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Carbon nanotube doped poly(3,4-ethylenedioxythiophene) for the electrocatalytic oxidation and detection of hydroquinone

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ABSTRACT

A sensitive amperometric sensor for the selective detection of hydroquinone in cosmetics was developed based on the excellent electrocatalytic property of carbon nanotube (CNT) doped poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer toward the oxidation of hydroquinone. The oxidation potential of hydroquinone on the PEDOT/CNT modified carbon paste electrode was much lower than that on the bare electrode, and the charge transfer rate constant for the oxidation of hydroquinone was significantly increased from 0.45 to 1.84 s^{-1} after the modification with PEDOT/CNT. Under optimal conditions, the differential pulse voltammetry current of the sensor was linear with hydroquinone concentration across a 1.1–125 μM range and associated with a detection limit of 0.3 μM. Significantly, the detection limit is comparable or better than many current electrochemical hydroquinone assays, and the sensor is potentially much cheaper and easier for fabrication. The sensor was capable not only of comfortably quantifying hydroquinone in the presence of common interferences but also doing this in real cosmetics samples with satisfying accuracy.

1. Introduction

Hydroquinone (HQ) is widely used in many fields such as reducing agent, antioxidant, polymerization inhibitor, black white film developer, anthraquinone dye, azo dyestuff and other chemical intermediate [1,2]. HQ sometimes was overdosed in the bleaching creams for its certain role of fading sunspots and lightening pigmented areas of the skin. Because of the hazards of long-term treatments, the European Committee and China have banned the use of HQ in cosmetics and formulations, and it is available only through prescription by physicians and dermatologists. However, HQ has been being added to some cosmetics illegally by certain manufacturers to increase the bleaching efficacy of the cosmetics. Several analytical methods such as high performance liquid chromatography [3], spectrophotometry [4,5] and electroanalysis [6] have been used for the determination of HQ in samples of cosmetic creams. Among these, electrochemical assays promise most in terms of low cost, flexibility and sensitivity [7–9].

Carbon nanotubes (CNTs) have attracted enormous interest in the past years due to their superior electrical properties, high specific surface area, and chemical stability, which make them attractive for sensing applications [10,11]. As another kind of widely used material, conducting polymers, including polypyrrole, polythiophene, and their derivatives have also been used extensively in the development of sensors because of their interesting electrical, optical and electrocatalytic properties. In recent years, considerable interest has been shown in the synthesis of conducting polymer/CNTs composites that exhibit special properties of both individual components in a synergistic manner [12]. The addition of CNTs to the polymer can significantly increase the mechanical property of the polymer, and at the same time enhance the electrical property by facilitating the charge-transfer process between these two components [13]. Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been considered as the most promising one because its ordered and well-defined chemical structure offers outstanding conductivity and stability [14,15]. It has been reported that the electrical properties of neural electrodes can be greatly improved by surface coating with PEDOT conducting polymer [16,17].

In our previous work [18], we have reported the preparation of highly stable CNT doped PEDOT for neural stimulation. Here, CNT doped PEDOT was chemically synthesized and used for the modification of carbon paste electrode (CPE). The electrochemical oxidization of HQ at the PEDOT/CNT modified CPE was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and a sensitive and selective HQ sensor was further developed based on the excellent catalytic property of PEDOT/CNT toward the oxidization of HQ. Due to the lowered oxidization

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potential and enhanced oxidative current, the prepared sensor was free from common interferences and could be successfully used for the practical determination of HQ in cosmetics.

2. Experimental

2.1. Materials and apparatus

Multi-walled CNTs with the length of 10–30 mm and diameter of 20–30 nm were purchased from Cheap Tubes Inc. (Brattleboro, USA). 3,4-Ethyl-enedioxythiophene (EDOT) and HQ were purchased from Aladdin Chemistry Co. Ltd. A stock solution of 0.5 mM HQ was prepared in 0.2 M Britton–Robinson (B–R) buffer (pH 3.0). Working HQ solutions were prepared using the required quantity from the stock solution, and adjusted with NaOH (Carlo Erba) to obtain the desired pH. All reagents used are of analytic grade, and Milli-Q (Waters) water was used in all processes.

The electrochemical experiment was carried out with the CHI660D electrochemical work station (CH Instruments), using a conventional three-electrode system with the platinum wire as the counter electrode, a saturated calomel electrode as the reference electrode and the CPE or the PEDOT/CNT modified CPE as the working electrode. All the electrochemical tests were carried out at room temperature (20 ± 1 °C). The surface morphologies and microstructures of the modified electrodes were examined using a field emission scanning electron microscopy (SEM) instrument (JSM-7500 F, Hitachi High- Technology Co., Japan), with an acceleration voltage of 5.0 kV.

2.2. Preparation of PEDOT/CNT

According to our previous work [18], the CNTs were pretreated by dispersing 200 mg CNTs in 100 mL 1:3 concentrated HNO_3 and H_2SO_4 solution with sonication for 2 h. The suspension was then kept at room temperature overnight. After the acid treatment, the CNTs were washed with water and separated using ultracentrifugation repeatedly until the pH of the washing solution was neutral. Finally, the CNTs were collected and dried at 60 °C.

The synthesis of CNT doped PEDOT composite is referred to the literature [19]. Briefly, 10 mg of acid-treated CNTs was dispersed in 5 mL of deionized water, and the suspension was heated to 70 °C and maintained under magnetic stirring for 20 min. Following the dropwise addition of 10.5 mg 3,4-ethylenedioxythiophene to the above suspension, 0.68 mg of $FeCl_3 \cdot 6H_2O$ was immediately added, and the suspension was vigorously stirred again for 2 h at 70 °C. After cooling, the resulting material was recovered and subjected to a series of centrifugation (15 min at 3000 rpm) and washing cycles. The obtained precipitate was dispersed in 10 mL water and stored for further use.

2.3. Preparation of the PEDOT/CNT modified CPE

The CPE was prepared according to previous work [20]. 3.0 g graphite powder and 0.75 g solid paraffin were heated at 80 °C for 2 h, and ground intensively to obtain a uniform carbon paste. The hot carbon paste was tightly packed into the cave of a glass tube (diameter 4 mm) and a copper wire was introduced for electrical contact. The carbon paste was cooled down to room temperature under pressure.

The CPE was smoothed on a weighing paper, and subsequently 10 μL of the prepared PEDOT/CNT suspension was drop-coated on the CPE and dried under the ambient temperature (20 ± 1 °C). The obtained electrode was denoted as PEDOT/CNT/CPE.

For comparison, 10 μL of CNTs suspension without PEDOT was used to prepare CNT modified CPE (CNT/CPE).

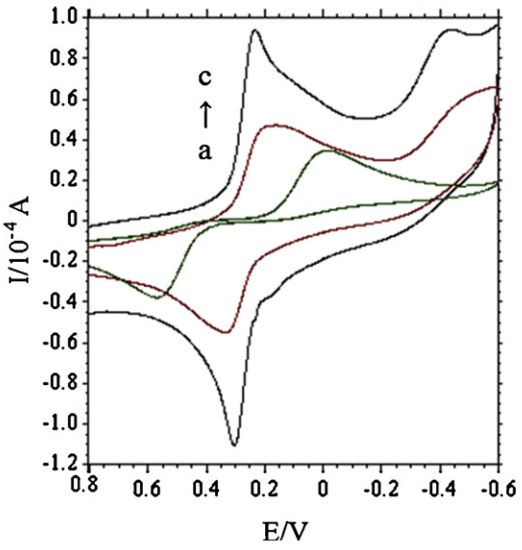

Fig. 1. CVs of 0.5 mM HQ on (a) CPE, (b) CNT/CPE and (c) PEDOT/CNT/CPE in B–R buffer (pH 3.0). Scan rate: 100 mV/s.

2.4. Electrochemical experiments

All the electrochemical experiments were performed in 0.2 M pH 3.0 B–R buffer. The CV experiments were scanned from −0.6 to 0.8 V or 1.0 V, with a scan rate of 100 mV/s, unless otherwise stated. The DPV experiments were scanned from −0.6 to 1.0 V, with a scan rate of 100 mV/s and an accumulation time of 60 s.

For the real sample analysis, 10 mg of cosmetic sample was accurately weighed and dispersed in 10 mL of B–R butter with the aid of ultrasonic agitation for 15 min, and the prepared sample was measured with the PEDOT/CNT/CPE using DPV.

3. Results and discussion

3.1. Electrochemical behavior of hydroquinone at the PEDOT/CNT/CPE

Fig. 1 shows the typical CVs of HQ obtained at the bare CPE (curve a), CNT/CPE (curve b) and PEDOT/CNT/CPE (curve c), respectively. As can be seen, the peak-potential separation between the E_{pa} and the E_{pc} (ΔE_p) at the PEDOT/CNT/CPE (73 mV) is much smaller than that at bare CPE (584 mV) and CNT/CPE (141 mV), which indicates that the PEDOT/CNT on the surface of the CPE can significantly increase the velocity of electron transfer for the redox of HQ. Simultaneously, the redox peak currents of HQ are remarkably increased at the PEDOT/CNT/CPE. This may be attributed to the electrocatalytic property of the PEDOT/CNT film, which greatly lowered the redox overpotential of HQ.

The SEM images of the CPEs modified with PEDOT/CNT and pure CNTs are shown in Fig. 2. Clearly, entangled network-like microstructures were formed on both electrode surfaces, and the diameter of the tubes/wires of the PEDOT/CNT was significantly wider than that of the pure CNTs. These results indicate that the formed PEDOT polymer prefers to grow around the CNTs, and the CNTs are evenly coated by a layer of PEDOT and formed nanocable-structured PEDOT/CNT nanocomposite. The formed PEDOT/CNT nanocomposite possesses a highly porous structure in the nanoscale with enlarged surface area, which can minimize the diffusion path and enlarge the electrode–electrolyte interface for ions to move in and out of the PEDOT/CNT film, and thus favoring the electrochemical reaction of HQ.