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The Effects of Laser Pulse Irradiation at Glassy Carbon Electrode on the Electrochemistry of Dopamine and Ascorbic Acid

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In this research, we found that treatment of a glassy carbon (GC) electrode using laser pulse irradiation offers substantial improvements of its selectivity and sensitivity toward voltammetric determination of dopamine (DA) in the presence of ascorbic acid (AA). In phosphate buffer of pH 7.0, oxidation of DA at an untreated GC electrode was controlled by a mixture of both adsorption and diffusion but at the treated GC electrode diffusion-controlled became dominant. When cyclic voltammograms of DA were measured with the untreated and treated GC electrode, the oxidation peak current at the treated GC electrode was five times larger than that at the untreated GC electrode. The midpoint potential (E_m) at the treated GC electrode shifted about 0.03 V to a negative potential and the peak separation (ΔE_p) decreased from 0.16 V at the untreated GC to 0.04 V at the treated GC. The enhancement in the oxidation peak current by the use of the treated GC electrode was probably due to activation of the GC electrode and an increase in electrode surface area because of roughening the electrode surface by laser pulse irradiation. Similar results were found for AA. The oxidation peak potential of AA at the treated GC electrode shifted about 0.47 V to a more negative potential, compared with that at the untreated GC electrode. In addition, the oxidation peak current at the treated GC electrode increased about twice larger than that at the untreated GC electrode. The enhancement in the oxidation peak of AA is not only due to an increase in electrode surface area but also due to activation of the GC electrode by laser pulse irradiation. Using the treated GC electrode by laser pulse irradiation, two oxidation peaks of DA and AA could be separated with a potential difference enough to distinguish between them in cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Based on this result, the voltammetric determination of DA could be performed in the presence of AA.

Keywords: Ascorbic acid, dopamine, glassy carbon, laser pulse irradiation, voltammetry

1. INTRODUCTION

Dopamine (DA) is one of the important catecholamine neurotransmitters in the central nervous system, which is related to several diseases such as schizophrenia and Parkinson's [1-3]. Consequently, determination of DA and related catecholamines is indispensable in neurochemical and brain science studies. Thus, there is a continuing interest in the development of simple, sensitive, and reliable method for the determination of DA. Taking into account the fact that DA and other catecholamines are easily oxidized, voltammetric techniques can be employed for the determination of DA. However, the voltammetric determination of DA is complicated by the coexistence of relatively high levels of ascorbic acid (AA) in body fluid. AA is oxidized at a potential close to that for DA at almost all electrode materials and consequently overlapped voltammetric responses severely hinder the accurate determination of DA [1, 4].

A surface condition of a working electrode is one of the most important aspects of voltammetric measurements, and at the same time one of the most difficult problems to solve. It is necessary to maintain the surface condition of the working electrode constant with a high activity, at least during a single experiment [5]. In electroanalytical chemistry, various treatments for solid electrodes have been attempted for higher sensitivity and selectivity in the determination of DA. Several modification methods have been reported, such as coating an electrode surface with polymeric films [6-15], entrapping modifiers in polymeric [16, 17], and modifying an electrode surface with self assembled monolayers [18-23]. However, a serious drawback of electrodes modified by these methods is that the electrode surface can not be renewed in the event of leakage, contamination or passivation [1]. Further, in some modification methods, expensive modifiers such as carbon nanotubes [24-28], nanoparticles [29-31], or synthetic modifiers that required complicated and time consuming preparation methods [32-37] are needed. Incorporation of various modifiers, such as zeolites [38], organic molecules [39], and surfactant [40], into a carbon paste electrode (CPE) has been also reported for the selective determination of DA. A main drawback of these incorporated CPEs is that the modifiers are in loose association or physical contact with the electrode. Thus, the electrodes may easily degrade over time due to depletion of modifier especially in solvents in which they have a high level of solubility [1].

On the other hand, unlike the chemical modification methods described above, a physical treatment of solid electrodes by laser pulse irradiation has been suggested [41-44]. Since a solid electrode is only irradiated with strong laser pulses in a sample solution in this treatment, the treatment does not need complicated modification procedures and essentially does not contaminate a sample solution. The treatment has been applied to various carbon electrodes such as a GC electrode and a highly ordered pyrolytic graphite (HOPG) electrode, and can not only remove contaminants on the electrodes but also activate the electrodes. In this paper, based on the advantages of this treatment, we examined voltammetric behaviors of DA and AA at a GC electrode treated by laser pulse irradiation.

2. EXPERIMENTAL

2.1. Chemicals

Dopamine hydrocloride (Aldrich), ascorbic acid (Merck), KH_2PO_4 (Merck), and Na_2HPO_4 (Merck) were of analytical grade and used as received. Deionized water was used for all solutions. Phosphate buffer solutions (PBS) were prepared by dissolving appropriate amount of KH_2PO_4 and Na_2HPO_4 in deionized water to get the desired pH. Stock solutions of DA and AA were freshly prepared as required. Nitrogen gas was used to bubble through the test solution to remove dissolved oxygen.

2.2. Apparatus

Figure 1 shows an experimental setup for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with the treatment by laser pulse irradiation. A Q-switched Nd:YAG laser (Quantel, Brilliant ω) was used for irradiating a GC rod 1.0 mm in diameter. The wavelength was 1064 nm, the pulse width was 5 ns, and the laser spot was ca. 5 mm in diameter. The energy was adjusted to 100 mJ/pulse by placing several slide glass plates between the electrolytic cell and the laser. The pulse energy was measured with a laser power meter (OPHIR, 30A-P-SH, A/N2) in the atmosphere. The spot of laser was carefully positioned at the center of the GC electrode with a fine adjustable X-Y stage.

Voltammetric measurements were carried out with a potentiostat (Huso, HECS 972) and a potential sweep unit (Huso, HECS 980). A conventional three electrode system was used for all voltammetric experiments. The GC rod and a platinum spiral wire served as a working electrode (WE) and as a counter electrode (CE), respectively. All potentials were referred to an Ag/AgCl (NaCl 3 M) as a reference electrode (RE). A sample solution was purged with nitrogen gas (99.9%) for at least 15 min before each voltammetric measurement.

2.3. Preparation of the working electrodes

The GC rod was connected with a copper wire and inserted into a glass tube 5 mm in diameter and embedded with epoxy cement. The copper wire was used for electrical contact to the potentiostat. Before the GC electrode was inserted into the electrolytic cell, it was polished with 0.3 μm alumina powder slurry and ultrasonically rinsed with deionized water. The GC electrode was then horizontally placed in the electrolytic cell (Figure 1). Before each measurement, the GC electrode was irradiated with laser pulses at 20 Hz for 2 s.

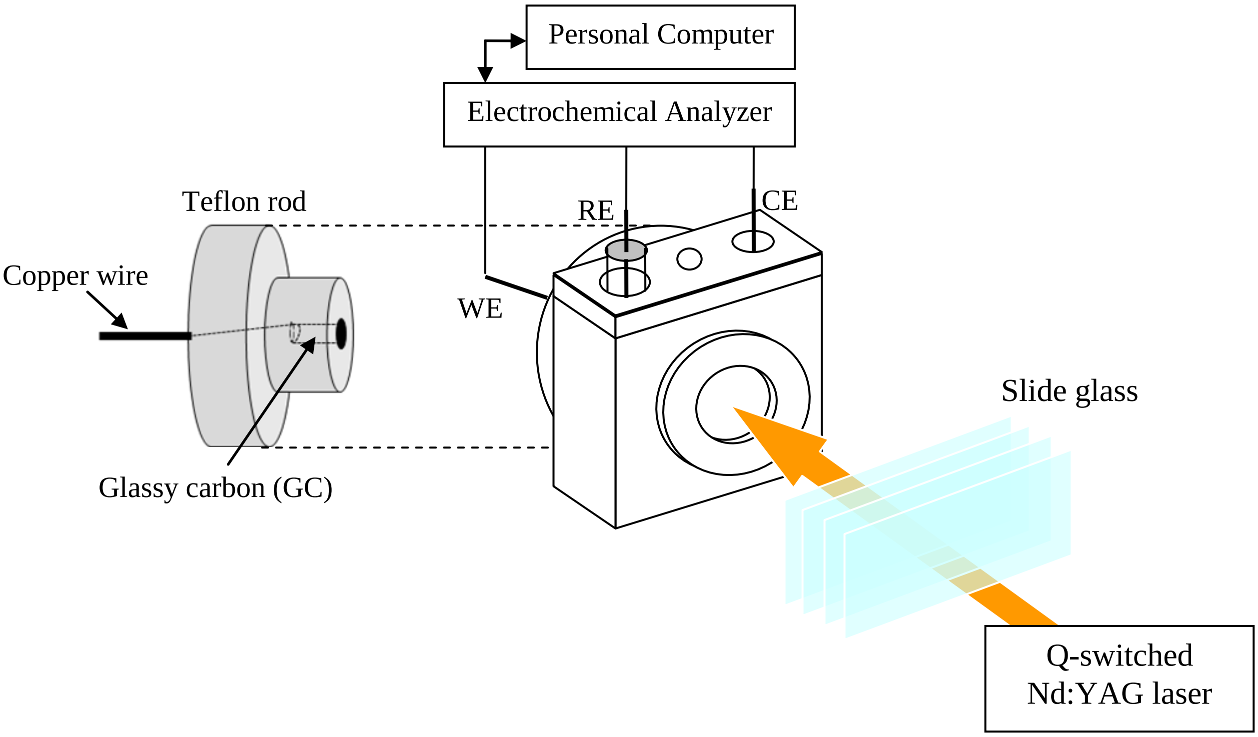

Figure 1. Schematic diagram of experimental setup

3. RESULTS & DISCUSSION

3.1. Voltammmetric behavior of DA at GC electrodes untreated and treated by laser pulse irradiation

Figure 2 shows cyclic voltammograms (CVs) of DA in PBS pH 7.0 obtained with the untreated and treated GC electrode. In this connection, the reaction scheme of DA is shown in Figure 3. The two CVs were significantly different in shape. The oxidation and reduction waves in the CV obtained with the untreated GC were broader than those obtained with the treated GC. At the untreated GC, the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}) were 0.29 and 0.13 V, respectively, and the peak separation ($\mathit{\Delta} E_p$) was 0.16 V. In addition, the anodic peak current (I_{pa}) and cathodic peak current (I_{pc}) were 1.79 and 1.24 µA, respectively. On the other hand, at the treated GC, E_{pa} and E_{pc} were 0.20 and 0.16 V, respectively, and $\mathit{\Delta} E_p$ was 0.04 V. In addition, I_{pa} and I_{pc} were 9.59 and 4.74 µA, respectively. The results are listed in Table 1. As can be seen from the results, the treatment by laser pulse irradiation caused a negative shift in E_ps, a decrease in $\mathit{\Delta} E_p$, and an increase in I_ps. The negative shift indicates that the oxidation of DA at the treated GC needs energy less than that at the untreated GC. Both the decrease in $\mathit{\Delta} E_p$ and increase in I_ps suggest that the oxidation at the treated GC occurs faster (is more reversible) than that at the untreated GC.

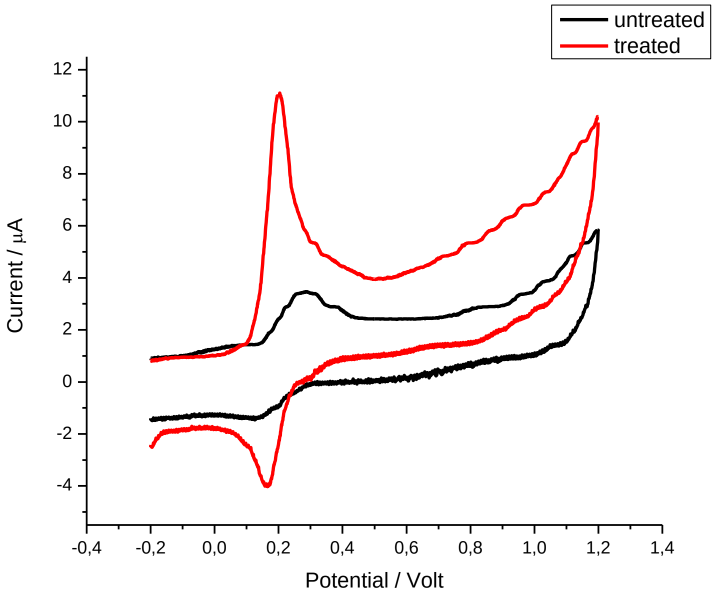

Figure 2. Cyclic voltammograms of DA. The sample solution contained 1 mM DA in PBS pH 7.0. The cyclic voltammograms were obtained with the untreated and treated GC electrode at a scan rate of 100 mVs^{-1}.

Table 1. Comparison of CV's parameters of DA at the untreated and treated GC electrode

Electrode	E_{pa} / V	E_{pc} / V	ΔE_p / V	I_{pa} / µA	I_{pc} / µA
Untreated GC	0.29	0.13	0.16	1.79	1.24
Treated GC	0.20	0.16	0.04	9.59	4.74

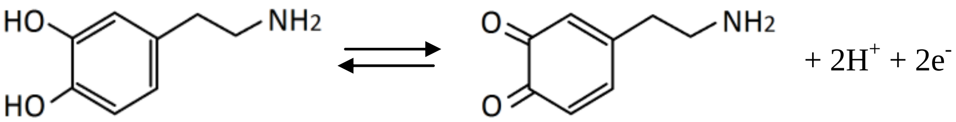

Figure 3. The reaction scheme of DA

To confirm this suggestion, we examined the influence of the scan rate (*v*) on the oxidation peak currents of 1 mM DA in PBS pH 7.0 at the untreated and treated GC electrode. Plots of I_{pa} *vs* *v* and I_{pa} *vs* $v^{1/2}$ are shown in Figures 4 and 5, respectively. Comparison between two figures clearly shows that R^2 of I_{pa} *vs* *v* and I_{pa} *vs* $v^{1/2}$ plots for the untreated GC electrode have values that are not much different, 0.9663 and 0.9793, respectively. It implies that the oxidation of DA at the untreated GC was controlled by a mixture of both adsorption and diffusion. While for the treated GC electrode, the I_{pa} *vs* $v^{1/2}$ plot was linear, which suggests that diffusion-controlled became dominant. However, slopes of the I_{pa} *vs* $v^{1/2}$ plots were significantly different with each other, i.e., 2.23 µA (mV)$^{-1/2}$ at the treated GC and 0.46 µA (mV)$^{-1/2}$ at the untreated GC. In general, the peak current is proportional to the electrode surface area in cyclic voltammetry [45]. Consequently, the increase in the slope for the I_{pa} *vs* $v^{1/2}$ plot from the untreated to treated GC electrode is partially attributable to an increase in surface area of the GC electrode caused by the treatment by laser pulse irradiation. On the other hand, the peak current depends on the reversibility, described above [45]. As the electrode reaction is improved more reversible, larger peak currents can be observed. Consequently, considering the decrease in ΔE_p by the treatment, the increase in the slope is attributed to the improvement of the electrode reaction by activation of the GC electrode caused by the treatment of laser pulse irradiation.

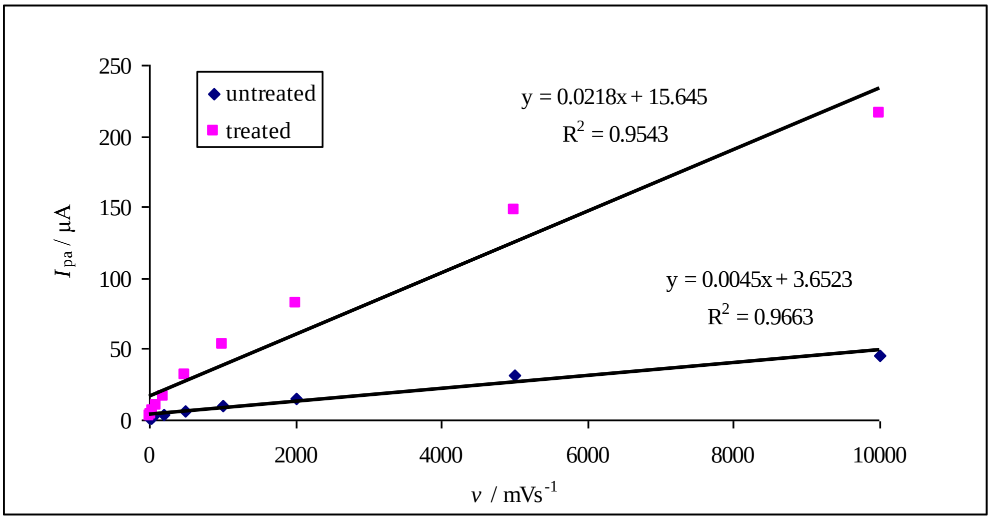

Figure 4. Plot of I_{pa} vs v. The sample solution contained 1 mM DA in PBS pH 7.0. The cyclic voltammograms were obtained with the untreated and treated GC electrode at various scan rates.

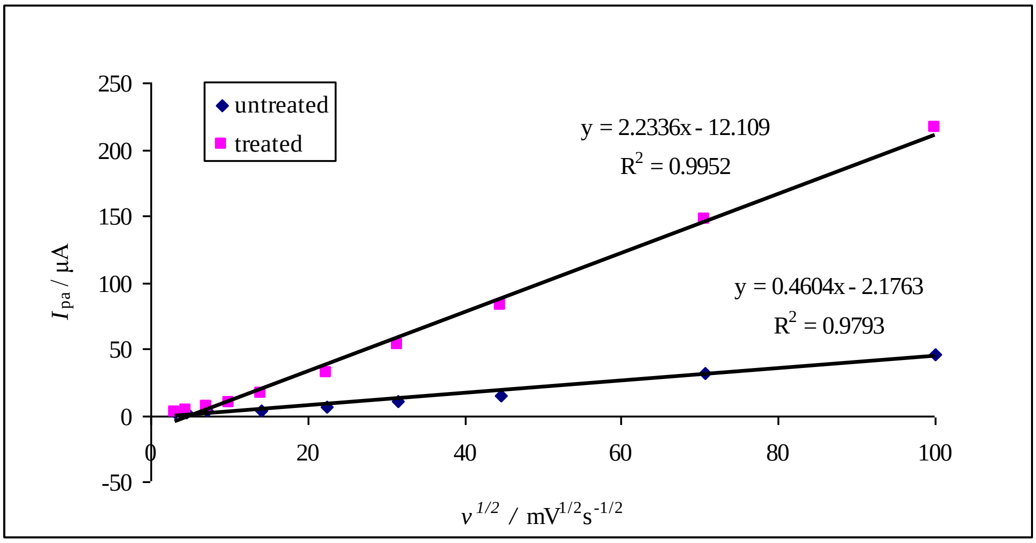

Figure 5. Plot of I_{pa} vs $v^{1/2}$. The sample solution contained 1 mM DA in PBS pH 7.0. The cyclic voltammograms were obtained with the untreated and treated GC electrode at various scan rates.

Differential pulse voltammograms (DPVs) of DA at the treated GC electrode showed that the peak potential slightly shifted to more positive potentials with increasing concentration of DA from 0.2 to 1.0 mM, i.e., 10 mV/mM. Although a calibration curve in this concentration range was linear with the equation, I_{pa} (µA) = 12.43 C (mM) + 11.36 with R^2 of 0.9911, the intercept of this equation significantly deviated from the origin. This suggests that an adsorption of DA occurred in the concentration range of 0.2 to 1.0 mM. At lower concentrations, no potential shift was found, suggesting that no adsorption of DA occurred.

3.2. Voltammetric electrochemistry of AA at the untreated and treated GC electrode

Figure 6 shows the CVs of 5 mM AA in PBS of pH 7.0 obtained by using the untreated and treated GC electrode. The CVs at the both electrodes showed only oxidation waves. This has been reported in many works, since AA is finally oxidized to dehydroascorbic acid, which is not electroactive, through a complicated process [43]. The reaction scheme of AA is shown in Figure 7. At the untreated electrode, E_{pa} was found at 0.48 V with I_{pa} of 7.81 µA. On the other hand, E_{pa} was found at 0.01 V with I_{pa} of 18.00 µA at the treated GC. The results are listed in

Table 2.

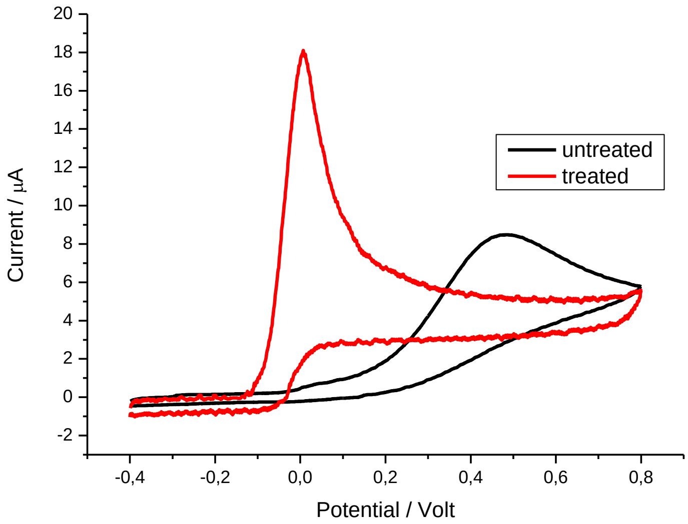

Figure 6. Cyclic Voltammogram of AA. The sample solution contained 5 mM AA in PBS pH 7.0. The cyclic voltammograms were obtained with the untreated and treated GC electrode at a scan rate of 100 mVs^{-1}.

Table 2. Comparison of CV's parameters of AA at the untreated and treated GC electrode

Electrode	E_{pa} / V	I_{pa} / µA
Untreated GC	0.48	7.81
Treated GC	0.01	18.00

In a similar way of the oxidation of DA, the oxidation of AA was improved more reversible at the treated GC, leading the negative shift of E_{pa} and the larger I_{pa} in CV. Further, the increase in surface area by the treatment of laser pulse irradiation can partially contribute to the increase in peak current [5,42], as it was found for DA oxidation.

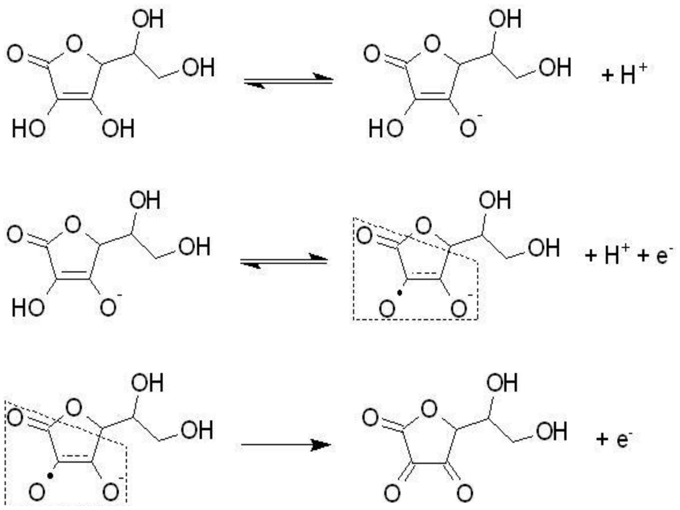

Figure 7. The reaction scheme of AA

To confirm the mechanism of AA oxidation at the untreated and treated GC electrode, we also studied the influence of scan rate on I_{pa}. A linear correlation was found between I_{pa} *vs* $v^{1/2}$ at both electrodes (Figure 8), which confirmed that the oxidation of AA was controlled by a diffusion process at both electrodes.

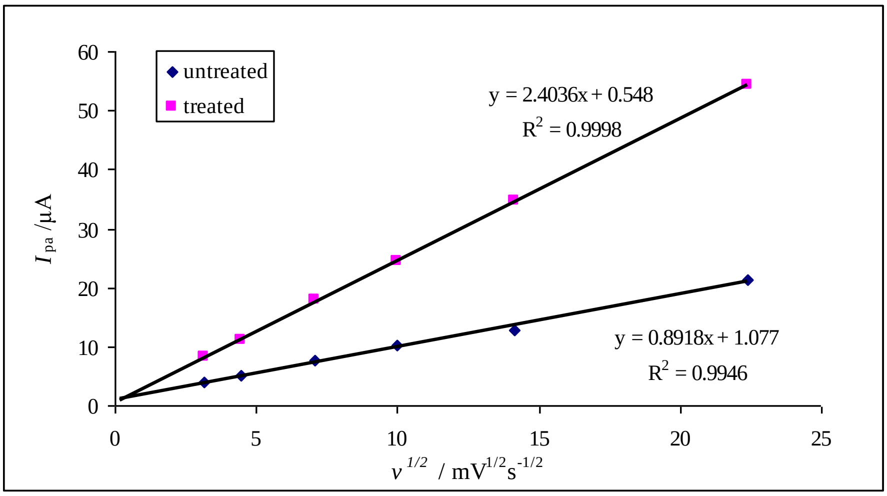

Figure 8. Plot of I_{pa} vs $v^{1/2}$. The sample solution contained 5 mM AA in PBS pH 7.0. The cyclic voltammograms were obtained with the untreated and treated GC electrode at various scan rates.

3.3. Voltammmetry of a mixture of DA and AA at the untreated and treated GC electrode

Remarking the availability of the treatment of the GC electrode by laser pulse irradiation, the determination of DA in the presence of AA was attempted by CV. Figure 9 shows the CVs of the mixture of 1 mM DA and 10 mM AA in PBS pH 7.0. The CV obtained by using the untreated GC only had one peak at potential of 0.52 V. However, CV obtained by using the treated GC gave two well-separated oxidation waves. The CV shows that the oxidation peak of DA was found at 0.23 V with I_{pa} of 2.88 μA and that of AA at 0.01 V with I_{pa} of 25.15 μA, as shown in Table 3. I_{pa} of AA was much higher than that of DA since we used the concentration of AA which is ten times higher than that of DA. The separation between the peaks of DA and AA is enough to determine DA. Well separated peaks were also obtained using DPV technique (not shown), which could be used for sensitive determination of DA in the presence of excess AA.

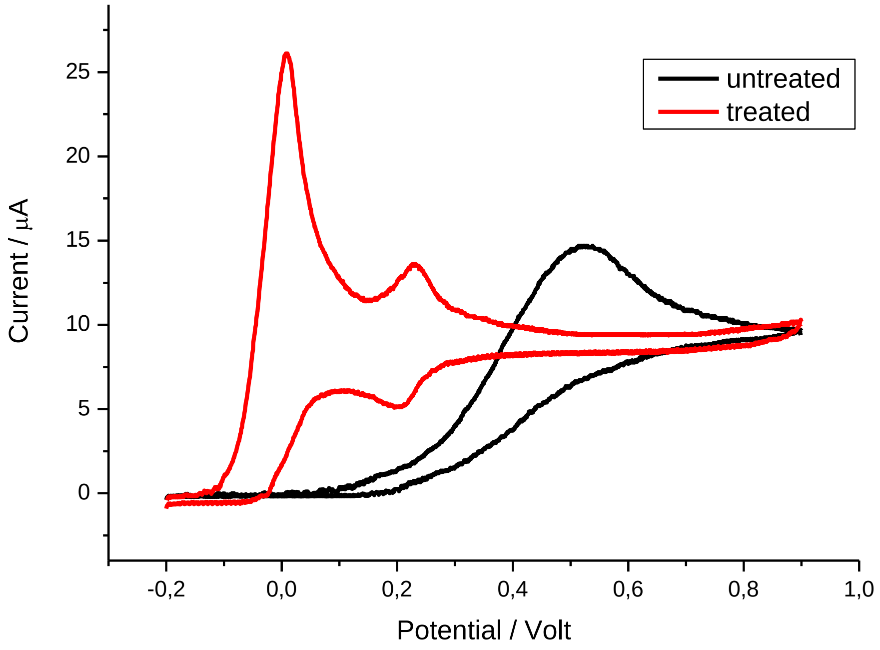

Figure 9. Cyclic voltammograms of DA in the excess of AA. The sample solution contained 1 mM DA and 10 mM AA in PBS pH 7.0. The untreated and treated GC electrodes were used and the scan rate was 20 mVs^{-1}.

Table 3. CV's parameters of a mixture of DA and AA at the untreated and treated GC electrode

Electrode	E_{pa} / V	DA		AA	
		E_{pa} / V	I_{pa} / μA	E_{pa} / V	I_{pa} / μA
Untreated GC	0.52	-	-	-	-
Treated GC	-	0.23	2.88	0.01	25.15

4. CONCLUSION

It had been shown that a GC electrode treated with laser pulse irradiation exhibits an improvement of voltammetric sensitivity of DA and AA, because the irradiation not only increases the electrode surface area but also improve the electrode reactions of DA and AA. Because of the oxidation peak potential shift on the treated irradiated GC electrode, the oxidation waves of DA and AA could be separated well from each other. Based on these results, the determination of DA is possible in the presence of excess AA.

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