

# Electrochemical Determination of Hydroquinone and Catechol Using Multi-walled Carbon Nanotubes/ eosin Y Modified Glassy Carbon Electrode

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Received: 12 March 2019 / Accepted: 7 May 2019 / Published: 10 June 2019

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A new glassy carbon electrode modified with eosin Y (EY) and multiwalled carbon nanotubes (MWCNTs) film was fabricated. The modified electrode was used for highly selective and sensitive determination of hydroquinone (HQ) and catechol (CC). The electrode combined the advantages of using EY and MWCNTs, and exhibited a dramatic electrocatalytic effect on the oxidation of HQ and CC. The modified GCE showed two well-defined redox peaks for HQ and CC in cyclic voltammetry (CV) with a peak potential separation of 110 mV, which ensured the anti-interference ability of the electrochemical sensor and made simultaneous determination of dihydroxybenzene isomers possible in real samples. The oxidation peak currents were linear to HQ/CC in the range from  $4.0 \times 10^{-7}$  to  $5.0 \times 10^{-5}$  M with the detection limits of  $1.0 \times 10^{-8}$  M (S/N=3) for HQ and  $1.5 \times 10^{-8}$  M (S/N=3) for CC, respectively. In addition, the proposed sensor was successfully applied to the simultaneous determine HQ and CC in real water samples with reliable recovery.

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**Keywords:** Hydroquinone; Catechol; eosin Y; Multi-walled carbon nanotubes; Simultaneous determination

## 1. INTRODUCTION

Phenolic compounds are widely used chemical raw materials, and also a class of organic pollutants that are harmful to both humans and environment. Catechol (CC) and hydroquinone (HQ) are each other's isomers, owing to their similar physical and chemical properties, they usually coexist in environmental samples and interfere with each other [1, 2]. Therefore, it is difficult to separate and analyze quantitatively by chemical or physical methods. To date, various methods have been developed for simultaneously determining dihydroxybenzene isomers, such as high performance liquid

chromatography [3], synchronous fluorescence [4], chemiluminescence [5], spectrophotometry [6], capillary electrophoresis [7] and electrochemical methods [8–13]. Among them, the electrochemical methods with the advantage of low cost, automatic and fast analysis, excellent sensitivity and selectivity and free of complicated sample pretreatment procedures have triggered enormous research activities, but it is essential to prepare a suitable working electrode to extend the dynamic range for the analytical determination if the electrochemical techniques are used.

In practice, significant advantages have been achieved using organic molecules to develop electrochemical sensors for measuring chemical compounds. Organic molecules can be easily prepared as film electrodeposited over different substrates with good stability, reproducibility, more active sites, homogeneity in electrochemical deposition and strong attachment to electrode surface [14, 15]. Organic dyes, such as crystal violet [16, 17], malachite green [18] and thionine [19] have been used for electrode modified materials for simultaneously determination of HQ and CC. Eosin Y (2', 4', 5', 7'-tetrabromofluorescein disodium salt), a xanthene dye containing bromine atoms, is widely used as fluorescent probe, sensitizer and so on [20–22]. As demonstrated in previous study, an eosin Y film modified electrode can also be applied to study the electrocatalytic properties of catechol (CC) and hydroquinone (HQ) [23].

Carbon nanotubes (CNTs) have captured much attention as an electrode material because of their high surface area, specific conductivity formation, stable chemical property and tensile strength [24–27]. CNTs have excellent ability to mediate fast electron transfer kinetics for electrochemical sensing and show electrochemical catalytic activity towards theophylline [28] and hydrogen peroxide [29]. CNT/conducting polymer composites are often used to fabricate the modified electrode as the electrical and mechanical properties of polymers can be improved by the CNTs [30, 31] and the obtained CNT/conducting polymer composites possess properties of the individual components with a synergistic effect [32–34].

In the present study, for the first time, we benefited from multi-walled carbon nanotubes (MWCNTs) high electrical conductivity and high surface area as well as good stability and reproducibility ability of eosin Y along with low toxicity. We explored to fabricate a novel nanocomposite combining MWCNTs and eosin Y on the GCE by coating MWCNTs on to the electrochemically deposited eosin Y surface. At the MWCNTs / EY /GCE, HQ and CC exhibited two corresponding, well-defined oxidation peaks with sufficiently differing peak potential and enhanced peak currents. The detection performance for HQ and CC was examined by differential pulse voltammetry (DPV) and a real analysis in local tap water also carried out.

## 2. MATERIALS AND METHODS

### 2.1 Materials

MWCNTs were purchased from Chengdu Institute of Organic Chemistry (China). Hydroquinone (HQ), catechol (CC) and eosin Y were obtained from Sigma-Aldrich (USA). All other reagents were of analytical grade and provided by Shanghai Chemical Reagent Co., Ltd (China). For study of pH effect 0.1 mol·L<sup>-1</sup> phosphate buffer solutions (PBS) with different pH values were used.

The stock solution ( $1 \text{ mmol}\cdot\text{L}^{-1}$ ) of HQ or CC was freshly prepared by dissolving HQ or CC in a PBS ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ , pH 6.85). The water used was double-distilled.

## 2.2 Apparatus

The electrochemical experiments were conducted on a CHI660C electrochemical workstation (ShangHai ChenHua Instruments, China). A conventional three-electrode cell was used in the experiments, consisting of the modified electrodes and bare GCE ( $\Phi = 3 \text{ mm}$ ), an Ag/AgCl reference electrode and a platinum wire auxiliary electrode, was employed. Ultrasonic cleaner (BRANSON2000, USA) was used in this experiment. The pH value of buffer solution was measured with a pHs-3C meter (Leici Devices Factory of Shanghai, China).

## 2.3 Preparation of the modified electrode

The glassy carbon electrode (GCE) was polished with 1, 0.3 and  $0.05 \mu\text{m}$  alumina powder, respectively, and then washed ultrasonically in 1:1  $\text{HNO}_3$  (v/v), ethanol and doubly distilled water for 30 s, respectively. After rinsing with distilled water, the electrode was electrochemically subjected to potential cycling between  $-0.4$  and  $1.6 \text{ V}$  in  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$  at  $100 \text{ mV}\cdot\text{s}^{-1}$  until a steady state was reached. Then, the pretreated GCE was obtained. The eosin Y film in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  of phosphate buffer solution (PBS) (pH = 7.0) containing  $1.0\times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  eosin Y was prepared on the surface of the pretreated GCE by electrodeposited with a scanning rate of  $100 \text{ mV}\cdot\text{s}^{-1}$  from  $-1.6$  to  $1.5 \text{ V}$  for 15 cycles. Thus, a EY/GCE was obtained. One milligram of treated MWCNTs was dispersed in 2 mL DMF/ $\text{H}_2\text{O}$  (1:1) with the aid of an ultrasonic bath for 30 min. the eosin Y/GCE was treated by dropping  $5 \mu\text{L}$  of the MWCNTs suspension ( $0.50 \text{ mg}\cdot\text{mL}^{-1}$ ) and dried for 4 h at room temperature. The modified electrode was donated as MWCNTs/EY/GCE. The MWCNTs/GCE was prepared through similar procedure for comparison. The electrodes were stored at  $4 \text{ }^\circ\text{C}$ .

## 2.4 Electrochemical determination of HQ and CC

Before voltammetric measurements, the modified electrodes were firstly activated with a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$  in  $0.1 \text{ mol}\cdot\text{L}^{-1}$  PBS (pH 6.85). Then, cyclic voltammetric (CV) behavior of two dihydroxybenzene isomers (HQ or CC) was characterized between  $-0.4 \text{ V}$  and  $0.4 \text{ V}$  in a PBS ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ , pH 6.85) respectively. Based on the voltammetric behavior, a simple analytical method to determination of HQ and CC was carried out by differential pulse voltammogram (DPV) technique.

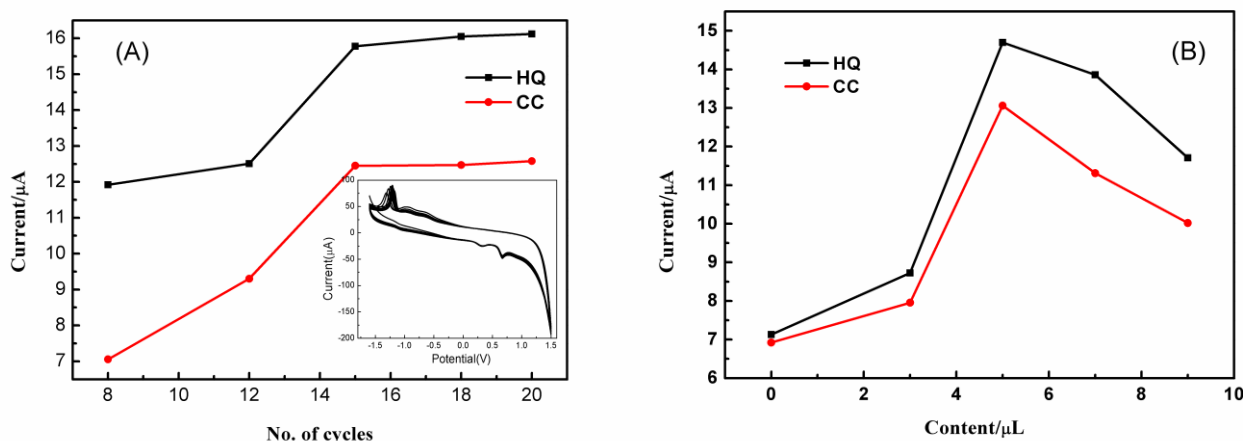
## 3. RESULTS AND DISCUSSION

### 3.1 Optimization of experimental conditions

#### 3.1.1 Optimization of electrochemical polymerization cycles

It is well known that the thickness of the polymer film is directly related to the number of potential cycles during electrodeposited [35-37] owing to the growth of the polymer films on the

electrode is continuous with the increase of cycle number of CV. Film thickness can be effectively controlled by changing the scan cycle number during the electrodeposition process. The effect of film thickness, determined by the number of electrodeposited scans, was studied on the response of HQ and CC. The prepared GC electrode was electrochemically deposition with different cycles. Then, the same concentration (0.5 mg/mL) of MWCNTs with 5  $\mu\text{L}$  was coated on the EY/GCE. The catalysis of CC and HQ were studied by the MWCNTs/EY/ GC modified electrode. Figure 1A showed that the catalytic current increased with the increase of electrodeposited cycles to 15. A further increase in the number of cycles caused the current response to be slightly lowered. This behavior indicated the charges or electrons of HQ and CC would take longer time to transfer through a thicker EY film to the electrode surface. A thick film is not beneficial for electrode response due to the increase in diffusion barrier. the activity of polymer films was reduced most probably owing to thicker films [19, 36-38]. So, 15 cycles of electrodeposited was chosen as the optimum condition and used in further experiments.



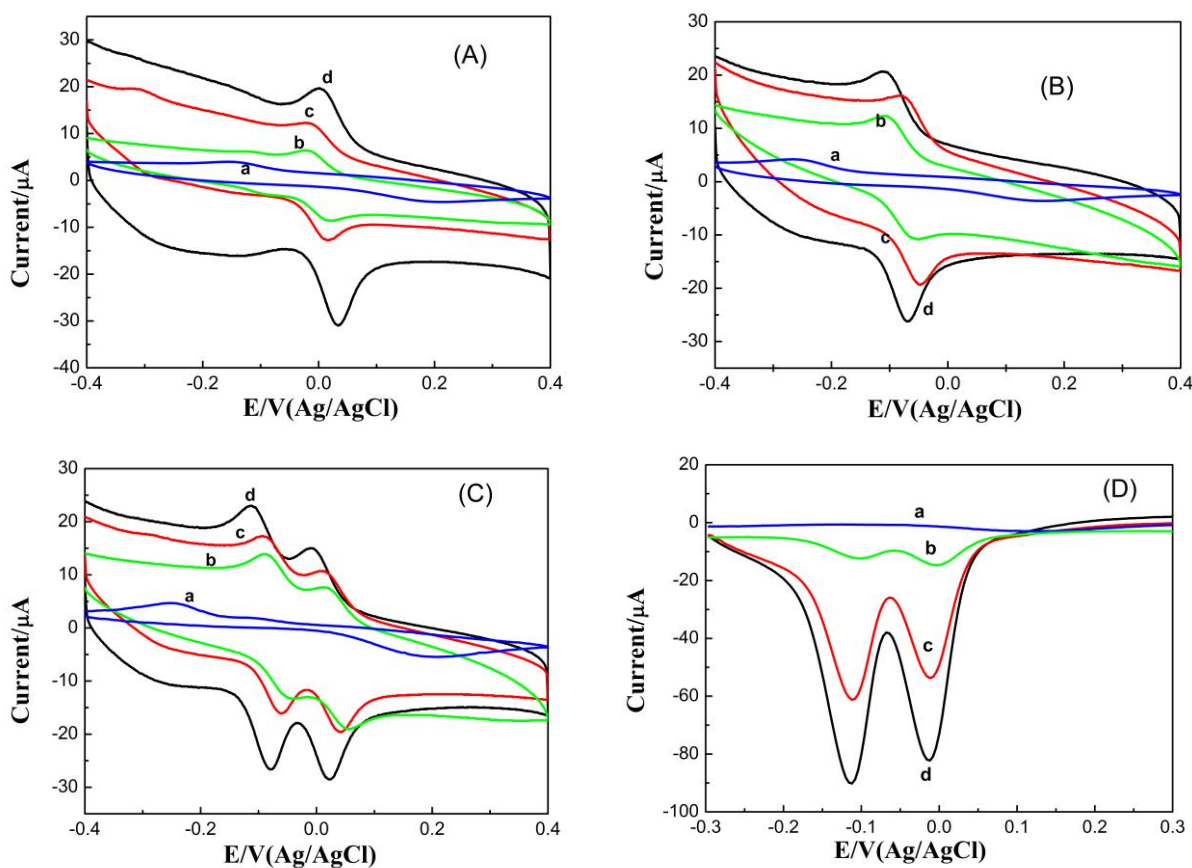
**Figure 1.** (A) Dependence of the anodic peak currents of HQ and CC (0.5 mM of each) on the number of cycles of CVs during the electrodeposition of eosin Y, the inserted chart is CV of the electrodeposition of eosin Y; (B) Dependence of the anodic peak currents of HQ and CC (0.4 mM of each) on MWCNTs content, scan rate:  $50 \text{ mV} \cdot \text{s}^{-1}$ .

### 3.1.2 Optimization of MWCNTs content

The prepared GCE was electrochemically deposition of eosin Y with 15 cycles. Then, the same concentration (0.5 mg/mL) of MWCNTs with different volume of 3, 5, 7, 9  $\mu\text{L}$  was modified on the EY/GCE. Fig. 1B showed the variations in the electrocatalytic nature of the MWCNTs/EY/ GCE with the different content of MWCNTs. The catalytic current increased with the increase of MWCNTs but reduced when the content of MWCNTs was more than 5  $\mu\text{L}$ . That means the film become certain thicker, which hindered the electron transfer and was not conducive enough to react with the substrate. So, 5  $\mu\text{L}$  MWCNTs was chosen as the optimum content.

## 3.2 Electrochemical behaviors of HQ and CC on the MWCNTs/EY/GCE

Figure 2A and B showed the electrochemical responses of  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  HQ and CC in  $0.1 \text{ mol} \cdot \text{L}^{-1}$  pH 6.85 PBS at different electrodes, respectively. At the bare GCE, the redox peaks of HQ and CC were shown at  $-0.265/0.165$  and  $-0.156/0.211 \text{ V}$ , respectively. The differences between anodic and cathodic peaks ( $\Delta E_p$ ) were determined to be  $430 \text{ mV}$  and  $367 \text{ mV}$ , respectively. Correspondingly, for the EY modified electrode (curve b), the current peaks of HQ and CC greatly increased and the  $\Delta E_p$  were reduced to  $60 \text{ mV}$  and  $45 \text{ mV}$ , respectively. At the MWCNTs/GCE (curve c), the  $\Delta E_p$  were extensively reduced to  $35 \text{ mV}$  and  $36 \text{ mV}$ . The further increased peak currents were observed at the MWCNTs/PEY modified electrode (curve d), the redox peaks were measured at  $-0.111/-0.068$  and  $0.001/0.034 \text{ V}$  and the  $\Delta E_p$  were extensively all reduced to  $33 \text{ mV}$ .



**Figure 2.** CVs of  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  CC (A),  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  HQ (B), a mixture of  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  HQ and  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  CC (C) and DPV of the mixture of HQ and CC at the different modified electrodes based on GCE (curve a), EY/GCE (curve b), MWCNTs/GCE (curve c) and MWCNTs/EY/GCE (curve d) in  $0.1 \text{ M}$  phosphate buffer (pH 6.85) at scan rate:  $100 \text{ mV} \cdot \text{s}^{-1}$ .

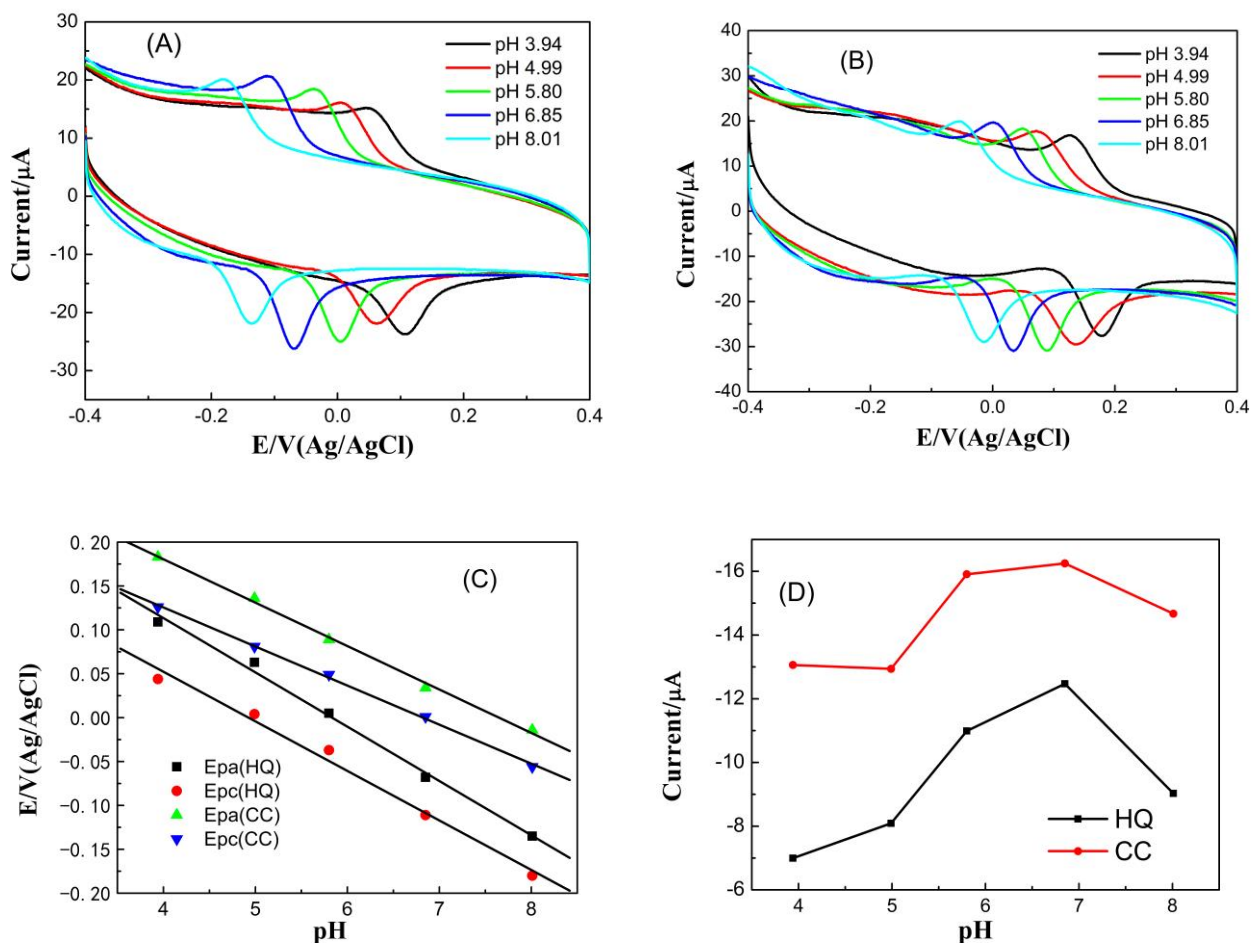
Figure 2C showed the cyclic voltammetric electrochemical responses of the mixture of HQ and CC in  $0.1 \text{ mol} \cdot \text{L}^{-1}$  pH 6.85 PBS at four electrodes. At a bare GCE, the mixture of HQ and CC exhibited a poor electrochemical response (Fig. 2, curve a) and the redox responses of HQ and CC could not be distinguished. Except for the bare GCE, two pairs of peaks were exhibited, which indicated that the oxidation and reduction peaks of HQ and CC can be separated at other three

modified electrodes. And, at the EY/GCE (curve b), two small redox peaks appeared. Although both the oxidation and the reduction peaks of CC and HQ separated well at the MWCNTs/GCE (curve c), their peak currents were still smaller than those at the MWCNTs/EY/GCE (curve d). As shown in Fig. 2D, the oxidation peaks of HQ and CC were clearly resolved in DPV with peak potentials of - 0.111 V and - 0.001 V and peak separation of 110 mV, at the MWCNTs/EY/GCE. Obviously, the inset of the electrochemical response was consistent with that of CVs. The excellent performance of MWCNTs/EY/GCE demonstrated that the MWCNTs/EY composite film act as an efficient promoter to enhance the electrochemical process, which was probably caused by the synergistic effect of the electro-catalytic property of EY and MWCNTs. These results indicated that the MWCNTs/EY composite film modified electrode can not only identify the HQ and CC simultaneously, but also improved the detection sensitivity.

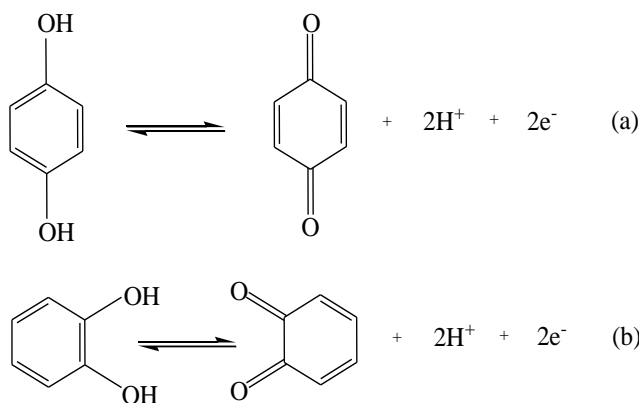
### 3.3 Effect of the experimental conditions

#### 3.3.1 Effect of solution pH

Acidity of electrolyte has a significant effect on the HQ and CC electrooxidation because protons participate in the electrode reaction. In this work, some supporting electrolytes, such as phosphate buffer solution ( $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ , PBS),  $\text{NaOH-KH}_2\text{PO}_4$ , acetate buffer solution ( $\text{HAc-NaAc}$ ) and Britton-Robinson buffer solution (B-R) were investigated to optimize the response of HQ and CC at MWCNTs/EY/GCE. The results showed that in  $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$  buffer solution, both HQ and CC exhibited well-defined and sensitive peaks. Therefore, the supporting electrolyte of PBS was the best choice. The influence of pH on the response of HQ and CC at MWCNTs/EY/GCE was studied by CV in PBS over a pH range of 3.94-8.01 (Fig. 3(A) and 3(B)). The formal peak potentials of both HQ and CC negatively shifted with the increase of solution pH from 3.94 to 8.01 (Fig. 3(C)). The equations for peak potential with the pH for HQ and CC can be expressed as:  $E_{pa}(\text{HQ}) = 0.361 - 0.0618 \text{ pH}$  ( $R=0.997$ ),  $E_{pc}(\text{HQ}) = 0.278 - 0.0565 \text{ pH}$  ( $R=0.992$ ),  $E_{pa}(\text{CC}) = 0.309 - 0.0453 \text{ pH}$  ( $R=0.999$ ) and  $E_{pc}(\text{CC}) = 0.378 - 0.0495 \text{ pH}$  ( $R=0.998$ ), respectively. The slopes of the four regression equations were close to the theoretical value of 59 mV per pH unit for an equal number of electrons ( $e^-$ ) and protons ( $\text{H}^+$ ) process based on the Nernst Equation. Therefore, the oxidation of the reaction mechanism of HQ and CC at MWCNTs/EY/GCE followed the 2 electron and 2 proton transfer process [19, 39] as scheme 1. Fig. 3(D) showed that the anodic peak currents of HQ and CC increased as pH change from 3.94 to 6.85, decreased with further increase of pH. Thus, this value of 6.85 was selected as the optimum pH for the determination of HQ and CC.



**Figure 3.** CVs of MWCNTs/ EY /GCE in pH 3.94.0–8.01 PBS containing  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  HQ (A) and  $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  CC (B). (C)  $E_p$ –pH relationships of HQ and CC. (D)  $I_{pa}$ –pH relationships of HQ and CC.

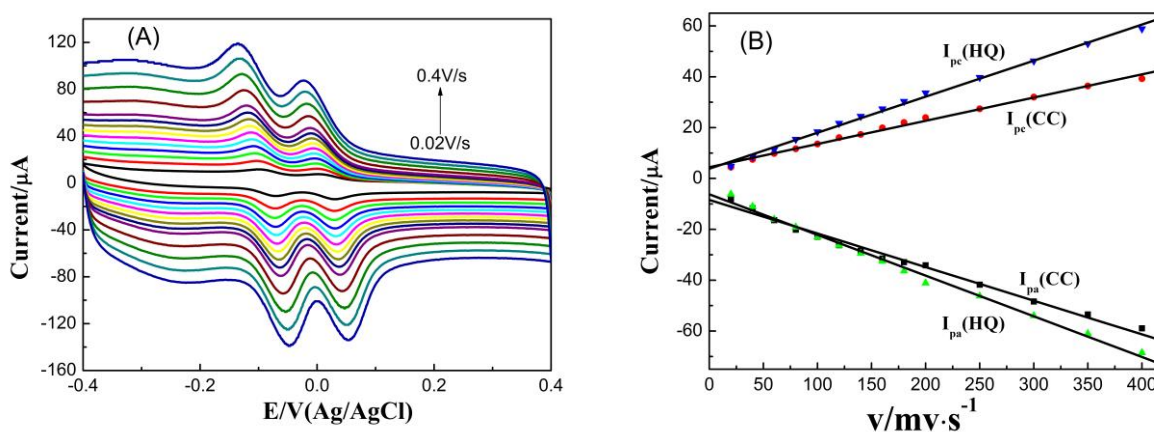


**Scheme 1.** the reaction mechanism of HQ (a) and CC (b) on the modified electrode

### 3.3.2 Effect of scan rate

The influence of scan rate on the peak current of HQ ( $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) and CC ( $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) in the mixture was also examined at MWCNTs/EY/GCE by CV. It can be seen that both the

redox peak currents of HQ and CC enhanced regularly with increase of scan rates from 20 to 400  $\text{mV}\cdot\text{s}^{-1}$ . Moreover, further studies indicated that the peak current ( $I$ ) and the scan rate ( $\nu$ ) showed a typical linear relationship with the equations: HQ:  $I_{pc}$  ( $\mu\text{A}$ ) =  $0.1417\nu + 3.8400$  ( $\nu$  in  $\text{mV}\cdot\text{s}^{-1}$ ) ( $R=0.998$ ) and  $I_{pa}$  ( $\mu\text{A}$ ) =  $-0.1600\nu - 6.1931$  ( $R=0.995$ ), CC:  $I_{pc}$  ( $\mu\text{A}$ ) =  $0.0913\nu + 4.4506$  ( $\nu$  in  $\text{mV}\cdot\text{s}^{-1}$ ) ( $R=0.995$ ) and  $I_{pa}$  ( $\mu\text{A}$ ) =  $-0.1322\nu - 8.3936$  ( $\nu$  in  $\text{mV}\cdot\text{s}^{-1}$ ) ( $R=0.991$ ). As we know, linear relationship between scan rate and peak currents was a typical adsorption-controlled process [39].



**Figure 4.** (A) CVs of MWCNTs/EY/GCE with  $4\times 10^{-5}$  M HQ and CC in PBS (pH 6.85) at different scan rates from inter to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400  $\text{mV}\cdot\text{s}^{-1}$ . (B) The plots for the dependence of peak current on scan rate.

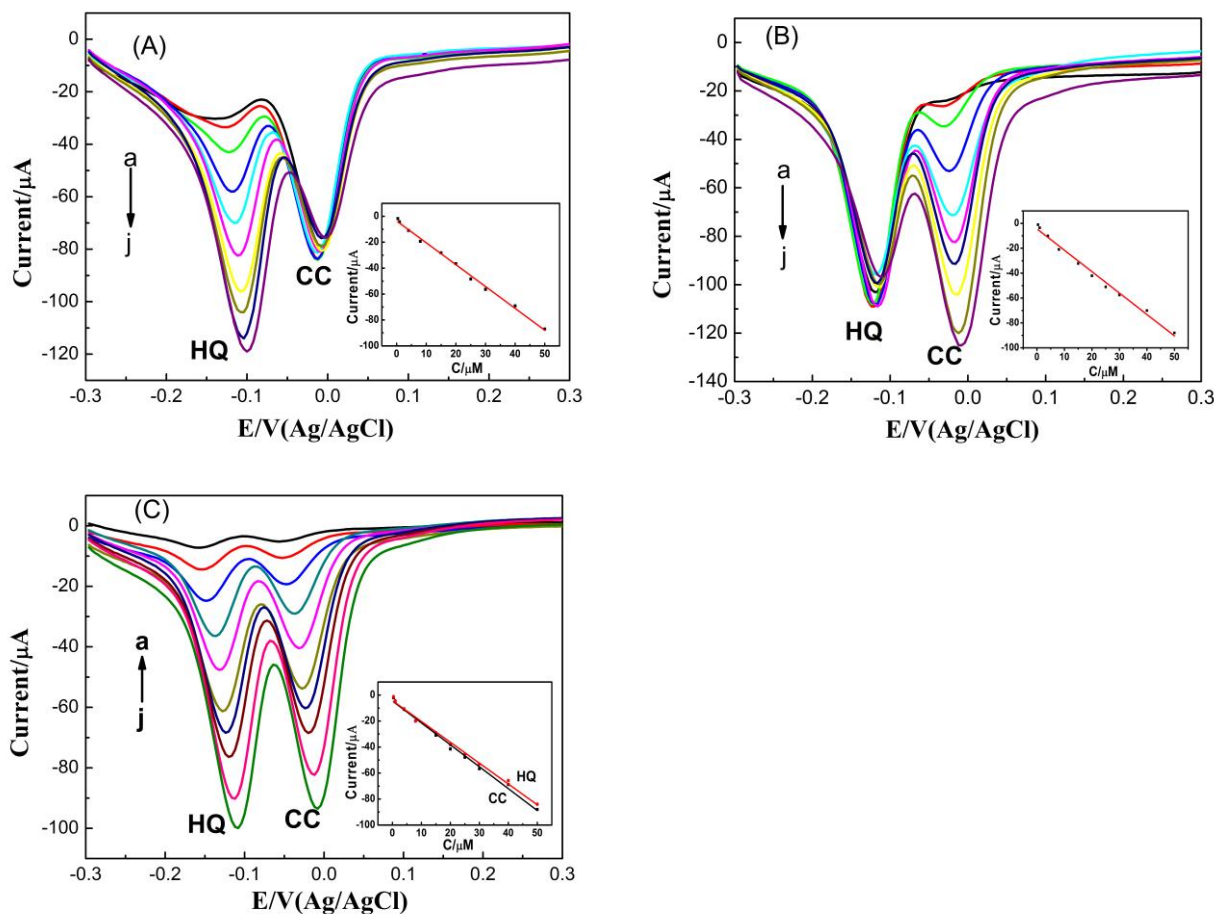
### 3.4. Simultaneous determination of HQ and CC using differential pulse voltammetry

Due to the higher current sensitivity and better resolution of differential pulse voltammetry (DPV) compared with CV, DPVs of HQ and CC at MWCNTs/EY/GCE were recorded and showed in Fig 5. Under the optimal conditions, individual determination of HQ or CC was performed at the MWCNTs/EY/GCE when the concentration of one specie changed and the other specie remained constant. Fig. 5(A) and (B) showed DPV curves of different concentrations of HQ and CC in pH 6.85 PBS with coexisting of  $3\times 10^{-5}$  M isomer. From the inset of Fig. 5(A), the oxidation peak current of HQ was linear with its concentration from  $4\times 10^{-7}$  M to  $5\times 10^{-5}$  M. The regression equation for HQ was  $I_{pa}$  ( $\mu\text{A}$ ) =  $-1.6866C$  ( $\mu\text{M}$ ) -  $3.5966$  ( $R=0.998$ ) with the detection limit of  $5\times 10^{-8}$  M ( $S/N = 3$ ). Similar patterns were observed for CC as shown in (Fig. 5B), the anodic peak current was proportional to the concentration of CC in the range of  $4\times 10^{-7}$  M -  $5\times 10^{-5}$  M with a regression equation of  $I_{pa}$  ( $\mu\text{A}$ ) =  $-1.7205C$  ( $\mu\text{M}$ ) -  $4.3789$  ( $R=0.993$ ) and the LOD was  $8\times 10^{-8}$  M ( $S/N = 3$ ). These results indicated that the oxidation of HQ and CC at MWCNTs/EY/GCE took place independently without any mutual interference.

Fig. 5(C) showed DPV curves of HQ and CC in the mixture solution by simultaneously changing their concentrations. Two well-defined oxidation peaks appeared and the separation of the oxidation peak potentials of HQ and CC was got as 110 mV. The oxidation peak currents ( $I_{pa}$ ) of HQ and CC increased linearly with concentration of their own in the range of  $4\times 10^{-7}$  M -  $5\times 10^{-5}$  M. For HQ, the regression equation was  $I_{pa}$  ( $\mu\text{A}$ ) =  $-1.6044C$  ( $\mu\text{M}$ ) -  $4.2211$  ( $R=0.997$ ), while for CC, the



regression equation was  $I_{pa} (\mu\text{A}) = -1.6856C (\mu\text{M}) - 4.5493$  ( $R=0.997$ ). These results indicated that MWCNTs/EY/GCE can be used effectively can simultaneous determination of HQ and CC without interference. The analytical performance of the MWCNTs/EY/GCE was compared with previously other modified electrodes as shown in Table 1. It showed that for the detection of HQ and CC the proposed method showed lower detection limit and larger linear range than previously reported other modified electrodes [40-44]. So, this MWCNTs/EY modified electrode was efficient and sensitive in simultaneous determination of the isomers.



**Figure 5.** (A) DPV of HQ at MWCNTs/EY/GCE in the presence of  $3 \times 10^{-5}$  M CC and HQ concentrations (from a to j): (a)  $4 \times 10^{-7}$  M, (b)  $1 \times 10^{-6}$  M, (c)  $4 \times 10^{-6}$  M, (d)  $8 \times 10^{-6}$  M, (e)  $1.5 \times 10^{-5}$  M, (f)  $2 \times 10^{-5}$  M, (g)  $2.5 \times 10^{-5}$  M, (h)  $3 \times 10^{-5}$  M, (i)  $4 \times 10^{-5}$  M, (j)  $5 \times 10^{-5}$  M. Supporting electrolyte: 0.1 M PBS (pH 6.85) (B) DPV of CC at MWCNTs/EY/GCE in the presence of  $3 \times 10^{-5}$  M HQ and CC concentrations (from a to j): (a)  $4 \times 10^{-7}$  M, (b)  $1 \times 10^{-6}$  M, (c)  $4 \times 10^{-6}$  M, (d)  $8 \times 10^{-6}$  M, (e)  $1.5 \times 10^{-5}$  M, (f)  $2 \times 10^{-5}$  M, (g)  $2.5 \times 10^{-5}$  M, (h)  $3 \times 10^{-5}$  M, (i)  $4 \times 10^{-5}$  M, (j)  $5 \times 10^{-5}$  M. (C) DPV of various concentrations of HQ and CC (from a to j): (a)  $4 \times 10^{-7}$  M, (b)  $1 \times 10^{-6}$  M, (c)  $4 \times 10^{-6}$  M, (d)  $8 \times 10^{-6}$  M, (e)  $1.5 \times 10^{-5}$  M, (f)  $2 \times 10^{-5}$  M, (g)  $2.5 \times 10^{-5}$  M, (h)  $3 \times 10^{-5}$  M, (i)  $4 \times 10^{-5}$  M, (j)  $5 \times 10^{-5}$  M. Inset: Variation of the DPV oxidation peak currents against their concentration for HQ (inset of 6A), CC (inset of 6B) and mixture of HQ and CC (inset of 6C), respectively.

**Table 1.** Comparison of analytical performances at different materials-based electrochemical sensors for the simultaneous electrochemical determination of HQ and CC.

Modified electrodes	Analytes	Linear range ( $\mu\text{M}$ )	Detection limit (nM)	Reference
RGO–MWCNTs/GCE <sup>a</sup>	HQ	8.0-391	2600	[40]
	CC	5.5-540	1800	
Graphene/chitosan/GCE	HQ	1-300	750	[41]
	CC	1-400	750	
GQDs/GCE	HQ	0.5-100	80	[42]
	CC	0.5-100	80	
p-rGO/GCE	HQ	5-90	80	[43]
	CC	5-120	180	
UiO-66/MC3/GCE	HQ	0.5-100	56	[44]
	CC	0.4-100	72	
MWCNTs/EY/GCE	HQ	0.4-50	10	This work
	CC	0.4-50	15	

<sup>a</sup> RGO-MWCNTs: reduced graphene oxide- multi-walled carbon nanotubes.

### 3.5. Repeatability, reproducibility and stability of MWCNTs/EY/GCE

The repeatability of MWCNTs/EY/GCE was investigated by conducting a series of repetitive measurements, the peak currents of DPV in the mixture solution containing HQ and CC in five successive measurements. The relative standard deviations (*RSD*) for HQ and CC were 2.90% and 2.31%, respectively. The fabrication reproducibility was estimated by using four modified electrodes independently prepared by the same procedure, the *RSD* was 2.74% and 3.88% for HQ and CC, respectively. Additionally, the modified electrode was stored at room temperature for two weeks, the oxidation peak current decreased with the signal change of 4.10% for HQ and 3.51% for CC. This suggested that the MWCNTs/EY/GCE has good repeatability and reproducibility along with a considerable average stability.

### 3.6. Interference studies

The influences of some possible interfering substances on the detection of  $5.0 \times 10^{-5}$  M HQ and CC were performed in 0.1 M PBS (pH 6.85). Experimental results showed that 100-fold  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Fe}^{3+}$ ,  $\text{S}^{2-}$  and 20-fold glucose, ascorbic acid, uric acid did not interfere with the determination (signal change below 5%). MWCNTs/EY/GCE exhibited good selectivity and favorable ability of anti-interference for the simultaneous determination of HQ and CC.

### 3.7. Analytical application

Simultaneous determination of HQ and CC in local tap water (Hefei, PR China) was tested for the assessment of the practical feasibility of the modified electrode by the standard addition method with the results shown in Table 2. A good recovery of HQ (98.53–103.20%) for and CC (97.90–103.45%) was obtained, indicated practical applicability and good reliability of the fabricated MWCNTs/EY electrode for simultaneous determination of HQ and CC.

**Table 2.** Recovery results for HQ and CC in tap water samples

Sample	Analyte	Added ( $\mu\text{M}$ )	Found <sup>a</sup> ( $\mu\text{M}$ )	RSD <sup>b</sup> (%)	Recovery (%)
1	HQ	10	9.99 $\pm$ 0.12	1.77	99.90
	CC	20	20.69 $\pm$ 0.14	1.69	103.45
2	HQ	20	20.64 $\pm$ 0.18	2.16	103.20
	CC	10	9.92 $\pm$ 0.23	2.18	99.20
3	HQ	15	14.78 $\pm$ 0.19	1.82	98.53
	CC	15	14.69 $\pm$ 0.15	1.86	97.90

<sup>a</sup> Standard addition method. <sup>b</sup> Relative standard deviation for 5 successive measurements.

## 4. CONCLUSION

The present study demonstrated an excellent approach for the simultaneous determination of CC and HQ based on MWCNTs/EY composite film modified GC electrode. The improvement of peak current together with sharpness of the peak shape clearly indicated that the MWCNTs/EY composite film acted as an efficient promoter to enhance the electrochemical process, which was probably caused by the synergistic effect of the electrocatalytic property of eosin Y and MWCNTs. Moreover, MWCNTs/EY/GCE was also successfully used for the detection of HQ and CC in tap water and showed reliable recovery. All results show that MWCNTs/EY electrode is a promising candidate for designing effective dihydroxybenzene sensor.

## ACKNOWLEDGEMENTS

This work was supported from National Natural Science Foundation of China (11804003), the stable talent program and the outstanding talent program of Anhui Science and Technology University, the key discipline of Anhui Science and Technology University (AKZDXK2015A01), the first discipline of Anhui Science and Technology University.

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