



Immobilization of phosphotungstic acid on multiwalled carbon nanotubes with cetyltrimethyl ammonium bromide as the molecular linker for enhanced oxidation of hydroxylamine



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ABSTRACT

Hydroxylamine, widely used as reducing agent in chemical and pharmaceutical industries, has been recognized as a mutagen. Modest levels of hydroxylamine are toxic to humans, animals and even plants. The development of a sensitive method for the detection of HA is very important. In this work, phosphotungstic acid (PTA)/cetyltrimethyl ammonium bromide (CTAB)/multiwalled carbon nanotube (MWCNT) nanocomposite with sandwich structure was prepared by means of the immobilization of PTA on carboxylated MWCNT. CTAB acts as the molecular bridge to immobilize PTA molecules on the surface of MWCNT. The surface of the MWCNT is negatively charged owing to the abundant distribution of carboxyl groups. PTA is a strong acid, which ionizes completely in aqueous solutions by losing protons. CTAB is a quaternary ammonium surfactant, which is positively charged in aqueous solutions. The formation of PTA/CTAB/MWCNT nanocomposite is due to the electrostatic attraction between CTAB, PTA and MWCNT. PTA/CTAB/MWCNT shows excellent electrocatalytic ability towards the oxidation of hydroxylamine (HA) by significantly enhancing its oxidation current. On PTA/CTAB/MWCNT modified glassy carbon electrode (GCE) (PTA/CTAB/MWCNT/GCE), the oxidation current of HA is linear with its concentration in the range of 0.3–100 μM with a detection limit of 0.06 μM .

1. Introduction

HA is an intermediate in biological nitrification. During the biological nitrification, NH_3 was first oxidized to HA under the mediation of ammonia monooxygenase [1]. HA was further oxidized to nitrite by hydroxylamine oxidoreductase [2]. As a reducing agent, HA has been widely used in pharmaceutical industry and chemical industry for the synthesis of intermediates and final products. It is well-known that HA is a mutagen which causes highly specific mutations [3–6]. Because HA is toxic to organisms including humans, animals and plants, the development of a sensitive sensor for the detection of HA is cardinal significance.

Although the applications of HPLC [7] and spectrophotometry [8] in the detection of HA have been reported, the most commonly used methods are electrochemical methods due to their simplicity, feasibility, high sensitivity and low detection limit. Recently, many electrocatalysts have been developed for the determination of HA. The nanomaterials of metals or metal chalcogenides have been widely applied in the fabrication of HA sensors. HA sensors based on sol-gel film/gold NPs [9], ruthenium oxide [10], gold NPs/polypyrrole nanowires

[11], TiO_2 NPs [12], Pt/polypyrrole nanocomposite [13], gold/polypyrrole nanocomposite [14], Pt NPs/choline film [15], ferric oxide/copper hexacyanoferrate(II) nanocomposite [16], zirconia NPs [17], silver NPs [18], ZnO NPs [19] have been reported by many researchers. As a novel one-dimensional carbon based nanomaterials, carbon nanotubes (CNTs) [20–28] and CNTs functionalized with compounds or metal cations such as rutin [29], baicalin [30], chlorogenic acid [31] and Co(II) [32] exhibits excellent electrocatalytic ability towards the oxidation of HA. Many CNT-based composite materials such as CNT/ZnO [33,34], CNT/conducting polymer coated palladium NPs [35], fullerene/CNT/ionic liquid [36] and gold NPs/CNT [37], prussian blue/MWCNTs [38] have been developed for the determination of HA. The graphene is a sheet of carbon atoms, which is only one-atom thick. The carbon atoms of graphene are arranged in honeycomb-shape. As a novel two-dimensional carbon nanomaterial, graphene has been extensively explored for its sensor applications. Many novel sensing interfaces have been constructed taking advantage of the excellent catalytic abilities of graphene oxide (GO) [39], reduced graphene oxide (rGO) and their composites such as poly(3,4-ethylenedioxythiophene)/GO nanocomposite [40] and rGO/ Fe_3O_4 nanoparticles [41].

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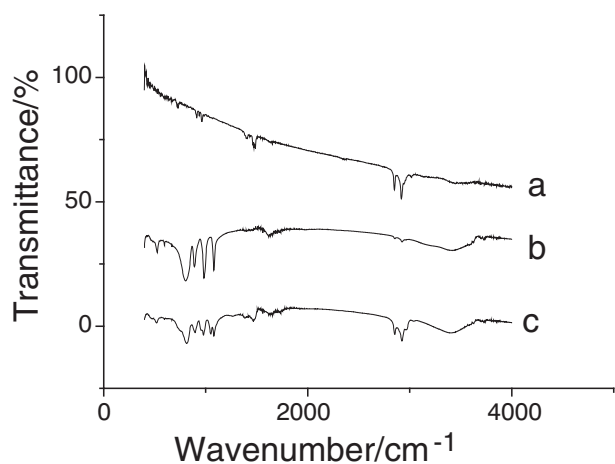


Fig. 1. FT-IR spectrum of pure CTAB (curve a), pure PTA (curve b) and PTA/CTAB/MWCNT (curve c).

A polyoxometalate (POM) is a closed 3-dimensional framework composed of three or more transition metal oxyanions. These transition metal oxyanions are linked together by shared oxygen atoms. As the simplest POM, PTA on various supports such as montmorillonite [42], fullerene [43], MWCNT [44,45], GO [46], rGO [47–52] and LaFeO₃ nanoparticles [53] have been proven efficient catalysts for many electrochemical processes.

Carbon-based nanomaterials such as MWCNT have been widely employed in the fabrication of electrochemical sensors [54–56]. MWCNT is an efficient catalyst for the oxidation of HA [20–28]. It has also been reported that MWCNT is an ideal support for PTA due to its large specific surface area, extraordinary mechanical, and electrical properties [44,57,58]. In this work, a novel method to load PTA on MWCNT support was developed. PTA/CTAB/MWCNT, a sandwich structured nanocomposite, was prepared via the electrostatic attraction between PTA, CTAB and MWCNT. PTA and MWCNT have been widely used as catalysts for many electrochemical processes. By combining the catalytic effect of both PTA and MWCNT, PTA/CTAB/MWCNT exhibits excellent catalytic ability towards the oxidation of HA. As a novel HA sensor, CTAB/PTA/MWCNT/GCE shows low limit of detection, high sensitivity and wide detection range.

2. Experimental

2.1. Chemicals and reagents

PTA was purchased from Tianjin Dingshengxin Chemical Industry Co., LTD. CTAB was purchased from Tianjin Hedong Hongyan Reagent Factory. Hydroxylammonium chloride was purchased from Sinopharm Chemical Reagent Co., LTD. Sodium tetraborate was purchased from Tianjin Zhiyuan Chemical Reagent Co., LTD. All chemical reagents were of analytical grade and used as received. MWCNT was purchased from Chengdu Organic Chemicals Co., LTD. (Chinese Academy of Sciences). Twice-distilled water was used throughout the experiment. 0.1 M

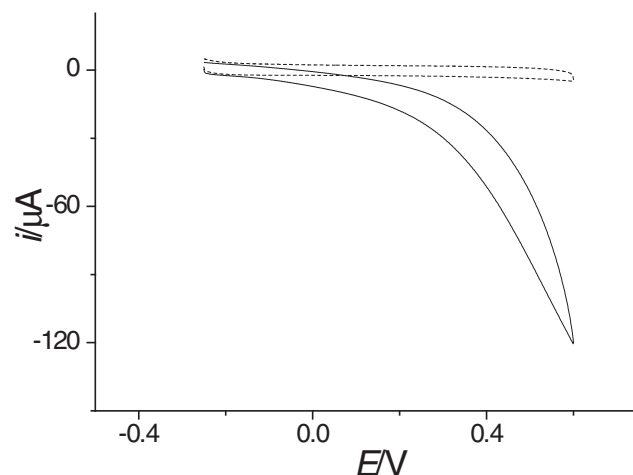


Fig. 3. The cyclic voltammograms of PTA/CTAB/MWCNT/GCE in 0.1 M pH 10.1 borate buffer in the absence (dashed line) and presence (solid line) of 5 mM hydroxylamine.

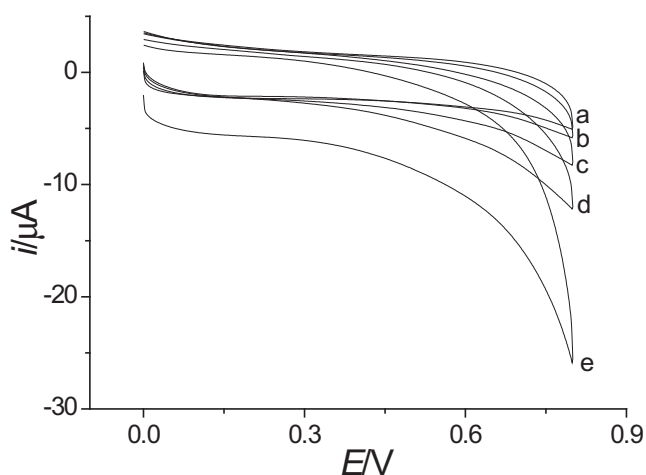


Fig. 4. The cyclic voltammograms of PTA/CTAB/MWCNT/GCE in 0.1 M pH 6.0 phosphate buffer (curve a), 0.1 M pH 7.0 phosphate buffer (curve b), 0.1 M pH 8.0 phosphate buffer (curve c), 0.1 M pH 9.3 borate buffer (curve d) and 0.1 M pH 10.1 borate buffer (curve e) containing 2.5×10^{-4} M HA.

pH 10.1 borate buffer solution was prepared by mixing 50 mL 0.05 M sodium tetraborate, 46 mL 0.2 M sodium hydroxide and 4 mL water.

2.2. Carboxylation treatment of MWCNT

According to a method reported in the literature, carboxylated MWCNT was prepared by acid treatment of pristine MWCNT using a mixture of 98% sulfuric acid and 66–68% nitric acid [59,60]. For mixed acid, the volume ratio of sulfuric acid to nitric acid is 3:1. The acid treatment procedures are as follows: 150 mg pristine MWCNT was added into a 500 mL round bottom flask containing 150 mL mixed acid.

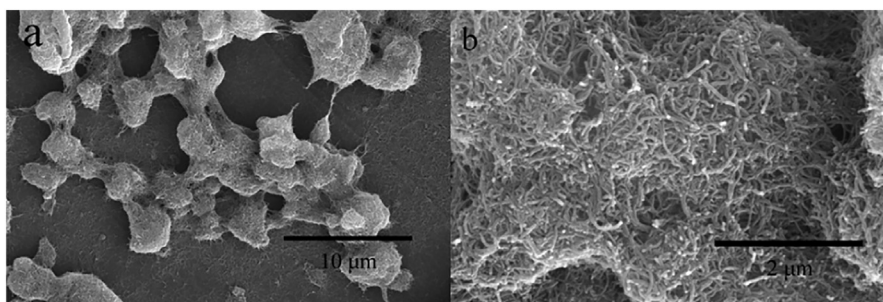


Fig. 2. (a) FE-SEM image of PTA/CTAB/MWCNT/GCE; (b) FE-SEM image of PTA/CTAB/MWCNT/GCE with higher magnification.

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