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ELECTROCATALYTIC ACTIVITY OF BAMBOO-LIKE MULTI WALLED CARBON NANOTUBES FOR THE DETERMINATION OF ASCORBIC ACID

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ABSTRACT

Bamboo-like multi walled carbon nanotubes (b-CNTs) were synthesized by chemical vapour deposition technique (CVD) using copper supported catalyst and the obtained product were purified by a simple acid treatment. Purified CNTs were characterized by FE-SEM and HR-TEM analysis, which clearly reveals the formation of multi layers of graphitic carbon tubular structures and having diameter between 4 – 10 nm, respectively. The purified CNTs were used for the modification of carbon paste electrode (CPE) to determine ascorbic acid (AA) by using cyclic voltammetry (CV) technique. The modified electrode exhibited a rapid response to AA within 5s and showed a linear correlation to AA concentration in a range from 10×10^{-6} to 50×10^{-6} M. Stability of the modified electrode was also evaluated by repeating the experiment for 20 days and results show good stability. From this study, we confer that without using redox mediator, CNTs with carbon paste will results in good electrocatalytic activity towards oxidation of AA.

KEY WORDS: Bamboo-like multi walled carbon nanotubes, CVD, Ascorbic acid, Carbon paste electrode

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INTRODUCTION

Ascorbic acid is a water soluble vitamin, which can be found in natural sources such as fruits and fresh vegetables. It was used as an antioxidant in food, animal feed, beverages, cosmetic applications and pharmaceuticals [1, 2]. It plays a significant role in biological metabolism such as development of bones, blood vessels and skin. It is also important for the prevention and treatment of common cold, infertility, scurvy, mental illness and cancer [3, 4]. Determination of AA is most essential due to the significant role in life cycle. Various methods are available for determination of AA like titration [5], colorimetry [6], HPLC [7], spectrometry [8], among them electrochemical sensors are considered as one of the most convenient method, owing to their high sensitivity, simplicity and accuracy. Generally AA can easily undergo oxidation at conventional electrodes [9, 10]. However, which requires high over potential for the direct oxidation of ascorbic acid at bare electrodes and also leads to low selectivity, poor reproducibility and low sensitivity [11]. Modified electrodes with nanomaterials have been introduced and developed to resolve these issues. Among them CNTs modified electrodes have played a crucial role in sensor applications. In recent years CNTs have received much interest after their discovery by Sumio Iijima in 1991 [12]. They have obtained remarkable attention in chemical, physical, material and medical fields due to their outstanding novel properties. CNTs can promote charge transfer reaction easily in electrode materials [13], because of their excellent electronic properties, huge surface area and efficient catalytic activity. Furthermore CNTs are extensively using in electrochemical studies for sensor and supercapacitor applications. Simultaneous determination of Ascorbic Acid, Uric acid and Dopamine has been reported by many researchers. To the best of our knowledge only a few studies have published, in individual determination AA without redox mediators by electrochemical method. In this paper we described, carbon paste electrode fabrication with bamboo structured CNTs and their electrocatalytic activity against ascorbic acid molecules.

MATERIALS AND METHODS

Reagents

Reagent grade L-Ascorbic Acid, $Cu(NO_3)_2.3H_2O$ and Graphite powder (<20µm) were purchased from Sigma-Aldrich. Eicosane, α-Al_2O_3 nano powder and other chemicals (Fisher) used were of analytical grade. Double distilled water was used to prepare all the solutions. 0.1M phosphate buffer solution (PBS) of pH 7 was prepared using K_2HPO_4 and KH_2PO_4.

Apparatus

Voltammetric measurements were carried out with a CHI660D electrochemical workstation and a conventional three-electrode system. The CPEs were used as working electrode and platinum wire, Ag/AgCl electrodes were the auxiliary and reference electrodes, respectively. All the electrochemical measurements were conducted in 0.1 PBS using an electrochemical cell at 27 ± 1 ºC.

Synthesis of bamboo-like multi walled carbon nanotubes (b-CNTs) and its purification

The CVD process was carried out in horizontal tubular furnace at atmospheric pressure according to our previous investigations [14 – 16]. Quartz boat containing 10 wt% Cu/Al_2O_3 catalyst were placed at the middle of the alumina tube. The furnace temperature increased gradually up to reaction temperature of 700 °C under N_2 gas flow at a rate of 500 sccm. Then N_2 flow was stopped and purged C_2H_2 gas with flow rate of 40 sccm for 10 minutes into the reaction tube. C_2H_2 flow was discontinued and N_2 flow was continuously purged to cool down the chamber to room temperature. The black carbon product were purified using 5 M NaOH solution by continuously stirring for 2 hrs at room temperature and then washed several times with distilled water until the filtrate become neutral. Then the obtained product were treated with 5 M HCl solution as above procedure to remove catalyst particles from the nanotubes and dried at 60 °C for 4 hrs.

Fabrication of carbon paste electrodes

Carbon paste electrode were prepared by thoroughly mixing the graphite powder (<20µm) and eicosane in a ratio of 70:30 on watch glass while they were heated at 70 °C. A portion of the paste was put into plastic cylindrical tube holder with the 1.2 mm inner diameter to form bare CPE. Electrical contact to the paste was established by inserting a copper wire into the plastic tube. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and then polished with a weighing paper. Modified CPE was also prepared in a similar way by mixing graphite powder (<20 µm), eicosane and b-CNTs in a ratio of 60:30:10. The paste electrodes were kept at room temperature prior to use.

Characterization

Field Emission Scanning Electron Microscope (FE-SEM) SU-6600, Hitachi, Japan, operated at an accelerating voltage of 15 kV was performed to study the morphology of the carbon product. The structure and tube diameter were estimated by High Resolution Transmission Electron Microscope (HRTEM) JEOL 3010, 300 kV instrument with a UHR pole piece.

RESULTS AND DISCUSSION

FE-SEM and HR-TEM Analysis

The obtained product was examined through FE-SEM to predict the morphology of synthesized material. Purified product consists of tubular material with smooth outer wall in micron lengths and diameter within the nanometer range, which depicted in Figure 1(a). There was no other morphology observed in the carbon product, which is also evident from HR-TEM image in Figure 1(b) clearly shows the formation of carbon nanotubes with good crystanility and also shows the individual compartments inside the tubes, which indicated the bamboo structure CNTs [15 – 17]. The product consists of uniform diameter tubes ranging from 4 – 8 nm and lengths in microns. FE-SEM and HR-TEM observations confirm the final product was pure and no other impurities found in the material.

Determination of AA by Cyclicvoltammetric technique

The modified electrode with b-CNTs and bare electrode were tested for oxidation of AA at a concentration of 50 µM. Fig. 2 shows CV data for the oxidation of AA of modified b-CNTs/CPE in comparison with bare electrode. The result confirms that the b-CNTs/CPE electrode shows a better sensitivity in comparison to the bare CPE. An irreversible process was observed for the oxidation of AA, this is due to absence of reduction peak in voltammogram, which clearly depicted in Fig. 2. The oxidative peak current of AA raised 21.20 µA at positive potential of 500 mV. This indicates the b-CNTs/CPE without redox mediator which produced more enhancement in the oxidative peak current, when compared to bare CPE. This is due to the presence of CNTs in the modified electrode which improves the relative electron transfer at faster rate [18 – 20]. In this case b-CNTs provided the improved performance due to greater number of active sites induced by multiple joint structures and higher surface area. This implies that the presence of active sites for interface electrochemical reaction and facilitating the direct electron transfer between analyte and electrode [21]. Thus the synthesized b-CNTs even without mediator act as a good electrochemical sensor for the determination of AA when compared to other carbon materials such as activated carbon, carbon black etc [22 – 24].

Effect of ascorbic acid concentration

Electrocatalytic activity of b-CNTs/CPE was investigated at different concentrations of AA i.e. (i) 10 µM, (ii) 20 µM, (iii) 30 µM, (iv) 40 µM and (v) 50 µM. The oxidative peak current at different concentrations were shown in Fig. 3. The voltammograms shows that the peak current decreased with the decrease in the AA concentration from 50 µM to 10 µM. From Fig. 4, the relationship was found to be $y = 0.142 x + 13.650$, with an R^2 value of 0.986. The results obtained from b-CNTs modified CPE, which gives a sensitivity response for this electrode and was found to be 1.4×10^{-7} M (S/N=3). The limit of detection of AA was calculated to be 2.1×10^{-6} M, according to LOD = 3 SD/m, where SD is the standard deviation of the blank response and m is the slope of the calibration plot. This

suggests that the sensitivity of the b-CNTs/CPE electrode is higher than bare CPE.

Reproducibility and stability

The electrode capability for the generation of a reproducible surface was examined by the determination of 50 µM ascorbic acid in a 0.1 M PBS supporting electrolyte. Five successive determinations were conducted on different days with from five separately prepared b-CNTs/CPE electrodes for each run. A relative standard deviation (RSD) value of 2.4% was obtained which shown in table 1, indicating that the b-CNTs/CPE electrode has good reproducibility. In addition, the long-term stability of the b- CNTs/CPE was tested over a three-week period. All the CV's experiments were recorded at room temperature and the b- CNTs/CPE electrode was stored at room temperature. There was no noticeable change in the peak potential for AA oxidation. Thus the modified electrode showed stability up to 20 days period.

Table 1

Repeatability of ascorbic acid determination at MWCNTs/CPE

S.No	Repeat No	Peak Current
1.	1	21.20
2.	2	20.85
3.	3	19.93
4.	4	21.16
5.	5	20.84
6.	Mean	20.80
7.	SD	0.512
8.	RSD (%)	2.46

Figure 1

(a) FE-SEM image of CNTs and (b) HR-TEM image of b-CNTs

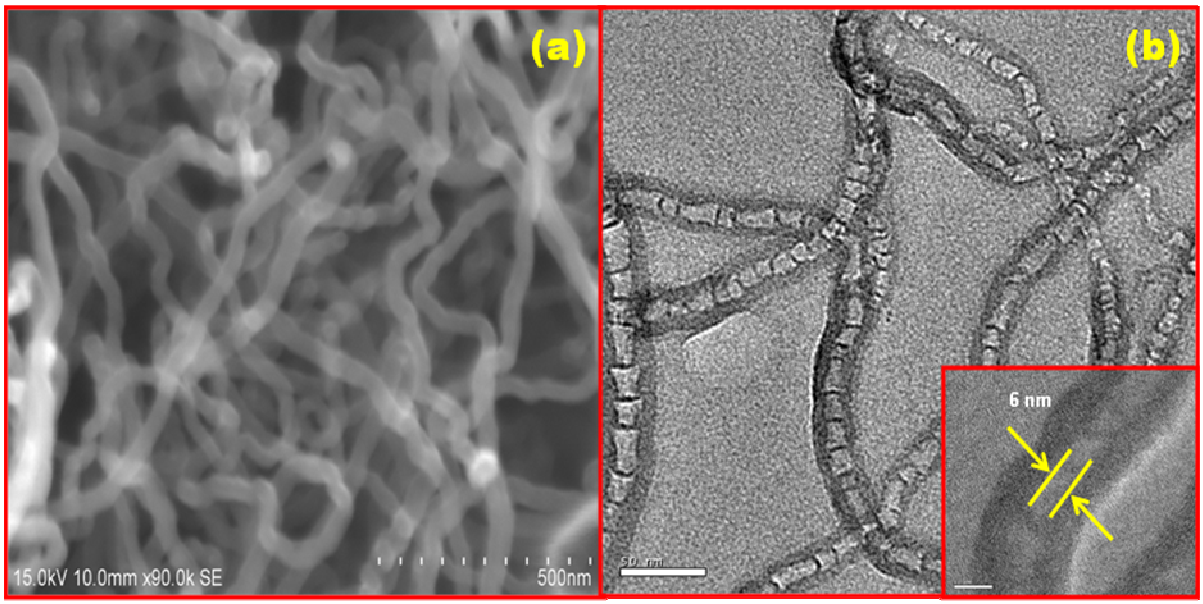


Figure 2

Cyclic voltammograms for the oxidation of 50 µM ascorbic acid in 0.1 M PBS at a scan rate 100 mV/s using (a) bare CPE, (b) b-CNTs modified CPE

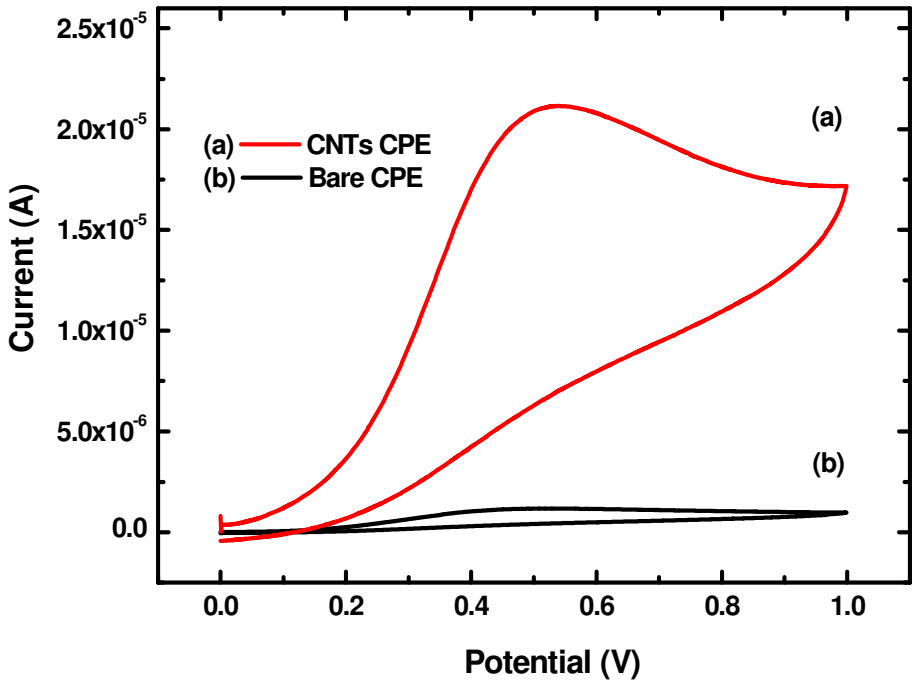


Figure 3

Cyclic voltammograms of b-CNTs-modified electrode in 0.1 M PBS at a scan rate 100 mV/s with increasing ascorbic acid concentration (a) 10 µM, (b) 20 µM, (c) 30 µM, (d) 40 µM and (e) 50 µM

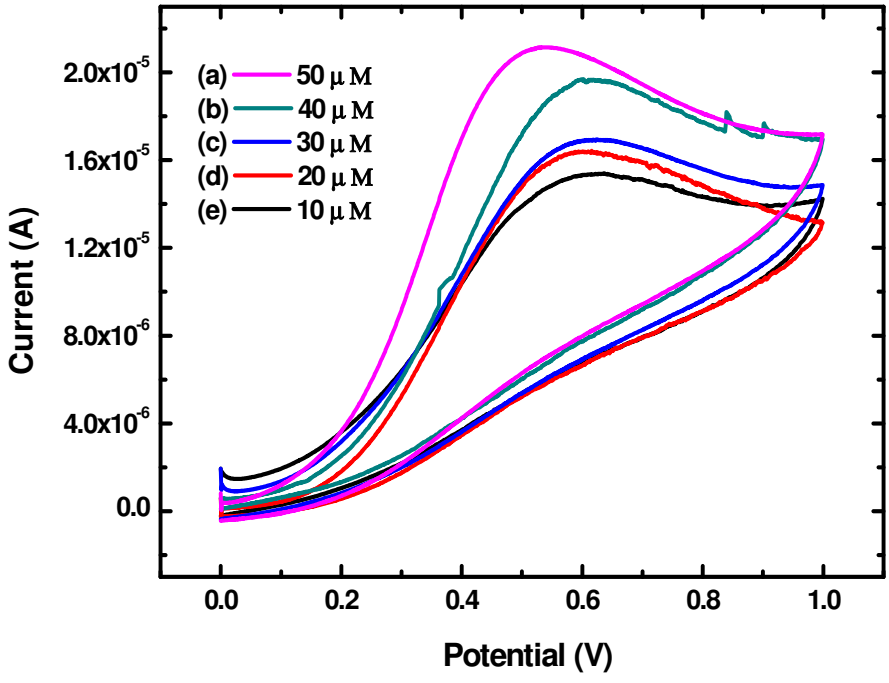
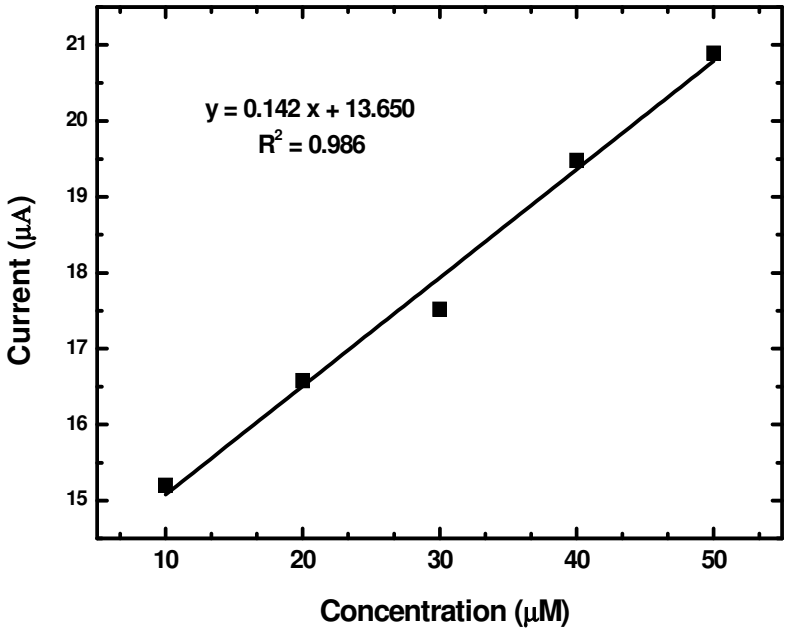


Figure 4
Calibration curve of the oxidation current response of the b-CNTs/CPE versus concentration of AA in 0.1 M PBS, pH 7, with the scan rate 100 mV/s at 27 ± 1 ºC.



CONCLUSION

We have prepared b-CNTs from Cu/Al_2O_3 catalyst by thermal CVD and were purified by a simple acid treatment. Carbon paste electrode (CPE) and modified Carbon paste electrode with b-CNTs were fabricated for the determination of AA at low concentration levels. Application of b-CNTs into the carbon paste showed an excellent electrocatalytic activity towards oxidation of AA, without using any redox mediator. The modified electrode exhibited a rapid response to AA within 5s and shows a linear correlation to AA concentration in a range from 10×10^{-6} to 50×10^{-6} M. The modified electrode also showed good reproducibility and stability.

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