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# Grafted Polymer with Nano Materials (CNT, $C_{60}$ and Activated Carbon) Using As Working Electrodes in Cyclic Volta metric Technique

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## ABSTRACT

Acrylonitrile was grafted on polystyrene and modified with nano materials such as CNT, $C_{60}$ and activated carbon using gamma-irradiation technique. This process was carried out at various gamma doses 0.2-1.5 Mrad (0.002-0.015 MGry) and used different percentage (w/w %) of monomer (Acrylonitrile) and catalyst ferrous ammonium sulfate (FAS). The new grafted polymer modified with nanometrials has good physical and chemical properties of hardness, insolubility, and stability. Also the sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, electrolyte and scan rate. The grafted polymer modified with nano materials was used in different applications in electrochemistry such as in cyclic voltammetric technique by fabrication of working electrodes from these materials as a substitute of glassy carbon electrode, platinum electrode, gold electrode…etc. and self modified these electrodes with nanomaterials.

**Keywords**: Grafted Polymer Electrodes, CNT, $C_{60}$, AC, Cyclic Voltammetry.

# تعديل البوليمر المطعم بمواد نانوية (الكاربون نانوتيوب والكاربون60 والكاربون المنشط) واستخدامه في الاقطاب العاملة في تقنية الفولتامتري الحلقي

## الخلاصة

تم تعديل البولي ستايرين المطعم بالاكريلونايترايل بمواد نانوية مثل الكاربون نانوتيوب والكاربون 60 والكاربون المنشط باستخدام تقنية التشعيع باشعة كاما. حيث استخدمت اشعة كاما بجرع مختلفة 0.2-1.5 Mrad (0.002-0.015 MGry). تم استخدام نسب مختلفة من المونومير (الاكريلونايترايل) ومن العامل المساعد كبريتات الامونيوم الحديدية. حيث تم الحصول على بوليمر مطعم ومعدل بمواد نانوية اكسبته صفات فيزياوية وكيمياوية جيدة من حيث الصلابة والثبوتية والذوبانية والاستقرارية وكذلك تحسسه العالي لتقنية الفولتامتري الحلقي في دراسة الحامضية المختلفة والمذيبات المختلفة وسرع المسح المختلفة.

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وتم استخدام هذه البوليمرات المطعمة في تطبيقات الكيمياء الكهربائية بتقنية الفولتامتري الحلقي وذلك بتصنيع الاقطاب العاملة كبديل للاقطاب العاملة التجارية مثل قطب الكاربون الزجاجي والبلاتين والذهب وغيرها. كذلك يمكن استخدام هذه الاقطاب كاقطاب عاملة ومعدلة ذاتيا بالمواد النانوية.

## INTRODUCTION

Composites of $C_{60}$ fullerene and carbon nanotubes with polymers are attractive for a wide range of applications. The combination of the unique physicochemical and optoelectronic properties of the carbon structures with the characteristics of some well-known polymers has proven to yield some interesting effects. Various synthetic approaches to making these advanced polymeric composites have been suggested along with novel methods for micro structuring the materials into aligned or patterned forms [1]

Fabrication and electrochemically characterized of two types of individual carbon nanotube electrodes: an as-produced multi-walled carbon nanotube (MWNT) electrode and a modified MWNT electrode. Open-ended modified MWNT electrodes were fabricated by using a reactive ion etching treatment under an oxygen atmosphere. Also, the measurements of cyclic voltammetry were used to detection of aqueous dopamine solutions with different concentrations. The modified electrode was capable of detecting dopamine at the picomolar level. Therefore, an individual modified MWNT electrode has potential for applications to active components in nanobiosensors [2].

The chemistry of CNT is a current subject of intense research, which produces continuous advances and novel materials. However, the controlled functionalization of CNT has not yet been fully achieved. Solubility continues to be an issue, and new purification and characterization techniques are still needed. It is hoped that, with the effort carried out in many laboratories, we will be able to witness full control of size and shape, with new interesting applications in composites and electronics [3].

In its conducting form, carbon has proven to be a versatile, robust and high performing electrode material in areas such as energy conversion, energy storage and even medical bionics. In our laboratories we have been interested in the fabrication and utilization of nanostructured electrodes based on more recently discovered forms of carbon. These include carbon nanotubes and grapheme [4].

The improvement of interfacial adhesion in polystyrene – carbon nanotubes composites by grafting polystyrene chains onto the nanotube surface was studied. The polystyrene was covalently bond onto the nanotube surface with an average molecular weight of about 104 g $mol^{-1}$ from which composites with different nanotube weight fraction were synthesized. it is shown that short chains polymer grafting, (i) enhanced the dispersion of the nanotubes within the matrix, (ii) increased the Young modulus below Tg, and (iii) increased the stress breaking of the nanocomposites. [5].

Working electrodes acts as a source or sink of electrons for exchange with molecules in the interfacial region, and must also be an electronic conductor and electrochemically inert. Commonly used working solid electrode materials for cyclic voltammetry include platinum, gold and glassy carbon. Other materials (e.g., semi-conductors, for example ITO, indium-tin oxide, or conductive polymers or grafted polymer) are also used, for more specific applications. Polystyrene is a polymer made from the monomer styrene. At room temperature, polystyrene is normally a solid thermoplastic, colorless and harder plastic, it has low thermal conductivity 0.08 W/(m•k) and electrical conductivity (σ) is 10-16 S m-1, a copolymer of acrylonitrile and styrene, toughened with polybutadiene. Conductive polymers are good candidates for preparation of conducting grafted copolymers [6-8]. The thermal degradation of a grafted copolymer in which acrylonitrile is grafted on to polystyrene has been studied by thermogravirnetric analysis [9]. Abstraet Polystyrene-polyacrylonitrile copolymers have been prepared by the direct radio-induced grafting method [10].

In this work, grafted polymer electrode (GPE) was fabricated from grafted polystyrene with Acrylonitrile using gamma irradiation, also the self modified grafted polymer electrodes with nanomaterials such as carbon nanotude, $C_{60}$ and activated carbon. It was successfully to using these new working electrodes in cyclic voltammetry with high advantages comparison with other working electrodes like GCE, Pt-E, and Au-E and modified these electrodes with nano materials. GPE was characterized electrochemically in aqueous electrolyte which it was proved successfully with good results.

## EXPERIMENTAL PART

### Synthesis of Grafted Polymer (GP)

Polystyrene as a polymer was grafted using acrylonitrile as a monomer using gamma-irradiation, with chloroform as a solvent and ferrous ammonium sulphate (FAS) as a catalyst, also can modify the grafted polymer with nanomaterials (1% carbon nanotude, 1%$C_{60}$ and 1%activated carbon). The new grafted polymers obtained in different percentages of grafting have been investigated and characterized [11-13].

### Instrument and Electro analytical Methods

Electrochemical workstations of Bioanalytical system Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring software were connected to PC computer in order to perform cyclic voltammetry (CV), chronoamperometry (CC), and chronoamperometry (CA). An Ag/AgCl (3M NaCl) and platinum wire (1mm diameter) were used as the reference and counter electrodes, respectively. The working electrode used in this study was grafted polymer electrode (GPE) (see below). The voltammetric experiments were carried out with 0.1M KCl as supporting electrolyte. Solution was degassed with nitrogen for ten minutes prior to recording the voltammogram.

### Reagents

All reagents were analytical reagents or electrochemical grade purity. All solutions were prepared using distilled water. Unless otherwise specified, the supporting electrolyte was used 0.1M KCl in aqueous media at room temperature.

### Preparing the new grafted polymer electrode (GPE)

GPE has been fabricated from grafted polymer and grafted polymer modified with nanomaterials. The grafted polymer with diameter of electrode of 3 mm was done a hole (1mm) to allow 1cm length of platinum wire out from other side of electrode. A copper wire was then joined with the platinum wire. After that, all parts of fabricated electrode was covered with glassy tube and then fixed with epoxy resin.

## RESULTS AND DISCUSSION

### Effect of GPE on the Redox Reaction of Potassium Ferricyanide during CV

Potassium Ferricyanide is commonly used as a reference standard for the purpose of calibrating a voltammetric system in aqueous solutions. During the calibration process of an electro analytical workstation (BAS Model 50W) using GCE, Pt-wire and GPE. Oxidative current of Fe (III)/Fe (II) redox couple appears to be significantly enhanced by the GPE as in Figure (1). Comparison of Figure (1a and b) the cyclic voltammetric of $Fe^{3+}$ in the presence Figure (1a) and absence of GP Figure (b) shows conclusion that the enhancement of redox current of $Fe^{3+}$.

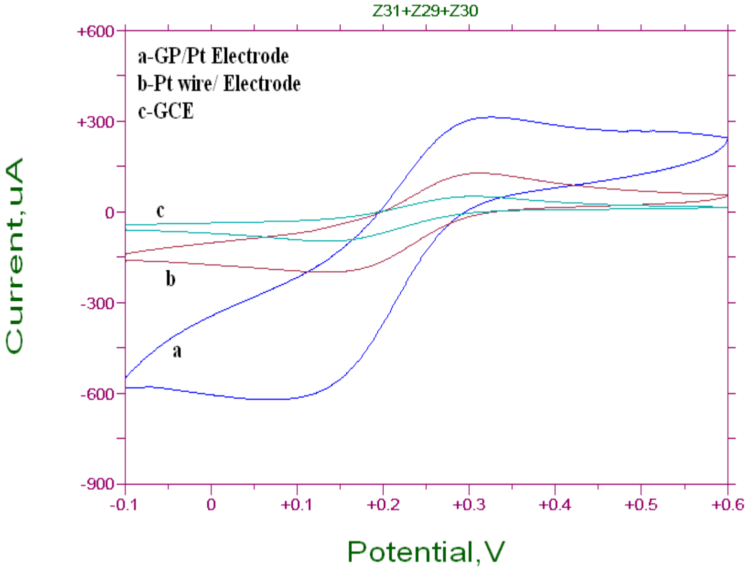


**Figure (1) Cyclic voltammetry of different electrodes (a) GP/Pt electrode (b) Pt wire electrode and (c) GCE in 1mM $K_3Fe(CN)_6$ with 0.1M KCl as supporting electrolyte versus Ag/AgCl and 100 $mVsec^{-1}$.**

It was also observed that the redox potential with Epa = +227 mV and Epc= +320 mV with peak separation of 93 mV (for n=1) in 0.1M KCl electrolyte indicates the reversible reaction of the Fe(III)/Fe(II) couples in KCl solution and agree well with the accepted values. In subsequent studies, various chemical and physical effects were assessed in order to determine the optimum conditions under which maximum current response at the GPE can be obtained.

Figure (2) shows the two redox peaks of $Fe (CN)_{63}^{-}$ when the working electrode GPE is used as working electrode in 0.1M KCl as supporting electrolyte. The first redox process of Fe (III)/Fe (II) at +0.1V and +0.3V for reduction and oxidation peaks respectively. While the second redox process of Fe (II)/Fe (0) at -0.3V can be assigned for the reduction and -0.05V for oxidation.

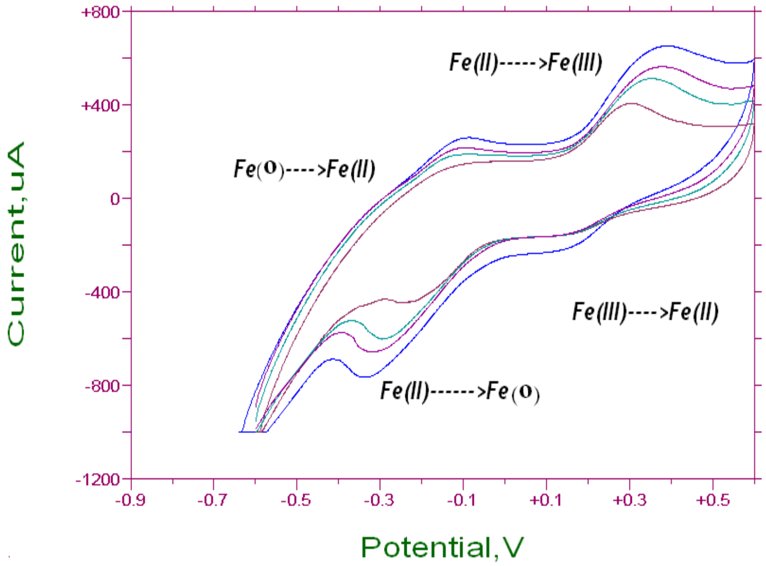


**Figure (2) Cyclic Voltammetry of GPE in different concentration of 1mM $K_3Fe$ $(CN)_6$ and 0.1M KCl two redox of Fe versus Ag/AgCl and 100 $mVsec^{-1}$.**

## Potential window of different electrodes

The working potential window of GCE (where electroactivity due to electrode materials and electrolyte is negligible) was found to be in the range (-1.5 - +1.2V) with small significant peak appearing at -0.4 and +1.0V. A considerable extension of the working window with absence of each esp. at the anodic region is observed when GPE is used. Although the working window at anodic and cathodic region deteriorate due to the “electrocatalysed” oxidation-reduction of the aqueous electrolyte or the reactivity of GPE giving rise to a limiting current appearing at about -1.5 to +2.0 V. This limiting current, however diminishes in subsequent cycles allowing potential working window to be widened at the anodic region to near 2.0 V as show in Figure (3). It shows that GPE is useful for redox reaction studies appearing at a more negative potential of up to at least -2.0 volt esp. if 2nd cycle is used. Figure (4) show the CV of Fe $(CN)_{63}^{-}$ in 0.1M KCl is taken at varying working electrodes. In general degrees of sensitivity of response that it’s evident for various solid electrodes appear as:

GPE > GCE > Au-E > Pt-E It is interesting to note that GPE has quite a similar enhancement in capacitance current as compared with the GC electrode (3 mm diameter) followed by Au and Pt (1 mm diameter) due to area effect over potential.

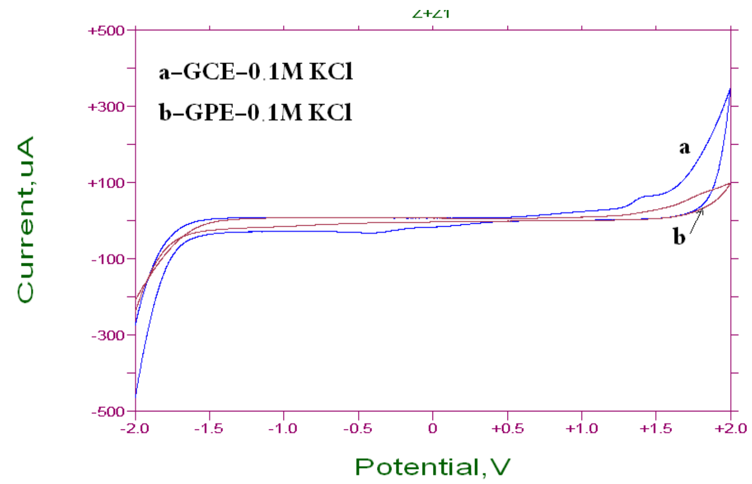


**Figure (3) Cyclic voltammograme of (a) GCE (b) GPE in 0.1M KCl. SR=100 mVsec$^{-1}$versus Ag/AgCl.**

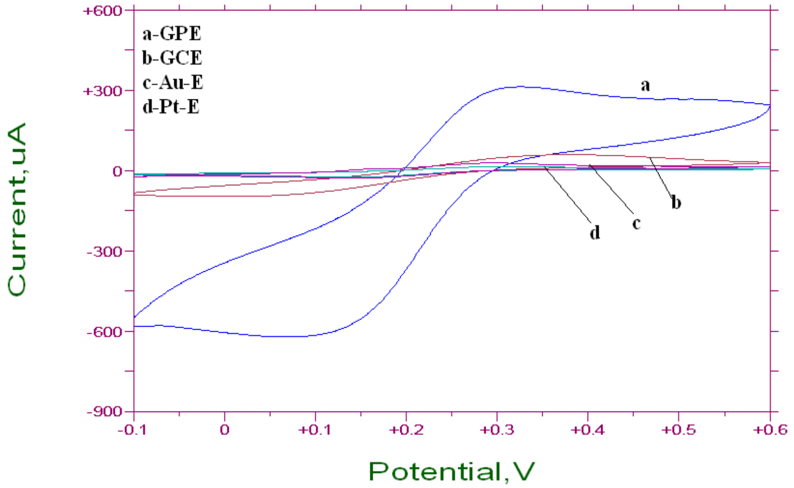


**Figure (4) Cyclic Voltammetry of different electrodes (a) GPE (b)GCE (c) Au-Electrode (d) Pt-Electrode in 1mM $K_3Fe(CN)_6$ with 0.1M KCl as supporting electrolyte versus Ag/AgCl and 100 mVsec$^{-1}$.**

## Effect of Varying Scan Rate

The effect of varying scan rates on the cyclic voltammograms using GPE as working electrode in 0.1M KCl supporting electrolyte was studied with 1mM $K_3Fe(CN)_6$ over a scan rate ranging of 5 – 1000 mV/s. Oxidation and reduction currents of Fe(III)/Fe(II) couple was observed to increase with scan rate due to heterogeneous kinetics and IR effect as shown in Figure (5).

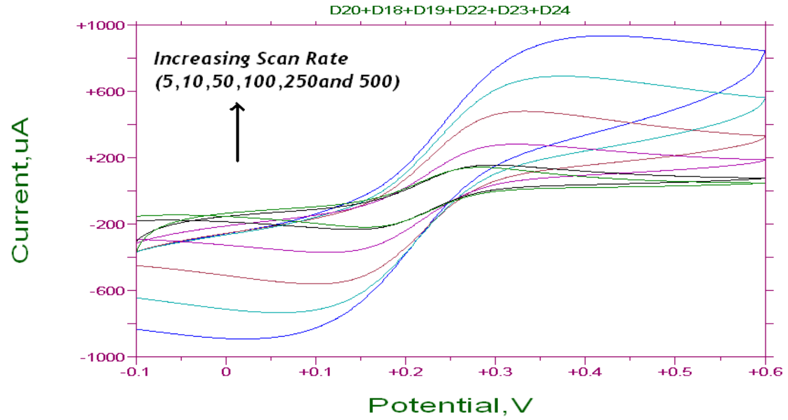


**Figure (5) Cyclic Voltammetry of GPE in 0.1M KCl and 1mM $K_3Fe\ (CN)_6$ at different scan rate (5,10, 50, 100, 250 and 500 mV $sec^{-1}$) Versus Ag/AgCl and $100mVsec^{-1}$.**

Based on a plot of log (Ipa) versus log (scan rate) for oxidation current of the first cycle, a straight line was obtained in Figure (6) fulfilling the equation y = 0.4388X+1.7912 with $R^2$=0.9988. A slope of 0.44 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process.

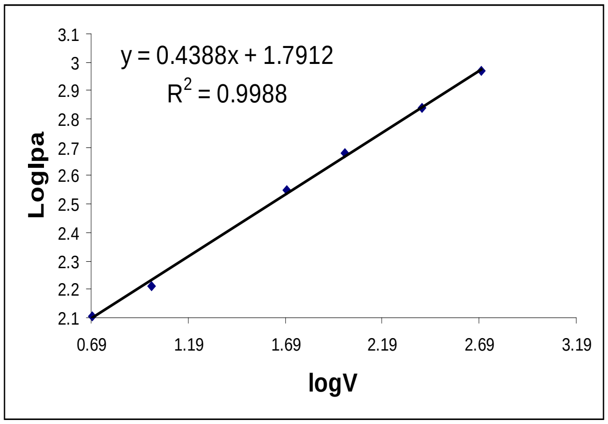


**Figure (6) Plot Log Ipa(anodic current) versus Log SR(scan rate) of GPE in 0.1M KCl and 1mM $K_3Fe(CN)_6$ versus Ag/AgCl.**

## Effect of Varying $K_3Fe\ (CN)_6$ Concentration

Figure (7) shows the linear current dependent on K3Fe(CN)6 concentration was observed at concentration range of 1-10mM which is described by the equation of y=41.802X - 69.113 with $R^2$=0.9484. The slope of linear line for K3Fe (CN) 6 showed that a considerably high sensitivity response of 41.8µA/mM is readily obtained at GP electrode during cyclic voltammetry.

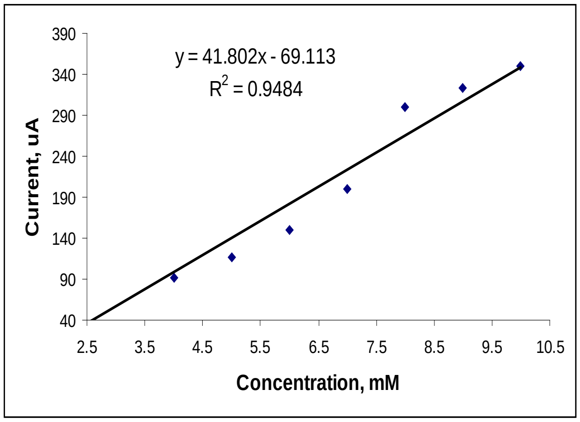


**Figure (7) Plot Ipc(cathodic current) versus different concentration $K_3Fe(CN)_6$ (1-10mM) in 0.1M KCl at scan rate 100mVsec$^{-1}$ Using GPE versus Ag/AgCl.**

## Chronoamperometry and Chronocoulometry studies

Figure (8) shows the monotonous rising and decaying current transient in accordance to the theoretical expectation of the Cottrell equation [14, 15] based on the diffusion process to a planar electrode. Diffusion coefficient (D) of in 0.1M KCl using GPE as a working electrode is $3.2\times10^{-7}$ cm$^2$/sec. It was found that the GPE has a total charge transferred of 12.8µC/m$^2$ in Fe $(CN)_{63}^{-}$ ion as in Figure (9).

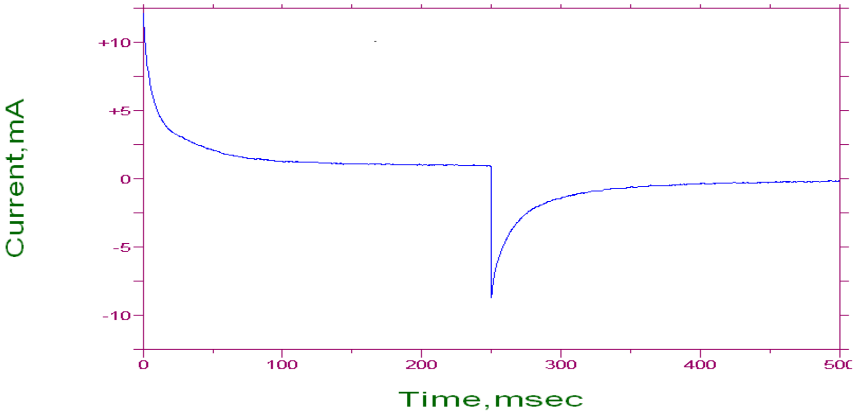


**Figure (8) Chronoamperograms or Cottrell plot obtained For 1mM $K_3Fe(CN)_6$ and 0.1M KCl as supporting electrolyte Using GPE versus Ag/AgCl. Potential was scanned in a negative direction from -1800 to +1800mV with 250 msec. pulse width.**

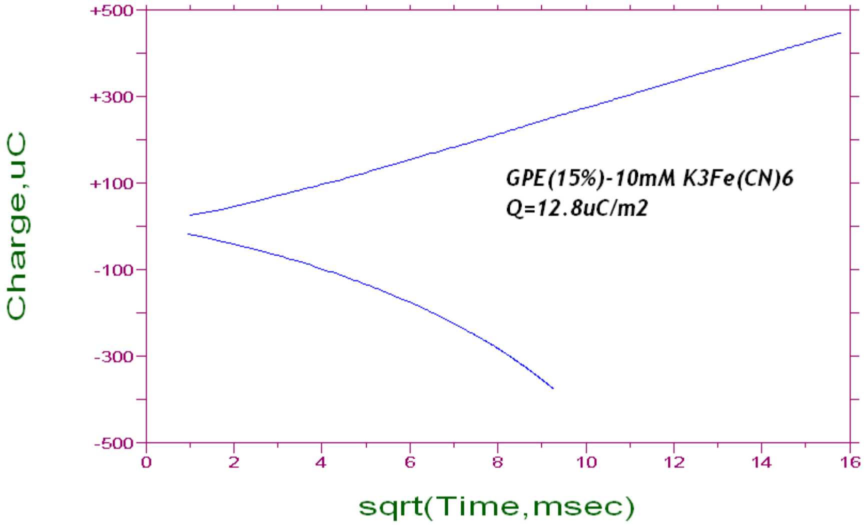
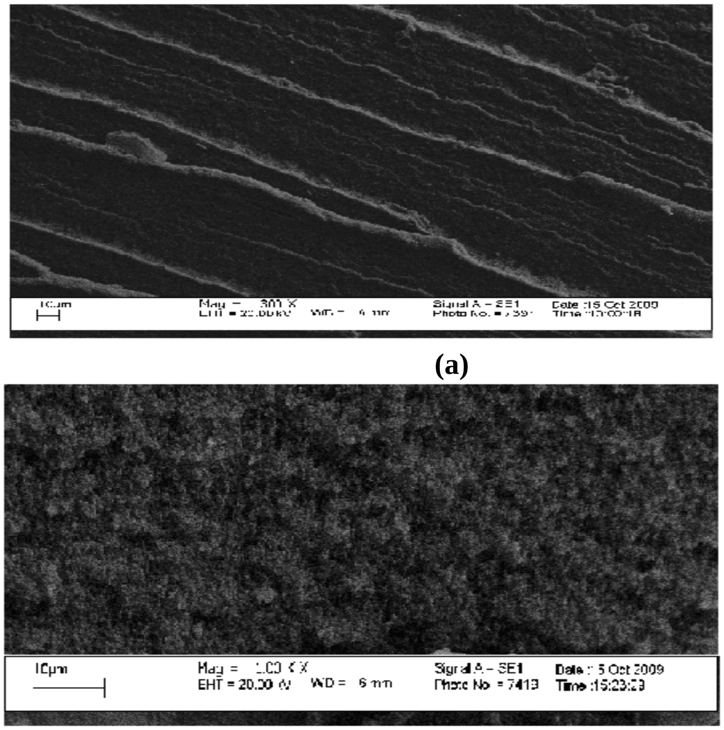


**Figure (9) Choronocoulomogram or Anson plot of charge, Vs. t1/2 obtained for the redox of 1mM $K_3Fe(CN)_6$ and 0.1M KCl as supporting electrolyte using GPE versus Ag/AgCl.**

### Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) of the grafted polymer GP was studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 kV. The scanning electron photographs were recorded at a magnification of 100k X depending on the nature of the sample. Samples were dehydrated for 45 minutes before being coated with gold particle using the Baltec SC030 Sputter Coater. SEM was used to examine the morphology of grafted polymer (GP) before and after electrolysis. Figure(10a) GPE before electro analysis, in $K_3Fe(CN)_6$ by cyclic voltammetry, GP surface appears compact, nonporous, the uniformity of GP surface is marred by a wavelike protrusion but slightly increase as occurrence of protrusion is observed phase an absence of microcrystalline structure. Figure (10b) after electro analysis the GPE was subjected to continuous 10 potential cycling during CV in the presence of $Fe(CN)_6^{3-}$ solution, although many of the microparticles still remain at about <1 µm, there are some of the GP/Fe(0) microparticles that appear to increase in size. The slight increase in size can be due to the presence of $Fe^0$.



**(a)**

**(b)**

**Figure (10) Scanning electron micrographs (SEM) of Grafted Polymer as electrode (a) before and (b) after electroanalysis with Potassium Ferricyanide in aqueous solution 0.1M KCl.**

## CONCLUSIONS

A Grafted Polymer Electrode (GPE) has an extended potential working region as compare to GCE. The stability of GPE as a working electrode was evaluated by using $K_3$Fe (CN) 6 solution. Redox peaks of Fe (CN) $_{63}^{-}$ / Fe (CN) $_{64}^{-}$ obtained at GPE appears high current comparing with GCE. Although the oxidative and reductive region is limited with high rang +2.0 to -2.0V, the use of potential cycling helps to widen the redox working potential range significantly. Electro catalytic activity of GPE is therefore evident in this study. GPE was studied by redox process of $K_3$Fe(CN)6 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, pH, Temperature, electrolyte and scan rate.

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