



## EDTA-modified PANI/SWNTs nanocomposite for differential pulse voltammetry based determination of Cu(II) ions

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### ABSTRACT

Differential pulse voltammetry (DPV) based electrochemical sensor dedicated for the determination of Cu(II) ion concentration is reported in this research. Sensor was based on electrochemically synthesized polyaniline (PANI) and single walled carbon nanotubes (SWNTs) nanocomposite (PANI/SWNTs), which was additionally functionalized by ethylenediaminetetraacetic acid (EDTA) in order to get structure (EDTA-PANI/SWNTs) with advanced selectivity towards Cu(II) ion. Synthesis of PANI/SWNTs nanocomposite was performed by potential cycling, dodecyl benzene sulphonic acid sodium salt (DBSA) was used as a surfactant during the synthesis of PANI/SWNTs nanocomposite to get a uniform suspension of SWNTs at room temperature. In the next step, PANI/SWNTs nanocomposite was further modified by the EDTA solution containing 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) as activating agent, which is activating carboxyl groups, utilizing dip coating technique at room temperature. Differential pulse voltammetry (DPV) technique was applied for the electrochemical detection of Cu(II) ion. DPV based response of EDTA-PANI/SWNTs structure towards Cu(II) ion was investigated. Analytical signals reveal that EDTA-PANI/SWNTs structure is suitable for selective determination of Cu(II) ion in the presence of interfering Pb(II), Cd(II), Ni(II) and Co(II) ions.

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### 1. Introduction

Sensitive and selective detection of heavy metal ions is very important and challenging research area. Among many metal ions Cu(II) shows essentiality as micronutrient element, it also has significant importance in biochemistry and metabolic processes of many living organisms [1,2]. Deficiency of Cu(II) may be responsible for the anemia, ischemic heart diseases, bone demineralization, cardiovascular effects, skin diseases etc. [3]. But recently, due to contamination instead of being an essential element, excessive doses of Cu(II) ion become threatening life issue for the living organisms [4]. Therefore, numerous methods and technologies have been developed for the sensitive and selective detection of metal ions. Most popular and well-known techniques are liquid chromatography, electrophoresis, spectrophotometry, solid-phase extraction coupled with atomic absorption spectroscopy, atomic emission spectroscopy, and induc-

tively coupled plasma mass spectrometry [5–10] etc. However these methods are still expensive, time-consuming and require experienced staff for the handling of these instruments.

Therefore, electrochemical techniques for the detection of metal ions are grasping the attention of researchers due to their advantages such as simple and cost effective instrumentation and fast analytical response [11–13]. In addition, the complexation by organic molecules containing coordinating site [1,14] and chemically modified electrodes [15–20] could be applied in order to increase both selectivity and sensitivity of electrochemical methods. The desired sensitivity of chemical sensors can be achieved by a modification of electrode surfaces with suitable chemical reagents such as metals, semiconductors, carbon based materials and polymeric materials [21–24]. Chelating ligands are also used as metal ion complexing agents [25–29].

The modification of electrode surfaces with nanocomposite materials such as carbon nanotubes and conducting polymer nanocomposite can increase environmental stability and electrical conductivity [30–33]. Polyaniline and their derivatives are used in chemical sensors [34–38]. Conducting polymers (CPs) are also very useful materials for modification of electrodes due to their conductivity, easy synthesis, low resistance [39], high accessible surface area, environmental stability etc. [40,41]. These enlisted ideal properties as well as su-

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perior electrical and structural properties, better adhesion ability of CPs makes them most considerable material for the development of sensors, especially for the detection of metal ions [42,43]. However, due to continuous charge, discharge process during repeated interpolation as well as depletion of ions considerable volume change occurs in the CPs, which is responsible for the reduction of mechanical stability for various applications [44,45]. Among different types of nanomaterials, carbon nanotubes are used as preferred materials due to their excellent electrical properties, better charge transfer channels, and high surface to volume ratio etc. [46–50]. In spite of admirable properties of CNTs, they are hydrophobic in nature and pristine CNTs can lack functional binding groups on their surfaces which lead towards the weak response to metal ions [51]. Surface modification of CNTs with various functional groups can tackle these issues. Chelating ligands are binding central metal ion, which can be applied in order to form a complex structures. Chelating ligands form very stable complexes with the most of the transition metals. Thus, chelating ligand modified organic materials; particularly conducting polymers can be used for the determination of heavy metal ions by adjusting different values of pH [52]. M. A. Rahman et al. [29] have reported EDTA-CPME electrode, which was fabricated by polymerization of 3', 4'-diamino-2, 2'; 5'2"-terthiophene monomer on glassy carbon electrode by utilizing the electrochemical technique. The CPME was further functionalized by immersing CPME in EDTA solution containing additional crosslinking agent. The electrochemical response of EDTA modified CPME was successfully tested for various metal ions viz. Co, Ni, Zn, Cd, Cu, Fe, Pb & Hg. There are several reports for the detection of metal ions using conducting polymers, carbon nanotubes and chelating ligand complexes with conducting polymers [53–58].

Conducting polymers and carbon nanotubes have their own advantages and disadvantages in the detection of heavy metals, we intended to exploit the advantageous properties of these materials to fabricate polyaniline/carbon nanotube nanocomposite with good conductivity and worthy water stability. Therefore, the effective combination of these two materials will not only make full use of respective advantages but also be vital for advanced efficiency.

Present investigation, is focused on the synthesis of polyaniline and single walled carbon nanotubes based composite structure and its applicability for monitoring of Cu(II) ion concentration. In this investigation we have carried out electrochemical synthesis of polyaniline and single walled carbon nanotubes and further it was modified by chelating ligand-EDTA.

## 2. Materials and methods

### 2.1. Reagents

Aniline of reagent grade was purchased from Sigma Aldrich (Bangalore, India); Dodecyl benzene sulphonic acid sodium salt (DBSA) was purchased from Kemphasol (Bombay, India) and it was used as a surfactant and the organic solvent to form a fine suspension of SWNTs.  $H_2SO_4$  of HPLC grade obtained from Rankem (Bombay, India), SWNTs functionalized with carboxyl groups (-COOH) were purchased from Nanoshel LLC. Ethylenediaminetetraacetic acid (EDTA) was purchased from Fisher Scientific, 1-ethyl-3(3(dimethylamino)propyl)-carbodiimide (EDC) was procured from Sigma Aldrich (Bangalore, India). Phosphate buffer with pH 7, and other chemicals were reagent grade quality and they were used as received. Stainless steel electrode (SSE) type 304, 0.5 mm thick and area  $1 \times 1 \text{ cm}^2$  was purchased from SSD Enterprises (Jalna, India). An ac-

etate buffer solution was prepared by adjusting 0.1 M acetic acid to the desired pH by adding 0.1 M sodium acetate. Other solvents and chemicals were of analytical grade.

### 2.2. Methods

All the electrochemical measurements were carried out in a single compartment cell containing three electrode system with a CHI660C electrochemical workstation from CH Instruments (Texas, USA). Fourier transform infrared (FTIR) spectrum of the sample was recorded by FTIR spectrophotometer Bruker-Alpha from Bruker (Germany). Atomic force microscope Park system XE-7 (South Korea) was used for AFM visualization in non-contact mode (NC-AFM) to examine the surface morphology of the PANI/SWNTs and EDTA-PANI/SWNTs. All measurements were carried out at room temperature and under an atmospheric environment.

### 2.3. Preparation of PANI/SWNTs nanocomposite

Electrochemical synthesis of PANI/SWNTs nanocomposite was carried out in solution containing 20 wt.% of SWNTs with respect to aniline monomer. Prior to use, SWNTs were mixed with 1 ml of DBSA at SWNTs to DBSA volume ratio of 1:10, in order to homogenize the solution and to disperse SWNTs bundles uniformly SWNTs dispersion in DSBA (SWNTs+DSBA) was ultra-sonicated for 4 h at room temperature. Then 0.25 M emulsion of aniline monomer in 0.5 M solution of  $H_2SO_4$  (Aniline+ $H_2SO_4$ ) was prepared and in order to homogenize it was stirred for 20 min. Then Aniline+ $H_2SO_4$  was further transferred to the flask containing the ultra-sonicated suspension of SWNTs. The reaction mixture of (Aniline+ $H_2SO_4$ +SWNTs) was mechanically stirred for 20 min at room temperature to form a uniform electrolyte of PANI/SWNTs nanocomposite. Prior to the electrochemical deposition of PANI/SWNTs layer, SSE was thoroughly cleaned with piranha solution, acetone and then air dried. SSE with  $1 \text{ cm}^2$  area was used for electrochemical deposition of the nanocomposite. PANI/SWNTs nanocomposite based layer was deposited on a SSE by 20 potential cycles between +0.1 and +1.0 V at a potential sweep rate of 0.1 V/s. Three electrode system with a SSE based working electrode (geometrical area of  $1 \text{ cm}^2$ ), Platinum (Pt) plate as a counter electrode and Ag/AgCl electrode in saturated KCl (Ag/AgCl<sub>(sat.KCl)</sub>) as a reference electrode was used for electrochemical deposition of PANI/SWNTs layer. The electrochemical formation of PANI/SWNTs nanocomposite was observed as a dark green colored coating on SSE electrode. After the deposition of PANI/SWNTs layer, the SSE was washed with reagent grade distilled water and then it was air dried at room temperature.

### 2.4. Modification of PANI/SWNTs nanocomposite by EDTA

Further, modification of PANI/SWNTs nanocomposite with EDTA was performed using dip-coating technique. In order to form covalent bonds between the carboxyl groups of EDTA with amino groups of PANI/SWNTs nanocomposite the PANI/SWNTs nanocomposite film was immersed in a phosphate buffer, pH 7, containing 0.1 M of EDC, which served as crosslinker and 0.01 M of EDTA for the time period of 12 h. the modification was conducted under continuous stirring at room temperature. The resulting EDTA modified PANI/SWNTs nanocomposite modified electrode (EDTA-PANI/SWNTs/SSE) was further rinsed carefully with distilled water and air-dried.

### 2.5. Procedure for electrochemical detection

The electrochemical determination of Cu(II) ions was performed in 40 ml electrochemical cell using three-electrode setup at room temperature, acetate buffer solution with pH 4.5, was used for the preparation of Cu(II) ion-containing solution and 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as blank electrolyte solution for the stripping of Cu(II) ions. The EDTA-PANI/SWNTs/SSE was used as a working electrode, (Ag/AgCl<sub>(sat.KCl)</sub>) as a reference electrode and Pt plate as a counter electrode. Before differential pulse voltammetry (DPV) experiment, a EDTA-PANI/SWNTs/SSE was dipped into the electrolyte containing different concentrations (from 2 mM to 4 μM), of Cu(II) ion under constant stirring to allow trace amounts of Cu(II) ion to be pre-concentrated at the EDTA-PANI/SWNTs/SSE surface. After the pre-concentration step DPV detection step by potential sweep from -0.35 V to 0.00 V (with a potential step increment of 0.004 V, amplitude of 0.05 V, and pulse period of 0.5 s) was carried out for the determination of Cu(II) ion using EDTA-PANI/SWNTs/SSE surface.

## 3. Results and discussion

### 3.1. Electrochemical deposition and characterization of PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite

Fig. 1a shows the typical cyclic voltammogram recorded during potential cycling based synthesis of PANI/SWNTs nanocomposite. Continuous potential cycling leads to the formation of a uniform dark green colored coating on the SSE. As it is seen from the voltammogram the oxidation of aniline monomer starts at 0.2 V. The CV recorded during a continuous scan shows that both oxidation and reduction current are increasing by each successive cycle of the voltammogram, which confirms that electrically conducting nature of formed PANI/SWNTs nanocomposite. The thickness of the film increases by increasing number of potential cycles. The voltammogram of PANI/SWNTs nanocomposite shows clear reduction peaks, which indicate the tendency of material to acquire electrons at low electrode potential. Fig. 1b (curve 1), represents CV registered using PANI/SWNTs/SSE and Fig. 1b (curve 2) using EDTA-PANI/SWNTs/SSE electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> based electrolyte. It is clearly observable that after the modification of PANI/SWNTs/SSE electrode by EDTA, the electrical capacitance of EDTA-PANI/SWNTs/SSE, which can be estimated from voltammogram, is getting decreased. On the other

hand PANI/SWNTs/SSE shows higher current density compared to that of EDTA-PANI/SWNTs. The decrease in peak current of the EDTA modified nanocomposite exhibits the dominant effect of the electrostatic interactions, which reflects on the current density of nanocomposite. These results can be also attributed to the formation of strong complex and chelating interaction between nanocomposite structure and EDTA molecules.

### 3.2. FTIR study of the PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite

Fig. 2 shows FTIR spectra of PANI/SWNTs nanocomposite (Fig. 2a) and EDTA-PANI/SWNTs nanocomposite (Fig. 2b). The band at 837 cm<sup>-1</sup> is attributed to the N—H out of plane bending in the PANI/SWNTs nanocomposite structure. The bands around 1425 cm<sup>-1</sup> and 1637 cm<sup>-1</sup> are characteristic for the emeraldine salt form of PANI in PANI/SWNTs nanocomposite. FTIR spectrum of PANI/SWNTs nanocomposite shows the appearance of the characteristic band at 1037 cm<sup>-1</sup>, which confirms high concentration of SWNTs in PANI/SWNTs nanocomposite structure [59]. This band also represents charge transfer and confirms interaction between SWNTs and a quinoid ring of PANI [59]. The C—N stretching vibrations of aromatic groups in the PANI/SWNTs nanocomposite and EDTA-PANI/SWNTs structures were observed at 1192 cm<sup>-1</sup> and 1264 cm<sup>-1</sup> respectively. Band at 1720 cm<sup>-1</sup> for C=O and 3600 cm<sup>-1</sup> for O—H were observed in EDTA-PANI/SWNTs structure, which was initially absent in the FTIR spectrum of unmodified PANI/SWNTs nanocomposite. It also confirms that the EDTA moieties were covalently attached to the surface of PANI/SWNTs nanocomposite.

### 3.3. Morphological investigations of PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite

The morphological investigations of PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite were performed using AFM. Fig. 3a shows AFM images of PANI/SWNTs nanocomposite and Fig. 3b represents AFM images of EDTA-PANI/SWNTs nanocomposite. The AFM image represented in Fig. 3a clearly shows that the PANI is formed on the surface of SWNTs, resulted in forming a nanocomposite layer where SWNTs acts as the backbone. The nanocomposite structure shows rod-like structures distributed in an irregular manner with more rigid features compared to that of EDTA-PANI/SWNTs (Fig. 3b) in which the coating of EDTA dominates the rod-like struc-

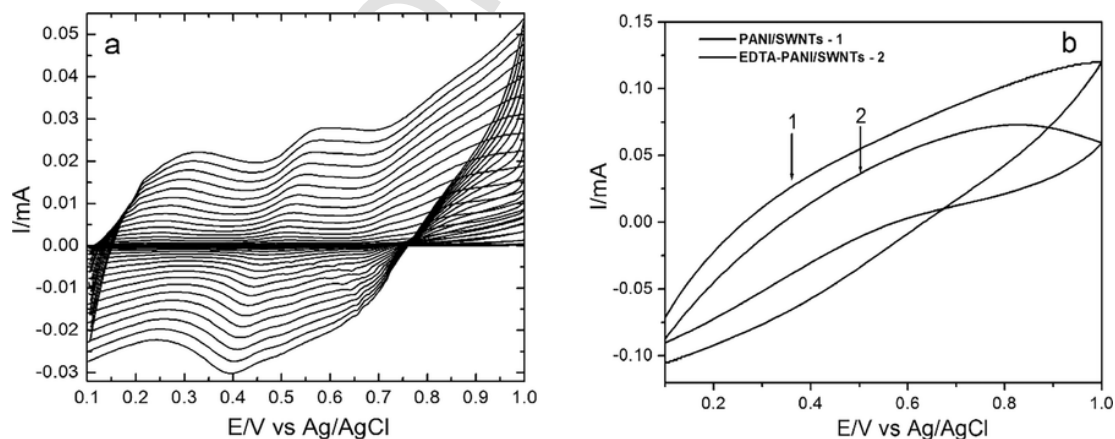


Fig. 1. Cyclic Voltammograms (a) recorded during the deposition of PANI/SWNT nanocomposite layer on SSE (b) PANI/SWNTs nanocomposite (curve 1) and EDTA-PANI/SWNTs nanocomposite (curve 2).

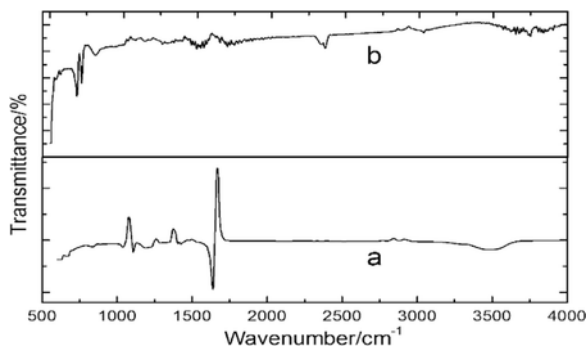


Fig. 2. FTIR spectra of (a) PANI/SWNTs nanocomposite, (b) EDTA-PANI/SWNTs nanocomposite structure.

ture. Fig. 3b shows AFM image of EDTA-PANI/SWNTs with agglomerated form due to the bonding of EDTA molecules on nanocomposite surface. EDTA molecules occupy all space available on the PANI/SWNTs nanocomposite. Fig. 3b confirms the accumulation of EDTA on the nanocomposite surface.

Thus, the AFM images are confirming that, in nanocomposite formation, SWNTs are getting covered with PANI layer, which further acts as a conducting backbone of nanocomposite. The  $\pi$ - $\pi^*$  stacking

between conducting polymer and SWNTs must have lead towards the enhancement of the charge carrying capacity, which results in faster signal transduction that will be beneficial for the faster charge transfer and ultimately fast sensor response. In PANI/SWNTs nanocomposite SWNTs will not expose directly to the analyte thereby, overcoming the hurdle of hydrophobic nature of SWNTs, lower stability in the harsh environment and contamination by the analyte. EDTA will be responsible for increased response towards metal ions, and the advance of EDTA-PANI/SWNTs-based sensor selectively by adjustment of pH.

Fig. 4a shows the comparative single scan image of the (Fig. 4a, curve 1) PANI/SWNTs and (Fig. 4a, curve 2) EDTA-PANI/SWNTs. EDTA-PANI/SWNTs layer is more complex in comparison to PANI/SWNTs layer, which confirms that the PANI/SWNTs layer become rougher after the modification by EDTA, which could be easily revealed by Fig. 4b via the observed parameters expressed by Max(nm) is the maximum roughness profile, Rpv Peak-to-Valley Roughness, Ra the average roughness of the absolute value of the profile height, Rz ten point average roughness, Skewness (RsK) the third moment of profile amplitude probability density function used to measure the profile symmetry about mean line, Kurtosis (Rku) fourth moment of profile amplitude probability density function and corresponds to a measure of surface sharpness, root mean-square factor Rq [RMS], the value of

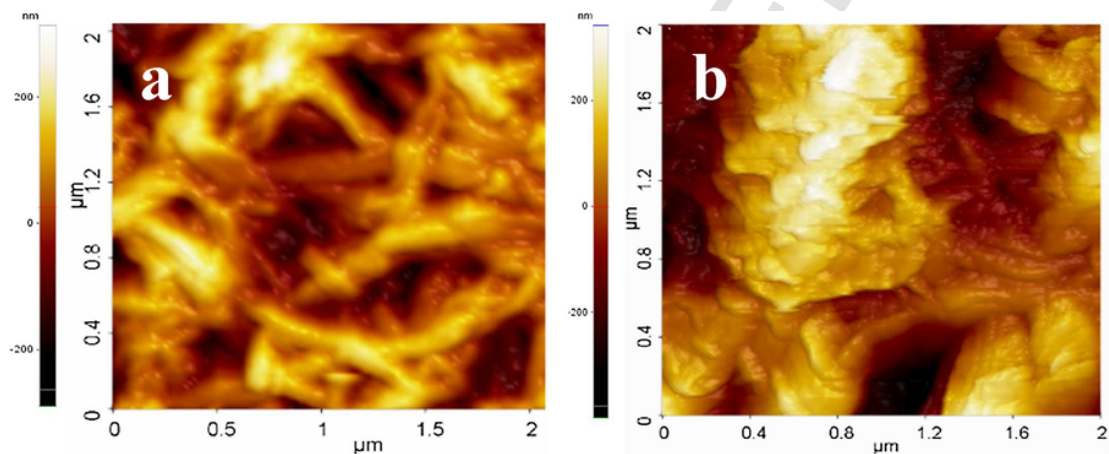


Fig. 3. AFM image of (a) PANI/SWNTs nanocomposite, (b) EDTA-PANI/SWNTs nanocomposite.

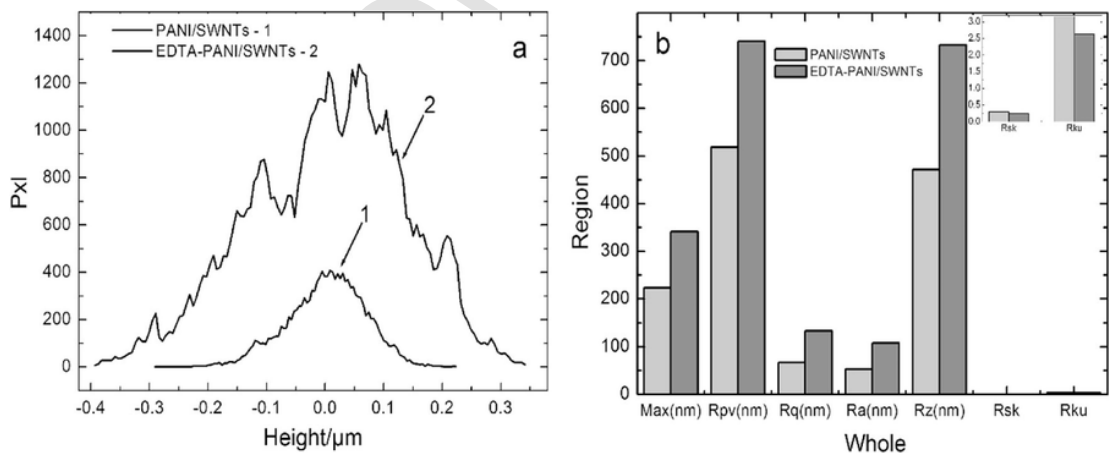


Fig. 4. (a) Single scan by AFM of PANI/SWNTs layer (curve 1) and EDTA-PANI/SWNTs nanocomposite (curve 2), (b) Roughness parameters of PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite.

the highest single peak above the center line [Rp], the mean levelling depth [Rpm], the deepest valley below the centre line [Rv].

### 3.4. Comparative study of bare PANI/SWNTs and EDTA modified PANI/SWNTs nanocomposite electrodes towards Cu(II) ion sensing

In order to study the impact EDTA on sensing, the comparative study sensing abilities of bare PANI/SWNTs/SSE and EDTA modified PANI/SWNTs/SSE for the determination of Cu(II) ion concentration was investigated. The bare PANI/SWNTs/SSE and EDTA modified PANI/SWNTs/SSE were incubated in the analyte solution containing 2 mM of Cu(II) ions in an acetate buffer solution, pH 4.5. The EDTA modified PANI/SWNTs/SSE electrode exhibits significant DPV peak response for Cu(II) ions, however, bare PANI/SWNTs/SSE electrode exhibits almost negligible response (Fig. 5). The better response was observed for EDTA-PANI/SWNTs/SSE due to selective chelation ability of EDTA molecules towards Cu(II) ions.

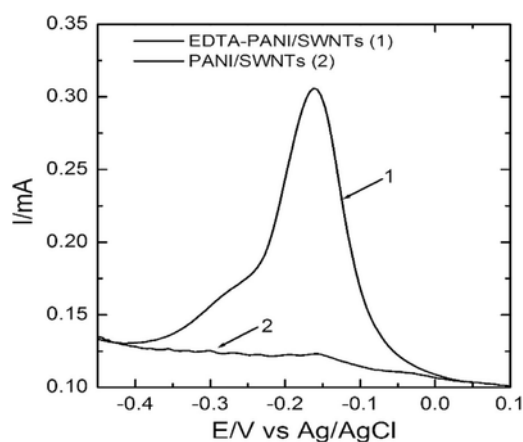


Fig. 5. DPV based response of PANI/SWNTs and EDTA-PANI/SWNTs towards 2 mM of Cu(II) ions followed by stripping with DPV technique in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

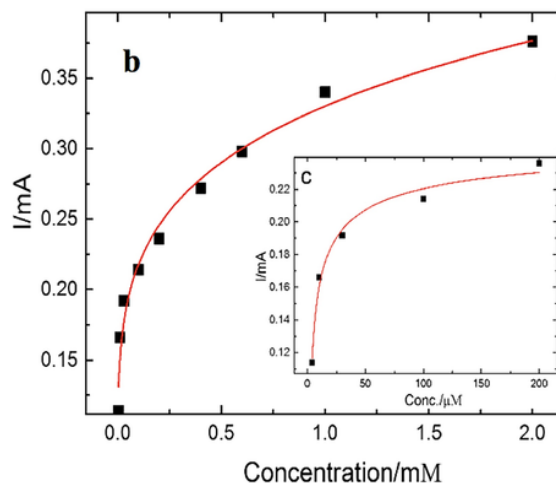
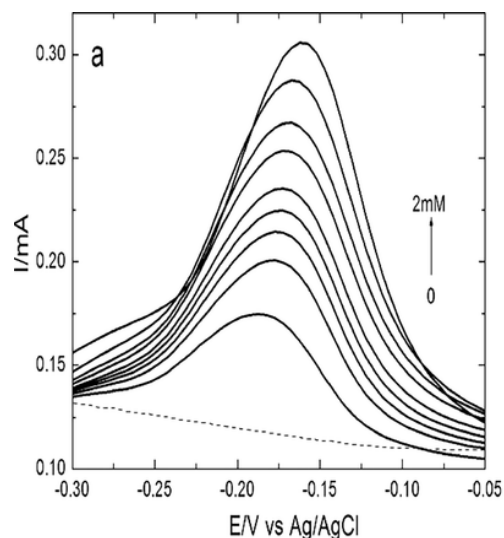


Fig. 6. (a) Differential pulse voltammograms of EDTA-PANI/SWNTs/SSE registered in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different Cu(II) ion concentrations of 4 μM, 10 μM, 1 × 10<sup>2</sup> μM, 4 × 10<sup>2</sup> μM, 6 × 10<sup>2</sup> μM, 1 mM, and 2 mM, 2 × 10<sup>2</sup> μM, 30 μM, respectively (b) DPV peak currents plotted against Cu(II) concentrations, respectively; approximated by hyperbolic equation  $y = a - b / (1 + c \times x)^{1/d}$ . (c) DPV peak currents plotted against Cu(II) concentrations in shorter concentration diapason, approximated by hyperbolic equation  $y = a - b / (1 + c \times x)^{1/d}$ .

### 3.5. Electrochemical response of PANI/SWNTs-EDTA towards Cu(II) ion

Interaction of analyte with EDTA-PANI/SWNTs/SSE was studied by electrochemical DPV technique at 2 mM–4 μM Cu(II) ion concentrations. The metal ions were collected on the surface of EDTA-PANI/SWNTs nanocomposite by simply immersing EDTA-PANI/SWNTs/SSE into the acetate buffer, pH 4.5, containing Cu(II) ions by varying incubation time from 10 min to 1 min without applying electrode potential, which is mostly used in accumulation step of DPV experiment for advanced accumulation of metal ions. Elimination of additional electrode potential protected the sensing EDTA-PANI/SWNTs from contamination and damaging of the surface. Clear anodic DPV peaks were obtained for different concentrations of Cu(II) ions. The voltammograms along with a standard addition plot of metal ions concentration versus peak current are shown in Fig. 6a.

The DPV peak currents registered during Cu(II) ion determination over the potential range between −0.30 V to −0.05 V. DPV voltammograms for different Cu(II) ion concentrations determined by EDTA-PANI/SWNTs/SSE are presented in Fig. 6a. The dotted line (Fig. 6a) represents the reference curve recorded for blank solution without Cu(II) ions.

Fig. 6b represents the dependences of concentration of Cu(II) ions on the analytical signals, it can be approximated by hyperbolic function;  $y = a - b / (1 + c \times x)^{1/d}$  with parameters, which are represented in Table 1. The approximation with respect to concentration of Cu(II) ion with hyperbolic function measure for very broad concentration region, however in shorter region to simplify calculation of Cu(II) concentration. The limit of detections (LODs) for Cu(II) ion was calculated using following formula:

$$LOD = 3.3 \times (\text{standard deviation of the regression line } (\sigma)) / \text{Slope}(S)$$

**Table 1**

Represents corresponding parameters of applied hyperbolic equation  $y = a - b / (1 + c \times x)^{(1/d)}$ . DPV was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> based supporting electrolyte.

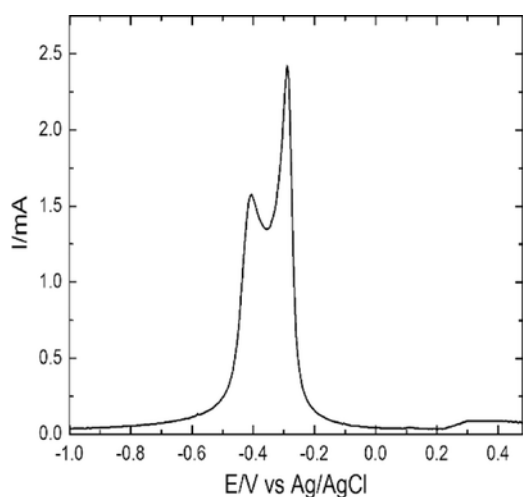
Model	Hyperbola Gen	Value	Standard Error
Equation	$y = a - b / (1 + c \times X)^{(1/d)}$		
Reduced Chi-Sqr.	2.00453E-4		
Adj. R-Square	0.97185		
A		0.04708	0.15393
B		-0.01831	10.86388
C		256334.34977	6.89194E8
D		-4.54881	3.04121

The calculated value of limit of detection (LOD) for Cu(II) was 1.4 μM and the calculated value of sensitivity from slope of the linear calibration curve was 189 mA/μM.

### 3.6. Selective determination of Cu(II) ion in the presence of interfering Pb(II), Cd(II), Ni(II), Co(II) ions

Fig. 7 shows DPVs of EDTA-PANI/SWNTs/SSE in acetic acid buffer solution, pH 4, containing Cu(II) and Pb(II) ions. The EDTA-PANI/SWNTs/SSE was immersed in a solution containing 2 mM/L of Pb(II), Cd(II), Ni(II), Co(II), Cu(II) ions for 10 min. The DPV plot shows clear anodic peaks only for Cu(II) and Pb(II). EDTA is also sensitive for Pb(II) ions at the pH of 4.9. Herein, we have pre-concentrated Cu(II) ions in acetate buffer solution of pH 4.5 which is closer to the accumulation pH of Pb(II) ions. However, EDTA-PANI/SWNTs/SSE showed some sensitivity towards Pb(II) ions, but without significant interference on the determination of Cu(II) ion determination. However, no DPV peaks were observed for Cd(II), Ni(II), Co(II) ions, which confirms good selectivity of EDTA-PANI/SWNTs/SSE for Cu(II) ion.

As listed in Table 2, spectroscopic and colorimetric techniques are often used for the determination of metal ions. However, these techniques have several limitations in their regular use. While electrochemical techniques are less time consuming, easy to handle and still accurate enough. In present investigation the EDTA-PANI/SWNTs nanocomposite shows good DPV-based response with better sensitivity and selectivity towards Cu(II) ions.



**Fig. 7.** DPV registered during the determination of 2 mM of Cu(II) ion in the presence of 2 mM Pb(II), Cd(II), Ni(II) and Co(II) ions in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

**Table 2**

Review of some analytical systems for Cu(II) ion determination.

Sr. No.	Sensing Material	Detection limit	Detection technique	Ref.
01	Alkyl-terminated porous silicon nanoparticles	4 μM	Spectroscopic	[60]
02	Glycine on Hydrazine-Adsorbed Gold Nanoparticles	2 μM	Raman Spectroscopy	[61]
04	Peptide immobilized gold nanoparticles	10 μM	Colorimetric	[62]
05	water-soluble polymer containing pendant rhodamine units	20 μM	Spectroscopy	[63]
06	Protein	0.1 mg	Spectroscopy	[64]
07	Biosynthesized silver nanoparticles	20 μM	Spectroscopy	[65]
08	Copper-silver RF sputtered thin film	~10 μM	Potentiometric	[66]
09	Polyethyleneimine	2 μM	Spectroscopy	[67]
10	Polydopamine	1 nM	Spectroscopy	[68]

## 4. Conclusions

Bare CNTs have no specific affinity towards metal ions due to the absence of functional groups, but here described composite structure based on PANI, SWNTs and EDTA is suitable for Cu(II) ion determination, CNTs enables faster transfer of electrical signal due to its electric conductivity and polymeric layer of PANI provides immobilization of PANI/SWNTs composite on the metal sensor surface. In this research electrochemical synthesis of PANI/SWNTs nanocomposite and further modification by EDTA was successfully carried out. An electrochemical, spectroscopic and morphological characterization of PANI/SWNTs and EDTA-PANI/SWNTs confirmed some chemical and morphological differences between PANI/SWNTs and EDTA-PANI/SWNTs nanocomposite. To the best of our knowledge, there are no reports on heavy metal ion detection by nanocomposite based on conducting polymer and carbon nanotubes, which in our research was further modified with EDTA. EDTA is serving as agent, which is providing advanced selectivity and sensitivity towards metal ions due to its chelation ability. Therefore during this research designed EDTA-PANI/SWNTs/SSE showed good sensitivity and selectivity towards Cu(II) ions.

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