



Trade Science Inc.

June 2010

ISSN : 0974-7419

Volume 9 Issue 2

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAJ, 9(2) 2010 [286-290]

Study on the electrochemical behavior of catechol at a multiwall carbon nanotubes /poly (3-methylthiophene) modified glassy carbon electrode

He Zhang, Jinsheng Zhao*, Houting Liu, Renmin Liu, Huaisheng Wang
Department of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, (P.R.CHINA)

E-mail : j-s-zhao@hotmail.com

Received: 5th February, 2010 ; Accepted: 15th February, 2010

ABSTRACT

The electrochemical behavior of catechol at the multiwall carbon nanotubes (MWNTs)/poly (3-methylthiophene) (P3MT)/glassy carbon electrode (GCE) was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The experimental results suggested the modified electrode combined the advantage of P3MT and MWNTs, they exhibited electrocatalytic effect on the oxidation of catechol, and resulted in enhancement of rate of charge-transfer. In 0.1 mol L⁻¹ phosphate buffer solution (PBS, pH 6.4), the peak currents of DPV were linear with the catechol concentration in two intervals, viz. 0.2-0.6 μmol L⁻¹ and 0.6-1.0 μmol L⁻¹, with the correlation coefficients were 0.9996, 0.9967 mentioned above respectively. The detection limit of catechol can be estimated to be 5 × 10⁻⁸ mol L⁻¹ (S/N = 3). The effects of scan rates, pH for the voltammetric behavior and detection of catechol were also discussed. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Catechol;
Multiwall carbon nanotubes;
Poly (3-methylthiophene);
Electrochemical behavior;
Electrocatalytic.

INTRODUCTION

Catechol as important phenolic compound in nature, it is often used in industrial processes, such as developer, depressor, antioxidant, secondary coloring matters and so on. Meanwhile, most of them are highly toxic to the environment and the human^[1-3]. Therefore, the detection, identification and quantification of catechol have gained significance in environmental protection, food safety and human health. 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 sen-

sitivity, time-consuming and complicate pretreatment.

In recent years, polymer-modified electrodes have attracted extensively interest, because of their good reproducibility, stability, more active sites and so on^[8]. Poly (3-methylthiophene) (P3MT) is an electronically conducting polymer, which is easily deposited onto electrodes by electro-oxidation of its monomer, and many reports about its preparation and characterization have been published^[9-15]. As far as we know, 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 phenolic compounds^[16-20], dopamine^[21], 8-Hydroxy-2'-deoxyguanosine (8-OH-dG)^[22].

Carbon nanotubes (CNTs) have received more at-

tention since their discovery in 1991^[23], due to their exceptional mechanical and electrical properties. Generally, there are two kinds of nanotubes: single-walled carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs). MWNTs have high surface area, specific conductivity formation, stable chemical property and the character of mechanical strength, so MWNTs attract scientists' extensive attention in sensors research^[24-30]. Recently, polymer/MWNTs modified electrodes have excellent electro-catalytic ability for some biological molecules because of their adsorption onto the surface of the MWNTs through strong π - π stacking force to the modified film^[31].

In this work, we prepared the modified glassy carbon electrode (GCE) by coating the MWNTs onto the electrochemical polymerized P3MT surface. This modified electrode combined the advantage of P3MT and MWNTs, exhibited dramatic electro-catalytic effect on the oxidation of catechol, and resulted in enhancement of rate of charge-transfer. The effects of scan rates, pH for the voltammetric behavior and detection of catechol were also discussed.

EXPERIMENTAL

Apparatus

Cyclic voltammetry (CV) and the differential pulse voltammetry (DPV) were performed using a CHI760C electrochemical workstation (CH Instruments, Shanghai, Chenhua Equipments, China). The conventional three-electrode system was employed with a bare GCE, a P3MT/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-methylthiophene (3MT) was obtained from Acros and 3MT was used without further purification, MWNTs was purchased from Chengdu Organic Chemicals Co.Ltd. (Chengdu, China), Acetonitrile (LC grade), NaClO₄ and catechol were all obtained from Aldrich. 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 P3MT modified GCE (P3MT / GCE) has been described in previous works^[19,21,22]. Briefly, prior to the polymer electro-synthesis, the surface of the GCE (diameter 3.0mm) was polished with 0.05 μ m alumina slurry and cleaned by ultra-sonication in twice distilled water. P3MT was electro-deposited on a GCE surface from a solution containing 0.1 M 3MT and 0.1M NaClO₄ dissolved in acetonitrile. Both CV and the potentiostatic mode were adapted for P3MT film preparation. Cyclic voltammograms (CVs) were recorded between 0.0 and 1.7 V vs. Ag/AgCl at a scan rate of 20mV 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 PBS 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 100mV s⁻¹ until a stable background was obtained. Thus, the P3MT-modified GCE was achieved.

The MWNTs were treated by the mixture of concentrated H₂SO₄ and concentrated HNO₃ (1/3, v/v), it is well known that this treatment causes segmentation and carboxylation of MWNTs at their terminuses^[21]. 1.0 mg/mL MWNTs dispersion was made by 1.0 mg solubilizing MWNTs in 1.0mL twice distilled water, and sonicating for 100 s. Following this step, 5 μ L MWNTs dispersion were scrupulously dropped onto the surface of P3MT/GCE. The electrode was treated in pH 7.0 PBS by repetitive scanning in the potential range of -0.2-0.6 V vs. Ag/AgCl at a scan rate of 100mV s⁻¹ until a stable background was obtained. Thus, the MWNTs / P3MT modified electrode was achieved. The prepared electrodes were stored in a dry chamber before

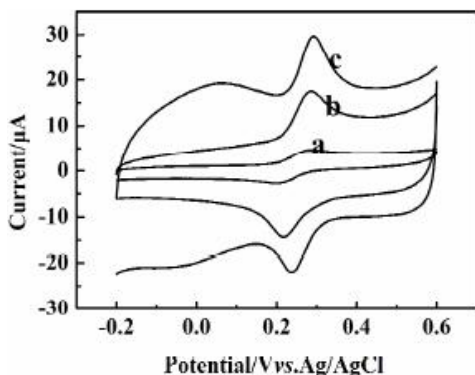


Figure 1 : CVs of $1 \times 10^{-5} \text{ mol L}^{-1}$ catechol at the bare GCE (a), P3MT/GCE (b) and MWNTs/P3MT/GCE (c) in 0.1 mol L^{-1} pH 6.4 PBS. Scan rate: 100 mV s^{-1}

Full Paper

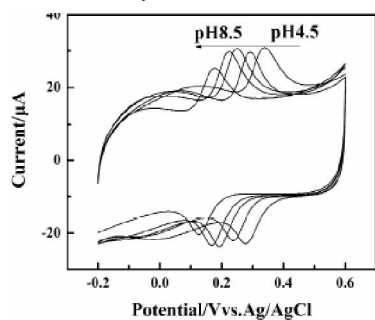


Figure 2(A)

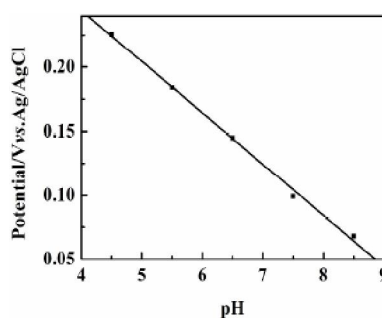


Figure 2(B)

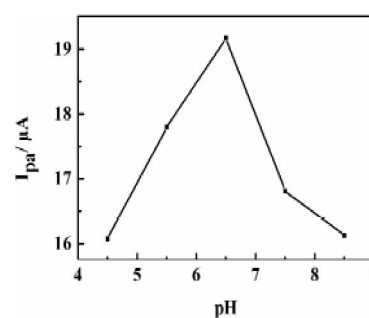


Figure 2(C)

Figure 2 : CVs of $1 \times 10^{-5} \text{ mol L}^{-1}$ catechol at the MWNTs/P3MT/GCE with various pH values (4.5-8.5) in 0.1 mol L^{-1} PBS. Scan rate: 100 mV s^{-1} (A). The relationship between E_{pa} and pH (B), relationship between I_{pa} and pH (C)

use to keep their surface dried.

Electrochemical experiments

The DPV and CV experiments were performed in 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 6.4) containing certain concentrations of 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 catechol at the modified electrodes

CVs of catechol at three different electrodes were shown in figure 1. At the bare GCE (Figure 1, curve a), a couple of broad, ill-defined redox waves were observed with ΔE_p ($80 \text{ mV vs. Ag/AgCl}$). However, a couple of well-defined redox waves as well as enhanced electrochemical response of catechol appeared at P3MT/GCE, MWNTs/P3MT/GCE with ΔE_p , $60 \text{ mV vs. Ag/AgCl}$ and $40 \text{ mV vs. Ag/AgCl}$, respectively. Figure 1, curve (c) suggested that the film of MWNTs/P3MT/GCE can combine the advantage of P3MT and MWNTs, which can effectively catalyze the electro-oxidation of catechol, improve the peak shape and accelerate electron transfer; moreover, result in increased response towards the redox of catechol in contrast to P3MT or GCE alone. That is to say, the MWNTs/P3MT/GCE had better electrocatalytic activity for the catechol.

Effect of pH on the response at the modified electrode

The pH value of the supporting electrode has a

significant influence on the CV of catechol at the MWNTs/P3MT/GCE as shown in figure 2 (A). It can be seen that the anodic peak potential shifts toward negative values with the increase of the supporting electrolyte pH from 4.5 to 8.5, indicating that the electrochemical process of catechol was associated with a proton-transfer process. The relationship between the anodic potential (E_{pa}) of catechol and the pH was linear and a linear regression equation $E_{pa} \text{ (mV vs. Ag/AgCl)} = 0.4042 - 0.03999 \text{ pH}$ can be obtained over the 4.5-8.5 pH with the correlation coefficient of 0.9986 (Figure 2 (B)). The slope of $dE_p/d(\text{pH}) = 0.03999$ implied that the uptake of electrons was accompanied by an equal number of protons^[3,32].

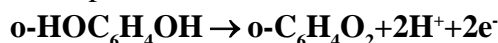


Figure 2 (C) showed the higher peak current appeared at pH range of 6.0-7.0, we used catechol pH value at 6.4 throughout the work.

Effect of the scan rate on electrochemical response of catechol at the MWNTs/P3MT/GCE

The effect of the scan rates on the electrochemical behavior of $1 \times 10^{-5} \text{ mol L}^{-1}$ catechol at the MWNTs/P3MT/GCE in 0.1 mol L^{-1} pH 6.4 PBS was investigated by CV and the results were shown in (Figure 3(a)). It can be seen that the anodic peak current increased and the peak potential shifts towards more positive values with the increase of scan rates. The plot of $\log I_{pa}$ against $\log V$ was linear over the range of $20\text{-}200 \text{ mV s}^{-1}$ and the linear regression equation $\log I_{pa} = -0.1668 + 0.6406 \log V$ (I_{pa} in μA and V in mV s^{-1}) with a correlation coefficient of 0.9996 was obtained I_{pa} against square root of V , which suggested that catechol undergoes an adsorption-controlled process at the MWNTs/P3MT modified glassy carbon electrode surface.

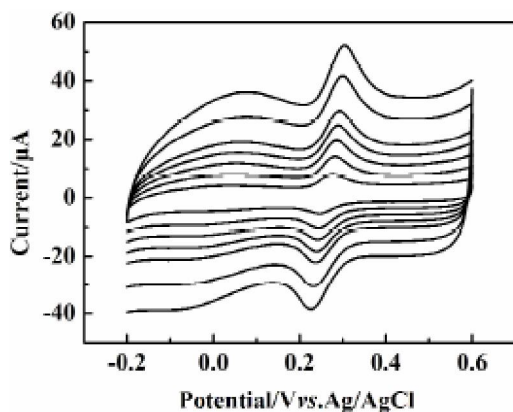


Figure 3(a)

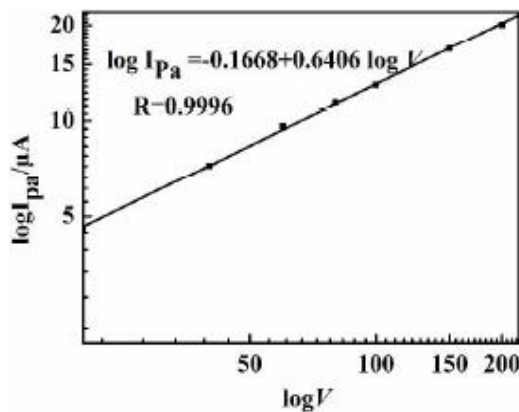


Figure 3(b)

Figure 3: CVs of $1 \times 10^{-5} \text{ mol L}^{-1}$ catechol at the MWNTs/P3MT/GCE in 0.1 mol L^{-1} pH 6.4 PBS with scan rates of 200, 150, 100, 80, 60, 40, 20 mV s^{-1} (a). The relationship between $\log I_{pa}$ and $\log V$ (b)

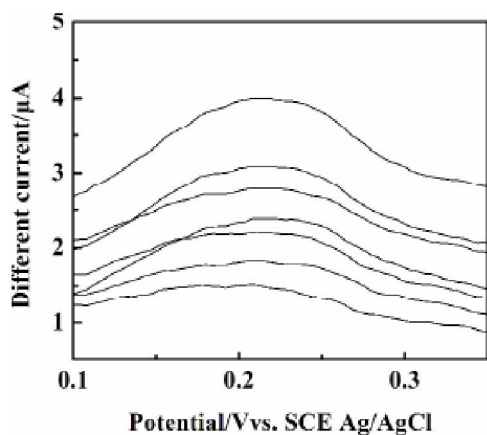


Figure 4(a)

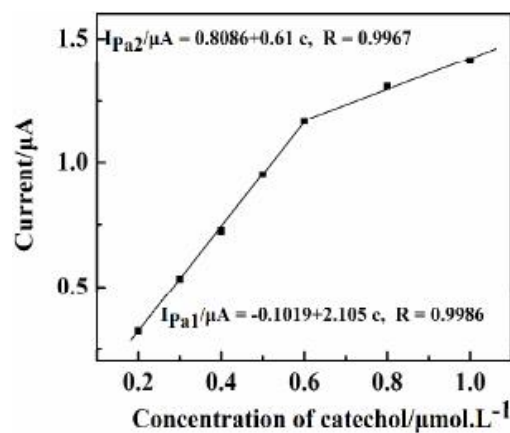


Figure 4(b)

Figure 4: (a) DPV (background correction) of different concentrations catechol at MWNT/P3MT/GCE. Concentrations: 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, $1.0 \mu\text{mol L}^{-1}$. Potential range: $-0.2-0.4 \text{ V}$ (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. (b) The linear relationships in different concentrations catechol at the MWNT/P3MT/GCE

DPV for detection catechol at the MWNTs/P3MT modified electrode

DPV was used for the determination of catechol, because of its much higher current sensitivity and better resolution than CV. Figure 4(a) showed the DPV of different concentrations catechol at MWNT/P3MT/GCE. A preconcentration time of 300s was needed for the determination. The relative deviation was 2.1% for 7 successive determinations at $0.2 \mu\text{mol L}^{-1}$ catechol, which indicated that the modified electrode has a good reproducibility for catechol. After each of determination the electrode was treated in pH 7.0 PBS by repetitive scanning until a stable background was obtained.

Figure 4(b) showed the linear relationships in different concentrations catechol at the MWNTs/P3MT/GCE. Two linear relationships were found differential

pulse peak heights of catechol with its different concentrations, the linear regression equations, respectively:

$$I_{pa1}/\mu\text{A} = -0.1019 + 2.105 c/(\mu\text{mol L}^{-1})$$

$$R = 0.9986 (0.2-0.6 \mu\text{mol L}^{-1})$$

$$I_{pa2}/\mu\text{A} = 0.8086 + 0.61 c/(\mu\text{mol L}^{-1})$$

$$R = 0.9967 (0.6-1.0 \mu\text{mol L}^{-1})$$

The corresponding slopes (sensitivity) were 2.105, $0.61 \mu\text{A}/(\mu\text{mol L}^{-1})$ in the two linear regression equations, the correlation coefficients were 0.9986, 0.9967 mentioned above respectively, the detection limit was $5 \times 10^{-8} \text{ mol L}^{-1}$ ($S/N = 3$).

CONCLUSION

A glassy carbon electrode modified with MWNTs/P3MT film was fabricated. Compared with P3MT/GCE

Full Paper

and MWNTs/P3MT/GCE, the MWNTs/P3MT/GCE can combined the advantages of P3MT and MWNTs, which can effectively catalyze the electro-oxidation of catechol, improve the peak shape and accelerate electron transfer; moreover, result in increased response towards the redox of catechol. The modified electrode also showed better reproducibility and stability. In 0.1 mol L⁻¹ pH 6.4 PBS, the peak currents of DPV were linear with catechol concentration in two intervals, with the detection limit of 5×10^{-8} mol L⁻¹ catechol (S/N=3).

ACKNOWLEDGEMENTS

Financial supports from the National Natural Science Foundation of China (no. 20906043) and the Taishan Scholarship of Shandong Province are gratefully acknowledged.

REFERENCES

- [1] L.Taysse, D.Troutaud, N.A.J.Khan; *Toxicol.*, **98**, 207 (1995).
- [2] D.M.Zhao, X.H.Zhang, L.J.Feng, L.Jia, S.F.Wang; *Colloids and Surfaces B: Biointerfaces*, **74**, 317 (2009).
- [3] C.X.Chen, C.Sun, Y.H.Gao; *Electrochimica Acta*, **54**, 2575 (2009).
- [4] H.Cui, C.X.He, G.W.Zhao; *J.Chromatogr.A.*, **171**, 855 (1999).
- [5] S.C.Moldoveanu, M.Kiser; *J.Chromatogr.A.*, **90**, 1141 (2007).
- [6] P.Nagaraja, R.A.Vasanth, K.R.Sunitha; *Talanta*, **55**, 1039 (2001).
- [7] M.F.Pistonesi, M.S.D.Nezio, M.E.Centuri3n, M.E.Palomeque, A.G.Lista, B.S.F.Band; *Talanta*, **69**, 1265 (2006).
- [8] G.Y.Jin, F.Huang, W.Li, S.N.Yu, S.Zhang, J.L.Kong; *Talanta*, **74**, 815 (2008).
- [9] G.Erdogdu, A.E.Karagozler; *Talanta*, **44**, 2011 (1997).
- [10] J.W.Thackeray, H.S.White, M.S.Wrighton; *J.Phys. Chem.*, **89**, 5133 (1985).
- [11] A.E.Karagozler, O.Y.Ataman, A.Galal, Z.L.Xue, H.Zimmer, H.B.Mark Jr.; *Anal.Chim.Acta*, **248**, 163 (1991).
- [12] J.Roncali, A.Yassar, F.Garnier; *J.Chem.Soc. Chem. Commun.*, 5812 (1988).
- [13] J.Roncali, F.Garnier; *J.Chem.Soc.Chem. Commun.*, 783 (1986).
- [14] R.W.C.Li, L.Ventura, J.Gruber, Yoshio Kawano, L.R.F.Carvalho; *Sensors and Actuators,B.*, **131**, 646 (2008).
- [15] T.Ahujaa, I.A.Mira, D.Kumara; *Rajeshb.Biomaaterials.*, **28**, 791 (2007).
- [16] W.B.Zhang, S.J.Dong; *Acta Chim.Sin.*, **51**, 229 (1993).
- [17] W.B.Zhang, S.J.Dong; *Acta Chim.Sin.*, **50**, 427 (1992).
- [18] W.B.Zhang, H.M.Ji, S.J.Dong; *Acta Chim.Sin.*, **50**, 417 (1992).
- [19] J.Wang, R.L.Li; *Anal.Chem.*, **61**, 2809 (1989).
- [20] L.Agu3, B.Serra, P.Y3ñez-Sede3o, A.J.Reviejo, J.M.Pingarr3n; *Electroanalysis*, **13**, 1231 (2001).
- [21] H.S.Wang, T.H.Li, W.L.Jia, H.Y.Xu; *Biosensors and Bioelectronics*, **22**, 664 (2006).
- [22] T.H.Li, W.L.Jia, H.S.Wang, R.M.Liu; *Biosensors and Bioelectronics*, **22**, 1245 (2007).
- [23] S.Lijima; *Nature*, **354**, 56 (1991).
- [24] Z.H.Wang, J.Q.L.Liang; *Electroanal.Chem.*, **540**, 129 (2003).
- [25] H.S.Wang, D.Q.Huang, R.M.Liu; *Electroanal. Chem.*, **570**, 83 (2004).
- [26] J.J.Gooding; *Electrochim.Acta*, **50**, 3049 (2005).
- [27] A.Merkoci; *Microchim.Acta*, **152**, 157 (2006).
- [28] A.Bouvier, J.F.Feller, M.Castro, Y.Grohens, M.Rinaudo; *Sensors and Actuators, B.*, **138**, 138 (2009).
- [29] H.A.Mohammed, U.Sundararaj; *Carbon*, **47**, 2 (2009).
- [30] F.A.Matthew, E.V.Wytze; *J.Am.Soc.Mass Spectrom.*, **13**, 1170 (2002).
- [31] A.G.Mohamed; *Electrochem.Comm.*, **9**, 2501 (2007).
- [32] S.L.Mu; *Biosens.Bioelectron.*, **21**, 1237 (2006).