ELECTROCHEMICAL OXIDATION OF ASCORBIC ACID MEDIATED BY CARBON NANOTUBES /Li^+/ CARBON PASTE MODIFIED SOLID ELECTRODE

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Abstract

Multi-walled carbon nanotube (MWCNT) was used to modify BPPG electrode because of its unique structure and extraordinary properties. MWCNT modified electrode exhibited obvious enhancing and electrocatalyzing effects to the oxidation of ascorbic acid using cyclic voltammetry technique. MWCNT was bonded on BPPG electrode surface using carbon paste with ratio of 30% (w/w) carbon paste (binder): 70% (w/w) MWCNT. This method of modification has lowered the capacitance background current and enabled lower detection limit of ascorbic acid concentration. The electrical conductivity property of MWCNT modified electrode was further improved with the intercalation with lithium ion and resulted in current enhancement of 2 times on the oxidation current of ascorbic acid.Parameters of pH and temperature showed significant relation to the sensitivity of MWCNT modified electrode. Under the optimized parameters, the calibration curve constructed was linear up from 50 µM to 5 mM with sensitivity of 34.5 mA M^{-1}. The practical application of MWCNT modified electrode was demonstrated with Vitamin C pill and orange juice. Good reproducibility and recovery of ascorbic acid concentration showed the feasibility of MWCNT modified electrode to be used in the detection of ascorbic acid in aqueous solution. This also proposed MWCNT modified BPPG electrode possessed advantages such as low detection limit, high stability, low cost and simplicity in fabrication.

Keywords: Multi-walled carbon nanotube; Ascorbic acid; Basal plane pyrollitic graphite electrode; Cyclic voltammetry; Modified electrode

Introduction

The fabrication of chemically modified electrode (CME) has been widely reported to improve sensitivity and selectivity in determining amino acids, vitamins, DNA and etc. in recent years [5-9]. Generally, CME incorporates a thin film of a selected conducting compounds or polymers which is bonded to or coated on the electrode surface to detect the presence of biomolecules of interest [1-6].

CNT is another allotrope of carbon other than graphite, diamond and fullerene [2]. These carbon allotropes have entirely different structures and properties. The characteristic that contributes to these differences is mainly due the different hybridization types. CNT possesses high electrical conductivity, high chemical stability and strong mechanical strength [10]. CNT can be divided to two categories: single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). These unusual properties are mainly due to the special architecture of bonded carbon.

Ascorbic acid is water soluble type of organic acid, which is also known widely as Vitamin C. Ascorbic acid is essential in human body due to its importance in antioxidant property. Besides, ascorbic acid also plays role in metabolisms include collagen synthesis, amino acid metabolism, synthesis of adrenalin, synthesis of anti-inflammatory steroids and certain hormones and neurotransmitters synthesis [3, 12].

This report illustrates incorporation of CNT to the basal plane pyrolytic electrode to determine the presence of ascorbic acid in tablet fruit juices.

Experimental

Instrumentation

Voltammetric experiments were carried out with a BAS (Bioanalytical Systems, West Lafayette, Indiana, USA): CV-50W electrochemical workstation, which was controlled by external computer. Conventional three-electrode system was employed with platinum wire as the counter electrode and silver-silver chloride (Ag/AgCl, 3 M NaCl) as the reference electrode. The working electrode used was 3 mm diameter basal plane pyrolytic graphite electrode (BPPGE).

Chemicals and materials

Multi-walled carbon nanotube (MWCNT) was obtained from Dynamic Enterprises Ltd., with 98% purity, with 20-50 nm x 5-20 μm diameter x length, metal salts from Sigma Aldrich. Vitamin C tablet brand named Redoxon and fruit juices by Marigold Peel Fresh were obtained from leading pharmacy in Kuala Lumpur. All other chemicals used were of analytical reagent grade and used without further purification.

Fabrication of modified CNT electrode and determination of ascorbic acid in tablet and juices

The surface of bare basal plane pyrolytic graphite electrode (BPPGE) was cleaned using 0.05 μm alumina powder, followed by ultrasonic cleaning for about 2-3 minutes. The BPPG electrode was dried with lint-free tissue paper.

The mechanical attachment method was employed to modify the working electrode surface by attaching the MWCNT with using carbon paste as binder [13]. The working electrode surface with a well-coated layer of MWCNT was then tested with various voltammetric characterizations. Unless otherwise mentioned, the voltammetric experiments were carried out at temperature (25 ± 2) °C using 0.1 M potassium dihydrogen phosphate (KH_2PO_4) as a supporting electrolyte. Solutions were degassed with nitrogen for about ten minutes prior to recording the voltammogram. Doping of MWCNT/BPPGE with Li^+ was carried out by continuous potential cycling in the supporting electrolyte. The practical application of MWCNT/Li^+ carbon paste modified electrode was demonstrated with two different samples. The first contained a known manufacturer specified amount of Vitamin C tablet (1000 mg of Vitamin C per tablet). Recovery experiments on the tablet were determined. The second was fruit juices (mango juice and orange juice) with unknown amount of ascorbic acid. Standard addition method was used to determine the concentration of ascorbic acid in juices. Conditions of 0.1 M KH_2PO_4 at pH 4.2 were employed for all the samples.

Results and Discussion

Fabrication of modified multi-walled carbon nanotube (MWCNT) electrode

Mechanical attachment of MWCNT on BPPGE surface using nafion and carbon paste as binders gave oxidative current enhancement in comparison with the bare BPPGE. Figure 1 shows the voltammograms of MWCNT/BPPGE using two types of binders; nafion and carbon paste. It was noted that the use of nafion binder gave enhancement factor of 2.0 whilst using carbon paste binder showed 1.7. However, carbon paste was chosen to bind with MWCNT due to its low capacitative charging current which would possibly facilitate lower detection limit of ascorbic acid as compared to nafion. Nafion was known as a cation-exchange polymer which possessed impermeable effect and may cause high capacitative charging current due to its good ion exchange property [4]. Therefore, nafion binder was not used in the following report.

The peak potential of ascorbic acid oxidative current shifted approximately 180 mV to less positive potential which indicated the electrocatalytic effect of the modified MWCNT/BPPG electrode. Metal ion such as Li^+ was introduced to the MWCNT/BPPG modified electrode to enhance the electrocatalysis effect in determination of ascorbic acid [14]. The deposition of Li^+ to MWCNT/BPPGE caused peak potential of ascorbic acid oxidative current to decrease 70 mV which indicated less potential was required for the oxidative peak to appear, and signified the activation energy for this reaction to be slightly lower. The sensitivity of MWCNT/BPPG doped Li^+ electrode increased as shown by the enhancement factor of 2.3 in comparison to bare BPPG electrode (Figure 2).

Theoretically, the hexagonal lattice of CNT has radius of 1.2 Å, while Li^+ has 0.72 Å in radius [5]. Thus, it was suggested that the Li^+ not only capable to dope outside the cylinder graphene layer and the edge of the graphene layer, but also into the inner core space of MWCNT [5]. MWCNT with multiple graphene layers increased the capacity for Li^+ intercalation and featured the stronger metallic characteristic with high electronic density [10].

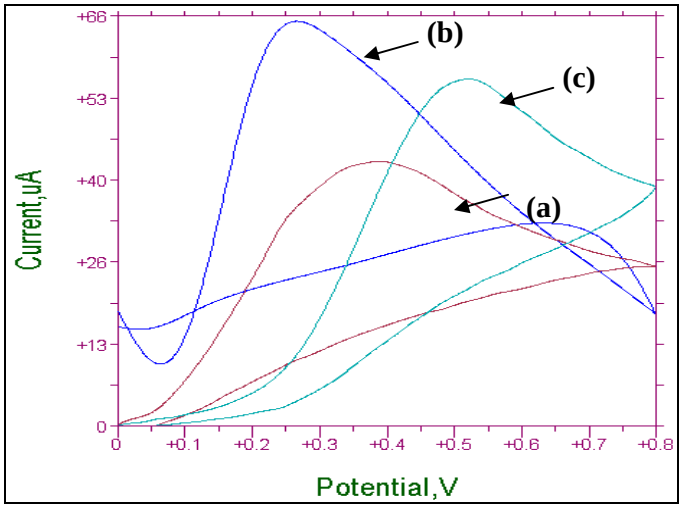

Fig 1: Voltammograms obtained at a 3mm diameter BPPG electrode for oxidation of 2.0 mM ascorbic acid in a 0.1M KH_2PO_4 supporting electrolyte at pH 4.2 with a potential scanning in a positive direction at a scan rate of 100mV/s at 25°C. (a) oxidative current of ascorbic acid using bare BPPG electrode, (b) oxidative current of ascorbic acid using Nafion-MWCNT/BPPG modified electrode, (c) oxidative current of ascorbic acid using 30% (w/w) carbon paste : 70% (w/w) MWCNT/BPPG modified electrode.

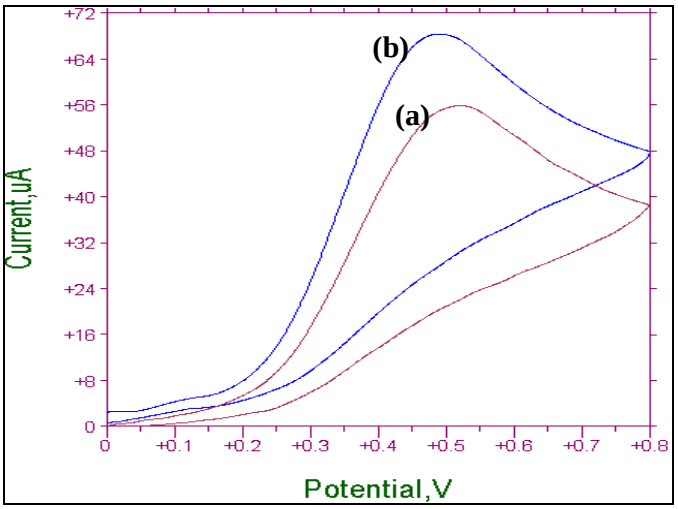

Fig 2: Voltammograms comparison between modified electrodes before and after Li ion doped at a 3mm diameter BPPG electrode for oxidation of 2.0 mM ascorbic acid in a 0.1M KH_2PO_4 supporting electrolyte at pH 4.2 with a potential scanning in a positive direction at a scan rate of 100mV/s at 25°C, oxidative current of ascorbic acid using 30% (w/w) carbon paste: 70% (w/w) MWCNT modified BPPG electrode; (a) before Li^+ doped and (b) after Li^+ doped.

Ascorbic acid concentration

The concentration of standard ascorbic acid was determined using MWCNT/ Li^+/BPPG modified electrode as shown in Figure 3. Optimization of pH and temperature were performed to obtain best sensitivity towards ascorbic acid. pH of 4.2 at 25°C were found to be optimum condition to detect ascorbic acid (voltammogram was not shown in this report). Linear response was achieved over the concentration range from 0 to 5 mM, which showed excellent correlation of 0.999 R^2 value. The sensitivity of the modified electrode obtained from the linear equation slope was 34.5 mA M^{-1}. Besides, the detection limit of ascorbic acid using MWCNT/Li^+/BPPG modified electrode was found to be 50 μM.

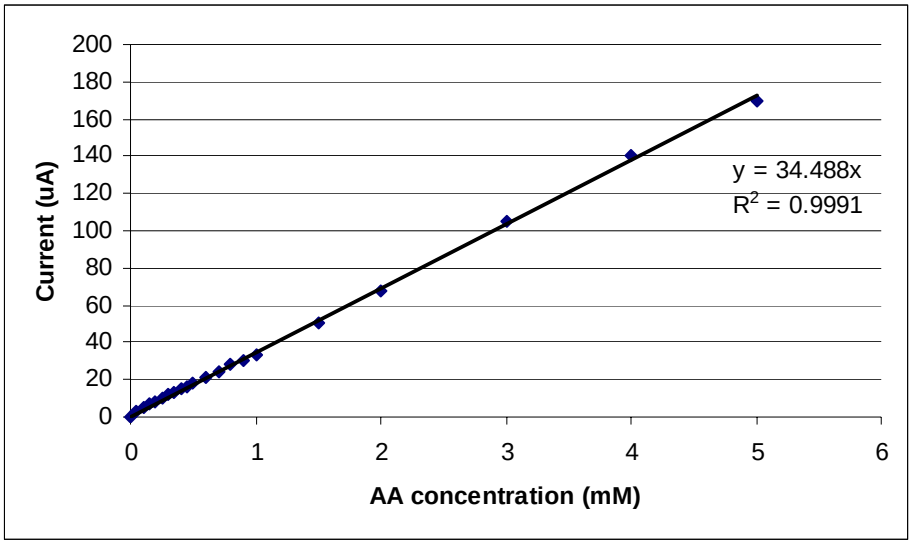

Fig 3: Concentration of ascorbic acid using 30% (w/w) carbon paste: 70% (w/w) MWCNT/Li^+/BPPG modified electrode with potential scanning in a positive direction from 0 to 800 mV at pH 4.2, a scan rate of 100mV/s and at 25°C.

Recovery concentration of ascorbic acid in tablet and fruit juices

The validity of MWCNT/Li^+/BPPG modified electrode for the determination of ascorbic acid was assessed by direct calibration using calibrated graph shown in Figure 3. Redoxon vitamin C tablet of 1000 mg ascorbic acid was diluted to prepare 1.0 mM and 0.5 mM solution. Five replications were carried out as shown in Table 1. Good recovery rates of 97 ± 3.08% (for 1.0 mM ascorbic acid) and 102.6 ± 2.33% (for 0.5 mM ascorbic acid) were obtained.

Recovery concentration of ascorbic acid compared to the ascorbic acid content stated by the manufacturer indicated the high reproducibility and reliability of the modified electrode.

The feasibility of MWCNT/Li+/BPPG modified electrode was further assessed using fruit juices. This section, standard addition method was used to determine the unknown concentration of ascorbic acid in these juices. Table 2 shows the ascorbic acid concentration found in mango juice was 0.84 ± 3.55% mM and for orange juice was 0.5 ± 4% mM.

The accuracy of MWCNT/Li^+/BPPG modified electrode was further determined to support the findings. 0.5 mM of standard ascorbic acid solution was added to perform standard addition method. Every 0.5 mM ascorbic acid added, current increment of 17.3 (±0.05) μA was resulted, which corresponded with the sensitivity equation obtained from the calibration graph from section 3.2.

Table 1: Recovery concentration of Redoxon vitamin C tablet using freshly prepared modified electrode and diluted solution for both 1.0 and 0.5 mM ascorbic acid concentration, determined using carbon paste-MWCNT/Li^+/BPPG electrode under optimized conditions in 0.1M KH_2PO_4 supporting electrolyte.

Real life sample	Recovered concentration (mM)		Recovery rate (%)		Mean recovery (%)		RSD (%)	
	1.0	*0.5*	*1.0*	*0.5*	*1.0*	*0.5*	*1.0*	*0.5*
1	1.01	0.51	101	102				
2	1.0	0.5	100	100				
3	0.96	0.48	96	104	97	102.6	3.08	2.33
4	0.95	0.49	95	101				
5	0.94	0.47	94	106				

Table 2: Recovery concentration of ascorbic acid in Marigold Peel Fresh- Tropical Mango juice and freshly squeezed orange juice, determined using carbon paste-MWCNT/Li^+/BPPG modified electrode under optimized conditions in 0.1M KH_2PO_4 supporting electrolyte.

Real life sample	Unknown concentration (mM)	Mean (mM)	RSD (%)
Marigold Peel Fresh- Tropical Mango juice			
1	0.80		
2	0.81		
3	0.85	0.84	3.55
4	0.80		
5	0.87		
Freshly squeezed orange juice			
1	0.48		
2	0.48		
3	0.53	0.5	4.0
4	0.52		
5	0.50		

Conclusion

A MWCNT modified BPPG electrode has been successfully fabricated using carbon paste as the binder using mechanically attached method. MWCNT modified electrode enhanced the ascorbic acid oxidative current. Further doping with Li^+ onto the MWCNT showed the ability to further enhance the oxidative current of ascorbic acid. Under optimum condition, carbon paste-MWCNT/Li^+/BPPG modified electrode exhibits the best enhancement factor of 2.3 with sensitivity of 34.5 mA M^{-1}. The ascorbic acid peak current is linear from concentration range of 50µM to 5.0mM with excellent R^2 value of 0.999. The detection limit of this modified electrode was found to be 50µM (with two sigma values). Determination of ascorbic acid in tablet, commercial mango juice and freshly prepared orange juice were found to give excellent recovery data and highly reproducible data.

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