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Sensitive voltammetric determination of chloramphenicol by using single-wall carbon nanotube–gold nanoparticle–ionic liquid composite film modified glassy carbon electrodes

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Abstract

A novel composite film modified glassy carbon electrode has been fabricated and characterized by scanning electron microscope (SEM) and voltammetry. The composite film comprises of single-wall carbon nanotube (SWNT), gold nanoparticle (GNP) and ionic liquid (i.e. 1-octyl-3-methylimidazolium hexafluorophosphate), thus has the characteristics of them. The resulting electrode shows good stability, high accumulation efficiency and strong promotion to electron transfer. On it, chloramphenicol can produce a sensitive cathodic peak at −0.66 V (versus SCE) in pH 7.0 phosphate buffer solutions. Parameters influencing the voltammetric response of chloramphenicol are optimized, which include the composition of the film and the operation conditions. Under the optimized conditions, the peak current is linear to chloramphenicol concentration in the range of 1.0×10^{-8}–6.0×10^{-6} M, and the detection limit is estimated to be 5.0×10^{-9} M after an accumulation for 150 s on open circuit. The electrode is applied to the determination of chloramphenicol in milk samples, and the recoveries for the standards added are 97.0% and 100.3%. In addition, the electrochemical reaction of chloramphenicol and the effect of single-wall carbon nanotube, gold nanoparticle and ionic liquid are discussed.

Keywords: Chloramphenicol; Ionic liquid; Gold nanoparticles; Single-wall carbon nanotubes; Voltammetry

1. Introduction

Chloramphenicol (CAP) is a broad-spectrum antibiotic, exhibiting activity against a group of microorganisms such as Gram-positive and Gram-negative bacteria [1]. It was isolated from *Streptomyces venezuelae* in 1947 and is widely used in the treatment of serious infections including typhoid fever and other forms of salmonellosis. Its chemical structure is as shown in Scheme 1. Owing to its low cost and notable efficiency, it is also widely applied in animal production. However, recent research reveals that CAP has two toxic side effects on the haemopoietic system: one is the frequently occurring mile anaemia with reticulocytopenia, sometimes accompanied by leucopenia and thrombocytopenia; another is the aplastic anaemia [2,3]. Hence, its clinical application is controlled now [4]. Further more, it has been banned for use in foodstuffs of animal origin in the European Union and United States [5,6]. In order to monitor the level of CAP, sensitive qualitative and quantitative methods are required. Several techniques have been developed for the determination of CAP in different biological materials. They are photoinduced chemiluminescence [7], HPLC with UV, single MS and tandem MS detection [8], capillary zone electrophoresis with amperometric detection [9], and surface plasmon resonance biosensor [10]. Although these methods have advantages of sensitivity and accuracy, their high cost and complicated operation limit their extensive application. Electrochemical methods are simple, speedy, sensitive and inexpensive, thus they are attempted for CAP determination. Agui et al. [11] developed a voltammetry for chloramphenicol with electrochemically activated carbon fiber microelectrodes; the linear range was 1.0×10^{-7}–1.0×10^{-5} M and the detection limit was 4.7×10^{-8} M. Chen et al. [12] developed a novel one-off amperometric sensor incorporating a three- electrode configuration for direct detection of CAP, and the detection limit was 4.2×10^{-7} M. To our knowledge, hitherto ionic liquid-based

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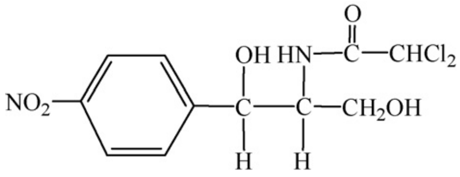

Scheme 1. Chemical structure of CAP.

modified electrodes have not been reported for the determination of CAP.

Room temperature ionic liquids (RTILs), initially reported in 1914, are novel solvent comprising of organic cations and various anions [13]. They exhibit many unique advantages such as good chemical and thermal stability, negligible vapor pressure, good ionic conductivity, wide electrochemical windows, and are widely applied in organic synthesis, electrochemistry, lubrication, and solar cell etc. [14]. Recently, some reports on the application of RTILs in electrochemical analysis can be noted. Maleki et al. [15] reported a high-performance carbon composite electrode using ionic liquid as binder. This electrode combined the advantages of edge plane pyrolytic graphite electrode and the low cost of carbon paste electrode together with the robustness of metallic electrode. It could decrease markedly the over voltage of some biomolecules such as NADH, dopamine, and ascorbic acid. Lopez et al. [16] developed an amperometric glucose biosensor based on polymerized ionic liquid microparticles; the biosensor can be employed in aqueous and non-aqueous media for glucose determination of human serum samples. Increasing attention has been paid on the modified electrodes with ionic liquids and nanomaterial composite in hope for combining their unique advantages. Hong et al. [17] studied the direct electrochemical and electrocatalytic properties of heme proteins immobilized on ionic liquid–clay–nanoparticle composite films. Yan et al. [18] reported the voltammetric determination of uric acid with a glassy carbon electrode coated by paste of multi-walled carbon nanotubes and ionic liquid, and found that the electrode exhibited higher sensitivity and selectivity. Li et al. [19] presented a glucose oxidase–ionic liquid–gold nanoparticles composite coated glassy carbon electrode for glucose sensing, which showed good stability and sensitivity. Obviously, RTILs are promising material for constructing sensors.

In the present paper, a novel composite film coated electrode is fabricated. It consists of gold nanoparticle (GNP), single-wall carbon nanotube (SWNT) and room temperature ionic liquids. The resulting electrode gives good performance in sensing chloramphenicol.

2. Experimental

2.1. Reagents

The single-walled carbon nanotubes used (diameter <10 nm, length 1–2 μm, purity $\geq$ 95%) came from Shenzhen Nanotech Port Co. Ltd. (Shenzhen, China). The ionic liquids 1-octyl-3-methylimidazolium hexafluorophosphate ($OMIMPF_6$) and 1-butyl-3-methylimidazolium hexafluophosphate ($BMIMPF_6$, purity 98%) were purchased from Acros Organics and used as received. 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) and 1-butyl-3- methylimidazolium bromine (BMIMBr) were synthesized according to [20]. *N*,*N*-Dimethylformamide (DMF) was obtained from Sinopharm Group Chemical Reagent Co. (Shanghai, China). Chloramphenicol was the product of Beijing Chemical Plant (Beijing, China), and its stock solution (0.010 M) was prepared with anhydrous ethanol. The working solutions were prepared by diluting the stock solution with phosphate buffer solution and water. All other chemicals used were of analytical reagent grade. The water used was redistilled.

2.2. Apparatus

Cyclic voltammetric (CV) and linear sweep voltammetric (LSV) experiments were performed with a CHI 660B electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional three-electrode system was adopted. The working electrode was a modified glassy carbon electrode (GCE, 3 mm in diameter), the auxiliary and reference electrodes were platinum wire and saturated calomel electrode (SCE), respectively. The scanning electron microscope (SEM) image was obtained using a HITACHI X-650 SEM (Hitachi, Japan).

2.3. Treatment of SWNT and preparation of modified electrode

The SWNT was purified by refluxing in HNO_3–H_2SO_4 (v/v, 1:1) mixture for 2 h at 55 °C and then for 3 h at 80 °C, washed with redistilled water and dried under vacuum. The GNP–SWNT hybrid was prepared according to [21]. In brief, 20 mL 5 mM $HAuCl_4$ and 70 mL water was transferred into a flask, stirred and heated until boiling. Then 10 mL 0.75% $NaBH_4$ aqueous solution (40 mM) was rapidly added to the boiling solution. The solution color changed rapidly from clear to burgundy red, indicating nucleation and GNP formation. After refluxing for 15 min, the solution was cooled to room temperature, filtered with a membrane filter (diameter 0.22 μm, Millipore Inc.), and the gold colloid was collected and stored at 4 °C. SWNT (final concentration 1.0 mg mL^{-1}) was added to the gold colloid and the resulting suspension was ultrasonicated for 2 h. After that, $OMIMPF_6$ (final concentration (v/v) 2.0%) was dispersed in the GNP–SWNT hybrid with aid of ultrasonication. Thus, a uniform $OMIMPF_6$–GNP–SWNT hybrid suspension was obtained. $OMIMPF_6$–DMF–SWNT suspension was prepared through similar procedure.

Before modification, the GCE was polished to mirror smooth with 0.05 μm Al_2O_3 slurry, and then rinsed with water, ultrasonicated in water and ethanol bath for several minutes. Five microliters of the $OMIMPF_6$–GNP–SWNT suspension was dropped on the GCE and let it dry at room temperature for about 1 h, thus a uniform film coated electrode ($OMIMPF_6$–GNP–SWNT/GCE) was obtained. The SWNT/GCE, $OMIMPF_6$/GCE, GNP–SWNT/GCE, and $OMIMPF_6$–SWNT/GCE were fabricated through similar method.