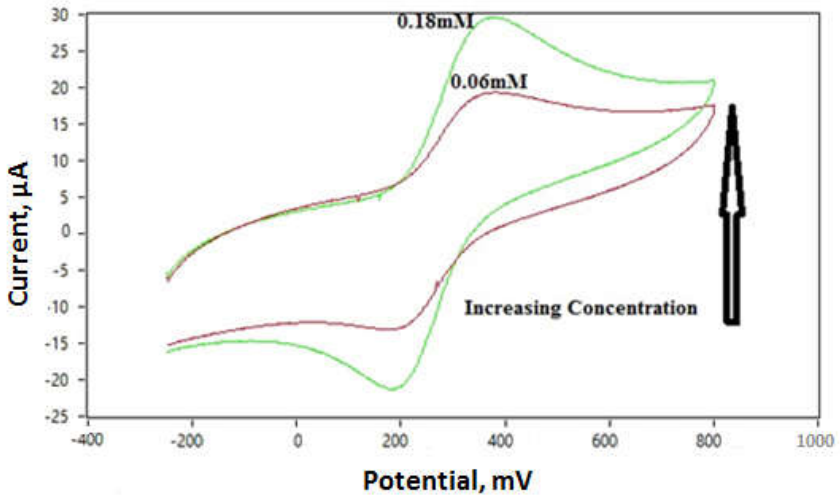

Figure 2. Cyclic voltammogram of different concentration (0.06–0.2 mM) of $K_4[Fe(CN)_6]$ in 1 M KCl solution on the modified electrode (PANI NPs/GCE) at Ag/AgCl as reference electrode and scan rate of 0.1 Vs^{-1}.

Effect of different scan rate

The scan rate difference was studied from 0.01 to 0.1 Vs^{-1} for the oxidation-reduction current peaks of FeII/FeIII in the 1M KCl solution as an electrolyte on the modified electrode (PANI NPs/GCE) as shown in Figure 5. The redox current peaks of FeII/FeIII were enhanced by increasing the scan rate. The diffusion layer at a slow voltage scan grows much further from the electrode in comparison to a fast scan rate. Thus, at slow scan rates, the flux to the electrode surface is smaller than it is at faster scan rates. The current becomes least at slow scan rates and higher at high scan rates because the current is proportional to the flux towards the electrode [15].

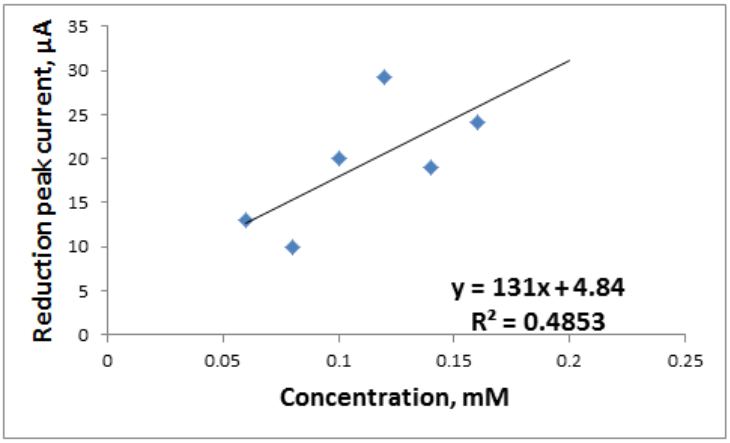

Figure 3. Relationship between cathodic peak current of different concentration (0.06-0.2) mM of $K_4[Fe(CN)_6]$ in 1 M KCl.

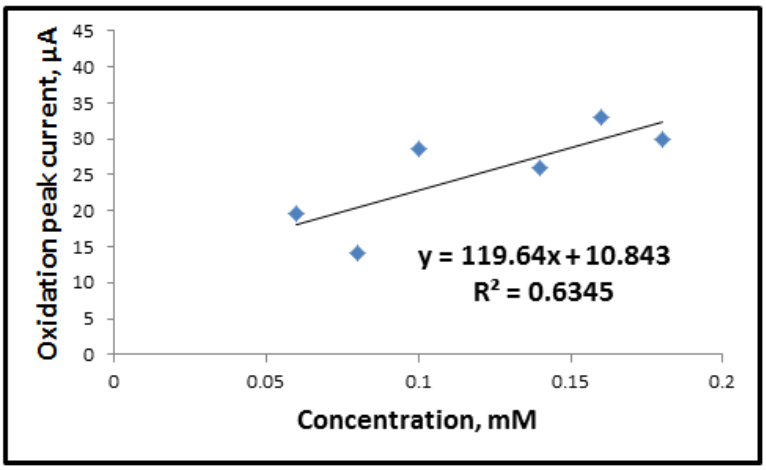

Figure 4. Relationship between anodic peak current of different concentration (0.06-0.2) mM of $K_4[Fe(CN)_6]$ in 1 M KCl.

The relationship between anodic current peak (I_{pa}) versus the scan rate (SR) and cathodic current peak (I_{pc}) versus SR are shown in Figures 6 and 7, respectively. It was shown that the current increases linearly with the scan rate for both the oxidation and reduction current. A straight line relationship was obtained from Figures 6 and 7, which represent I_{pa} and I_{pc} against to the SR with the equations $y = 175.5x + 7.3083$, $R^2 = 0.9891$ and $y = 135.7x + 6.2094$, $R^2 = 0.9781$, respectively [16].

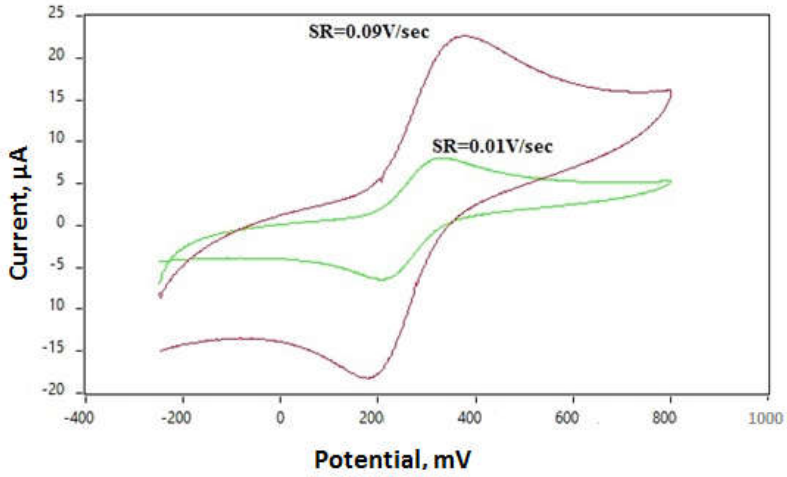

Figure 5. Cyclic voltammogram of oxidation-reduction for FeII/FeIII in 1 M KCl solution on (PANI NPs/GCE) at different scan rate (0.01-0.1 Vs^{-1}).

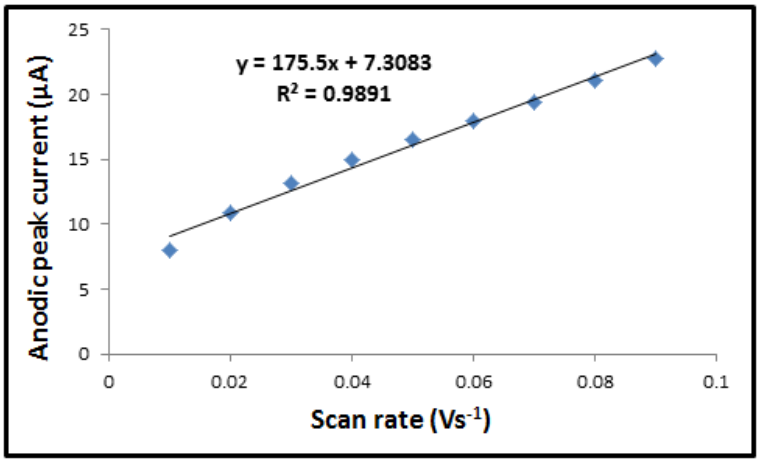

Figure 6. Relationship between anodic peak current versus different scan rates.

Diffusion Coefficient Determination

Randles-Seveik equation can be used to determination the diffusion coefficient value, which is described as the reversible oxidation-reduction current peaks was found [17, 18]:

$$I_p = (2.69 \times 10^5)\, n^{3/2}\, AC\, D_f^{1/2}\, V^{1/2} \quad (1)$$

where, I_p denotes the current peak, as n and A indicates the number of electrons moles that transferred in this reaction and the electrode area (cm^2), respectively. D_f and V indicate the diffusion coefficient (cm^2/s) and its applied potential (v/s), respectively. The diffusion coefficient

values of oxidation-reduction reaction for Fe(II)/Fe(III) ions in KCl solution on PANI NPs/GCE was determined as $D_{fa} = 5.127 \times 10^{-5}$ cm^2/s and $D_{fc} = 1.676 \times 10^{-5}$ cm^2/s, respectively. Figures 8 and 9 show the relationship of anodic and cathodic peak current of Fe(II)/Fe(III) on the sensor of PANI nanoparticles on GCE with the different scan rates in the voltammetric technique respectively, the diffusion coefficient values of the oxidation-reduction reaction of FeII/FeIII on the new sensor (PANI NPs/GCE) has nearly equal values which indicated the reversible process of iron ions [19].

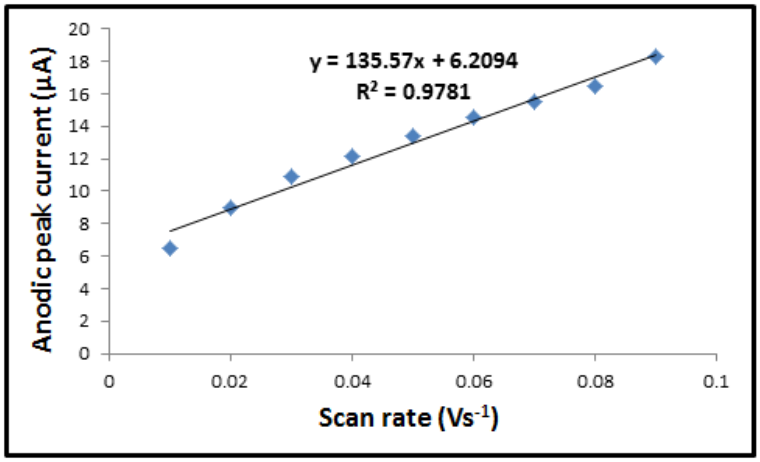

Figure 7. Relationship between cathodic peak current versus different scan rates.

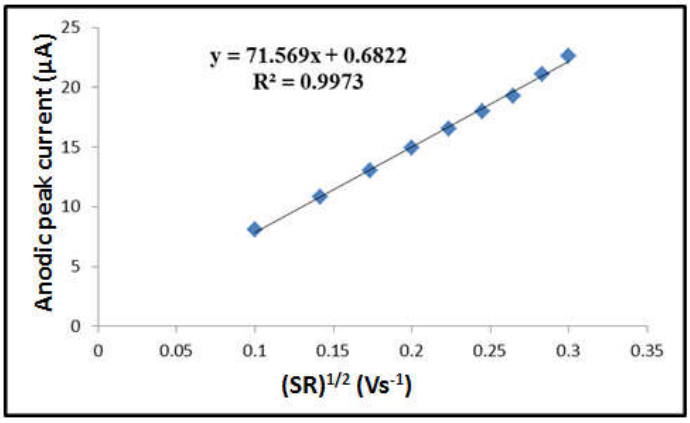

Figure 8. Relationship between anodic current peak of FeII/FeIII in KCl on the PANI NPs/GCE against to square root of scan rate.

Effect of different pH

Characterization studies of the modified electrode PANI NPs/GCE are electrochemical properties by different pH each of acidic and alkaline media. The redox current peaks of 0.2 mM

K4[Fe(CN)6] on the nano sensor has the relationship between the anodic and cathodic peak current of Fe(II)/Fe(III) with different pH (2-8). It was found from the results that acidic medium act as electrochemical catalyst which enhanced the redox peaks, while alkaline medium has inverse properties that decreased the redox current [20].

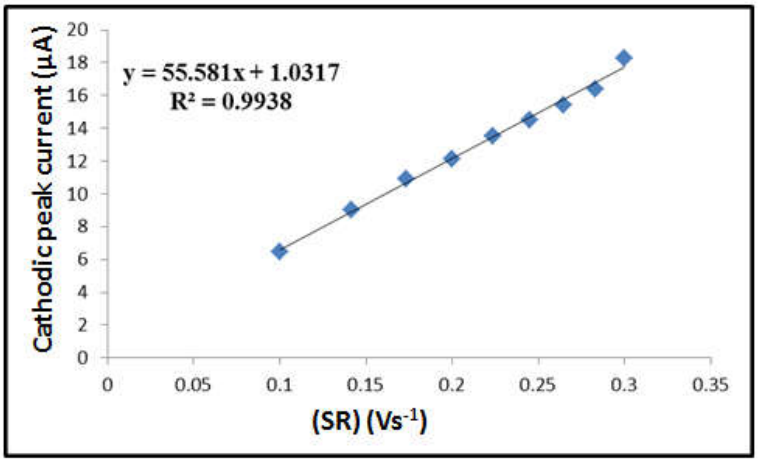

Figure 9. Relationship between anodic current peak of FeII/FeIII in KCl on the PANI NPs/GCE against to square root of scan rate.

Reliability and stability study

The new modified GCE with polyaniline nanoparticles (PANI NPs) was studied the stability in KCl electrolyte using cyclic voltammetry by the reliability with ten times of scanning as shown in Figure 10. The relative standard deviation (RSD) was determined for each oxidation and reduction current peaks of FeII/FeIII on PANI NPs/GCE are ± 0.261% and ± 0.214%, respectively [21].

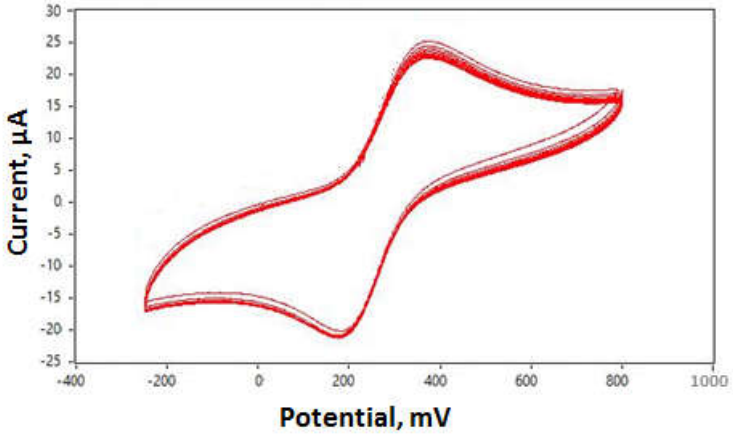

Figure 10. Cyclic voltammogram of ten times scanning for FeII/FeIII on PANI NPs/GCE in KCl as an electrolyte.

CONCLUSION

Polyaniline nanoparticles were studied by cyclic voltammetry technique as modified nanomaterials to find the electrochemical behavior of Fe(II)/Fe(III) in KCl as electrolyte. The study involved various concentrations, pH, scanning rates and a study of the reliability and stability of nanoparticles on a glassy carbon electrode. It can be concluded that the new nanosensor prepared in this study has good electrochemical properties which have high electrical conductivity by enhancing the comparison of the redox current peaks with GCE. PANI NPS/GCE has a low detection limit for iron ion concentration in KCl which found a range of 0.06-0.18 mM. It was also found that the acidic pH = 2 acts as electrochemical catalyst by enhanced the redox current peaks of iron ions. Moreover, the study demonstrated that the stability of the nanopolymer on the surface of GCE has high reliability results with the RSD of the redox peaks having values of ±0.261% and ±0.214%, respectively.

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