Nano Biomed Eng
2018, 10(1): 10-15. doi: 10.5101/nbe.v10i1.p10-15.

Research Article

Electrochemical Characterisation of the Redox Couple of Fe(II)/Fe(III) Mediated by Nano SiO_2 Modified GCE Using Cyclic Voltammetry

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Received: Dec. 4, 2017; **Accepted:** Jan. 14, 2018; **Published:** Feb. 13, 2018.

Citation: Muhammed Mizher Radhi, Ahmed Ali Moosa, and Ishraq Abd-Alkareem Khalaf, Electrochemical Characterisation of the Redox Couple of Fe(II)/Fe(III) Mediated by Nano SiO_2 Modified GCE Using Cyclic Voltammetry. *Nano Biomed. Eng.*, 2018, 10(1): 10-15.
DOI: 10.5101/nbe.v10i1.p10-15.

Abstract

A new modified working electrode of glassy carbon electrode with nanoparticles of SiO_2 (SiO_2 nanoparticles/GCE) was prepared by mechanical attachment method. The modified electrode (SiO_2 nanoparticles/GCE) was characterised by electrochemical analysis using cyclic voltammetric technique to evaluate this electrode as nano-sensor. A standard solution of 1 mM $K_4[Fe(CN)_6]$ with 1 M KCl as an electrolyte was used to study the redox current peaks of FeII/FeIII ions on the modified electrode at different concentrations, scan rates, pH, determination of diffusion coefficient (D_f), reliability and stability of the modified electrode. It was found the new nano-sensor (SiO_2 nanoparticles/GCE) had enhancement for the oxidation and reduction current peak of FeII/FeIII ions of about 1.29 and 1.58 µA, respectively. The current ration value of the new modified electrode was I_{pa}/I_{pc} = 1.7 with the peak separation of $\Delta E_{pa\text{-}c}$ = 140 mV, which demonstrated that the new modified electrode acted in electrolyte as irreversible and heterogeneous reaction, had low detection limit, and enhanced the redox current peaks in acidic pH with good reliability and stability of nanoparticles on the surface of GCE.

Keywords: SiO_2 nanoparticles; Cyclic voltammetry; GCE; FeII/FeIII; KCl

Introduction

Scientists studied different modified working electrodes with nanoparticles to produce high-quality sensors with low detection limit by cyclic voltammetry [1-6].

Silica (SiO_2) nanoparticles were studied by electrochemical method and micro-calorimetry; the particles interacted with the monolayer of dioleoyl phosphatidylcholine on a mercury (Hg) film electrode. The result illustrated that the extent of interaction was inversely proportional to the particle dimeter. Scanning electron microscopy (SEM) images showed that the nanoparticles bound to the dioleoyl phosphatidylcholine [7]. Different photo-luminescent SiC-dots/SiO_2 were synthesised by heating reaction, and the electrochemical application was studied. The electrical properties of the photoluminescence were found stable, low-toxic, low-cost and with great economic potential in many applications such as light-emitting diodes, photo-luminescent windows and fuel cells [8]. Through the electrochemical method, a silicon layer was synthesised on a molybdenum (Mo) electrode in a $CaCl_2$ which melt containing silicon oxide (SiO_2) nanoparticles at 850 °C. The oxidation of electrode-posited silicon in $CaCl_2$ melt, producing a redox couple at positive potentials of the deposition potential [9]. SiO_2 nanotubes were fabricated by hard-template growth method and evaluated as an anode for Li-ion batteries. The high-aspect-ratio character of these nanotubes allows for a relatively scalable fabrication method of nanoscale SiO_2-based anodes [10]. Silicon dioxide thin films were studied with Cu/Cu^+ by cyclic voltammetry. The diffusion coefficient and the mobility of Cu ions in SiO_2 were calculated [11]. The synthesis of polyaniline-SiO_2 composites by chemical oxidation polymerisation was carried out in the presence of phosphoric acid and was evaluated for protection of mild steel from corrosion in strong aggressive medium. A higher protection efficiency up to 99% was achieved [12].

In this study, silicon dioxide nanoparticles were used as modified materials on the glassy carbon electrode (GCE), and the electrochemical characterisation was carried out by cyclic voltammetric method.

Experimental

Materials and methods

Nano silica (20-30 nm, Hongwu International Group Ltd, China), KCl powder (SCRC, China), NaOH (BDH Company), 0.1 N HCl solution and deionise water were used in this work.

Apparatus and method

Potentiostat (EZstat series Potentiostat/Galvanostat, NuVant Systems Inc. USA) was used in the experiment. The electrochemical bio-analytical cell was connected to a potentio-stat device and monitored by the special software to perform cyclic voltammetry (CV). Silver/silver chloride reference electrode (Ag/AgCl in 3 M NaCl) was used as a reference electrode, and a platinum wire with the diameter of 1 mm as an auxiliary electrode. The GCE was used in this study after being cleaned with alumina solution and treated with ultrasonic path water for 10 min; the other working electrodes were modified by GCE with nanoparticles of SiO_2 using mechanical attachment method by doping GCE with SiO_2 nanoparticles [13]. The three electrodes were immersed in cyclic voltammetric cell (10 mL) with the solution. Throughout this paper, the modified GCE with nano-silica particles will be referred to as SiO_2 nanoparticles (NPs)/GCE.

Results and Discussion

Enhancement of different electrodes

Different electrodes were used in electrochemical analysis by cyclic voltammetry for GCE and SiO_2 NPs/GCE to be characterised by standard solution of 1mM $K_4[Fe(CN)_6]$ with 1 M KCl as an electrolyte. Fig. 1 illustrates the oxidation-reduction current peaks of FeII/FeIII ions on GCE and SiO_2 NPs/GCE, which shows an enhancement of both redox current peaks at modified GCE with SiO_2 NPs. This nanoparticle-layer of SiO_2 on the surface of GCE acted as an electro-catalyst as revealed in Table 1 [14].

Table 1 shows the enhancement of oxidation-reduction current peaks of FeII/FeIII ions in KCl solution as an electrolyte on two different electrodes. For GCE and SiO_2 NPs/GCE electrodes, the oxidation-reduction enhancement of the current peak of FeII/FeIII are 1.3 and 1.6 fold, respectively. The oxidation current peak was shifted to lower potential and the reduction peak to higher potential [15-17].

Calibration graph

The characterisation of the new modified working electrode nano SiO_2/GCE was carried out with different

Table 1 Anodic and cathodic current peaks enhancement of modified electrode

	Anodic peak		
SiO_2 NPs/GCE	I_{pa} = 69.2	E_{pa} = 339 mV	Enhancement =1.3
GCE	I_{pa} = 53.6	E_{pa} = 339 mV	
	Cathodic peak		
SiO_2 NPs/GCE	I_{pc} = −41.2	E_{pc} = 199 mV	Enhancement=1.6
GCE	I_{pc} = −26.1	E_{pc} = 157 mV	

concentrations of standard solution of $K_4[Fe(CN)_6]$ in 1 M KCl as the supporting electrolyte to determine the calibration curve and to calculate the detection limit of the nano sensor. Fig. 2 illustrates the cyclic voltammogram of the low and high concentrations (4-19 mM) of $K_4[Fe(CN)_6]$ for the modified electrode nano SiO_2/GCE to find the oxidation-reduction current peak of FeII/FeIII. Fig. 3 & 4 show the calibration graph of the oxidation-reduction peak by equations y = 0.0397x + 3.1017 with the sensitivity of R^2 = 0.8508, and y = 0.0806x + 2.3135 with R^2 = 0.9295, respectively. The new modified electrode SiO_2 NPs/GCE had good detection limit, and so it can be used in the electrochemical analysis of samples of material traces in different concentrations. This is in agreement with the work by Orata et al. [18].

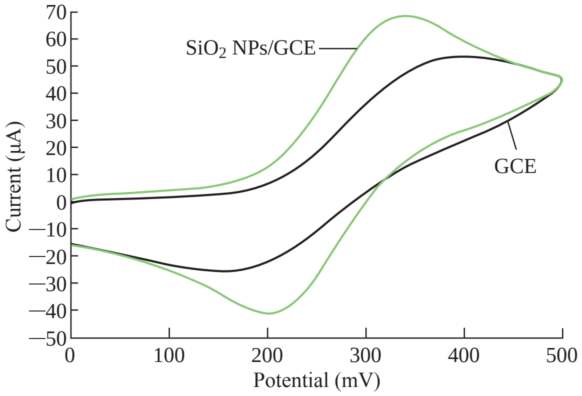

Fig. 1 Cyclic voltammogram of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on GCE and SiO_2 NPs/GCE versus Ag/AgCl as reference electrode and 100 mV/sec.

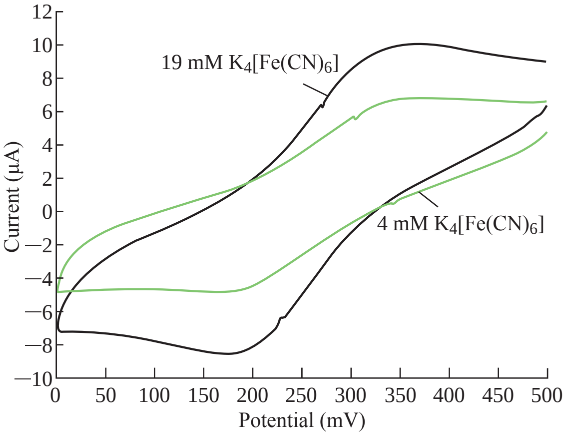

Fig. 2 Cyclic voltammogram of $K_4[Fe(CN)_6]$ at different concentration (4-19 mM) in 1 M KCl on SiO_2 NPs/GCE versus Ag/AgCl as reference electrode and 100 mV/sec.

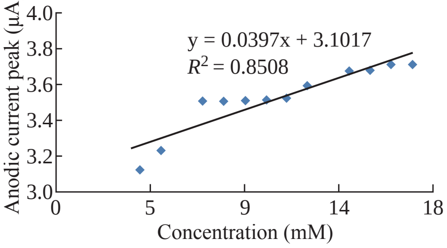

Fig. 3 Relationship between anodic current peak at different concentration of $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE.

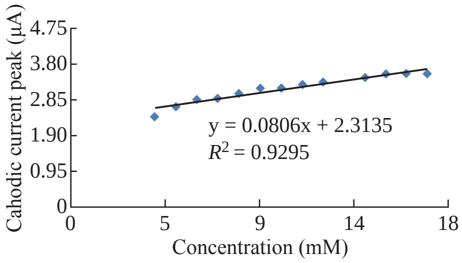

Fig. 4 Relationship between cathodic current peak at different concentration of $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE.

Effect of scan rate (SR)

One important study in cyclic voltammetric technique is the different scan rates on SiO_2 NPs/GCE which effected on the redox current peaks of FeII/FeIII ions by enhancing the oxidation current peak from 23.2 to 68.7 μA at scan rate 0.1 V/sec, and for reduction

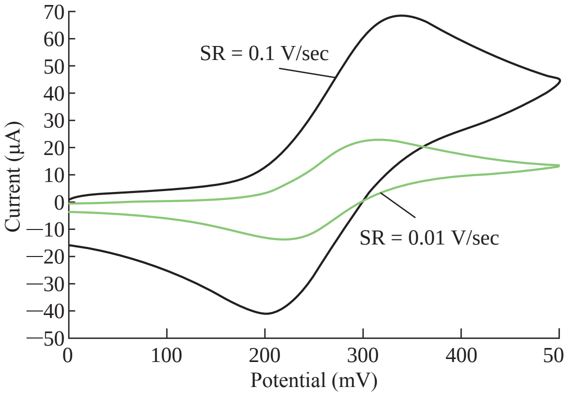

Fig. 5 Cyclic voltammogram of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on modified SiO_2 NPs/GCE versus Ag/AgCl as reference electrode at different scan rate (0.01-0.1 V/sec).

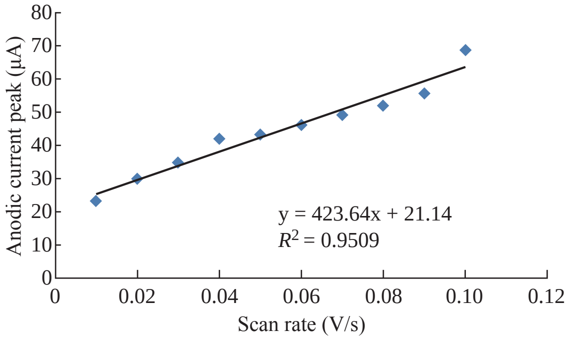

Fig. 6 Relationship between the oxidation current peak of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE versus different scan rate (0.01-0.1 V/sec).

current peak from –14.2 to –41.2 μA at scan rate 0.01 V/sec as shown in Fig. 5.

Fig. 6 shows the relationship between the oxidation current peak against the scan rate as in the equation $y = 423.64\ x + 21.14$ with a good sensitivity of $R^2 = 95.09$. Fig. 7 shows the reduction current peak of FeIII/FeII as in the equation $y = 264.06\ x + 15.747$ with a good sensitivity of $R^2 = 9155$. This is in agreement with the work done by of Orata et al. and Abdullah et al. [18, 19].

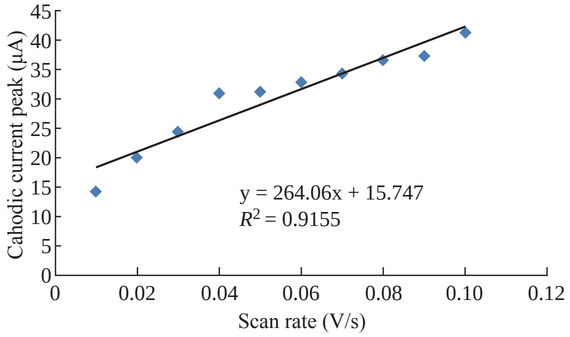

Fig. 7 Relationship between the reduction current peak of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE versus different scan rate (0.01-0.1 V/sec).

Diffusion coefficient determination

The diffusion coefficient of the redox process for FeII/FeIII ions in the 1 M KCl as an electrolyte was calculated from the Randles-Seveik equation which describes it as a reversible redox couple [20, 21].

$$I_p = (2.69 \times 10^5)\ n^{3/2}\ A C\ D_f^{1/2}\ v^{1/2} \qquad (1)$$

where, I_p is the current peak (μA), n is the number of moles of electrons transferred in the reaction, A is the area of the electrode (cm^2), Df is the diffusion coefficient (cm^2/sec), and V is the scan rate of the applied potential (V/sec)..

It was found the diffusion coefficient of oxidation-reduction reaction of FeII/FeIII ions in KCl solution on SiO_2 NPs/GCE was $D_{fa} = 2.0 \times 10^{-5}$ and $D_{fc} = 7.3 \times 10^{-6}$ cm^2/sec respectively, while the diffusion coefficient values of the oxidation-reduction ions on GCE were $D_{fa} = 1.1 \times 10^{-5}$ and $D_{fc} = 1.9 \times 10^{-6}$ cm^2/sec. The diffusion coefficient on the modified electrode was higher than on the GCE, which indicated that the thin film of nano-materials on the surface of working electrode acted as an electro-catalyst in the electrolyte [22].

Different pH study

It is scientifically known that different pH values effect directly on the oxidation-reduction current peaks of FeII/FeIII ions in KCl as electrolyte on nano-sensors SiO_2 NPs/GCE [23]. The electrochemical analysis of FeII/FeIII ions in both acidic (pH = 2) and alkaline (pH = 12) is shown in Fig. 8, which reveals the acidic medium enhanced redox current peaks about two folds than that in alkaline medium. Hence, acidic pH acted as an electro-catalyst on the surface of GCE by SiO_2 NPs layer. Fig. 9 & 10 show the electrochemical behaviour of oxidation-reduction current peaks of FeII/FeIII ions in acidic and alkaline media respectively [24]. But both redox current peaks began to decline gradually after

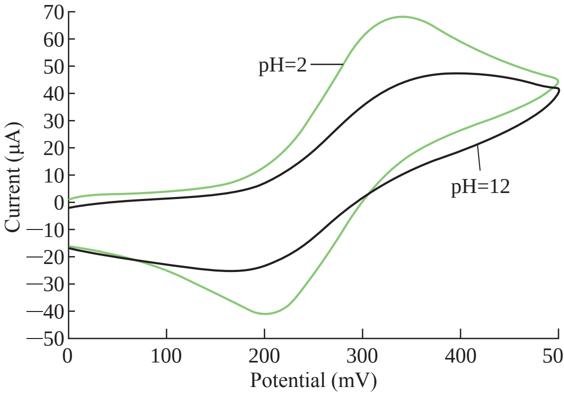

Fig. 8 Cyclic voltammogram of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on modified SiO_2 NPs/GCE at different pH (2-12).

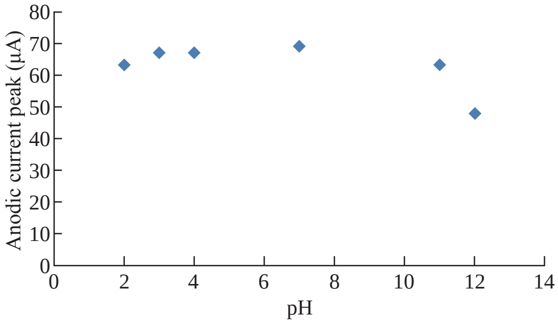

Fig. 9 Relationship between the oxidation current peak of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE versus different pH (2-12).

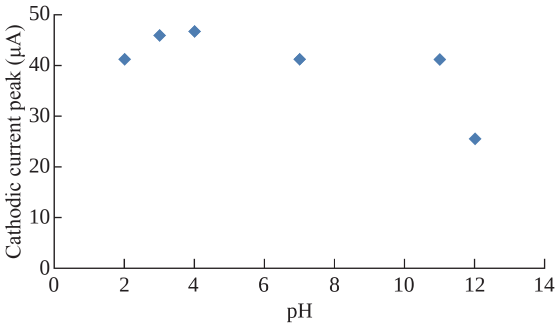

Fig. 10 Relationship between the reduction current peak of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE versus different pH (2-12).

the rise of pH to 12 due to the bulky molecule and the difficulty of transmission through the electrolyte [25].

Reliability and stability study

Fig. 11 shows the reliability and stability of nanoparticles of SiO_2 on the surface of GCE in electrolyte using cyclic voltammetric technique. The relative standard deviation (RSD) was determined from the range of oxidiation-reduction current peak values at 10 times by cycling voltammogram with accepted results of ± 0.5% and ± 0.61%, respectively which was in agreement with the work of Karimi et al. and Naseri et al. [25, 26].

Transmission Electron Microscopy (TEM) study

Fig. 12 shows the morphology structure of SiO_2 NPs by TEM. It was found that the spherical shape of nanoparticles was in fine picture with dimeters of 20-30 nm.

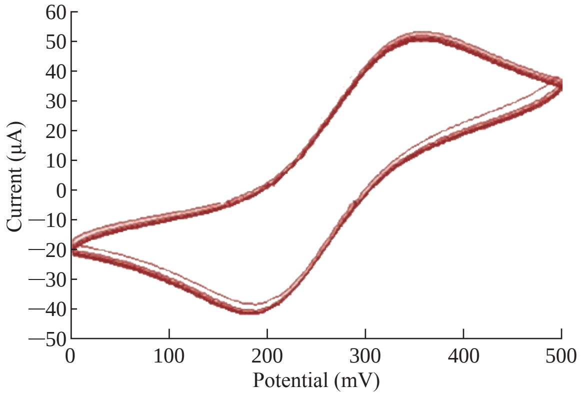

Fig. 11 Cyclic voltammogram of 1 mM $K_4[Fe(CN)_6]$ in 1 M KCl on SiO_2 NPs/GCE at ten times.

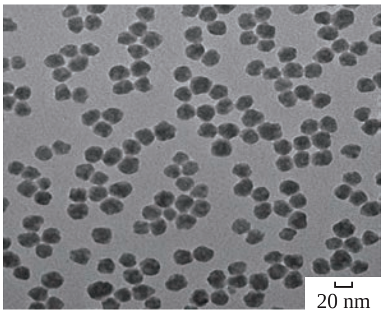

Fig. 12 TEM of SiO_2 NPs.

Conclusions

It can be said that the modified working electrode as prepared in the laboratory, the nano-sensor SiO_2 NPs/GCE, had good electrochemical properties in the cyclic voltammetric analysis. The results also indicated that the new modified electrode had good reliability, stability, high enhancement in conductivity and low detection limit, acted as electro-catalyst in acidic pH, and showed irreversible heterogeneous process in aqueous solution. Diffusion coefficient values of redox current peaks of FeII/FeIII ions on the modified electrode were calculated from Randel equation, which was $D_{fa} = 2.0 \times 10^{-5}$ cm^2/sec and $D_{fc} = 7.3 \times 10^{-6}$ cm^2/sec. It appeared that the silica micro-particles were non-conductive, but conductive in their nano dimeter, and the conductivity of the working electrode was enhanced in cyclic voltammetry.

Conflict of Interests

The authors declare that no competing interest exists.

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