Nano Biomed Eng
2018, 10(1): 34-39. doi: 10.5101/nbe.v10i1.p34-39.

Research Article

Nanoparticles of TiO_2-ZnO Modified Polystyrene-Acrylonitrile Characterization Using Glassy Carbon Electrode

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Received: Dec. 10, 2017; **Accepted:** Feb. 15, 2018; **Published:** Mar. 7, 2018.

Citation: Emad Abbas Jaffar Al-Mulla, Nanoparticles of TiO_2-ZnO Modified Polystyrene-Acrylonitrile Characterization Using Glassy Carbon Electrode. *Nano Biomed. Eng.*, 2018, 10(1): 34-39.
DOI: 10.5101/nbe.v10i1.p34-39.

Abstract

Grafted polystyrene with acrylonitrile modified nanoparticles of TiO_2-ZnO was successfully prepared to study its electrochemical characterization by cyclic voltammetric (CV) method. It was found the new modified copolymer had good electrochemical properties and was a semi-conductor material. The ratio redox current peak (Ipa/Ipc) was equal to 2; the separation potential peak (Epa-Epc) was equal to 113 mV. Normal saline was used as a good electrolyte to enhance the solution of peaks of redox current for $K_4Fe(CN)_6$. Different concentrations, scan rates, and pH values were studied of the modified glassy carbon electrode (GCE). Diffusion coefficient values of the ions were determined using Randles-Sevcik equation. Scanning electron microscope (SEM) and atomic force microscope (AFM) images for the new grafted polymer modified nanoparticles were studied. The product could be used in various industrial applications due to its electrochemical properties.

Keywords: ZnO/TiO_2 nanoparticles; Polystyrene-acrylonitrile; Cyclic voltammetry; Modified GCE; SEM; AFM

Introduction

Scientists have conducted various studies on the use of cyclic voltammetry (CV) to electrochemical characterization of conductive polymers [1-5]. Enhancement in photocatalytic activity was obtained using nano ZnO/TiO_2 in an electrochemical study [6]. CV analysis was studied for the degradation of methylene blue on photo-catalysts using ZnO/TiO_2 nanoparticles in the average dimension of 30-100 nm. The results of the research were expanding their applications, as a photo-anode for photo-electrochemistry [7]. Use of ZnO/TiO_2-Ti nanocomposite (NC) as a photo-anode electrode in solar cell increased electron transport, electron lifetime and dye absorption [8].

CV was studied for the application of potential cycling on gold electrode using polyaniline/titanium dioxide and polyaniline/zinc oxide as a conducting polymer NC. [9]. Composites of ZnO/TiO_2 materials were synthesized by deposition of TiO_2 thin film by a sol-gel method onto ZnO nanoparticle hydrothermally grown on an ITO electrode. Photo-electrochemical study of $ITO/ZnO/TiO_2$ working electrode was carried out in an acetonitrile solution in ferrocene as a redox medium, which illustrated an enhance

in redox current peaks in comparison to ITO/ZnO working electrode upon illumination with a xenon arc lamp [10]. The electrochemical properties of TiO_2/ZnO hybrid nano-wires were investigated using 1.5 M tetraethyl-ammonium-tetrafluoro-borate in acetonitrile as an electrolyte. The results demonstrated the fabrication of new geometrical architectures of the well adhered interfaces in inorganic hybrid nanowires [11]. TiO_2, ZnO and bilayer TiO_2/ZnO dye were synthesized for solar cells using organic dyes [12]. Hydrothermal method was used to develop GZnO-Au NCs as a photocatalyst. Au NC grips great potential as a photo-catalyst in the dismissal of organic pollutants in different media [13]. Tomiyuki et al. used sodium gluconate, zinc sulfate and benzyldimethyl phenylammonium chlorideto to prepare Zn-TiO_2-ZnO NCs with the grain size in the range of 10-15 nm [14].

In this study, grafted polystyrene-acrylonitrile was modified with ZnO/TiO_2 nanoparticles; its electrochemical properties were characterized of by CV method.

Materials and Method

Instrument and electro-chemical analysis methods

An instrument of EZ Stat Series (Potentiostat/Galvanostat), Nu Vant Systems Inc., USA was used. Ag/AgCl with 3 M NaCl, platinum of 1 mm diameter and glassy carbon wire of 0.3 cm diameter were utilized as a reference, a counter electrode and a working electrode, respectively. Solution evaporation technique was used to prepare nano ZnO-TiO_2-GP/GCE.

Reagents

Nanoparticles of ZnO and TiO_2 were from BDH Limited Poole England, Normalsaline (0.9% NaCl) was from ADWIC Pharmaceutical Division, Egypt. $K_4[Fe(CN)_6]$ and KCl were from Seelze-Hannover, Germany. All solutions were prepared by using deionized water. Aqueous media with 0.1 M KCl at 25 ^oC provided conditions of the supporting electrolyte.

Preparation of nano ZnO-TiO_2-GP modified glassy carbon electrode (GCE)

The evaporation solution method was used to modify the working electrode on a clean GCE; a homogenous mixture was obtained by dissolving nano ZnO-TiO_2-GP sample in chloroform. One microliter of the mixture was placed on the surface of GCE and vaporized by hot air to leave a modified grafted polymer thin film on the GCE.

Results and Discussion

Calibration graph

The characterization study of the modified GCE with ZnO-TiO_2 nanomaterials and grafted polymer (GP) used the electrochemical analysis by CV method. The new modified working electrode was characterized by standard solution of 0.1 M $K_4[Fe(CN)_6]$ at different concentrations in 1 M KCl as an electrolyte. Fig. 1 and 2 show the calibration graph of oxidation-reduction current peaks of FeII/FeIII at different concentrations, respectively. The relationship between the redox current with different concentrations of Fe ions in aqueous electrolyte (KCl) had a good relationship with the equation $Y = 4.59X + 7.205$ and $R^2 = 0.5747$ for oxidation reaction which is an accepted result. Also, the reduction current peak of Fe III/Fe II demonstrated the equation $Y = 29.6X + 14.8$ and $R^2 = 0.6839$ [15].

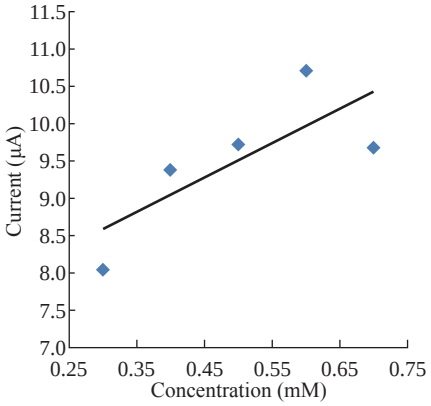

Fig. 1 Relationship between the oxidation current peak of $K_4[Fe(CN)_6]$ in KCl solution against different concentrations on the modified GCE versus Ag/AgCl reference electrode and at the scan rate of 100 mV/sec.

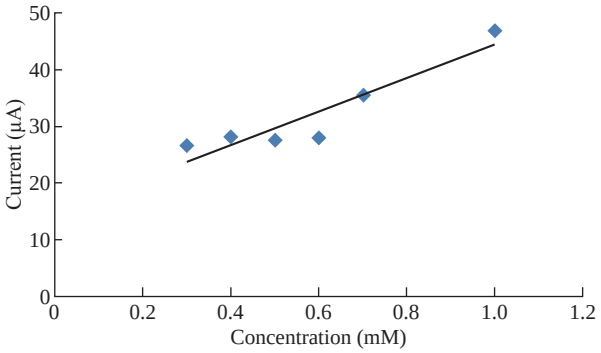

Fig. 2 Relationship between the reduction current peak of $K_4[Fe(CN)_6]$ in KCl solution against different concentrations on the modified GCE versus Ag/AgCl reference electrode and at the scan rate of 100 mV/sec.

The new working electrode showed low detection limit by the nanomaterials which had high conductivity [16].

Different scan rates

Fig. 3 illustrates the cyclic voltammogram of oxidation/reduction current peaks of Fe II/ Fe III at different scan rates to characterize the modified GCE with nanomaterials of ZnO-TiO_2 on GP. It can be seen that the increasing of scan rate caused increasing in the redox current peaks [17]. The relationship of current-scan rate was studied, as shown in Fig. 4 and 5. A good line of relationship for oxidation-reduction current peaks was demonstrated as the equation Y = 71.4X + 2.738, with high sensitivity of R^2 = 0.9956, and Y = 49.783X + 0.6731 with the sensitivity R^2 = 0.9976, respectively [18].

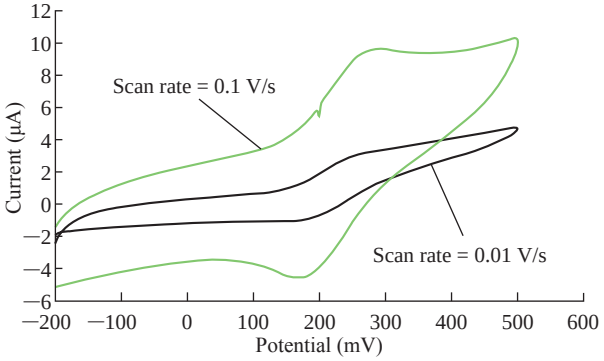

Fig. 3 Cyclic voltammogram of redox current peaks of $K_4[Fe(CN)_6]$ in KCl solution at different scan rates (0.01-0.1 V/sec) on the modified GCE versus Ag/AgCl reference electrode.

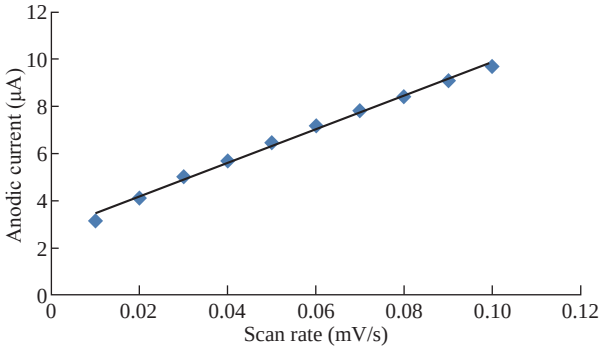

Fig. 4 Relationship between the oxidation current peak of $K_4[Fe(CN)_6]$ in KCl solution against different scan rates (0.01-0.1 V/sec) on the modified GCE versus Ag/AgCl reference electrode.

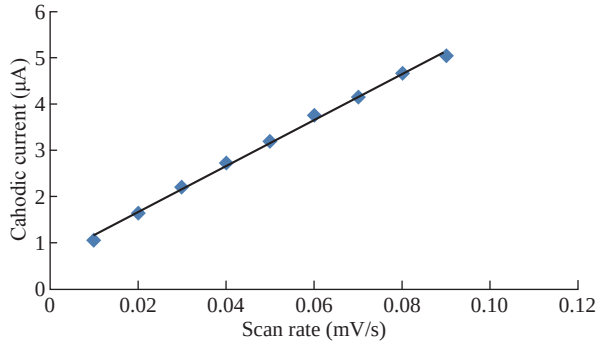

Fig. 5 Relationship between the reduction current peak of $K_4[Fe(CN)_6]$ in KCl solution against different scan rate (0.01-0.1 V/sec) on the modified GCE versus Ag/AgCl reference electrode.

Diffusion coefficient

One of the important applications of scan rate is the determination of diffusion coefficient (D_f) value peaks of redox current of K_4 $[Fe(CN)_6]$ in KCl solution for the modified working electrode ZnO-TiO_2 nanoparticles-GP/GCE from Randles-Sevcik equation [19]:

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

where I_p is the current peak, n is the number moles of electrons transferred in the medium, A is the area of the electrode, C, is concentration of K_4 $[Fe(CN)_6]$, D_f is the diffusion coefficient, and V is the applied potential scan rate.

The diffusion coefficient of oxidation-reduction current peaks of Fe II/ Fe III in KCl electrolyte as the modified electrode was 4.4 × 10^{-7} and 1.1 × 10^{-7} cm^2/sec, respectively [20].

Different pH values

The study on modified electrode with nanoparticles in different pH explained the electrochemical behavior of the new electrode in acidic and alkaline media. It was found that acidic pH enhanced the oxidation current peak of FeII/FeIII and reduced the reduction current peak with shifting both redox peaks to higher potential, as shown in Fig. 6. The acidic medium acted as an electro-catalyst for the surface of modified GCE by electronic layer on the grafted polystyrene-

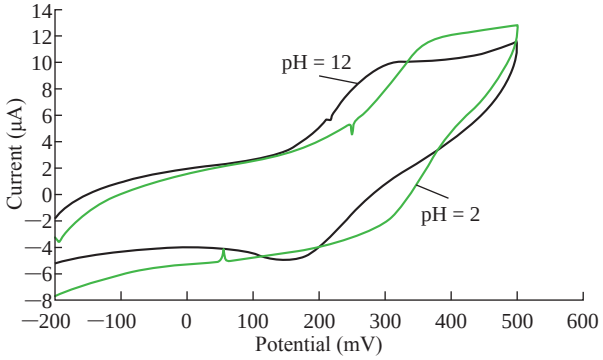

Fig. 6 Cyclic voltammogram of 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl at the modified working electrode in different pH values (2, 12) versus Ag/AgCl reference electrode at 100 mV/sec.

acrylonitrile with nanoparticles, enhancing the oxidation current, as shown in Fig. 7. However, the alkaline medium acted as an inhibition reagent for the oxidation current peak and shifted it to lower potential, as shown in Fig. 8 [21].

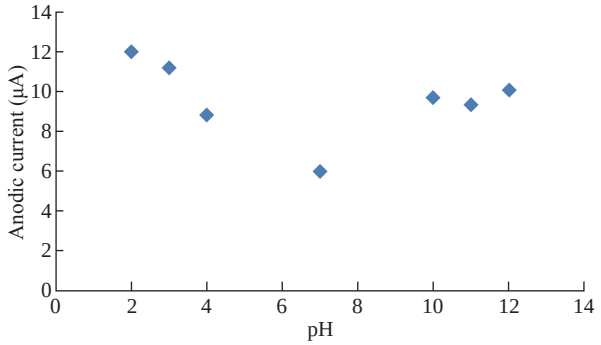

Fig. 7 Relationship between the oxidation current peak of $K_4[Fe(CN)_6]$ in KCl solution against different pH values (2-13) on the modified GCE versus Ag/AgCl reference electrode.

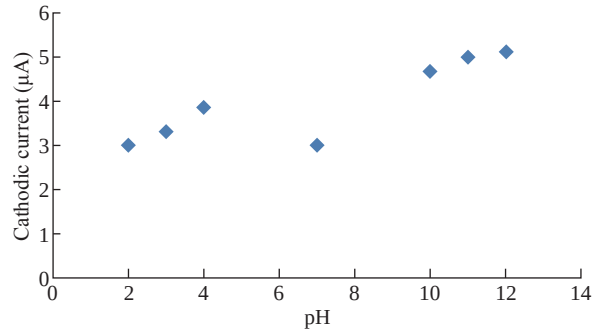

Fig. 8 Relationship between the reduction current peak of $K_4[Fe(CN)_6]$ in KCl solution against different pH values (2-13) on the modified GCE versus Ag/AgCl reference electrode.

Reliability and stability

Reliability and stability studies are very important to evaluate the activity of new modified electrode. It was found that the relative standard deviation (RSD) for oxidation-reduction current peaks was ±2.5% and ±3.7%, respectively. Fig. 9 presented the applicability of the cyclic voltammogram at 10-time cycling with good stability and good reliability. This electrode can be used in electro-analysis for its precision in addition to its good sensitivity [22].

Scanning electron microscopy (SEM)

Fig. 10 and 11 demonstrate the scanning electron microscopy (SEM) for the grafted polystyrene-acrylonitrile before and after modification with nanoparticles of $ZnO\text{-}TiO_2$, respectively, which showed morphology of the polymer layer.

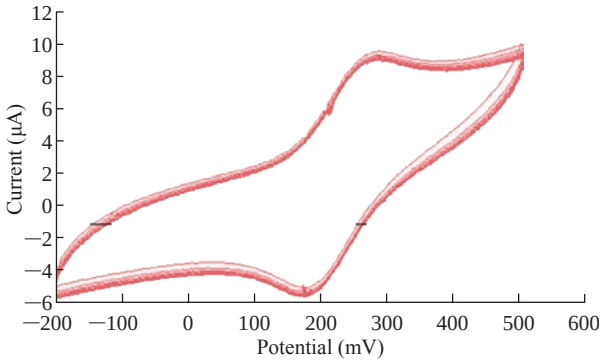

Fig. 9 Cyclic voltammogram of 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl on modified GCE at 10 times versus Ag/AgCl reference electrode at 100 mV/sec.

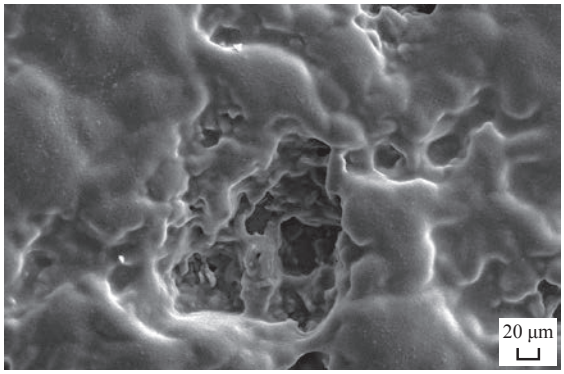

Fig. 10 SEM of grafted polystyrene-acrylonitrile on 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl.

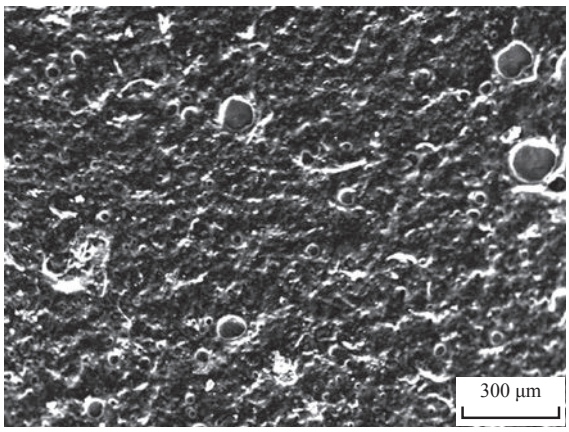

Fig. 11 SEM of grafted polystyrene-acrylonitrile modified with nano $ZnO\text{-}TiO_2$ on 0.5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl.

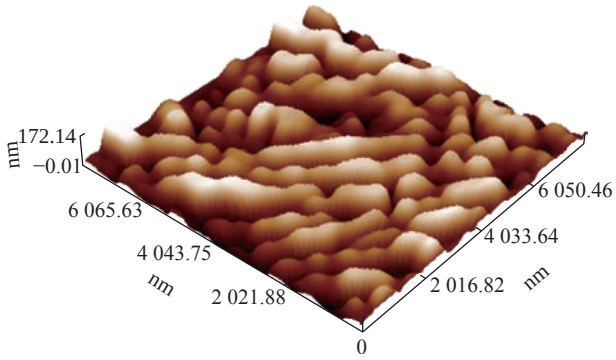

Fig. 12 AFM of the grafted polystyrene-acrylonitrile modified with $ZnO\text{-}TiO_2$ nanoparticles.

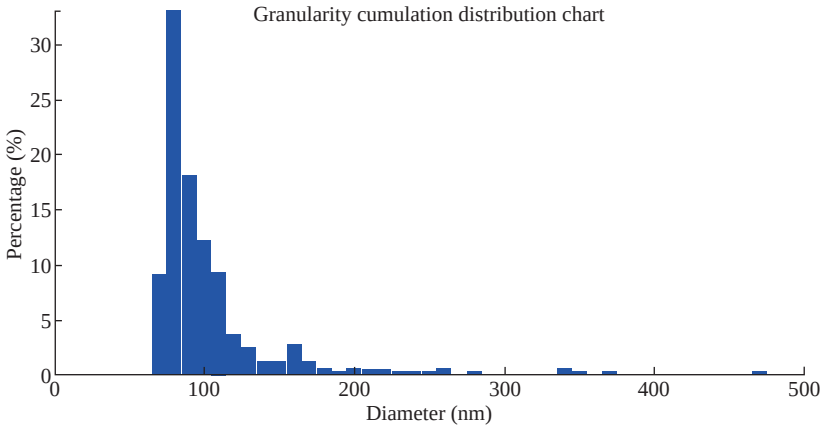

Fig. 13 Contribution of the percentage of diameter in nanoscale for ZnO-TiO_2 nanoparticles.

Atomic force microscopy (AFM)

Fig. 12 and 13 illustrate the diameter of ZnO-TiO_2 nanoparticles through the grafted polymer which had the range of 50-100 nm.

Conclusions

A significant redox current peaks of FeII/FeIII was observed using nano ZnO-TiO_2-GP modified GCE by $K_4[Fe(CN)_6]$ solution in normal saline as supporting electrolyte. The results also reveal that the new modified electrode with nanoparticles has good sensitivity and enhanced the oxidation current peak of FeII/FeIII in acidic pH and inhibited of alkaline medium. Diffusion coefficient values of oxidation and reduction current peaks were found with different scan rate of $4.4x10^{-7}$ and $1.1x10^{-7}$ cm^2 sec^{-1}, respectively according to Randles-Sevcik equation, which indicates the redox process is reversible. Many studies were done to characterize the modified grafted polymer with the nanoparticles at different concentration, pH, scan rate. Both of SEM and AFM samples show the morphological images and diameters (50-100 nm) of modified grafted polymer nanoparticles.

Conflict of Interest

The authors declare that they have no conflict of interest.

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