

The Modified Electrode by PEDOP with MWCNTs-Palladium Nanoparticles for the Determination of hydroquinone and Catechol

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Poly-ethylenedioxyppyrrrole (PEDOP) coated thiolated multiwall carbon nanotubes palladium nanoparticles (MWCNTs-Pd) modified glassy carbon electrode (GCE) [PEDOP/MWCNTs-Pd/GCE] for the determination of hydroquinone (HQ) and its isomer catechol (CA) were synthesized and compared with bare GCE and thiolated multiwall carbon nanotubes (MWCNTs-SH/GCE). The modification could be made by simple processes on a GCE with MWCNTs-Pd covered by PEDOP in a 0.05 M tetrabutylammonium perchlorate (TBAP)/MeCN solution system. A well-defined peak potential evaluation of the oxidation of hydroquinone to quinone at 0.05 V (vs. Ag/AgCl), and electrochemical reduction back to hydroquinone were found by cyclic voltammetry (CV) in phosphate buffered saline (PBS) at pH 7.4. Peak current values increased linearly with increasing hydroquinone contents. The peak separation between the anodic and cathodic peaks at the PEDOP/MWCNTs-Pd/GCE was $\Delta E_p = 40$ mV for HQ and $\Delta E_p = 70$ mV for CA, resulting in a higher electron transfer rate. Moreover, good reproducibility, excellent storage stability, a wide linear range (0.1 μ M - 5 mM for HQ and 0.01 μ M - 6 mM for CA), and low detection limits (2.9×10^{-8} M for HQ and 2.6×10^{-8} M for CA; S/N = 3) were determined using differential pulse voltammetry (DPV) and amperometric responses; this makes it a promising candidate as a sensor for determination of HQ and CA.

Key Words : Hydroquinone, Catechol, Electrochemical sensor, Carbon nanotubes, MWCNTs-palladium nanoparticles

Introduction

Since its introduction for clinical use in 1961, hydroquinone (HQ; 1,4-dihydroxybenzene) has been a popular depigmenting agent, inhibiting melanin formation.^{1,2} Accordingly, it has been used not only in cosmetic creams and tanning but also pesticides, flavoring agents, medicines, photography chemicals, organic constituent of tobacco smoke, and widely distributed throughout nature.³⁻⁶ Nevertheless, HQ and its isomers, catechol (CA; 1,2-dihydroxybenzene) and resorcinol (RE; 1,3-dihydroxybenzene), are harmful to both humans and animals, even at low concentrations, and they are difficult to degrade due to their coexistence and interference during determination.⁷⁻¹⁰ Moreover, they are considered to be environmental pollutants by the United States Environmental Protection Agency (EPA) and the European Union (EU) and banned its use in cosmetics and such formulations.¹¹ But some researchers have acknowledged that these dihydroxybenzenes not only affect activities of some enzymes, but also have biological importances such as antioxidation and antivirus characteristics, thus are environmentally significant as antioxidants and antiviral agents.¹² Therefore, various methods for their determination have been carried out by spectrophotometric and chromatographic techniques.¹³⁻¹⁵ Unfortunately they possess high cost and low sensitivity, require complicated pretreatments, and consume much time. So, it's demanding to develop simple, rapid, and electrochemical

methods with low cost, high sensitivity, and ease of operation.^{16,17} From previous reports, they demonstrated that a GCE modified by multiwall carbon nanotubes (MWCNT) can separate oxidation peaks of HQ and CA.¹⁸⁻²⁰

Recently our group has successfully used poly-ethylenedioxyppyrrrole (PEDOP) coated multiwall carbon nanotube-palladium nanoparticles (MWCNTs-Pd) modified on a glassy carbon electrode (PEDOP/MWCNTs-Pd/GCE) to determine hydrazine, showing significant and positive results.²¹ The purpose of this work is to suggest a very simple electrochemical method for simultaneous detection of HQ and CA with a PEDOP/MWCNTs-Pd/GCE-modified electrode using CV and DPV. Well-defined oxidation peak appeared at HQ at 0.05 V and CA at 0.17 V, thus the dihydroxybenzene isomers were identified and separated.

Experimental

Chemicals. All MWCNTs were purchased from Carbon Nano Tech. Co., Ltd. (Pohang, South Korea). The diameter and length ranged between 20-30 nm and 1.0-2.0 μ m, respectively. 3,4-Ethylenedioxyppyrrrole (EDOP), Nafion, HQ, CA, RE, and tetrabutylammonium perchlorate (TBAP) were purchased from Aldrich. All other reagents used were of analytical grade and without further purification. Phosphate buffered saline (PBS) was used as the supporting electrolyte solution and was made from Na_2HPO_4 with distilled water and adjusted to various pH values with 0.1 M

NaOH or 0.1 M H₃PO₄ solutions. All the aqueous solutions were prepared with doubly distilled water with a resistivity over 18 MΩ cm in a quartz apparatus. A 15 mL electrolytic cell with 5.0 mL PBS were deaerated by high-purity argon gas at room temperature (25 ± 2 °C) for at least 5 min to remove oxygen prior to the beginning of a series of experiments. All the electrochemical experiments were performed with a fast response initial stirring time of 10 s.

Apparatus. A three-electrode cell was employed, consisting of a modified glassy carbon electrode (3.0 mm diameter) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (3.0 M NaCl) electrode supplied by BAS (Model MF-2052) as the reference electrode. The CVs and DPVs were performed using a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN, USA). All pH measurements were performed with the pH glass electrode of a JENCO meter. The scanning electron microscopy (SEM) observations were carried out in a JSM-7500 F, JEOL.

Preparation of the Modified Electrode. MWCNTs-Pd nanoparticles were prepared by previous method²¹ with MWCNTs first oxidized in a hot acid solution of HNO₃ and H₂SO₄ (1:3 by volume) at 90 °C for 3 hr to remove impurities and generate surface functional groups. Then dispersed in THF and a NaSH aqueous solution was added afterwards, to produce the surface thiol groups. Thiolated MWCNT-supported Pd catalysts were synthesized at room temperature using a Pd colloidal solution. Sodium tetrachloropalladate (II) (Na₂PdCl₄, 249.83 mg) was dissolved in deionized water, followed by addition of a 4-dimethylaminopyridine (DMAP, 119.9 mg) solution. Afterwards, thiolated MWCNTs (223.8 mg) in 100 mL of deionized water were added to the solution. While vigorously stirring, NaBH₄ solution was slowly dropped into the mixture for 30 min until the color changed from pale yellow to black. The resulting slurry was filtered, washed thoroughly with deionized water, and dried in a vacuum oven to give MWCNTs-Pd nanoparticle.

The GCE surface was carefully polished with alumina powder on chamois leather to a mirror-like finish, washed thoroughly with methanol, and rinsed with distilled water. Then, the GCE surface was coated with 5 μL of the black MWCNTs-Pd suspension (1.0 mg/mL) in distilled water and dried in room temperature. The MWCNTs-Pd-coated GCE was covered again by electropolymerization of 1.0 mM EDOP under the conditions of sweeping potentials 1.5 to -1.5 V, at a scan rate of 0.1 V/s in a 0.05 M TBAP/MeCN solution for 10 cycles using CV. The resulting modified electrode was thoroughly rinsed with distilled water.

Results and Discussion

Surface Morphology of PEDOP/MWCNTs-Pd/GCE. A thin, dark-blue film was produced uniformly at the surface of the GCE, indicating that the EDOP was successfully electropolymerized. Morphologies of the PEDOP/MWCNTs-Pd/GCE and MWCNT-Pd/GCE (without electropolymeri-

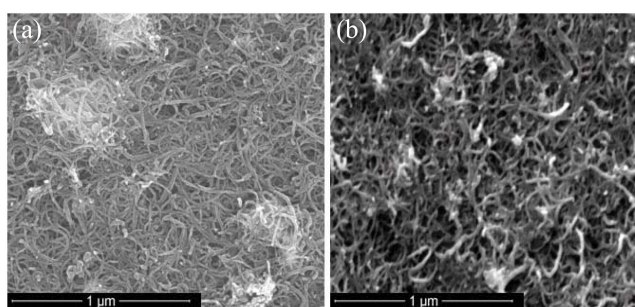


Figure 1. SEM images of GCE with (a) MWCNTs-Pd, (b) PEDOP/MWCNTs-Pd.

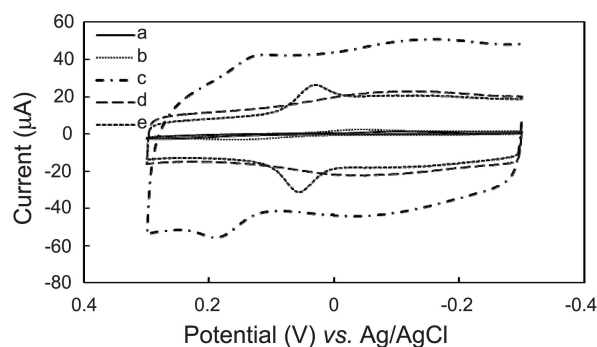


Figure 2. CVs of bare GCE (a), PEDOP/GCE (b), PEDOP/MWCNTs-SH/GCE (c) were performed in the presence of 100 μM HQ; PEDOP/MWCNTs-Pd/GCE were performed in the absence (d) and presence (e) of 100 μM HQ in 0.1 M pH 7.4 PBS with scan rate of 0.1 V/s. Initial stirring time 10 s.

zation) were studied by SEM shown in Figure 1. Magnified images show that PEDOP are attached to MWCNTs-Pd and covered the surface significantly.

Electrochemical Behavior of HQ at the Modified Electrode. Figure 2 shows the cyclic voltammograms of PEDOP/MWCNTs-Pd/GCE and other electrodes in 0.1 M pH 7.4 PBS at 0.1 V/s. Insignificant, small peaks were observed at the bare GCE (curve a) and PEDOP/GCE (curve b) due to polymeric film formation, causing electrode fouling.²² However, a couple of well-defined reversible redox peaks were observed at PEDOP/MWCNTs-Pd/GCE (curve e) and PEDOP/MWCNTs-SH/GCE (curve c), with a formal potential of +0.05 V and potential range from -0.3 to +0.3 V. The background current of PEDOP/MWCNTs-Pd/GCE and PEDOP/MWCNTs-SH/GCE was larger than others, indicating larger surface area, strong absorptive abilities, effective accumulation to HQ and CA and improves their surface concentration. But PEDOP/MWCNTs-Pd/GCE shows stronger peak and requires less potential advantageously.

Same larger currents were obtained with increasing concentrations (Fig. 3) with peak separation (ΔE_p) between the anodic and cathodic peaks of HQ (40 mV) and CA (70 mV) was smaller for PEDOP/MWCNTs-Pd/GCE compared with GCE, showing higher electron transfer rate kinetics and improved reversibility.^{10,23} The improved detection of HQ and catechol can be attributed to MWCNTs-Pd interaction. This interaction induces a particular modification of the

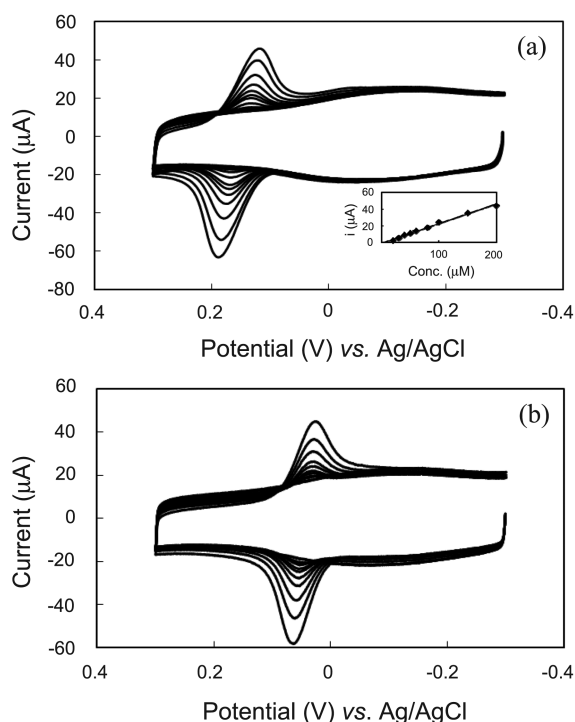


Figure 3. CVs of HQ from 0.0 μM up to 300.0 μM (a) and CA from 0.0 μM up to 200.0 μM (b) with PEDOP/MWCNTs-Pd/GCE in 0.1 M PBS (pH 7.4). Scan rate 0.1 V/s. Inset: plots of peak current *versus* concentration. ($y = 0.133x + 0.424$; $R^2 = 0.996$ for HQ and $y = 0.233x - 0.927$; $R^2 = 0.993$ for CA).

electron density in Pd nanoparticles.

Optimization of General Procedures. Initial stirring time was chosen to be 10 s based on experimental results; the redox currents can decrease due to thick deposits and create a major resistance to electron transport.²³ The influence of pH was investigated on the response of dihydroxybenzenes at the modified electrode by CV using 0.1 M PBS with different pH values ranging from 3.4–11.4. From these, the anodic peak potentials were found to be decreased with an increase in the solution pH (Fig. 4).

The slopes of the equations (-0.054 V) were close to -0.059 V, involving the same number of protons and electrons, thus considered to be two-electron process.²⁴ Low pH values showed much more positive potentials that would cause interference but high values of pH formed a broad hump. Moreover, the peak current of both the HQ and CA reached maximum values at approximately pH 7.4 (data not shown) and then decreased with increasing pH. Thus, pH 7.4 was chosen for this work.

Electrochemical Behaviours of Dihydroxybenzene Mixtures. In order to evaluate the selectivity and sensitivity of the PEDOP/MWCNTs-Pd/GCE, dihydroxybenzene isomers were investigated by performing CV and DPV due to its advantage of reducing the background current and better resolution. It was reported that it was impossible to use bare GCE for voltammetric determination of the dihydroxybenzene isomer mixtures. However, PEDOP/MWCNTs-Pd/GCE gave clear separate peak detections in coexisting isomer

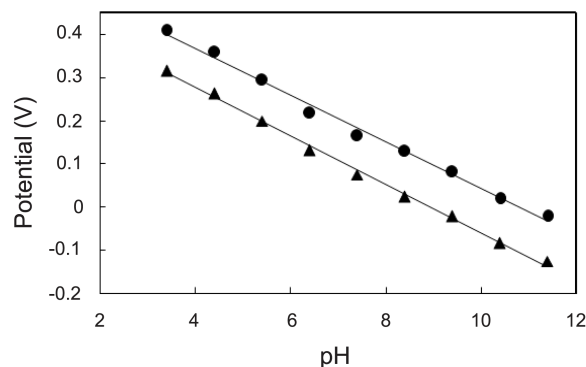


Figure 4. Plots showing the pH dependence of HQ & CA oxidation potentials obtained from CV's of HQ & CA in 0.1 M PBS with different pH values. Scan rate 0.1 V/s. Initial stirring time 10 s. HQ (\blacktriangle) $y = -0.054x + 0.480$, $R^2 = 0.996$ and CA (\bullet) $y = -0.054x + 0.585$, $R^2 = 0.993$. $Q + 2H^+ + 2e^- \leftrightarrow HQ$.

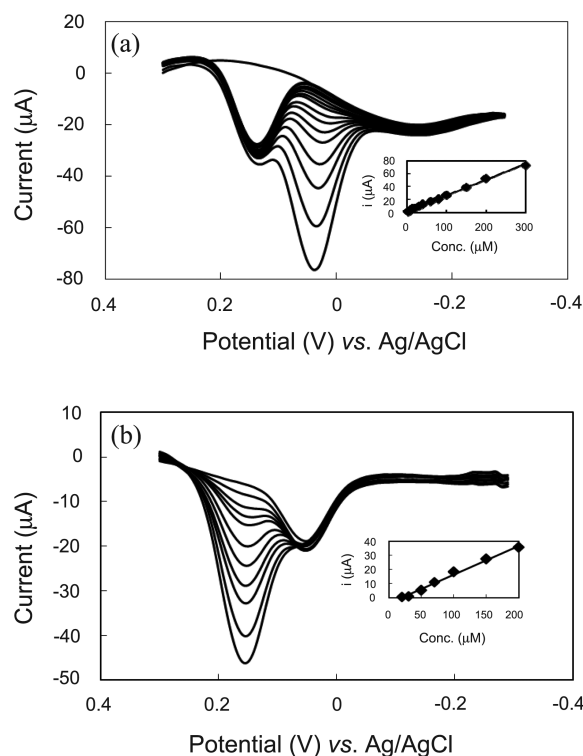


Figure 5. DPVs (background correction) of 0.0 μM up to 300.0 μM HQ in the presence of 100 μM CA (a) and 0.0 μM up to 200.0 μM CA in the presence of 100 μM HQ (b) at PEDOP/MWCNTs-Pd/GCE in 0.1 M PBS (pH 7.4). Scan rate 0.05 V/s. Inset: plots of peak current *versus* concentration. ($y = 0.244x + 1.914$, $R^2 = 0.997$ for HQ DPV (a) and $y = 0.203x - 3.732$, $R^2 = 0.992$ for CA DPV (b)).

mixtures. Figure 5 shows well-defined oxidation peaks at the potentials of HQ and CA at various concentrations, respectively, in the presence of constant concentrations of the counter parts and were found at the same positions as in separate solutions (data not shown). This proves that oxidation of dihydroxybenzene isomers in the mixture solutions take place independently at the PEDOP/MWCNTs-Pd/GCE.

It might be due to the density of the electron cloud orderly lowering from HQ to CA, therefore electroactivity de-

Table 1. The comparison of characteristics obtained from some literatures and this work

Electrodes	pH	Linear range, M		Eox, V (difference of HQ & CA's ox/peak potential)	LOD, M		Reference
		HQ	CA		HQ	CA	
MWCNTs/P3MT/GCE	6.4	5.0×10^{-7} to 2.0×10^{-4}	5.0×10^{-7} to 1.5×10^{-4}	0.101	1.2×10^{-8}	4.0×10^{-8}	26
MWCNT/ β -CD/CILE	7	1.2×10^{-7} to 2.2×10^{-3}	7.0×10^{-7} to 1.0×10^{-3}	0.07	4.0×10^{-8}	8.0×10^{-8}	27
PAIUCPE	5.6	-	-	0.12	-	-	28
AuNPs/MWCNTs/SPE	7	2.0×10^{-6} to 7.3×10^{-4}	2.0×10^{-6} to 7.3×10^{-4}	> 0.1	3.9×10^{-7}	2.6×10^{-7}	29
Sweet potato tissue/ Graphite	-	7.5×10^{-5} to 1.6×10^{-3}	-	-	8.1×10^{-6}	-	2
LDHf/GCE	-	3.2×10^{-6} to 2.4×10^{-3}	6.0×10^{-7} to 6.0×10^{-3}	0.112	1.0×10^{-6}	1.0×10^{-7}	23
OMC/GCE	5	-	-	0.154	7.6×10^{-8}	1.0×10^{-7}	10
Activated GCE	7	5.0×10^{-7} to 2.0×10^{-4}	-	0.049	1.6×10^{-7}	1.1×10^{-7}	25
[Cu ₂ (HL)(Oac)](ClO ₄) ₂ ...	7.5	6.0×10^{-5} to 2.5×10^{-3}	-	-	3.0×10^{-7}	1.0×10^{-6}	3
PEDOP/MWCNTs-Pd/GCE	7.4	1.0×10^{-7} to 5.0×10^{-3}	1.0×10^{-8} to 6.0×10^{-3}	0.12	2.9×10^{-8}	2.6×10^{-8}	Our work

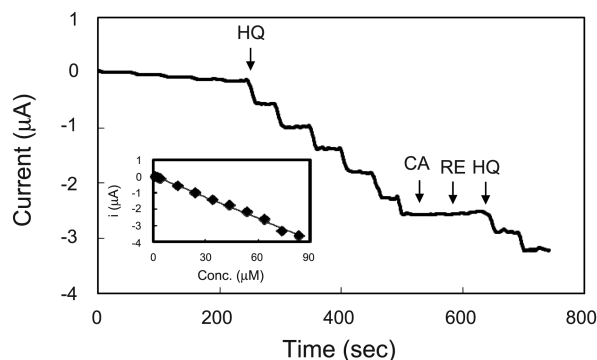


Figure 6. Amperometric response of the sequential additions of 1 μ M and 10 μ M HQ, adding 10 μ M CA (a) and 10 μ M RE (b) with applied potential of +70 mV (vs. Ag/AgCl) at PEDOP/MWCNTs-Pd/GCE in 0.1 M PBS (pH 7.4). Inset: calibration curve for HQ without isomer mixtures. $y = -0.041x + 0.022$, $R^2 = 0.996$.

creases.¹⁰ Thus, simultaneous determination of HQ and CA could be achieved even if they coexisted. The anodic current of HQ increased linearly as the concentration of HQ (up to 300 μ M) increased, while the peak current of CA was nearly unchanged (a). Similar behaviour was observed with anodic current of CA (up to 200 μ M), respectively (b). Potential difference for HQ and CA oxidation was 0.12 V, indicating that simultaneous and quantitative determination of HQ and CA was achieved successfully at this modified electrode. Table 1 shows comparison of HQ and CA result characteristics with other references.

Simultaneous Determination of Dihydroxybenzene Isomers. An amperometric response of sequential addition of 1 μ M and 10 μ M HQ with addition of 10 μ M CA (a); 10 μ M RE (b) was studied at applied potential of 70 mV (vs. Ag/AgCl) (Fig. 6).

The interference of common substances with the determination of 10 μ M dihydroxybenzene isomer mixtures was studied. If the presence of interfering chemicals altered the current signal of the isomers by less than 5%, it was considered to have no effect. Oxidation currents were not seriously affected by common cations such as, Na⁺, K⁺, Ca²⁺, Ba²⁺, Al³⁺, Mg²⁺, NH₄⁺, and Cu²⁺ and anions such as

NO₃⁻, SO₄²⁻, and H₂PO₄⁻, indicating an excellent anti-interference ability of the proposed method.

Conclusion

Dihydroxybenzene isomers, HQ and CA, were electrochemically tested first time with PEDOP/MWCNTs-Pd/GCE in 0.1 M PBS (pH 7.4) and gave significantly more well-defined redox peaks than other electrodes mentioned here. Also in the mixture solution of HQ and CA, their oxidation peak potential difference was separated by approximately 0.12 V, proving that they can be used to detect HQ and CA in mixtures. PEDOP/MWCNTs-Pd/GCE gives significant better results proving that it's a promising sensor for HQ and CA.

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