



Layer-by-layer assembly of poly(*p*-aminobenzene sulfonic acid)/quaternary amine functionalized carbon nanotube/*p*-aminobenzene sulfonic acid composite film on glassy carbon electrode for the determination of ascorbic acid

Lingling Xi ^{a,*}, Danwei Zhang ^a, Fengli Wang ^a, Zhongping Huang ^b, Ting Ni ^a

^a Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China

^b College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

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ABSTRACT

An excellent *p*-aminobenzene sulfonic acid (*p*-ABSA) monolayer film was fabricated on glassy carbon electrode (GCE) by situ electrochemical oxidation. Then a novel kind of homogeneous quaternary amine-functionalized carbon nanotube (q-CNT) film was adsorbed onto *p*-ABSA/GCE through electrostatic interaction to produce q-CNT/*p*-ABSA/GCE. Finally an electropolymerized poly(*p*-ABSA) film was formed on q-CNT/*p*-ABSA/GCE. The electrostatic layer-by-layer assembly process of the modified electrode poly(*p*-ABSA)/q-CNT/*p*-ABSA/GCE was well characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The modified electrode exhibited excellent electrocatalytic activity toward ascorbic acid (AA) oxidation at a low potential of +0.02 V in pH 7.0 PBS. Amperometric experiments were performed for the sensitive determination of AA. Linear responses in two concentration ranges of 0.002–0.06 and 0.1–3.20 mM were obtained with the detection limit of 0.5 μM (S/N = 3). The electrostatic interaction of the positively charged q-CNTs with the monolayer *p*-ABSA film and the poly(*p*-ABSA) film promoted to form a stable poly(*p*-ABSA)/q-CNT/*p*-ABSA composite film on GCE. So the poly(*p*-ABSA)/q-CNT/*p*-ABSA/GCE showed good reproducibility and stability, and was successfully employed for the determination of AA in vitamin C tablet and human urine real samples with satisfactory results.

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1. Introduction

Ascorbic acid (AA, vitamin C), which is mainly present in fruits and vegetables, is a soluble vitamin and an essential component of human nutrition [1–2]. It is commonly used for the prevention of scurvy and the treatment of common cold, mental illness, infertility and cancer. Also it is widely used as an antioxidant agent in food and beverages to stabilize color and aroma of products [3–4]. So the determination of ascorbic acid has attracted great attention in clinical, pharmaceutical and food industries. Reported methods for AA determination include enzymatic method [5], spectrophotometry [1], fluorometry [6], chromatography [7] and chemiluminescence [8]. Among the various methods, electrochemical technique is a preferred method for its simplicity, high efficiency and sensitivity [9]. However, the major problem of electrochemical detection of AA is the high over-potential and the irreversible contamination caused by accumulation of its reaction products on traditional bare electrode surface, which results in poor detection reproducibility. In order to resolve these problems, many strategies

have been used to modify the traditional bare electrodes with self-assembled monolayer [10], nanomaterials [11–12] and polymer film [13–14].

Since their discovery, carbon nanotubes (CNTs) have been extensively studied due to their unique properties such as high surface area, strong adsorption ability, good biocompatibility and fast electron transfer ability [15–16]. Chemically modified electrodes (CMEs) based on CNTs can offer superior performances in terms of promoting electron-transfer rate, improving reversibility of electrochemical reaction and enhancing electrochemical response signal. So CNTs have been widely used as modifying material in the preparation of electrochemical sensors for the detection of many biomolecules [17] such as glucose [18], hydrogen peroxide [19–20], amino acids [21–22] and some neurotransmitters [23–24]. However, because of the surface hydrophobicity and strong Van der Waals interaction, the synthesized CNTs are often bundled together. The poor dispersion of CNTs in many solvents especially in water hinders the potential application of CNTs in electrochemical sensor field, because some characteristics of CNT sensors such as electrocatalytic activity, detection reproducibility and sensitivity are relevant to the dispersion homogeneity of CNTs on surface of electrodes. In recent years, great efforts have been made to disperse CNTs

* Corresponding author.
E-mail address: xll98731@zju.edu.cn (L. Xi).

into aqueous solutions by noncovalent method, which is using surfactants [25], polymers [26], ionic liquids [27], etc. as dispersing agents. Additionally, covalent functionalization has been found to be another efficient way to render CNTs soluble in aqueous solutions by attaching some functional groups such as COOH [28], F [29], OH [30], NH₂ [31–32] and quaternary amine [33] to CNTs. Correspondingly, various modified electrodes could be fabricated with these functionalized CNTs or their composites [34]. But up to now, most of the hitherto-developed strategies for preparing CNT electrochemical sensors were based on the carboxyl-functionalized CNTs (CNT-COOH), and most of the preparation methods are mainly focus on simply incorporating CNT-COOH into polymer matrices such as nafion [35] and chitosan [36], or depositing metals on CNT-COOH film [37–39]. Recently, many attempts have also been performed to fabricate electrochemical sensors by combining carboxyl-functionalized CNTs and organic conducting polymers, since these polymers have good conductivity, stability, homogeneity and film-forming ability [40–42]. Additionally, the layer-by-layer self-assembly modified gold electrode based on the poly(*m*-aminobenzene sulfonic acid) functionalized single-walled CNTs has also been prepared [43]. From an electrochemical point of view, the preparation of homogeneous CNT dispersion aqueous solutions is a challenging task, and the methods for the preparation of CNT modified electrodes are still needed.

In the present work, based on a novel kind of quaternary amine functionalized CNTs (q-CNTs), a new CNT composite film electrochemical sensor was prepared for the determination of AA. Firstly a stable *p*-aminobenzene sulfonic acid (*p*-ABSA) monolayer film was fabricated on glassy carbon electrode (GCE) by situ electrochemical oxidation. Then a novel kind of quaternary amine functionalized carbon nanotubes, which was used to fabricate electrochemical sensor for the first time, was electrostatically assembled to the *p*-ABSA monolayer film modified glassy carbon electrode (*p*-ABSA/GCE). A stable and homogeneous q-CNT film was formed on *p*-ABSA/GCE owing to the admirable dispersibility of q-CNTs in water and the electrostatic interaction between the positively charged q-CNTs and the negatively charged *p*-ABSA/GCE surface. Further *p*-ABSA was electropolymerized on q-CNT/*p*-ABSA/GCE to obtain the poly(*p*-ABSA)/q-CNT/*p*-ABSA composite film modified GCE. Combining the characteristics of poly(*p*-ABSA) and CNTs, the new composite film modified electrode poly(*p*-ABSA)/q-CNT/*p*-ABSA/GCE showed excellent electrocatalytic activity toward the oxidation of AA, and was used successfully for AA determination in real samples with good stability and reproducibility.

2. Experimental

2.1. Chemicals

p-ABSA was purchased from the Shanghai Aladdin Chemical Reagent Company (Shanghai, China). Ascorbic acid was obtained from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). CNTs (≥95%) were supplied by the Institute of Material

Physics and Microstructure of Zhejiang University, China. Vitamin C tablets (10 mg per tablet) were purchased from Shanghai Harvest Pharmaceutical Company. After the vitamin C tablets were treated by mechanical grinding, the powder sample was dissolved in 40 mL 0.1 M pH 7.0 PBS. After filtration, the AA sample solution was transferred into a 100 mL measuring flask and diluted with 0.1 M pH 7.0 PBS. All other chemicals used in our experiment were of analytical grade. Freshly prepared solutions of AA were used in all experiments. The phosphate buffer solutions (PBS) at various pH values were prepared using Na₂HPO₄ and NaH₂PO₄, then adjusted by 0.1 M HCl or NaOH. Double distilled water employed in all experiments was obtained from a Millipore-Milli-Q system.

Quaternized CNTs were prepared following the reported method [44]: Raw multi-walled CNTs were suspended in 200 mL mixture of concentrated H₂SO₄/HNO₃ (3:1, v/v). This mixture was sonicated at 40 °C for 30 min in an ultrasonic bath, then stirred and heated to reflux at 70 °C for 3 h under dry nitrogen. After diluting with cold deionized water, the obtained mixture was filtered with a 0.22 μm cellulose acetate membrane and washed repeatedly until the filtrate was neutral. The final black solid was dried under vacuum for 24 h at 60 °C to obtain acidified CNTs (CNT-COOH). 20 mL mixture of methylamine (2.8%, v/v) and 1,4-butanediol diglycidyl ether (7.2%, v/v) was added to 500 mg CNT-COOH, then the suspension was heated to 65 °C for 1 h, later filtered and rinsed with deionized water. Thus, CNTs with positively charged quaternary amine groups (q-CNTs) were obtained. 5 mg of the q-CNTs was dispersed in 5 mL deionized water and sonicated for 30 min, obtaining homogeneous black q-CNT suspension (1 mg mL⁻¹).

2.2. Apparatus

The electrochemical measurements such as cyclic voltammetry (CV) and amperometry were performed on the CHI 660 electrochemical work station (CH Instrument Co., Austin, TX, USA) with a conventional three electrode system, which comprises a bare 3 mm (Φ) or modified glassy carbon electrode as working electrode, a Pt wire as counter electrode and a KCl saturated Ag/AgCl as reference electrode. A Hitachi Scientific Instruments (London, UK) model S-3000H scanning electron microscope at an accelerating voltage of 15 kV was used for surface image measurements. Electrochemical impedance spectroscopy (EIS) was performed on the VMP2 potentiostat system (PARC Co., USA) in a frequency range from 0.1 to 10⁴ Hz with a potential amplitude of 5 mV. All pH measurements were performed on a Suntex model SP-701 pH meter (Jiangsu, China).

2.3. Preparation of poly(*p*-ABSA)/q-CNT/*p*-ABSA/GC modified electrode

Prior to surface modification, GCE was firstly polished with alumina slurry (0.05 μm) on a soft polishing cloth (Buehler). Then it was cleaned by sonication in ethanol and water successively. Finally the GCE was washed with deionized water and dried in nitrogen atmosphere.

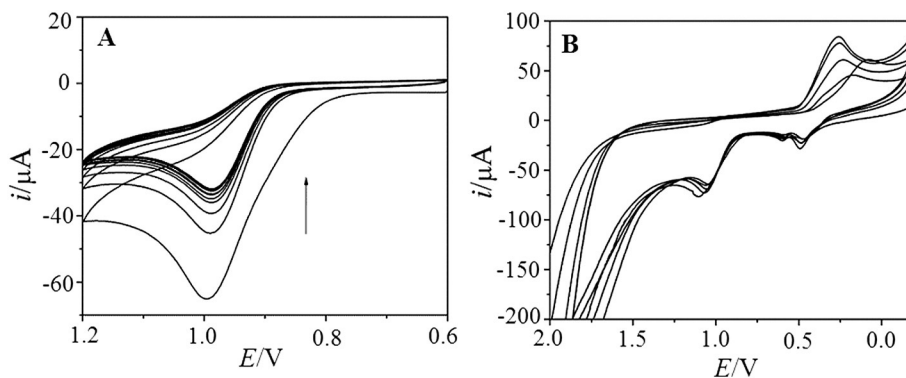


Fig. 1. (A) CVs of GCE in 0.1 mol L⁻¹ KCl solution containing 0.002 mol L⁻¹ *p*-ABSA. (B) CVs of *p*-ABSA electropolymerization on the surface of q-CNT/*p*-ABSA/GCE.

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