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Electrochemical Detection of Hg (II) Ions Using EDTA-PANI/SWNTs Nanocomposite Modified SS Electrode

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Abstract. Detection of Hg (II) ions using EDTA modified polyaniline (PANI) and single walled carbon nanotubes (SWNTs) nanocomposite (PANI/SWNTs) was performed electrochemically via cyclic voltammetry (CV) technique. Dodecyl benzene sulphonic next step, PANI/SWNTs nanocomposite was modified acid sodium salt (DBSA) was used as a surfactant during this synthesis to get uniform suspension SWNTs. In the by EDTA solution containing crosslinking agent 1-ethyl-3-(3-(dimethylamino) propyl) - carbodiimide (EDC) utilizing dip coating technique. The sensitivity of EDTA modified PANI/SWNTs nanocomposite towards Hg (II) ions was investigated. Differential pulse voltammetry (DPV) technique was applied for the electrochemical detection of Hg (II) ions.

Keywords: Hg(II) ions, Nanocomposite, Electrochemical, DPV, cross linker

PACS: 81

INTRODUCTION

Earth contains a number of natural constituents to balance the ecological and biological system for living organisms [1]. Heavy metal ions are one of them which play an essential role in the fundamental physiological processes in organisms, from bacteria to mammals [2]. Irrespective atomic mass or density of metal ions as well as in the concentration that causes an unfavorable activity to human or environment confirms them as toxic heavy metal ions [1,3]. Mercury (Hg) is nominated as sixth most toxic amongst the most toxic compounds [2, 4]. The mercury shows binding affinity towards the proteins and nucleic acids of human body which interrupts the biological activity in the cells resulting in severe health risks [5].

Traditionally mercury based electrodes recognized as the most sensitive electrodes for the detection of heavy metal ions due to their high sensitivity towards target metal ion, reproducibility, purity of surface, amalgam formation ability etc. [6, 7]. Though, in spite of all these excellent performances, mercury has been severely restricted or banned for future regulations and occupational health consideration due to its high toxicity [8, 9].

Conducting polymer and carbon nanomaterial have shown great promise because of an ample of reasons. The most distinct reason behind the potential use of

these materials is their application in potentiometry, voltammetry and as electrochemical biosensors [10-12]. Thus, to utilize the idyllic properties of these materials, in the present study we have reported an electrochemical sensor for detection of Hg (II) ions based on EDTA-PANI/SWNTs composite structure.

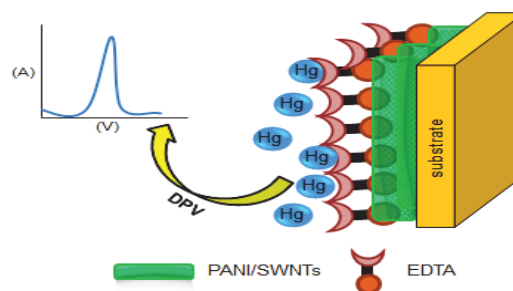


FIGURE 1. Schematic of EDTA-PANI/SWNTs composite.

In this combination non-covalent bonding between PANI and SWNTs will take place, where SWNTs will utilize for the faster signal transduction and EDTA will bind with π - π interaction to the PANI surface. EDTA will serve the purpose of sensitive detection of Hg (II) ions. Scheme 1 represents the EDTA modified composite structure and analysis of Hg (II) ions.

EXPERIMENTAL DETAILS

The PANI/SWNT composite was synthesized by electrochemical method in the presence of single wall carbon nanotube (SWNTs) on commercial grade stainless-steel (SS). 20% wt. SWNTs w.r.t. aniline monomer was dispersed in a solution of Sodium Dodecyl benzene Sulphonate (SDBS) in water and stirred for 4hr. The resulting SWNTs solution was immersed in electrolyte containing 0.25M aniline with 1M H_2SO_4 and stirred for 20 min. The electrochemical polymerization was carried out by cyclic voltammetry (CV) technique at a potential range 0.0V to 1.0V at 0.1 V/s scan rate. The dark green coating on SS obtained.

Electrochemically synthesized PANI/SWNTs nanocomposite film was then immersed in a phosphate buffer solution of pH 7 containing 0.1M EDC (activating agent) and 0.01 M EDTA for 12 hrs. with continuous stirring for the covalent bonding between COOH- in EDTA with NH_2 groups of PANI/SWNTs nanocomposite structure.

RESULTS AND DISCUSSIONS

Electrochemical Analysis of PANI/SWNTs and EDTA-PANI/SWNTs Structure

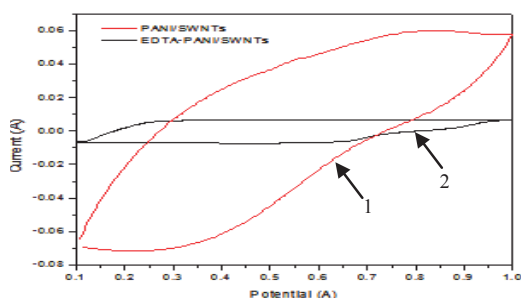


FIGURE 2. Comparative CV of (1) PANI/SWNTs and (2) EDTA- PANI/SWNTs nanocomposite structure

Fig. 2 shows the comparative electrochemical characterization of PANI/SWNTs and EDTA-PANI/SWNTs composite nanostructure. From comparative voltammogram observed that PANI/SWNTs composite structure is showing higher current density means more conductive in nature compared to EDTA modified EDTA-PANI/SWNTs composite nanostructure. In another way decrease in conductivity of EDTA-PANI/SWNTs nanocomposite means EDTA structure is dominating the electrostatic interactions of PANI/SWNTs composite nanostructure. Dominating effect on conductivity of composite structure shows the presence of EDTA

molecules on the PANI/SWNTs composite nanostructure.

FTIR Analysis of PANI/SWNTs and EDTA-PANI/SWNTs Structure

Fig. 3 represents the FTIR spectra of electrochemically synthesized PANI/SWNTs and EDTA modified PANI/SWNTs nanocomposite structures. The peak at 835 cm^{-1} confirms the N-H band for out-of-plane bending absorption. The Presence of benzoid band around 1470 cm^{-1} vibration indicates the emeraldine salt form of PANI in PANI-SWNTs composite structure. Strong N-H stretching band of aromatic ring of PANI in PANI/SWNTs composite structure confirms at 3400 cm^{-1} . The appearance of band nearly 1037 cm^{-1} at composite structure confirms the presence of SWNTs in PANI/SWNTs structure. Band in between $1720\text{-}1740\text{ cm}^{-1}$ for C=O and 3600 cm^{-1} for O-H were observed in EDTA-PANI/SWNT structure, which were completely absent in the PANI/SWNTs nanocomposite structure confirms the presence of EDTA covalent bonding towards PANI/SWNTs composite structure.

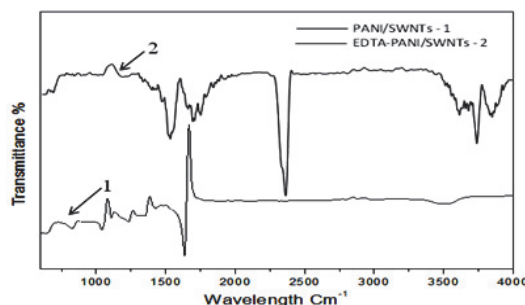


FIGURE 3. Comparative FTIR spectra of (1) PANI/SWNTs and (2) EDTA- PANI/SWNTs nanocomposite structure

Morphological Analysis of PANI/SWNTs and EDTA-PANI/SWNTs Structure

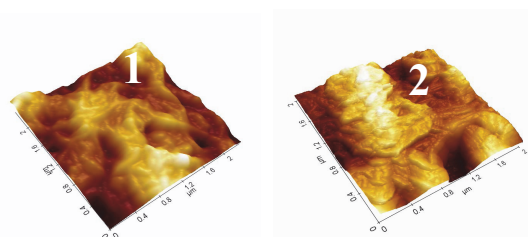


FIGURE 4. Comparative AFM images of (1) PANI/SWNTs and (2) EDTA- PANI/SWNTs nanocomposite structure

Fig. 4 shows the comparative atomic force microscopy (AFM) micrographs of the PAN/SWNTs and EDTA-PANI/SWNTs composite structure. From above

micrographs we can observe a strong change in morphology of composite structure from PANI/SWNTs composite to EDTA-PANI/SWNTs structure. EDTA-PANI/SWNTs composite structure shows rougher surface compared to PANI/SWNTs composite structure which confirms the presence of EDTA molecules on PANI/SWNTs composite structure.

Analytical Analysis of Hg (II) Ions by EDTA-PANI/SWNTs Structure

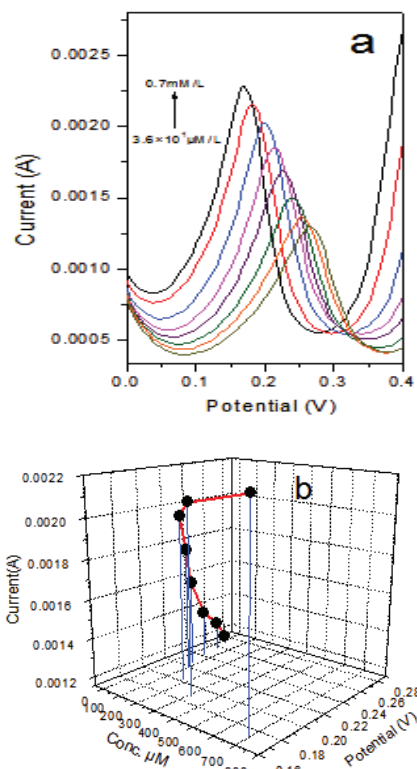


FIGURE 5. (a) DPV stripping signals for various concentrations (0.7 mM to $3.6 \times 10^1 \mu\text{M L}^{-1}$ from top to bottom) of Hg (II) ions on the EDTA-PANI/SWNTs electrode. Supporting electrolyte: $0.5 \text{ M H}_2\text{SO}_4$. (b) The effect of concentration of Hg (II) ions on current (A) and Potential (V)

As mentioned above, the conductive and rich chelating groups of the EDTA-PANI/SWNTs through DPV utilized for the electrochemical determination of Hg (II) metal ions. The PANI/SWNTs-EDTA nanocomposite electrode was immersed in solution of Hg (II) ions for 20min. The investigation was conducted at room temperature at various concentrations of Hg (II) ions, i.e. 0.7 mM , $3.2 \times 10^2 \mu\text{M}$, $1.8 \times 10^2 \mu\text{M}$, $1.1 \times 10^2 \mu\text{M}$, $8.1 \times 10^1 \mu\text{M}$, 5.9×10^1

μM , $4.5 \times 10^1 \mu\text{M}$, $3.6 \times 10^1 \mu\text{M}$. The metal ions were collected on the surface of EDTA-PANI/SWNTs-EDTA nanocomposite structure by immersing into the solution containing Hg (II) ion for 20min without applying potential (for accumulation of metal ions). After the mechanical pre-concentration, followed by a positive-going DPV scan (with a step increment of 0.004 V , amplitude of 0.05 V , and pulse period of 0.5 s) from 0.0 V to 0.4 V was carried out for the removal of Hg (II) metal ions from PANI/SWNTs-EDTA electrode surface. Clear anodic DPV peaks were obtained for different concentrations of Hg (II) ions (Fig. 5a).

From Fig. 5b we can observe that, as the concentration of Hg (II) ions increased intensity of current is also getting increased w.r.t. potential in increased order. For more accumulated Hg (II) ions more stripping voltage required. Decrease in steady state of current (A) and Potential (V) is proportional to Hg (II) ion concentration. EDTA-PANI/SWNTs layer showed good electrochemical response towards analysis of Hg(II) ions. A detection limit obtained for Hg(II) ions was in the range of $3.6 \times 10^1 \mu\text{M L}^{-1}$.

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