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ORIGINAL RESEARCH ARTICLE

ELECTROCHEMICAL SENSING OF HEAVY METAL IONS (NI) WITH ORGANIC CONDUCTING POLYMER (PANI)

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ABSTRACT

The aim of this work was to synthesise The conducting polymer (PANI)in the modified electrochemical sensors included (Dimethyl Giyoxime) to use in the electrochemical sensing of heavy metal ions with (Ni). Electrochemical synthesis experiments were used throughout this study. The polypanlin films (pani) were electrochemically synthesised by cyclic voltammetry on CHI-660C electrochemical device with (H_2SO_4) represents the anionic dopant. The solution typically contained 0.1 M aniline and 0.12 M H_2SO_4 in (H_2O concentration about 5% (v/v)).Traditional techniques used to characterize the films,FAM was used for studding the structural properties and (FT-IR , UV-visible) were used for studding the spectroscopy properties.The results of this study was presented to report the use of the electrochemical sensors to sense the heavy metal ions (Ni) with organic conducting polymer (PANI).

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INTRODUCTION

As heavy metal ions severely harm human health, it is important to develop simple, sensitive and accurate methods for their detection in environment and water (Nicholson, 2003 .water pollution can occur through natural processes, most of the pollution is the result of anthropogenic activities. Wastewaters arising from these activities are generally discharged into water resources and because of the high toxicity associated with heavy metals in particular, some of these metals represent a risk for human health even at low (μgL^{-1}) levels (Boulanger, 2004). Various electroactive compounds with reactivity towards metal ions can be employed to obtain enhanced selectivity for the identified metal ions of interest (MacDiarmid, 2001). PAni has generally been synthesized by both chemical and electrochemical methods. Recently, (PAni)has been synthesized using a novel mechano-chemical route (Chiang, 1986). Electrochemical synthesis is one of the excellent methods to synthesize conducting polymers because their area and thickness can be controlled.

Recently years, conducting polymers have conjured great interest in the work of research because of their various chemical, physical properties and their numerous possible applications (Skotheim, 1986). Conducting polymer PANi attracted much attention because of its physical and chemical properties which make it interesting material for applications in different areas such as Light-weight batteries (Wallace, 2013; Matsunaga, 1990; Huang, 1993; Nicolass-Debarnot, 2003), capacitors (Wallace, 2003), electrochromic devices (Matsunaga, 1990; Huang *et al.*, 1993), photoelectric cell (Li *et al.*, 2000; Ayad, 1994), light emitting diodes (Yang, 1992), biosensors (Mu, 1996), sensors (Mirmohseni, 2002), switchable membranes (Mirmohseni, 1995), anti-corrosive coatings on metals (Tallman *et al.*, 2002). Polyaniline and the other conducting polymers such as polythiophene, polypyrrole, and PEDOT/PSS contain conjugating (π) electron system i.e. they are members of the same class of polymers, and have potential for applications due to their light weight, conductivity, mechanical flexibility and low cost. They have been intensively studied from both experimental (Kanazawa *et al.*, 1979/ 80; Tourillon, 1982; Chung *et al.*, 1984; Hotta, 1983) and theoretical (Ford, 1983; Bredas, 1983; Bredas,1983) points of view.

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Polyaniline is especially attractive because it is relatively inexpensive, has three distinct oxidation states with different colors,it's high conductivity, easy synthesis and has an acid/base doping response (Wu *et al*., 2008; John, 2008; Rodriguez, 2009; Han *et al*., 2008). PANi has high stability in air in the oxidized state, which can be reversibly doped in aqueous medium from a semi conducting state ($\sigma \approx 10^{-8}\ \Omega^{-1}cm^{-1}$) to a conducting state ($\sigma \approx 10^{2}\ \Omega^{-1}cm^{-1}$) (Kaufman, 1984)

The microstructure of conductive PANi can vary greatly with the preparing methods and processing conditions. Zhang *et al* prepared a series of polyaniline/Carbon nanotube array composite electrodes by cyclic voltammetry electrode position, to improve the capacitive performance of PANi/CNTA Composites (Zhang *et al*., 2009). Sazou *et al* reported polyaniline coating on stainless steel by potentiodynamic and potentiostatic deposition (Sazou, 2007). Wu *et al* recently studied the PANi counter electrode coated on conductive glasses using a chemical synthesis method (Li, 2008). The aim of this work was to synthesize The conducting polymer (PANI)in the modified electrochemical sensors included (Dimethyl Giyoxime) to use in the electrochemical sensing of heavy metal ions with (Ni). The application of this compound in electroanalysis was evaluated to determine the response of this compound for the heavy metal ions (Ni).

EXPERIMENTAL

Polyaniline (PAni) films were synthesized by the electrochemical technique of aniline monomer on conducting substrates (platinum). The solution typically contained 0.1 M aniline and 0.12 M H_2SO_4 in (H_2O concentration about 5% (v/v)), the mixture was placed and stirred in a cell (All chemicals and materials were available in the lap). Traditional techniques were used to characterize the films, FAM was used for studding the structural properties and (FT-IR, UV-visible) were used for studding the spectroscopy properties. Synthesis of PANI was carried out by cyclic voltammetry on CHI-660C electrochemical device. To increase the adsorption capacity and selectivity toward the metal ions (Ni) for (PANI) films, 0.001 M (Dimethy – lglyoxime) in 0.01 M (EDC) solution was used as the chemical modification by Dip technique. PANI films were immersed on the solution for (24 hours).

For the electrochemical sensing of heavy metal ions, Ni ions used as heavy metal ions of concentration 0.1 M. On CHI-660C electrochemical work station differential pulse voltammetry DPV technique used for electrochemical sensing of Ni ions. First, DPV scan was recorded in 0.1 M KCl solution of modified polyanilin film as working (sensing) electrode, while Ag/AgCl and platinum plate as reference and counter electrodes respectively After the reference solution scan the films were immersed in 0.1 M Ni ion solution for 5 minutes. After 5 min. again DPV scan taken in 0.1 M KCl solution in the same parameters as above and same steps repeat with the immersing time at 10,15 and 20 minutes.

RESULT AND DISCUSSION

1-Synthesis of organic conducting polymer (PANI)

CV is performed by cycling the potential of a working electrode, and measuring the resulting current. The potential of the working electrode is measured against a reference electrode which maintains a constant potential, and the resulting applied potential produces an excitation signal such as that of figure1 In the forward scan of figure1, the potential first scans positively, starting from a lower potential and ending at a greater potential.

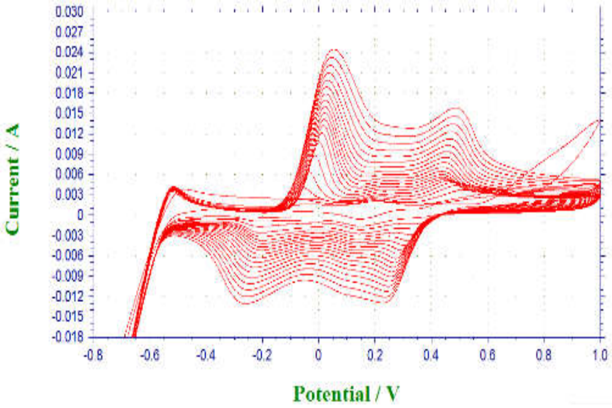


Fig.1 Electrochemical Synthesis of Polyaniline by Cyclic Voltammetry Technique

The potential at (1V) is call the switching potential, and is the point where the voltage is sufficient enough to have caused an oxidation or reduction of an analyte. The reverse scan occurs from (1V) to (-0.65V), and is where the potential scans negatively. Figure 1 shows a typical oxidation occurring from (-0.65V) to (1V) and an reduction occurring from (1V) to (-0.65V).This cycle is repeated as shown in the figure 1.

The oxidation process occurs from (-0.65V)the initial potential to (1V) the switching potential. In this region the potential is scanned potential to cause a oxidation. The resulting current is called anodic current (Ipa). The corresponding peak potential occurs at (0.025V), and is called the anodic peak potential (Epa). and is reached when all of the substrate at the surface of the electrode has been oxidized After the switching potential has been reached (1V), the potential scans negatively from (1V) to (-0.65V). The resulting current is called cathodic current (ipc). The corresponding peak potential occurs at (-0.275V), and is called the cathodic peak potential (Epc). The Epc is reached when all of the substrate at the surface of the electrode has been reduced. These measurements approximately identical with the electrochemical properties of PANI (http://www.hindawi.com/journals/tswj/2013/940153/). That means Cyclic voltammetry measurements were used to identify the redox processes at the PANI composite films are achieved the electrochemical properties of PANI.

2-FT-IR Spectra (absorption)

FT-IR device ALPHA type was used to characterize the spectra of films in the region 4000cm^{-1} to 600 cm^{-1} In a spectrum the band observed at 3679.81 cm^{-1} is due to N-H stretching. The polymer shows the absorption bands at 2356.00 cm^{-1} is due to asymmetric C-H stretching . The absorption peaks observed at 1686.46, 1651.37 and 1524.86 cm^{-1} were attributed to C=C stretching in aromatic nuclei. Absorption bands at 1460.82 cm^{-1} evidenced to C=N stretching. The polymer shows absorption bands at 1288.66 cm^{-1} which confirms the C-N stretching.

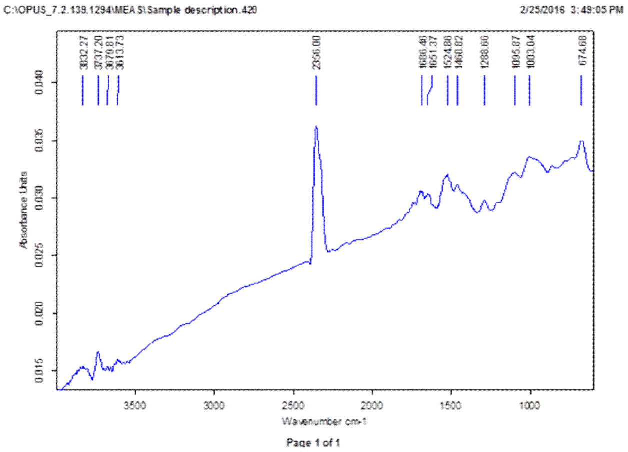


Fig .2 FT-IR spectra of PANI samples doped with H_2SO_4 acid

The absorption bands appeared at 1095.87and 1003.04 cm-1 reveals the C-H bending vibrations. The absorption bands lies below 1000 cm-1 are the characteristics of mono substituted benzene. The same finding has been reported in literature values (Vivekanandan *et al*. 2011). SO The absorption peaks of the FTIR spectra confirms that, polymer was prepared using H_2SO_4 as dopant anions is successfully synthesized Polyanilin film.

3-UV-Visiable Spectra (transmittion)

The UV-VIS spectra of the PANI films were done by using UV-visible spectroscopy device in the region 1200 cm-1 to 200cm-1 with the help of DFF (C_3H_7NO) as the reference liquid.

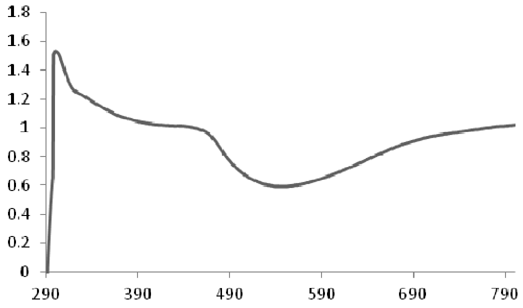


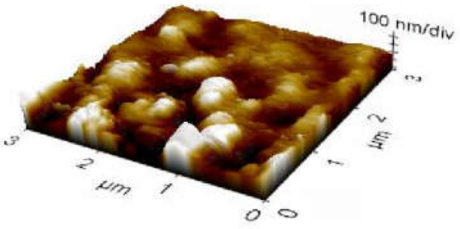
Fig.3 UV-VIS spectra of the PANI film

The UV-VIS spectra of the PANI film with the help of DFF (C_3H_7NO) as the reference liquid is shown in Fig.3 .The band observed at 297 nm for the PANI samples corresponds to π- π^* transitions of aniline (S. Journal of Atomic, Molecular, Condensate & Nano Physics Vol. 3, No. 1,pp. 27–33, 2016 ISSN 2349-2716 (online); 2349-6088 (print) Published by RGN Publications). Fig.3 shows that when increasing the voltage, the absorption peak intensity also increases (high intensity peak at (1.5111ev) due to the regular arrangement of monomer units in electrochemical polymerization.

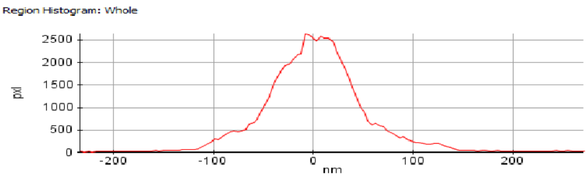
4- AFM (Topographical Properties)

Atomic Force Microscopy was used to study the Topographical Properties of PANI. The 3*3 μm^2 area was scanned for topographical study .The table(1) shows the values of parameters was used. The topographic image for the Polyaniline film was taken for the area 3*3 μm^2. Fig. (4a) shows tow dimensional (2D) topographic image of the scanned area and (4b) shows the three dimensional (3D) view of the image and line parameter of the same.

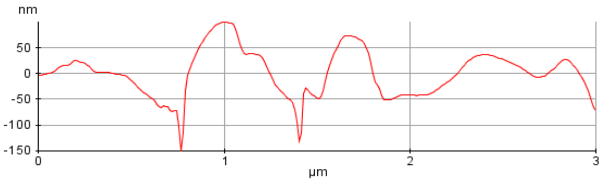
(4a) 2D image



(4b) 3D image



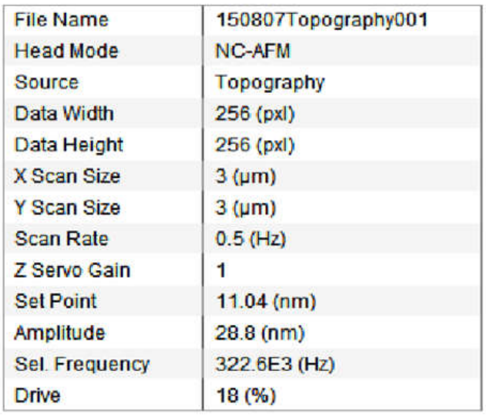
(4c)Region Histogram



(4d)Line Profile

3D view of nanocomposite illustrated thickness ~200nm with 40 nm average roughness of the nanocomposite film. The cloudy appearance of the film as attributed to the conclusion of deposition of Polyaniline (PANI).

Table 1. Parameters value



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Head Mode	NC-AFM
Source	Topography
Data Width	256 (pxl)
Data Height	256 (pxl)
X Scan Size	3 (µm)
Y Scan Size	3 (µm)
Scan Rate	0.5 (Hz)
Z Servo Gain	1
Set Point	11.04 (nm)
Amplitude	28.8 (nm)
Sel. Frequency	322.6E3 (Hz)
Drive	18 (%)

5-Electrochemical detection of heavy metal ions (Ni).

Electrochemical detection of heavy metal ions (Ni) gives the sensing of the Ni ions (Fig. 5) at potential of -0.25 V because Nickel has oxidation potential of -0.25 V.

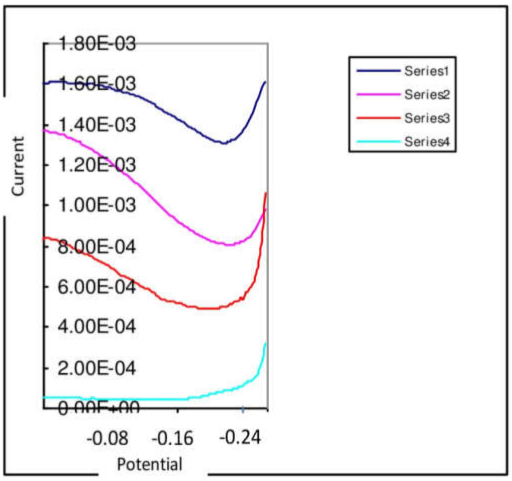

Fig5. Electrochemical detection of Ni ion with Dimethy-lglyoxime modified PANI Films

This means that Nickel ions reacts with (Dimethyl Glyoxime) and forms coordination bond between Nickel as central metal atom and (Dimethyl Glyoxime) as ligand. In the DPV scan at the oxidation potential (i.e. -/+ 0.25 V) coordination bond between Nickel metal and (Dimethyl Glyoxime) breaks, which results Nickel ions leaves the (Dimethyl Glyoxime) ligand, which causes flow of electrons or current and observed peak at the oxidation potential (i.e. -/+ 0.25 V) as shown in Fig. 5

Conclusion

The conclusions arrived from the studies are as follows:

- Cyclic voltammetry measurements were used to identify the redox processes at the PANI composite films are achieved the electrochemical properties of PANI.
- The FTIR analysis and UV spectral confirm that, we have successfully synthesized Polyaniline films.
- The π- π* transitions of aniline were confirmed from the UV spectral studies.
- Nickel ions reacts with (Dimethyl Glyoxime) and forms coordination bond between Nickel as central metal atom and (Dimethyl Glyoxime) as ligand. In the DPV scan at the oxidation potential (i.e. -/+ 0.25 V) coordination bond between Nickel metal and (Dimethyl Glyoxime) breaks, which results Nickel ions leaves the (Dimethyl Glyoxime) ligand, which causes flow of electrons or current and observed peak at the oxidation potential (i.e. -/+ 0.25 V)

(That means there is response to heavy metal ions (Ni), so our films can be used to sense the heavy metal ions (Ni)).

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