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Voltammetry of nanomolar leveled environmental hazards on the polymer/CNT coated electrodes

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ABSTRACT

4-tert-Octylphenol is toxic even at nanomolar levels but widely used as an intermediate substance. The detection methods for 4-tert-octylphenol at nanomolar levels are however missing in literature. We investigate in this paper the voltammetric response and electrochemical detection of nanomolar leveled 4-tert-octylphenol in water. A polymer/CNT film coated electrode was applied. The electrode was prepared by firstly coating a polished and clean glassy carbon electrode with a CNT film and then covering the CNT film coated electrode with a conducting film from L-lysine. On this electrode, 4-tert-octylphenol is electrochemically oxidized at 0.60 V vs. SCE. This irreversible oxidation process is controlled by adsorption. The anodic peak current is proportional to the concentration of 4-tert-octlyphenol in the range of 6.5–20 nM. The detection limit is 0.5 nM. This electrode has been applied for the detection of 4-tert-octylphenol in lake and river water. The relative standard derivation (RSD) of these measurements is less than 4.3%.

1. Introduction

Alkyl phenols are important industrial chemicals and have been widely used in that they are high production-volume substances to synthesize phenolic resins and ethoxylates to produce surfactants [1–3]. For example, 4-tert-octylphenol (4-(1,1,3,3-tetramethylbutyl) phenol), one of the most important substances and intermediates, had a consumption of approximately 23,000 tons in 2001 inside European Union. The demand is expected to grow further. 4-tert-Octylphenol has a water solubility of 19 mg L^{-1} (90 μM) at 22 °C, while it is not readily biodegradable and is hard to be removed by hydrolysis or photolysis [2]. It therefore exists in fresh and marine waters and sediments, waste water treated plants, soil, air, and even in predatory wildlifes [1–3].

On the other side, 4-tert-octylphenol is considered toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment [2]. It is known that the presence of 4-tert-octylphenol in water will lead to estrogenic activity [4–8]. The predicted no-effect concentration of 4-tert-octylphenol in fresh water on aquatic organisms is 0.12 μg L^{-1} (0.6 nM). It can also adversely affect the endocrine systems of certain organisms, in some cases (e.g. aquatic snails) even at concentrations lower than 0.12 μg L^{-1} (0.6 nM) [2]. Unfortunately, the concentration of 4-tert-octylphenol in surface water is generally about 1 μg L^{-1} (4.8 nM) [2]. Some higher concentrations are found in trade and sewage effluents. The highest value is 10.8 mg L^{-1} (48.4 μM), reported from an untreated trade effluent from a 4-tert-octylphenol manufacturing plant [2]. However, these predicted concentrations are likely to be overestimated in some cases because of limitations of present methods (poor sensitivity and high detection limits) to detect 4-tert-octylphenol, especially at nanomolar concentration levels. Currently the methods are mainly based on separation techniques such as liquid chromatography [9,10] and mass spectrometry [11,12].

We are thus interesting in developing a novel method for the detection of 4-tert-octylphenol at nanomolar concentration levels. Electrochemical detection is our choice because it has advantages of high sensitivity, low detection limit, fast response, low cost, simple instrumentation, facile miniaturization, and low power requirement. Moreover, some phenols have been successfully detected using electrochemical methods [13,14]. As shown previously, carbon nanotube (CNT) is one of the best sensing materials for electrochemical and biochemical applications [15–21]. We therefore modify the glassy carbon electrode with a carbon nanotube (CNT) film and further cover the CNT film coated electrode with a conducting polymer film. The modified electrodes prepared in this way combine super properties of CNTs (e.g. larger surface area, high catalytic activity, etc.) with advanced features of conducting polymers (e.g. porous structures, accumulation ability), resulting in a longer life-time and a better sensing performance than those obtained only on the CNT film coated electrodes. The

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small-sized L-lysine molecule was chosen as the monomer for the electrochemical polymerization because it has multi-functional and chargeable groups ($-NH_2$ and COOH), which are perfect to accumulate analytes from solutions. Better sensitivity and a lower detection limit for the detection of 4-tert-octylphenol is thus expected. In this paper we report the fabrication and characterization of this polymer/CNT modified electrode. More attentions have been paid to voltammetric response of 4-tert-octylphenol on the modified electrode and the detection of nanomolar leveled 4-tert-octylphenol with this electrode (including the optimization of detection conditions and the analysis of real samples).

2. Experimental

4-tert-Octylphenol and L-lysine were purchased from Shanghai Zhenxiang Institute of Chemical Reagents (Shanghai, China). Other reagents are analytical grade and were used as received. Multi-walled carbon nanotubes (CNTs) with approximately 95% purity were obtained from Shenzhen Nanotech Port (Shenzhen, China).

The purification and functionalization of CNTs were conducted in a way as reported [22,20,23]. Briefly, 500 mg of CNTs were oxidized at 400 °C for 30 min to remove amorphous carbon particles. The oxidized CNTs were dispersed in 60 ml of 6.0 M HCl for 4 h in an ultrasonic bath to eliminate metal oxide catalysts. Then CNTs were washed with water until the solution pH was close to 7.0. Finally, they were air dried at room temperature. In order to generate carboxylic acid functionalized surface, the purified CNTs were further oxidized in a mixture of concentrated sulfuric and nitric acid (v/v = 3:1) with the aid of ultrasonication for 6 h at 50–60 °C. The resultant solution was filtered through a poly(tetra fluoroethylene) membrane with a 200 nm pore size. The solid powders were washed thoroughly with water to remove any residual acid and then dried at 60 °C for 2 h. The functionalized CNTs (1.0 mg) were then dispersed in 10 mM L-lysine in pH 7.6 phosphate buffer. This suspension (1.0 mg mL^{-1}) was used to form a CNT film on the glassy carbon electrode.

Electrochemical measurements were carried out on a CHI760B electrochemical station (Shanghai Chenhua, China) with a conventional three-electrode system at room temperature. A saturated calomel electrode (SCE) acted as the reference electrode and a platinum foil constituted as the counter electrode. Either a bare or a modified glassy carbon electrode was used as the working electrode.

The modified electrodes were prepared in two steps. The first step was the formation of a CNT film on a glassy carbon electrode by direct casting. Prior to experiments, a glassy carbon electrode (3.0 mm in diameter) was firstly polished with emery paper and alumina slurry, cleaned in sonication bath for 10 min and thoroughly rinsed with distilled water. Then one drop (8 μL) of CNT suspension was cast on the clean glassy carbon electrode. The electrode was then air dried at room temperature. The second step was the formation of a poly(L-lysine) film on the CNT film coated electrode by electrochemical polymerization. The electrochemical polymerization was conducted in a 10 mM L-lysine solution in a potentiodynamic mode. The potential range was from −1.0 to 2.5 V and the scan rate was 100 mV s^{-1}. The scanning cycles during the electrochemical polymerization were used to control the thickness of the polymer film. After washing adequately with water, the modified electrode was fabricated.

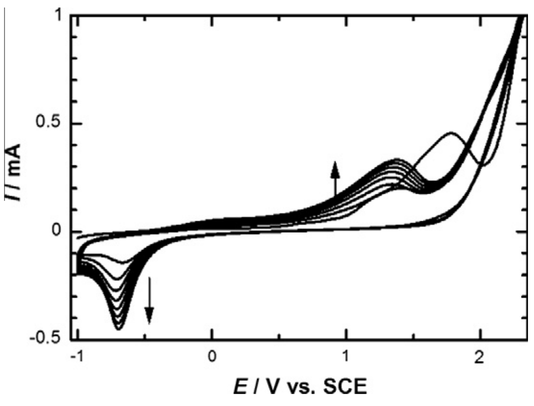

Fig. 1. Cyclic voltammograms for the polymerization of L-lysine on the CNT film coated glassy carbon electrode. The potential range is from −1.0 to 2.5 V and the scan rate is 100 mV s^{-1}. The polymerization solution is 10 mM L-lysine in 10 mM pH 7.6 phosphate buffer.

3. Results and discussion

3.1. Formation and characterization of the modified electrode

The modified electrode was fabricated in two steps as demonstrated in experimental section. The first step is the modification of a polished and clean glassy carbon electrode with a CNT film. The CNT film coated electrodes have been widely characterized and applied as electrochemical and biochemical sensors for different analytes [15–21]. The disadvantage of this electrode is its poor stability due to the stripping of CNTs from the electrode surface. As the second step of the fabrication of the modified electrode, we therefore cover the CNT film coated electrode with a conducting film. Fig. 1 shows cyclic voltammograms for electrochemical polymerization of L-lysine on the CNT film coated electrode. In the first cycle, an anodic wave at 1.8 V is seen together with a cathodic wave at −0.7 V. In the second and following cycles, the anodic peak shifts to 1.4 V while the peak position of the cathodic wave does not change. An increase in cycle number results in the enhancement of both cathodic and anodic peak currents. After 8 cycles, a shiny and light green color was found on the electrode surface, indicating the fabrication of a polymer film on the CNT film coated electrode.

The modified electrode was characterized regarding its conductivity, surface area and electrochemical activity. The redox couples of $[Fe(CN)_6]^{3-/4-}$ were adopted as probe molecules. Fig. 2 shows cyclic voltammograms of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ on a bare glassy carbon electrode (a), a CNT film coated electrode (b), a polymer film coated electrode (c), and a polymer/CNT film coated electrode (d). Well-defined oxidation and reduction peaks are observed on all electrodes without significant difference in separation of peak-to-peak potentials, indicating good conductivities of all electrodes. On four electrodes, both cathodic and anodic peak currents are proportional to square roots of scan rates, indicating diffusion-controlled electrode processes. The highest peak current is obtained on the polymer/CNT film coated electrode, suggesting the biggest electroactive surface area. According to the Randles–Sevcik equation [24], the electroactive surface area for the polymer/CNT film coated electrode was calculated to be 0.18 cm^2, which is close to that (0.15 cm^2) of a polymer film coated electrode but larger than that (0.09 cm^2) for a CNT film coated electrode and 0.08 cm^2 for a bare glassy carbon electrode. The increase in electroactive surface area might result from porous structure of the conducting polymer film.

These electrodes were further checked with electrochemical impedance spectroscopy, which provides the information about kinetics of electrode reactions on electrodes. For example, the semicircular portion at higher frequencies in a Nyquist plot corresponds to the electron transfer limited process and its diameter is equal to the resistance for electron transfer process, R_{et}. This value indicates