

Electrochemical study of glassy carbon electrode mediated by carbon nanotubes for detection of trace Mn(II)

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ABSTRACT

Carbon nanotubes CNT was modified on the surface of glassy carbon electrode (GCE) using mechanical method to prepare working electrode CNT/GCE and CNT/Li⁺/GCE were used in cyclic voltammetry analysis. The nanostructured electrodes showed individual voltammetric of Mn²⁺ two reduction peaks at +800 and +100 mV. The reduction current of Mn²⁺ on CNT/Li⁺/GCE was largely influenced by low concentration comparing with GCE and CNT/GCE. It was obtained the detection of Mn²⁺ by CNT/Li⁺/GCE in aqueous 0.1M KCl, 0.1M urea, seawater and blood samples as a supporting electrolyte, the relative standard deviation RSD of two electrodes is very good on CNT/Li⁺/GCE and CNT/GCE. The study to determine the efficiency of best electrode for Mn²⁺ detection, it was founded wide linear range and good repeatability relative standard deviation (RSD) of $\pm 1.9\%$ when used CNT/Li⁺/GCE and the limit of detection was found to be 10^{-4} - 10^{-3} mM of Mn²⁺, while the limit of detection was determined 3×10^{-4} - 10^{-3} mM when used CNT/GCE with RSD of $\pm 3.3\%$.

Key words: CNT/GCE, CNT/Li⁺, Cyclic Voltammetry, Manganese ion analysis, Electrocatalysis.

INTRODUCTION

Carbon nanotubes are a newly created material combining two previously discovered allotropes of carbon; carbon nanotubes and fullerenes¹. The most common oxidation state of manganese are +2, +3, +4, +6 and +7, though oxidation states from +1 to +7 are observed. Manganese compounds where manganese is in oxidation state +7 are powerful oxidizing agents². Carbon nanotubes CNT are allotropes of carbon with a nanostructure that can have a length to diameter ratio of up to 28,000,000:1, which is significantly larger than any other material³. CNT are long, thin cylinders of carbon^{4,5}. The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis⁶. The behavior of multi wall carbon nanotubes in water solution depending on concentration electrolytes and/or biomolecules was

studied by methods of evaluation of electroconductivity. There were found that study could be the method of preliminary testing new materials for biocompatibility of multiwall carbon nanotubes in studied polymer matrixes changes the nanocomposites surface chemistry and influence on their biocompatible properties⁷. Novel multipurpose electrode materials that have various catalytic applications are developed. The materials are composites based on multiwalled carbon nanotubes and electroconducting of Nanoparticles of metallic platinum and compounds of transition metals. It is demonstrated experimentally that the materials possess high electronic and protonic conductance, thermal stability, hydrophilicity, large specific surface area, and considerable porosity⁸. Carbon nanotubes CNT, modified with manganese dioxide, were synthesized. Electrochemical characteristics of the oxygen electrodes containing manganese dioxide modified nanotubes in active

layer were investigated. It was shown, that deposition of manganese dioxide on surface of carbon nanotubes results in improvement of electrochemical characteristics in comparison with manganese dioxide as a separate phase⁹. A novel electrochemical DNA-based biosensor for the detection of deep DNA damage was designed employing the bionanocomposite layer of multiwalled carbon nanotubes, thus confirming a strong effect of multiwalled carbon nanotubes on the enhancement of the electroconductivity of the electrode surface which distribution at the electrode surface¹⁰. Various carbon materials including carbon nanotubes and graphitised nanofibres used as supports in heterogeneous catalysis are considered. The methods for modification of catalysts and the results obtained as applied to three important processes of organic synthesis¹¹. In this work, CNT was modified GCE by mechanical method and CNT/Li⁺/GCE was modified by LiOH solution and cyclic voltammetry to resulting composites modified electrodes were successfully applied to detect trace Hg²⁺ by cyclic voltammetry with different results¹².

MATERIAL AND METHODS

Materials

CNT (Fluka, 98%). Other chemicals and solvents were used of annular grade and as received from the manufacturer. Distilled water was used for the preparation of aqueous solutions. All solutions were deaired with oxygen free nitrogen gas for 15 minutes prior to making the measurement.

Instruments

Electrochemical workstations of Bioanalytical System Inc. USA: Models BAS CV 50W with potetiostate driven by electroanalytical measuring softwares were connected to PC computer to perform cyclic voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire were used as a reference and counter electrode respectively. The working electrodes used in this study were GC electrode and modified GCE with CNT by mechanical attachment method¹³⁻¹⁵, also the CNT/GCE was doping with Li⁺ ion by cyclic voltammetry, a platinum wire (1mm diameter) counter electrode and an Ag/AgCl (3M NaCl) reference electrode were used in CV analysis.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) the fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 kV. The scanning electron photographs were recorded at a magnification of 1000X to 6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 minutes before being coated with goal particle using SEM coating unit baltec SC030 sputter Coater. SEM was used to examine the morphology of CNT microcrystals by mechanical attached on a graphite electrode surface before and after electrolysis by cyclic voltammetry. Figure 1a is SEM of CNT attached on to 6 mm diameter basal plane graphite electrode exhibits an array of microcrystals with 2µm diameter. Figure 1b is SEM of CNT after electrolysis with Mn²⁺ using cyclic voltammetry on to 5 mm diameter basal plane graphic electrode with 2µm diameter.

RESULTS AND DISCUSSION

Comparison the different modified electrodes CNT and CNT/Li⁺ on GCE

Voltammograms of GC, CNT/GC and CNT/Li⁺/GC electrodes with 1mM Mn²⁺ shows the effect of using chemically modified electrodes on electrochemical reduction of Mn²⁺ in Figure 2, it was observed that the reduction current peaks of Mn²⁺ appear on the two modified electrodes was higher in current especially at the CNT/Li⁺/GCE. However, the reduction process appears to be mediated by the presence of CNT with and without Li⁺ doping since CNT/Li⁺ the modified GCE enhance the reduction current of Mn²⁺ nearly twice folds but the reduction peak shifted to higher potential when compared to other electrodes was used during cyclic voltammetry that the modification causes as an electrocatalyst.

Evidently degree of sensitivity response increases in the order of

CNT/Li⁺/GCE > CNT/GCE > GCE.

Electrochemical performance of CNT/Li⁺/GCE for Mn²⁺ detection

In aqueous 0.1M KCl solution

The CNT/Li⁺/GCE was applied for the successive determination of Mn²⁺ by different concentration ranges in 0.1M KCl were investigated.

To examine the performance of the two modified electrodes CNT/GCE and CNT/Li⁺/GCE as a method in Mn²⁺ detection, the differential pulse for cathodic CV by different electrodes to get the most results with high accuracy.

However, the CNT/Li⁺/GCE exhibited excellent performance of Mn²⁺ analysis as show in

Figure 3B and a well defined was observed at +0.55V corresponding to the reduction peak of Mn²⁺ and at +0.6V on CNT/GCE as in Figure 4B. It was clear that Mn²⁺ ion was selectively deposited on CNT/Li⁺/GCE rather than CNT/GCE surface.

The calibration plots were performed at the CNT/Li⁺/GCE in the Mn²⁺ the concentration range of 0.0001-0.001mM as show in Figure 3A and the CNT/GCE in the Mn²⁺ at concentration range of 0.0003-0.001mM in Figure 4A. It was found a very good linearity of peak current versus Mn²⁺

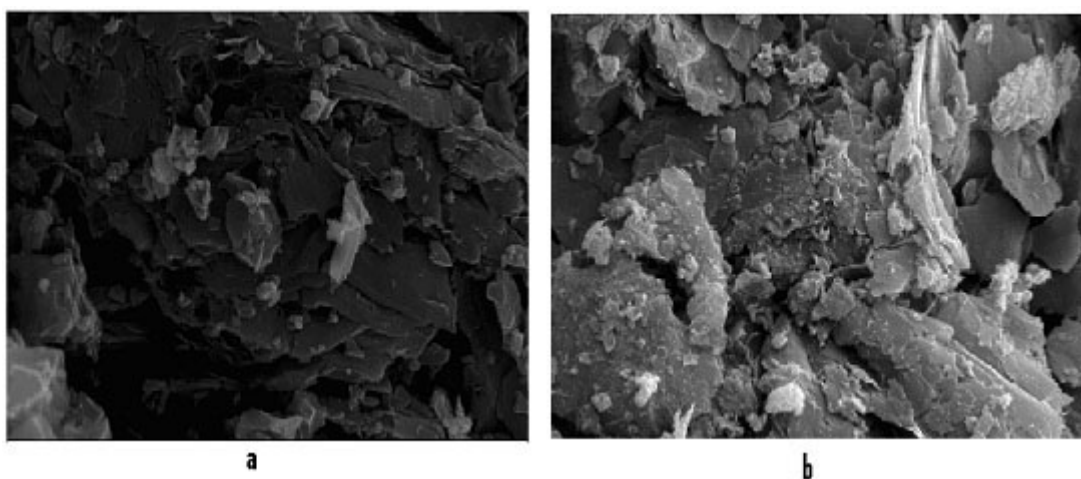


Fig. 1: Scanning electron micrographs of CNT microparticles mechanically attached to a basal plane pyrolytic graphite electrode (a) before and (b) after electroanalysis with Mn²⁺

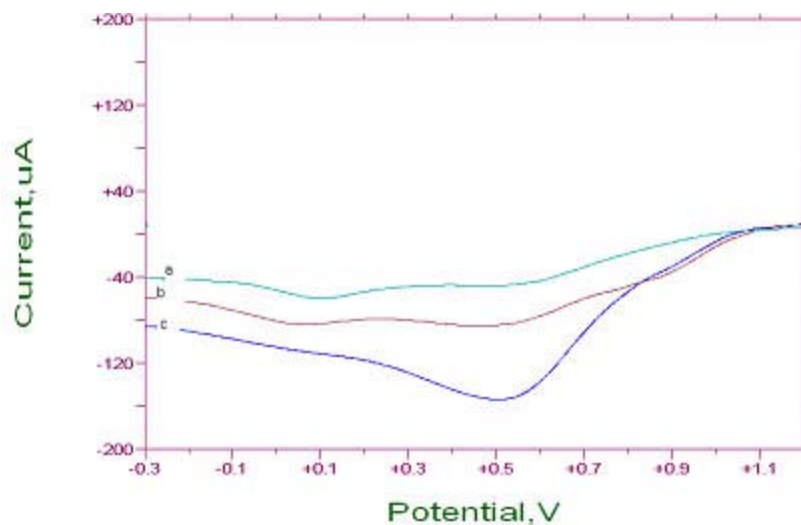


Fig. 2: Voltammogram for the reduction peak of 1mM Mn²⁺ in 0.1M KCl as supporting electrolyte at scan rate 100mvs⁻¹ using (a) GCE (b) CNT/GCE and (c) CNT/Li⁺/GCE

concentration with correlation coefficient of $R^2=0.9828$ when use CNT/Li⁺/GCE with concentration range from 0.0001mM to 0.001mM with good linearity by $Y= 65396X+13.837$ while, the linearity of cathodic current versus Mn²⁺

concentration with correlation coefficient of $R^2=0.9621$ and $Y=76777X-0.899$ when used CNT/GCE.

The reduction peak current remarkably

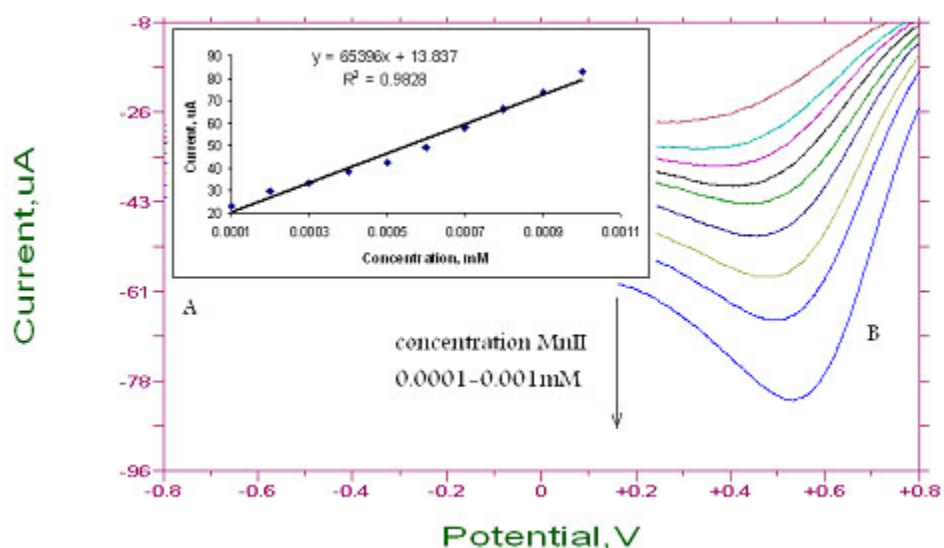


Fig. 3: (A) Calibration Plot of cathodic current versus different concentration 0.0001-0.001mM MnCl₂, (B) Voltammogram of cathodic current versus different concentration 0.0001-0.001mM MnCl₂ in 0.1M KCl as a supporting electrolyte using CNT/Li⁺-GCE versus Ag/AgCl

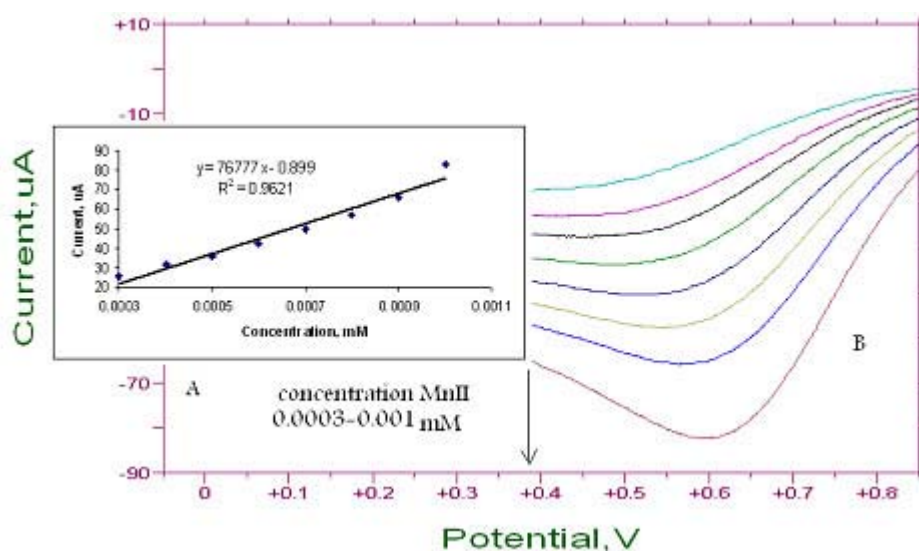


Fig. 4: (A) Calibration Plot of cathodic current versus different concentration 0.0003-0.001mM MnCl₂, (B) Voltammogram of cathodic current versus different concentration 0.0003-0.001mM MnCl₂ in 0.1M KCl as a supporting electrolyte using CNT-GCE versus Ag/AgCl.

enhanced at the CNT/Li⁺ surface on GCE which may be attributed to the larger effective surface area and better electrochemical reacting ability resulting

from Mn²⁺ supported on the CNT/Li⁺ surface. In order to compare the electrochemical properties of CNT/Li⁺/GCE and CNT/GCE calibration plots were

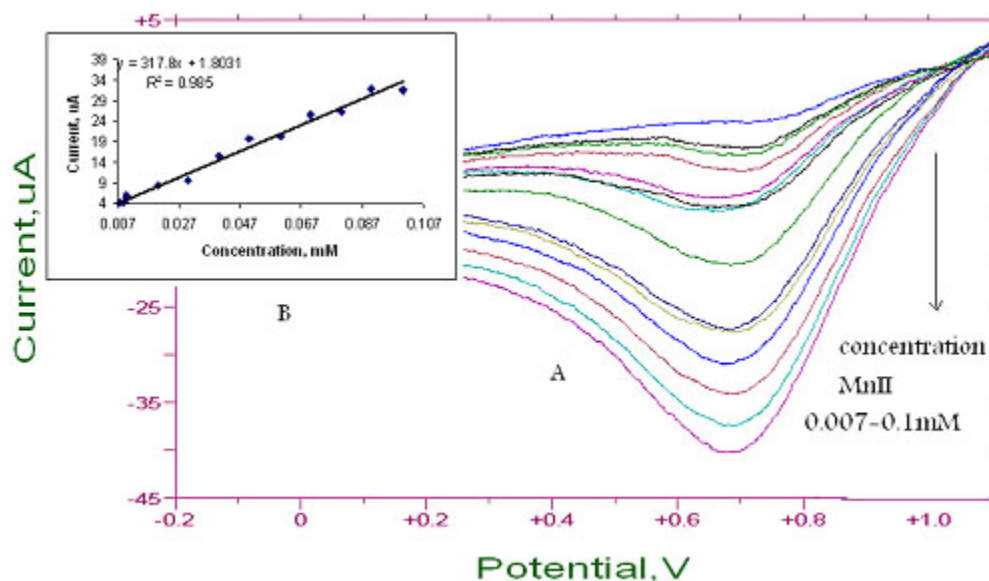


Fig. 5: (A) Voltammogram of cathodic current versus different concentration 0.007-0.1mM MnCl₂ in 0.1M urea as a supporting electrolyte using CNT/Li⁺/GCE versus Ag/AgCl. (B) Calibration Plot of cathodic current versus different concentration 0.007-0.1mM MnCl₂

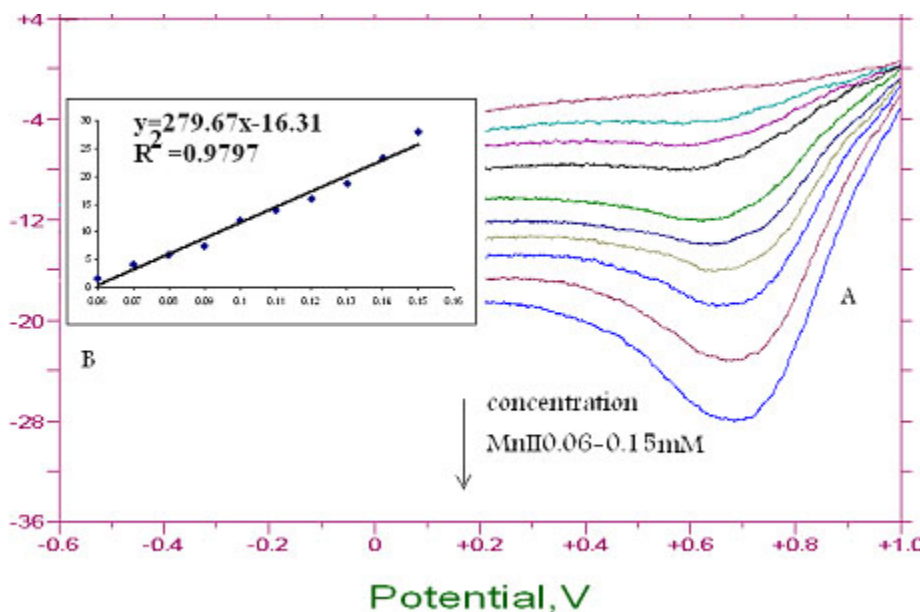


Fig. 6: (A) Voltammogram of cathodic current versus different concentration 0.06-0.15mM MnCl₂ in 0.1M urea as a supporting electrolyte using CNT/GCE versus Ag/AgCl. (B) Calibration Plot of cathodic current versus different concentration 0.06-0.15mM MnCl₂

performed in Mn^{2+} concentration ranges, the low concentration conditions, a very good linearity of reduction peak current versus Mn^{2+} concentration as in CNT/Li⁺/GCE that gives high sensitivity and good results.

In 0.1M urea solution

The CNT/Li⁺/GCE was applied for the successive determination of Mn^{2+} by different concentration ranges in 0.1M urea solution as a supporting electrolyte were investigated to examine

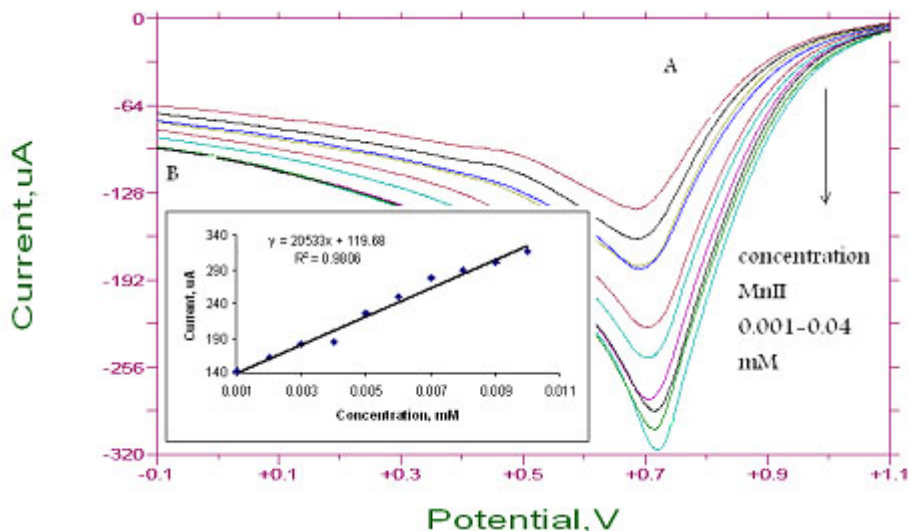


Fig. 7: (A) Voltammogram of cathodic current versus different concentration 0.001-0.03mM $MnCl_2$ in 0.1M seawater as a supporting electrolyte using CNT/GCE versus Ag/AgCl. (B) Calibration Plot of cathodic current versus different concentration 0.001-0.03mM $MnCl_2$

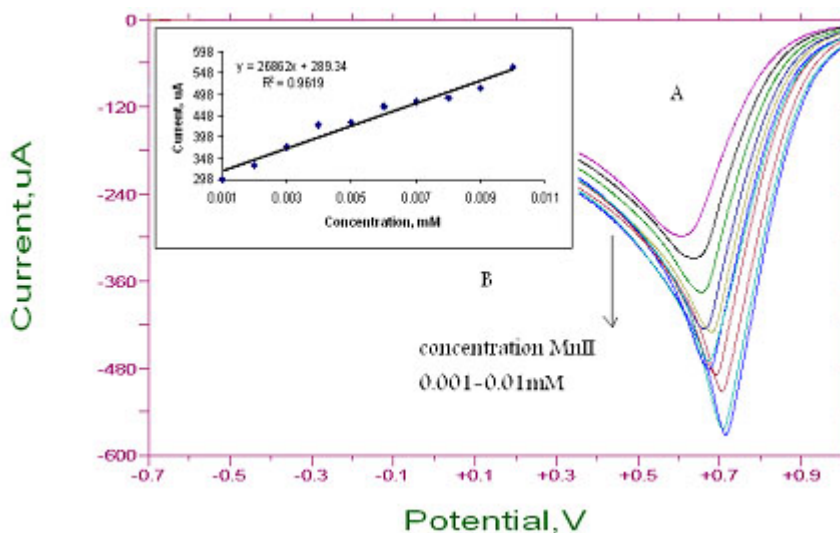


Fig. 8: (A) Voltammogram of cathodic current versus different concentration 0.001-0.01mM $MnCl_2$ in 0.1M seawater as a supporting electrolyte using CNT/Li⁺/GCE versus Ag/AgCl. (B) Calibration Plot of cathodic current versus different concentration 0.001-0.01mM $MnCl_2$

the performance of the two modified electrodes CNT/GCE and CNT/Li⁺/GCE as a method in Mn²⁺ to detection using CV method get the most results with high accuracy of Mn(II) ions.

However, the CNT/Li⁺/GCE exhibited excellent performance of Mn²⁺ analysis as in Figure 5A and a well defined was observed at +0.7V corresponding to the reduction current peak of Mn²⁺ and also, at CNT/GCE as in Figure 6A. It was clear that Mn²⁺ ion was selectively deposited on CNT/Li⁺/GCE rather than CNT/GCE surface.

The calibration plots were performed at the CNT/Li⁺/GCE in the Mn²⁺ the concentration range of 0.007-0.1mM in 0.1M urea solution as show in Figure 5B and the CNT/GCE in the Mn²⁺ at concentration range of 0.06-0.15mM as show in Figure 6B. It was found a very good linearity of reduction current peak versus Mn²⁺ concentration with correlation coefficient of R²=0.985 when use CNT/Li⁺/GCE with good linearity by Y= 317.8X+1.8031. While, the linearity of cathodic current versus Mn²⁺ concentration with correlation coefficient of R²=0.9797 and Y=279.67X-16.31 when used CNT/GCE.

The cathodic current remarkably enhanced at the CNT/Li⁺ surface on GCE which may be attributed to the larger effective surface area and better electrochemical reacting ability resulting from Mn²⁺ supported on the CNT/Li⁺ surface. In order to compare the electrochemical properties of CNT/Li⁺/GCE and CNT/GCE calibration plots were performed in Mn²⁺ concentration ranges, the low concentration conditions, a very good linearity of reduction peak current versus Mn²⁺ concentration as in CNT/Li⁺/GCE that gives good results.

In seawater sample

The CNT/Li⁺/GCE was applied for the successive determination of Mn²⁺ by different concentration ranges in seawater sample as a supporting electrolyte were investigated to examine the performance of the two modified electrodes CNT/GCE and CNT/Li⁺/GCE to detection the Mn²⁺ ion using CV method to get the most results with high accuracy of Mn(II). However, the CNT/GCE exhibited performance of Mn²⁺ analysis as in Figure 7A and a well defined was observed at +0.7V corresponding to the reduction peak of Mn²⁺ and also, on CNT/Li⁺/GCE as show in Figure 8A. It was clear that Mn²⁺ ion was selectively deposited on CNT/Li⁺/GCE rather than CNT/GCE surface.

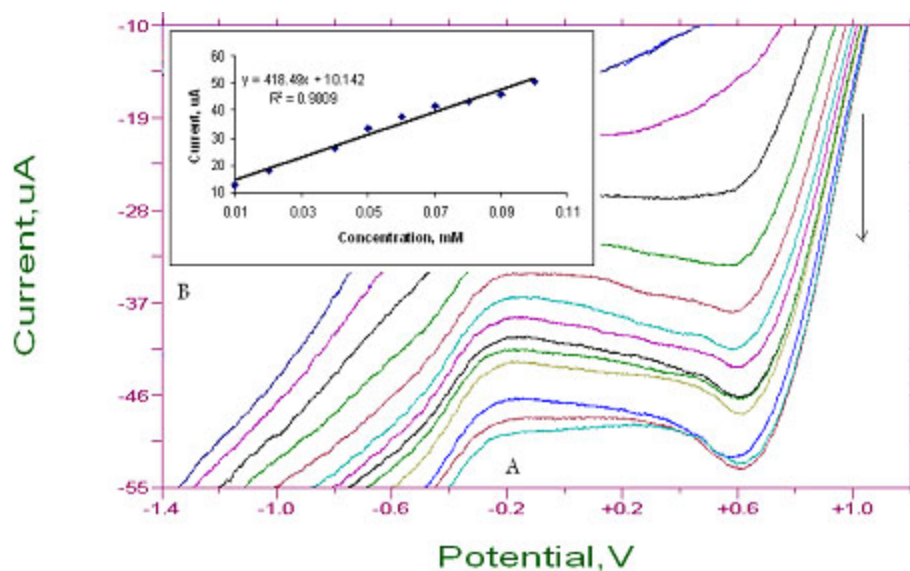


Fig. 9: (A) Voltammogram of cathodic current versus different concentration 0.01-0.1mM MnCl₂ in blood sample using CNT/Li⁺/GCE versus Ag/AgCl. (B) Calibration Plot of cathodic current versus different concentration 0.01-0.1mM MnCl₂

The calibration plots were performed at the CNT/GCE in the Mn^{2+} the concentration range of 0.001-0.04mM in 0.1M urea solution as show in Figure 7B and the CNT/Li⁺/GCE in the Mn^{2+} at concentration range of 0.001-0.01mM as show in Figure 8B. It was found a very good linearity of peak current versus Mn^{2+} concentration with correlation coefficient of $R^2=0.9619$ when the modified electrode was used CNT/Li⁺/GCE with good linearity by $Y= 2686.2X+289.34$. While, the linearity of cathodic current versus Mn^{2+} concentration with correlation coefficient of $R^2=0.9806$ and $Y=20533X-119.68$, when it was used CNT/GCE as show in Fig. 7B.

In blood sample

The study of effect blood (chose mouse blood) on the Mn^{2+} was carried out by using different concentration of Mn^{2+} (0.01-0.1mM) was spiked in to the blood using CNT/Li⁺/GCE. Figure 9A shows a well defined was observed at +0.6V corresponding to the reduction peak of Mn^{2+} . The calibration plots were performed at the CNT/Li⁺/GCE in the Mn^{2+} the concentration range of 0.01-0.1mM in blood sample as show in Figure 9B. It was found a very good linearity of cathodic peak current versus Mn^{2+} concentration with correlation coefficient of

$R^2=0.9809$ when use CNT/Li⁺/GCE with good linearity by $Y= 418.49X+10.142$.

CONCLUSIONS

The CNT/GCE and CNT/Li⁺/GCE have been successfully fabricated by different methods to study Mn^{2+} detection by cyclic voltammetry analysis in different supporting electrolytes (0.1M KCl, 0.1M Urea, Seawater and Blood samples) . As a resulting composite modified electrodes which produced favorably the bulk quantities of the renewable sensors and electrocatalyst.

The CNT/Li⁺/GCE exhibits an improved performance for Mn^{2+} analysis in comparison with CNT/GCE. The Mn^{2+} detection by CNT/Li⁺/GCE gives a very good sensitivity with high correlation coefficient with wider linear range and lower detection limit than the other modified electrode and GCE alone.

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