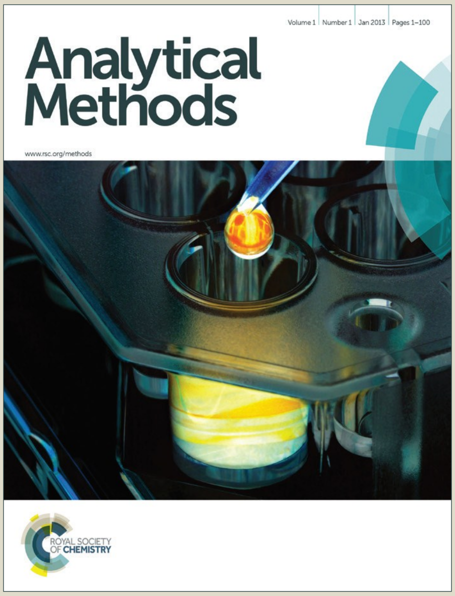
Analytical Methods



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Microsensor for hydroquinone and catechol based on poly (3, 4-ethylenedioxythiophene) modified carbon fiber electrode

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A rapid and highly sensitive miniaturized sensor for differential pulse voltammetric (DPV) and amperometric determination of hydroquinone and catechol based on carbon fiber electrode modified by poly (3, 4-ethylenedioxythiophene) was presented. This low-cost diphenol microsensor was constructed by several simple steps and displayed excellent electrochemical activity toward the oxidation of hydroquinone and catechol in 0.1 M phosphate buffer solution (pH 7.0). Furthermore, the microsensor had the virtue of good stability and high sensitivity. Under the optimal working conditions, linear relationships between the amperometric current response and the concentration of substrates were obtained in the ranges of 5.3×10^{-7} M to 8.6×10^{-4} M for hydroquinone and 5.2×10^{-7} M to 4.9×10^{-3} M for catechol, with the detection limits (S/N = 3) of 4.2×10^{-7} M and 1.6×10^{-6} M, respectively. The proposed microsensor was applied on the determination of the mixture of hydroquinone and catechol, and satisfying results were obtained.

1. Introduction

Catechol (1, 2-dihydroxybenze, CC) and hydroquinone (1, 4-dihydroxybenze, HQ) are two significant isomers of dihydroxybenzene, they are produced as contaminants in many industrial processes, such as tanning, cosmetics, dying and in the chemical and pharmaceutical industries.[1] Because HQ may cause fatigue, headache, kidney damage and CC may cause liver function decrease,[2] the accurate determination of HQ and CC is needed urgently. So far, a great deal of methods have been established for their determination, including synchronous fluorescence,[3] chemiluminescence,[4] spectrophotometry,[5] pH based-flow injection analysis,[6] solid-phase extraction,[7] pulse radiolysis[8] and high performance liquid chromatography.[9, 10] However, most of these methods have disadvantages such as time consuming, high cost, low sensitivity and complicated pretreatment. In recent years, electrochemical detection of HQ and CC has gained increasing attention for its high catalytic ability, good stability and broad potential window.[11, 12] A number of new materials used to modify the electrodes for simultaneous determination of HQ and CC have been developed, including carbon nanotubes,[13, 14] electrospun carbon nanofiber,[15] mesoporous Pt,[12] mesoporous carbon,[16] graphene,[17-19] etc.. However, it is still a challenge to explore novel electrode materials for the determination of HQ and CC with wider linear range and higher sensitivity.

Recently, microsensors have been developed rapidly in analysis fields and showed outstanding performance. Although having small surface area and faint signal, it provides high signal-to-noise ratio and short response time in case of a small amount of sample.[20,21] The electrode miniaturized enough to match with the small space in biological microenvironments, such as single cell or certain locations in tissues appears to have great advantages over other electrodes with ordinary size.[22] Many applications have been developed on microsensor, such as pH measurement,[23] detection of nitric oxide,[24] glucose,[25] ascorbic acid,[26] dopamine,[27] etc.. Carbon fiber is one of the most promising candidate materials for microsensor due to its tiny size, sensitivity and selectivity.[28] Carbon fiber electrode (CFE) was invented in the late 1970s by Francois Gonon and his colleagues,[29] and modified CFE has been utilized in various cases.[30-32]

Conducting polymers (CPs) have been studied most intensively due to its easy synthesis, high conductivity, environmental stability and unique electrochemical redox properties.[33] The various excellent electronic properties of CPs result from the various types of charge carriers in these materials, which are entirely different from that of conventional semiconductors. Cps, such as polyacetylene (PA), polyaniline (PANI), polyfuran (PF), polypyrrole (PPy), poly (p-phenylenevinylene) (PPV), poly (3, 4-ethylenedioxythiophene) (PEDOT), polyvinylidene fluoride (PVDF) and other polythiophene (PTh) derivatives, can be used as thin film transistors,[34] polymer light emitting diodes (LEDs),[35] corrosion resistance materials,[36] electromagnetic shielding,[37] sensor technology,[38] molecular electronics,[39] supercapacitors,[40] and electrochromic devices.[41] Polymer modified electrodes can be designed through polymer screening to provide tremendous improvements of the electrode response to detect a variety of analytes.[42] Their lower cost, mass production, better mechanical stability, easier surface functionalization and more edge sites on the outer wall compared with traditional electrodes make them possess outstanding advantages.

In this work, an electrochemical microsensor was constructed based on carbon fiber modified by poly (3, 4-

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ethylenedioxythiophene) (PEDOT), and used for the amperometric determination of diphenol materials (HQ and CC). The PEDOT modified CFE exhibited excellent electrocatalytic activity towards the oxidation of HQ and CC, and satisfying amperometric response for microscale analysis of the above substrates.

2. Experimental

2.1 Reagents

Carbon fiber (T300, 12K) was purchased from Toray Chemical Industry, Tokyo, Japan. A 3, 4-ethylenedioxythiophene (EDOT) was obtained from XZL Bio-Technology Co., Ltd. Hydroquinone, catechol and $LiClO_4$ were purchased from Guangfu Fine Chemical Research Institute. Conductive silver glue was purchased from Dongguan Yihui Adhesive co., Ltd. Acetonitrile and acetone were taken from Tianjin Kemiou Chemical Reagent Co., Ltd and Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd, respectively. All other chemicals were of analytical grade and used without further purification.

2.2 Instrumentation

Electrochemical measurements were carried out with LK2006A electrochemical workstation (Tianjin Lanlike Chemical and Electron High Technology Co., Ltd.). A field emission scanning electron microscopy (FE-SEM, S4800, Hitachi) was used to characterize the PEDOT modified CFEs.

2.3 Preparation of the working electrodes

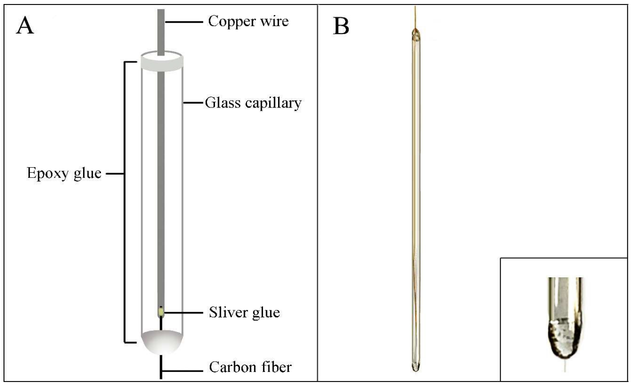
The carbon fiber was initially cleaned by sonicating in acetone, alcohol and doubly distilled water separately each for 2 min and cut into a desired length, then the carbon fiber was connected to a copper wire for conductance by silver glue. After a period of drying, the copper wire together with carbon fiber were inserted through a capillary and sealed with epoxy glue, followed by drying completely at room temperature, and used as carbon fiber electrode (CFE). The schematic diagram of the prepared CFE was shown in Scheme 1.

2.4 Preparation of the PEDOT modified CFE

The tip of CFE was firstly cut at the length of 1 mm, followed by scanning over the potential range of + 0.0 V to + 1.7 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 solution for about 25 min until stable voltammograms were obtained. A potentiostatic method was used to deposit PEDOT films onto CFE, which was performed by applying a potential at + 1.4 V for appropriate time at 0.01 M EDOT acetonitrile solution containing 0.1 M lithium perchlorate ($LiClO_4$). After electropolymerization, the PEDOT modified CFE was washed with ethanol and deionized water and then dried by N_2.

2.5 Electrochemical measurement

A three-electrode electrochemical cell was used in the voltammetric and amperometric experiments. Electrochemical behaviors of bare and PEDOT modified CFE were investigated by cyclic voltammetry in the potential range between − 0.2 V and + 0.6 V vs. Ag/AgCl at a scan rate of 100 mVs^{-1} in 0.1 M PBS. The applied potential was set at + 0.13 V and + 0.25 V for the amperometric determination of HQ and CC, and DPV was set −100 to +500 mV at 20mV pulse amplitude with 0.1 s and 0.2 s pulse width and pulse period, respectively.



Scheme 1 Schematic diagram (A) and real picture (B) of CFE. Insert: Partial magnified picture of CFE.

3. Results and discussion

3.1 Characterization of PEDOT modified CFE

Bare carbon fiber (~6μm) coated with PEDOT and magnified images were observed on FE-SEM, as shown in Fig. 1. The surface of the polymer coating was rough and its thickness varied spatially along the fiber (Fig.1A). Porous structure[43] was also observed on the detail with enlarged scale (Fig.1B), which indicated that PEDOT has been successfully polymerized on the carbon fiber. Furthermore, the increased superficial area can facilitate both electron and mass transfer process of the substrates.

The electrochemical behavior of PEDOT modified CFE was further characterized by electrochemical impedance spectroscopy (EIS). A typical shape of a Faradic impedance spectrum includes a semicircle region (at higher frequencies) and a straight line portion (at lower frequencies). The semicircle portion corresponds to the charge-transfer limited process, and the linear portion represents the diffusion-limited process. The semicircle diameter in the impedance spectrum equates to the electron transfer resistance, Ret, at the electrode surface. The experimental Faradaic impedance spectra were fitted using a general Randles electronic equivalent circuit (Fig. 2c), which is used to model interfacial phenomena,[44] including the ohmic resistance of the electrolyte solution, Rs, the Warburg impedance, Zw, the double layer capacitance, Cdl and the electron transfer resistance, Ret.

Impedance spectrum of PEDOT modified CFE compared with bare CFE in solution containing 2.5 mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ was shown in Fig. 2. For bare CFE, the value of electron

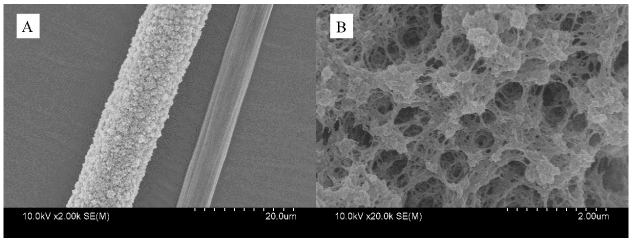


Fig. 1 FE-SEM images of bare and PEDOT-modified CFE (A) and detail with enlarged scale of modified CFE (B).

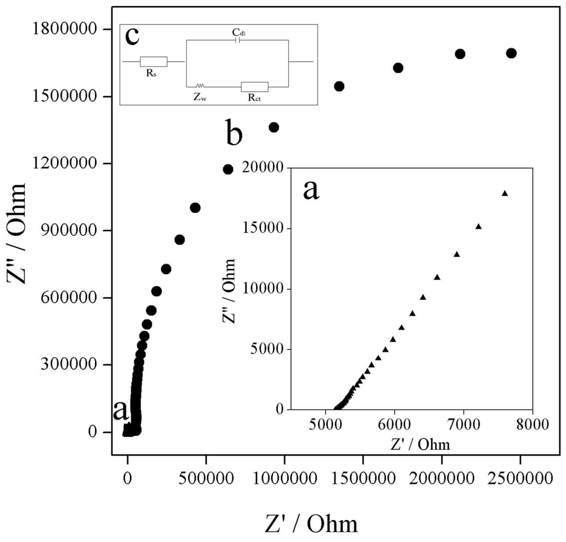


Fig. 2 Nyquist plots obtained from bare CFE (●) and PEDOT modified CFE (▲) in 2.5 mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ solution.

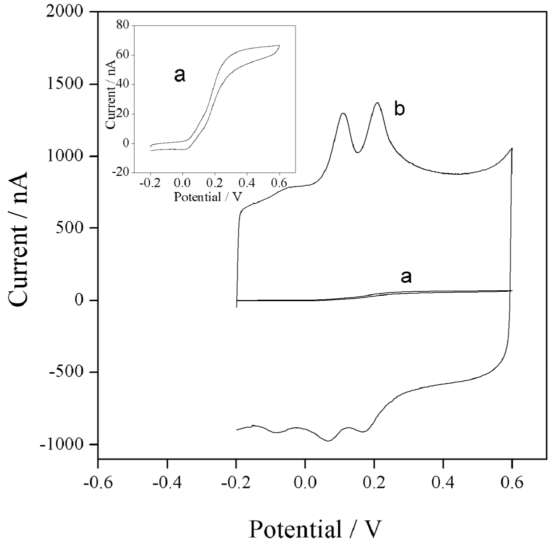


Fig. 3 Cyclic voltammograms of bare (a) and modified CFE (b) in PBS (pH 7.0) containing 100 µM HQ and 100 µM CC. Scan rate: 100 mVs^{-1}.

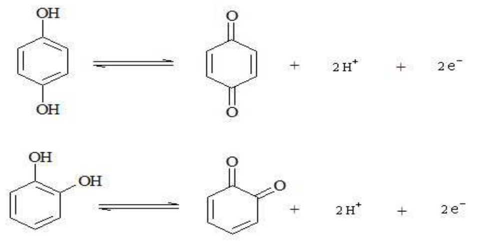
transfer resistance (Ret) is about 5 MΩ (Fig. 2, curve b), after modifying PEDOT, the Ret value decreased to 5140 Ω (Fig. 2, curve a), and the result was very similar to P. Salazar's work.[31] It demonstrated that the conductivity of PEDOT modified CFE was greatly enhanced under the help of the PEDOT film.

3.2 Electrochemical properties of HQ and CC on bare CFE and PEDOT modified CFE

The electrochemical behavior of HQ and CC on bare and PEDOT modified CFE was studied by cyclic voltammetry. Fig. 3 displayed the cyclic voltammograms of bare and modified CFE (electropolymerization time 10 s) in PBS (pH 7.0) containing HQ and CC. A weak and broad oxidation peak around + 0.25 V was found in Fig. 3, curve a, which resulting from the overlapped oxidation peaks of both HQ and CC. By contrast, two pairs of clear redox peaks (at potentials of + 0.13 V and + 0.25 V) with much larger current response were observed on PEDOT modified CFE, shown in Fig. 3, curve b. The ratio of current density between bare and modified electrode could be calculated based on the response current and their geometry area. For example, the response current (HQ fixed at 100 µM) of bare and modified electrode was 0.02426 µA and 1.544 µA with the geometry area of 0.01884 mm^2 and 0.0408 mm^2, respectively. So the ratio value was 29.38, this means that the current density of modified CFE increased almost 30 times compared with the bare one. This is the good conductivity, excellent catalytic activity of PEDOT film[45] and increased superficial area that resulted in the enhanced electrochemical signals.

The effect of pH on the electrochemical oxidation of HQ and CC was also investigated, and shown in Fig. 4. The cyclic voltammograms of HQ and CC on PEDOT modified CFE in 0.1 M PBS at different pH (5-9) were shown in Fig. 4A. It was found clearly that the redox potential of both HQ and CC shift negatively with the increasing pH, and the linear relationship between the formal peak potential and pH were found clearly in the pH range of 5-9, showed in Fig. 4D with the linear regression equation of $E^{0\prime}(V)=0.46-0.053pH$ ($r^2=0.996$) for HQ and $E^{0\prime}(V)=0.55-0.051pH$ ($r^2=0.999$) for CC, which indicates that an equal number of electron and protons were involved in the redox process of HQ and CC. It coincided the reaction mechanism of the substrates,[46] shown in scheme 2. The slopes of the two regression equations were very close to the theoretical value of 59 mV/pH for two electrons and two protons process.[47] From Fig. 4B and Fig. 4C, it can be seen that the peak currents of HQ and CC increased with the increasing pH from 5 to 7 and then decreased when pH increased from 7 to 9. It may be due to both HQ and CC were of no advantage to the oxidation reaction in low pH solution, and they were apt into anions in high pH solution, decreased peak current caused because of electrostatic repulsion[17] between two dihydroxybenzen isomers and modified CFE. Thus, pH 7 was chosen as the optimum pH for the following experiments.

The cyclic voltammograms of PEDOT modified CEFs in buffer containing HQ and CC at different concentrations were further studied, and the results were shown in Fig. 5. In Fig. 5A, the concentration of CC was fixed at 100 µM and that of HQ varied from 10 µM to 100 µM. No change was found for the oxidation peak of CC in the presence of different concentration of HQ,



Scheme 2 Mechanism of redox reactions of HQ and CC at PEDOT modified CFE.

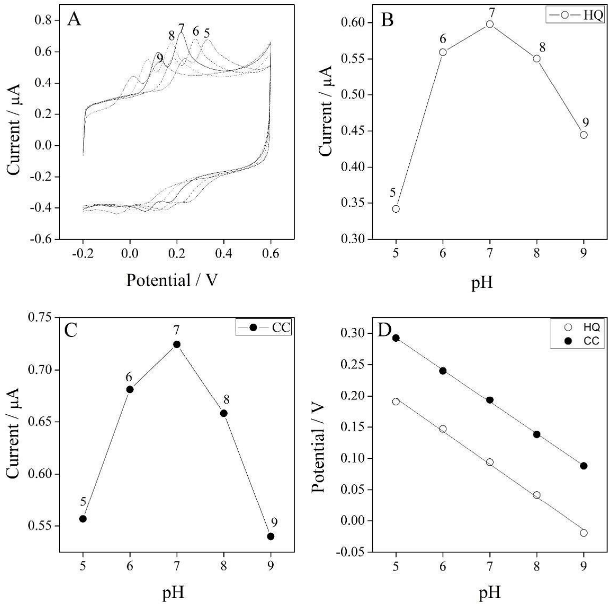


Fig. 4 Cyclic voltammograms of PEDOT modified CFE in 0.1 M PBS containing HQ and CC (A) at different pH (from 5 to 9).The effect of pH on the peak current of HQ (B) and CC (C) and the dependence of peak potentials of HQ and CC (D) on the pH of the buffer at PEDOT CFE.

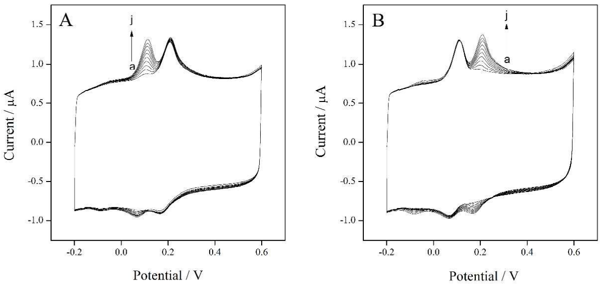


Fig. 5 Cyclic voltammograms of PEDOT modified CFE in 0.1 M PBS (pH 7.0) containing (A) 100 μM CC and different concentration of HQ: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μM (from a to j), and (B) 100 μM HQ and different concentration of CC: 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μM (from a to j).

which indicating that HQ has no influence on the redox process of CC. The similar results were also obtained when the concentration of HQ was fixed and that of CC varied (shown in Fig. 5B). It is inferred that the redox process of one dihydroxybenzene do not affect the other one, which makes it possible for the simultaneous determination of the two substrates.

3.3 Simultaneous determination of HQ and CC

To develop a sensitive analytical method for the analysis of HQ and CC, DPV was employed. As shown in Fig. 6, no obvious interference can be observed for the determination of one species coexisting with the other one. Peak currents linearly increased with increasing concentration of CC from 1 μM to 250 μM (Fig.6A), while keeping the concentration of HQ constant at 50 μM. A similar result was also obtained with HQ (1-150 μM) in the presence of 50 μM CC (Fig. 6B).

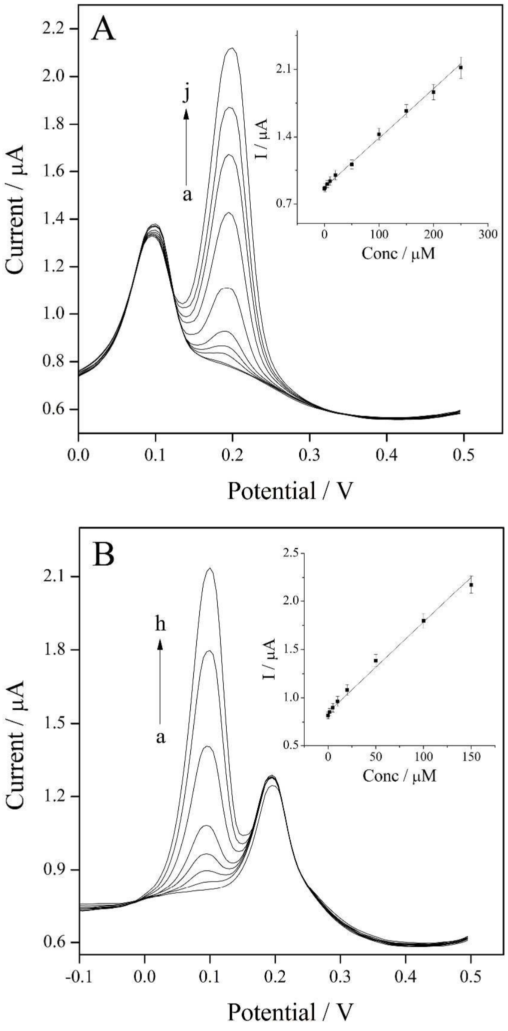


Fig. 6 Differential pulse voltammetry of PEDOT modified CFE in 0.1 M PBS (pH7.0) (A) containing 50 μM HQ and different concentrations of CC from 0 to 250 μM. Insert: Calibration plots of CC. (B) containing 50 μM CC and different concentrations of HQ from 0 to 150 μM. Insert: Calibration plots of HQ.

After calculation, the linear regression equations were I_h = 0.8680 + 0.00897 C (I_h : μA, C: μM) (r^2=0.993) for HQ and I_c = 0.8725 + 0.00514 C (I_c : μA, C: μM) (r^2=0.995), and the detection limits was 0.8 μM and 0.5 μM (S/N=3) for HQ and CC, respectively. Thus, the selective and sensitive determination of HQ and CC was achieved simultaneously at this modified electrode.

3.4 Amperometric determination of HQ and CC

The quantitative amperometric determination of HQ and CC at the three electrodes was carried out by using the standard addition method. Fig. 7 shows the steady-state current-time response of the PEDOT modified electrode for the incremental addition of HQ and CC to a continuously stirring 0.1 M PBS at an applied potential + 0.13 V for HQ and + 0.25 V for CC, respectively (baseline had been calibrated). It can be observed from Fig. 7A and 7C that the responses of the modified electrode reach relative steady catalytic current values within

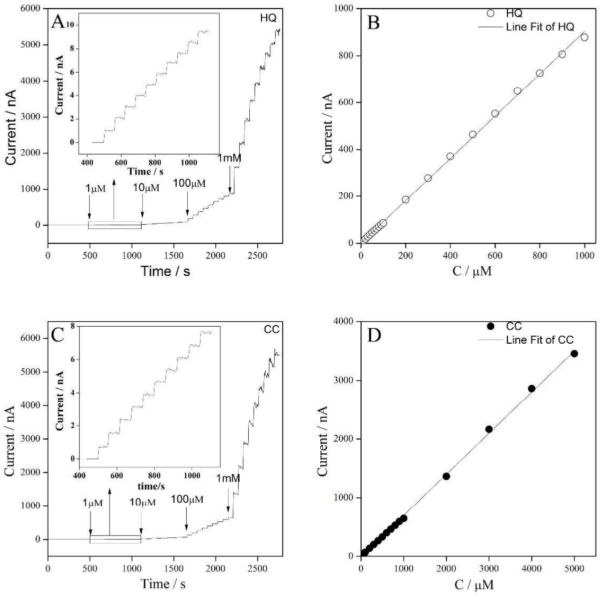


Fig. 7 Typical current–time response curves of the PEDOT modified CFE to the successive additions of HQ (A) and CC (C) and calibration curves of HQ (B) and CC (D) based on their respective current–time response curve.

about 10 s response time (t_R , time taken to reach 95% of the maximum current) at various concentration of HQ and CC, and current altered with small change for dozens of seconds. Furthermore, the catalytic current increased steadily with increasing the substrate concentration, and seemed to be saturated for 1 mM HQ or 5 mM CC. The fast response might be owned to the interactions between the substrates and the reduced or oxidized forms of PEDOT polymer, and its catalytic activity toward to HQ and CC might due to the unique structure and good conductivity of PEDOT.[48] Fig. 7B and 7D showed the current response versus concentrations based on the data from Fig. 7A and 7C, respectively, which suggested that the PEDOT modified CFE offered a useful linear calibration plot in the concentration rang of 5.3×10^{-7} M to 8.6×10^{-4} M for HQ and 5.2×10^{-7} M to 4.9×10^{-3} M for CC. The linear regression equations were $I_h = 1.35 + 0.90\ C$ (I_h : nA, C: μM) ($r^2 = 0.999$) for HQ and $I_c = -6.8 + 0.70\ C$ (I_h : nA, C: μM) ($r^2 = 0.999$) for CC, and the detection limits was 0.42 μM and 1.6 μM (S/N = 3) for HQ and CC respectively.

Compared with DPV, amperometric determination provided lower sensitivity but larger detection range, so samples with low concentration were analyzed by DPV and chronoamperometry was suggested to detect samples with large concentration range.

The possibility for quantitive determination of a mixture of HQ and CC was further investigated. Amperometric response of HQ and CC at + 0.13 V (A) and + 0.25 V (B) was shown in Fig. 8. It was seen that when keeping the potential at + 0.13 V, an obvious current increase was obtained with the addition of HQ and no current change observed with the addition of CC, indicating that only HQ could be oxidized at this potential. However, both HQ and CC could cause current increase as they were added to the system after shifting the potential to + 0.25 V, as shown in Fig. 8B, indicating that both HQ and CC could be electrochemical oxidized at this potential. So the concentration of HQ could be calculated from I_h and the regression equation ($I_h = 1.35 + 0.90\ C$) at the potential of + 0.13 V, the response current of CC was the algebraic difference between I_{h+c} and I_h ($I_c = I_{h+c} - I_h$), and the concentration of CC could also obtained at the potential of + 0.25 V based on the regression equation mentioned above, $I_c = -6.8 + 0.70\ C$.

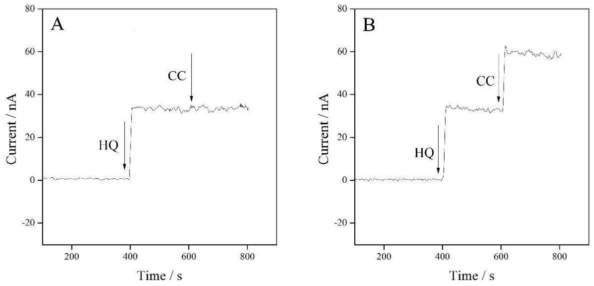


Fig. 8 Current–time response of both HQ and CC at different potentials: (A) + 0.13 V and (B) + 0.25 V.

3.4 Reproducibility, stability and selectivity of this sensor

The electrochemical signal provided by this microsensor is largely depended on the length of exposed carbon fiber and experimental conditions for polymerization. So, reproducibility can be guaranteed if these variables are under control. The fabrication reproducibility for five PEDOT modified CFEs was investigated by comparing the oxidation peak current of 100 μM HQ and 100 μM CC in mixed solution. The relative standard deviation (RSD) was 3.8 % for HQ and 4.1 % for CC. After 20 days, the peak currents of HQ and CC decreased by 13 % for HQ and 14 % for CC (data not shown here), indicating an acceptable reproducibility and stability.

The influence of some coexist inorganic ions and organic compounds on the determination of HQ and CC was also investigated. The results showed that 100-fold of Na^+, K^+, NO_3^-, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, and 10-fold of urea acid, glucose and ethanol did not interfere with the oxidation signal of 100 μM HQ and CC (peak current change < ±5 %).

The properties obtained in the present work were also compared with other traditional electrodes, and linear range and detection limit were listed in Table 1. It was found clearly that larger linear range and satisfying detection limit were obtained in the present work compared to other traditional electrode materials. Furthermore, the advantage of PEDOT modified CFE is embodied in its small size, detection can be carried out in case of a small amount of samples, there's undoubtedly that this kind of microsensor could expand the detection scope of dihydroxybenzene.

3.5 Real samples analysis

To evaluate the validity of the proposed method, the PEDOT modified CFE was applied for the determination of CC and HQ in local tap and lake water. The results demonstrated that no target analytes were detected with the modified electrode. The standard solution was added to the tap and lake water samples to determine the recovery of CC and HQ. The recoveries for CC and HQ (shown in Table 2) were 98.2–105.6%.

Table 1 Comparison of analytical performances at various electrodes for the determination of HQ and CC.

Modified electrode	pH	Analyte	Linear range (μM)	Detection limit (μM)	Reference
(CMWNTs[a]-NHCH$_2$CH$_2$NH)$_6$ /GCE	7.0	HQ	10-120	2.3	[2]
		CC	5-80	1.0	
MWNT/GCE	4.5	HQ	1-100	0.75	[13]
		CC	0.6-100	0.20	
SWNT/GCE	5.6	HQ	0.4-10	0.26	[14]
		CC	0.4-10	0.30	
ECF-CPE[b]	7.0	HQ	1-200	0.40	[15]
		CC	1-200	0.20	
CMK-3[c]/GCE	7.0	HQ	1-30	0.10	[16]
		CC	0.5-35	0.10	
CNCs-RGO[d]/GCE	4.0	HQ	1-300	0.87	[17]
		CC	1-400	0.40	
IL-G[e]/GCE	7.0	HQ	2-400	1.0	[18]
		CC	1-300	0.85	
Pyridinic-NG[f]/GCE	5.5	HQ	5-200	0.38	[19]
		CC	5-200	0.10	
PEDOT/CFE	7.0	HQ	0.53-861	0.42	This work
		CC	0.52-4920	1.6	

[a] Carboxylated-MWNTs
[b] Electrospun carbon nanofiber-modified carbon paste electrode
[c] Mesoporous carbon CMK-3
[d] Carbon nanocages-reduced grapheme oxide
[e] Ionic liquids-functionalize graphene
[f] Pyridinic nitrogen doped graphene

Table 2 Determination of HQ and CC in water samples.

Samples		Original (μM)	Added (μM)	Found[a] (μM)	Recoveries (%)	RSD (%)
Tap water	HQ	-	5	4.91	98.2	2.57
	CC	-	5	5.21	104.2	4.17
Lake water	HQ	-	5	5.19	103.8	3.46
	CC	-	5	5.13	105.6	3.85

- Not detected
a Average of five determinations

Conclusion

A simple and sensitive electrochemical microsensor for quantitative detection of HQ and CC was developed using PEDOT modified CFE in neutral phosphate buffer solution. The PEDOT modified CFE showed two well-defined redox peaks with enhanced peak currents compared to the bare electrode, DPV and amperometric determination were employed in the analysis, and satisfying results were obtained. The linear detection ranges of 5.3×10^{-7} M to 8.6×10^{-4} M for HQ and 5.2×10^{-7} M to 4.9×10^{-3} M for CC were obtained, with the detection limits (S/N=3) of 0.42 μM and 1.6 μM, respectively. The wide linear range, high sensitivity, fast and stable response to the dihydroxybenzene isomers in case of a small amount of sample as well as the effective discrimination to the possible interferences at PEDOT modified CFE make it a promising candidate for designing effective dihydroxybenzene sensor.

Acknowledgements

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Notes and references

1. B. Unnikrishnan, P.-L. Ru and S.-M. Chen, Sensors and Actuators B: Chemical, 2012, **169**, 235-242.
2. S. Feng, Y. Zhang, Y. Zhong, Y. Li and S. Li, Journal of Electroanalytical Chemistry, 2014, **733**, 1-5.
3. M. F. Pistonesi, M. S. Di Nezio, M. Centurion, M. E. Palomeque, A. G. Lista and B. S. F. Band, Talanta, 2006, **69**, 1265-1268.
4. H. Cui, Q. Zhang, A. Myint, X. Ge and L. Liu, Journal of Photochemistry and Photobiology A: Chemistry, 2006, **181**, 238-245.
5. A. Afkhami and H. A. Khatami, Journal of Analytical Chemistry, 2001, **56**, 429-432.
6. J. A. Garcia-Mesa and R. Mateos, J Agr Food Chem, 2007, **55**, 3863-3868.
7. Á. Kovács, M. Mörtl and A. Kende, Microchemical Journal, 2011, **99**, 125-131.
8. B. Mishra, K. I. Priyadarsini, M. Sudheerkumar, M. K. Unnikrishhnan and H. Mohan, Radiat Phys Chem, 2006, **75**, 70-77.
9. E. A. Podolina, O. B. Rudakov, E. A. Khorokhordina and L. A. Kharitonova, Journal of Analytical Chemistry, 2008, **63**, 468-471.
10. W. Gao and C. Legido-Quigley, Journal of Chromatography A, 2011, **1218**, 4307-4311.
11. B. D. Malhotra, A. Chaubey and S. P. Singh, Anal Chim Acta, 2006, **578**, 59-74.
12. M. A. Ghanem, Electrochemistry Communications, 2007, **9**, 2501-2506.
13. H. Qi and C. Zhang, Electroanalysis, 2005, **17**, 832-838.
14. Z. Wang, S. Li and Q. Lv, Sensors and Actuators B: Chemical, 2007, **127**, 420-425.
15. Q. Guo, J. Huang, P. Chen, Y. Liu, H. Hou and T. You, Sensors and Actuators B: Chemical, 2012, **163**, 179-185.
16. J. Yu, W. Du, F. Zhao and B. Zeng, Electrochimica Acta, 2009, **54**, 984-988.
17. Y. H. Huang, J. H. Chen, X. Sun, Z. B. Su, H. T. Xing, S. R. Hu, W. Weng, H. X. Guo, W. B. Wu and Y. S. He, Sensors and Actuators B: Chemical, 2015, **212**, 165-173.
18. C. Wang, Y. Chen, K. Zhuo and J. Wang, Chemical communications, 2013, **49**, 3336-3338.
19. H.-L. Guo, S. Peng, J.-H. Xu, Y.-Q. Zhao and X. Kang, Sensors and Actuators B: Chemical, 2014, **193**, 623-629.
20. C. Amatore and E. Maisonhaute, Anal Chem, 2005, **77**, 303A-311A.
21. N. Baltes, L. Thouin, C. Amatore and J. Heinze, Angewandte Chemie-International Edition, 2004, **43**, 1431-1435.
22. R. Mohammadzadeh Kakhki, Arabian Journal of Chemistry, 2014, DOI: 10.1016/j.arabjc.2014.11.058.
23. A. Lale, A. Tsopela, A. Civélas, L. Salvagnac, J. Launay and P. Temple-Boyer, Sensors and Actuators B: Chemical, 2015, **206**, 152-158.
24. D. Kato, M. Kunitake, M. Nishizawa, T. Matsue and F. Mizutani, 2005,**108**, 384-388.
25. T. Yasukawa, Y. Yoshimura and F. Mizutani, Electrochemistry, 2012, **80**, 15-17.
26. E. A. Hutton, R. Pauliukaitė, S. B. Hocevar, B. Ogorevc and M. R. Smyth, Analytica Chimica Acta, 2010, **678**, 176-182.
27. B.-X. Shi, Y. Wang, K. Zhang, T.-L. Lam and H. L.-W. Chan, Biosensors and Bioelectronics, 2011, **26**, 2917-2921.
28. S. Tiwari and J. Bijwe, Procedia Technology, 2014, **14**, 505-512.
29. F. Gonon, M. Buda, R. Cespuglio, M. Jouvet and J.-F. Pujol, Nature, 1980, **286**, 902-904.
30. C.-S. Park, J. Park and D.-W. Lee, Microelectronic Engineering, 2009, **86**, 1250-1253.
31. P. Salazar, R. D. O'Neill, M. Martín, R. Roche and J. L. González-Mora, Sensors and Actuators B: Chemical, 2011, **152**, 137-143.
32. P. Salazar, M. Martin, R. Roche, J. L. Gonzalez-Mora and R. D. O'Neill, Biosensors & bioelectronics, 2010, **26**, 748-753.
33. K. Saranya, M. Rameez and A. Subramania, European Polymer Journal, 2015, **66**, 207-227.
34. K. Wolff and U. Hilleringmann, Solid-State Electronics, 2011, **62**, 110-114.
35. C.-Y. Li, T.-C. Wen, T.-F. Guo and S.-S. Hou, Polymer, 2008, **49**, 957-964.
36. H. Wang, D. Gao, Y. Meng, H. Wang, E. Wang and Y. Zhu, Progress in Organic Coatings, 2015, **82**, 74-80.
37. A. Gupta and V. Choudhary, Composites Science and Technology, 2011, **71**, 1563-1568.
38. K. He, X. Wang, X. Meng, H. Zheng and S.-i. Suye, Sensors and Actuators B: Chemical, 2014, **193**, 212-219.
39. A. Burke, Journal of Power Sources, 2000, **91**, 37-50.
40. Y. Zhao and P. Jiang, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, **444**, 232-239.
41. P. Camurlu and C. Gültekin, Solar Energy Materials and Solar Cells, 2012, **107**, 142-147.
42. U. Lange, N. V. Roznyatovskaya and V. M. Mirsky, Analytica Chimica Acta, 2008, **614**, 1-26.
43. S. Y. Heo, J. K. Koh, J. K. Kim, C. S. Lee and J. H. Kim, Electrochimica Acta, 2014, **137**, 34-40.
44. Y. Liu, X. H. Qu, H. W. Guo, H. J. Chen, B. F. Liu and S. J. Dong, Biosensors & bioelectronics, 2006, **21**, 2195-2201.
45. B. Bezgin, A. Yagan and A. M. Onal, Journal of Electroanalytical Chemistry, 2009, **632**, 143-148.
46. H. Du, J. Ye, J. Zhang, X. Huang and C. Yu, Journal of Electroanalytical Chemistry, 2011, **650**, 209-213.
47. H. S. Han, J.-M. You, H. Seol, H. Jeong and S. Jeon, Sensors and Actuators B: Chemical, 2014, **194**, 460-469.
48. F. Sekli-Belaidi, P. Temple-Boyer and P. Gros, Journal of Electroanalytical Chemistry, 2010, **647**, 159-168.

A microsensor for hydroquinone and catechol was constructed based on carbon fiber electrode modified by poly (3, 4-ethylenedioxythiophene) by several simple steps. This microsensor exhibited excellent electrochemical activity toward the oxidation of substrates, and the fast current response, wide linear range and low detection limit in the amperometric determination of the two diphenol isomers.