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ORIGINAL PAPER

Electrochemical determination of diphenols and their mixtures at the multiwall carbon nanotubes/poly (3-methylthiophene) modified glassy carbon electrode

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Abstract A glassy carbon electrode modified with poly (3-methylthiophene) (P3MT) and coated with multiwall carbon nanotubes (MWNTs) film was fabricated and used for highly selective and sensitive determination of hydroquinone and catechol. The electrode combines the advantages of using P3MT and MWNTs, and exhibits a dramatic electro-catalytic effect on the oxidation of hydroquinone and catechol. This resulted in a marked enhancement of the current response. The peaks for hydroquinone and catechol are separated by about 101 mV in pH 6.4 phosphate buffer which enables simultaneous determination of both via cyclovoltammetry. Good linear relationships between the peak current and concentration were observed for single solution of hydroquinone (or catechol) by differential pulse voltammetry. The detection limits are 12 nmol L^{-1} and 40 nmol L^{-1} (at an S/N of 3). When simultaneously changing the concentration of both hydroquinone and catechol, the linear responses are in the range from 0.5 to 200 μmol L^{-1} for hydroquinone, and from 0.5 to 150 μmol L^{-1} for catechol, and the detection limits are 50 nmol L^{-1} (S/N=3) for both hydroquinone and catechol. This method is simple, rapid, and accurate.

Keywords Hydroquinone · Catechol · The multiwall carbon nanotubes · Poly(3-methylthiophene) · Glassy carbon electrode · Electro-catalytic activity

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Introduction

Hydroquinone and catechol are two important isomers of phenolic compounds in nature, they are often used as developer, depressor, antioxidant, and secondary coloring matters, and so on. Meanwhile, most of them are highly toxic to the environment and the human, so design and development of quick, simple analytical methods have some important meanings in recent decades [1–3]. So far, several methods have been applied to determine phenols, including liquid chromatography [4], gas chromatography/mass spectrometry [5], spectrophotometer [6], and synchronous fluorescence [7]. However, some of these mentioned methods have the disadvantages of expensive, low sensitivity, time-consuming and complicate pretreatment. Thus, the design and development of quick, simple and effective analytical methods are of great importance in practice.

Poly (3-methylthiophene) (P3MT) is a widely used conducting polymer, which can be easily electrodeposited onto electrode surface by electro-oxidation of its monomer [8]. P3MT modified electrodes have been extensively reported and have shown excellent electro-catalytic effect on some compounds which have conjugated double bond in molecular structure, such as 8-Hydroxy-2′-deoxyguanosine (8-OH-dG) [9], dopamine [10], phenolic compounds [11–15]. The multiwall carbon nanotubes (MWNTs) have high surface area, specific conductivity formation, stable chemical property and the character of mechanical strength, so MWNTs attract scientists' extensive attention in conducting polymer research [16–24].

The simultaneous determination of hydroquinone and catechol at a glassy carbon electrode modified with multiwall carbon nanotubes has been proposed [2, 25]. In this work, we successfully prepared the modified glassy carbon electrode (GCE) by coating the MWNTs onto the

electrochemical polymerized P3MT surface (MWNTs/P3MT/GCE). This modified electrode combined the advantages of P3MT and MWNTs, they exhibited dramatic electro-catalytic effect on the hydroquinone and catechol. Separation of the two peaks for hydroquinone and catechol was about 101 mV vs. Ag/AgCl in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution, which made it suitable for simultaneous determination of these compounds. Moreover, the peak currents of hydroquinone and catechol increased at the MWNTs/P3MT/GCE compared with some previous reports [2, 25–27]. The electrochemical methods for the simultaneous determination of hydroquinone and catechol were simple and rapid with high accuracy.

Experimental

Apparatus

Cyclic voltammetry (CV) and the differential pulse voltammetry (DPV) were performed using a CHI760C electrochemical workstation (CH Instruments, Chenhua Corp. Shanghai, China, http://chi.instrument.com.cn). The conventional three-electrode system was employed with a bare GCE or a MWNTs/ P3MT/GCE as working electrode, a platinum wire as auxiliary electrode, and the reference electrode was a saturated Ag/AgCl.

Chemicals and reagents

3-methythiohene (3MT) was obtained from Acros (http://www.acros.com) and 3MT was used without further purification, MWNTs was purchased from Chengdu Institute of Organic Chemistry of Academy of Sciences (http://www.timesnano.com), Acetonitrile (LC grade), $NaClO_4$, hydroquinone and catechol were all obtained from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China, http://www.china-reagent.com). All other reagents were analytical reagent grade, and all solutions were prepared using twice distilled water.

Fabrication of modified glassy carbon electrode

The preparation of the P3MT-modified GCE has been described in previous works [9, 10, 14, 21]. Briefly, prior to the polymer electro-synthesis, the surface of the GCE (diameter 3.0 mm) was polished with 0.05 μ m alumina slurry and cleaned by ultra-sonication in twice distilled water. P3MT was electrodeposited on a GCE surface from a solution containing 0.1 M 3MT and 0.1 M $NaClO_4$ dissolved in acetonitrile. Both cyclic voltammetry and the potentiostatic mode were adapted for P3MT film preparation. Cyclic voltammograms were recorded between 0.0 and 1.7 V vs. Ag/AgCl at a scan rate of 20 mV s^{-1} for three cycles, and then the film was grown in potentiostatic mode at a potential of 0.7 V vs. Ag/AgCl for 10 s. After the polymerization, the electrode was treated in pH 7.0 phosphate buffer solution by repetitive scanning in the potential range of 0.0 and 1.7 V vs. Ag/AgCl for 10 cycles and then between −0.2 and 0.5 V vs. Ag/AgCl at a scan rate of 100 mV s^{-1} until a stable background was obtained. Thus, the P3MT-modified GCE (P3MT/GCE) was achieved.

MWNTs were treated by the mixture of concentrated H_2SO_4 and concentrated HNO_3 (1/3, v/v), it is well known that this treatment causes segmentation and carboxylation of MWNTs at their termini [10]. 1.0 mg/mL MWNTs dispersion was made by 1.0 mg solubilizing MWNTs in 1.0 mL twice distilled water, and sonicating for 100 s. Following this step, 5 μL MWNTs dispersion were scrupulously dropped onto the surface of P3MT/GCE. The electrode was treated in pH 7.0 phosphate buffer solution by repetitive scanning in the potential range of −0.2–0.6 V vs. Ag/AgCl at a scan rate of 100 mV s^{-1} until a stable background was obtained. Thus, the MWNTs/P3MT modified GCE (MWNTs/P3MT/GCE) was achieved. The prepared electrodes were stored in a dry chamber before use to keep their surface dried.

Electrochemical experiments

The DPV and CV experiments were performed in 0.1 mol L^{-1} phosphate buffer solution (pH 6.4) containing certain concentrations of hydroquinone, catechol or mixed systems of hydroquinone and catechol. Under the various conditions, the DPV and CV were recorded in a suitable potential range. All experiments were carried out at ambient temperature (about 25 °C) under a nitrogen atmosphere.

Results and discussion

Electrochemical behaviors of hydroquinone and catechol by CV

Figure 1 showed the electrochemical responses of hydroquinone in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution at two different electrodes. At a bare GCE (Fig. 1, **curve A**), hydroquinone exhibited a poor electrochemical response. But at the film of MWNTs/P3MT/GCE (Fig. 1, **curve B**), better redox peak of hydroquinone was observed. The separation between peak potentials (ΔE_P) was about 45 mV vs. Ag/AgCl. Compared with bare GCE, the film of MWNTs/P3MT/GCE increased the peak current and a more reversible electron process to hydroquinone. Thus, this modified electrode had electro-catalytic activity for the hydroquinone.

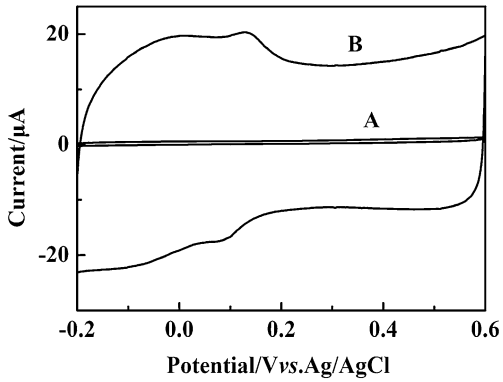

Fig. 1 Cyclic voltammograms (CVs) of 1×10^{-5} mol L^{-1} hydroquinone at the bare GCE (A) and the MWNTs/P3MT/ GCE (B) in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution with a scan rate of 100 mV s^{-1}

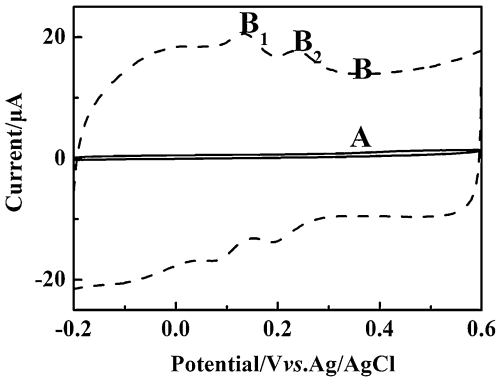

Fig. 3 CVs of 1×10^{-5} mol L^{-1} hydroquinone and 1×10^{-5} mol L^{-1} catechol at the bare GCE (A) and the MWNTs/P3MT/GCE (B) in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution with a scan rate of 100 mV s^{-1}

A similar experiment was done with catechol as shown in Fig. 2. Compared with that at a bare GCE (Fig. 2, **curve a**), the separation between peak potentials (ΔE_{Pa1})=80 mV vs. Ag/AgCl. The remarkable enhancement in the peak currents provided clear evidence of the electro-catalytic effects of the modified electrode toward catechol (Fig. 2, **curve b**). The separation between peak potentials (ΔE_{Pa2})=40 mV vs. Ag/AgCl, indicating that the film of MWNTs/P3MT/GCE was superior to the GCE for the detection of catechol, and had better electro-catalytic activity for the catechol.

The voltammetric behaviors of the mixture which had hydroquinone and catechol were investigated using CV. At a bare GCE, the mixture of certain concentrations hydroquinone and catechol exhibited a poor electrochemical response (Fig. 3, **curve A**). Figure 3, **curve B** showed that the mixture of hydroquinone and catechol yield two well-defined redox peaks, whose separation of the two peaks for hydroquinone and catechol was about 101 mV vs. Ag/AgCl at the MWNTs/P3MT/GCE. Meanwhile, the peak currents also increased remarkably. Combined with the advantages of MWNTs and P3MT, they exhibited catalytic effects toward the oxidations of hydroquinone and catechol, resulting in increasing peak current. Consequently, the electron transfers of hydroquinone and catechol at the MWNTs / P3MT/GCE were facilitated. That is to say, the MWNTs/P3MT/GCE had electro-catalytic ability toward the oxidation of hydroquinone and catechol.

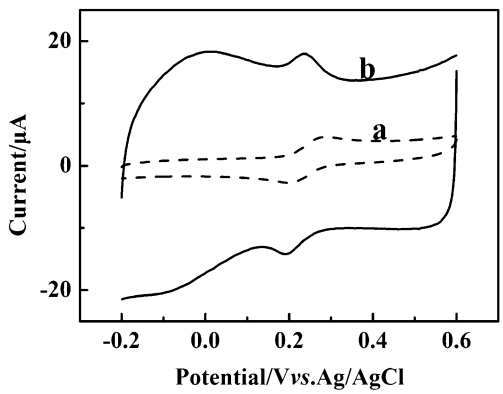

Fig. 2 CVs of 1×10^{-5} mol L^{-1} catechol at a bare GCE (a) and the MWNTs/P3MT/ GCE (b) in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution with a scan rate of 100 mV s^{-1}

DPV for the detection single solution of hydroquinone and catechol

DPV was used for the determination of dipheonls, because of its much higher current sensitivity and better resolution than cyclic voltammetry. Figure 4 showed DPVs of different concentrations hydroquinone in 0.1 mol L^{-1} pH 6.4 phosphate buffer solution. Before each of determination need enrichment stirring 300 s. The relative deviation was 2.5 % for seven successive determinations at 0.02 μmol L^{-1} hydroquinone, which indicated that the modified electrode

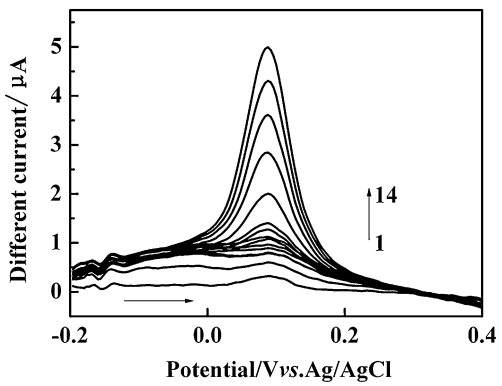

Fig. 4 DPVs (background correction) of different concentrations hydroquinone at the MWNTs/P3MT/GCE. Concentrations: 0.02,0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.8, 1, 2, 4, 6, 8, 10 μmol L^{-1}. Potential range: −0.2–0.4 V (vs. Ag/AgCl); Incr E (V): 0.004; Amplitude (V):0.05; Pulse Width (sec): 0.2; Sample Width (sec): 0.02; Pulse Period (sec): 0.5; Quiet Time (sec):2

has a good reproducibility for hydroquinone. After each of determination the electrode was treated in pH 7.0 phosphate buffer solution by repetitive scanning until a stable background was obtained. As shown in Fig. 4, it was evident that electron transfer reaction was enhanced, and the modified electrode showed positive and effective electro-catalysis for the oxidation of hydroquinone. It can be found that the differential pulse peak heights of hydroquinone were linearly related to the hydroquinone concentration over three concentration intervals, viz. 0.02–0.06 μmol L^{-1}, 0.08–0.4 μmol L^{-1} and 0.8–10 μmol L^{-1} as shown in Fig. S1 and Fig. S2 (see Supplementary material), the linear regression equations, respectively:

$$I_{Pa1}/\mu A = 0.2157 + 0.806\ c/(\mu mol\ L^{-1}), (R = 0.9995)(0.02 - 0.06\ \mu mol\ L^{-1})$$
$$I_{Pa2}/\mu A = 0.2536 + 0.3977\ c/(\mu mol\ L^{-1}), (R = 0.9936)(0.08 - 0.4\ \mu mol\ L^{-1})$$
$$I_{Pa3}/\mu A = 0.8229 + 0.3942\ c/(\mu mol\ L^{-1}), (R = 0.9967)(0.8 - 10\ \mu mol\ L^{-1})$$

The corresponding slopes (sensitivity) were 0.806, 0.3977, 0.3942 μA/(μmolL^{-1}), the correlation coefficients were 0.9995,0.9936,0.9967 mentioned above respectively. The detection limit was 12 nmol L^{-1}(S/N=3). From the decreased slopes with increasing hydroquinone concentrations, it can be presumed that the main contributions to the peak currents of hydroquinone were changed gradually from the absorption of hydroquinone at the electrode surface into the diffusion of hydroquinone to the electrode surface.

A similar experiment was done with catechol, and the results as shown in Fig. S3, the relative deviation was 2.1% for seven successive determinations at 0.1 μmol.L^{-1} catechol, which indicated that the modified electrode has a good reproducibility for catechol. The differential pulse peak heights of catechol were linearly related to the catechol concentration over three concentration intervals, viz. 0.1–0.4 μmol L^{-1}, 0.4–0.6 μmol L^{-1} and 0.8–10 μmol L^{-1} as shown in Fig. S4 and Fig. S5, the linear regression equations, respectively:

$$I_{Pa1}/\mu A = 0.03725 + 1.895\ c/(\mu mol\ L^{-1}), R = 0.9986(0.1 - 0.4\ \mu mol\ L^{-1})$$
$$I_{Pa2}/\mu A = 0.3647 + 0.91\ c/(\mu mol\ L^{-1}), R = 0.9973(0.4 - 0.6\ \mu mol\ L^{-1})$$
$$I_{Pa3}/\mu A = 1.173 + 0.2777\ c/(\mu mol\ L^{-1}), R = 0.9940(0.8 - 10\ \mu mol\ L^{-1})$$

The corresponding slopes (sensitivity) were 1.895, 0.91, 0.2777 μA/(μmol L^{-1}), the correlation coefficients were 0.9986,0.9973,0.9940 mentioned above respectively. The detection limit was 40 nmol L^{-1} (S/N=3). The slopes of the three linear regions also decreased with increasing concentrations of catechol, the reason for which was similar with that of hydroquinone. By contrast with the latest work by Zhao et al. [2], in which the poly-amidosulfonic acid (PASA)/MWNTs composite film modified glassy carbon electrode was used for detection of hydroquinone and

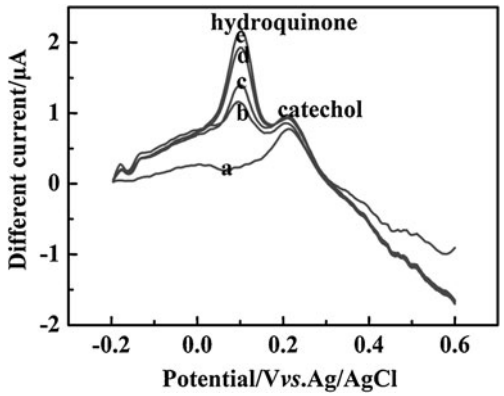

Fig. 6 DPVs (background correction) of various concentrations of hydroquinone in 5×10^{-7} mol L^{-1} catechol solution at the MWNTs/P3MT/GCE. Concentrations: a. no hydroquinone; b.1 μmol L^{-1}; c. 2 μmol L^{-1}; d. 3 μmol L^{-1}; e. 5 μmol L^{-1}. Other conditions were the same as in Fig. 4

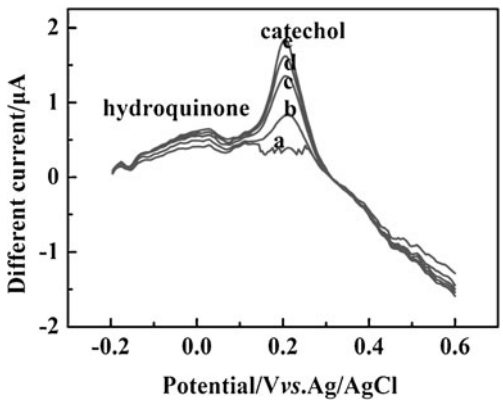

Fig. 5 DPVs (background correction) of various concentrations of catechol in 5×10^{-7} mol L^{-1} hydroquinone solution at the MWNTs/P3MT/GCE. Concentrations: a. no catechol; b.1 μmol L^{-1}; c. 2 μmol L^{-1}; d. 3 μmol L^{-1}; e. 5 μmol L^{-1}. Other conditions were the same as Fig. 4

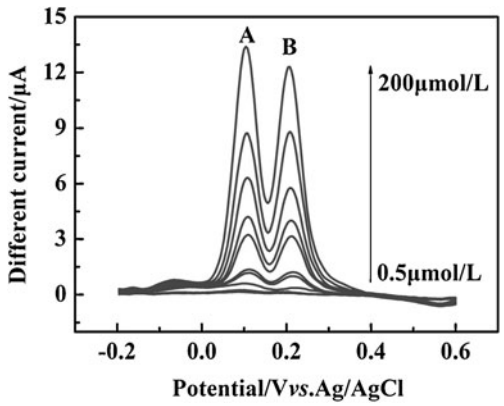

Fig. 7 DPVs (background correction) of hydroquinone and catechol at the MWNTs/P3MT/GCE. Concentrations of both hydroquinone and catechol were simultaneously changed, hydroquinone = catechol: 0.5, 1.0, 2.0, 3.0, 5.0, 10, 20, 50, 100, 200 μmol L^{-1}. Other conditions were the same as in Fig. 4

catechol, and the detection limit was about 1.0 μmol L^{-1} for both dipheonls, which was somewhat higher than that of the MWNTs/P3MT/GCE proposed in the present work. Compared with the broader mono-liner range of the poly (aniline-co-aminophenol)/GCE (5–500 μmol L^{-1}) [28], the present electrode was more suitable for the detection of the low concentrations of diphenols.

DPV for the detection mixed systems of hydroquinone and catechol

To learn more about the electrochemical response when hydroquinone and catechol coexist, we tested the voltammetric behaviors of hydroquinone (or catechol) by DPV in 0.1 mol L^{-1} phosphate buffer solution (pH 6.4). Figure 5 showed the DPV of 5×10^{-7} mol L^{-1} hydroquinone with coexisting catechol from 0 to 5 μmol L^{-1}(**a–e**). It can be seen that further increasing the catechol concentration will cause the oxidation peak of hydroquinone to disappear.

A similar experiment was done with catechol, and the results were shown in Fig. 6. When the concentration of coexisting hydroquinone increased from 0 to 5 μmol L^{-1}(**a–e**), the response of 5×10^{-7} mol L^{-1} catechol at the MWNT/P3MT/GCE remained unchanged. Although there is a competitive absorption of hydroquinone and catechol at the MWNTs/P3MT/GCE, the competitive absorption equilibrium can be attained at suitable concentrations. Thus, this method was suitable for the simultaneous determination of hydroquinone and catechol concentrations.

The utilization of the MWNTs/P3MT/GCE for the simultaneous determination of hydroquinone and catechol were demonstrated by simultaneously changing their concentrations, as shown in Fig. 7. The DPV results indicated that the simultaneous determination of hydroquinone and catechol with a well-distinguished two peaks at potentials 102 mV vs. Ag/AgCl and 203 mV vs. Ag/AgCl, corresponding to the reduction hydroquinone and catechol, respectively, could be possible at the MWNTs / P3MT/GCE.

As shown in Fig. S6 and Fig. S7, the peak currents of hydroquinone and catechol increased linearly with the concentrations of their own in the range of 5×10^{-7}–2×10^{-4} mol L^{-1}. The differential pulse peak heights of hydroquinone were linearly related to the hydroquinone concentration over two concentration intervals, viz. 0.5–5.0 μmol L^{-1} and 10–200 μmol L^{-1}, the linear regression equations, respectively:

$$I_{Pa1}/\mu A = 0.03045 + 0.2791\ c/(\mu mol\ L^{-1}), R = 0.9870(0.5 - 5.0\ \mu mol\ L^{-1})$$
$$I_{Pa2}/\mu A = 3.211 + 0.05184\ c/(\mu mol\ L^{-1}), R = 0.9950(10 - 200\ \mu mol\ L^{-1})$$

The corresponding slopes (sensitivity) were 0.2791, 0.05184 μA /(μmol L^{-1}) in the two linear regression equations, the correlation coefficients were 0.9870 and 0.9950 mentioned above respectively.

Figure S7 showed the differential pulse peak heights of catechol were linearly related to the catechol concentration over two concentration intervals, viz. 0.5–5.0 μmol L^{-1} and 10–150 μmol L^{-1}, the linear regression equations, respectively:

$$I_{Pa1}/\mu A = -0.07694 + 0.2622\ c/(\mu mol\ L^{-1}), R = 0.9905(0.5 - 5.0\ \mu mol\ L^{-1})$$
$$I_{Pa2}/\mu A = 3.153 + 0.04795c/(\mu mol\ L^{-1}),\ R = 0.9894(10 - 150\ \mu mol\ L^{-1})$$

The corresponding slopes (sensitivity) were 0.2622, 0.04795 μA/(μmol L^{-1}) in the two linear regression equations, the correlation coefficients were 0.9905 and 0.9894 mentioned above respectively.

The detection limit was 50 nmol L^{-1} (S/N=3) for hydroquinone and catechol at the MWNTs / P3MT/GCE, which suggested that the fabricated electrode was suitable for the simultaneous detection of mixed systems of diphenols, and the method was simple, rapid, and accurate. The detection limit was lower than the PASA/MWNTs composite film modified glassy carbon electrode (1.0 μmol L^{-1}) [2]. Further work will be undertaken for the simultaneous detection of diphenols in real wastewater samples.

Conclusion

This work developed a direct simultaneous determination method for hydroquinone and catechol by CV and DPV at the MWNTs/P3MT/GCE. The significant increase in peak current together with the sharpness of the peak was observed at the MWNTs/P3MT/GCE, which clearly demonstrated the MWNTs/P3MT/GCE acted as an efficient promoter to enhance the kinetics of the electrochemical process of hydroquinone and catechol. The DPV results indicated that the simultaneous determination of hydroquinone and catechol with a well-distinguished two peaks at potentials 102 mV vs. Ag/AgCl and 203 mV vs. Ag/AgCl, corresponding to the reduction hydroquinone and catechol, respectively, could be possible at the MWNTs/P3MT/GCE. The results showed that the methods were simple and rapid with high accuracy. Thus, the MWNTs/P3MT/GCE has a better application prospect for the highly selective quantitative determination of hydroquinone and catechol, alone or mixed as commonly found in water samples.

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