Selective Electrochemical Response of Dopamine against 3,4-Dihydroxyphenylacetic Acid at Bare Indium–Tin Oxide Electrode

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Electrochemistry of dopamine and 3,4-dihydroxyphenylacetic acid at ITO were investigated. The oxidation of dopamine significantly depended on pH and supporting electrolyte. The peak current increased more than one hundred folds with increasing pH from 2.5 to 10.0 in phosphate buffer. Moreover, selective oxidation of dopamine against 3,4-dihydroxyphenylacetic acid at bare ITO was observed. It is the first electrode material that can be produced in large scale for selective oxidation of dopamine. Selective catecholamine detection at ITO is suggested.

Dopamine plays a very important role in the functioning of the central nervous, cardiovascular, renal, and hormonal systems, as well as in drug addiction and Parkinson's disease.[1–3] The basal dopamine concentrations in blood samples are very low, and low dopamine concentrations of pM order can be electrochemically detected without labeling.[4] This makes the electrochemical method a very promising approach for the real time detection of dopamine in biological samples.[4–9]

The electrochemistry of dopamine at metal and carbon electrodes has been extensively studied, and depended significantly on electrode surface properties.[10–16] Indium–tin oxide (ITO) is a degenerate n-type semiconductor with highly populated positively and negatively charged sites.[17] The interesting surface states of ITO result in its numerous use as substrates for self-assembly and in electroanalytical sensors.[18–21] Matsue's group studied the electrochemistry of dopamine at a bare ITO and a platinum particle-modified ITO electrode in order to improve the electrochemical reaction rate of dopamine.[22] Recent studies show that the adsorption of catecholamines on the electrode surface play an important role in the electron transfer, the variable surface properties of ITO may enable us to achieve highly sensitive and selective electroanalysis for catecholamines.[10] In this study, we report that dopamine was oxidized much easily than 3,4-dihydroxyphenylacetic acid at ITO using suitable supporting electrolyte and pH.

ITO films were formed on microscope glass from an In_2O_3–5%SnO_2 ceramic target using RF sputter deposition equipment (SEED Lab. Kanagawa, Japan) in pure argon gas. Prior to deposition, the chamber pressure was reduced to 2×10^{-6} Pa and then filled with argon. The RF power was 50 W. The substrate was kept at room temperature and rotated at 10.7 rpm. The sputtering time was 90 min.

Electrochemical experiments were performed using an ALS/CHI 750A electrochemical analyzer (CH Instruments, Inc. USA). Unless otherwise noted, all potentials were reported with respect to an Ag/AgCl/3 M KCl reference electrode. The ITO working electrode area was defined by using a piece of adhesive tape with a hole. For the cyclic voltammogram experiments, the electrode area was 3.14 mm^2. The pH of phosphate buffer was changed by changing the H_3PO_4, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4 ratio.

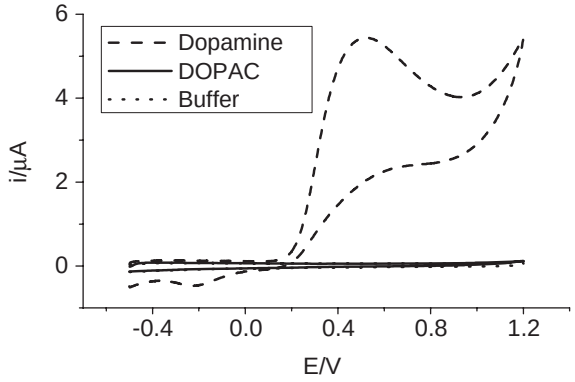

Figure 1. CV of 1 mM dopamine and 1 mM DOPAC in 2/15 M pH 7.4 phosphate buffer. Scan rate 0.1 V/s.

Figure 1 shows cyclic voltammograms (CV) of dopamine and 3,4-dihydroxyphenylacetic acid (DOPAC) at ITO electrodes. The dopamine was easily oxidized. The redox process of dopamine was less reversible than that at the glassy carbon and metal electrodes, indicating that the reduction of the quinone form to catechol was particularly suppressed at the ITO electrode. Unlike dopamine, DOPAC was not oxidized in the potential range investigated (Figure 1). Dopamine and DOPAC have simliar structures and generally exhibit similar voltammograms at glassy carbon and metal electrodes, the noticeable difference between the CVs of dopamine and DOPAC shows that the amine group of dopamine promoted the oxidation of catechol, and the carboxylic group of DOPAC inhibited the oxidation of catechol.

Recent studies have shown that the adsorption of catechols is essential for rapid electron transfer, and alkylphosphonates can adsorb more strongly onto ITO than carboxylic acids and amines.[10,18,19] We deduced that the adsorption of phosphate promoted dopamine adsorption (pK_b 8.87) and inhibited the adsorption of negatively charged DOPAC, resulting in the noticeable difference between the voltammograms of dopamine and DOPAC. To confirm this idea, the effect of supporting electrolyte on electrochemistry of dopamine, DOPAC, and ferrocyanide was studied.

DOPAC was easily oxidized and dopamine anodic current decreased in acetate buffer (Figure 2). Ferrocyanide was more easily oxidized in acetate buffer than in phosphate buffer, indicating the adsorption of phosphate. The dependence of catechol-

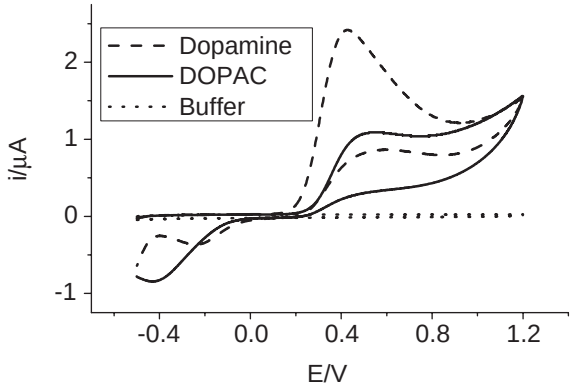

Figure 2. CV of 1 mM dopamine and 1 mM DOPAC in 2/15 M pH 7.4 acetate buffer. Scan rate 0.1 V/s.

amine electrochemistry on the supporting electrolyte is attributed to the competitive adsorption between the supporting electrolyte and catechols, and the interaction between the adsorbed supporting electrolyte and catechols. When acetate buffer was used as the supporting electrolyte, the interaction between the acetate and the ITO surface is not as strong as the interaction between phosphate and the ITO surface. As a result, both DOPAC and dopamine directly adsorbed onto the ITO surface in acetate buffer. The adsorption of DOPAC resulted in the oxidation of DOPAC in acetate buffer. On the other hand, the less negatively charged ITO surface reduced the amount of adsorbed dopamine and led to a decrease in the oxidation current.

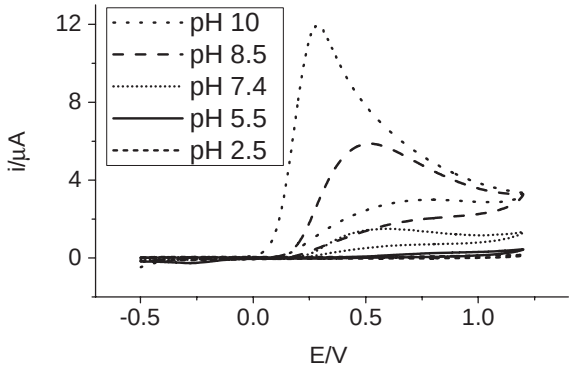

Figure 3. pH dependence of CV for 1 mM dopamine in 2/15 M phosphate buffer. Scan rate was 0.1 V/s. pHs were 2.5, 5.5, 7.4, 8.5, and 10.0.

For further confirmation of the importance of the dopamine adsorption, we studied pH effect in phosphate buffer (Figure 3). The oxidation peak potential shifted negatively with increasing pH from 2.5 to 10.0 at both ITO and glassy carbon electrodes. Interestingly, the peak current increased more than one hundred folds at ITO and less than 50% at the glassy carbon electrode with increasing pH from 2.5 to 10.0. The sharp current increase at the ITO is due to the deprotonation of adsorbed phosphate and the adsorption of more dopamine molecules that catalyzed the oxidation of dopamine.[10]

In conclusion, it is easy to oxidize dopamine, and is difficult to oxidize DOPAC at bare ITO using phosphate buffer as supporting electrolyte. This result suggests that bare ITO may be employed for the selective detection of dopamine. Further studies on the selective detection of dopamine against interfering molecules, such as L-ascorbic acid and uric acid, are under way.

References

1 B. J. Venton and R. M. Wightman, *Anal. Chem.*, **75**, 414A (2003).
2 J. Wang, B. M. Tian, and E. Sahlin, *Anal. Chem.*, **71** 3901 (1999).
3 J. M. Zen and P. J. Chen, *Anal. Chem.*, **69**, 5087 (1997).
4 O. Niwa, H. Tabei, B. P. Solomon, F. M. Xie, and P. T. Kissinger, *J. Chromatogr., B*, **670**, 21 (1995).
5 R. D. O'Neil, *Analyst*, **119**, 767 (1994).
6 J. Wang and A. Walcarius, *J. Electroanal. Chem.*, **407**, 183 (1996).
7 J. Wang, P. V. A. Pamidi, G. Cepria, S. Basak, and K. Rajeshwar, *Analyst*, **122**, 981 (1997).
8 O. Niwa, M. Morita, and H. Tabei, *Electroanalysis*, **3**, 163 (1991).
9 O. Niwa and H. Tabei, *Anal. Chem.*, **66**, 285 (1994).
10 S. H. Duvall and R. L. McCreery, *J. Am. Chem. Soc.*, **122**, 6759 (2000).
11 R. L. McCreery, in "Electroanalytical Chemistry; Carbon Electrodes: Structural Effects on Electron-Transfer Kinetics," ed. by A. J. Bard, Dekker, New York (1991), Vol. 17, p 221.
12 G. E. Cabaniss, A. A. Diamantis, W. R. Murphy, R. W. Linton, and T. J. Meyer, *J. Am. Chem. Soc.*, **107**, 1845 (1985).
13 R. L. McCreery, in "Voltammetric Methods in Brain Systems, Carbon Electrode Surface Chemistry: Optimization of Bioanalytical Performance," ed. by S. A. A. Boulton, G. B. Baker, and R. N. Adams, Humana Press, Totowa, NJ (1995), p 1.
14 M. Deakin, P. Kovach, K. Stutts, and R. M. Wightman, *Anal. Chem.*, **58**, 1474 (1986).
15 E. Laviron, *J. Electroanal. Chem.*, **164**, 213 (1984).
16 M. P. Soriaga and A. T. Hubbard, *J. Am. Chem. Soc.*, **104**, 2735 (1982).
17 F. Nuesch, L. J. Rothberg, E. W. Forsythe, Q. T. Le, and Y. L. Gao, *Appl. Phys. Lett.*, **74**, 880 (1999).
18 T. Gardner, C. Frisbie, and M. J. Wrighton, *J. Am. Chem. Soc.*, **117**, 6927 (1995).
19 S. H. Brewer, D. A. Brown, and S. Franzen, *Langmuir*, **18**, 6857 (2002).
20 S. Y. Oh, Y. J. Yun, D. Y. Kim, and S. H. Han, *Langmuir*, **15**, 4690 (1999).
21 C. Donley, D. Dunphy, D. Paine, C. Carter, K. Nebesny, P. Lee, D. Alloway, and N. R. Armstrong, *Langmuir*, **18**, 450 (2002).
22 T. Matsue, A. Aoki, T. Abe, and I. Uchida, *Chem. Lett.*, **1989**, 133.

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