Short Communication

Selective Determination of Catechol in the Presence of Hydroquinone at Bare Indium Tin Oxide Electrodes via Peak-Potential Separation and Redox Cycling by Hydrazine

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Abstract
The electrochemical, selective determination of catechol (CT) in the presence of hydroquinone (HQ) is not readily achieved, because the formal potentials of two phenolic compounds are very close. Here, we have developed a simple electrochemical method for the selective determination of CT by using bare indium tin oxide electrodes and employing CT redox cycling by hydrazine. The cyclic voltammetry of CT and HQ was investigated in Tris buffer (pH 9.0), phosphate buffered saline buffer (pH 7.4), and acetate buffer (pH 4.5). Especially in Tris buffer, the anodic peak potential of CT is much lower than that of HQ, resulting in a large difference between two peak potentials (ca. 0.4 V). The difference allows the selective determination of CT in the presence of excess HQ. The anodic current of CT is amplified using CT redox cycling by hydrazine, which also helps to stabilize CT and HQ in Tris buffer for several hours. The detection limits of CT in Tris buffer containing 0.1 mM HQ are 1 μM and 10 μM in the presence and absence of hydrazine, respectively.

Keywords: Indium tin oxide, Catechol, Hydroquinone, Hydrazine, Redox cycling

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The determination of phenolic compounds is of great importance in terms of environmental monitoring, neurochemistry, and clinical chemistry [1]. Among phenolic compounds, catechol (CT) and hydroquinone (HQ) (i.e., isomers of dihydroxybenzenes) are widely used for photographic chemicals, pesticides, medicines, etc. [2]. CT is a significant environmental pollutant with high toxicity, and it exists with HQ in environmental samples [3]. CT even in low concentrations in foods and cigarette smokes may cause mutagenesis and cancerous alteration [4–6]. Moreover, CT is readily adsorbed from the gastrointestinal tract, causing renal tube degeneration, liver function decrease, etc. [7]. Because of its high toxicological potential, the accurate determination of CT in the presence of HQ is very important. However, CT and HQ have similar structure and properties, which makes it difficult to determine CT selectively. Accordingly, it is crucial to develop a selective and simple method for CT determination without any previous separation or treatment [1, 8].

The formal potentials of CT and HQ are also very close, which makes it difficult to obtain two separate anodic peaks corresponding to the oxidation of two compounds in voltammetric experiments [9–14]. The separation of two anodic peaks can be obtained using chemically modified electrodes [9–13] or micelles [14]. All methods are based on the high electrocatalysis of one compound along with the lower (or higher) electrocatalysis of the other compound. The main effort is to improve the electrocatalysis of CT or HQ. However, the difference between two peak potentials is not large, at most 100 mV, resulting in limitation in obtaining low detection limits [10, 13, 14].

Indium tin oxide (ITO) electrodes have been used as working electrodes in electrochemical sensors because of their wide potential window and low background current [15–18]. However, the electrocatalytic properties of ITO electrodes are inferior to noble metal and glassy carbon electrodes. Especially, ITO electrodes show poor electrocatalytic properties for phenolic compounds such as *p*-aminophenol [15]. Thus, large overpotentials are required for the electrooxidation of phenolic compounds, i.e., anodic peak potentials occur at higher potentials. Importantly, the overpotential depends highly on the type of phenolic compounds [15]. Although ITO electrodes give large overpotentials for CT and HQ oxidation, the difference between two peak potentials of CT and HQ could be increased compared to that in case of highly electrocatalytic electrodes.

The redox cycling using interdigitated array electrodes was used for the selective determination of dopamine in the presence of ascorbic acid and uric acid [19]. During redox cycling, the oxidized product of dopamine is reduced back to dopamine at the adjacent electrodes, whereas the reduction of oxidized products of ascorbic acid and uric acid is suppressed. Recently, we showed that redox cycling by hydrazine can be used to increase the anodic current of *p*-aminophenol [20]. In this approach, the redox cycling was

achieved simply by adding hydrazine to a solution without using microfabricated interdigitated array electrodes.

Here, we describe a simple electrochemical technique for selective determination of CT in the presence of HQ. Bare ITO electrodes allow a large difference in peak potentials especially in Tris buffer (pH 9.0) (Fig. 1), which is due to different electrocatalytic properties of ITO electrodes for CT and HQ. CT is oxidized to *o*-benzoquinone, which is reduced back to CT by hydrazine. The regenerated CT is reoxidized at ITO electrodes. CT redox cycling by hydrazine increases the anodic current of CT.

To investigate electrocatalytic behavior of CT and HQ at bare ITO electrodes, cyclic voltammograms were obtained in three different buffers (Figure 2). The anodic peak potentials of CT are 0.19, 0.52, and 0.65 V in Tris buffer (pH 9.0), PBS buffer (pH 7.4), and acetate buffer (pH 4.5), respectively (Fig. 2a). The sequence of peak potentials shows that CT electrooxidation in Tris buffer is much faster than in PBS and acetate buffers. The anodic peak current is also higher in Tris buffer. In case of HQ (Figure 2b), the anodic peak potentials appear at more than 0.4 V in three buffers. It indicates that HQ electrooxidation is very slow on bare ITO electrodes. The difference between two anodic peak potentials of CT and HQ is ca. 0.4 V in Tris buffer, which is sufficiently enough for the selective determination of CT in the presence of HQ. Moreover, HQ electrooxidation is negligible almost up to 0.4 V in Tris buffer, while CT electrooxidation is considerable. Considering that the adsorption of CTs is essential for fast electron transfer [21, 22], the better electrooxidation of CT seems to be due to the easy adsorption of CT on ITO electrodes in Tris buffer.

To test the feasibility of CT redox cycling by hydrazine, cyclic voltammograms were obtained in Tris buffer containing CT, HQ, and hydrazine (Fig. 3). In the presence of hydrazine, the anodic peak current of CT is 10-times larger than in the absence of hydrazine (Fig. 3a). The disappearance of cathodic peak in the presence of hydrazine is attributed to CT redox cycling by hydrazine. The oxidized product of CT, *o*-benzoquinone, is easily reduced back to CT

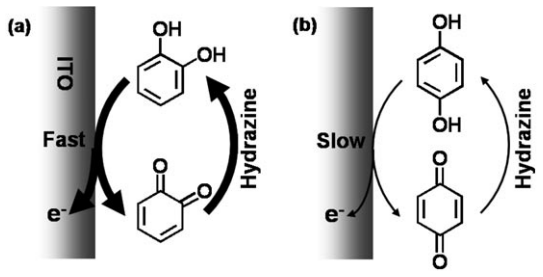

Fig. 1. Schematic diagrams for a) CT and b) HQ electrooxidation and redox cycling by hydrazine.

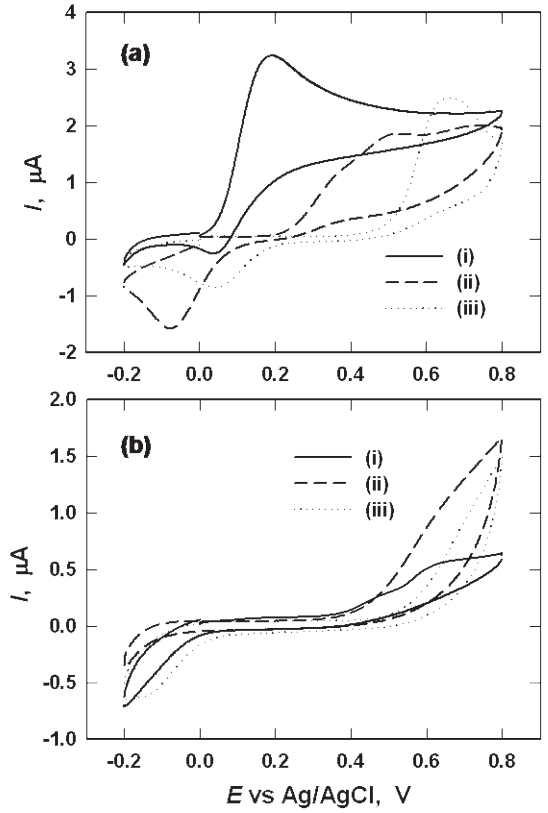

Fig. 2. Cyclic voltammograms obtained with bare ITO electrodes in i) Tris buffer (pH 9.0), ii) PBS buffer (pH 7.4), and iii) acetate buffer (pH 4.5) containing a) 0.1 mM CT or b) 0.1 mM HQ (scan rate = 10 mV/s).

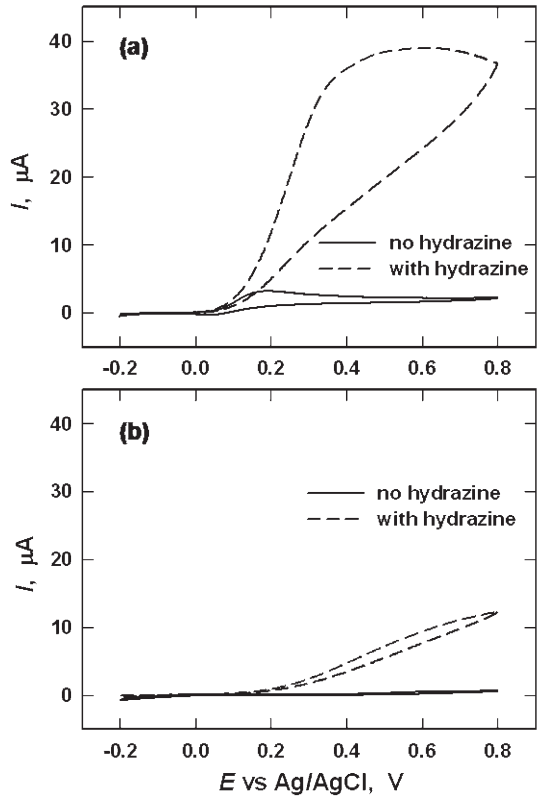

Fig. 3. Cyclic voltammograms obtained with bare ITO electrodes in Tris buffer (pH 9.0) containing a) 0.1 mM CT or b) 0.1 mM HQ in the absence and presence of 1 mM hydrazine (scan rate = 10 mV/s).

by hydrazine. However, the current does not show a simple limiting-current behavior. It seems that the actual mechanism is more complex. On the other hand, HQ redox cycling by hydrazine also occurs (Fig. 3b). However, the current is much smaller, because the electrooxidation of HQ is slow in this potential range.

It is well known that CT and HQ are easily oxidized at high pH values [9]. However, CT and HQ are stable for several hours in Tris buffer (pH 9.0) in the presence of hydrazine, because hydrazine acts as an antioxidant. Therefore, hydrazine plays a crucial role in stabilizing CT in Tris buffer as well as increasing the anodic current of CT.

The detection limits of CT in the presence and absence of hydrazine have been determined by using differential pulse voltammetric technique. Figure 4a shows the concentration-dependent differential pulse voltammograms of CT in the presence of 0.1 mM HQ and 1 mM hydrazine. The anodic peak potential of CT appears at 0.26 V, where the oxidation current of HQ is negligible. The anodic peak current increases gradually with increasing CT concentration. The calibration plots for CT are shown in Figure 4b. The peak currents in the presence of hydrazine are much larger than in the absence of hydrazine because of CT redox cycling by hydrazine. In the presence of 1 mM hydrazine, the anodic peak current in Tris buffer containing 1 μM CT is 2.11 ± 0.26 μA, which is clearly higher than the anodic current of 0.1 mM HQ at 0.26 V (1.51 ± 0.05 μA). The results show that the detection limit of CT is 1 μM in the presence of excess concentration of HQ (0.1 mM) and 1 mM hydrazine. On the other hand, the detection limit of CT is 10 μM in Tris buffer containing 0.1 mM HQ in the absence of hydrazine. The CT redox cycling by hydrazine lowers the detection limit by one order of magnitude.

In summary, bare ITO electrodes have been used for the selective determination of CT in the mixture of CT and HQ. The large difference between two peak potentials of CT and HQ and the redox cycling by hydrazine enables us to obtain a low detection limit, which is obtained without using chemically modified electrodes and simply by adding hydrazine to a solution. This approach can be applied to environmental analysis of CT in the presence of HQ.

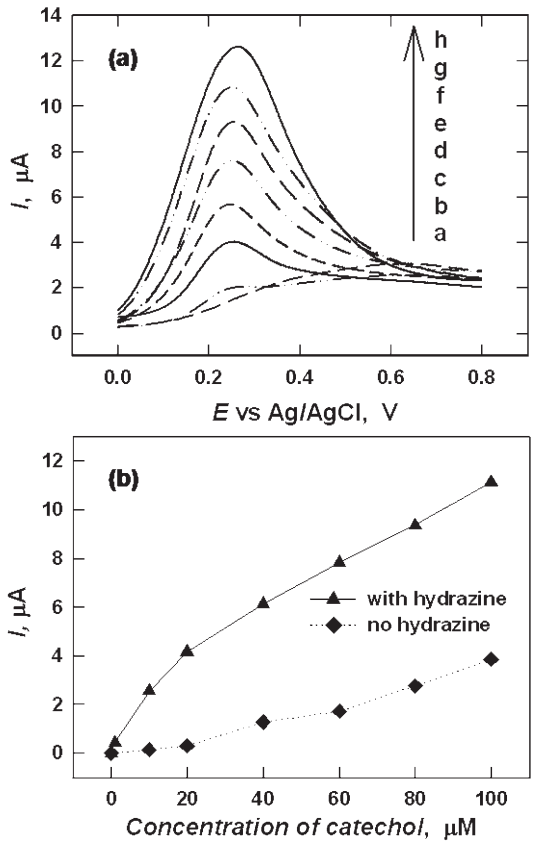

Fig. 4. a) Differential pulse voltammograms obtained with bare ITO electrodes in Tris buffer (pH 9.0) containing 0.1 mM HQ and different concentrations of CT in the presence of 1 mM hydrazine. [CT] = a) zero, b) 1, c) 10, d) 20, e) 40, f) 60, g) 80, and h) 100 μM. B) Calibration plots for CT in Tris buffer containing 0.1 mM HQ in the absence and presence of 1 mM hydrazine.

Experimental

The electrochemical experiments were performed using a CHI 617 (CH Instruments). The electrochemical cell consisted of a pretreated ITO working electrode, a Pt counter electrode, an Ag/AgCl (3 M KCl) reference electrode. All electrochemical experiments were carried out without removing oxygen from the analyte solution.

ITO-coated glasses were supplied by Geomatec (www.geomatec.co.jp). CT, HQ, and hydrazine monohydrate were purchased from Sigma-Aldrich. All reagents for preparing buffer solutions were obtained from Sigma-Aldrich or Fluka. All reagents were used without any further purification, and doubly distilled water was used for the preparation of aqueous solutions. The Tris buffer (pH 9.0) consisted of 50 mM tromethamine, 10 mM KCl, 1 g/L $MgCl_2$, and 7 mM HCl. The phosphate buffered saline (PBS, pH 7.4) buffer consisted of 0.01 M phosphate, 0.138 M NaCl, and 0.0027 M KCl. The acetate buffer (pH 4.5) consisted of 62.4 mM acetic acid and 37.6 mM sodium acetate.

ITO electrodes were washed with trichloroethylene, ethanol, and water consecutively to remove polar and nonpolar contaminants, and dried at 60 °C. The cleaned electrodes were pretreated at 70 °C for 1.5 h in a mixed solution of H_2O, H_2O_2 (30%), and NH_4OH (30%) in a ratio of 5:1:1.

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