



# One-step electrodeposition of poly (3,4-ethylenedioxythiophene) on carboxylated multi-wall carbon nanotubes and its application in ascorbic acid sensing



Xin Du <sup>a,1</sup>, Zhenguo Zhang <sup>b,1</sup>, Cong Zhang <sup>b</sup>, Yanyan Zhang <sup>b</sup>, Qiang Chen <sup>b,\*</sup>

<sup>a</sup> Shandong Normal University, Institute of Biomedical Sciences, College of Life Science, Jinan, China

<sup>b</sup> Nankai University, College of Life Science, China

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## ABSTRACT

The poly (3,4-ethylenedioxythiophene) (PEDOT) nanomaterial was synthesised by a facile electrodeposition on a glassy carbon electrode (GCE) modified by carboxylated multi-wall carbon nanotubes (CA-MWCNTs). The nanocomposite was characterized using transmission electron microscopy, scanning electron microscope, energy-dispersive X-ray spectroscopy and fourier transform infrared spectroscopy. Moreover, a highly sensitive ascorbic acid (AA) sensor was developed based on the nanocomposite. Owing to the combination of the advantages of CA-MWCNTs and PEDOT, the modified electrode exhibited excellent electro-catalytic activity for AA detection which was investigated in detail by cyclic voltammetry and chronoamperometry. The cationic PEDOT film on CA-MWCNTs could interact with anionic AA in neutral PBS at a low potential and distinguish the oxidation peaks of common interfering species. The effects of electrodeposition time and pH value on the current responses of the modified electrode towards AA were optimized to obtain the maximal sensitivity. The prepared AA sensor demonstrated high sensitivity ( $1699.36 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ), wide linear range detection (100  $\mu\text{M}$  to 20 mM), low detection limit (4.2  $\mu\text{M}$ ), rapid response time (less than 4 s), good selectivity and long-term stability. This work presented a facile approach for future research in AA amperometric sensors.

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## 1. Introduction

Ascorbic acid ( $\text{H}_2\text{A}$ , AA), which known as vitamin C, is present in many vegetables and fruits as an essential nutrient for humans [1]. It plays an important role in biological metabolism, such as scavenging free radicals, healing of injuries, promoting the cell development and helping the synthesis of tendons, bones collagen and blood vessels [2–4]. Therefore, a rapid and sensitive method for the determination of AA is of great interest to scientists. Many conventional methods have been developed, including liquid chromatography [5], enzymatic method [6], spectrophotometric method [7], UV-detection [8]. Recently, owing to its sensitivity, low cost and simplicity, the electrochemical method for the detection of AA has received increasing attention [9–11]. However, the oxidation of AA on the bare electrode appears in a high potential. Moreover, in the process of detection of AA, the oxidation peaks of co-existing interferences, such as dopamine (DA) and uric acid (UA), will overlap the peak of AA which leads to low sensitivity and poor reproducibility of the modified electrode. So, preparing appropriate nanomaterial to modify the electrode is vital and challenging.

Carbon nanotubes (CNTs), composed of  $\text{sp}^2$ -hybridized carbon atoms, were discovered by Iijima in 1991 [12] which have large surface area, excellent electrical conductivity and good stability [13,14]. Due to those remarkable properties, CNTs have been used in many different fields including electrochemical detection [15–17]. Many methods were devoted to modify the surface of CNTs in order to enhance their performance. Among the methods, the method of introducing the carboxyl groups onto the surface of CNTs was widely used because the carboxyl groups could not only improve the solubility of CNTs but also offer more active sites for the following modification [18–20].

Many conducting polymer materials, including polypyrrole (PPy) [21] and polyaniline (PANI) [22], have been used to modify the electrode for various applications. Among them, poly (3,4-ethylenedioxythiophene) (PEDOT) has received much attention owing to it has high charge injection limit, good conductivity and excellent stability [23–25]. Furthermore, uniform PEDOT film can be synthesised by facile electrodeposition.

In our work, we prepared the CA-MWCNTs-PEDOT modified electrode by electrodeposition and used it in AA electrochemical determination. Combining advantageous features of CA-MWCNTs and PEDOT, the modified electrode has superb electro-catalytic activity to AA. In previous works using PEDOT to detect DA or UA, AA usually was considered as interfering substance. To our knowledge, it is the first time to prepare

\* Corresponding author.

E-mail address: [qiangchen@nankai.edu.cn](mailto:qiangchen@nankai.edu.cn) (Q. Chen).

<sup>1</sup> These authors contributed equally to this work.

a sensor focused on AA detection based on CA-MWCNTs-PEDOT modified electrode. In this paper, we mainly studied the electrochemical performance of AA sensor and the effect of experimental parameters to the AA sensor in detailed. Moreover, the prepared AA sensor displayed larger linear detection range, higher sensitivity and lower detection limit than most papers previously reported.

## 2. Experimental

### 2.1. Chemicals and reagents

MWCNTs (20  $\mu\text{m}$  average length, 20–30 nm diameter and >95% purity) were purchased from Alpha Nano Technology Co., Ltd. (China). Concentrated hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were obtained from Tianjin Damao Chemical Reagent Co., Ltd. (China). 3,4-ethylenedioxythiophene was supplied by Shanghai Macklin Biochemical Co., Ltd. AA, DA and UA were purchased from Sigma–Aldrich (USA). Phosphate buffer solution (PBS, 0.1 M, pH = 7.0) was prepared by  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ . All aqueous solutions were prepared using doubly distilled water.

### 2.2. Measurements

Electrochemical measurements were performed by a conventional 283 Potentiostat-Galvanostat electrochemical workstation (EG & G PARC with M270 software) at room temperature. An electrochemical cell connected with a standard three-electrode system was employed for all electrochemical measurements. An Ag/AgCl (saturated KCl) electrode was used as the reference electrode. A 3-mm-diameter modified GCE and a platinum wire (1 mm diameter) were used as the working electrode and the counter electrode, respectively. In steady-state amperometric experiments, the potential was set at 50 mV in stirring PBS. Images of transmission electron microscopy (TEM) and fourier transform infrared spectroscopy (FTIR) were collected on Tecnai G2 F20 equipped with energy-dispersive X-ray spectroscopy (EDX, Philips Holland) and Bruker TENSOR 37 instruments, respectively.

### 2.3. Fabrication of carboxylated MWCNTs and the modified electrode

MWCNTs were dispersed in the mixed solution of HCl and  $\text{HNO}_3$  with the volume ratio was 3:1 and then ultrasonically shook for 4 h. After that, the dark homogeneous solution was centrifugated and cleaned by doubly distilled water until the pH became neutral. The solution was dried and the CA-MWCNTs were obtained. The CA-MWCNTs were dispersed in doubly distilled water again ( $1 \text{ mg mL}^{-1}$ ) for the following application.

Bare GCE was first carefully polished with alumina powders (0.3 and 0.05  $\mu\text{m}$ ) to remove the oxide layers in the surface of GCE. After polishing, GCE was ultrasonically cleaned using double distilled water and ethanol for 20 min which could remove the physically adsorbed substance. Then, the electrode was dried immediately by nitrogen gas. CA-MWCNTs films were prepared through dropping 10  $\mu\text{L}$  of CA-MWCNTs suspension onto the surface of GCE. The CA-MWCNTs-PEDOT modified GCE was obtained by electrodeposition in a 20 mL solution (20 mM EDOT, 0.1 M HCl) and then, a constant potential at 900 mV was applied for 240 s.

## 3. Results and discussion

### 3.1. Characterization of the materials

Fig. 1 displays the TEM photos of CA-MWCNTs and CA-MWCNTs-PEDOT under different magnification. As we can see from Fig. 1a and b, CA-MWCNTs were core-shell fibrous structure and the average diameter was about 10–20 nm. After the electrodeposition of PEDOT, the average diameter of CA-MWCNTs-PEDOT was much wider (about 20–30 nm) than that of CA-MWCNT as shown in Fig. 1c and d. Furthermore, we can see clearly CA-MWCNTs had been wrapped by the irregular material which was the PEDOT after electrodeposition. In the process of electrodeposition, the CA-MWCNTs worked as crystal nucleus and then EDOT could adhere to the surface of CA-MWCNTs to form PEDOT under the continuous potential. The EDX analysis was also done to confirm the formation of PEDOT as shown in Fig. 2a. We can see that the peak of C was the highest which attributed to CA-MWCNTs and PEDOT. Furthermore, the peak of S was the typical peak of PEDOT and the peak of Cu was due to the Cu substrate.

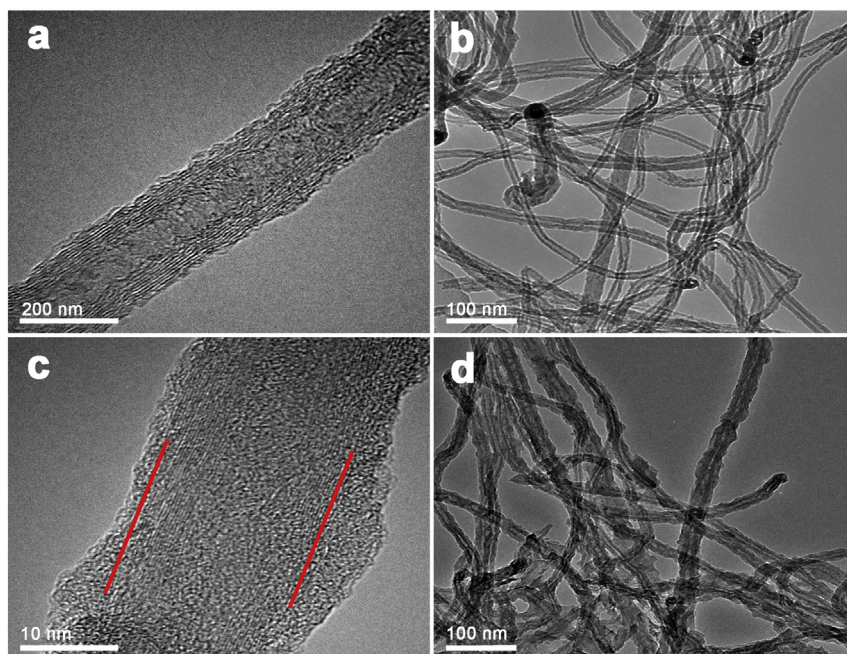


Fig. 1. Typical TEM images of CA-MWCNTs (a, b) and CA-MWCNTs-PEDOT (b, c) under different magnification.

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