Electrocatalytical oxidation and sensitive determination of acetaminophen on glassy carbon electrode modified with graphene–chitosan composite

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ABSTRACT

The electrochemical behaviors of acetaminophen (ACOP) on a graphene–chitosan (GR–CS) nanocomposite modified glassy carbon electrode (GCE) were investigated by cyclic voltammetry (CV), chronocoulometry (CC) and differential pulse voltammetry (DPV). Electrochemical characterization showed that the GR–CS nanocomposite had excellent electrocatalytic activity and surface area effect. As compared with bare GCE, the redox signal of ACOP on GR–CS/GCE was greatly enhanced. The values of electron transfer rate constant (k_s), diffusion coefficient (D) and the surface adsorption amount (Γ^*) of ACOP on GR–CS/GCE were determined to be 0.25 s^{-1}, 3.61×10^{-5} cm^2 s^{-1} and 1.09×10^{-9} mol cm^{-2}, respectively. Additionally, a 2e$^-$/2H$^+$ electrochemical reaction mechanism of ACOP was deduced based on the acidity experiment. Under the optimized conditions, the ACOP could be quantified in the range from 1.0×10^{-6} to 1.0×10^{-4} M with a low detection limit of 3.0×10^{-7} M based on 3S/N. The interference and recovery experiments further showed that the proposed method is acceptable for the determination of ACOP in real pharmaceutical preparations.

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1. Introduction

As an acetyl aniline drug, acetaminophen (ACOP) has antipyretic and analgesic functions, which is suitable for the remedy of fever, headache, joint ache, rheumatism pain and various neuralgia, migraine and dysmenorrhea [1]. However, the overdoses of ACOP are harmful to the human body including the digestive, urinary, blood and respiratory systems [2,3]. Therefore, it is very valuable to establish new methods to accurately monitor and detect the content of this drug. Up to now, many methods have been developed for the analysis of ACOP, which includes spectrophotometry [4], titrimetry [5], fluorescence spectroscopy [6], chromatography [7] and electrochemical methods [8–11]. Compared with the other technologies, the electrochemical method shows the advantages of simplicity, low cost and high sensitivity [8–11]. However, the poor electrochemical response of ACOP on the common electrodes often limits its application in practical analysis. In order to overcome this disadvantage, the chemically modified electrodes are often designed and applied. For example, Boopathi et al. [8] have reported the electrocatalysis of ACOP on a conducting copper ion-containing terthiophene carboxylic acid polymer (Cu-poly-TTCA) modified electrode. The results showed that the electrochemical response of ACOP on the modified electrode was greatly promoted due to Cu(II) species. The similar promotions of ACOP electrochemistry were also observed on the electrode modified with nano-sized materials like polyaniline-multi-walled carbon

nanotubes (PANI-MWCNTs) composite [9], Pd nanoparticles incorporated poly(3-methylthiophene) composite [10], Co(OH)$_2$ [11], etc.

Graphene (GR), a one-atom-thick sp^2-bonded carbon sheet has attracted extensive attention of scientific and technological researchers since it was first discovered in 2004 by Novoselov and Geim [12]. Due to its high surface area, excellent conductivity and mechanical strength, the material displays its promising potential for application in the fields of microelectrical device, filed-effect transistor and ultrasensitive sensor [13,14]. The application of graphene as a novel electrochemical sensing material attracts considerable attention, and it has been reported that many biological molecules such as dopamine [15], cytochrome c [16], glucose oxidase [17] and DNA [18], and the inorganic metal ions of Pb^{2+} [19] and Cd^{2+} [20] all showed enhanced electrochemical response on the graphene modified electrodes.

Chitosan (CS) is one of the most widely used biopolymers for sensor applications due to its nontoxic nature, excellent film-forming ability, good mechanical strength, high permeability and cost-effectiveness characteristics [21,22]. However, in its normal state, CS film has very low electrical conductivity and high degree of swelling, which often results in a low sensitivity for the determination of the analytes [21,23]. In order to circumvent these problems, doping with some conductive nanoparticles like carbon nanotubes [24,25], gold nanoparticles [26] and SiO$_2$ [27] is often adopted, by which the analytical performance of the modified electrodes can be dramatically improved because of the synergistic effect from the chitosan and the nanoparticles.

In this work, a nanocomposite of graphene–chitosan (GR–CS) was fabricated and applied to modify glassy carbon electrode (GCE). The obtained modified electrode (GR–CS/GCE) was electrochemically

characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using $[Fe(CN)_6]^{3-/4-}$ as redox probe. The results showed that the modified electrode showed excellent conductivity and surface area effect, and meanwhile the modified film of GR–CS on GCE revealed good stability due to the remarkable film-forming property of CS. The electrochemical behaviors of ACOP were carefully studied on GR–CS/GCE, which showed that GR–CS/GCE exhibited excellent electrocatalytic activity toward the redox of ACOP. Under the optimized conditions, the sensor shows high sensitivity, good selectivity and low detection limit for the determination of ACOP.

2. Experimental

2.1. Chemicals and reagents

ACOP was purchased from Sinopharm Chemical Reagent Co., Ltd (China); Chitosan was provided by Sanland Chemical Co., Ltd (USA); The graphene sheets were prepared in our lab according to the modified Hummer's method [28]; N, N-dimethylformamide (DMF) was purchased from Xilong Chemical Co., Ltd (China); Britton–Robinson (B–R) buffer solutions of required pH were prepared by adding 0.4 M acetic acid and 0.4 M boric acid into a solution of 0.4 M phosphoric acid. The pH was adjusted with the appropriate amount of 0.2 M NaOH. All the other chemicals were of analytical reagent grades and were purchased commercially. Doubly distilled water (DDW) was used throughout this experiment.

2.2. Apparatus

The scanning electron microscopic (SEM) morphologies of the chemically reduced GR nanosheets and its composite with chitosan (GR–CS) were recorded on a LEO 1530 scanning electron microscope (Germany). A CHI 650 C electrochemical analyzer (Shanghai CH Instrument, China) was used for all the electrochemical measurements. A conventional three-electrode system consisted of a bare or GR–CS modified GCE (GR–CS/GCE) as working electrode, a platinum wire as auxiliary electrode and an Ag/AgCl/3 M KCl as reference electrode. The nominal surface area of the bare GCE was calculated to be 0.031 cm^2 according to the disk diameter of 2 mm. All the peak current densities were determined based on the nominal surface area of the bare GCE.

2.3. Preparation of the GR–CS/GCE

Prior to use, the bare GCE was polished to a mirror-like surface with 0.05 μm, 0.3 μm and 0.5 μm α-Al$_2$O$_3$, respectively, and rinsed ultrasonically with DDW, absolute ethanol and DDW, in turn. A chitosan solution (0.3%) was prepared by dissolving about 0.003 g of chitosan in 1 mL acetic acid, and then 1 mg GR dissolved in 1 mL DMF was added and ultrasonically dispersed for 1 h to obtain a well-dispersed black suspension. Then 10 μL of the prepared GR–CS solution was cast on the pretreated GCE and allowed to dry at room temperature. Before use, the modified electrode was carefully rinsed with DDW to remove the loosely attached GR–CS, and thus a GR–CS/GCE was obtained. For comparison, the CS modified GCE (CS/GCE) or GR modified GCE (GR/GCE) was also prepared by the same way except replacing the GR–CS nanocomposite solution with the single-component CS or GR solution.

3. Results and discussion

3.1. Morphological and electrochemical characterization of GR–CS

Fig. 1A shows the SEM images of pristine graphene nanosheets and their composite with chitosan, GR–CS. For the pristine graphene, a typical wrinkle and thin-flake structure can be clearly observed
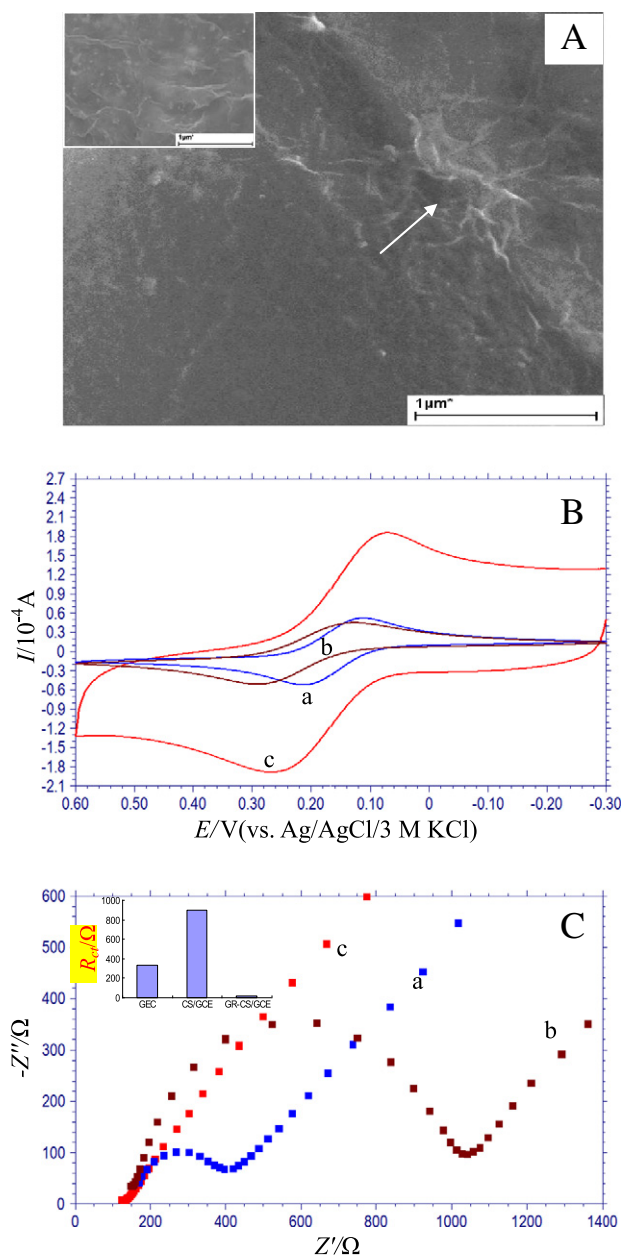

Fig. 1. (A) SEM images of pristine GR (inset) and GR–CS nanocomposite (main panel). CV (B) and EIS (C) images of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ with 0.1 M KCl at bare GCE (a), CS/GCE (b) and GR–CS/GCE (c).

(inset), suggesting the successful preparation of GR nanosheets in this work. When the GR material was dispersed in the CS gel solution by ultrasonication, a stable and dark suspension was formed, and the SEM image shows that nanocomposite film (main panel) becomes more uniform and flat in comparison with pristine graphene nanosheets due to the good film-forming property of CS. Additionally, the specific wrinkle structure of GR can also be seen on the local position of the GR–CS film (see the arrow), indicating that the GR nanosheets are not aggregated in the nanocomposite and the high surface area of GR is maintained.

The electrochemistry of GR–CS was characterized by CV in a mixture of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl. As shown in Fig. 1B, a pair of well-defined redox peaks is observed on the bare GCE with the peak-to-peak separation (ΔE_p) of 0.10 V. The oxidative peak current density (j_{pa}) and the reduction peak current density (j_{pc}) were determined to be −1.90 mA cm^{-2} and 1.87 mA cm^{-2} (curve a), respectively. When the same solution was detected with CS/GCE, j_{pa} and j_{pc} were decreased to −1.64 mA cm^{-2} and 1.45 mA cm^{-2} (curve