

Simultaneous Determination of Dihydroxybenzene Isomers by MWCNTs-NTiO₂ Modified Glassy Carbon Electrode

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In this paper, multi-wall carbon nanotubes and nano-titanium dioxide (MWCNTs-NTiO₂) modified electrode is easily prepared by one-step coating. The nano-TiO₂ colloid is prepared by sol-gel method at room temperature to improve the dispersion and electrical conductivity of original MWCNTs on glass carbon electrode (GCE). The electrochemical behaviors of dihydroxybenzene isomers are investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at MWCNTs-NTiO₂/GCE. Hydroquinone (HQ), catechol (CC) and resorcinol (RC) all exhibit sensitive responses at original MWCNTs modified electrode. However, the peak currents of HQ, CC and RC present much enhanced signals at MWCNTs-NTiO₂ modified electrode, proving a good synergetic effect of NTiO₂ and MWCNTs. The individual and simultaneous determination of HQ, CC and RC at MWCNTs-NTiO₂/GCE are studied, and obtains good linear relations in a wide range. The limits of detection for HQ, CC and RC are 93 nmol L⁻¹, 210 nmol L⁻¹ and 32 nmol L⁻¹ (S/N = 3), respectively. This kind of sensor has been applied for simultaneous determination of HQ, CC and RC in artificial wastewater and obtained good results.

Keywords: dihydroxybenzene; electrochemical sensor; MWCNTs; NTiO₂; isomer

1. INTRODUCTION

Hydroquinone (HQ), catechol (CC) and resorcinol (RC) are three isomers of dihydroxybenzene which are widely used in dyes, pharmaceuticals and cosmetics for industrial chemicals [1]. Meanwhile, their high toxicity and low degrade ability attract too much attention [2]. The US Environment Protection Agency (EPA) and the European Union (EU) stipulate that the maximum amount of

phenols in waste water has to be lower than 1 ppm [3]. Owing to their similar structures, properties and coexistence in environment samples and chemical production, it is hard to differentiate them. Therefore, it is essential to develop a simple and high sensitive method for the simultaneous quantitative determination for HQ, CC and RC. There has been many methods to determine the dihydroxybenzene isomers, such as ultraviolet spectrometry [4], gas chromatography/mass spectrometry [5], fluorescence [6], chemiluminescence [7] and electrochemical methods [2, 8, 9]. In recent years, the electrochemical methods raised more concern for its extraordinary advantages of fast response, high selectivity, and low limit of detection [10], especially for the simultaneous determination of isomers with a low cost.

Several materials have been reported for the simultaneous determination of dihydroxybenzene on modified electrode, such as Ag/SiO₂/MWCNT [2], RGO/Au-NPs composite [11], Zn/Al layered double hydroxide film [12], chit-Fe₃O₄-GO/GCE [13] and so on. It can be seen that carbon series nano-materials, nano-particles of metal and metallic oxide are widely used in modified electrode. In this work, MWCNTs and NTiO₂ suspension is coated on GCE for a MWCNTs-TiO₂/GCE easily.

It is well-known that MWCNTs have very high specific surface area (up to 1300 m² g⁻¹), leading to high attractive forces which have to be overcome by a dispersion process [14]. The traditional pretreatment of MWCNTs is needed to be mixed in acid for several hours. It can result in improved dispersion [15], but the structure of the nanotubes can be destroyed and the length can be shortened which will lead to reduced electric properties [16]. In order to solve this problem, nano-TiO₂ is mixed with MWCNTs to improve the dispersion in this experiment. For preparing TiO₂ nanoparticles, various protocols like ionothermal, solvothermal, hydrothermal, co-precipitation, combustion and sol-gel have been reported [17]. Traditional nano-TiO₂ preparation process all need high temperature for several hundreds degrees centigrade. But in present study, room temperature is adopted to prepare nano-TiO₂ collid by sol-gel method. MWCNTs solution is obtained through only dispersion of original MWCNTs in organic solvent without any further treatment. The MWCNTs-NTiO₂ suspension is obtained by an appropriate ratio of volume.

In this manuscript, we are reporting for the first time such facily prepared MWCNTs-NTiO₂ obtained modified glassy carbon electrode for simultaneous determination of dihydroxybenzene isomers. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) shows a satisfied result about the sensitivity, selectivity, repeatability and low limit of detection. The reason is explained by synergistic effect of the nano-composite to improve the dispersion of MWCNTs by their optical micrographs and morphologies. The MWCNTs-NTiO₂/GCE is expected to be a dihydroxybenzene sensor for practical applications.

2. EXPERIMENTAL

2.1 Chemicals

MWCNTs (≥95%) are obtained from The center for eco environment research, Chinese Academy of Science, tetra-n-butyl titanate is obtained from Sinoharm Chemical Reagent Co., Ltd. HQ,

CC, RC and all other chemicals are of analytical reagent grade and used without further purification. Phosphate buffer solution (PBS) is prepared from 0.1 mol L^{-1} KH_2PO_4 and K_2HPO_4 , and the pH can be adjusted by H_3PO_4 and NaOH . All solutions are freshly prepared with doubly distilled water at room temperature.

2.2 Apparatus

Electrochemical experiments are performed with a LK2010 electrochemical workstation (Lanlike, Tianjin, China) [18]. The three-electrode system is used with glassy carbon electrode (GCE, 3mm diameter) or modified electrode as working electrode, platinum electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The optical micrographs of MWCNTs and MWCNTs- NTiO_2 nano-composites films are analyzed using optical microscope (OM, Olympus, BX051). The morphologies of MWCNTs and MWCNTs- TiO_2 nanocomposites are obtained by field-emission scanning electron microscopy (FE-SEM, Zeiss, Ultra55). Besides, ultrasonic cleaner, magnetic stirrer and infrared lamp are used for oscillation, mixing and evaporation, respectively, and detailed use will be mentioned following.

2.3 Preparation of MWCNTs- NTiO_2 Suspension

The MWCNTs- NTiO_2 suspension is prepared by three steps. First, adding 20mg MWCNT into 40 mL anhydrous alcohol and sonicate for 4 hours, then 0.5 mg mL^{-1} MWCNTs is obtained. Second, adding 1 mL tetra-n-butyl titanate and 20 mL 0.2 mol L^{-1} HNO_3 dropwise into 20 mL anhydrous alcohol at room temperature under magnetic stirring, followed by keeping it at $25 \text{ }^\circ\text{C}$ in the oven for 24 h, then 0.074 mol L^{-1} NTiO_2 colloid is obtained. Last, mix the two solutions above in various proportion and then the MWCNTs- NTiO_2 suspension is obtained.

2.4 Electrode Modification

The GCE with diameter of 3mm is polished with alumina/water slurry (Lanlike, Tianjin, China) and then sonicated with water, acetone and ethanol, respectively [19]. Finally, various volumes of the MWCNTs- NTiO_2 suspension is coated on GCE surface, and dried by an infrared lamp.

2.5 Experimental procedure

The cyclic voltammetry is performed with three electrodes by scanning from -300 mV to 900 mV at a scan rate of 100 mV s^{-1} . For differential pulse voltammetry (DPV) measurement, the potential is performed from -50 mV to 900 mV , the step potential is 2 mV , the amplitude is 50 mV , the pulse width is 160 ms and the pulse period is 320 ms . All dihydroxybenzene solutions, except as specially provided, are prepared with 0.1 mol L^{-1} phosphate buffer solution of pH 5.8 as supporting electrolyte for HQ, CC and RC detection.

3. RESULTS AND DISCUSSION

3.1 The electrochemical properties of the MWCNTs-NTiO₂

The macrostructure of different modified electrodes are characterized by OM in Fig. 1. It has been reported that MWCNTs adhere heavily to themselves due to the strong van der Waals force between the MWCNTs caused by their large aspect ratio and nanoscale size [20]. Fig. 1 A reveals severely agglomeration of MWCNTs. Conversely, according to Fig. 1 B, after adding titanium dioxide to MWCNTs, the dispersion quality increases significantly. Then the surface morphologies of MWCNTs and MWCNTs-NTiO₂ nanocomposites are analyzed by SEM in Fig. 2. The MWCNTs shows a heavy agglomeration with themselves in Fig. 2 A. The MWCNTs-NTiO₂ nanocomposites film falls partly and therewith a mass of MWCNTs fractures appear in Fig. 2 B and Fig. 2 C. It is probably the reason that the MWCNTs-NTiO₂/GCE conducts a higher electrical conductivity than MWCNTs/GCE. Thus it can be seen that NTiO₂ plays a vitally important role for the uniform distribution of MWCNTs.

[Fe(CN)₆]^{3-/4-} has been widely used as a molecular probe in the electrochemical studies for its good reversible redox properties [21], which is a single electro transfer reaction ($n = 1$). The active surface area of the modified electrodes is evaluated by Randles-Sevcik formula $i_{pa} = 2.69 \times 10^5 AD^{1/2} n^{2/3} \nu^{1/2} C$, A is the activity of the electrode surface area (cm²), D is the diffusion coefficient of molecules in solution (cm² s⁻¹), n is the number of electro transfer, ν is the scan rate of potential. Under the same conditions of the experiment, except different modified electrodes, the formula can be abbreviated to $i_{pa} = kA$, k is a constant. The electrochemical properties of the MWCNTs-NTiO₂ is characterized by cyclic voltammetry in 1 mmol L⁻¹ K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution containing 0.1 mol L⁻¹ KCl. The cyclic voltammograms of [Fe(CN)₆]^{3-/4-} measured with the bare GCE, MWCNTs/GCE and MWCNTs-NTiO₂/GCE are shown in Fig. 3.

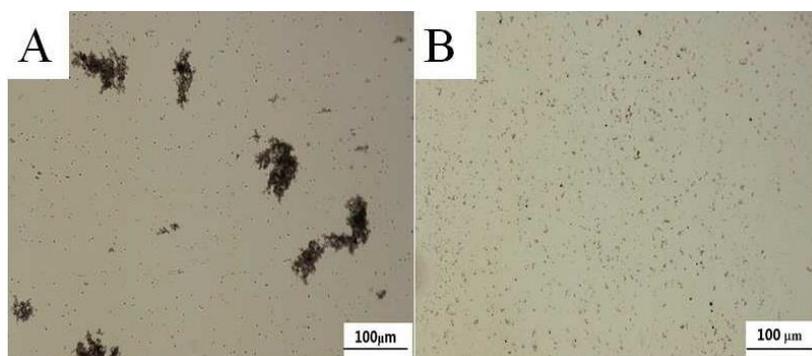


Figure 1. Optical micrographs of the suspensions: (A) MWCNTs, (B) MWCNTs-NTiO₂.

There is a low peak current at the bare GCE (curve a). At the MWCNTs/GCE (curve b), the peak current is higher than that of curve a, and a pair of broad oxidation-reduction peaks appears at 255 mV and 121mV, the redox peak potential separation (ΔE_p) is 134 mV, indicating the excellent electro-catalytic activity of MWCNTs. At the same time, the peak current of MWCNTs-NTiO₂/GCE

(curve c) is 2.54 times than that of MWCNTs/GCE, and ΔE_p of curve c decreases to 80 mV, which is closer to the ideal value of 59 mV. In general, the MWCNTs-NTiO₂/GCE exhibits the highest electrochemical activity. The reason is probably the good dispersion of MWCNTs, which are distributed evenly in GCE to enlarge the surface area of electrode. Therefore, it can be concluded that NTiO₂ can effectively enhance electrical conductivity of MWCNT, and should have a good electrochemical behavior.

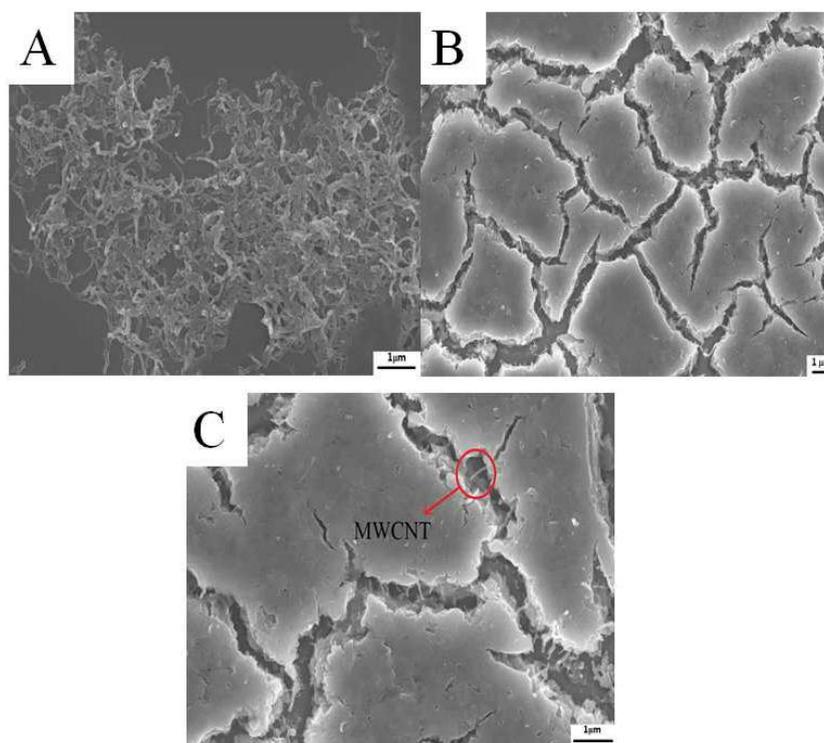


Figure 2. SEM images of the suspensions: (A) MWCNTs (magnification times is 10 k), (B) MWCNTs-NTiO₂ (magnification times is 5 k), (C) MWCNTs-NTiO₂ (magnification times is 10 k).

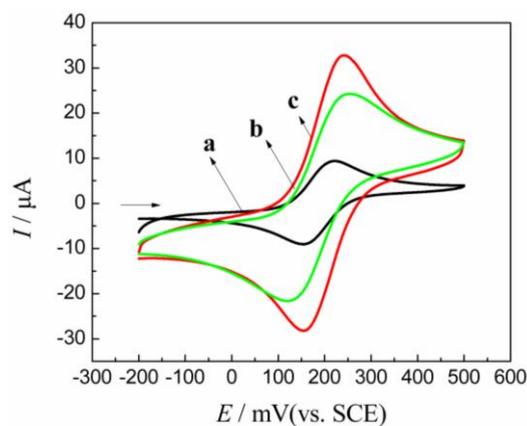


Figure 3. Cyclic voltammograms of different electrodes in pH 7.0 1 mmol L⁻¹ K₃[Fe(CN)₆]/K₄[Fe(CN)₆] containing 0.1 mol L⁻¹ KCl. (a) GCE, (b) MWCNTs/GCE, (c) MWCNTs-NTiO₂/GCE.

3.2 Voltammetric behavior of dihydroxybenzene isomers

The cyclic voltammograms of dihydroxybenzene isomers at bare GCE (curve a), NTiO₂/GCE (curve b), MWCNTs/GCE (curve c), MWCNTs-NTiO₂/GCE (curve d) are shown in Fig. 4. For the bare GCE, there is only one peak, which shows no sharpness of separation for these three isomers. For the NTiO₂/GCE, there are two broad oxidation peaks at the potentials of 377 mV and 778 mV, which indicate that the oxidation peaks overlapped to form a weak and wide oxidation peak. Although there are three obvious redox peaks at MWCNTs/GCE, which reveals HQ, CC and RC can be separated, the peak currents are rather small. These three isomers of dihydroxybenzene all have two hydroxies on a benzene of analogical forms, but for their different structures, their cyclic voltammogram behaviors are different. It is reported that the molecular property is closely related to the molecular orbital structure, the higher the molecular orbital energy is, the more difficult to be oxidized [22]. When the two hydroxy groups in para-position of the benzene, it has the largest charge density, followed with a-position and meta-position being the minimum. Zhenhui compared the HOMO, LUMO and the total molecular energy of o-, m- and p-aminophenol, and concluded that the aminophenol isomers' electro-oxidized sequence is p-aminophenol, o-aminophenol and m-aminophenol, respectively [23]. Benzenediol isomers have the same result as aminophenol, for hydroxyl and amidogen are both electron-donating group. Hence, the order of the peak is HQ, CC and RC, respectively, and it can also be proved in the individual determination of dihydroxybenzene. While at the MWCNTs-NTiO₂/GCE, their oxidation peaks of HQ, CC and RC are 2.37 times, 2.59 times and 2.12 times higher, respectively when compared with curve c, and their separation of oxidation peak potentials are 129 mV and 359 mV, which strongly demonstrates that NTiO₂ plays an important role in the simultaneously, selectively and sensitively determination of HQ, CC and RC.

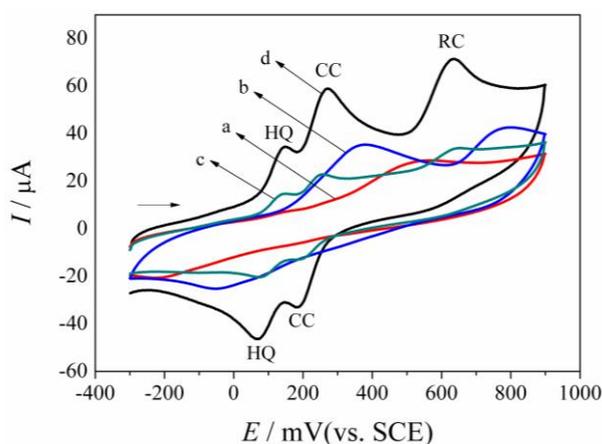


Figure 4. Cyclic voltammograms of 500 $\mu\text{mol L}^{-1}$ HQ, CC and RC in pH 5.8 PBS at different electrodes. (a) GCE, (b) NTiO₂/GCE, (c) MWCNTs/GCE, (d) MWCNTs-NTiO₂/GCE.

Furthermore, the electrochemical behaviors of HQ, CC and RC on MWCNTs-NTiO₂/GCE with different scan rates are studied. It can be seen in Fig. 5 that both the oxidation and reduction peak potentials shift positively and their peak currents increase when improving the scan rate from 40 to 200

mV s^{-1} (a→i). Further study indicates that the peak currents of the three isomers increasing proportionately, which suggest that the electrode process of HQ, CC and RC are adsorption controlled [24].

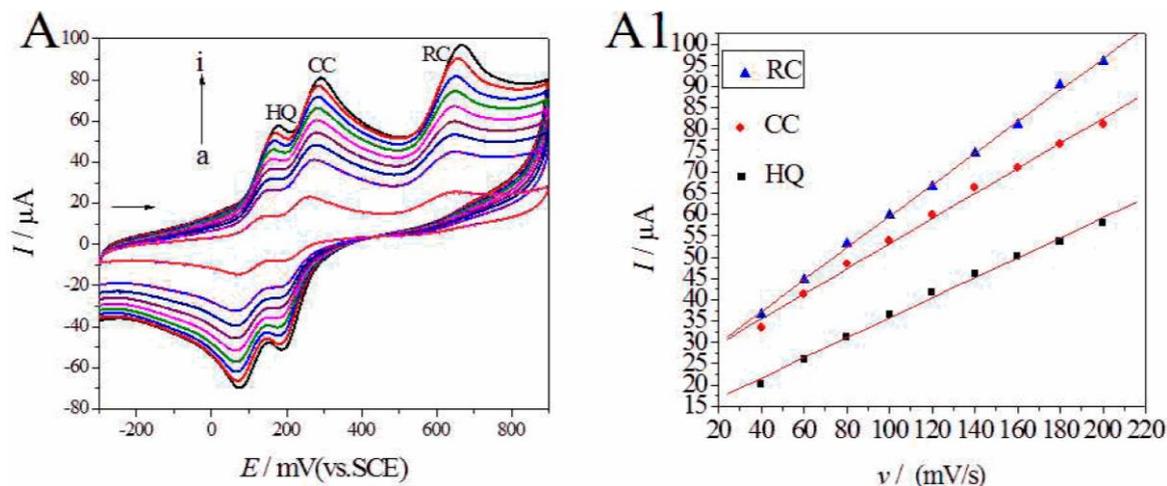


Figure 5. (A). Cyclic voltammograms of $500 \mu\text{mol L}^{-1}$ HQ, CC and RC in pH 5.8 PBS at different scan rates of (a→i): 40, 60, 80, 100, 120, 140, 160, 180, 200 mV s^{-1} . (A1) The relationship of scan rate and i_{pa} of HQ, CC and RC in 0.1 mol L^{-1} PBS.

3.3 Choice of experimental conditions

MWCNTs-NTiO₂ suspension is the mixture of MWCNTs and NTiO₂ colloid, the proportion is a key factor in improving the electrochemical properties of the modified electrode. And the film thickness, which is determined by the coating amounts, is also an important factor that should be studied. The electrochemical behaviors of the MWCNTs-NTiO₂ are characterized by cyclic voltammetry in $1 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution containing $0.1 \text{ mol L}^{-1} \text{ KCl}$. Fig. 6 A shows the trend of oxidation peak currents with different MWCNTs-NTiO₂ volume ratios, and they are set as 1:1, 2:1, 3:1, 4:1, 5:1 and 1:2 ($v_{\text{MWCNTs}}/v_{\text{NTiO}_2}$) respectively. The MWCNTs-NTiO₂ film is prepared by coating the mixture above on GCE. It can be seen in Fig. 6 the MWCNTs-NTiO₂/GCE exhibits the most excellent electrochemical activity in $1 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution containing $0.1 \text{ mol L}^{-1} \text{ KCl}$ when the ratio of MWCNTs and NTiO₂ is 4:1 (v/v). Too much NTiO₂ can weaken the electrical conductivity of the modified electrode, while too little NTiO₂ can not disperse the MWCNTs completely. Therefore, the ratio 4:1 (v/v) of MWCNTs and NTiO₂ is chosen at the MWCNTs-NTiO₂/GCE.

Fig. 6 B shows the trend of oxidation peak currents with different coating amount of MWCNTs-NTiO₂ suspension. With the rise of coating amount from 3 to 6 μL , the peak currents are increasing obviously. While the coating amount is increasing over 6 μL , the peak currents is decreasing. Hence, the coating amount of 6 μL is selected at the MWCNTs-NTiO₂/GCE.

Furthermore, the pH effect is investigated by cyclic voltammetry of HQ, CC and RC in the range of pH from 5.0 to 6.2 at MWCNTs-NTiO₂/GCE. Fig. 6 C shows the relationship of pH and the

current response. It can be seen that the oxidation peak currents reach a maximum at pH 6.0 for CC and RC detection. But the most sensitive pH of HQ detection is 5.6. It can be explained by the electrochemical oxidation processes of HQ, CC and RC and their adsorption at the MWCNTs-NTiO₂/GCE [25]. Thus, for the simultaneous determination of HQ, CC and RC, the pH 5.8 is selected in the whole experiments.

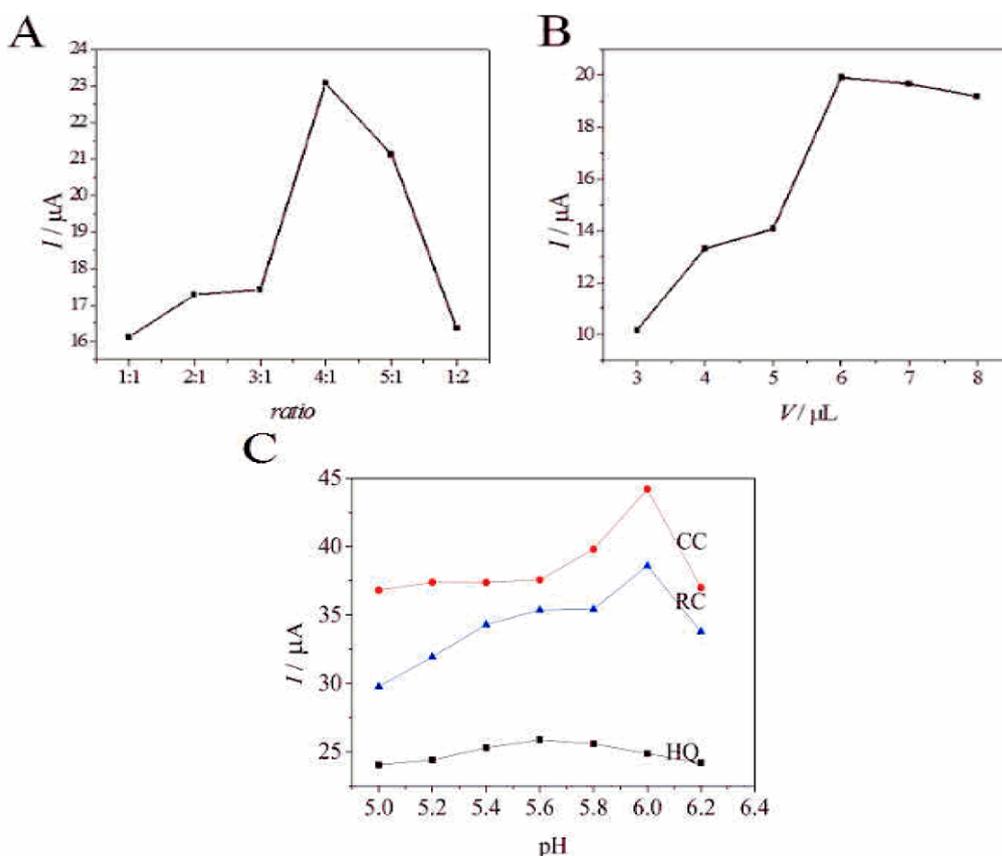


Figure 5. (A) The relationship of the volume ratio of MWCNTs and NTiO₂ and oxidation peak currents. (B) The relationship of the coating amount of MWCNTs-NTiO₂ and oxidation peak currents. (C) The relationship of pH and *i*_{pa} of HQ, CC and RC in 0.1 mol L⁻¹ PBS.

3.4 Electrochemical Determination of HQ, CC and RC

Differential pulse voltammetry (DPV) is used for the electrochemical determination of HQ, CC and RC at the modified electrode for its higher current sensitivity and better resolution than cyclic voltammetry. Fig. 7 compares the oxidation responses for the mixture of 500 μmol L⁻¹ HQ, 500 μmol L⁻¹ CC and 500 μmol L⁻¹ RC at the bare GCE and MWCNTs-NTiO₂/GCE. Actually, the bare GCE (curve a) have a small response at the peak potentials of 82 mV and 194 mV, but it is impossible to separate the three components for low sensitivity and even no response to RC. In contrast, the MWCNTs-NTiO₂/GCE (curve b) shows a high sensitivity for all the three and can be completely resolved in the peak potentials of 197 mV, 283 mV and 609 mV, respectively.

The individual determination of dihydroxybenzene isomers is first performed at MWCNT-NTiO₂/GCE. Fig. 8 A is the DPV curves of different concentrations of HQ in pH 5.8 PBS. Fig. 8 A1

shows the i_{pa} is proportional to the concentration of HQ in the range of 0.5 to 100 $\mu\text{mol L}^{-1}$. Fig. 8 B is the DPV curves of different concentrations of CC in pH 5.8 PBS. Fig. 8 B1 shows the i_{pa} is proportional to the concentration of CC in the range of 1 to 100 $\mu\text{mol L}^{-1}$. Fig. 8 C is the DPV curves of different concentrations of RC in pH 5.8 PBS. Fig. 8 C1 shows the i_{pa} is proportional to the concentration of RC in the range of 0.5 to 100 $\mu\text{mol L}^{-1}$. Their linear regressions are listed in the corresponding calibration plots. It can be seen there is a good linear relationship and high sensitivity of HQ, CC and RC in their individual determination at MWCNTs-NTiO₂/GCE.

Then the simultaneous determination of dihydroxybenzene isomers is performed, Fig. 9 presents the DPV curves of the MWCNTs-NTiO₂/GCE upon changing the concentrations of HQ, CC and RC simultaneously in pH 5.8 PBS. The three linear equations are obtained as following: $i_{pa} = 3.73005 + 0.23243 c$ (μA , $\mu\text{mol L}^{-1}$, $R = 0.9981$) in the range of 0.8 to 80 $\mu\text{mol L}^{-1}$ for HQ; $i_{pa} = 2.73167 + 0.19221 c$ (μA , $\mu\text{mol L}^{-1}$, $R = 0.9974$) in the range of 0.8 to 80 $\mu\text{mol L}^{-1}$ for CC and $i_{pa} = 1.34778 + 0.03052 c$ (μA , $\mu\text{mol L}^{-1}$, $R = 0.9963$) in the range of 1.6 to 160 $\mu\text{mol L}^{-1}$ for RC, respectively.

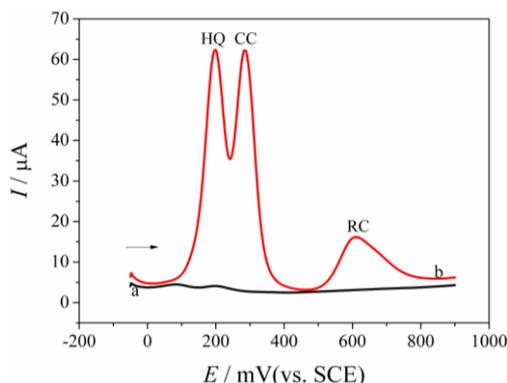
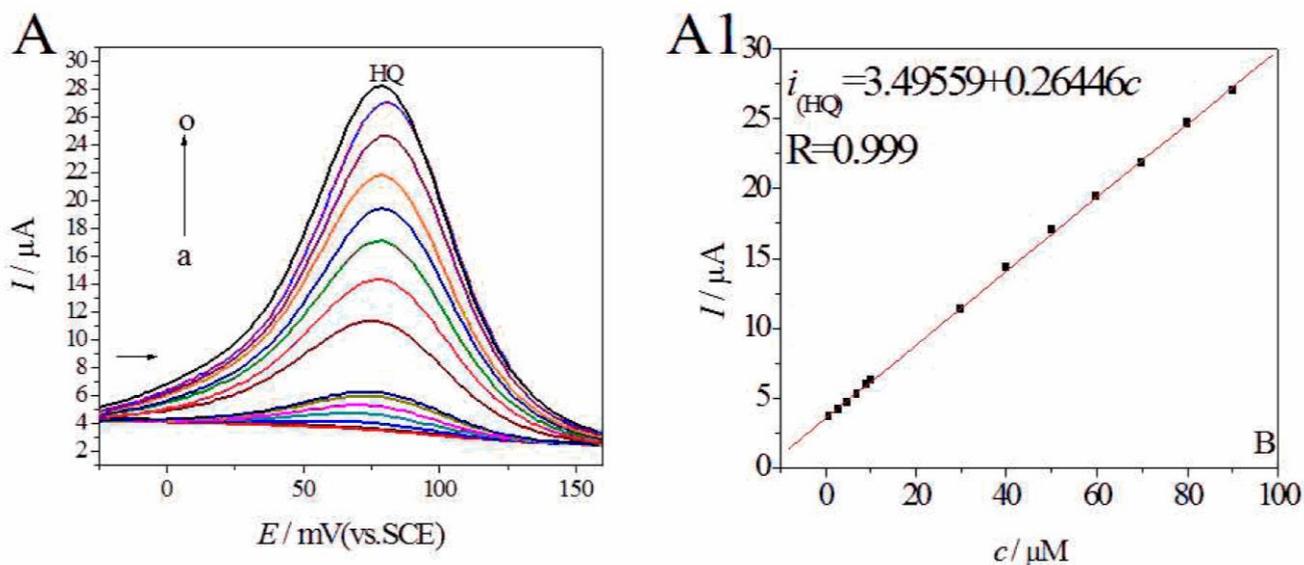


Figure 7. Differential pulse voltammetry of HQ, CC and RC of all their concentrations are 500 $\mu\text{mol L}^{-1}$ in pH 5.8 PBS at different electrodes. (a) GCE, (b) MWCNTs-NTiO₂/GCE.



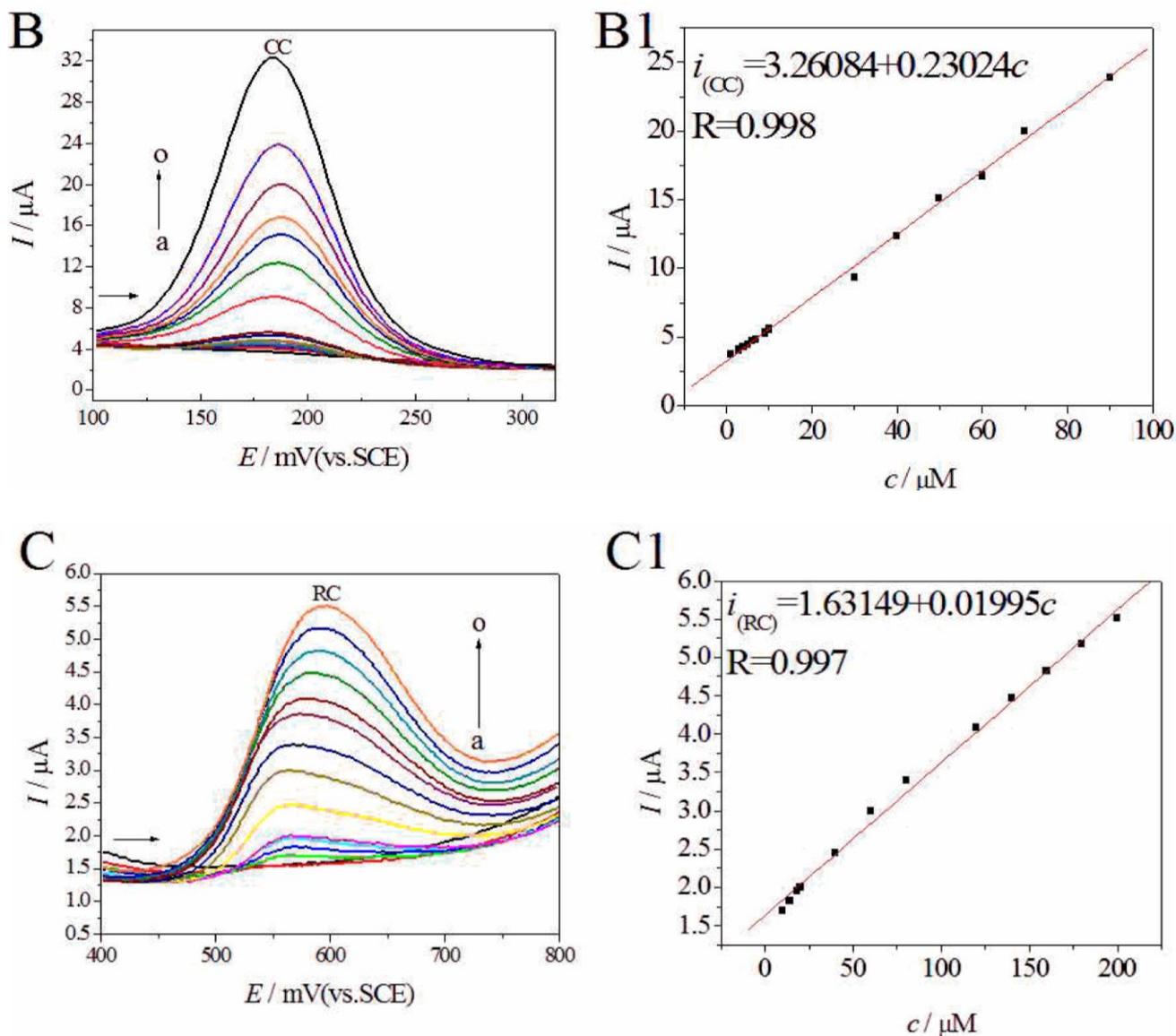


Figure 8. (A) DPV graphs of (a→o): 0.5, 0.8, 3, 5, 7, 9, 10, 30, 40, 50, 60, 70, 80, 90, 100 $\mu\text{mol L}^{-1}$ of HQ in pH 5.8 PBS, (A1). Calibration plots of HQ; (B) DPV graphs of (a→o): 1, 3, 4, 5, 6, 7, 9, 10, 30, 40, 50, 60, 70, 90, 100 $\mu\text{mol L}^{-1}$ of CC in pH 5.8 PBS, (B1). Calibration plots of CC; (C) DPV graphs of (a→o): 2, 6, 10, 14, 18, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 $\mu\text{mol L}^{-1}$ of RC in pH 5.8 PBS, (C1). Calibration plots of RC.

The detection limit is 93 nmol L^{-1} , 210 nmol L^{-1} and 32 nmol L^{-1} ($S/N = 3$) respectively for HQ, CC and RC. Electrochemical performance of the other reported methods to dihydroxybenzene isomers are compared in Table 1 [8, 10, 26-28]. It reveals that the proposed electrode is more comparable with previously reported for the simultaneous determination of HQ, CC and RC. Thus, the selective and sensitive determination of dihydroxybenzene isomers is achieved simultaneously determination at MWCNTs-NTiO₂/GCE.

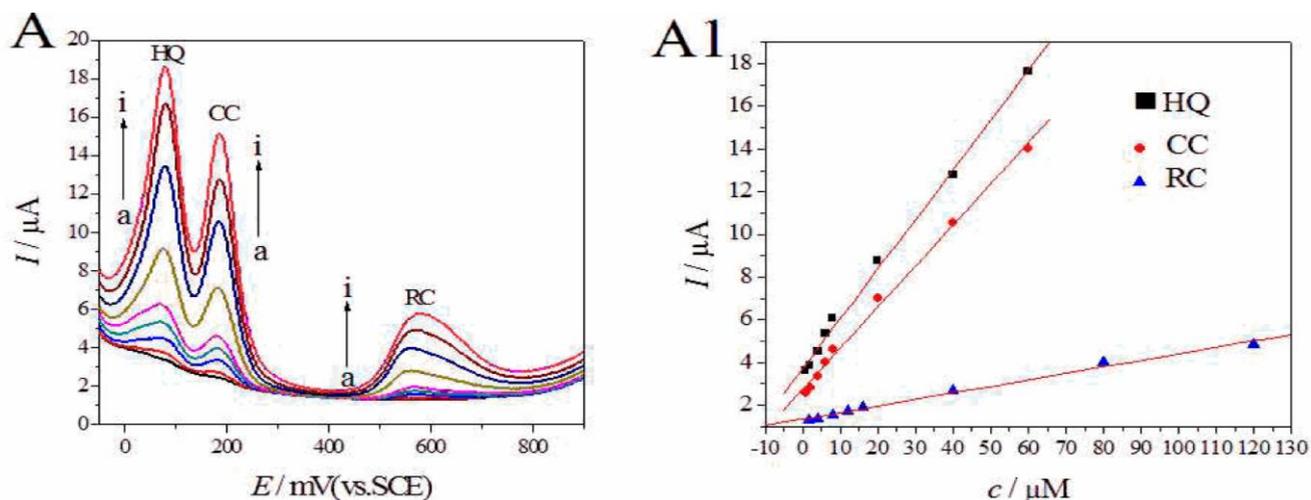


Figure 9. (A) DPV graphs of both HQ and CC (a→i): 0.8, 2, 4, 6, 8, 20, 40, 60, 80 μmol L⁻¹ and (a→i): 1.6, 4, 8, 12, 16, 40, 80, 120, 160 μmol L⁻¹ for RC in pH 5.8 PBS. (A1) Calibration plots of HQ, CC and RC.

Table 1. Comparison of different electrochemical sensors for the detection of HQ, CC and RC

Modified electrode	Linear range / (μM)			Detection limit / (μM)			Reference
	HQ	CC	RC	HQ	CC	RC	
Ag doped TiO ₂	--	--	0-15	--	--	24.9	[8]
CFG	1-190	5-250	--	200	600	--	[10]
RGO / Au-NPs	3-90	3-300	15-150	150	120	780	[11]
Chit-Fe ₃ O ₄ -GO	1.5-150	1-140	--	20	250	--	[26]
PAIUCPE	5-500	3-500	4-400	200	200	120	[27]
MWCNTs-NTiO ₂	0.8-80	0.8-80	1.6-160	93	210	32	Present work

*[a] CFG: Carboxyl functionalized graphene, [b] PAIUCPE: pre-anodized inlaying ultrathin carbon paste electrode, [c] μM: μmol L⁻¹

3.5 Interference studies

Add 500 fold Na⁺, Cu²⁺, Ca²⁺, K⁺, Mg²⁺, NH₄⁺, SO₄²⁻, NO₃⁻, Cl⁻, Ac⁻, alcohol and acetone in in pH 5.8 PBS in the presence of the mixture of 500 μmol L⁻¹ HQ, 500 μmol L⁻¹ CC and 500 μmol L⁻¹ RC, for these ions are common in waste water. As a result, the detected concentrations decreased to 98.93%, 95.42% and 95.67% for HQ, CC and RC, respectively. It is reported that if the coexisting interferences brought the detection current signal deviation below 5%, it is considered the above substances have no interference. Similarly, the MWCNTs-NTiO₂/GCE is thought to have strong anti-interference ability.

3.6 Analytical application

In order to discuss the practical applicability of the proposed modified electrode, MWCNTs-NTiO₂/GCE is applied for the simultaneous determination of HQ, CC and RC in different water samples that are prepared by adding different amounts of HQ, CC and RC in artificial wastewater, and the results are listed in Table. 2. It can be seen that satisfied results are obtained with the recovery rate being 93.37% to 106.25 for HQ, 93.48% to 102.00% for CC and 94.04% to 99.56% for RC, respectively. And relative standard deviation (RSD) are from 0.97 to 2.89 for them, which all indicate the good reproducibility and applicability on MWCNTs-NTiO₂/GCE to simultaneous determination of HQ, CC and RC in the real samples.

Table 2. Recovery results for HQ, CC and RC in artificial wastewater samples for simultaneously determination

Target analytes (μM)	Content (μM)	Added (μM)	Founded %	Recovery %	RSD
HQ	5	5	10.31	106.25	1.17
	7	5	12.03	100.58	1.84
	9	5	13.67	93.37	1.56
CC	5	5	10.86	93.48	1.20
	7	5	11.92	98.52	1.56
	9	5	14.10	102.00	2.85
RC	10	10	19.40	94.04	2.89
	14	10	23.71	97.13	0.97
	18	10	27.96	99.56	1.57

*[a] μM : $\mu\text{mol L}^{-1}$

4. CONCLUSIONS

In this paper, MWCNTs-NTiO₂ modified electrode is easily obtained by one-step coating. The electrocatalytic property of original MWCNTs is strongly enhanced with the help of NTiO₂. This sensor shows a wide linear response and low limit of detection for the simultaneous determination of HQ, CC and RC in pH 5.8 PBS. It can be applied in artificial wastewater samples with a satisfied recovery rate and low RSD to demonstrate a promising sensor for the determination of HQ, CC and RC simultaneously in environmental samples.

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