

Voltammetric Determination of Ascorbic Acid and Dopamine Simultaneously at a Single Crystal Au(111) Electrode

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A single-crystal Au(111) electrode was used for the simultaneous determination of dopamine (DA) and ascorbic acid (AA) in a phosphate buffer solution at pH 6.9. The single-crystal Au(111) electrode displayed excellent electrocatalytic activity for DA and AA oxidation in comparison to a Au disk electrode. Although the anodic peaks of both reagents overlapped on the Au disk electrode, the anodic peak potentials of DA and AA in their mixture were well separated since the peak potential of AA was shifted to more negative values by cyclic and differential pulse voltammetry. The oxidation peak current increased linearly with the concentration of DA in the range of 5×10^{-6} - 5×10^{-4} mol/L in the presence of 5×10^{-4} mol/L AA. The detection limit of DA was 5×10^{-7} mol/L. The peak current also linearly increased with increasing AA concentration in the presence of 5×10^{-4} mol/L DA in the range of 1×10^{-6} - 5×10^{-4} mol/L. The detection limit of AA was 5×10^{-8} mol/L (s/n = 3). The single-crystal Au(111) electrode showed excellent electrocatalytic activity to both AA and DA, probably because hydrogen flame treatment made the single-crystal electrode surface a well-defined atomic structure.

Key Words: Au(111) single-crystal electrode, dopamine, ascorbic acid, voltammetry, simultaneous determination.

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Introduction

Dopamine (DA) plays an important physiological role in the functioning of the central nervous system, and cardiovascular, renal, and hormonal systems as well as in drug addiction and Parkinson's disease. Similarly, ascorbic acid (AA) has been used for the prevention and treatment of the common cold, mental illness, infertility, and even cancer and AIDS.¹⁻³

DA and other neurotransmitter catecholamines are easily oxidized, and electrochemical methods have been used to monitor their concentration based on anodic oxidation. A major problem in analysis of DA is the coexistence of AA in high relative concentrations, which is oxidized at very similar potentials for most electrode materials. Therefore, the presence of AA constitutes a serious interference in the voltammetric determination of DA. Considerable efforts have been devoted to overcome this problem, and, among the methods developed, electrochemical sensors have attracted wide attention due to their advantages of simplicity, inexpensiveness, and fast analysis in combination with high sensitivity and selectivity.

Most studies on DA and AA determination describe several methods to separate either AA⁴⁻⁶ or DA⁷⁻¹⁰ by selecting particular potentials or using different membranes or modified electrode surface. Selective determination of DA was achieved using polypyrrole,¹¹ nafion,¹² and stearic acid¹³ membranes based on the cationic permeability of the polymer. Many efforts have been made to separate the oxidation signals including pretreatment with laser activation on the electrode surface to obtain heterogeneous electron transfer at the glassy carbon electrode,¹⁴ employing heat on the carbon electrodes,¹⁵ using polyeugenol modified platinum electrode¹⁶ and overoxidized poly(1,2-phenylenediamine)-coated carbon fiber electrode,¹⁷ and gold electrode modified with self-assembled monolayers such as cysteamine¹⁸ and homocysteine.¹⁹ Gold nano particle modified electrodes prepared by electrochemical²⁰ or chemical^{21,22} techniques have received extensive interest for the simultaneous determination of AA and DA. Even though good selectivity and sensitivity have been achieved using these modified electrodes, adsorption of the analytes requires surface renewal after each experiment. As a result, there is still an expanding demand to develop simple, reliable, and efficient sensors for effective detection of AA and DA simultaneously.

The surface energy of well-defined single-crystal Au electrodes is minimized by means of reconstruction with a flame-annealing procedure.²³ The signal of analyte should be separated on electrode surfaces from the other electroactive constituent interferences, which oxidize close to the potential of the analyte on various types of electrodes. To the best of our knowledge, only self-assembled mercaptopropionic acid monolayer modified Au(111) single-crystal electrodes have been used for electrochemical detection of DA in the presence of AA²⁴ within gold-based electrodes. The present study is concerned with the simultaneous determination of DA and AA using single-crystal Au(111) electrodes treated with a hydrogen flame to maintain the well-ordered atomic structure with low charge transfer resistance.

Experimental

Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a BAS 100B electrochemical workstation (Bioanalytical System). The working electrodes were single-crystal Au(111) and Au disk

electrodes, while the auxiliary and reference electrodes were platinum wire and Ag/AgCl, respectively.

Au wire (99.99% in purity, Tanaka Kikinzoku Kogyo Co., Ltd.) was used for preparing the Au(111) single-crystal electrodes using the flame-annealing-quenching method with successive mechanical polishing to obtain a shiny surface for electrochemical measurements as described elsewhere in detail.²⁵ The freshly annealed single crystal Au(111) surface was cooled in a hydrogen gas stream and then immediately immersed into hydrogen saturated ultra-pure water. The electrode surface was protected with a water droplet prior to immersion in an electrochemical cell. To close the circuit, a single crystal Au(111) electrode was put in contact with the solution using hanging meniscus geometry. The quality of the single crystal plane was judged by measuring the cyclic voltammogram in a 0.1 M H₂SO₄ solution.²⁶

Reagents and solutions

DA and AA were purchased from Merck. The electrolytes were prepared from analytical grade NaOH and H₂SO₄, and NaH₂PO₄ salts. Ultra-pure water obtained from Milli-Q Elga System (18.2 MΩcm) was used throughout the study. All standard solutions were freshly prepared using deaerated ultra-pure water. The pH was adjusted by means of a Metrohm E 510 pH-meter with a combined glass electrode. The buffer and analytes containing solutions were purged with nitrogen for at least 10 min prior to the experiments. Nitrogen atmosphere was maintained over the solutions during the experiments. All experiments were carried out at room temperature.

Results and Discussion

Electrochemical behavior of DA and AA at gold electrodes

Initial studies were conducted to investigate the voltammetric behavior of DA and AA alone at gold disk and single crystal Au(111) electrodes to compare the performance characteristics of these 2 electrodes. Figure 1 shows the cyclic voltammogram of 5×10^{-4} M DA prepared in a pH 6.9 phosphate buffer solution at Au disk and Au(111) electrodes. On the gold disk electrode, the oxidation of DA takes place at around 260 mV (vs. Ag/AgCl) and in the reverse scan a pair of reduction peaks at 145 and -260 mV were observed. The first reduction peak was revealed to have a 2-electron process accompanied by transfer of 2 protons forming a reduction product as DA *o*-quinone. As reported earlier, in neutral and alkaline media, the second cathodic peak appears due to a 2-electron reduction of aminochrome, a cyclization product of *o*-quinone.²⁷

The response of DA at the single crystal Au(111) electrode displayed a well-established oxidation peak at 198 mV that lies at 60 mV more negative potentials compared to that of the disk electrode. A well-defined sharp oxidation peak with obviously increased current response was obtained at the single crystal Au(111) electrode. The flame annealing procedure yielded a well-ordered atomic structure with low charge transfer resistance. Therefore, the single crystal Au(111) electrode surface plays an important role in accelerating the electron transfer and increasing the peak current.

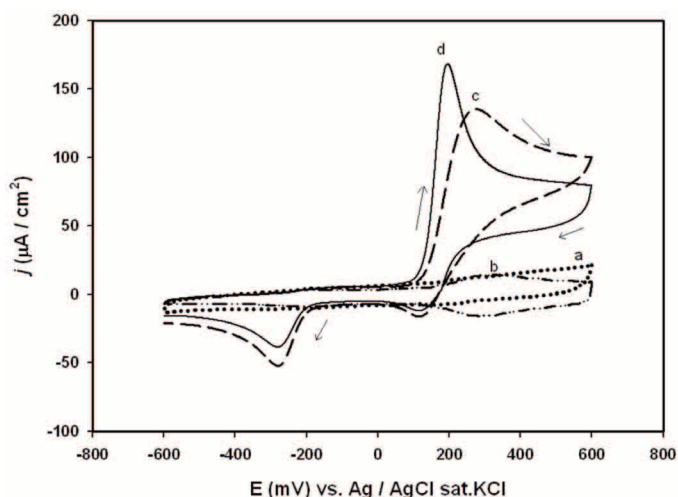


Figure 1. Cyclic voltammogram in a 0.10 M phosphate buffer solution at pH 6.9 at bare Au (a: dash-dotted line), Au(111) (b: dotted line) and in the presence of 5.0×10^{-4} M DA at bare Au (c: long dash line), Au(111) (d: solid line) electrodes with a scan rate of 50 mVs^{-1} .

Finally the results clearly indicate that single crystal electrodes have an electrocatalytic effect on DA oxidation. On the other hand, the difference between the anodic and cathodic peak potentials ($E_{pa} - E_{pc}$) was calculated as 130 mV at the Au disk electrode and 55 mV at the single crystal electrode, respectively, suggesting that the reversibility of the DA electrode reaction was improved by the single crystal Au(111) electrode.

The formal potential of DA estimated from the average value of anodic (E_{pa}) and cathodic peak potentials (E_{pc}), $(E_{pa} + E_{pc}) / 2$ were 170 mV and 195 mV vs. Ag/AgCl at the Au(111) single crystal electrode and Au disk electrode, respectively.

Figure 2 shows the cyclic voltammograms of 5×10^{-4} M AA in a phosphate buffer solution. AA displayed a single irreversible oxidation peak at both electrodes but the peak potential obtained on the gold disk electrode (165 mV) changed to 40 mV when the single crystal Au(111) electrode was used. This decrease in oxidation overpotential of about 125 mV and the increase in peak current clearly indicate an electrocatalytic effect of the single crystal Au(111) for oxidation of AA. The peak was significantly sharper and peak current became larger compared to those obtained at the Au disk electrode. The potential shift in oxidation peak of AA was important for further studies on the simultaneous determination of DA and AA by the separation in oxidation peak potential of each compound. A broad peak at around 350 mV in Figure 2 at the single crystal Au(111) electrode could be the oxidation of gold or Au(I) in the presence of AA or DHAA (dehydroascorbic acid, which is the oxidation product of AA), because a small broad oxidation peak for gold was observed at the single crystal Au(111) electrode at the same potential.

Figure 3 shows the cyclic voltammogram of a mixture containing 5×10^{-4} M DA and AA. A broad anodic peak at 230 mV was observed for the Au disk electrode with poor peak separation for DA and AA oxidation. In the reverse scan 2 small reduction peaks at 134 and -250 mV were observed for DA. However, as shown by curve d in Figure 3 the anodic peak potentials of the AA and DA oxidations were clearly seen separately at 40 and 198 mV, respectively, at the single crystal Au(111) electrode with a decrease in overpotential.

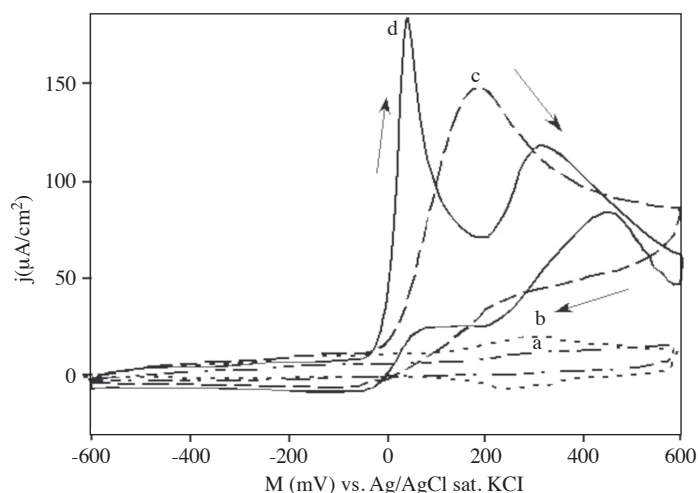


Figure 2. Cyclic voltammograms in a 0.10 M phosphate buffer solution at pH 6.9 at bare Au (a: dotted line), Au(111) (b: dash-dotted line) and in the presence of 5.0×10^{-4} M AA at bare Au (c: long dash line), Au(111) (d: solid line) electrodes with a scan rate of 50 mVs^{-1} .

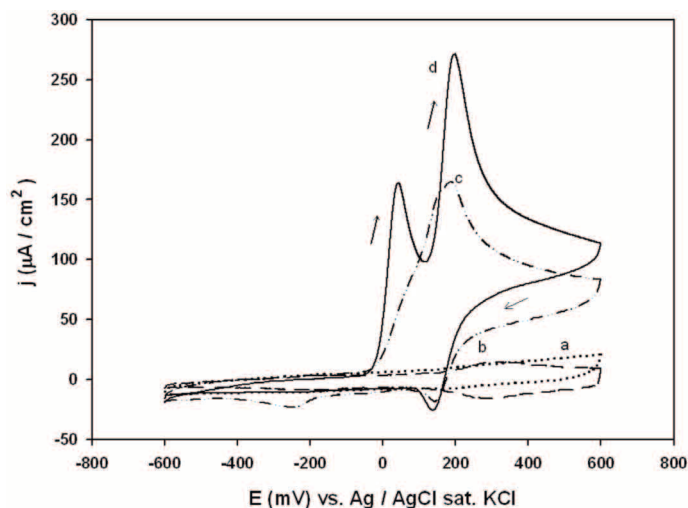


Figure 3. Cyclic voltammograms in a 0.10 M phosphate buffer solution at pH 6.9 at bare Au (a: dash-dotted line), Au(111) (b: dotted line) and in the presence of 5.0×10^{-4} M AA and DA at bare Au (c: long dash line), Au(111) (d: solid line) electrodes with a scan rate of 50 mVs^{-1} .

The broad peak at 350 mV for AA shown in Figure 2 at the single crystal electrode disappeared in the presence of DA (see Figure 3). This would be due to a stronger interaction between the electrode surface and DA than the interaction between Au(I) and AA or DHAA. The results indicate that the single crystal Au(111) electrode showed excellent electrocatalytic activity for oxidation of AA and DA, since hydrogen flame treatment provides a well-defined atomic structure. Further studies were carried out to understand the electron transfer mechanism of DA and AA at a single crystal Au(111) electrode. The CV current responses were found to be

linear with the square root of scan rates in the range of 20-200 mV/s indicating that the electrode reactions were diffusion-controlled (Figures 4 and 5).

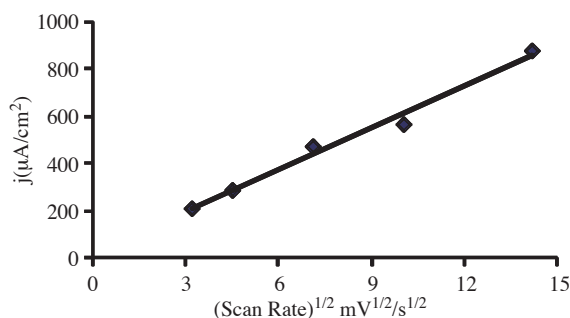


Figure 4. The dependence of peak current of 1.0 mM AA on scan rate at an Au(111) single crystal electrode in a 0.10 M phosphate buffer solution at pH 6.9.

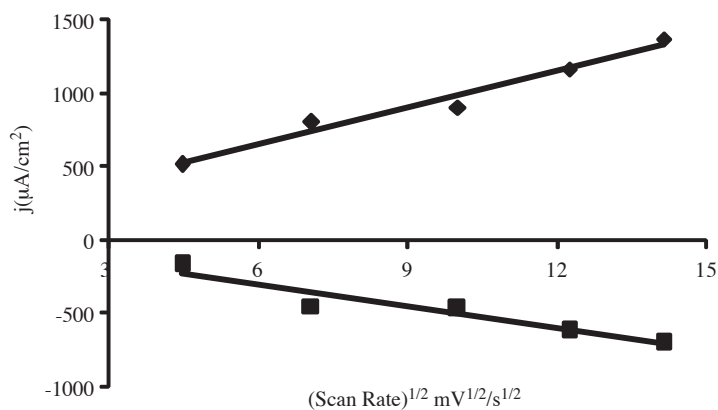


Figure 5. The dependence of peak current of 1 mM DA on scan rate at an Au(111) single crystal electrode in a 0.10 M phosphate buffer solution at pH 6.9.

Simultaneous determination of DA and AA

Simultaneous determination of both DA and AA is a difficult task in electroanalytical chemistry. The main goal of the present study was to display the well resolved oxidation peaks for AA and DA using a single crystal Au(111) electrode. Figure 6 shows the differential pulse voltammograms (DPV) of AA and DA that coexist in a solution at Au disk and Au(111) single crystal electrodes. As illustrated in Figure 6 (curve c), the Au disk electrode cannot separate the responses of DA and AA and gave a large response due to homogeneous catalytic oxidation of AA by the oxidized DA. On the other hand, the well resolved oxidation peaks for both compounds can be seen at -8 mV for AA and 155 mV for DA at the single crystal Au(111) electrode (Figure 6, curve d). This voltammogram was obtained by treating the single crystal electrode surface with a hydrogen flame to obtain a well-ordered atomic structure. It is generally accepted that the treatment of an electrode surface with a hydrogen flame results in more AuOH sites, which are the active species for oxidation, on a

single crystal electrode surface in neutral and alkaline solutions. The procedure also helps to give low charge transfer resistance on the surface of a single crystal electrode. Therefore, the linear increase in peak current of AA molecule in the presence of excess DA can be seen in Figure 7. Almost a stable peak current was observed for 5.0×10^{-4} M DA oxidation while the AA peak increased with increasing AA concentration into

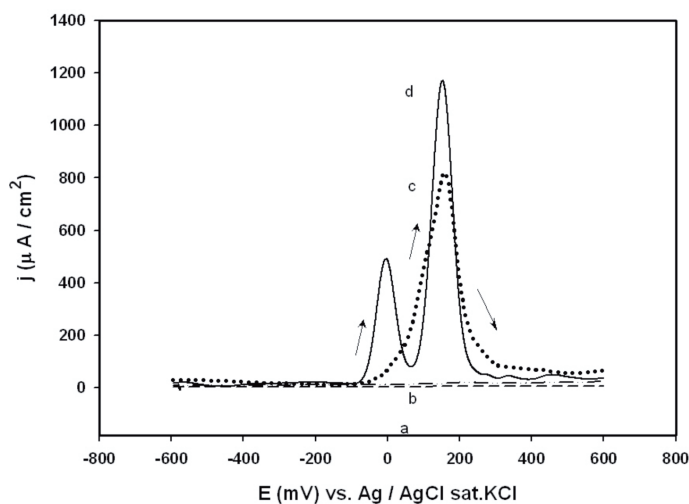


Figure 6. DP voltammograms recorded in a 0.10 M phosphate buffer solution at pH 6.9 Au disk (a: dash-dot-dash line), Au(111) (b: medium dash) electrodes, and in the presence of 5.0×10^{-4} M AA and DA at bare Au (c: dotted line) and Au(111) (d: solid line) electrodes with a scan rate of 20 mVs^{-1} .

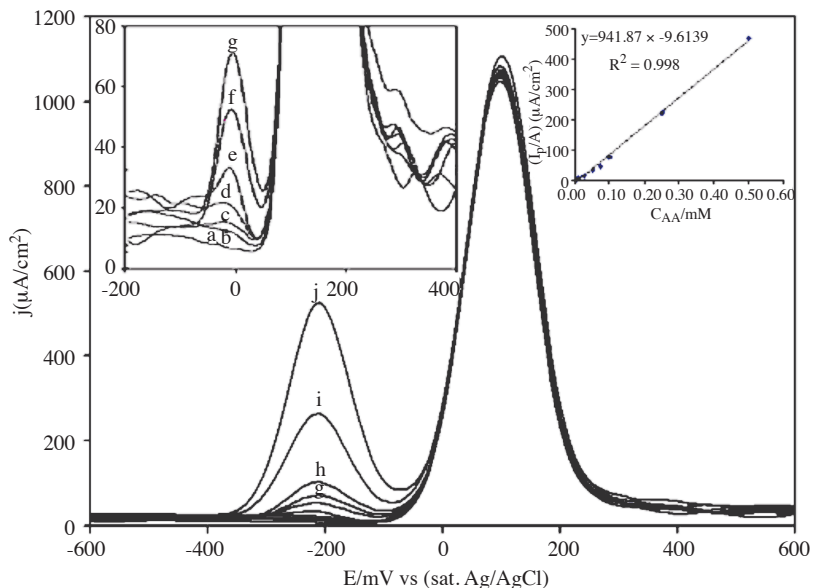


Figure 7. DPVs of Au(111) single crystal electrode in the presence of 5.0×10^{-4} M DA in a 0.10 M pH 6.9 phosphate buffer solution mixed with AA: (a) 0.0; (b) 1.0×10^{-6} ; (c) 5×10^{-6} ; (d) 1.0×10^{-5} ; (e) 2.5×10^{-5} ; (f) 5.0×10^{-5} M; (g) 7.5×10^{-5} ; (h) 1.0×10^{-4} ; (i) 2.5×10^{-4} ; (j) 5.0×10^{-4} M AA. Pulse height: 50.0 mV; pulse width: 120 ms; pulse period: 0.5 s.

the electrochemical cell. Thus, the homogeneous catalytic oxidation of AA by oxidation of DA was able to be eliminated by using a single crystal electrode. Figure 8 shows the DP voltammetric signals of 5×10^{-4} mol/L AA spiked with DA in a wide range of concentrations. No homogeneous catalytic oxidation was obtained and the oxidation signal of AA was unaltered by the addition of DA. The dependence of peak current on the concentration was linear in the range of 1×10^{-6} - 5×10^{-4} for AA and 5×10^{-6} - 5×10^{-4} for DA with correlation coefficients of 0.998 and 0.990. The correlation coefficients were obtained from the calibration curves depicted in the insets in Figures 7 and 8, respectively. Detection limits were estimated to be 3×10^{-8} mol/L for AA and 2×10^{-7} mol/L for DA using 3σ /slope ratio, where σ is the standard deviation of the mean value for 5 independent voltammograms of the blank solution.

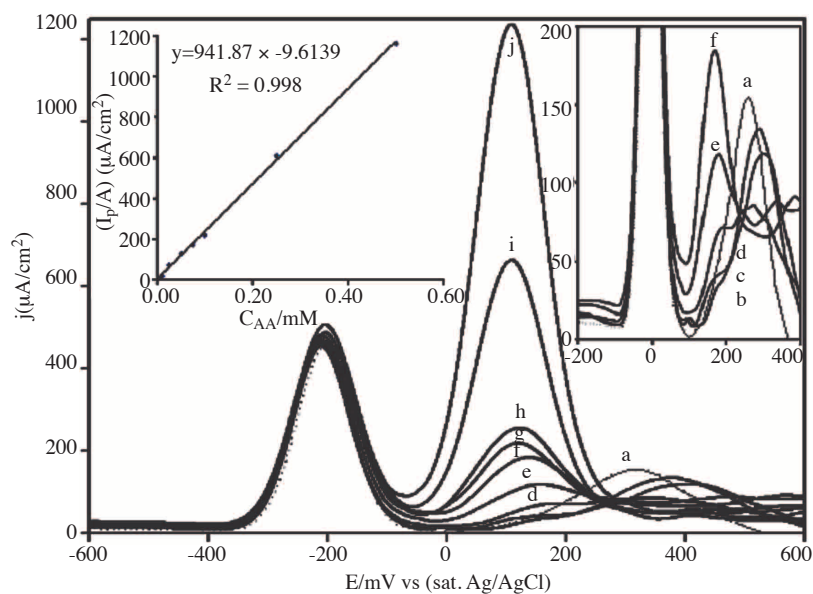


Figure 8. DPVs of Au(111) single crystal electrode in the presence of 5.0×10^{-4} M AA in a 0.10 M pH 6.9 phosphate buffer solution mixed with DA: (a) 0.0; (b) 5.0×10^{-6} ; (c) 7.5×10^{-6} ; (d) 1.0×10^{-5} ; (e) 2.5×10^{-5} ; (f) 5.0×10^{-5} M; (g) 7.5×10^{-5} ; (h) 1.0×10^{-4} ; (i) 2.5×10^{-4} ; (j) 5.0×10^{-4} M AA. Pulse height: 50.0 mV; pulse width: 120.0 ms; pulse period: 0.5 s.

Conclusion

Although gold electrodes have weak catalytic properties in acidic solutions²⁵ their catalytic effect increases with increasing pH. At pH 6.9, some active AuOH sites could be formed on the single crystal electrode surface and the number of active AuOH sites increased after the single crystal electrode was treated by hydrogen flame to maintain a well-ordered atomic structure with low charge transfer resistance. The present study revealed that the single crystal Au(111) electrode exhibits highly electrocatalytic activity towards oxidation of AA and DA in a binary mixture with enhanced sensitivity and selectivity compared to the Au disk electrode. By this means the single crystal Au(111) electrode can be successfully used to detect AA and/or DA sensitively and selectively in the presence of excess of each other at pH 6.9.

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