Bull Environ Contam Toxicol (2007) 79:5–10
DOI 10.1007/s00128-007-9147-1

Simultaneous Voltammetry Determination of Dihydroxybenzene Isomers by Poly-bromophenol Blue/Carbon Nanotubes Composite Modified Electrode

Pinghua Yang · Wanzhi Wei · Chunyuan Tao · Jinxiang Zeng

Received: 25 September 2006 / Accepted: 19 March 2007 / Published online: 3 May 2007

Abstract A novel modified electrode was constructed by electropolymerization of bromophenol blue at a multi-walled carbon nanotubes modified glassy carbon electrode. The electrode developed was used for the simultaneous determination of the isomers of dihydroxybenzene in environmental samples using a voltammetry method. There was a linear relationship over the range 10^{-6}–10^{-4} mol L^{-1} of hydroquinone, catechol and resorcinol; the detection limits was 3×10^{-7} mol L^{-1}. The constructed electrode showed excellent reproducibility and stability. Actual water samples were analyzed and satisfactory result was obtained.

Keywords Bromophenol blue · Carbon nanotubes · Dihydroxybenzene isomers · Voltammetry determination

Dihydroxybenzene is an important industrial raw and processed material and is widely used in the photography, dye, cosmetic, chemical and pharmaceutical industries. Catechol, resorcinol and hydroquinone are the isomers of dihydroxybenzene. Hydroquinone and catechol are significant airborne toxic environmental pollutants (www.epa.gov). Due to their similar structure and character, it is crucial to develop a simultaneous and simple analytical method for dihydroxybenzene isomers. The current methods for the simultaneous determination of dihydroxybenzene isomers are chromatography (N. A. Penner et al., 2001), spectrophotometry (P. Nagaraja et al., 2001) and electrochemical methods (Rosangela M. et al., 2000). However, these techniques have some disadvantages, such as the requirement for previous separation, complicated operation, intricate chemometric treatments of the analytical signals and a narrow linear range. There are few direct and simultaneous determination methods for dihydroxybenzene isomers.

Electrochemical methods are one of the favored techniques in environmental and biological analysis because of their low cost, high sensitivity and simple operation (Eric Bakker, 2004). With their specifically functionalized surfaces, good stability and reproducibility, chemically modified electrodes are an important component for electrochemical analysis (Qiantao Cai et al., 1994). Methods used for electrode modification included electropolymerization, physical coating and covalent attachment. Electropolymerized dye electrodes show good selectivity and catalytic property (Guiying Jin et al., 2005, F. Valentini et al., 2004).

Since the discovery of their unique electronic structures, and high specific surface area and electrical conductivity, carbon nanotubes have been attractive candidates for use as chemical sensors and biosensors (Joseph Wang, 2005, Qiang Zhao et al., 2002). Multi-walled carbon nanotubes (MWNTs) have been used as electrode modified carbon materials and have exhibited excellent catalytic properties (Joseph Wang et al., 2003). Bromophenol blue (BPB) is an acid–base indicator and has been used as an spectrophotometric and electrochemical reagent for protein assay (Ma et al., 1997, Sun et al., 2005). However, there are no reports of electropolymerized of bromophenol blue with carbon nanotubes for environmental applications.

P. Yang · W. Wei (✉) · J. Zeng
State Key Laboratory of Chemical, Biological Sensing Technologies & Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082
P. R. China
e-mail: weiwz2003@126.com

P. Yang · C. Tao
College of Chemistry and Chemical Engineering, Jiujiang University, Jiujiang 332005, P. R. China

For derivative voltammetry, cyclic voltammetric curves were treated using the *n*th-order derivative technique. The derivative voltammetric curve allows the avoidance of linear interference between the background and noise and increases signal sensitivity and resolution power. To date, the method has been widely applied in electrochemical fields (Jeremiah Mbindyo et al., 2000, Y. Bonfil et al., 2000; http://www.epa.gov).

In this article, a novel modified electrode was fabricated by electropolymerization of bromophenol blue at a multi-walled carbon nanotubes modified glassy carbon electrode. The resulting electrode combined the catalytic properties of carbon nanotubes with the selectivity of the polymerized film and was used for the simultaneous determination of the isomers of dihydroxybenzene with good reproducibility and stability.

Materials and Methods

Multi-walled carbon nanotubes (MWNTs) were obtained from Shenzhen Nanotech Port Co. Ltd. with a typical diameter of 10–30 nm and length of 1–2 µm; their purity was 95–98%. Other chemicals were analytical reagents, and were used as received. Doubly distilled water was used throughout the experiments. All of the procedure was carried out at room temperature.

Scanning electron microscopy (SEM) images were obtained by using a JSM-6700F field emission SEM (JEOL Ltd., Japan). All electrochemical experiments were carried out on a CHI660B electrochemical workstation (Chenhua Instrument Company of Shanghai, China) in a conventional three-electrode cell. The working electrode was a glassy carbon disk electrode (GCE) with a diameter of 3 mm, the auxiliary electrode consisted of a platinum wire, and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials reported in this paper are relative to the SCE.

Prior to use, the 3 mm GC working electrode was carefully polished with a chamois leather containing 0.05 µm Al_2O_3 slurry and then ultrasonically cleaned in ethanol and distilled water, and finally electrochemically treated by potential cycling between –1.0 and 1.6 V in 0.5 mol/L H_2SO_4 until a steady state was reached. The MWNTs were treated according to a previously described procedure (Hidefumi Hiura et al., 1995). Ten milligrams of purified and functionalized MWNTs was dispersed with the aid of ultrasonic agitation in 10 mL of N,N-dimethylformamide (DMF) to give a 1.0 mg/mL black suspension. The MWNT modified GCE was prepared by dropping 4 µL of the suspension of MWNTs onto the clean GC electrode surface well, and evaporating the solvent using an infrared lamp. The electropolymerization of bromophenol blue was performed in pH 6.0 phosphate buffer solutions with 0.5 mM bromophenol blue by cyclic voltammetry between –1.0 V and 1.8 V. The scan rate was 0.1 V/s.

Firstly, the modified electrode was activated by six successive voltammetric cycles from –0.1 to 0.90 V in pH 6.0 phosphate buffer solution (PBS). Next, linear sweep voltammograms (LSV) were recorded from –0.1 to 0.90 V in pH 6.0 PBS as the background. Then, the same sweep of LSV of dihydroxybenzene isomers was recorded. Finally, after subtracting the background, the LSV curves were treated with a first-order derivative technique on the CHI660B electrochemical workstation. Peak currents were measured at 0.11 V for hydroquinone, 0.22 V for catechol, and 0.63 V for resorcinol.

Results and Discussion

The electropolymerization of bromophenol blue was performed in pH 6.0 PBS with 0.5 mM bromophenol blue by cyclic voltammetry between –1.0 V and 1.8 V. The scan rate was 0.1 V/s. Figure 1 illustrates the typical set of cyclic voltammetry grams obtained from the electropolymerization of bromophenol blue on MWNT modified GCE. There was a broad reductive peak from –0.15 V to 0.40 V and three oxidative peaks from 0.27 to 0.90 V with steadily increasing current. The oxidative peak at 0.82 V indicates that the monomer of BPB was oxidized at a high potential. In the second cycle, a new pair of redox peaks appeared and the current increased across the scan, which is indicative of the buildup of a conducting polymer film at the electrode.

Figure 2 shows the typical morphology of the MWNTs/GCE (a) and poly-BPB/MWNT/GCE (b) characterized by scanning electron microscopy (SEM). It could be observed that the MWNTs distributed homogeneously on the glassy carbon electrode and displayed a special three-dimensional

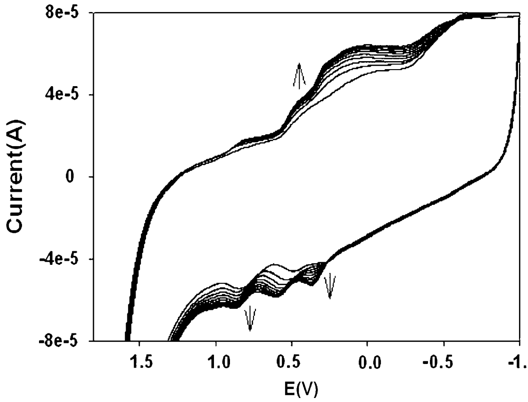

Fig. 1 Typical cyclic voltammograms of electropolymerization of 0.5 mM BPB at MWNT modified GCE. The arrows shows increasing current

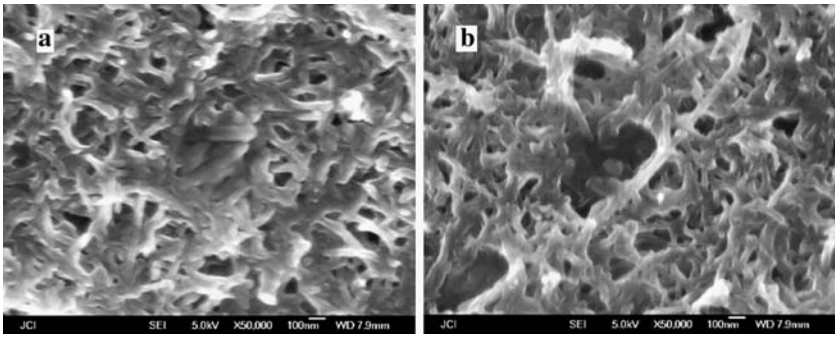

Fig. 2 SEM images of: (a) MWNTs, and (b) poly-BPB/MWNT modified electrodes

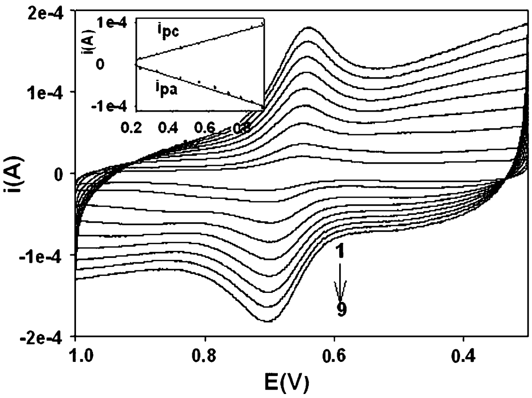

Fig. 3 Cyclic voltammograms of Poly-BPB/MWNT/GC electrode in 0.5M H_2SO_4 at 50, 100, 150, 200, 250, 300, 400, 500 and 600 mV/s (1–9). *Inset*: plots of cathodic peak currents (i_{pc}) and anodic peak currents (i_{pa}) versus the square root of the scan rate

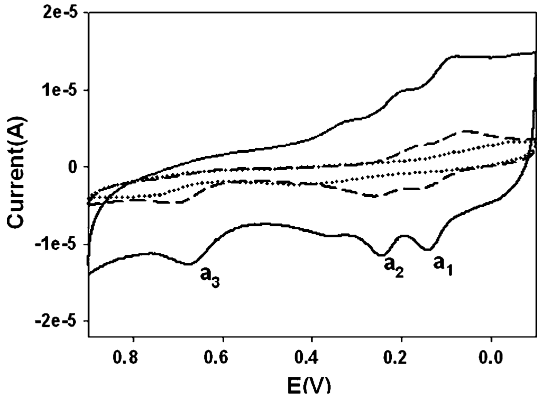

Fig. 4 Cyclic voltammograms of dihydroxybenzene at different electrodes in pH 6.0 PBS. Dotted line: bare GCE; long-dash line: poly-BPB/GCE; solid line: poly-BPB/MWNT/GCE. a_1, a_2 and a_3 are the oxidation peak potentials of hydroquinone, catechol and resorcinol, respectively. The concentration of catechol, hydroquinone and resorcinol was 0.1, 0.1 and 0.2 mM, respectively

structure. The poly-BPB/MWNTs nanocomposite on the glassy carbon electrode exhibited a similar structure to that of MWNTs, which means that the electrodeposited poly-BPB did not change the structure of the MWNTs. Therefore, it is difficult to discern the difference between the poly-BPB/MWNTs and MWNT modified GCE; this may be mostly due to the large amount of MWNT present while the electrodeposited poly-BPB is very thin. It is hoped that the poly-BPB/MWNT nanocomposites distributed homogenously on the electrode will provide a high signal-to-noise ratio since they are fully and easily accessible to analytes when used as an electrochemical sensing unit. The effect of the polymerizing potential was studied. When the upper limit of potential was less than 1.4 V or the lower limit of the potential was more than –0.6 V, electropolymerization had not occurred. The selective experimental parameter was similar to that for direct electropolymerization of BPB on bare GCE.

The cyclic voltammetry grams of the poly-BPB/MWNT/GCE are shown in Fig. 3 for different scan rates in 0.5M H_2SO_4. A pair of current peaks appeared in the range 0.62–0.70 V, the redox peaks of poly-BPB. The peak current increased with the scan rate. The inset figure shows the linear relationship between the peak current and the square root of the scan rate. This illustrates the transmission of electrons in the polymerized film in accord with the diffusion law.

The electrochemical behaviour of dihydroxybenzene isomers at different electrodes was investigated by cyclic voltammetry; the results are shown in Fig. 4. At the bare GC electrode, there are two oxidation peaks at potentials of 0.43 and 0.76 V. The oxidation peak of catechol and hydroquinone could not be divided and the peak current was low (Fig. 4, dotted line). Under the identical conditions, the isomers of dihydroxybenzene yielded three oxidation peaks whose potentials were 0.16, 0.26 and 0.71 V at the polybromophenol blue GCE (Fig. 4, long-dash line). The oxidation peaks of catechol and hydroquinone were divided with a difference of 100 mV. This illustrates that the poly-BPB GCE has better selectivity with respect to catechol and hydroquinone. However, the peak current was still low. In contrast, the poly-BPB/MWNT/GCE showed excellent electrocatalytic activity and the best selectivity for the isomers of dihydroxybenzene (Fig. 4, solid line). The difference in the oxidation peak potential between hydroquinone, catechol and resorcinol was 105 and 432 mV and the oxidation peak current was greater than for the other electrodes. These results illustrate that the poly-BPB/MWNT/GC electrode combined the catalytic effect and the selectivity from MWNTs and the polymerized film and that the modified electrode could be used in the analysis.

Cyclic voltammetry was used to investigate the effects of different supporting electrolytes. Different supporting electrolytes were tested: H_2SO_4, acetate buffer, Britton–Robinson buffer and phosphate buffer solution. We found that in PBS and H_2SO_4 solutions, the peak currents of the dihydroxybenzene isomers were larger and the peak was sharper. However, the peak potentials of hydroquinone, catechol and resorcinol were shifted towards positive values for increasing pH. This indicated that there had been a larger over-potential and greater interference. In this paper, PBS was chosen as the supporting electrolyte. The effect of the pH of the PBS was tested from 4.0 to 8.0. When the scan rate was constant, all peak potentials shifted towards negative values with increasing pH in the range 5.0–8.0. The relationship between the anodic peak potential and the pH was linear with the regression equation:

$$\text{Hydroquinone}: E_\text{p} = 0.475 - 0.0537\text{pH}(R^2 = 0.993),$$

$$\text{Catechol}: E_\text{p} = 0.594 - 0.0565\text{pH}(R^2 = 0.990),$$

$$\text{Resorcinol}: E_\text{p} = 1.081 - 0.0649\text{pH}(R^2 = 0.993).$$

The experimental results show that protons participate in the redox processes of dihydroxybenzene isomers at the modified electrode (Huaisheng Wang et al., 2004). In addition, the peak currents increased slightly with increasing pH. However, at low pH, the oxidation potentials were high and interference was serious. Therefore, a weak acidic solution was better for the experiments. In this work, pH 6.0 was chosen as the optimum pH.

Figure 5 illuminates the typical first-derivative recording of the background-subtracted LSVs of mixed isomers of dihydroxybenzene. Hydroquinone, catechol and resorcinol exhibited an excellent record with the signal height of the other two isomers remaining unchanged, thus proving that the responses to the dihydroxybenzene isomers were relatively independent. The calibration experiments were carried out by varying the concentration of one isomer in the presence of the other two in pH 6.0 PBS. (The concentration of catechol and hydroquinone was 0.1 mM; the concentration of resorcinol was 0.2 mM.)

The results show that the oxidative peak current has a linear relationship with concentration in the range 10^{-6} – 10^{-4} M (resorcinol, hydroquinone and catechol). The detection limits of hydroquinone, catechol and resorcinol were 3×10^{-7} M (a signal-to-noise ratio of 3). The calibration formulas and the linear correlation coefficients are (i_pa in A/s, C in mol/L): C in mol/L):

$$\text{Hydroquinone}: i_\text{pa} = 3.35 \times 10^{-2}C + 9.44 \times 10^{-8}(R^2 = 0.9999)$$

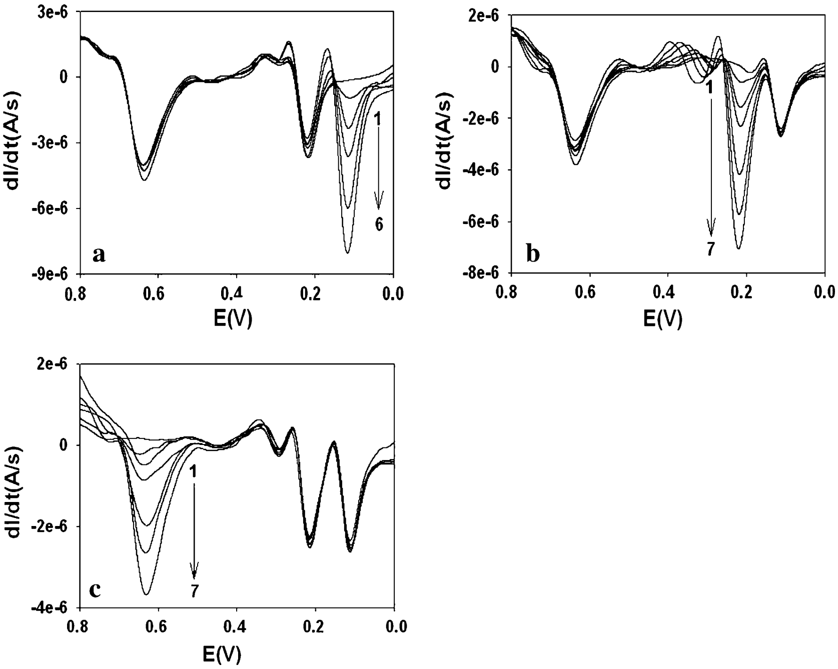

Fig. 5 Typical first-order derivative of linear sweep voltammograms of: (a) hydroquinone (1–6) at 0, 0.2, 0.6, 1, 2, and 3 × 10^{-4} M; (b) catechol (1–7) at 0, 0.2, 0.6, 1, 2, 3, and 4 × 10^{-4} M; (c) resorcinol (1–7) at 0, 0.04, 0.1, 0.2, 0.4, 1.2, and 2.0 × 10^{-4} M

Table 1 Determination of hydroquinone in a water sample

Water sample[a]	1			2			3			4[b]
Isomer	HQ	CA	RE	HQ	CA	RE	HQ	CA	RE	HQ
Added (10^{-5} M)	0.00	0.00	0.00	0.00	2.00	2.00	2.00	5.00	5.00	0.00
Found (10^{-5} M)	3.52	—	—	3.47	1.92	2.10	5.50	5.08	4.89	3.43
RSD (n = 6)	—	—	—	2.2%	3.0%	1.8%	2.7%	1.6%	2.1%	2.5%
Recovery (%)	—	—	—	—	96.0	105.0	99.0	101.6	97.8	—

[a] The waste sample was diluted 100 times. HQ = hydroquinone; CA = catechol; RE = resorcinol, average of six measurements

[b] The result of the spectroscopic method

$$\text{Catechol}: i_{\mathrm{pa}} = 2.20 \times 10^{-2} C + 2.44 \times 10^{-7} (R^2 = 0.9941)$$

$$\text{Resorcinol}: i_{\mathrm{pa}} = 5.49 \times 10^{-2} C + 1.40 \times 10^{-7} (R^2 = 0.9981)$$

The poly-BPB/MWNT/GCE was prepared repeatedly six times using the same GCE. Measurements of a standard sample mixed with 4×10^{-5} mol.L^{-1} dihydroxybenzene were carried out in parallel three times with relative standard deviations (RSD) of 2.43 %, 3.76 % and 2.89 % for hydroquinone, catechol and resorcinol, respectively. The results indicated that the poly-BPB/MWNT/GCE has excellent reproducibility and stability.

The effect of possible interference in the wastewater due to metal ions, anions and organic compounds was tested. A large number of compounds, such as Ca^{2+}, Zn^{2+}, Mg^{2+}, Cu^{2+}, Na^{+}, K^{+}, NO_3^{-}, Cl^{-}, SO_4^{2-}, PO_4^{3-} (each at concentrations of 5 mM) and ethanol, benzene, toluene (each at concentrations of 0.1 mM) had no influence on the dihydroxybenzene signals.

The water samples (D-72# develop waste) were obtained from a photo studio. The main ingredients of the D-72# developer liquid are methyl-p-aminophenol sulfate (w/w 0.3 %), sodium sulfite (w/w 4.5 %), hydroquinone (w/w 1.2 %), sodium carbonate (w/w 6.8 %) and potassium bromide (w/w 0.2 %). First, the waste was adjusted to weak acidity by added 0.5 M H_2SO_4. Then, the waste was diluted 100 times. Finally, the approach described above was used to measure dihydroxybenzene by direct determination and the standard added method. The results obtained by this method are compared with those from the spectroscopic method (A. Afkhami et al., 2001) in Table 1. The recovery was 96.0–105.0%. The results of the proposed method agree well with those obtained by the spectroscopic method, which suggests the accuracy and reliability of the approach, and that it has great potential for practical analyses.

Acknowledgements The authors gratefully acknowledge the financial support of the China Postdoctoral Science Foundation (No. 20020532007) and Key Sci/Tech Res. Project (no. 03123) of the Education Department, China.

References

Afkhami A, Khatami HA (2001) Indirect kinetic spectrophotometric determination of resorcinol, catechol, and hydroquinone. J Anal Chem 56(5):429–432

Bonfil Y, Brand M, Kirowa-Eisner E (2000) Trace determination of mercury by anodic stripping voltammetry at the rotating gold electrode. Analytica Chimica Acta 424:65–76

Cai QT, Khoo SB (1994) Poly (3, 3'-diaminobenzidine) film on a gold electrode for selective preconcentration and stripping analysis of selenium (IV). Anal Chem 66:4543–4550

Eric Bakker (2004) Electrochemical sensors. Anal Chem 76:3285–3298

Hidefumi H, Thomas WE, Katsumi T (1995) Opening and purification of carbon nanotubes in high yield. Advanced Materials 7:3275–276

Jeremiah Mbindyo, Liping Zhou, Zhe Zhang, James D Stuart, James F (2000) Rusling detection of chemically induced DNA damage by derivative square wave voltammetry. Anal Chem 72:2059–2065

Jin GY, Zhang YZ, Cheng WX (2005) Poly (p-aminobenzene sulfonic acid) – modified glassy carbon electrode for simultaneous detection of dopamine and ascorbic acid. Sensors Actuators B 107:528–534

Joseph W (2005) Carbon-nanotube based electrochemical biosensors: a review. Electroanalysis 17:7–14

Joseph W, Mustafa M (2003) Carbon nanotube/teflon composite electrochemical sensors and biosensors. Anal Chem 75:2075–2079

Ma CQ, Li KA, Tong SY (1997) Enhancement of Rayleigh light scattering of bromophenol blue by proteins and protein assay by the scattering technique. Analyst 122:361–364

Nagaraja P, Vasantha RA, Sunitha KR (2001) A sensitive and selective spectrophotometric estimation of catechol derivatives in pharmaceutical preparations. Talanta 55:1039–1046

Penner NA, Nesterenko PN, Rybalko MA (2001) Use of hypercrosslinked polystyrene for the determination of pyrocatechol, resorcinol, and hydroquinone by reversed-phase HPLC with dynamic on-line preconcentration. J Anal Chem 56:934–939

Rosangela MC, Cesar M, Lauro TK (2000) Simultaneous determination of phenol isomers in binary mixtures by differential pulse voltammetry using carbon fibre electrode and neural network with pruning as a multivariate calibration tool. Anal Chim Acta 420:109–121

Sun W, Han JY, Jiao K, Lu LD (2005) Studies on the interaction of protein with bromophenol blue by electrochemical method and its analytical application. Bioelectrochemistry 68:60–66

Valentini F, Salis A, Curulli A, Palleschi G (2004) Chemical reversibility and stable low-potential NADH detection with nonconventional conducting polymer nanotubule modified glassy carbon electrodes. Anal Chem 76:3244–3248

Wang HS, Huang DQ, Liu RM (2004) Study on the electrochemical behavior of epinephrine at a poly (3-methylthiophene)-modified glassy carbon electrode. J Electroanal Chem 570:83–90

Zhao Q, Gan ZH, Zhuang QK (2002) Electrochemical sensors based on carbon nanotubes. Electroanalysis 14:1609–1613