RSC Advances

Nitrogen doped carbon nanotubes for sensitive and selective determination of heavy metals

Journal:	*RSC Advances*
Manuscript ID	RA-ART-08-2015-015944.R1
Article Type:	Paper
Date Submitted by the Author:	05-Nov-2015
Complete List of Authors:	Joshi, Anju; Indian Institute of Technology Ropar, Department of Chemistry Nagaiah, Tharamani; Indian Institute of Technology ropar, Department of Chemistry
Subject area & keyword:	Electroanalytical < Analytical

Journal Name

ARTICLE

Nitrogen doped carbon nanotubes for sensitive and selective determination of heavy metals

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Anju Joshi and Tharamani C. Nagaiah*

The present study attempts to demonstrate the potential of nitrogen containing carbonaceous materials towards electrochemical determination of heavy metal ions. For this purpose, nitrogen doped carbon nanotubes (N-CNTs) has been synthesized from post treatment of oxidized carbon nanotubes (O-CNTs) in presence of NH_3 at three different temperatures of 200, 400 and 600 ^{o}C to analyse their relevance in heavy metal ions determination. The electrocatalytic activity of these materials towards determination of Cd, Pb and Cu metal ions was examined by means of square wave stripping voltammetry (SWSV) technique which demonstrates the suitability of all temperature variants for the desired purpose. Eventually, N-CNTs treated at 600 ^{o}C (N-CNT 600) displayed comparatively better sensitivity towards the investigated heavy metal ions (Cd, Pb and Cu) as compared to other temperature variants of N-CNTs (N-CNT 200 & N-CNT 400). Role of nitrogen groups was assessed in comparison with O-CNTs as it eliminates the requirement of pre-concentration step by efficient complexation with heavy metal ions. The peak current for Pb and Cd metal ions increased linearly with in the concentration range of 0.01 µM – 70 µM and 0.1 µM – 100 µM respectively (individual as well as simultaneous determination). The limit of detection (LOD) was calculated out to be 0.001 µM and 0.005 µM (3σ method) for simutaneous determinaton of Pb and Cd metal ions respectively. Further, a real time application of N-CNT 600 modified GCE was probed by electrochemical detection of Cd and Pb metal ions in tap water and ground water.

Introduction

Heavy metal pollution is one of the most life threatening environmental problem which needs to be addressed at an imperative basis. Heavy metals being bio-accumulative in nature intrude into the environment due to anthropogenic activities like industrialization, agriculture and mining[1]. The toxicity due to heavy metal ions arise mainly because of their high affinity towards sulfhydryl groups present in various enzymes eventually leading to inhibition of glutathione metabolism[2]. In addition, heavy metals are also suspected to be causative agent for carcinogenesis, teratogenesis and mutagenesis[3] with association to various diseases like renal disorders, neurodegenerative diseases, lung diseases, muscular dystrophy (progressive skeletal muscle weakness), and multiple sclerosis[4, 5]. Mainly cadmium, lead, copper and arsenic are considered to be the major pollutants of drinking water[6]. Acceptable levels of cadmium, lead and copper has been reported to be 0.027 µM, 0.0452 µM, and 0.024 µM respectively according to USEPA[7].

These metal ions when exceed their permissible limits, pose severe detrimental effects to human health. Like cadmium at a concentration above 0.027 µM leads to inhibition of DNA, RNA and protein biosynthesis[8] while high concentration of copper (0.024 µM) lays down the foundation of severe neurological disorders[9]. Lead usually mimics the action of calcium in human body and hence considered toxic when inhaled in trace amount[10].

Thus, it is highly demanding to search for a rapid, sensitive and simple analytical method for detection as well as continuous monitoring of these environmental pollutants in natural water resources. At present, spectroscopic techniques like mass spectrometry, fluorescence spectrometry, atomic absorption spectrometry, and inductively coupled plasma spectrometry are the prominent means for detection of metal ions[11]. Unfortunately these techniques are cumbersome and hence inappropriate for onsite analysis thereby, limiting their practical applicability. However, electrochemical sensing of heavy metal ions using mercury electrode was quite popular over conventional spectroscopic techniques in the past decades but toxicity of mercury again prompted the requirement of new materials for determination of heavy metal ions. In this direction, numerous efforts have been dedicated towards development of materials such as bismuth carbon nanocomposites[12], Au-Pt nanoparticles (NPs)[13], Au NPs amplified DNA-gold electrode[14], molecular imprinted polymer[15] and alike. In addition, a wide variety of carbonaceous materials including graphite nanofibers[16], ordered mesoporous carbon[17], carbon nanotube thread[18], carbon nanotubes modified with dihexadecyl hydrogen

---

[a] *Dr. Tharamani C. Nagaiah, Anju Joshi*
Department of Chemistry
Indian Institute of Technology Ropar
Rupnagar, Punjab-140001, India
E-mail: tharamani@iitrpr.ac.in

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

phosphate (CNT-DHP)[19], heated graphite nanoparticle[20] and Bi-screen printed carbon nanotube electrode (Bi-SPCNTE)[21] have shown incredible potential for determination of heavy metal ions. However, complex synthesis procedure, reproducibility and requirement of longer pre-concentration time for efficient anchorage of metal ions restricts their applicability for onsite analysis in natural water resources. Hence, synthesizing novel and sensitive materials possessing high affinity towards metal ions is highly demanding in today's scenario.

Doping with heteroatoms like nitrogen seems an exciting approach for introducing novel functionalities to carbonaceous materials including extraordinary electronic properties and enhanced reactivity with increased defects sites to anchor guest molecules.

As a result of this, current research focuses on the application of nitrogen doped carbonaneous material for electrochemical sensing of heavy metal ions. For example, nitrogen doped porous carbon derived from direct pyrolysis of polypyrrole doped Al based metal organic framework (PPy@MOG)[22], nitrogen doped porous carbon-gold based nanocomposite[23], carbon nitride modified with bismuth[24] have been explored successfully for the desired purpose.

Nitrogen doped carbon nanotubes (N-CNTs) has been well recognized as an efficient adsorbent for metal ions especially Pb and Cd[25, 26]. However their potential as a highly sensitive electrochemical probe still remains unexplored. Motivated by aforementioned facts, in continuation with the ongoing research, the present study attempts to unravel the potential of various nitrogen containing functionalities (generated through exposure of NH_3 at various temperatures) towards highly sensitive determination of metal ions especially Pb and Cd using square wave stripping voltammetry (SWSV) technique.

For this purpose, controllable nitrogen content in N-CNTs were obtained using previously reported literature[27]. Briefly, the synthesis of N-CNTs were carried out by post treatment of oxidized CNTs (O-CNTs) under NH_3 atmosphere, at different temperatures of 200, 400 and 600 (N-CNT 200, N-CNT 400 & N-CNT 600).

The major focus of the present study remains in developing a highly sensitive probe for sensitive and selective determination of Pb and Cd metal ions without requirement of any pre-concentration or accumulation step hence fastening up the detection process which is quite crucial for onsite analysis.

Experimental

Reagents

Lead nitrate ($Pb(NO_3)_2$), cupric nitrate trihydrate ($(CuNO_3)_2.3H_2O$), cadmium chloride ($CdCl_2$) (anhydrous 95%) and Nafion were procured from Sigma Aldrich. Sulphuric Acid (0.05 M) of pH value 4.0 was prepared from stock solutions of 0.5 M sulphuric acid (98% pure). All chemicals used throughout the experiment were of analytical grade and were used without further purification. All aqueous solutions were prepared with deionized water obtained from a Millipore system (>12 MΩ cm^{-1}).

Synthesis of material:

N-CNTs were synthesized by post treating O-CNTs under NH_3 atmosphere using previously reported literature[27]. Briefly, CNTs with inner diameters of 20-50 nm and outer diameters of 70-200 nm were obtained from Applied Sciences Inc. (Ohio, USA). The polyaromatic impurities present on the surface of as-received CNTs were removed by thermal treatment under He flow at 800 °C for 1 hour. Before nitrogen functional group insertion, oxygen functional groups were introduced by HNO_3 vapour treatment[28]. In order to do so, first the thermally treated CNTs were oxidized using HNO_3 in the gaseous phase at 200 °C for 48 hours, cooled for some time and further dried at 60 °C overnight and termed as O-CNTs. Further, nitrogen functional groups were introduced to O-CNTs via post treatment of NH_3. For this, 200 mg of the O-CNTs were loaded into a tubular quartz reactor which was then heated under ammonia with a total flow rate of 25 sccm at 200 °C (N-CNT 200), 400 °C (N-CNT 400), 600 °C (N-CNT 600) and 800 °C (N-CNT 800) for 6 hours respectively.

Physical characterization:

The morphology of the synthesized CNTs was visualized using scanning electron microscope (SEM, JEOL, JSM-66101 V). CHN elemental analyses were carried out using Perkin- Elmer analyser PE2400 series II.

Electrochemical characterization:

For electrochemical measurements, glassy carbon electrode (GCE, Ø 3 mm) embedded in teflon was used as a support for the catalyst. Bare GCE was modified with different N-CNTs viz. N-CNT 200, N-CNT 400 & N-CNT 600 individually which served as working electrode (WE). Prior to its modification, bare GCE was polished with different grades of alumina slurry (3, 1, 0.3, 0.05 µm respectively, Pine Instrument, USA) using Nylon polishing cloth (SM 407052, AKPOLISH), rinsed thoroughly under running water and then deionized water. For surface modification of GCE, catalyst ink was prepared by sonicating 1.0 mg of the CNTs in 0.5 ml of deionized water along with 5 µl (0.002 % of 5 wt %) of Nafion using an ultrasonic bath and 20 µl of the prepared ink was drop casted on to GCE and dried at 50 ^{o}C for 20 min.

Electrochemical measurements were performed using Autolab, PGSTAT 302N, a modular electrochemical system driven by Nova 1.1.10 software. All measurements were conducted in a single compartment cell equipped with conventional three electrode configuration consisting of Pt wire as a counter electrode (CE). All experiments were performed at room temperature and the potentials were referenced to the Ag/AgCl/3M KCl reference electrode (RE). The sensitivity and selectivity performance of these CNTs towards determination of heavy metal ions was evaluated using cyclic voltammetry (CV) and square wave stripping voltammetry (SWSV). SWSV was carried out at a frequency of 15 Hz, step potential of 0.3 mV and pulse amplitude of 25 mV at a scan rate of 4.5 mV s^{-1}. All measurements, unless specified otherwise repeated at least five times.

Determination of heavy metal ions

SWSV was employed for determination of heavy metal ions under optimized conditions (frequency 15 Hz, step potential 0.3 mV and a pulse amplitude of 25 mV at a scan rate of 4.5 mV s^{-1}). Conventionally, SWSV involves accumulation of metal ions at an optimized potential under stirring conditions followed by stripping of the deposited metal to give stripping signal. Hence, in order to speed up the electrochemical determination of metal ions (Pb and Cd) we here propose to eliminate the time consuming pre-concentration or accumulation step by utilizing the high affinity of nitrogen rich functionalities towards Pb and Cd metal ions. High affinity of nitrogen functionalities leads to efficient complexation of metal ions which are reduced to form M^0 (M(II)→ M(0)), and are electro-oxidized (M(0)→ M(II)) using single step SWSV while stepping from -900 mV to - 300 mV after an equilibration time of 5 seconds. SWSV was carried out within a required potential range to record the corresponding current signal variance as a function of potential.

Results

As expected, the morphology of the N-CNTs shows tubular appearance without any damage after post-treatment with NH_3 at different temperatures. (Fig. S1, Supporting Information (SI)).

CHN analysis were carried out to gain insights into the elemental composition of the synthesized N-CNTs and nitrogen content was found to be 8.8%, 8.2%, 6.8% and 4.5% for N-CNT 200, N-CNT 400, N-CNT 600 & N-CNT 800 respectively. The detailed results are tabulated in Table S1, SI.

Electrochemical behaviour Cd and Pb metal ions

Preliminary analysis of the sensitivity of different N-CNTs and O-CNTs towards determination of lead (Pb) and cadmium (Cd) metal ions was performed by cyclic voltammetry (CV). GCE modified with different CNTs (O-CNT, N-CNT 200, N-CNT 400 and N-CNT 600) was probed in the solution comprising of $Pb(NO_3)_2$ (5 μM) and $CdCl_2$ (10 μM) in 0.05 M H_2SO_4 solution (pH 4) with in the potential range of -900 mV to -300 mV. It is clear from Fig. 1(a) that, CV does not show well pronounced peaks however, exhibited two small humps at potentials of ca. -780 mV and -500 mV which can be attributed to conversion of Cd(0) → Cd(II) & Pb(0) → Pb (II) respectively.

Appearance of peak for Pb can be attributed to the conversion of Pb(II)→Pb(0) during the reduction step which subsequently gets electro-oxidized back to Pb (II) on reverse sweep, leading to a pair of redox peaks centered at ca. -500 mV and -574 mV with a peak separation of 74 mV. Similar to Pb, Cd also shows a pair of redox peaks with an oxidative peak ca. -780 mV and a small broadened reduction peak at ca. -800 mV. Since O-CNTs are well recognized as a potent candidate for highly sensitive and selective determination of heavy metal ions, comparative analysis was carried out for O-CNTs, wherein O-CNTs also represent electro-oxidative peaks corresponding to Pb and Cd metal ions with reduced current response. Response of preliminary CV analysis necessitated further insights into the sensitivity determination of N-CNTs and O-CNTs.

This was accomplished by performing SWSV measurements for various CNTs under similar conditions as applied for CV within a potential range of -900 mV to -300 mV after equilibration time of 5 sec. (Fig. 1 b).

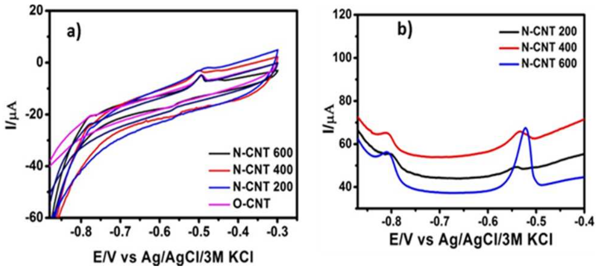


Fig. 1. a) Cyclic voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) solution containing 5 μM $Pb(NO_3)_2$ & 10 μM $CdCl_2$ solution at a scan rate of 5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl. b) Square wave voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) solution containing 5 μM $Pb(NO_3)_2$ solution & 10 μM $CdCl_2$ solution, SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl.

It is clear from Fig. 1 b that all CNTs exhibit two well defined peaks centered at ca. -780 mV and -500 mV corresponding to electrocatalytic based conversion of Cd(0)→ Cd(II) & Pb(0)→ Pb (II) respectively. However, N-CNT 600 possesses better current responses viz. 68.02 μA and 57.93 μA for detection of Pb and Cd metal ions respectively compared to other temperature variants of N-CNTs (N-CNT 200 & N-CNT 400) and O-CNTs. Better sensing response by N-CNT 600 could be ascribed to its superior spontaneous adsorbability and multiple nitrogen rich anchoring sites which act as trap centres for metal ions. However, all CNTs represented high affinity towards Pb metal ions as compared to Cd ions.

Effect of concentration of Cd and Pb metal ions

Contrary to the time consuming conventional electrochemical method which generally requires longer accumulation time, we here avoid the pre-concentration step and employed single step SWSV based determination of Pb and Cd metal ions utilizing the affinity of various nitrogen containing groups present in different temperature variants of N-CNTs. Hence, various N-CNTs (N-CNT 200, N-CNT 400 and N-CNT 600) modified GC electrodes were subjected towards electrochemical determination of Pb and Cd metal ions at their variable concentrations.

As it is clear from square wave stripping voltammograms (Fig. 2 & 3) all N-CNTs (N-CNT 200, N-CNT 400 and N-CNT 600) and O-CNTs shows a linear increase in peak current with subsequent increase in concentration of both Pb and Cd metal ions. The linear current response for Pb metal ions was obtained in the concentration range of 0.01 μM – 70 μM, whereas for Cd metal ions the concentration range was 0.1 μM- 100 μM.

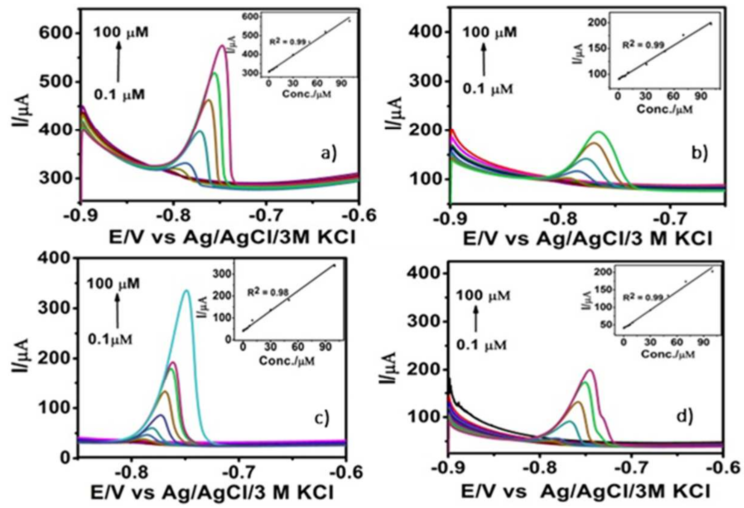


Fig. 2: Square wave voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) with varying concentrations of Cd metal ions for a) N-CNT 200, b) N-CNT 400, c) N-CNT 600 and d) O-CNT. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE:Ag/AgCl/3M KCl.

Calibration plots with 3 % error bars were also plotted for all the samples and are depicted in the respective insets of Fig. 2 & 3. N-CNT 600 shows better response in terms of enhanced peak current as compared to N-CNT 200 & N-CNT 400 and O-CNTs. But the response of O-CNTs (Fig. 2d) shows an additional small hump at higher concentrations which suggests that nitrogen containing groups present in N-CNTs leads to efficient anchorage of heavy metal ions resulting in excellent sensitivity towards electro-oxidation of Pb and Cd metal ions.

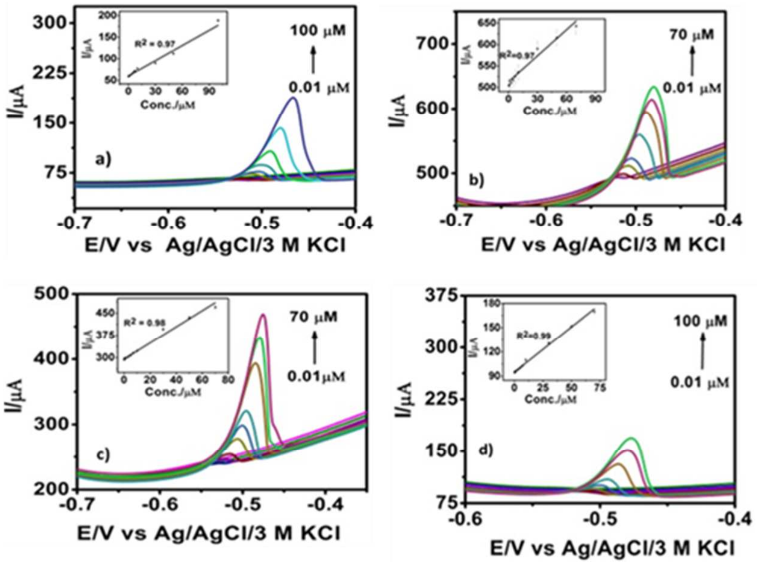


Fig. 3: Square wave voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) with varying concentrations of Pb metal ions for a) N-CNT 200 b) N-CNT 400 c) N-CNT 600 and d) O-CNT. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl.

In order to explore the potential of N-CNTs and O-CNTs towards simultaneous determination of Pb and Cd metal ions, ruling out mutual interference was carried out by increasing the concentration of one of the metal ions while keeping the other constant. It is clear from (Fig. 4 & 5) that electrochemical response for both Cd and Pb metal ions by various N-CNTs increases linearly with the increasing concentration of metal ions being varied, while the peak current of the other metal species remains constant as its concentration is kept same. Moreover, increasing the concentration of one heavy metal ions does not affect the peak current of the other metal ions which is desired for a highly selective sensor. Results of the above mentioned experiments suggest that at lower concentration of one metal ions there is no significant interference in the simultaneous determination of the other (varying Pb metal ions concentration and Cd metal ions remaining constant and vice-versa) using both N-CNTs (N-CNT-200, N-CNT-400 and N-CNT-600) and O-CNTs. Calibration plots were made similarly as done for individual determination of metal ions and are provided as insets.

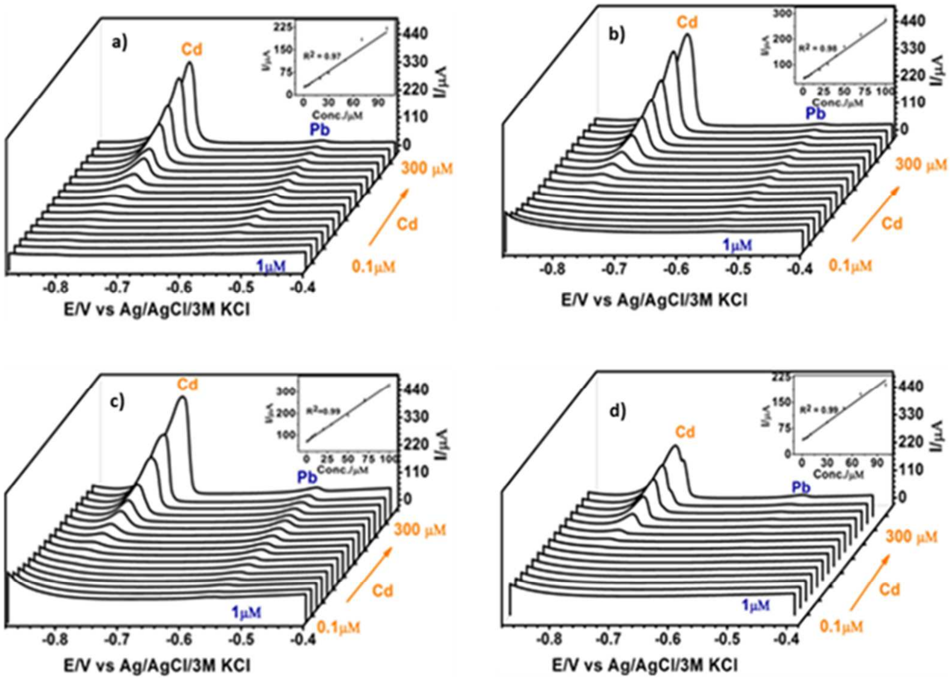


Fig. 4: Square wave voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) with varying concentrations of Cd metal ions in presence of 1 µM Pb metal ions for a) N-CNT 200 b) N-CNT 400 c) N-CNT 600 and d) O-CNT. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl.

The sensitivity and other analytical parameters for CNTs corresponding to simultaneous determination of metal ions are listed in Table S2 and S3, SI with their respective linear range and regression relations. N-CNT 600 depicted a high sensitivity of 118.18 µA $\mu M^{-1} cm^{-2}$ and 37.15 µA μM^{-1} cm^{-2} towards simultaneous determination of Pb and Cd metal ions respectively which is substantially higher compared to other N-CNTs and O-CNTs. The response of N-CNT 600 modified electrode has been compared with the state of art (well established) materials to realize the real advantage of N-CNT 600 for electrochemical sensing of Pb and Cd metal ions. Mercury (Hg) and bismuth (Bi) has been well known for electrochemical sensing of metal ions. Since Hg is toxic, response of Bi nanoparticle modified GCE (Bi/GCE) was subjected towards determination of Cd metal ions. For this purpose, Bi nanoparticles were electrodeposited onto GCE using previously reported literature[29] employing triple pulse voltage technique[30]. However, Bi/GCE fails to elicit a significant response towards determination of Cd metal ions even at high concentrations (70 µM) which confirms that bismuth nanoparticles require sufficient time for accumulation of metal ions (Fig. 6). In absence of pre-concentration / accumulation step bismuth lacks affinity towards Cd metal ions.

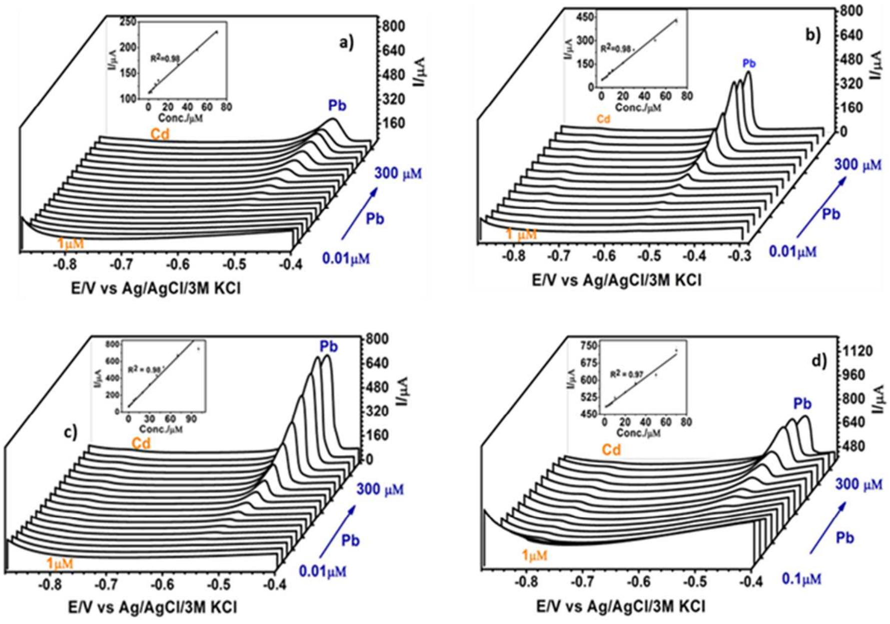


Fig. 5: Square wave voltammograms of various CNTs in 0.05 M sulphuric acid (pH 4.0) with varying concentrations of Pb metal ions in presence of 1 μM Cd metal ions for a) N-CNT 200 b) N-CNT 400 c) N-CNT 600 and d) O-CNT. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl.

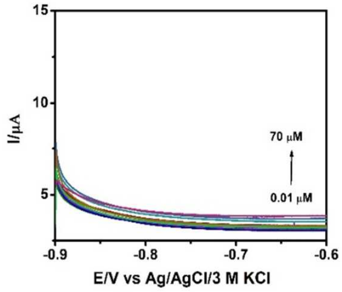


Fig. 6: Square wave voltammograms at Bi modified GCE in 0.05 M H_2SO_4 (pH 4.0) at various concentration of Cd metal ions ranging from 0.1 μM – 70 μM. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl.

Discussion

It can be deduced from the SWSV results obtained for both individual as well as simultaneous determination of Pb and Cd metal ions that N-CNTs possess various multi-adsorbing sites which can attract heavy metal ions from bulk solution to the electrode surface thus increasing the oxidative peak currents and hence sensitivity towards their determination. More importantly, eliminating the requirement of time consuming pre-concentration or accumulation step essentially required prior to the SWSV based determination of heavy metal ions. The mechanism responsible for the interaction between the metal ions and surface functional groups of CNTs can be speculated to be either-electrostatic attraction, sorption–precipitation and chemical interaction. Out of those sorption-precipitation mechanism seems to be more relevant[31-33] for understanding the interaction between metal ions and nitrogen containing functional groups.

CHN elemental analysis was performed for the synthesized N-CNTs (Table S1, SI) which indicates that with increase in temperature from 200 °C to 800 °C nitrogen content decreases from 8.8% to 4.5%. These results well compliments with the XPS data from our previously reported literature[27].

Hence, to gain a better understanding towards the excellent electrocatalytic activity of N-CNTs, XPS results has been correlated with the SWSV response obtained for determination of Pb and Cd metal ions.

As tabulated in Table S4 SI, XPS results suggests that with increase in temperature from 200 °C to 600 °C surface atomic concentration of both nitrogen and oxygen decreases from 6% to 4.3% & 19.4% to 2.4% respectively[27]. Mainly four different types of N-functional groups, but with varying content viz. pyridinic (N1), pyrrolic (N2), quaternary (N3) and pyridine N-oxide groups (N4) are generated on the surface of N-CNTs depending on the exposure of NH_3 at varying temperatures[27]. The differential distribution of nitrogen functional groups is responsible for different electrochemical response (SWSV studies), as obtained for various N-CNTs towards determination of Pb and Cd metal ions. As described previously[27], low temperature (200 °C) amination results in predominantly pyridinic (N1), and pyrrolic groups (N2) but as the temperature increased to 400 °C quaternary groups (N3) tends to appear on the surface of N-CNTs. Further increasing the temperature to 600 °C, pyridine N-oxide groups also appear on the surface of N-CNTs along with pyridinic, pyrrolic and quaternary groups. With further increase in temperature to 800 °C only traces of nitrogen and oxygen remains onto the surface of N-CNT 800. To gain further insights towards the role of nitrogen containing functionalities generated at high temperature (800 °C), response of N-CNT 800 has been evaluated towards individual determination of Cd and Pb metal ions (Fig. 7). However, a reduced current response with inability to detect low concentration (0.01 µM – 10 µM) of both metal ions was evident. We speculate that reduced response could be due to distorted structure of the N-CNT 800 with absence of sufficient anchoring sites for effective complexation of Pb and Cd metal ions.

Hence, it is highly evident that the right blend of different N-functional groups (N1, N2, N3 and N4) is required for high affinity towards Pb and Cd metal ions resulting in efficient interaction and hence better electrochemical determination.

Compared to N-CNT 600, N-CNT 400 possesses N1, N2 and N3 richly but lacks pyridine N-oxide surface moiety which compromises the extent of adsorbability to these heavy metal ions. This could be the reason of reduced sensitivity of N-CNT 400 towards Pb and Cd metal ions as evident from electrochemical studies. Similarly, N-CNT 200 contains only pyridinic and pyrrolic nitrogen groups whose electrochemical sensing ability was lesser than N-CNT 400.

Thus, the sensitivity of N-CNTs decreases in the order N-CNT 600 > N-CNT 400 > N-CNT 200 > N-CNT 800 which confirms the relevance of the type and right blend of nitrogen containing groups in determining the electrocatalytic activity of N-CNTs rather than the nitrogen content on whole. N-CNT 600 shows highest sensitivity as indicated by the enhanced peak currents obtained for SWSV experiments conducted for both individual and simultaneous determination of Pb and Cd metal ions. XPS studies indicates that presence of quaternary (N3) and pyridine-N-oxide(N4) type N-functional groups in N-CNT 600 enhances the electrocatalytic activity which suggests that there might be profound interaction between N3 and N4 with the heavy metal ions, thereby enhancing their sensitivity. These results suggest that firstly, the higher electrocatalytic activity is not proportional to the total amount of nitrogen and secondly it depends on the type of nitrogen containing groups present. In the present study to sense Pb and Cd metal ions, quaternary and pyridine N-oxide nitrogen containing groups played crucial role in determining the sensitivity towards these metal ions.

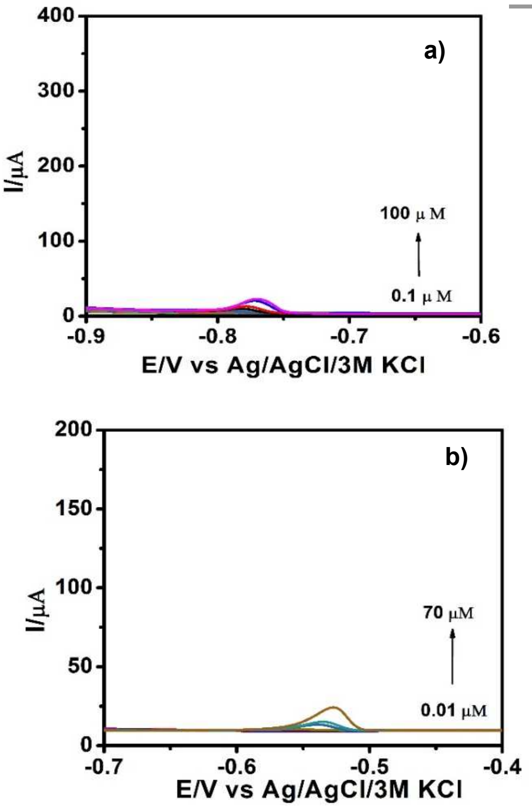


Fig. 7: Square wave voltammograms at N-CNT 800 modified GCE in 0.05 M H_2SO_4 (pH 4.0) at various concentration of a) Cd metal ions ranging from 0.1 µM – 100 µM b) Pb metal ions ranging from 0.1 µM – 70 µM. SWV conditions: frequency 15 Hz; step potential 0.3 mV; pulse amplitude 25 mV at a scan rate of 4.5 mV s^{-1}, CE: Pt wire, RE: Ag/AgCl/3M KCl

Evaluation of selectivity, stability and interference

Some other common heavy metal ions such as Cu (II) was also tested to evaluate the selectivity of the proposed sensor (N-CNT 600/GCE). It was found that copper can also be determined at -50 mV (Fig. S3, SI). But produce weak signals with broadened peaks, which suggests high affinity of nitrogen containing groups towards Pb and Cd metal ions. However, Cu metal ions produce characteristic peak which can be clearly distinguished and is well separated. Furthermore, this implies that N-CNT 600/GCE can be used as a highly sensitive and selective sensor for determination of Pb and Cd metal ions. In order to determine the stability of the proposed N-CNT 600/GCE, response of the sensor was observed over a period of 20 days. The current response decayed by about 2.3 % and 3.5 % for Pb and Cd metal ions respectively which shows excellent stability of N-CNT 600/GCE over a period of 20 days.

In addition, interference studies were also conducted using foreign substances including anions such as Cl^- by addition of such anions in a standard solution containing Cd and Pb metal ions. All N-CNT does not possess any significant influence of such anions on the determination of Pb and Cd metal ions. The performance of N-CNT 600/GCE has been compared with other well established potential candidates for simultaneous determination of Pb and Cd metal ions as depicted in Table 1.

Table 1 Comparative analysis of N-CNT 600 modified GCE for determination of Pb and Cd metal ions with existing literature

Electrode	Deposition time (min)	Deposition potential (mV)	Linear range (µM)		Ref.
			Pb(II)	Cd (II)	
AlOOH modified electrode	2 min	-1200 mV	0.2-0.8	0.2-0.8	[34]
SBA-15/IL/CPE	6 min	-1200 mV	0.4-90	0.6- 30	[35]
OMC[n]-Nafion modified GCE	5 min	-1000 mV	0.2- 2	-	[17]
CNT tower electrode	2 min	-1500 mV	0.5-3	1-4	[36]
SBA-15[a] /CPE	3 min	-800 mV	0.3-7	2-10	[37]
N-CNT 600/ GCE	-	-	0.01-70	0.1-100	Present work

[a] Nanostructured silica organofunctionalized with 2-benzothiazolethiol

[n] Ordered mesoporous carbon

Real Sample Analysis

For realization of practical application of the N-CNT 600/GCE, recovery studies on real samples were carried out using standard addition method. (Table S5, SI) The real sample was collected from tap water (IIT Ropar) as well as ground water taken from nearby village of Ropar. The real sample was diluted with 0.05 M sulphuric acid in 1:1 ratio to obtain final pH of the solution to be 4.0. No further sample treatment was done. Standard additions of Pb and Cd metal ions were performed in the diluted samples. The recovery studies were performed by adding known amount of target metal ions in real samples as depicted in Table S5, SI. The recovery for both the samples ranged from 96% - 110 %. These results reveal that the proposed N-CNT 600 modified GCE holds significant potential for determination of Cd and Pb metal ions in natural water resources.

Conclusions

N-CNTs were shown to possess excellent sensitivity towards the determination of heavy metal ions like Pb and Cd due to the presence of multiple nitrogen functional groups onto the surface of carbon nanotubes. In contrast to O-CNTs, N-CNTs shows sharp peaks with well separated potentials for the determination of Pb and Cd metal ions. Amongst them, N-CNT 600 illustrates better sensitivity towards simultaneous determination of Pb and Cd metal ions. These favourable features of N-CNTs offer great promise for simultaneous determination of Pb and Cd metal ions in natural water resources.

Acknowledgements

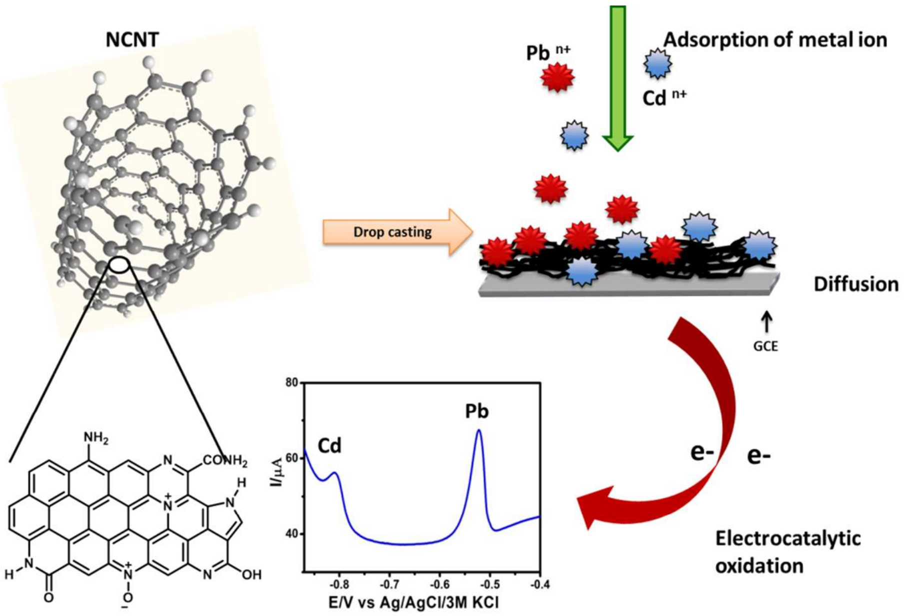
The authors are grateful to Department of Science and Technology (DST), India for Ramanujan Fellowship for financial support.

References

1. L. Järup, *British medical bulletin*, 2003, **68**, 167-182.
2. C. Chen, Q. Xie, L. Wang, C. Qin, F. Xie, S. Yao and J. Chen, *Analytical chemistry*, 2011, **83**, 2660-2666.
3. Y. Zhou, X.-L. Tian, Y.-S. Li, Y.-Y. Zhang, L. Yang, J.-H. Zhang, X.-R. Wang, S.-Y. Lu, H.-L. Ren and Z.-S. Liu, *Biosensors and Bioelectronics*, 2011, **30**, 310-314.
4. J. Duruibe, M. Ogwuegbu and J. Egwurugwu, *Int J Phys Sci*, 2007, **2**, 112-118.
5. S. Martin and W. Griswold, *Environmental Science and Technology briefs for citizens*, 2009, **15**, 1-6.
6. M. Li, H. Gou, I. Al-Ogaidi and N. Wu, *ACS Sustainable Chemistry & Engineering*, 2013, **1**, 713-723.
7. E. USEPA, 816-F-09-0004, National Primary Drinking Water Regulations, 2009.
8. F. Pinot, S. E. Kreps, M. Bachelet, P. Hainaut, M. Bakonyi and B. S. Polla, *Reviews on environmental health*, 2000, **15**, 299-324.
9. V. Desai and S. G. Kaler, *The American Journal of Clinical Nutrition*, 2008, **88**, 855S-858S.
10. D. O. Carpenter, *International journal of occupational medicine and environmental health*, 2001, **14**, 209-218.
11. X. Dai, O. Nekrassova, M. E. Hyde and R. G. Compton, *Analytical chemistry*, 2004, **76**, 5924-5929.
12. M. Gich, C. Fernandez-Sanchez, L. C. Cotet, P. Niu and A. Roig, *Journal of Materials Chemistry A*, 2013, **1**, 11410-11418.
13. J. Gong, T. Zhou, D. Song, L. Zhang and X. Hu, *Analytical chemistry*, 2009, **82**, 567-573.
14. Z. Zhu, Y. Su, J. Li, D. Li, J. Zhang, S. Song, Y. Zhao, G. Li and C. Fan, *Analytical Chemistry*, 2009, **81**, 7660-7666.
15. T. Alizadeh and S. Amjadi, *Journal of Hazardous Materials*, 2011, **190**, 451-459.
16. D. Li, J. Jia and J. Wang, *Talanta*, 2010, **83**, 332-336.
17. L. Zhu, C. Tian, R. Yang and J. Zhai, *Electroanalysis*, 2008, **20**, 527-533.
18. D. Zhao, X. Guo, T. Wang, N. Alvarez, V. N. Shanov and W. R. Heineman, *Electroanalysis*, 2014, **26**, 488-496.
19. K. Wu, S. Hu, J. Fei and W. Bai, *Analytica Chimica Acta*, 2003, **489**, 215-221.
20. G. Aragay, J. Pons and A. Merkoçi, *Journal of Materials Chemistry*, 2011, **21**, 4326-4331.
21. U. Injang, P. Noyrod, W. Siangproh, W. Dungchai, S. Motomizu and O. Chailapakul, *Analytica chimica acta*, 2010, **668**, 54-60.
22. L. Cui, J. Wu and H. Ju, *ACS applied materials & interfaces*, 2014, **6**, 16210-16216.
23. Q. Guan, W. Xiong, L. Zhou and S. Liu, *Electroanalysis*, 2015, DOI: 10.1002/elan.201500481, n/a-n/a.
24. D.-P. Wang, Y. Tang and W.-D. Zhang, *Microchimica Acta*, 2013, **180**, 1303-1308.

25. N. V. Perez-Aguilar, E. Munoz-Sandoval, P. E. Diaz-Flores and J. R. Rangel-Mendez, *Journal of nanoparticle research*, 2010, **12**, 467-480.
26. A. Osikoya, D. Wankasi, R. Vala, C. Dikio, A. Afolabi, N. Ayawei and E. Dikio, *Digest Journal of Nanomaterials & Biostructures (DJNB)*, 2015, **10**.

28. W. Xia, C. Jin, S. Kundu and M. Muhler, *Carbon*, 2009, **47**, 919-922.
29. C. Tharamani, H. Thejaswini and S. Sampath, *Bulletin of Materials Science*, 2008, **31**, 207-212.
30. E. C. Walter, M. P. Zach, F. Favier, B. J. Murray, K. Inazu, J. C. Hemminger and R. M. Penner, *ChemPhysChem*, 2003, **4**, 131-138.
31. C. Lu and C. Liu, *Journal of Chemical Technology and Biotechnology*, 2006, **81**, 1932-1940.
32. Y.-H. Li, J. Ding, Z. Luan, Z. Di, Y. Zhu, C. Xu, D. Wu and B. Wei, *Carbon*, 2003, **41**, 2787-2792.
33. C. Lu and H. Chiu, *Chemical Engineering Science*, 2006, **61**, 1138-1145.
34. C. Gao, X.-Y. Yu, R.-X. Xu, J.-H. Liu and X.-J. Huang, *ACS applied materials & interfaces*, 2012, **4**, 4672-4682.
35. P. Zhang, S. Dong, G. Gu and T. Huang, *Bulletin of the Korean Chemical Society*, 2010, **31**, 2949-2954.
36. X. Guo, Y. Yun, V. N. Shanov, H. B. Halsall and W. R. Heineman, *Electroanalysis*, 2011, **23**, 1252-1259.
37. I. Cesarino, G. Marino, J. do Rosário Matos and É. T. G. Cavalheiro, *Talanta*, 2008, **75**, 15-21.
27. T. C. Nagaiah, S. Kundu, M. Bron, M. Muhler and W. Schuhmann, *Electrochemistry Communications*, 2010, **12**, 338-341.


NCNT
Drop casting
Pb n+
Adsorption of metal ion
Cd n+
Diffusion
GCE
e-
e-
Electrocatalytic oxidation
NH2
CONH2
N
H
N
N
H
N
O
OH
N
O
Cd
Pb
80
60
40
I/μA
-0.8
-0.7
-0.6
-0.5
-0.4
E/V vs Ag/AgCl/3M KCl