

Selective determination of hydroquinone in the presence of catechol based on over-oxidized poly(hydroquinone)

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Abstract Selective determination of hydroquinone (HQ) in the presence of catechol (CC) was developed at an over-oxidized poly(hydroquinone) (PHQ) electrode. The electrochemical polymerization of HQ was carried out by potentiostatic method on a glassy carbon electrode. The resulting PHQ was over-oxidized in 0.10 mol/L NaOH solution and thus poly(*p*-benzoquinone) was obtained. Two dihydroxybenzene isomers, HQ and CC, show different voltammetric behavior at the over-oxidized PHQ electrode. The peak current of HQ is much larger than that of CC with the same concentration, which is attributed to the different position of the hydroxyl groups in benzene ring of the two isomers. The results from electrochemical impedance spectroscopy also demonstrates that the over-oxidized PHQ electrode has a stronger affinity for HQ over CC.

Keywords Selective determination · Hydroquinone · Catechol · Poly(hydroquinone) · Over-oxidation

Introduction

Hydroquinone (HQ) and catechol (CC) are two dihydroxybenzene isomers, and they usually coexist in biological and environmental samples. Because they usually interfere with each other in analysis, reliable determination of HQ or CC in the presence of the other isomer is a challenging and interesting

subject for researchers. Electrochemical detection based on various modified electrodes such as carbon-nanotube-modified glassy carbon electrode (GCE) [1, 2], mesoporous Pt-modified Pt electrode [3], ordered mesoporous carbon-modified GCE [4], poly(thionine)-modified GCE [5], graphene-chitosan composite film-modified GCE [6], photo-reduced graphene-polyoxometalate nanomaterials [7], and poly(malachite green)-coated multi-walled carbon nanotube film [8] has been employed for the simultaneous determination of HQ and CC. More recently, research on electrochemically activated GCE instead of chemically modified electrodes were reported [9, 10]. However, all these electrochemical methods provide a “simultaneous,” not a “selective” determination for one of the two isomers. So, it is of great importance to establish a reliable analytical method for the selective determination of HQ in the presence of CC, and vice versa. Recently, Yang et al. has proposed a poly(*p*-aminobenzene sulfonic acid)-modified GCE for selective determination of HQ in the presence of CC and resorcinol, and therefore electrochemical recognition of HQ and its isomers can be achieved by using this conducting polymer-modified GCE [11].

Poly(hydroquinone) (PHQ) is a kind of conducting polymer, and it can be electrochemically synthesized from hydroquinone (HQ) monomer [12]. Wang et al. [13] and Nakano et al. [14] reported that enzymatically prepared PHQ could be used as an amperometric sensor for the detection of glucose and DNA. However, as we all know, polyphenol is unstable in air since it undergoes an irreversible oxidation to form polyquinone [15].

In the present work, selective determination of HQ in the presence of CC is achieved successfully on the basis of different position of hydroxyl groups in benzene ring of HQ and CC. Instability of PHQ is utilized here, and further electrochemical over-oxidation of PHQ was carried out to accelerate the transfer from PHQ to poly(*p*-benzoquinone).

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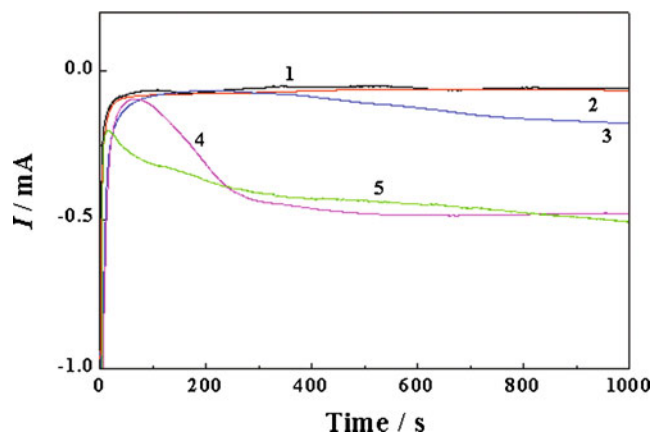


Fig. 1 Relationship between current and time during electrolysis of 0.02 mol/L HQ in 0.10 mol/L NaCl solution at various potentials of 1.2 (1), 1.5 (2), 1.8 (3), 2.0 (4), and 2.2 V (5)

The hydrogen bond between HQ and poly(*p*-benzoquinone) is much stronger than that between CC and poly(*p*-benzoquinone) because of the different stereo structure of HQ and CC, which results in a reliable determination of HQ at the over-oxidized PHQ electrode without the interference from CC existing in the electrolyte simultaneously.

Materials and methods

Reagents and apparatus

HQ and CC were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All other chemicals were of analytical grade and used without further purification. The solutions were prepared by doubly distilled water. A CHI 660D electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) was used for the electrochemical polymerization of HQ and square wave voltammetry of HQ and CC. Impedance analysis was conducted with a model VersaSTAT 3 electrochemical system (Princeton Applied Research, USA), and it was recorded with a frequency range from 10^4 to 0.1 Hz at a potential of 0 V. The amplitude of the applied sine wave potential was 10 mV.

Fabrication of over-oxidized PHQ electrode

A conventional three-electrode system, consisting of a GCE (3 mm in diameter) as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode as the reference electrode. The electrochemical polymerization was carried out in 0.10 mol/L NaCl containing 0.02 mol/L HQ, using potentiostatic method at 2.0 V for 1,000 s. The pH was adjusted to 2.0 with HCl. After the polymerization, a PHQ film was polymerized on the GCE. To accelerate the formation of poly(*p*-benzoquinone), the

prepared PHQ electrode was over-oxidized in 0.10 mol/L NaOH solution by applying a constant potential of 1.2 V for 800 s.

Selective determination of HQ in the presence of CC

Selective determination of HQ in the presence of CC was carried out in 0.50 mol/L H_2SO_4 containing 0.10 mmol/L HQ and different concentration of CC, using square wave voltammetry. Square wave amplitude of 10 mV, frequency of 5 Hz, and pulse increment of 1 mV were selected. The over-oxidized PHQ was used as the working electrode, and the auxiliary and the reference electrodes were the same as those used in the electrochemical polymerization of HQ.

Results and discussion

Potentiostatic electrolysis of HQ

Figure 1 shows the change of current with time during electrolysis of 0.02 mol/L HQ in 0.10 mol/L NaCl solution at different potentials, and its pH was adjusted to 2.0 with diluted HCl solution. An evident feature in Fig. 1 is that the shape of $I-t$ curve changes with potential. At 1.2 and 1.5 V (curves 1 and 2), the current first increases quickly with time and then reaches a plateau, i.e., the current hardly changes with time. In this case, the electrode reaction reaches a steady state, which is due to the reversible redox reaction of HQ at the GCE. After the electrolysis, PHQ was not found at the GCE, which indicated that the two potentials are not high enough for the polymerization of HQ. However, this current plateau disappeared as the potential increased from 1.5 to 1.8 V (curve 3). Finally, when the potential was set at 2.0 V, a sharp current peak appeared at about 70 s on curve 4, and then the current

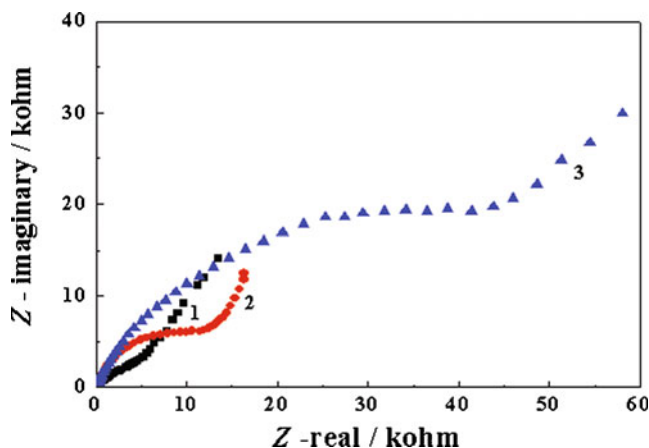
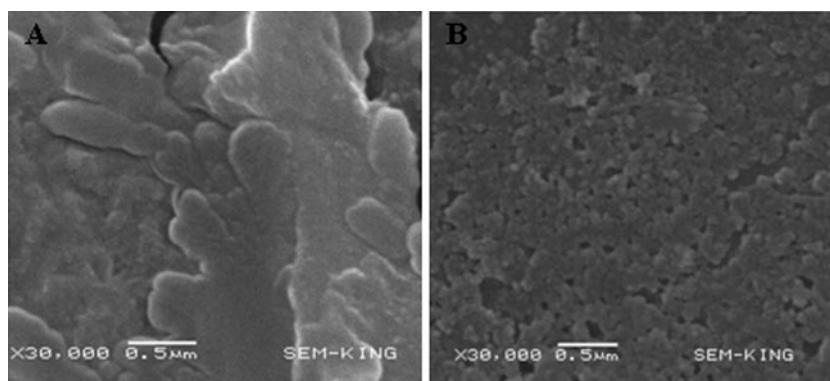


Fig. 2 Nyquist plots of the EIS for GCE (1), PHQ electrode (2), and over-oxidized PHQ electrode (3) in 0.10 mol/L NaCl solution containing 10 mmol/L $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ with a frequency range from 10^4 to 0.1 Hz at a potential of 0 V

Fig. 3 SEM images of PHQ before (a) and after over-oxidation (b)

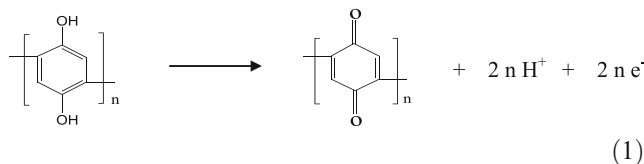


decreased with time and then remained constant. The increase of current in curve 4 indicated that the nucleation of PHQ; the decrease of current indicated the growth of PHQ film, because PHQ is an organic semiconductor which conductivity is lower than that of GCE. When the potential increased to more than 2.0 V (curve 5), the response became even faster. As a result, the current signal was difficult to be recorded in such short time. Thus, the potential for the polymerization of HQ is controlled at 2.0 V in the following experiments.

Over-oxidation of PHQ films

NaOH solution or PBS solution (pH 6.9) is beneficial to the over-oxidation of conducting polymers [16–19]. Because strong alkaline media make the transfer from PHQ to poly(*p*-benzoquinone) easier [20], 0.10 mol/L NaOH solution is chosen for the over-oxidation of PHQ. The oxidation peak potential of PHQ is usually lower than 0.80 V, so a potential of 1.2 V can make a complete over-oxidation of PHQ. Some references reported that oxygen-containing groups such as carbonyl groups were introduced as a result of over-oxidation, along with the loss of the cationic charge on the backbone of

conducting polymers [21, 22]. Therefore Cl⁻ is excluded from the over-oxidized PHQ films because of the disappearance of the electrostatic attraction between the over-oxidized PHQ and Cl⁻. At the same time, PHQ is transferred to poly(*p*-benzoquinone) with the loss of protons during the over-oxidation process (see Eq. 1). As a result, a strong hydrogen bond can be formed between HQ and the poly(*p*-benzoquinone).



Electrochemical impedance spectroscopy (EIS) can provide the information on the impedance changes of the PHQ films during the electrochemical over-oxidation. As can be seen in Fig. 2, the Nyquist plots of the bare GCE (curve 1), PHQ (curve 2), and over-oxidized PHQ electrode (curve 3) in 0.10 mol/L NaCl solution containing 10 mmol/L K₃[Fe(CN)₆]/K₄[Fe(CN)₆] are all constructed by a depressed semi-circle at high frequencies and a straight line at low frequencies, which indicate that the electrode process is controlled by electrochemical reaction at high frequencies and by mass-transfer at low frequencies. The diameter of the semicircle is equivalent to the charge transfer resistance (*R*_{ct}), which is the most directive and sensitive parameter that responds to changes of the electrode-solution interface [23]. It is found that the *R*_{ct} increases to ca. 15 kΩ after the GCE is covered by the PHQ films, implying that the resistance of the PHQ films is larger than that of the GCE. A significant increase of the *R*_{ct} to ca. 70 kΩ is observed after the over-oxidation of the PHQ films, which is due to the fact that the PHQ loses its electroactivity in parallel with the ejection of the dopants (Cl⁻). An obvious change in morphology after PHQ over-oxidation is shown in Fig. 3. As can be seen, the large-sized PHQ film with scale structure (Fig. 3a) disappears after over-oxidation; instead, clusters made up of nanoparticles are observable (Fig. 3b). This is caused by the over-oxidation of PHQ, and the clustered particles are poly(*p*-benzoquinone) nanoparticles. The porous structure of poly(*p*-benzoquinone) makes

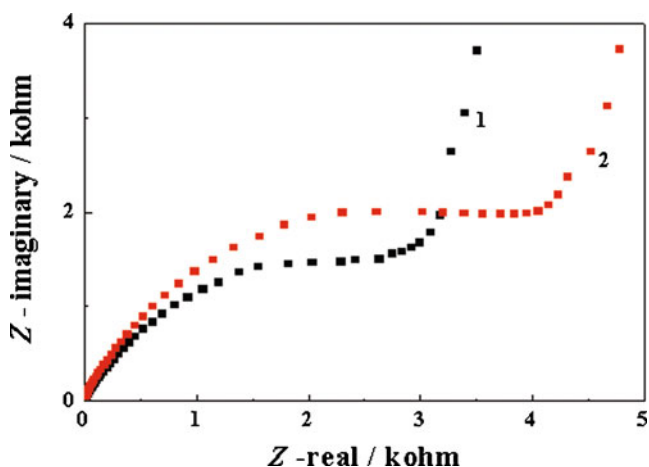
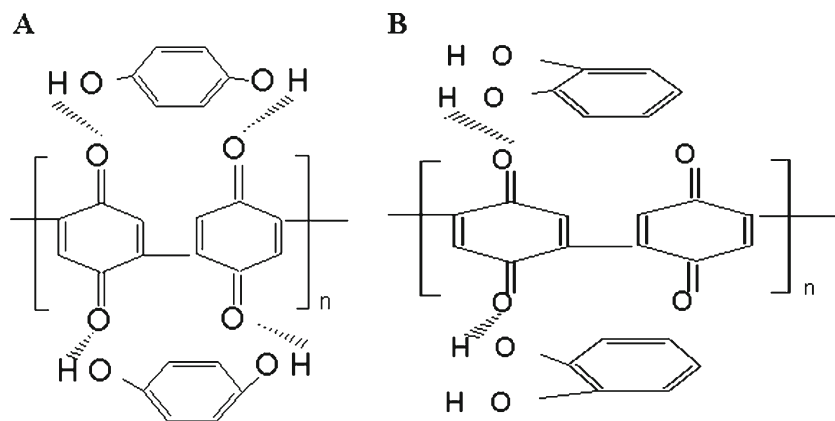


Fig. 4 Nyquist plots of the EIS for the over-oxidized PHQ in 0.50 mol/L H₂SO₄ solution containing 1.0 mmol/L HQ (1) and CC (2) with a frequency range from 10⁴ to 0.1 Hz at a potential of 0 V

Fig. 5 **a** The hydrogen bond between HQ and poly(*p*-benzoquinone). **b** The hydrogen bond between CC and poly(*p*-benzoquinone)



it easier for the dopants (Cl^-) and protons generated during the over-oxidation process to be excluded.

Selectivity of the over-oxidized PHQ for HQ

Figure 4 shows the EIS of the over-oxidized PHQ in 0.50 mol/L H_2SO_4 solution containing 1.0 mmol/L HQ (curve 1) and CC (curve 2). As can be seen, the R_{ct} of curve 1 is much smaller than that of curve 2. The results indicated that the over-oxidation of the PHQ made it easier for charge transfer of HQ than that of CC. The different R_{ct} for HQ and CC may be attributed to the different position of the hydroxyl groups in benzene ring of the two isomers. The hydrogen bond between HQ and poly(*p*-benzoquinone) is much stronger than that between CC and poly(*p*-benzoquinone), as shown in Fig. 5. The different hydrogen bonds resulted in different R_{ct} of HQ and CC in 0.50 mol/L H_2SO_4 solution.

Square wave voltammetry of HQ and CC on the over-oxidized PHQ electrode is carried out to test the selectivity of the over-oxidized PHQ for HQ. Figure 6 shows the square wave voltammograms of 1×10^{-4} mol/L HQ in the presence of

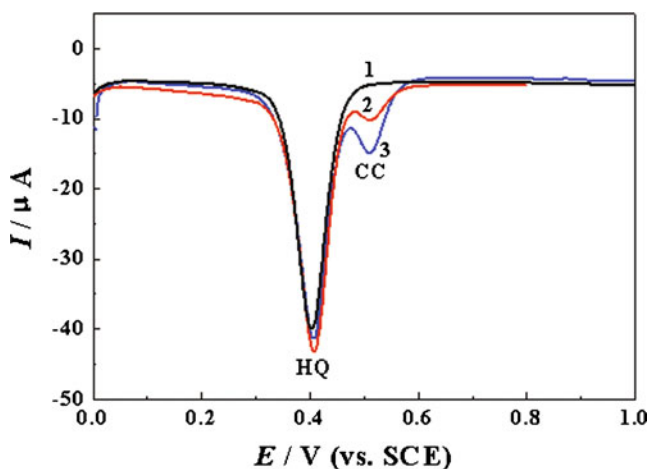


Fig. 6 Square wave voltammograms of 1×10^{-4} mol/L HQ in the presence of 5×10^{-6} mol/L (1), 2×10^{-5} mol/L (2), and 1×10^{-4} mol/L (3) CC in 0.50 mol/L H_2SO_4 solution

CC with different concentration in 0.50 mol/L H_2SO_4 solution. When the concentration of CC is 5×10^{-6} mol/L, no oxidation peak current is observed (curve 1), which indicates that the oxidation of CC at the over-oxidized PHQ electrode is seriously depressed. The peak current of CC increases with increasing concentration, however, the peak current of HQ is still much larger than that of CC with the same concentration (curve 3). It can be calculated that the peak current of HQ (34.46 μA) is about 7.3-fold of CC (4.72 μA) when the two isomers have a concentration of 1×10^{-4} mol/L. The results are quite different from previous work [10]. In that work, HQ and CC of 1×10^{-4} mol/L were determined simultaneous at an electrochemically activated GCE and the peak current of HQ (31.66 μA) is only 1.1-fold of CC (28.55 μA). It is obvious that the signal difference between HQ and CC is significantly magnified at the over-oxidized PHQ electrode compared with the electrochemically activated GCE. Because the hydrogen bonds between the two isomers and poly(*p*-benzoquinone) are quite different, the oxidation of CC at the over-oxidized PHQ electrode is depressed markedly. As a result, the over-oxidized PHQ electrode has good recognition ability to HQ. In this sense, a selective, not a simultaneous determination can be achieved for HQ at the over-oxidized PHQ electrode.

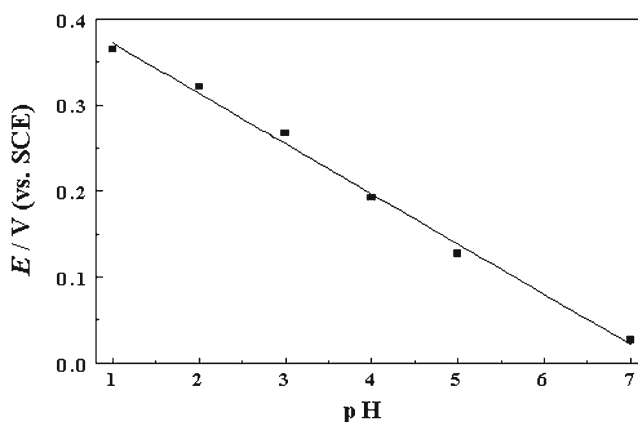


Fig. 7 Effect of pH on the peak potential of HQ at the over-oxidized PHQ electrode

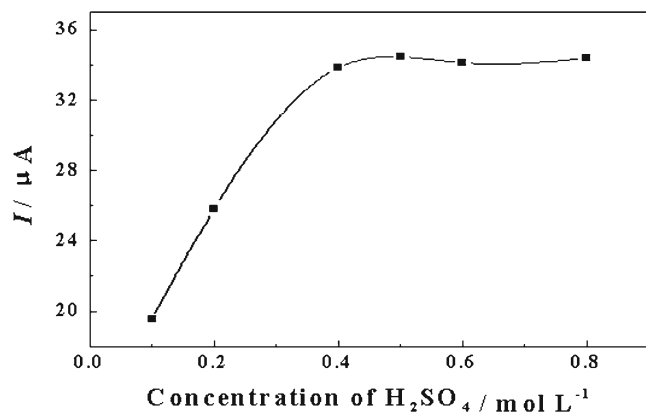


Fig. 8 Effect of H₂SO₄ concentration on the peak current of HQ at the over-oxidized PHQ electrode

Influences of pH and H₂SO₄ concentration

Influence of pH on the peak potential of HQ at the over-oxidized PHQ electrode was investigated by square wave voltammetry. The results indicated that the peak potential shifted negatively with the increase of the pH value. Within the range of pH 1.0–7.0, the peak potential is proportional to the pH value (Fig. 7). The linear regression equation is E_p (V)=0.4307–0.0584 pH ($r=0.9947$). The slope of the above equation is close to –59.2 mV, implying two protons are involved in the two-electron redox reaction [1].

In addition, the influence of H₂SO₄ concentration on the electrochemical response of HQ was also studied (Fig. 8). It was found that the oxidation peak current increased with increasing H₂SO₄ concentration. However, when the H₂SO₄ concentration was above 0.50 mol/L, the oxidation peak current of HQ remained almost unchanged. Therefore, 0.50 mol/L H₂SO₄ was employed as the supporting electrolyte for the selective electrochemical determination of HQ.

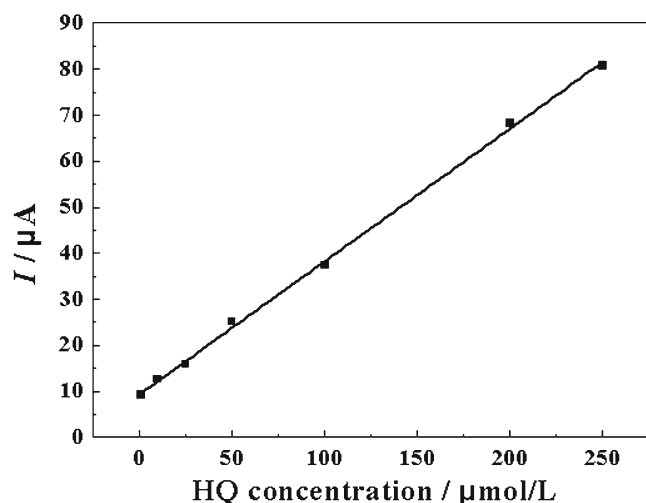


Fig. 9 Linear plot of the peak current with different concentration of HQ at the over-oxidized PHQ electrode

Interference from coexisting resorcinol

Resorcinol is another important isomer of HQ, and its interference on the determination of HQ at the over-oxidized PHQ electrode was also studied in this work. It is found that the peak current of HQ (34.46 μA) is as large as 19.9-fold of resorcinol (1.73 μA) when these two compounds have a concentration of 1×10^{-4} mol/L (figure omitted). Interestingly, the peak current of resorcinol at the unmodified GCE is about 8.81 μA, which is much larger than that of resorcinol at the over-oxidized PHQ electrode. This result indicates that the oxidation of resorcinol is significantly depressed at the over-oxidized PHQ electrode, and thus the over-oxidized PHQ electrode also has a stronger affinity for HQ over resorcinol.

Analytical performances of the over-oxidized PHQ electrode

The over-oxidized PHQ electrode shows a linear concentration range between 1 and 250 μmol/L HQ with a correlation coefficient of 0.9988, and the linear regression equation is I (μA)=9.3820+0.28866 C (μmol/L) (Fig. 9). The detection limit is as low as 0.055 μmol/L (S/N=3). The reproducibility of the over-oxidized PHQ electrode was checked by successive determinations ($n=5$) of 100 μmol/L HQ, and the relative standard deviation was calculated to be 1.70 %. It was found that the peak current of HQ on the over-oxidized PHQ electrode remained almost unchanged when the electrode was used again 2 weeks later, i.e., the stability is satisfactory. Table 1

Table 1 Comparison of over-oxidized PHQ electrode with other modified electrodes in determination of HQ

Electrodes	Linear range (μmol L ⁻¹)	Detection limit (μmol L ⁻¹)	References
Over-oxidized PHQ electrode	1–250	0.055	This paper
MWCNT ^a -modified GCE ^b	1–100	0.75	[1]
MWCNT-modified GCE	2–100	0.6	[2]
Mesoporous platinum	50–2000	–	[3]
Graphene–polyoxometalate-modified GCE	0.2–25	0.04	[7]
Polarized GCE	0.5–200	0.16	[9]
Electrochemically activated GCE	1–100	0.018	[10]
Organic polymer/MWCNT composite-modified GCE	6–400	1	[23]
Graphene-modified GCE	1–50	0.015	[24]
MWCNT/poly(3-methylthiophene)-modified GCE	0.5–200	0.05	[25]

^a Multi-wall carbon nanotubes

^b Glassy carbon electrode

presents the comparison of the present work with other published results with respect to linear concentration range and detection limit, indicating that the over-oxidized PHQ electrode displays a superior electroanalytical behavior for HQ compared with many other modified electrodes.

Conclusions

The PHQ film was synthesized at a GCE by potentiostatic method, and then it was over-oxidized in 0.10 mol/L NaOH solution to form poly(*p*-benzoquinone). The hydrogen bond between poly(*p*-benzoquinone) and HQ is much stronger than that between poly(*p*-benzoquinone) and CC, which leads to a selective determination of HQ in the presence of CC in a comparable concentration. HQ shows an electrocatalytic oxidation at the over-oxidized PHQ electrode, however, the oxidation of CC at the poly(*p*-benzoquinone) (over-oxidized PHQ) electrode is seriously depressed. Clearly, the novel over-oxidized PHQ electrode is one of the most challenging applications in the future for the selective determination of isomers.

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