Modification of glassy carbon electrode with Poly-melamine film : An application for the detection of hydroquinone, catechol and resorcinol

폴리-멜라민 필름을 이용한 유리탄소전극의
변형: 하이드로퀴논, 카테콜, 레조시놀
검출에 적용

2015년 2월

서울대학교 대학원
과학교육과 화학전공
김 은 경

Modification of glassy carbon electrode with Poly-melamine film: An application for the detection of hydroquinone, catechol and resorcinol

폴리-멜라민 필름을 이용한 탄소유리전극의
변형: 하이드로퀴논, 카테콜, 레조시놀
검출에 적용

지도교수 홍 훈 기

이 논문을 교육학 석사학위논문으로 제출함
2015년 2월

서울대학교 대학원
과학교육과 화학전공
김 은 경

김은경의 석사학위논문을 인준함
2015년 2월

위 원 장 _____노태희_____ (인)
부 위 원 장 _____홍훈기_____ (인)
위 원 _____안지현_____ (인)

CONTENT

Modification of glassy carbon electrode with Poly-melamine film: An application for the detection of hydroquinone, catechol and resorcinol

List of Schemes and Table

List of Figures

Abstract

Modification of glassy carbon electrode with Poly-melamine film: An application for the detection of hydroquinone, catechol and resorcinol

Eun-Kyoung Kim
Chemistry Education Major
Department of Science Education
The Graduate School
Seoul National University

In this study, we share findings about the development of a sensor using poly-melamine modified glassy carbon electrode (PMel/GCE) that is capable of detecting dihydroxybenzene isomers simultaneously in aqueous solution. We prepared poly-melamine film by electro-polymerization on GCE in acidic solution containing melamine monomer, then it was characterized by field emission scanning electron microscopy (FE-SEM), electrochemical impedance spectroscopy (EIS).

Cyclic voltammetry (CV) shows the electrochemical behaviors of dihydroxybenzene isomers at the PMel/GCE. Square wave voltammetry (SWV) was used for the simultaneous determination of dihydroxybenzene isomers. The two broad anodic peaks of dihydroxybenzene isomers at 0.380 V for hydroquinone and catechol and 0.712 V for resorcinol on the bare GCE resolved in three well-defined peaks at 0.084 V for hydroquinone, 0.184 V for catechol and 0.608 V for resorcinol vs. Ag/AgCl, respectively. It exhibited a good linearity to dihydroxybenzene isomers in the concentration range of 5-300 μM for hydroquinone, 5-500 μM for catechol and 3-200 μM for resorcinol with good sensitivity of 0.052, 0.055 and 0.038 μA/μM. And the detection limits were 0.65, 1.90 and 0.58 μM at a signal-to-noise ratio of 3. Furthermore, this sensor is expected to be utilized in detecting these isomers in local tap water sample with good anti-interference.

Key words: Melamine, Electrodeposition, Hydroquinone, Catechol, Resorcinol, Dihydroxybenzene isomers, Square wave voltammetry

Student Number: **2013-21425**

Modification of glassy carbon electrode with Poly-melamine film: An application for the detection of hydroquinone, catechol and resorcinol

1. Introduction

Hydroquinone (HQ), catechol (CA) and resorcinol (RE), known as dihydroxybenzene isomers, are largely used as antioxidants, flavoring agents, medicines, pesticides, photography chemicals and polymerization inhibitors. [1] Due to their high toxicity to human's health and difficulty to disintegrate, these isomers are considered to be environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU). [2] Furthermore, they commonly coexist in water samples, but it is hard to detect these isomers simultaneously because of their similar properties and structures. Therefore, it is important to establish effective analytical method for quantifying each isomers at the same time. Many techniques have been established to detect dihydroxybenzene isomers, including chromatography [3-5], spectrophotometry [6, 7], fluorescence [8, 9] and electrochemical analysis [10-12]. Among the techniques for determining dihydroxybenzene isomers, electrochemical methods are far preferable to others because of their favorable portability, easy operation process, high sensitivity, low cost and suitability for the *in situ* measurement. [13] For detecting dihydroxybenzene isomers, various conducting materials were used to improve electronic properties of conventional electrode. For example, there have been sensors based on graphene that have attempted to detect dihydroxybenzene isomers simultaneously. [14, 15] Other chemical sensors with noble metals for simultaneous

determination was reported as well. [16, 17] In addition to this, carbon nanotubes [18, 19] and polymers [20] have been used to modify conventional electrode for sensing dihydroxybenzene isomers.

Owing to chemical stability of polymeric film, high sensitivity, reproducibility, more active sites, strong adherence to electrode surface and intrinsic conductivity due to considerable π-electron of their conjugated backbone [21, 22], various polymers have been developed to improve electronic properties for simultaneous detection of the oxidation of dihydroxybenzene isomers. For instance, the composite of poly-aniline with MnO_2 [23], polymeric ionic liquid on multi-walled carbon nanotubes [24], poly-pyrrole encapsulated within Mesoporous Silica [25] or poly-(glutamic acid) [26] have been used as electrochemical sensors for detecting dihydroxybenzene isomers. However, electrodes modified with these materials still have some drawbacks such as inability for simultaneous determination of dihydroxybenzene isomers in their ternary mixture, a narrow linear range, a complicated modification process, a long synthesis time and high cost of modifying materials. This prompted us to be interested in finding a novel method for developing the dihydroxybenzene isomers sensor.

To overcome these drawbacks, we report a new modification method using electro-polymerization of melamine on glassy carbon electrode (GCE) in this paper. Recently, some electrochemical sensors using poly-melamine film have been reported for detection of various analytes such as serotonin [21] and to quantify simultaneously guanine and

adenine [27]. In literature, poly-melamine was also used for developing dihydroxybenzene isomers sensor because of its high catalytic current, large surface area, low cost, film stability and good sensitivity [21, 27]. The poly-melamine modified glassy carbon electrode (PMel/GCE) displays voltammetric responses with excellent analytical performances for simultaneous determination of dihydroxybenzene isomers.

2. Experimental

2.1. Apparatus and reagents

A CHI 760B electrochemical workstation (C.H. Instruments, Inc., U.S.A) was used for electrochemical measurements at the room temperature. The morphology of the poly-melamine film was examined on FE-SEM (Supra 55 VP (Carl Zeiss) Field-Emission Scanning Electron Microscope). Potentiometric experiments were performed in a conventional three-electrode electrochemical system with a bare or a modified GCE (3.0 mm diameter) as the working electrode, an Ag/AgCl/KCl (3.0 M) as the reference electrode and a platinum wire as counter electrode.

All reagents were of analytical grade without further purification, and aqueous solutions were prepared with deionized water (DIW) obtained from an ultra-pure water system (Human Co., Korea) (> 18 MΩ cm). Melamine ($C_3H_6N_6$, Sigma-Aldrich Co. (USA)) and sulfuric acid (H_2SO_4, Daejung Chemicals Co. (Korea)) were used for electro-polymerization. Hydroquinone, catechol and resorcinol (Dihydroxybenzene isomers, $C_6H_4(OH)_2$), potassium ferricyanide ($K_3Fe(CN)_6$) and potassium ferrocyanide ($K_4Fe(CN)_6$) were supplied by Sigma-Aldrich Co. (USA). Phosphate buffer solution (0.1 M PBS, pH 7.0) was used as the electrolyte by mixing the stock solutions of 0.1 M dipotassium hydrogen phosphate (K_2HPO_4, Sigma-Aldrich Co. (USA))

and 0.1 M monopotassium phosphate (KH$_2$PO$_4$,Sigma-Aldrich Co. (USA)), and the pH was adjusted with NaOH and HCl.

2.2. Preparation of the PMel/GCE

The PMel/GCE was prepared by a facile electro-polymerzation method. Before the electrodeposition, the GCE was polished with 0.3 μm and 0.05 μm alumina powders on a polishing cloth in regular sequence. After that it was thoroughly rinsed with water and sonicated by ultrasonication in DIW for 2 minutes. After being polished, the electrode was consecutively scanned using cyclic voltammetry (CV) from 0 to 1.6 V at a scan rate of 100 mVs^{-1} for 20 cycles in 0.1 M H$_2$SO$_4$ containing 1.0 mM melamine aqueous solution to form poly-melamine film on the surface of electrode. Then, the resulting PMel/GCE was rinsed with DIW to remove melamine monomer remaining at the surface of the electrode. After this step, the prepared electrode was washed with DIW and dried in the ambient condition. [21, 27, 28]

2.3. Electrochemical measurements

All electrochemical measurements were performed after purging oxygen gas in the PBS by high-purity nitrogen for about 15 minutes. Electroanalysis of dihydroxybenzene isomers concentration was

performed in a 10 mL of 0.1 M PBS (pH 7.0) by using square wave voltammetry (SWV) under a potential from -0.2 to 0.8 V at room temperature, and the conditions for employing SWV was an increment of 0.004 V, a pulse amplitude of 0.025 V and a frequency of 15 Hz.

3. Results and Discussion

3.1. Fabrication of the Poly-melamine film

Figure 1 shows the consecutive cyclic voltammograms (CVs) of melamine electro-polymerization at GCE in the solution of 1 mM melamine in 0.1 M H_2SO_4. It is observed respectively that anodic and cathodic peak potentials of poly-melamine film occur at 0.658 and 0.599 V. From observation the CVs of the PMel/GCE shows that as more and more number of potential cycles increase, current signals also continuously increase. These results suggest that the poly-melamine film was deposited on the surface of the GCE by CV. The peak current of the poly-melamine film obviously grows up at first, but later become stable after 17 cycles. Melamine can be easily assembled onto the surface of GCE as a thin polymer film through π-π electronic interactions between poly-melamine and GCE. It was amply demonstrated that potential and pH impact on the formation of and stabilization of melamine radical cation and electro-polymerization of that can occur at enough positive potential in highly acidic medium. We speculated that polymerization of melamine will occur on two oxidized amino groups and only form head-to-head coupling without head-to-tail and tail-to-tail coupling. This process is depicted in Scheme 1 [28]. CVs of electro-polymerization of melamine have been reported in previous work [21].
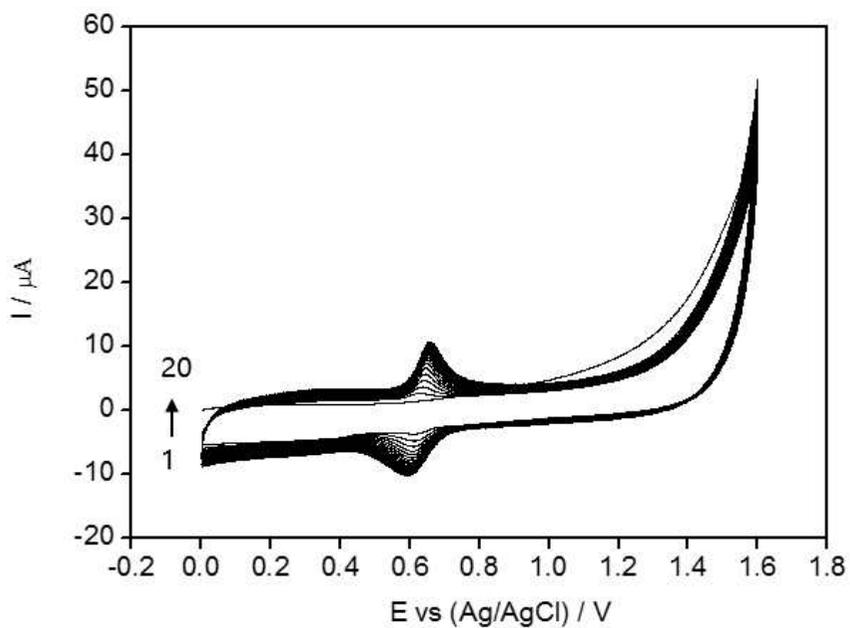
Figure 1. CVs for polymerization of Melamine on GCE. The voltammograms were recorded at 100 mVs^{-1} in 0.1 M H$_2$SO$_4$ solution containing 1 mM melamine.
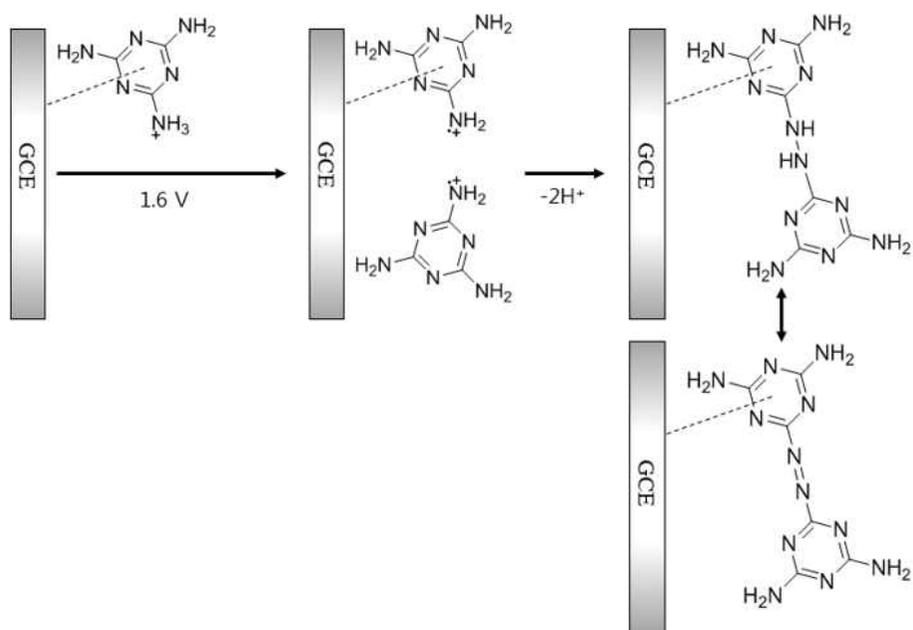
Scheme 1. Electro-polymerization mechanism of melamine at GCE.

3.2. *Characterization of the Poly-melamine film*

The morphological characteristics of the bare GCE and the PMel/GCE were examined by FE-SEM images. It is clear, from Figure 2A and 2B that poly-melamine film was assembled onto GCE. Figure 2A is indicative of the smooth surface of GCE, while the result in Figure 2B shows the uniform nanosheet branches of the poly-melamine film obtained by electrochemical polymerization. This kind of structure is far helpful that it increases the active surface area to offer more sites for the interaction with dihydroxybenxene isomers.
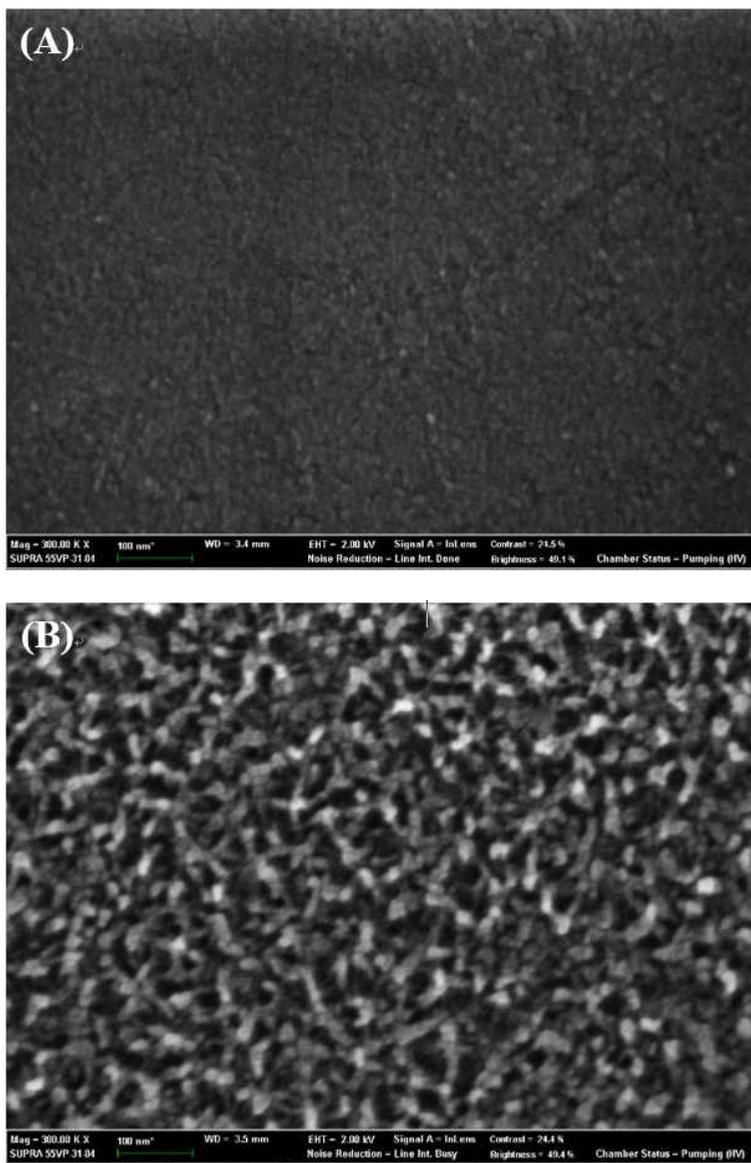
Figure 2. FE-SEM images for (A) the bare GCE and (B) the PMel GCE.

More characterization of the bare GCE and the PMel/GCE was investigated by electrochemical impedance spectroscopy (EIS). Figure 3 (a) and 3 (b) exhibits the Nyquist plots for EIS measurements of the bare GCE and the PMel/GCE in 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ containing 0.1 M KCl electrolyte at the potential of 0.22 V in the frequency range from 0.1 to 100,000 Hz. The charge-transfer resistance (Rct) related to the semicircular diameter in the Nyquist plot was obtained at high frequencies, and the mass transfer effect related to the Warburg linear line was exhibited at low frequencies. From this measurement, we can confirm the material adsorption status on the surface of the PMel/GCE. As shown in Figure 3 (a) and 3 (b), the Rct values were 40 Ω for the bare GCE (curve a) and 100 Ω for the PMel/GCE (curve b), respectively. The semicircular diameter of the PMel/GCE is larger than that of the bare GCE, which proved that the poly-melamine film was coated onto the GCE surface.
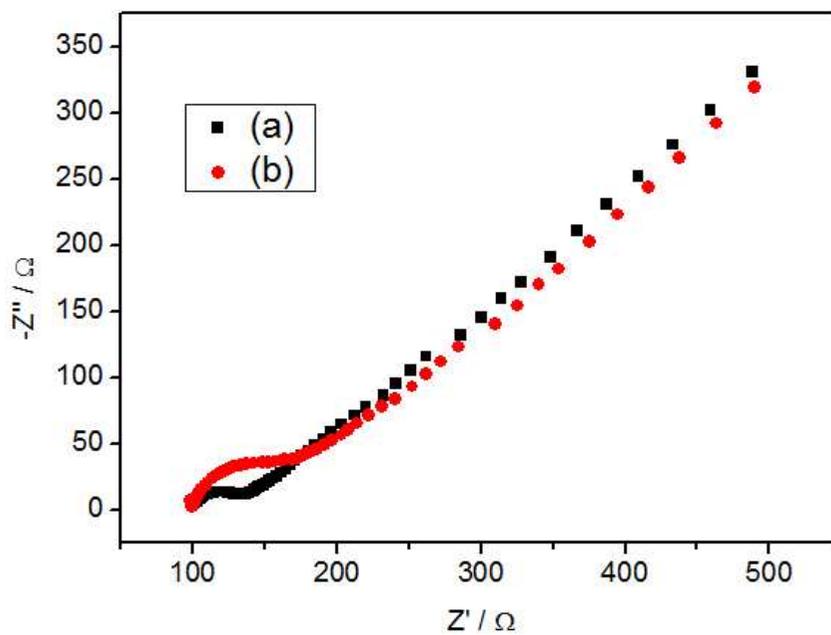
Figure 3. Nyquist plots of (a) the bare GCE and (b) the PMel/GCE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{3-}$ and 5 mM $[Fe(CN)_6]^{4-}$. Potential, 0.22 V; Frequency, 0.1-100,000 Hz.

3.3. Electrochemical behaviors of HQ, CA and RE

Figure 4 shows the CVs of 0.1 mM HQ, CA and RE at different electrodes in 0.1 M PBS (pH 7.0). As shown in curve a of Figure 4, two oxidation peaks are observed at the bare GCE. The anodic peak potentials of HQ and CA are overlapped at 0.344 V and for RE is 0.684 V, which indicated that the anodic peak potentials of dihydroxybenzene isomers are indistinguishable with the bare GCE. In case of reverse scan, the peak potentials for reduction of HQ and CA are found to be -0.057 and 0.072 V, while electrochemical redox reaction of RE on the surface of the bare GCE shows an irreversible peak. In contrast, Figure 4b presents well-defined oxidation peaks for HQ, CA and RE at the PMel/GCE. As it is seen, three well-defined anodic peak potentials can be observed obviously at 0.120 V, 0.215 V and 0.657 V, corresponding to the oxidation of HQ, CA and RE respectively. The peak-to-peak separation for HQ-CA is 0.095 V and for CA-RE is 0.442 V. At reverse scan, two well-defined reduction peaks are observed at 0.061 and 0.158 V, corresponding to HQ and CA, respectively. In common with redox reaction of RE on the surface of the bare GCE, that on the surface of the PMel/GCE shows only oxidation peak. The PMel/GCE shows a higher anodic (Ipa) and cathodic current (Ipc) for the redox reaction of HQ, CA and RE compared to that obtained with the bare GCE. This indicates that the poly-melamine film has significantly improved the electrochemical response of the electrode toward dihydroxybenzene isomers oxidation.

Moreover, the PMel/GCE exhibits enhanced redox peaks with lower peak potential separation values than the bare GCE. It was found from Figure 4a and 4b that the PMel/GCE leads to a negative shift of potentials for oxidation peaks and positive shift of potentials for reduction peak of dihydroxybenzene isomers. These results indicate that the PMel/GCE has a larger effective surface area and stronger electrocatalytic activity towards the redox process of dihydroxybenzene isomers than the bare GCE. This implies that simultaneous determination of HQ, CA and RE is feasible with the PMel/GCE.
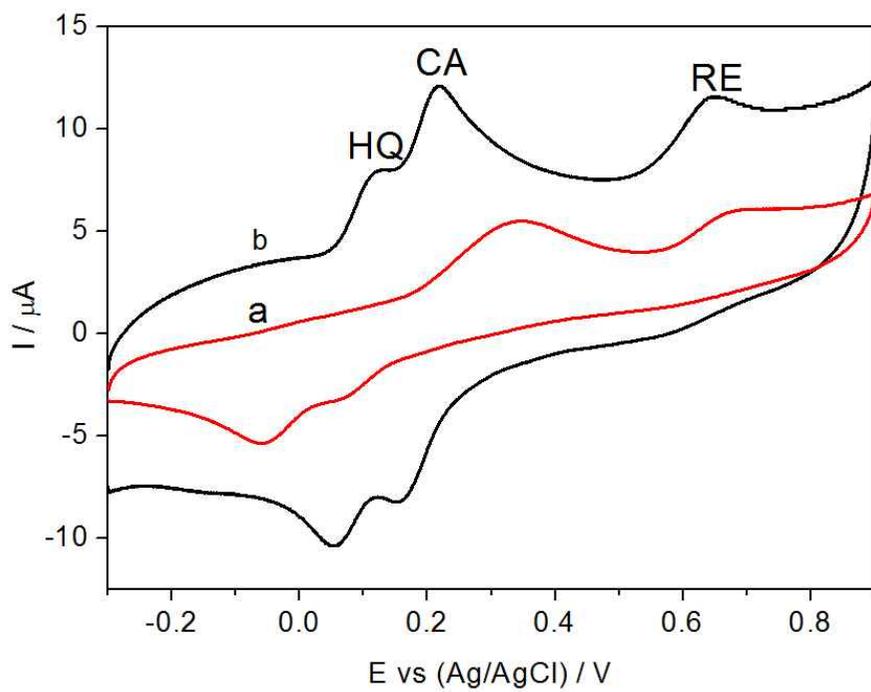
Figure 4. CVs of 0.1 mM HQ, CA and RE in 0.1 M (pH 7.0) at (a) the bare GCE and (b) the PMel/GCE at 100 mVs⁻¹.

3.4. *Effect of different scan rate.*

The influence of scan rate on the electrochemical response of 0.1 mM hydrquinone, catechol and resorcinol in 0.1 M PBS (pH 7) with the PMel/GCE was investigated by CV in the scan rates ranging from 40 to 400 mV s^{-1}; the results are shown in Figure 5 (A). With the PMel/GCE and under the experimental conditions used, HQ and CA show two pairs of symmetric redox peaks. However, only one oxidation peak appeared for RE, which confirms that the oxidation process of RE is irreversible. Both the anodic peak current (I_{pa}) and the cathodic peak current (I_{pc}) was found to be proportional to the square root of the scan rate (Figure 5 (B)), exhibiting a linear regression equation: I_{pa} (μA) = 0.5294 $v^{1/2}$ – 1.469, R^2 = 0.9996; I_{pc} (μA) = - 0.2468 $v^{1/2}$ – 0.1368, R^2 = 0.9942 for HQ, I_{pa} (μA) = 1.115 $v^{1/2}$ – 4.018, R^2 = 0.9969; I_{pc} (μA) = - 1.111 $v^{1/2}$ + 4.859, R^2 = 0.9959 for CA and I_{pa} (μA) = 0.1748 $v^{1/2}$ + 0.5963, R^2 = 0.9966 for RE. These out-comes verify that the reaction is controlled by diffusion of dihydroxybenzene isomers.
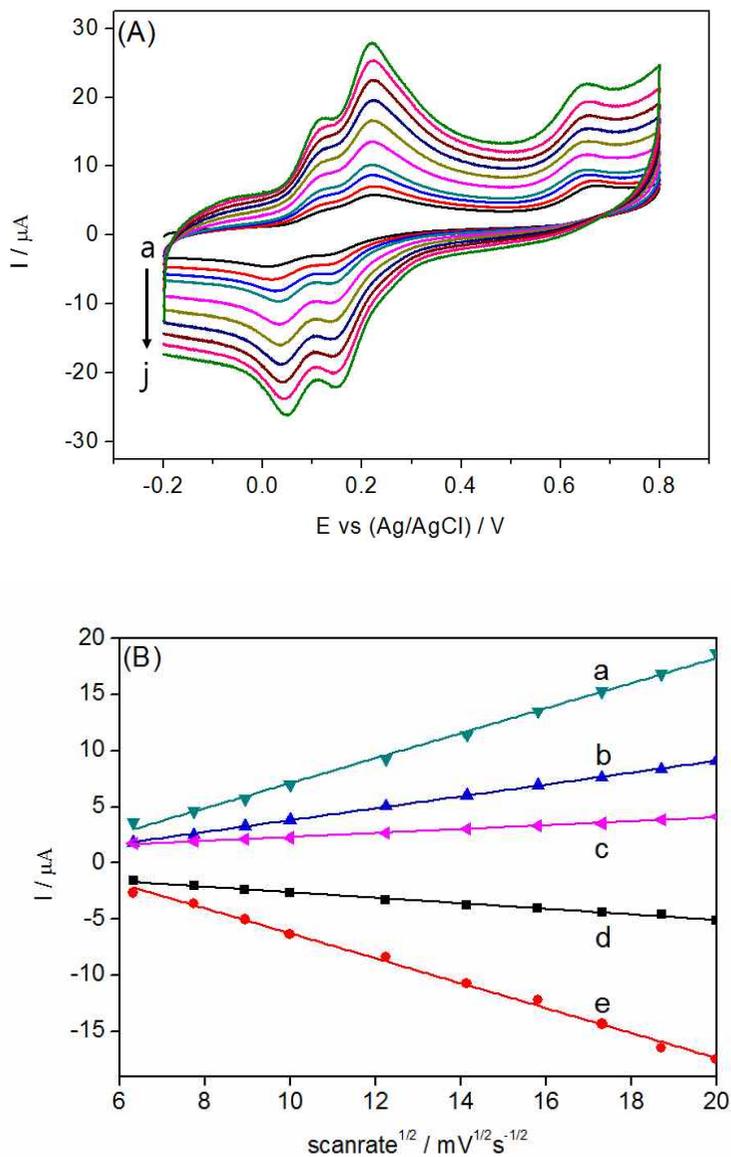
Figure 5. (A) CVs of 0.1 mM HQ, CA and RE in 0.1 M PBS (pH 7.0) at the PMel/GCE at different scan rate (a-j): 40, 60, 80, 100, 150, 200, 250, 300, 350, 400 mVs^{-1}. (B) Plotting of the I_{pa} (a, CA; b, HQ; c, RE) and the I_{pc} (d, HQ; e, CA) vs. square root of scan rate.

3.5. *Effect of buffer pH.*

The pH is an important factor to evaluate electrochemical behavior of the PMel/GCE. Figure 6 (A) shows the CVs for the effect of pH on the direct electron transfer between poly-melamine and catechol on the surface of the PMel/GCE at the scan rate of 100mVs^{-1} in different pH solutions (pH 4.0-9.0). According to Figure 6 (B), the results indicate that the PMel/GCE yields a relatively higher current response to catechol with the increasing pH until it reached 7.0 and gradually decreases at higher pHs (>7.0). We considered chemical affinity that lie behind the current variation and then correlated them with the electrostatic interaction between the poly-melamine film and catechol. At low pH, the amino groups of the poly-melamine film can be protonated and hydroxyl of catechol hardly become change into ionic form [29] due to the fact the pKa of melamine is 8.0 [30] and catechol is 9.48 [31]. At higher pH, over 8.0, the degree of deprotonation of amino groups in the poly-melamine film would increase. [32] And the increased hydroxyl ion in solution might compete with catechol, which would have changed to its mono- and dianion form. [33] It has generally been accepted that the pH value has an intense effect on the redox peak potential of CV. It is clear from Figure 6 (C) that with the increase of pH the oxidation peak potentials (E_{pa}) of the CA shift to negative values with the regression equation of E_{pa} (V) = - 0.0535 pH + 0.5967 (R^2 = 0.9976). The slopes of CA is close to the theory

value of 59 mV/pH (25∘C), implying that their oxidation reactions of CA occurs with two protons and electrons involved [23, 34].
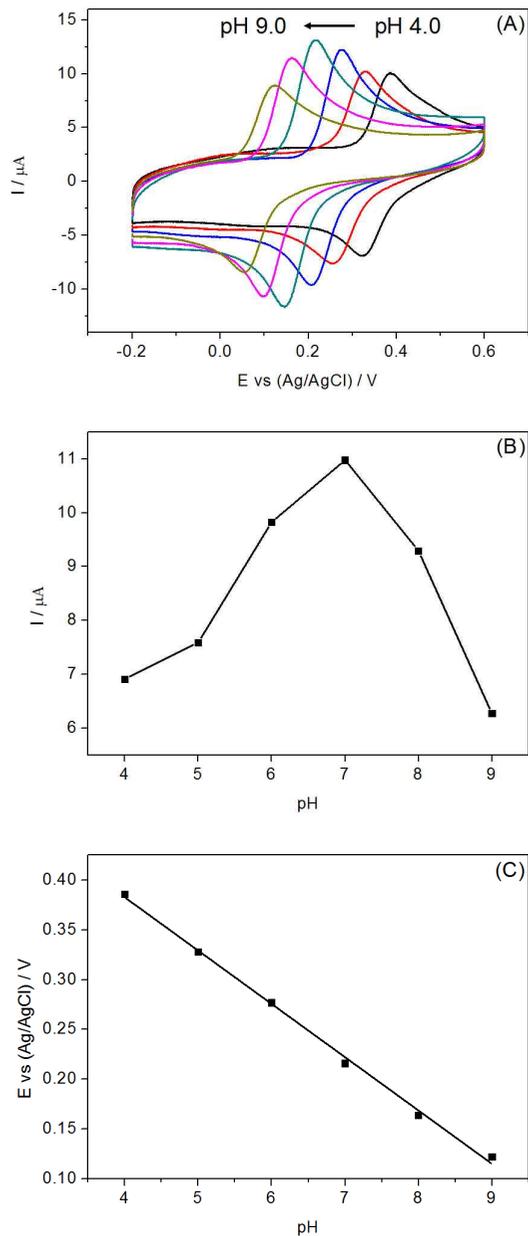
Figure 6. (A) CVs of 0.2 mM CA in 0.1 M PBS at different pH in the range of 4.0–9.0 at the PMel/GCE with scan rate 100 mVs^{-1}. Influences of pH on (B) the oxidation peak currents and (C) potentials.

3.6. Simultaneous determination of HQ, CA and RE.

The aim of our study was to develop a method with the capability of separating simultaneous electrochemical responses of HQ, CA and RE using the PMel/GCE. We investigated the simultaneous determination of 0.1 mM HQ, CA and RE in 0.1 M PBS (pH 7.0) with the bare GCE (curve a) and the PMel/GCE (curve b) by SWV techniques, as shown in Figure 7. It is clear, from Figure 7b that square wave voltammograms (SWVs) of these compounds reveal separated peak potentials at 0.084V for HQ, 0.184 V for CA and 0.608 V for RE with increased peak current significantly. By contrast, the bare GCE would not separate the signals of HQ, CA and RE as only two broad oxidation peak was obtained at 0.380 V for HQ and CA, 0.712 V for RE, respectively (Figure 7a). Moreover, the oxidation peaks of dihydroxybenzene isomers are narrower and located at a lower potential using the PMel/GCE than the bare GCE. These results infer that the simultaneous and quantitative determination of HQ, CA and RE is possible on the surface of the PMel/GCE in tertiary mixture samples.
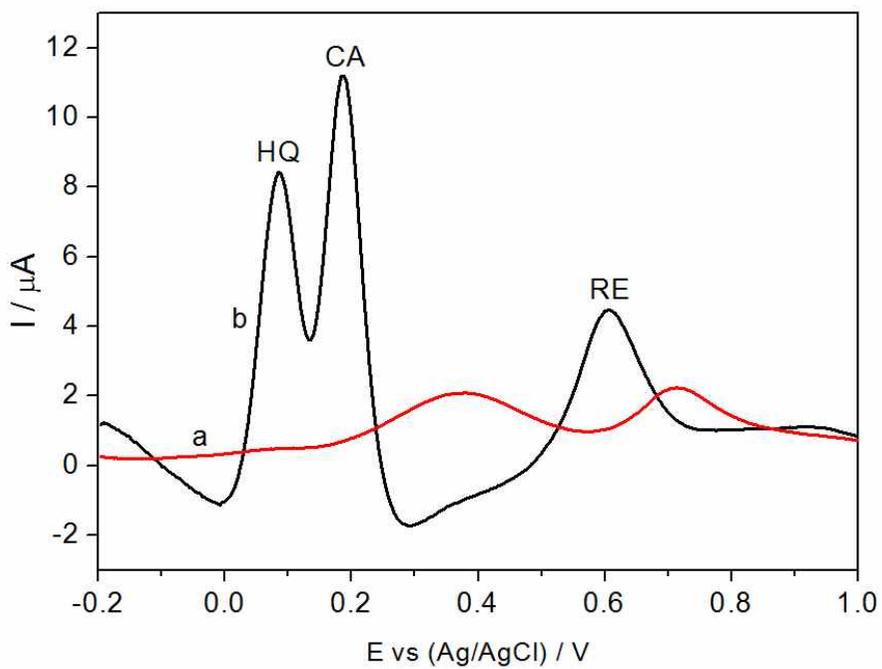
Figure 7. SWVs of 0.1 mM HQ, CA and RE in 0.1 M (pH 7.0) at (a) the bare GCE and (b) the PMel/GCE.

Figure 8 shows quantitative determination simultaneously for various concentrations of HQ, CA and RE at the PMel/GCE in 0.1 M PBS (pH 7.0) by using SWV. The calibration experiment of HQ, CA and RE in the mixture was investigated when the concentration of one isomer changed in the presence of the other two on optimized conditions. The oxidation peak current of each molecules linearly increased with their concentrations, while others remained constant. Figure 8 (A) shows the calibration graph for HQ on the PMel/GCE is linear from 5 – 300 μM and obeyed the equation I_{pa} (μA) = 0.0520 C (μM) + 1.612 (R^2 = 0.9912). And the linear relationships between oxidation peak currents and the concentrations of CA is I_{pa} (μA) = 0.0549 C (μM) + 1.674 (R^2 = 0.9917) in the range 5 – 500 μM (Figure 8 (B)). Similarly, as shown in Figure 8 (C), the peak current is linearly to the RE concentrations in the ranges of 3 – 200 μM and the regression is I_{pa} (μA) = 0.0384 C (μM) + 0.347 (R^2 = 0.9921). The detection limits of HQ, CA and RE calculated as Table 1 are 0.652, 1.898 and 0.576 μM, respectively (S/N = 3). A performance comparison of the PMel/GCE with comparable electrodes reported in the literature is listed in Table 1. As shown in Table 1, linear ranges of the PMel/GCE for oxidation of dihydroxybenzene isomers were much wider than many previously reported electrochemical sensors.
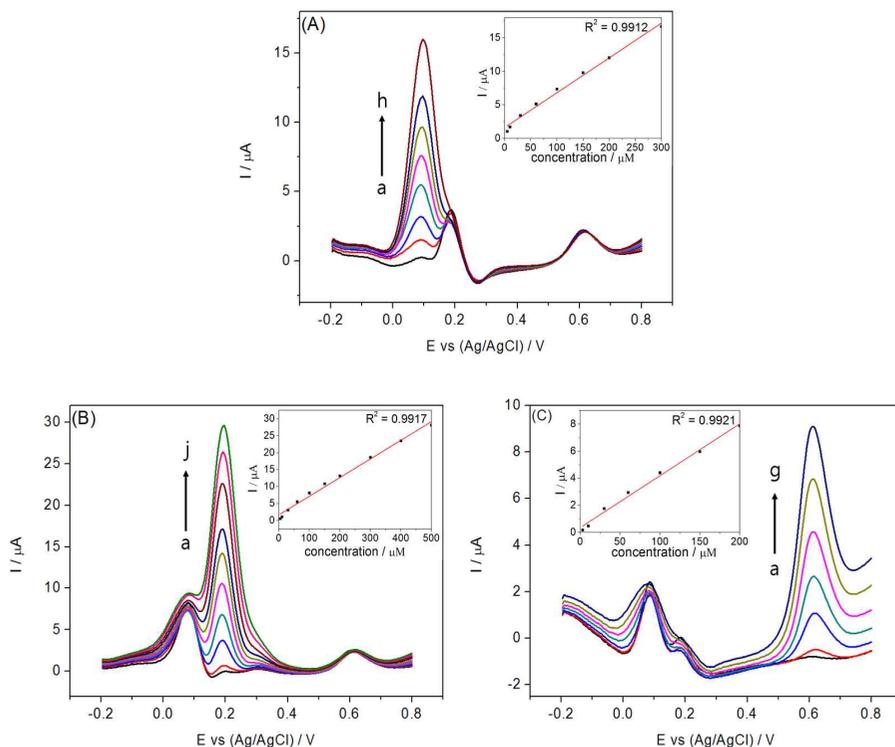
Figure 8. SWV responses at the PMel/GCE in 0.1 M PBS (pH 7.0) containing: (A) 50 µM CA, 50 µM RE and different concentrations of HQ (from a to h): 5, 10, 30, 60, 100, 150, 200 and 300 µM, (B) 50 µM HQ, 50 µM RE and different concentrations of CA (from a to j): 5, 10, 30, 60, 100, 150, 200, 300, 400 and 500 µM, (C) 20 µM HQ, 10 µM CA and different concentrations of RE (from a to g): 3, 10, 30, 60, 100, 150 and 200 µM. Insets show the calibration curves corresponding to the detection of dihydroxybenzene isomers concentration over each linear range.

Table 1. Comparison of the proposed electrode for HQ, CA and RE with other types of nanocomposite material modified electrode.

electrode	method	Linear range (µM)			Detection limit (µM)			Sensitivity (µA/µM)			Reference
		HQ	CA	RE	HQ	CA	RE	HQ	CA	RE	
Gr-Chitosan/GCE	DPV	1-300	1-400	1-550	0.75	0.75	0.75	0.056	0.059	0.025	[29]
WS$_2$-Gr/GCE	DPV	1–100	1-100	1-100	0.1	0.2	0.1	0.027	0.031	0.014	[35]
PANI- MnO$_2$/GCE	DPV	0.2-100	0.2-100	0.2-100	0.13	0.16	0.09	0.8	0.5	0.5	[23]
Polyfurfural/GCE	DPV	0.5–10	1-40	0.5-10	0.04	0.06	0.08	0.091	0.025	0.068	[36]
Nafion-FEPA-CNP-Gr/GCE	DPV	0.3–90	0.6-100	4-300	0.1	0.2	0.7	0.204	0.201	0.025	[37]
PMel /GCE	SWV	5–300	5-500	3-200	0.65	1.90	0.58	0.052	0.055	0.038	This work

3.7. Stability and Reproducibility.

The stability of the PMel/GCE was evaluated by examining its current response of 0.1 mM HQ, 0.1 mM CA and 0.1 mM RE in 0.1 M PBS (pH 7.0) at three PMel/GCE samples, stored in ambient condition at room temperature for 2 weeks. No serious decrease in the peak current was found as the sensor maintained 92.9 % for HQ, 96.7 % for CA and 95.3 % for RE of its original response, verifying the electrochemical stability of the PMel/GCE. Furthermore, we detected the current response of 0.1 mM dihydroxybenzene isomers simultaneously in 0.1 M PBS (pH 7.0) on five PMel/GCE samples. The PMel/GCE presented good reproducibility with a relative standard deviation (RSD) of 4.1 % for HQ, 5.5 % for CA and 3.6 % for RE, respectively.

3.8. Sample analysis.

Quantification of HQ, CA and RE in local tap water samples was performed to evaluate the performance of the PMel/GCE using the spike and recovery experiments. The results are presented in Table 2. The recovery ranges obtained from SWV response of local tap water samples are for HQ from 95.92 to 102.8 %, for CA from 102.3 to 103.6 % and for RE from 96.22 to 104.0 %, respectively. This shows that the PMel/GCE can be used to apply for the determination of dihydroxybenzene isomers in real samples.

Table 2. Determination of dihydroxybenzene isomers in local tap water samples.

Sample No.	Added (µM)			Found (µM)			RSD (%)			Recovery (%)		
	HQ	CA	RE	HQ	CA	RE	HQ	CA	RE	HQ	CA	RE
1	50	50	50	51.42	51.16	51.99	3.91	3.11	4.29	102.8	102.3	104.0
2	30	30	30	28.78	31.08	28.86	4.87	5.06	3.43	95.92	103.6	96.22

4. Conclusion

By using electrodepositon technique, a novel dihydroxybenzene isomers sensor has been easily fabricated and it realizes strong immobilization on the surface of GCE. The obtained poly-melamine film provides large electrochemically active surface area and electrocatalytic performance with good sensitivity for the dihydroxybenzene isomers redox reaction in comparison with the bare GCE. Under optimum conditions, the proposed sensor also exhibited ability to detect simultaneously toward dihydroxybenzene isomers with rapid response and outstanding wide linear range by using SWV. And also this sensor has an excellent stability as well as a good reproducibility. Moreover, it is concluded from our result of real sample analysis that the characteristics of poly-melamine film is useful for determining dihydroxybenzene isomers in real samples.

5. References

[1] J. Wang, J.N. Park, X.Y. Wei, C.W. Lee, Chemical Communications (2003) 628-629.

[2] T.Y. Xie, Q.W. Liu, Y.R. Shi, Q.Y. Liu, Journal of Chromatography A 1109 (2006) 317-321.

[3] H. Cui, C.X. He, G.W. Zhao, Journal of Chromatography A 855 (1999) 171-179.

[4] K. Fujino, T. Yoshitake, J. Kehr, H. Nohta, M. Yamaguchi, Journal of Chromatography A 1012 (2003) 169-177.

[5] Y.-B. Wu, J.-H. Wu, Z.-G. Shi, Y.-Q. Feng, Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences 877 (2009) 1847-1855.

[6] P. Nagaraja, R.A. Vasantha, K.R. Sunitha, Journal of Pharmaceutical and Biomedical Analysis 25 (2001) 417-424.

[7] P. Nagaraja, R.A. Vasantha, K.R. Sunitha, Talanta 55 (2001) 1039-1046

[8] M.F. Pistonesi, M.S. Di Nezio, M. Centurion, M.E. Palomeque, A.G. Lista, B.S.F. Band, Talanta 69 (2006) 1265-1268.

[9] X.H. Xia, H.W. Sun, Analytical Methods 5 (2013) 6135-6140.

[10] X. Zhang, S.O. Duan, X.M. Xu, S.A. Xu, C.L. Zhou, Electrochimica Acta 56 (2011) 1981-1987.

[11] D. Zhang, Y. Peng, H. Qi, Q. Gao, C. Zhang, Sensors and Actuators B: Chemical 136 (2009) 113-121.

[12] Y.P. Ding, W.L. Liu, Q.S. Wu, X.G. Wang, Journal of

Electroanalytical Chemistry 575 (2005) 275-280.

[13] F. Li, J. Song, C. Shan, D. Gao, X. Xu, L. Niu, Biosens Bioelectron 25 (2010) 1408-13.

[14] J. Du, L. Ma, D. Shan, Y. Fan, L. Zhang, L. Wang, X. Lu, Journal of Electroanalytical Chemistry 722 (2014) 38-45.

[15] W. Si, W. Lei, Z. Han, Q. Hao, Y. Zhang, M. Xia, Sensors and Actuators B-Chemical 199 (2014) 154-160.

[16] L. Han, X.L. Hang, Electroanalysis 21 (2009) 124-129.

[17] T.C. Canevari, P.A. Raymundo-Pereira, R. Landers, S.A.S. Machado, European Journal of Inorganic Chemistry 2013 (2013) 5746-5754.

[18] X. Yue, S. Pang, P. Han, C. Zhang, J. Wang, L. Zhang, Electrochemistry Communications 34 (2013) 356-359.

[19] X. Wang, M. Wu, H. Li, Q.J. Wang, P.N. He, Y.Z. Fang, Sensors and Actuators B-Chemical 192 (2014) 452-458.

[20] P.H. Yang, W.Z. Wei, L. Yang, Microchimica Acta 157 (2007) 229-235.

[21] P. Gupta, R.N. Goyal, Talanta 120 (2014) 17-22.

[22] U. Lange, N.V. Roznyatouskaya, V.M. Mirsky, Analytica Chimica Acta 614 (2008) 1-26.

[23] M.U.A. Prathap, B. Satpati, R. Srivastava, Sensors and Actuators B-Chemical 186 (2013) 67-77.

[24] X. Feng, W. Gao, S. Zhou, H. Shi, H. Huang, W. Song, Anal Chim Acta 805 (2013) 36-44.

[25] J. Dong, Y. Hu, J. Xu, X. Qu, C. Zhao, Electroanalysis 21 (2009) 1792-1798.

[26]   L. Wang, P. Huang, J. Bai, H. Wang, L. Zhang, Y. Zhao, International Journal of ELECTROCHEMICAL SCIENCE   2 (2007) 123-132.

[27]   X. Liu, L. Luo, Y. Ding, Q. Wu, Y. Wei, D. Ye, Journal of Electroanalytical Chemistry   675 (2012) 47-53.

[28]   S. Baskar, C.-W. Liao, J.-L. Chang, J.-M. Zen, Electrochimica Acta   88 (2013) 1-5.

[29]   H. Yin, Q. Zhang, Y. Zhou, Q. Ma, T. liu, L. Zhu, S. Ai, Electrochimica Acta   56 (2011) 2748-2753.

[30]   H.W. Sun, N. Liu, L.X. Wang, P. He, Journal of Chromatographic Science   48 (2010) 848-853.

[31]   Z.H. Wang, S.J. Li, Q.Z. Lv, Sensors and Actuators B-Chemical   127 (2007) 420-425.

[32]   L. He, Y. Su, X. Shen, Y. Zheng, H. Guo, Z. Zeng, J Sep Sci   32 (2009) 3310-8.

[33]   Y. Kwon, H.G. Hong, Bulletin of the Korean Chemical Society 34 (2013) 1755-1762.

[34]   S.K. Lunsford, H. Choi, J. Stinson, A. Yeary, D.D. Dionysiou, Talanta   73 (2007) 172-177.

[35]   K.J. Huang, L. Wang, Y.J. Liu, T. Gan, Y.M. Liu, L.L. Wang, Y. Fan, Electrochimica Acta   107 (2013) 379-387.

[36]   Y.H. Fu, Y.P. Lin, T.S. Chen, L.S. Wang, Journal of Electroanalytical Chemistry   687 (2012) 25-29.

[37]   L. Wang, Y. Meng, Q. Chen, J. Deng, Y. Zhang, H. Li, S. Yao, Electrochimica Acta   92 (2013) 216-225.

국문요약

본 연구는 폴리-멜라민 유리탄소전극 (PMel/GCE)을 이용해 개발한 센서가 수용액 속에 존재하는 디하이드록시벤젠 이성질체 (dihydroxybenzene isomers)를 동시에 검출해낼 수 있음을 보인다.

폴리-멜라민 필름은 멜라민 단량체를 포함한 산성 용액에서 전기중합 방법으로 유리탄소전극의 표면 위에 입혀졌다. 구조적 특성과 전기화학적 특성은 전계방사형 주사전자현미경 (field emission scanning electron microscopy; FE-SEM),전기화학적 임피던스법 (electrochemical impedance spectroscopy; EIS), 순환전압전류법 (Cyclic voltammetry; CV)을 통해 연구되었다. 또한, 디하이드록시벤젠 이성질체를 동시적으로 검출하기 위해 네모파 전압전류법 (Square wave voltammetry; SWV) 을 이용했다. 연구 결과, 폴리-멜라민을 입히지 않은 유리탄소전극에서는 두 개의 폭넓은 산화 봉우리가 0.380 V (하이드로퀴논, 카테콜), 0.712 V (레조시놀)에서 나타난 반면, 폴리-멜라민 유리탄소전극에서는 0.084 V (하이드로퀴논), 0.184 V (카테콜), 0.608 V (레조시놀)에서 뚜렷한 세 개의 산화봉우리가 나타났다. 선형성은 농도 범위 5-300 µM (하이드로퀴논), 5-500 µM (카테콜), 3-200 µM (레조시놀)에서 넓게 나타났고, 감도는 0.052 µA/µM (하이드로퀴논), 0.055 µA/µM (카테콜), 0.038 µA/µM (레조시놀), 검출한계 (S/N=3)는 0.65 M (하이드로퀴논), 1.90 M (카테콜), 0.58 M (레조시놀)임을 보였다.

본 연구에서 개발한 폴리-멜라민 유리탄소전극을 이용한 디하이

드록시벤젠 이성질체 센서는 간편한 전극 제작 과정, 저렴함 제작 비용, 넓은 선형 범위를 가진다는 장점이 있고, 더 나아가 다른 물질의 방해작용 없이 수돗물 속의 디하이드록시벤젠 이성질체를 검출하는데 활용될 수 있을 것이라 기대된다.

주요어: 멜라민, 전기도금, 하이드로퀴논, 카테콜, 레조시놀, 디하이드록시벤젠 이성질체, 네모파 전압전류법

학   번: 2013-21425