

Voltammetric characterization of polystyrene grafted with acrylonitrile electrode self modification with carbon nanotube (Psgacement)

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الخلاصة

تم تصنيع قطب جديد مصنع من البولي ستيرين المطعم اكرلوناترال والمعدل بهادة الكاربون نانوتيوب وباستخدام اشعة كاما والعامل المساعد كبريتات الامونيوم الحديدية. تم دراسة الصفات الكهروكيميائية للقطب المصنع حيث اعطى تحسناً في اداءه وذلك عن طريق استخدام الكاربون نانوتيوب الذي يزيد في التوصيلية الكهربائية لمادة البوليمر المطعم اثناء استخدامه في جهاز الفولتامترية الحلقي. وقد تم تشخيص الصفات السطحية للقطب الجديد باستخدام SEM و AFM. وكذلك تم استخدام محلول $K_3Fe(CN)_6$ كمادة قياسية في جهاز الفولتامترية الحلقي في تشخيص الصفات الكهروكيميائية للقطب. خواص التوصيل الكهربائي لـ GPESMCNT درست في 1 مولاري من KCl وبتراكيز مختلفة لـ $[K_3Fe(CN)_6]$ وعند درجات حرارة مختلفة باستخدام تقنية CV. وقد لوحظ أن القطب الجديد ساعد في تحسين أداء تقنية الفولتامترية الحلقي خاصة في استخدامه بتجربة القطب الدوراني التي لا يمكن استخدام الأقطاب المعدلة فيه. ان نتائج القياس اوضحت ان المادة النانوية لها اهمية في تركيبة البوليمر المطعم برفع قيمة التيار الكهربائي لقمته الاكسدة والاختزال للحديد Fe (II)/Fe (III) لمرت عديدة مقارنة مع الاقطاب التجارية مثل قطب الكاربون الزجاجي وقطب البلاتين وقطب الذهب.

الكلمات المفتاحية

قطب البولي ستيرين المطعم اكرلوناترال والمعدل بهادة الكاربون نانوتيوب، CNT جهاز الفولتامترية الحلقي.

Abstract

A novel self modification of grafted polystyrene-acrylonitrile working electrode with carbon nanotubes was success for fabrication from grafting polymer via gamma irradiation and ferrous

ammonium sulfate (FAS) as a catalyst. The electrochemical properties of the self modified grafted polymer with CNT (PSGACESMCNT) improved performance the working electrode at higher conducting surface was done through using in cyclic voltammetry (CV). Morphology of the surface of PSGACESMCNT was characterized by AFM and ASM. The characterization of electroconductivity properties of PSGACESMCNT was studied in 1M of KCl with different concentration of $K_3 [Fe(CN)_6]$, at different scan rates, temperature, and different concentrations using CV technique. The new PSGACESMCNT improved performance the working electrode in CV at different techniques such as rotating disc electrode (RDE). also, the nanomaterials in the chain of grafted polymer was enhanced the redox current peaks of Fe (II)/Fe (III) multi times than at commercial working electrodes such as GCE, Pt-electrode, Au-electrode.... etc.

Keywords

grafted polymer electrode self modified, CNT, cyclic voltammetry, $K_3 [Fe(CN)_6]$.

1. Introduction

The modification of grafted polymer with nano-deposits such as CNT, C₆₀ and activated carbon is very important for the scientists especially in the electrochemistry by cyclic voltammetric analysis field [1-5].

The unique chemical, physical, electronic (metallic or semiconducting) and high thermal properties of carbon nanotubes (CNTs) made them interesting materials for widespread application in the fields such as electrochemical sensors, biosensors, supports for heterogeneous metal catalysts in organic synthesis, fuel cells, semiconductors, batteries, random access memory cells, field effect transistor, field emission display, atomic force microscopy probes, microelectrodes, specific adsorbents to remove organic pollutants from water and waste water and as a potential drug carriers in cancer therapy [6-9].

Working electrodes must have electrically properties as conductor and electrochemically inert. Working solid electrode materials included platinum, gold and glassy carbon were used in cyclic voltammetry. Other materials (e. g., semiconductors, for example ITO, indium-tin oxide, or conductive polymers or grafted polymer) are also used, for more specific applications [10, 11].

Electrochemical behavior of famotidine has been studied at composite polymer membrane working electrode. Cyclic voltammetric method has been developed for the determination of drug in pharmaceutical formulation. A well-defined anodic peak was observed for famotidine in the entire pH range. The current increases steadily with scan rate and concentration. This composite

film showed good catalytic behavior, which includes a good current response. The result is compared with the glassy carbon electrode and it was found that the current with composite polymer electrode is of the order of 18.60 mA whereas with glassy carbon electrode it was around 565.00 μ A [12].

Electrochemical study behavior of terthiophene and its corresponding polymer, which is obtained electrochemically as a film by Cyclic Voltammetry (CV) on platinum electrode. The analysis focuses essentially on the effect of two solvents acetonitrile and dichloromethane on the electrochemical behavior of the obtained polymer. The voltammograms show that the film of polyterthiophene can oxidize and reduce in two solutions; in acetonitrile, the oxidation current intensity is more important than in dichloromethane. The impedance plots show the semicircle which is characteristic of charge-transfer resistance at the electrode/polymer interface at high frequency and the diffusion process at low frequency [13].

Grafted copolymer of polypyrrole has been synthesized by electrochemical polymerization of pyrrole in the presence of poly(para-chloromethylstyrene-co-styrene-copolyrrole-methylstyrene). The produced copolymer exhibits an electrical conductivity comparable to that of polypyrrole. This measurement showed that copolymer has excellent thermal stability. The response mechanism of this compound to sense a selection of gases and vapors was investigated, by measuring its electrical conductivity by four-point probe method. This gas sensor may have advantages over the other sensors in its

ability to operate at room temperature, lower gas and vapour sensing concentration, suitable solubility, stability in air, sufficient diffusion, and selectivity [14].

This review highlights the recent progress made in the area of thermoelectric (TE) applications of conducting polymers and related composites. Several examples of such materials and their TE properties are discussed. TE properties of new poly (2, 7-carbazole) derivatives are highlighted. References are also made to carbon nanotube/polymer composites and their improved electrical and TE performance. Studies on polymer/inorganic materials composites have also taken a step forward and have shown very promising TE properties [15].

In this work, grafted polymer was modified with carbon nanotubes to fabricate grafted polymer electrode self modified with carbon nanotubes. The new grafted polymer electrode was electrochemically characterized in $K_3 [Fe(CN)_6]$ with KCl aqueous electrolyte by CV technique.

2. Experimental

2.1. Synthesis of grafted polymer modified with carbon nanotubes (GP/CNT)

Polystyrene was grafted with acrylonitrile as a monomer and modified with nano-deposit (carbon nanotubes) and ferrous ammonium sulfate (FAS) as a catalyst using gamma-irradiation. The new grafted polymer modified with carbon nanotubes has been investigated and characterized [3].

2.2. Instrument and Electroanalytical Methods

Electrochemical workstations of NuVant

Systems Inc., USA (EZ stat series with potentiostat/galvanostat driven by electroanalytical measuring software) were connected to a PC computer in order to perform cyclic voltammetry (CV), chronoamperometry (CC), and chronopotentiometry (CA). An Ag/AgCl (3 M NaCl) and platinum wire (1 mm diameter) were used as the reference and counter electrodes, respectively.

The working electrode used in this study was grafted polymer electrode self modified with carbon nanotubes (PSGACESMCNT). The voltammetric experiments were carried out with $K_3 [Fe(CN)_6]$ and KCl as supporting electrolyte. Solution was degassed with nitrogen gas for ten to fifteen minutes prior to recording the voltammogram.

2.3. Reagents

All chemicals were analytical reagents or at spectroscopy grade purity. Also, solutions were prepared by double distilled water. It was used as the supporting electrolyte solution of 1M KCl in aqueous media at room temperature.

2.4. Fabrication of the new polystyrene-acrylonitrile electrode self modified with CNT (PSGACESMCNT)

PSGACESMCNT has been fabricated from grafted polymer modified with carbon nanotubes. The diameter of electrode was 3 cm. A hole was done (1mm) to allow 1cm length of platinum wire out from other side of electrode. A piece of copper wire was joined with the platinum wire. All parts of fabricated electrode were covered with glassy tube and then fixed by epoxy resin as shown in Fig.(1).



Fig.(1): PSGACESMCNT

3. Results and discussion

3.1. Electrochemical properties

$K_3Fe(CN)_6$ solution is commonly used as a reference standard solution for the purpose of calibrating a voltammetric system in KCl aqueous solution. During the calibration process of an electroanalytical workstation (EZ stat) using glassy carbon electrode (GCE) and grafted polymer self modified with carbon nanotubes electrode (GPESMCNT) as working electrode. The current of Fe (II) / Fe (III) redox couple appears to be significantly enhanced by the PSGACESMCNT. The enhancement of oxidation-reduction current peaks $+600 \mu A$ and $-200 \mu A$, respectively is comparison of GCE at very weak redox current peaks of $+70 \mu A$ and $-60 \mu A$ respectively as show in Fig.(2) and b.

3.2. Effect of different scan rate

The effect of varying scan rates (SR) on the cyclic voltammograms using grafted polymer electrode self modified with CNT as working electrode in 1M KCl as a supporting electrolyte was studied with 1mM $K_3Fe(CN)_6$ over a scan rate ranging from 5 – 1000 mV/s. Oxidation and reduction currents of Fe (II)/Fe (III) couple increased with the scan rate due to heterogeneous kinetics and IR effect. Fig.(3) is a reasonably linear dependence of PSGACESMCNT reduction current on the scan rate and is described by $y=0.48X - 1.225$, $R^2 =0.963$. The slope of graph $\text{Log } I_{pc}$ (reduction current) versus $\text{Log } (SR)$ is 0.48; which is significantly differ from the theoretical value of half for diffusion- controlled process, indicating presence of a complex. The relationship between oxidative potential and scan rate of PSGACESMCNT, shows a reduction peak

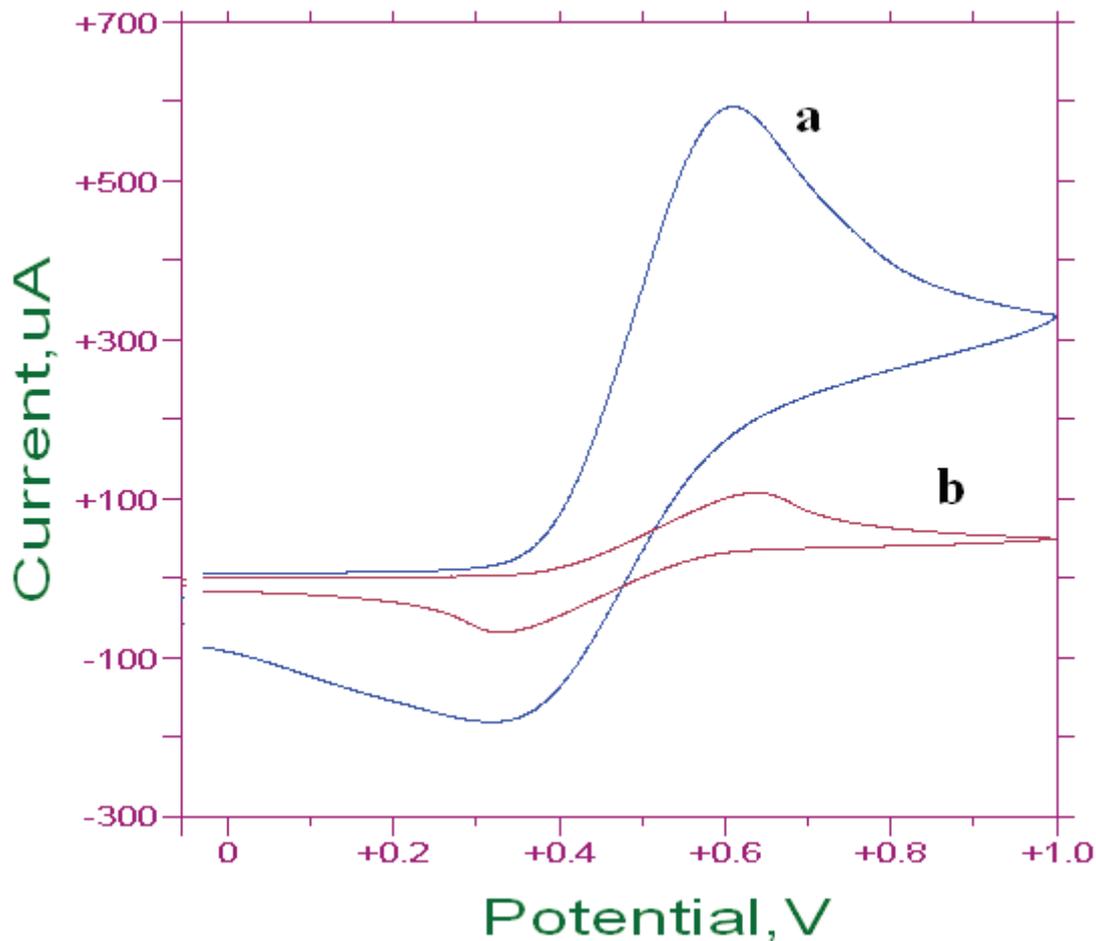


Fig.(2): cyclic voltammogram of $K_3(Fe(CN)_6)$ in 0.1M KCl (SR=100 mV/sec) versus Ag/AgCl using (a) GPESMCNT and (b) GCE.

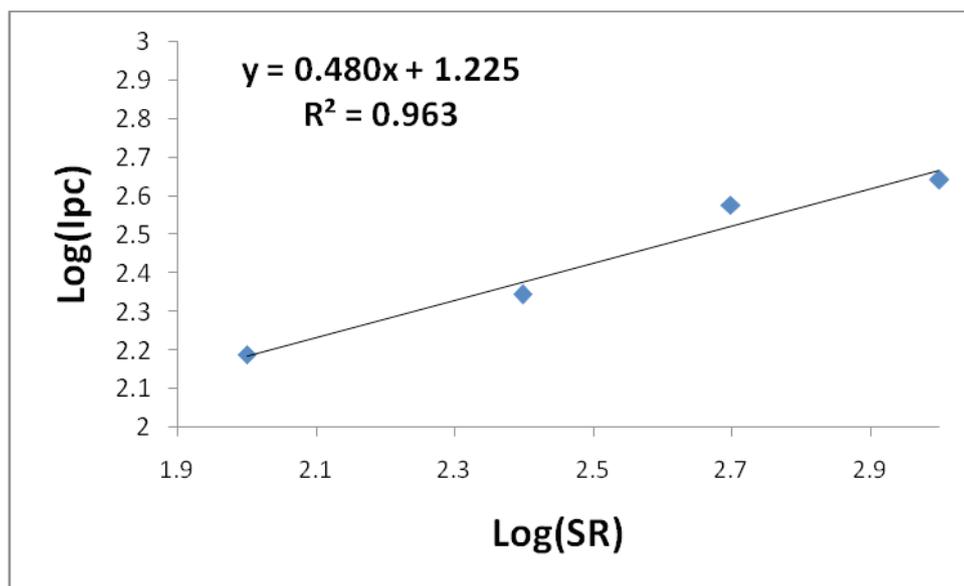


Fig.(3): Plot Log (Ipc) versus Log (SR) of 1mM $K_3Fe(CN)_6$ in 1M KCl at different scan rate (SR = 100, 250, 500, 1000 mV/sec) using PSGACESMCNT versus Ag/AgCl as reference electrode.

at 150 mV in low scan rate but increased more than 500 mV at high scan rate (Linearly with $Y=0.48X-1.225$ ($R^2=0.963$)). Surface intercepts process at zero current produces zero current potential ($E_0, 1$) of 150 mV for the reduction of PSGACESMCNT.

3.3. Effect of varying $K_3Fe(CN)_6$ concentration

Fig.(4) shows the linear current dependent on $K_3Fe(CN)_6$ concentration; observed at concentration range (5-10mM) which is described by the equation of $y=18x+221.2$ with $R^2=0.984$. The slope of the linear line for $K_3Fe(CN)_6$ showed that a considerably high sensitivity response of $18 \mu A/mM$ is readily obtained at GPESMCNT during cyclic voltammetry.

3.4. Reproducibility

The potential cycling of the redox of PSGACESMCNT in 1mM $K_3Fe(CN)_6$ and 1 M KCl aqueous solution as a supporting electrolyte was carried out during cyclic voltammetry. Continuous potential cycling did not seem to affect the redox current of PSGACESMCNT as the faradic activity appears reproducible even after 15 cycles, reflecting the stability and reproducibility at the surface of PSGACESMCNT.

3.5. Scanning electron microscopy (SEM) of GPE/CNT

Before electro-analysis polystyrene grafted acrylonitrile surface appears compact and nonporous. The uniformity of the grafted polymer surface slightly increases since occurrence of

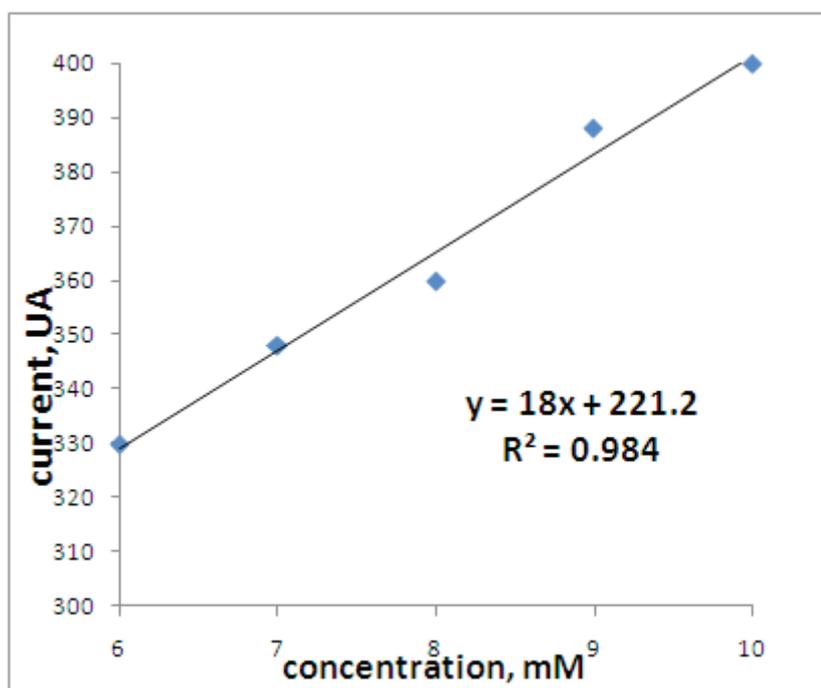
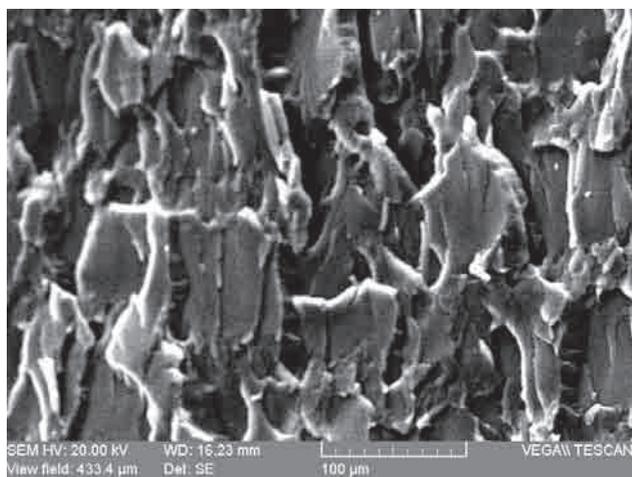


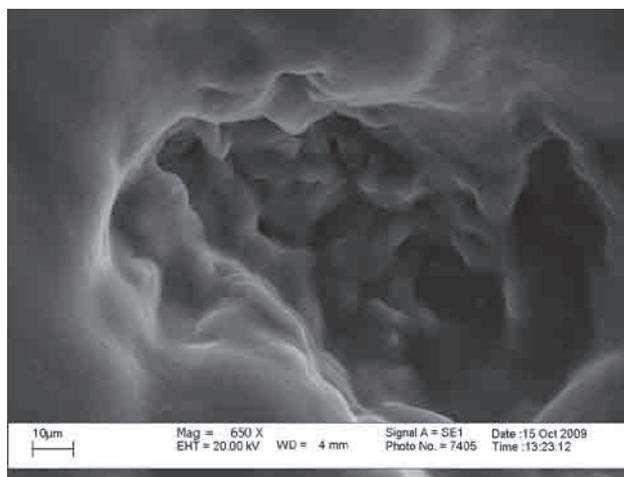
Fig.(4): plot cathodic current versus different concentration of $K_3Fe(CN)_6$ in 1M KCl scan rate=100 mV/sec using PSGACESMCNT versus Ag/AgCl as reference electrode.

protrusion observed phase as shown in Fig.(5) (a). After modification with CNT, although many of the nano deposits with homogenous distribution

of CNT still remain at about $<1 \mu\text{m}$ as show in Fig.(5) (b).



(b)



(a)

Fig.(5): SEM of (a) polystyrene grafted acrylonitrile (b) polystyrene grafted acrylonitrile modified with CNT

3. 6. Atomic force microscopy (AFM)

The surface image of AFM in an area of $20 \mu\text{m} \times 20 \mu\text{m}$ of the grafted polymer (polystyrene acrylonitrile) before and after modified with CNT as shown in Fig.(6). The surface of the electrode appeared to be compact and rough. According to AFM images, the average grain size and thickness of the film were estimated to be $11.23 \mu\text{m}$ and $28.69 \mu\text{m}$, respectively.

4. Conclusions

A polystyrene grafted acrylonitrile Electrode self modified with CNT (PSGACESMCNT) has an extended potential working region as a compared with solid electrodes and classical modification electrodes. The stability of PSGACESMCNT as a working electrode was evaluated by using $\text{K}_3\text{Fe}(\text{CN})_6$ in KCl electrolyte.

Redox peaks of Fe(II)/Fe(III) obtained at PSGACESMCNT showed high current as compared with bar GCE. Electro-catalytic activity of GPESMCNT is therefore evident in this study. GPESMCNT was studied by redox process of $\text{K}_3\text{Fe}(\text{CN})_6$ in KCl solution during cyclic voltammetry. The redox peaks potential shifts slightly to less negative value by about 100 mV for oxidative peak and 50 mV for reductive peak with current enhancement of about 3-5 folds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on the concentration and scan rate. It is an excellent reproducibility of the current which provided a fabricated electrode has a property in experiment without cleaning.

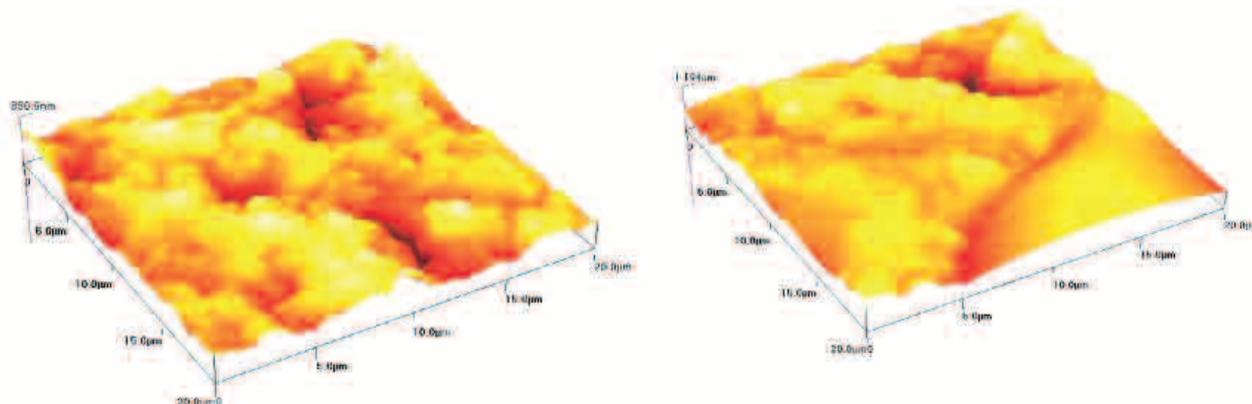


Fig.(6): AFM of Polystyrene grafted acrylonitrile

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