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Electrochemical Characterization of Redox FeII/FeIII Mediated by ZrO_2NPs/GCE Using Cyclic Voltammetry

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Abstract: In this article, experimental methods based on cyclic voltammetric technique were used to study the electrochemical analysis of a new modified electrode with zirconium dioxide molecules on the glassy carbon electrode (ZrO_2NPs/GCE) to characterize iron ions $K_4[Fe(CN)_6]$. These methods also allowed the study of current peaks for oxidation reduction of Fe(II)/Fe(III) using potassium chloride (KCl) solution as electrolytes at different concentration, pH, scanning rates, and stability (reliability) of which these parameters are important in assessing oxidation properties. Also, the diffusion coefficient values of oxidation-reduction reaction for iron ions on the new sensor (ZrO_2 NPs/GCE) was determined using Randles-Seveik equation as $D_{fa} = 2.03 \times 10^{-5}$ cm^2 /sec and $D_{fc} = 7.12 \times 10^{-5}$ cm^2 /sec, respectively. It was found the modified electrode ZrO_2NPs/GCE acts as a good sensor with high detection limit of iron ions in electrolyte. It can be used the modified electrode in different electrochemical applications because of its higher conductivity.
Keywords: cyclic voltammery, ZrO_2 NPs, FeII/FeIII, ZrO_2NPs/GCE, new sensor

1. Introduction

Recently, scientists focused in their studies on the nanoparticles, which have novelty in physical and chemical properties [1-5].

Zirconia has many interesting properties such as hardness, mechanical strength, chemical stability and ionic conductivity, among others. Different applications of zirconia as a multifunctional material in the field of electronics, optics, magnetism and biomedicine have been studied [6].

Zirconium oxide (ZrO_2) nanoparticles with high dielectric constant were prepared through a hydrothermal technique. The results indicate that the dielectric constant of the prepared Zirconium oxide nanoparticles is about 24 at a frequency of 10^6 Hz. This obtained dielectric constant value is three times more than the dielectric constant of the commercially available zirconium oxide [7].

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of 2 M KCl, KOH and $NaNO_3$ from electrolytes were used on modified electrode with ZrO_2 Nanoparticles / carbon black. The results have good reversibility and confirm that the electrical resistance would increase after 100 cycles [8].

UV-Vis spectra of Zirconium dioxide nanoparticles prepared by thermal treatment method using zirconium (IV) acetate hydroxide as the metal precursor showed a decrease in the band gap energy with increasing calcination temperature due to the enlargement of the particle size [9].

Altering the growth conditions during zirconia nanoparticle synthesis was resulted in strong changes in phase composition and morphology of zirconia nanoparticle. During the phase transformation, zirconia particles grow from roundish to dendritic shapes. The phase transition is controlled by kinetics rather than by thermodynamics [10].

MnO_2–ZrO_2 nano rods were prepared in the size of 20 nm by wet chemical method. Thermal stability of the nano rods was characterized by thermogravimetric and differential scanning colorimetric analysis. Cyclic voltammetric studies showed good adherent behavior on electrode surface with good electro-activity at a pH value of 1.0[11].

The specific capacitance and power performance of zirconia/graphene oxide (ZrO_2/GO) on the surface of the 316 stainless steel as an electroactive material were studied using different ZrO_2 : GO mass ratio (1:1, 1:2, and 2:1). The cyclic voltammetry was done to study the specific capacitance of the electroactive materials. Nanocomposites show a similar level of charge-discharge behavior with long-range ratability, indicating that manufactured ZrO_2 / GO electrodes are a

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promising candidate for high-performance energy storage devices [12].

The effect of nanostructures of zirconium dioxide can be significant in the interaction of matter and its minimization. Low-coordinated sites create defective conditions in the electronic structure and reduce the effective band gap, which can lead to enhanced interaction with deposited species and modified photocatalytic activity [13].

A stable single-phase tetragonal and monoclinic Fe-containing zirconia nanoparticles are is reported. The electrochemical properties of iron-doped zirconia particles obtained using the voltammetry of microparticles (VPM) Measurement Technology indicated the presence of a small fraction of iron ions in both types of crystalline iron-doped ZrO_2. Electrochemical data indicate that unidirectional solid solutions provide particularly high accessibility to enhance catalytic processes such as electrochemical [14].

In this study, zirconium oxide was modified on GCE to manufacture high sensitive sensor and then was characterized by electrochemical analysis using cyclic voltammetric technique and compared with other works [15-17].

2. Materials and Methods

2.1 Materials

Zircon dioxide nanoparticles (ZrO_2NPs) (20-40 nm) from EPRUI Nanoparticle and Microsphere com. (China), KCl powder from SCRC, (China), NaOH from BDH Company, 0.1 N HCl solution and deionized water were used in this study.

2.2 Apparatus and method

Potentiostat Galvanostat electroanalytical technique (EZstat Potentiostat / Galvanostat, NuVant Systems Inc. USA) is used in the area of this work. In general, the Biochemical Analytical Chemistry Cell has been linked to a powerful instrument and monitored by the Special Program for Measuring Periodic Periodic Voltage (CV). As a reference electrode, silver / silver chloride (Ag / AgCl) at 3M KCl was used, while a platinum wire auxiliary electrode with a diameter of 1 mm was used. Also in this study glassy carbon electrode (GCE) was used after cleaning with alumina solution and treated with ultrasonic pathway water for 10 minutes. Using the mechanical attachment method with nanoparticle powder the other working electrode was modified with ZrO_2NPs (ZrO_2NPs / GCE) ZrO_2 [18]. The three electrodes are inundated in a cyclic voltammetic cell (10 ml) with electrolyte.

3. Results and Discussion

In the present study many electrochemical properties were found for the ZrO_2 NPs in KCl as an electrolyte with $K_4[Fe(CN)_6]$ solution at different statues.

3.1 Different working electrodes

Figure 1 illustrates the cyclic voltammogram of different working electrodes (GCE and ZrO_2 NPs / GCE) to characterize the oxidation – reduction current peaks of Fe(II)/Fe(III) (0.1 M $K_4[Fe(CN)_6]$) using 0.1M potassium chloride (KCl) as supporting electrolyte. It was found that GCE had a range 25 and -25 uA of oxidation-reduction current peaks of Fe(II)/Fe(III) respectively, while the modified GC electrode with ZrO_2 NPs was enhanced about twice times for both oxidation and reduction current peaks. So, zircon nanoparticles act as a good sensing because of the high conductivity in electrolyte [19].

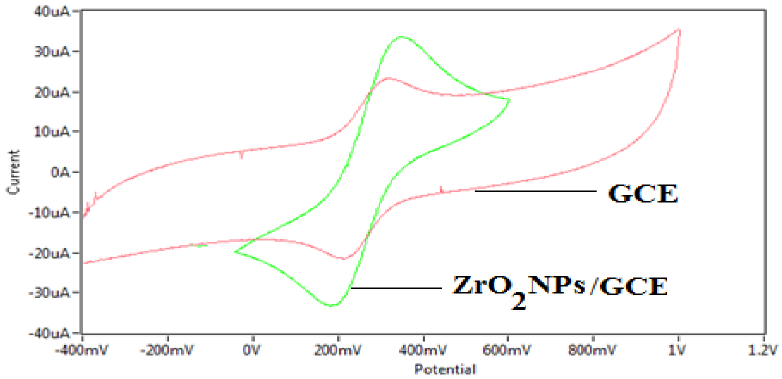

Figure 1. Cyclic voltammograms of $K_4[Fe(CN)_6]$ in 0.1M KCl on different working electrode (GCE and modified GCE with ZrO_2 NPs) versus a Ag/AgCl reference electrode at scan rate of 0.1Vsec^{-1}

3.2 Effect of different scan rates

At different scan rates in ranges from 0.01 to 0.1 V/sec for peaks of oxidation-reduction current of Fe(II)/Fe(III) with 1 M KCl solution as an electrolyte on the modified electrode (ZrO2 NPs/GCE) as shown in Figure 2. It was found that the redox peaks of Fe(II)/Fe(III) was enhanced with increasing the scan rate. Hence, the new modified electrode acted as electro-catalyst with the presence of zircon oxide nanoparticles on the surface of GCE. Using the Randles-Seveik equation, the diffusion coefficient value, which is described as the reversible oxidation waves peaks, was found [20-21]:

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

Where, Ip denotes the current peak, as n and A indicates the number of electrons moles that transferred in this reaction and the electrode area (cm2), respectively. D_f and V indicate the diffusion coefficient (cm2 / 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 ZrO_2 NPs/GCE was determined as $D_{fa} = 2.03 \times 10^{-5}$ cm^2 /sec and $D_{fc} = 7.12 \times 10^{-5}$ cm^2 /sec, respectively. Figure 3 shows the relationship of anodic and cathodic current peaks of Fe(II)/Fe(III) on the sensor of zirconium dioxide nanoparticles on GCE with the different scan rates in the voltammetric technique [22].

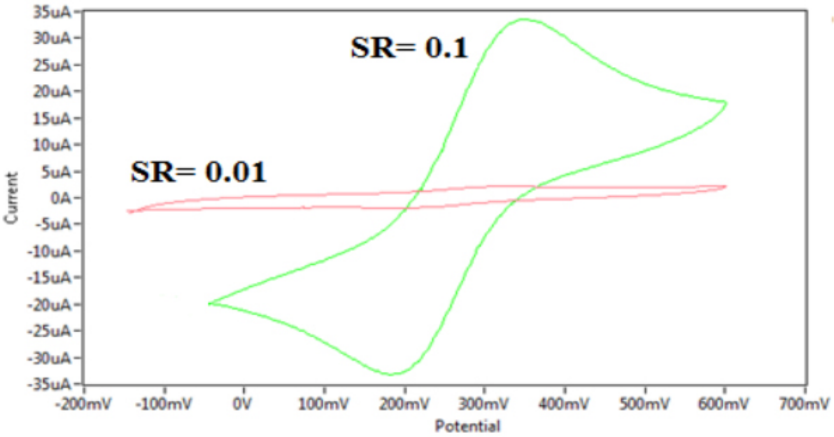

Figure 2. Cyclic voltammogram of $K_4[Fe(CN)_6]$ in 0.1M KCl on modified GCE with ZrO_2 NPs versus Ag/AgCl as reference electrode at different scan rate (0.01-0.1Vsec^{-1})

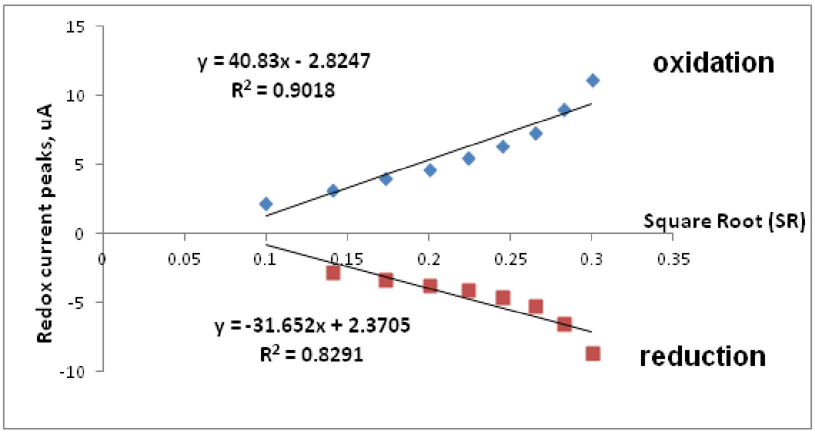

Figure 3. Relationship between oxidation-reduction current peaks and square root of different scan rates using $K_4[Fe(CN)_6]$ with 0.1M KCl on modified GCE with ZrO_2 NPs

3.3 Effect of different pH

Oxidation-reduction current peaks were studied at different pH, which is shown in Figure 4. The oxidation peak was enhanced in acidic medium pH from 6-3 and disappeared in alkaline medium, while the reduction peak remained in both media (acid and alkaline). Figures 5 and 6 show the relationship of current peaks to the oxidation reduction of Fe(II)/Fe(III) in acidic and alkaline media [23].

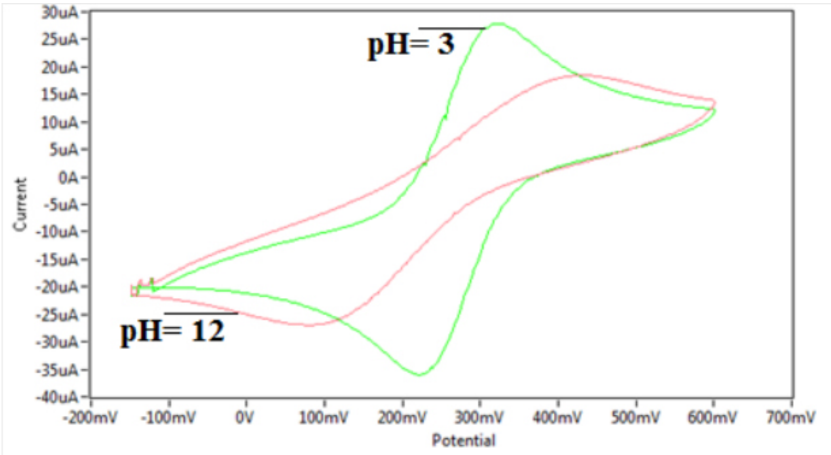

Figure 4. Cyclic voltammogram of $K_4[Fe(CN)_6]$ with 0.1M KCl on modified GCE with ZrO_2 NPs in different pH (acidic and alkaline) versus Ag/AgCl as reference electrode and scan rate $0.1 Vsec^{-1}$

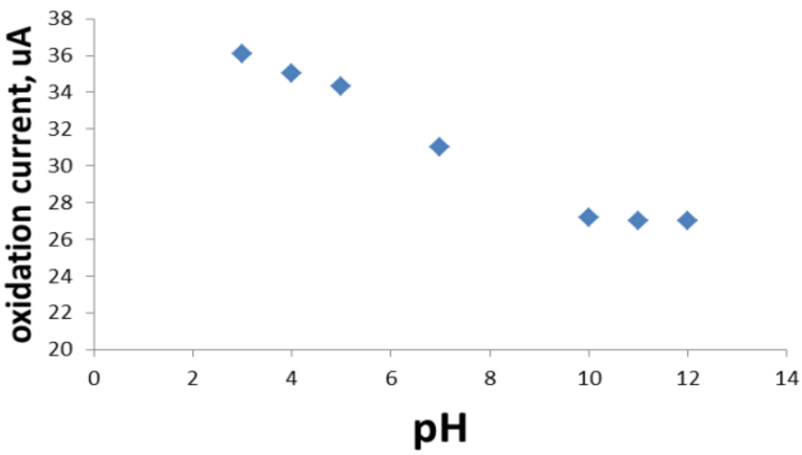

Figure 5. Relationship between oxidation current peak Fe(II)/Fe(III) and pH using $K_4[Fe(CN)_6]$ solution with 0.1M KCl on modified GCE with ZrO_2 NPs

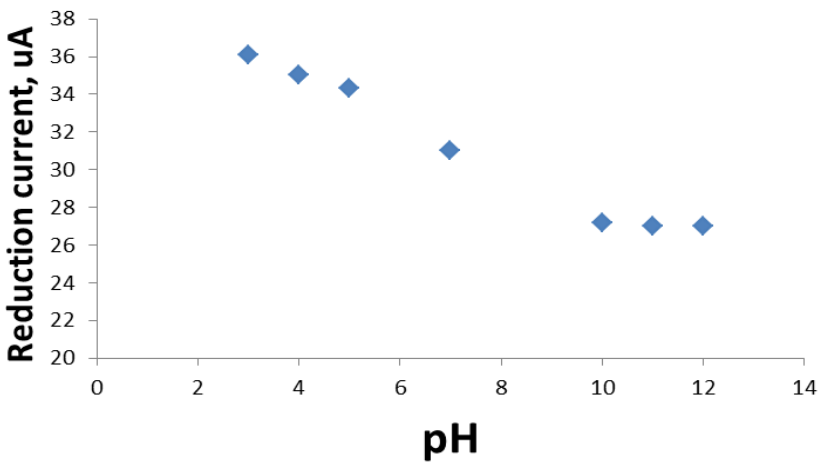

Figure 6. Relationship between reduction current peak (FeIII/FeII) and pH using $K_4[Fe(CN)_6]$ solution with 0.1M KCl on modified GCE with ZrO_2 NPs

3.4 Reliability and stability of the new modified electrode

The stability of modified nanomaterials on the GCE was studied for ten times of oxidation-reduction current peaks of $K_4[Fe(CN)_6]$ in KCl solution as shown in Figure 7. The relative standard deviation (RSD) of anodic and cathodic peaks was determined with good value of ± 0.5 and ± 0.2, respectively [24].

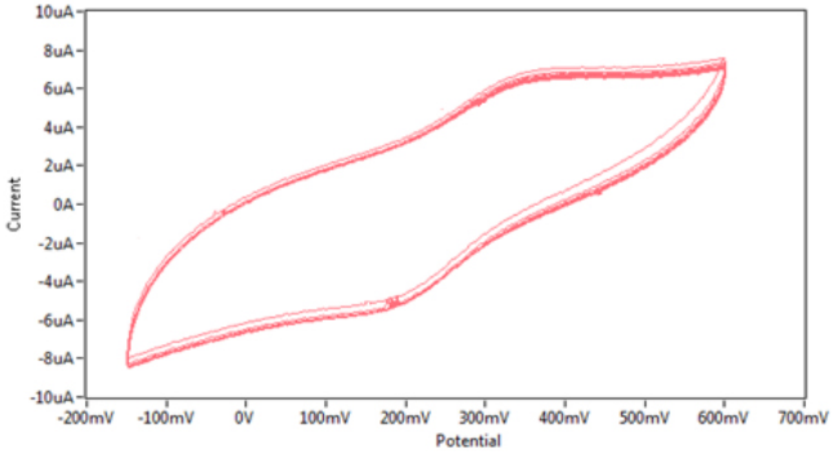

Figure 7. Cyclic voltammogram of $K_4[Fe(CN)_6]$ in 0.1M KCl electrolyte, on modified GCE with ZrO_2 NPs at ten time scanning versus Ag/AgCl as reference electrode at scan rate of $0.1Vsec^{-1}$

4. Conclusion

The most study of the behaviors of electro-conductivity of the zirconium dioxide nanoparticles are focusing on the cyclic voltammetric technique to evaluate the qualitative of the new sensor which used in different electro-analysis of traces of chemical compounds in electrolyte such as pollutant water or different media. The new modified electrode (ZrO_2 NPs/GCE) can be used to detect the traces ions after tested by electro characterization in voltammetric method. Through the work of study the electro-conductivity properties of the new nano-electrode (ZrO_2 NPs/GCE), it was observed that the electrode can be used as a high-precision sensor in the electrochemical analysis of pollutants in various electrolytes.

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