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The voltammetric sensor for sensitive determination of 8-hydroxyquinoline based on MWNTs/Nafion/GCE

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A multiwall carbon nanotube/Nafion composite modified glassy carbon electrode (MWNT/Nafion/GCE) was prepared and characterized by Atomic Force Microscopy (AFM) and Transmission Electron Microscope(TEM). This voltammetric sensor exhibited strong catalytic effect toward the oxidation of 8- hydroxyquinoline(8-HQ) in HAc-NaAc buffer solution (0.2M, pH 3.6). A new analytical method for determining 8-HQ was established. Under the optimized condition, the anodic peak current was linear with the concentration of 8-HQ in the range of 2×10^{-8}~1.0×10^{-5}M with a detection limit of 9×10^{-9} M. The practical application of MWNT/Nafion/GCE was carried out for determining 8-HQ in cosmetic sample with satisfactory results. The number of electron and proton taking part in the reaction was calculated, and then the electrode reaction mechanism was confirmed by UV-vis spectra.

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Keywords: Multi-wall carbon nanotubes, Nafion, Coliforms, Amperometric detection

1. Introduction

8-Hydroxyquinoline (8-HQ), known as an excellent preservative, bactericide, disinfector and deodorant, was widely used inthe production and preservation of cosmetic products for its strongantimicrobial property [1]. However, it was found that there wassome oncogenic potential when 8-HQ was transfused into themouse [2]. With the increasing use of cosmetic products in daily life, the harm to people caused by 8-HQ should be fully explored [3]. The regulations concerned the guarantee of consumer security had been constituted. According to the European Union Council Directive 76/768/EEC, 8-HQ was listed as the substance which must not form part of the composition in cosmetic products except for the use under the maximum authorized concentration restrictions of 0.3%(w/w) in rinse-off hair-care preparations and 0.03%(w/w) in nonrinse-off hair-care preparations. Therefore, the determination of 8-HQ in commercial cosmetic products was significant for quality control purposes and for checking their conformance to the current legislation [4]. However, some existing methods for determining 8-HQ are either toxic or expensive, such as polarography [5], thin layer chro-matography (TLC) [6], spectrophotometry [7], and liquid chroma-tography (LC) [8–10]. Compared with the analytical methodsmentioned above, electroanalytical method is environment friendly and low-cost [11], but the electro-activity of 8-HQ on bare electrode is too poor to detect. So far, there is no literature has been reported about determination of 8-HQ by electroanalytical method. Thus, it is imperative to develop a sensitive electroanalytical method for determining 8-HQ.

Carbon nanotubes (CNT), generated by rolling a single or several layers of graphite into a seamless and hollow cylinder, can be divided into multi-walled carbon nanotubes (MWNT) [12] and single-walled carbon nanotubes (SWNT) [13] based on the number of carbon atom layers. CNT has attracted much attention in the perspective of electrochemical sensor design [14]. Because of the excellent electrical properties, the ultrahigh ratio of surface area to volume, and the extreme sensitivity of its surface atoms to any surface adsorption reactions [15,16], CNT has the ability to mediate electron-transfer reactions with an electroactive species in solution when used as electrodes [17–19]. However, a major barrier for developing such CNT-based devices is the insolubility of CNTs in all solvents. To take advantages of its remarkable properties, CNTs need to be properly functionalized through its covalent [20] or noncovalent [21] modification. As we all know, Nafion is a good cation exchanger and can disperse MWNT readily with high stability [22]. Therefore, we combined the advantages of MWNT and Nafion (MWNT/Nafion) to modify a glass carbon electrode, signed as MWNT/Nafion/GCE. As a voltammetric sensor, it exhibits strong electrocatalysis toward the oxidation of 8-HQ.Then, an electroanalytical method for determining 8-HQ was established and its practical application was carried out in cosmetic sample with satisfactory results.

2. Experimental

Apparatus and reagents: A traditional three-electrode system consisting of an Ag/AgCl reference electrode, a platinum auxiliary electrode, and a glassy carbon working electrode modified with MWNT/Nafion film was employed. A transmission electron microscope (TEM)(Hitachi S-480) was used to observe the morphology of MWNT/Nafion. The UV–vis spectra were recorded by a Model UV-2102PC spectrophotometer (UNICO, Shanghai, China). MWNT (95% purity, 8nm diameter, 30 μm length) were obtained from Beijing Nachen S&T Ltd. The commercial samples of MWNT were pretreated according to the methods described in references [23,24]. Nafion 117(5%, w/v in alcoholic solution) was purchased from Alfa and was diluted to 0.1% (w/v) with ethanol beforeuse. 8-HQ was bought from Shang Hai SSS Reagent Co., Ltd. The stock solution of 8-HQ(1×10^{-2} M) was prepared with ethanol and kept darkly under 4℃. All other reagents were of analytical grade. Double distilled water was used for all preparations.

Preparation of MWNT/Nafion film modified electrode

Purified MWNT(2mg) was ultrasonically dispersed in a Nafion solution (0.1%) to give the final supernatant of 0.2mg/mL. The glassy carbon electrode was treated according to standardmethods and then ultrasonically cleaned in ethanol and double distilled water respectively. The MWNT/Nafion film was prepared by dropping the supernatant of MWNT/Nafion (5 μL) on the GCE surface and then evaporating the solvent naturally. After each determination of 8-HQ, MWNT/Nafion/GCE was cleaned by stirring in HAc-NaAc buffer solution (0.2M, pH 3.6) under a certain potential. The prepared electrode was stored in PBS (0.1M, pH 7.0) at 4℃ when it is not used. A Nafion film modified GCE (Nafion/GCE) was prepared by the same method as a contrast.

3. Results and discussion

TEM characterization of MWNT/Nafion composite

The TEM image of the MWNT/Nafion composite was shown in Fig. 1. It is clear that the Nafion/MWNTs composite formed a spaghetti-like porous reticular formation, exhibiting a special three-dimensional structure.

Electrochemical behavior of 8-HQ

The electrochemical behavior of 8-HQ at different electrodes was investigated by cyclic voltammetry (Fig. 2). In blank solution, there was no peak on the MWNT/Nafion/GCE (Fig. 2a). In 8-HQsolution (5×10^{-5}M), no electrochemical response was caused by GCE in the potential range between 0.6 V and 1.4V (Fig. 2b). The response on the Nafion/GCE was a small hump at 1.037V (Fig. 2c), suggesting that the Nafion film improved the accumulation of 8-HQ. Under the identical conditions, a sharp anodic peak at 0.97V was caused by MWNT/Nafion/GCE (Fig. 2d). The increase of the peak current and the negative shift of the oxidative potential were clear evidence that MWNT has strong catalysis toward 8-HQ. No reductive peak was observed during the reversing scan, indicating that the electrode reaction of 8-HQ was an irreversible process.

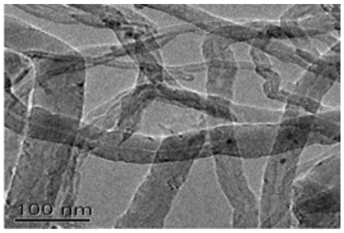


Fig. 1. TEM image of MWNT/Nafion composite.

The effect of scan rate

The effect of scan rate was investigated in the range of 50 mV/s–350 mV/s. As the scan rate increased, the peak current increasedand the peak potential moved to more positive value (Fig. 3A).The peak current was linear to the scan rate (Fig. 3B), suggesting an adsorption-controlled process occurring on the MWNT/Nafion/GCE.

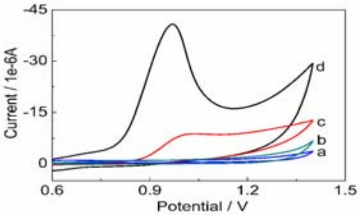


Fig. 2. The cyclic voltammograms of 8-HQ at different electrodes: (a) a MWNT/ fion/GCE in blank electrolyte solution; (b) a bare GCE in 8-HQ (5×10^{-5} M)solution; (c) a Nafion/GCE in 8-HQ (5×10^{-5} M) solution; (d) a MWNT/Nafion/GCE8-HQ (5×10^{-5} M) solution. Electrolyte: HAc-NaAc buffer solution (0.2 M, pH 3.6); scan rate: 100 mV/s.

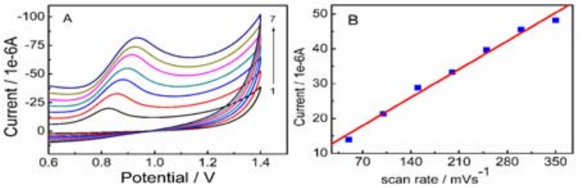


Fig. 3. The cyclic voltammograms of 8-HQ at different scan rates (A) and its ip ~ υ curve (B). Scan rates from 1–7: 50, 100, 150, 200, 250, 300, and 350 mV/s. Solution: HAc-NaAc (0.2 M, pH 3.6) + 8-HQ (1×10^{-5} M). Linear regression equation: $i_p = 9.834 + 0.116t$, $R = 0.994$.

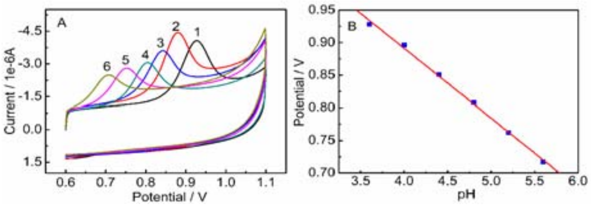


Fig. 4. The cyclic voltammograms of 8-HQ at different pH values (A) and its E_p ~ pH curve (B). Solution pH: (1)3.6, (2)4.0, (3) 4.4, (4) 4.8, (5) 5.2, (6) 5.6; solution: HAc-NaAc (0.2 M) + 8-HQ ((5×10^{-5}M); scan rate: 50 mV/s.

To get the best response of 8-HQ on MWNT/Nafion/GCE, several kinds of electrolyte were optimized. It was found that the peak current was higher in HAc-NaAc buffer solution (0.2M) and its peak shape was better than those obtained in other supporting electrolytes, such as phosphate buffer and B-R buffer solution. Thus, the effect of pH on the voltammetric response of 8-HQ was investigated in HAc-NaAc buffer solution (0.2M). Fig. 4A showed the effect of different pH on the response of 8-HQ (5×10^{-5}M) in the pH range of 3.6–5.6. The highest peak current and the best peak shape were obtained at pH 3.6. This could be explained by the fact that -OH group in 8-HQ was protonated as $-OH_2^+$ in acidic solution, and $-OH_2^+$ was easier to be adsorbed on MWNT/Nafion/GCE, since Nafion was a good cation-exchanger with high permeableness to $-OH_2^+$. Therefore, the lower pH was better for the absorption of 8-HQ. So, the following experiments were carried out in HAc-NaAc (0.2M, pH 3.6). In addition, the potential negatively shifted with the increase of pH, indicating that protons were involved in the electrode reaction.

Influence of accumulation time and accumulation potential

Accumulation step is usually a simple and effective way to enhance the sensitivity. In 8-HQ solution (5×10^{-7}M), the peak current increased with the accumulation time from 60s to 300s, then it was almost constant (data not shown), indicating that the adsorption was saturated after 300s. For getting a wider linear range, the accumulation time was selected as 120s. The accumulation potential has no effect on the peak current, which is a character of an adsorption process.

Calibration curve

The relationship between peak current and the concentration of 8-HQ was investigated by Differential Pulse Voltammetry (DPV). As shown in Fig. 5, the peak current increased with the concentration of 8-HQ. A wide linear range was attained between 2×10^{-8}M and 1×10^{-5}M, and the detection limit (defined as a concentration generating a signal that is three times larger than the noise [25,26]) was 9×10^{-9}M. The repeatability of this method was tested in 8-HQ solution (5×10^{-7}M) for six times with every interval of 24 h and the rela-tive standard deviation (RSD) was calculated as 3.42%, which demonstrated the good repeatability of this method and the stability of modified electrode. When not in use, MWNT/Nafion/GCE was stored in PBS (0.1 M, pH 7.0) at 4℃, and its response for 8-HQ solution (5×10^{-7} M) decreased little after 30 days.

Interferences

The purpose of establishing this analyticalmethod was to determine 8-HQ in cosmetic products. So, the interferential experiments were performed aiming on some materials usually exist in cosmetic products. The results showed that general concomitant substance in cosmetic products did not interfere with the determination of 8-HQ, such as, 300-fold (quality ratio) amount of coconut oil propylbetaine, sodium lauryl sulfacid, glycerol, citric acid, vitamin C and vitamin E. These data demonstrated that the MWNT/Nafion/GCE voltammetric sensor possessed high selectivity for 8-HQ.

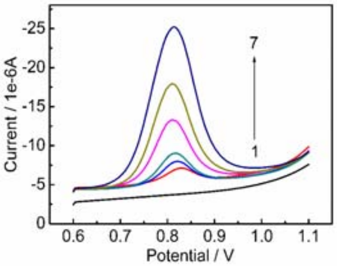
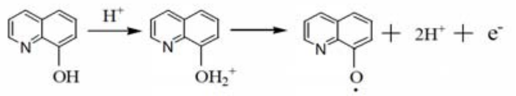


Fig. 5. The DPV curves of 8-HQ with different concentrations at the MWNT/Nafion/GCE (8-HQ): (1) 0; (2) 3×10^{-7}M; (3) 5×10^{-7}M; (4) 7×10^{-7}M; (5) 3×10^{-6}M; (6) 5×10^{-6}M; (7) 7×10^{-6}M. Electrolyte: HAc-NaAc buffer solution (0.2 M, pH 3.6). Linear regression equation: i_p (μA) = 1.046 + 2.105 C (8-HQ) (μM), R=0.995

Table 1. The results of determination of 8-HQ in cosmetic samples.

Samples	Measured value (mg/g)	Standard solution added	Standard solution found (μg)	Recovery (%)
1	0.1362	0.2901	0.2995	103.2
2	0.1351	0.5806	0.5788	99.7
3	0.1353	0.8709	0.8813	101.2
Average value	0.1355	—	—	101.4



Scheme 1. Proposed mechanism for the oxidation of 8-HQ.

Analysis of practical samples

To evaluate the applicability of the proposed method, one brand of shampoo was employed as practical sample and divided into two identical groups. Both were pretreated according literature [4]. The concentration of 8-HQ in the first group was determined by standard addition method. Meanwhile, in order to calculate the recovery, 8-HQ standard was added in the second group before the sample was pretreated. The analytical results were listed in Table 1, which demonstrated the reliability of the proposed method.

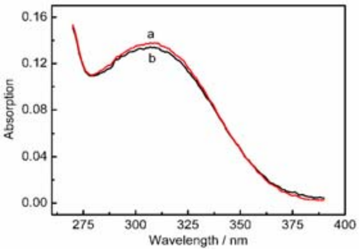


Fig. 6. The UV–vis spectra of 8-HQ solution (5×10^{-6}M) before and after fully electrolyzed.

The reaction mechanism of 8-HQ on MWNT/Nafion/GCE

The electrode reaction mechanism of 8-HQ was studied by cyclic voltammetry and UV–vis spectra. First, the electron number(n) of the electrode reaction was calculated from the data provided by Fig. 3. According to Laviron's theory [27,28], the ip~ υ relation can be described by the following equation: i_p = nFQυ/4RT. Obviously, the value of n could be calculated as long as the peak area Q was obtained under certain scan rate. Based on this theory, scan rates 50, 100, 150, 200, 250, 300 and 350 mV/s were put into the equation and the value of n was calculated as 1. Therefore, only one electron took part in the electrode reaction. Then, the number of proton taking part in the reaction was calculated according Nernstian Equation [29,30]:

$$E = E^0 + \frac{RT}{nF}\ln\frac{[O][H^+]^{\partial}}{[R]} = E^0 + \frac{RT}{nF}\ln\frac{[O]}{[R]} + \frac{\partial RT}{nF}\ln[H^+]$$

From Fig. 4B, the linear regression equation of E_p versus pH was obtained as E_p =1.360-0.115 pH (R=0.999). So the ratio value of ∂/n (∂ was the number of proton) was calculated as 1.95, which was approaching 2. Thus the number of proton taking part in the reaction could be regarded as two. On the basis of these data, we presumed the oxidation process as Scheme 1. This was also confirmed by UV–vis spectra. 8-HQ has a wide absorption band around 310 nm, which is caused by its conjugated structure [31]. Fig. 6 showed the UV–vis spectra of 8-HQ solution (5×10^{-6}M) before and after fully electrolyzed. The two spectra were almost identical, which indicated that the conjugated structure of 8-HQ molecule did not vary during the electrode reaction. Therefore, it was presumed that the hydroxyl group took part in the electrode reaction and generated a phenoxy radical.

4. Conclusion

In this paper, a voltammetric sensor was fabricated by dropping supernatant of MWNT/Nafion on a glassy carbon electrode. Theprepared sensor showed promising electrocatalysis toward the oxidation of 8-HQ because of the synergistic effect of MWNT and Nafion. Thus, a reliable voltammetric method of determining trace 8-HQ with wide linear rage, high sensitivity and selectivity was developed and suited well for the quality control assay of 8-HQ in cosmetic products. Compared with other analytical methods, this voltammetric method is environment-friendly and lower cost. Currently, it was the first report about determining trace 8-HQ in cosmetic products by electroanalytical method.

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