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Short Communication

Electrochemical Characterization of Carbon Nanotubes/Nafion/Aspartic Acid Modified Screen Printed Electrode in Development of Sensor for Determination of Pb(II)

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A screen printed electrode (SPE) based sensor for determination of Pb^{2+} has been developed by modifying the SPE with multiwall carbon nanotubes (MWCNTs), Nafion and aspartic acid for determination of Pb^{2+} using cyclic voltammetry. The electrochemical characteristics of CNTs /Nafion/aspartic acid modified SPE were examined in several conditions such as pH, different concentration of Pb^{2+} and reproducibility of the detection. It was observed that the CNTs/Nafion/aspartic acid modified SPE has significantly superior analytical performance in determination of Pb^{2+} compared to the unmodified electrode. The determination of Pb^{2+} by using modified electrode was reproducible with R.S.D of 1.76%. The electrochemical redox peak current of Pb^{2+} showed a linear response towards different concentration of Pb^{2+} and linear calibration curve was obtained in the range of 1 to 50 μM. The sensitivity expressed as the slope of the calibration curve is 5.22 μA/μM.

Keywords: Pb^{2+} detection; Aspartic acid; Modified electrode; Electrochemical

1. INTRODUCTION

Environmental monitoring of heavy metals is of great importance because of the growing environmental problems [1]. There are metals with an unpleasant effect like iron and other metals giving a very toxic effect such as lead which ranks second in the list of prioritized hazardous substances issued by the U.S. ATSDR (Agency for Toxic Substances and Disease Registry) in 1999 [1]. Common analytical methods for lead determination such as furnace atomic absorption spectroscopy and inductively coupled plasma have a good sensitivity but it is expensive and time consuming. Therefore simple and reliable instrument/method for example chemical and biosensor is highly needed to be developed as an alternative for these tedious and laborious procedures of metal analysis.

Many metal ion complexes of amino acids have been investigated [2-4]. Amino acid and peptides are known to bind with metal ions, in some cases very strongly. They contain a great number of potential donor atoms through the peptide backbone and amino acids side chains [5]. In nature, metal binding is achieved with a high degree of selectivity using peptide motifs rather than macrocyclic ligand [6]. In single amino acid, with non-coordinating side chain, there are two donor atoms that complex with the metal, the terminal amine and carbonyl oxygen or amide nitrogen. The coordination of the metal via amide nitrogen is capable through substitution of the nitrogen bound hydrogen. In this paper, we are presenting studies done on detection of Pb^{2+} using L-aspartic acid as the recognition element. L-aspartic acid can release totally three protons, two protons from carboxyl groups and one from amine group. L-aspartic acid would be expected to chelate with the metal by use of a functional group in the side chain (esters of α-amino acid) [7].

In recent years, carbon nanotubes (CNTs) based sensor for monitoring metal ion have attracted increased attention, because of their unique electronic, chemical and mechanical properties [8-14]. CNTs can be used as electrode materials with enhanced current due to its large surface area [15]. One of the problems for the preparation of sensors based on the use of CNTs is their insolubility in common solvent. Several strategies have been proposed for the immobilization of CNTs and amino acids on electrochemical transducers, like dispersion in different solvents or polyelectrolytes or incorporation in composites matrices using distinct binders [16]. The resolved methods are divided into two categories: direct solubility of CNTs in solvents and the attachment of functional groups to CNTs. In our research, we are using Nafion to solubilise the CNTs and at the same time as binder between CNTs and amino acid.

Nafion has an excellent miscibility with CNTs, a good film-forming ability and biocompatibility. Modified electrodes based on composite of Nafion, CNT and amino acids are anticipated to have a low charge current, which is quite beneficial for cyclic voltammetry (CV) measurements. Film forming ability of Nafion can facilitate the preparation of homogenous CNTs/Nafion/amino acids composite and permit various manipulations [17].

In this work, we have developed CNTs/Nafion/aspartic acid modified SPE to determine trace Pb^{2+} in aqueous media. The performance of the CNTs/Nafion/aspartic acid modified SPE for detection of Pb^{2+} was investigated using Cyclic Voltammetry (CV) technique.

2. EXPERIMENTAL

2.1 Materials

A multiwall carbon nanotubes (90%) was purchased from Sigma-Aldrich (Sydney, Australia). L-aspartic acid (98.5-100%) was purchased from Fisher (Japan) while Nafion (117 solution, ~5%)

from Fluka (Switzeland). Lead(II) nitrate (99.5%) and sodium hydroxide were purchased from Merck (Germany). Nitric acid and Tris-HCl were obtained from R&M Chemicals (United Kingdom).

2.2 Instrumentation

All electrochemical measurements were performed with μAutolab (Microchemie). Electrochemical measurements were performed using 3 systems electrode; 3-channelled SPE as the working electrode, Ag/AgCl/3M KCl as the reference electrode and platinum (Pt) rod as the counter electrode. Prior to any measurements, the solutions were deoxygenated by bubbling N_2 gas through the solution for 5 min at room temperature (25°C).

Signal of modified and unmodified screen printed electrode (SPE) were measured using cyclic voltammetry (CV) by scanning the potential from +1.25 to −1.25 V with a scan rate of 100 mV/s. 0.1 M Tris-HCl solution was used as supporting electrolyte. All measurements are based on the oxidative peak of the voltammograms.

2.3 Electrode preparation

The modification was done by casting CNTs/Nafion/aspartic acid solution onto the carbon active area on the 3-channelled SPE. An optimized amount of amino acids and CNTs is mixed by direct solubilisation in Nafion solution. This is followed by sonication for 30 minutes to improve the homogeneity. 10 μL of the homogenous black suspension is dropped onto the carbon active area on the 3-channelled SPE and air-dried for 30 minutes at room temperature.

3. RESULTS AND DISCUSSIONS

3.1 Electrochemical characterization of the CNTs/Nafion/aspartic acid modified SPE

The electrochemical experiments were performed on a CNTs/Nafion/aspartic acid modified SPE immersed in a cell containing 15 ml of 1 mM Pb^{2+} with 0.1 M Tris-HCl solution. Figure 1 show the effect of mass ratio of CNTs/aspartic acid on the oxidative current. The best ratio is 1:4 where the oxidative current is at the maximum value. At ratio 1:5, the oxidative current decreased due to the steric effect in the assembly of CNTs and aspartic acid on SPE.

The surface of electrode tends to be contaminated overtime when applied in detection of analytes in real sample. This will lead to a decrease in response and difficulty in the analysis of untreated samples due to irreversible adsorption of electro-active and other chemical species [18]. Modifying or protecting the electrode surface with polymer such as Nafion can lead to minimization of such effect. Nafion possesses several ideal properties such as permselective which represents sufficiently good discrimination against potential adsorbents and interfering species [18].

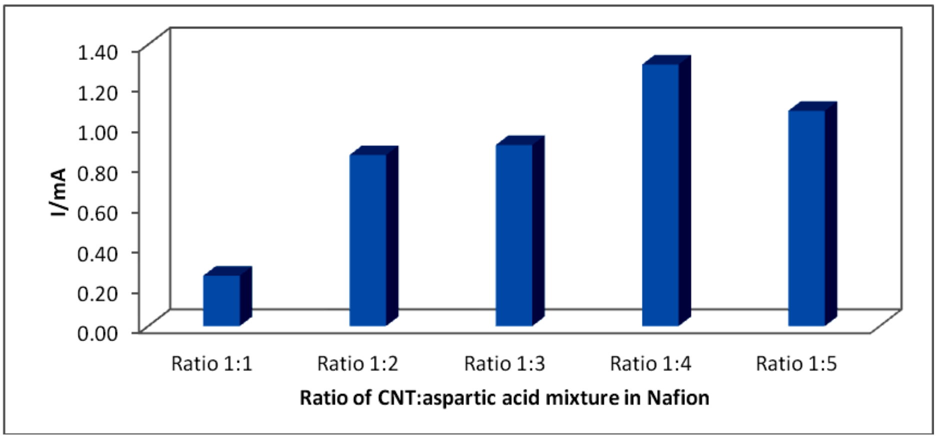

Figure 1. Effect of ratio of CNTs/aspartic acid mixture in Nafion on oxidative current of Pb^{2+}.

Figure 2 shows the CV of modified electrode for electrochemical oxidation of 1 mM Pb^{2+} in 0.1 M Tris-HCl solution as supporting electrolyte. The current responses were compared between unmodified SPE, CNTs modified SPE and CNTs/Nafion/aspartic acid modified SPE. It is observed that with unmodified electrode, a very low oxidative peak about 0.723 μA appears at -0.365 V. After modification with CNTs and CNTs/aspartic acid, the oxidative current increase significantly and shifted to more positive potential -0.211 V and 0.354 V, respectively. A distinct redox peak is observed in the presence of CNTs indicating reversible process which is possibly due to electrocatalytic properties of CNTs. The oxidative current increased significantly with addition of aspartic acid (at potential = 0.35 V), which suggest that a stable complex of Pb^{2+}–aspartic acid was formed. Only oxidation peak is observed for CNTs/aspartic acid modified electrode indicating irreversible process due to adsorption of complex Pb^{2+}–aspartic acid on the surface of electrode.

The enhancement of oxidation peak current for each modification is shown in Table 1. CNTs modified SPE have 6 folds of enhancement of oxidative current compared to unmodified electrode whereas CNTs/aspartic acid has 18 folds enhancement.

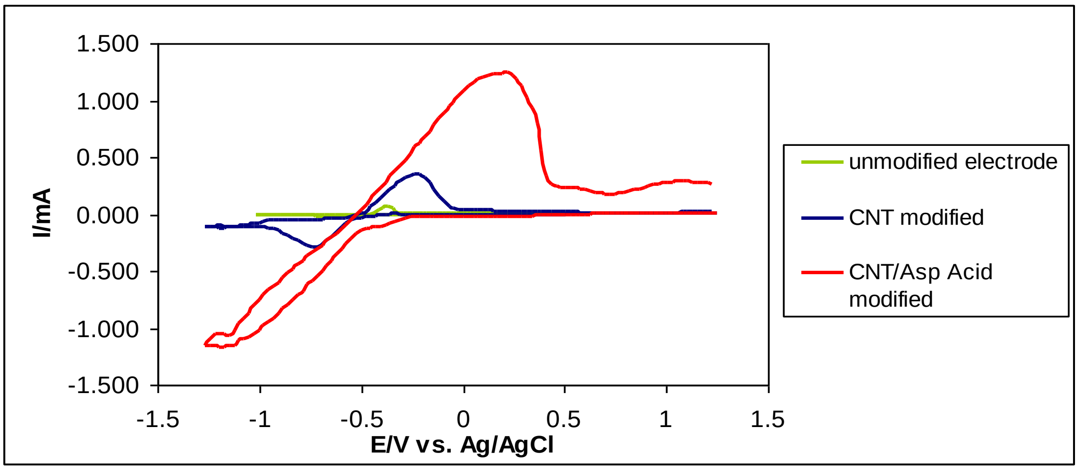

Figure 2. Cyclic voltammogram of modified SPE in 1 mM Pb^{2+} in 0.1 M Tris-HCl at scan-rate 100 mV/s with potential scanning commenced in negative direction over the range 1.25 to -1.25 V vs Ag/AgCl.

Table 1. Enhancement of oxidative current for modified SPE relative to unmodified SPE.

Modified SPE	**Current enhancement**
CNTs/AspAcid modified SPE	18 folds
CNTs modified SPE	6 folds

3.2 Electrochemical Characterization of the Modified Electrode at Different pH Value

The effect of pH on the oxidative current of the modified electrode was investigated using CV. The pHs of supporting electrolyte were varied from 1 to 8 to determine its effect on the current. The pH was adjusted using 0.1 M HNO_3 and 0.2 M NaOH. From Figure 3, it is observed that the oxidation current increases with an increase in pH from 1 to 2 and started to decrease beyond that.

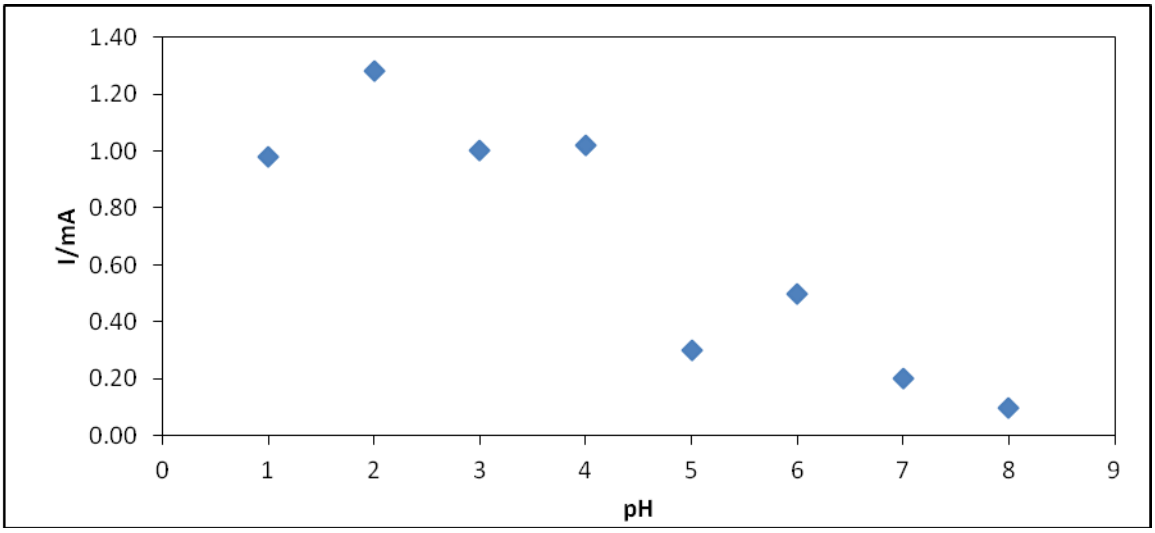

Figure 3. Effect of pH on oxidative current of CNTs/Nafion/aspartic acid modified SPE in 1 mM Pb^{2+} in 0.1 M Tris-HCl at scan-rate 100 mV/s with potential scanning commenced in negative direction over the range 1.25 to -1.25 V vs Ag/AgCl.

The side chains of aspartic acid are negatively charged above pH 3.0. It can form electrostatic interactions or “salt interactions” with opposite charge [19]. The current dropped sharply after pH 2 as the molecule carries no net charge at pH 2.77 (isoelectric point). At pH more than 5, white precipitation occurs due to formation of hydroxide. Therefore, alkaline condition is not suitable as the optimum pH.

The reproducibility of the detection system was studied by using 6 similarly constructed CNT/Nafion/aspartic acid modified SPE (as shown in Table 2). Good reproducibility with 1.76% relative standard deviation (R.S.D) was obtained for the determination of 1 mM Pb^{2+}.

Table 2. Reproducibility study of the determination of 1mM Pb^{2+} using CNTs/Nafion/aspartic acid modified SPE in 0.1 M Tris-HCl at scan-rate 100 mV/s.

No. of replicates	Current, I/mA
1	1.259
2	1.274
3	1.273
4	1.320
5	1.308
6	1.308

3.3 Analytical Application of the Developed Modified Electrode

In order to evaluate the sensitivity of CNTs/Nafion/aspartic acid modified electrode, voltammogram of the modified electrode in the presence of different concentration of Pb^{2+}were recorded. The result is shown in Figure 4. Anodic peak current increased with increasing of Pb^{2+} concentration. The sensitivity, expressed as the slope of the linear region of the calibration curve is 5.22 µA/µM. From these results it can be inferred that the presence of CNT/aspartic acid nanohybrid on the surface of SPE electrode facilitates the detection of Pb^{2+} at low concentration level. This can be explained by a large surface area and higher current density facilitated by CNTs [20].

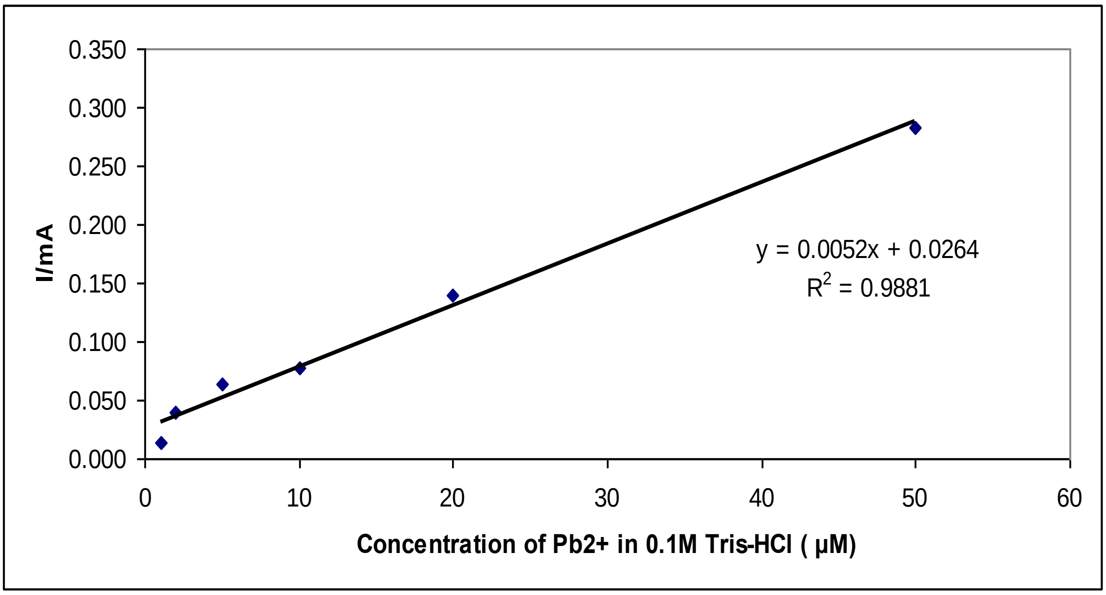

Figure 4. Calibration graph of Pb^{2+} in 0.1M Tris-HCl using CNTs/Nafion/aspartic acid modified SPE in 0.1 M Tris-HCl at scan-rate 100 mV/s. Potential scanning commenced in negative direction over the range 1.25 to -1.25 V vs Ag/AgCl.

4. CONCLUSION

In this paper, CNTs/Nafion/aspartic acid is used as modified SPE for determination of Pb^{2+} in 0.1 M Tris-HCl as supporting electrolyte. The prepared electrodes show sensitivity toward Pb^{2+} ions in solution. Nafion was used to serve as the electrode binder and also to solubilise the CNTs. The performance of the resulting modified electrode improved greatly compared to the unmodified electrode. The reported technique provides a potential way for determination of Pb^{2+} for routine sample analysis.

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