Notes

Amperometric Sulfite Sensor Using Electrodecorated Pt Particles onto Aminated Glassy Carbon Electrode Prepared by Stepwise Electrolysis

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Abstract

A novel modified glassy carbon electrode with platinum (Pt)-electrodecorated and nitrogen-containing functional groups was prepared by a stepwise electrolysis. The prepared electrode exhibited an electrocatalytic activity towards sulfite oxidation that was better than that of a bare glassy carbon electrode. The electrocatalytic activity of sulfite oxidation has been applied to an amperometric sulfite sensor. A favorable linear relationship between the current response (ΔI) and the sulfite concentration up to 500 μM was exhibited. The detection limit was estimated to be 3 μM based on the criterion of signal-to-noise (S/N) ratio of 3 under optimized conditions. In regards to the reproducibility, the RSD (n= 10) was 8.9% for 80 μM sulfite.

Keywords Amperometric sensor, sulfite, electrocatalytic oxidation, modified glassy carbon electrode
Introduction

Sulfite is an additive that is widely used in pharmaceutical, beverages, and food so as to prevent oxidation, inhibits bacterial growth, and control enzymatic reaction during production and storage.¹,² Despite these useful advantages, sulfite must be applied in extremely limited amounts due to its potential toxicity and harmful effects on human bodies. Exceeding the consumption limit may lead to headaches, nausea, diarrhea, asthma attacks, stomach irritation, nettle rash, and swelling.³-⁶ Existence of accurate methods for determining sulfite is fundamental for the food industry to ensure product quality. At present, a number of analytical methods for detecting sulfite such as iodimetric titration,⁷ high-performance liquid chromatography,⁸ fluorescence,⁹ chemiluminescence,¹⁰ capillary electrophoresis,¹¹ and electrochemical detection¹²,¹³ have been reported. Unlike these methods, electrochemical detection techniques realize simplicity, sensitivity, reliability, rapid detection, and also inexpensive.

Most researchers paid attention to the use of electrodes made of carbon material such as glassy carbon (GC; type of 2 dimensional shapes) and carbon felt (CF; type of 3 dimensional shapes) electrodes. Two electrodes are useful in the fields of
electrochemical sensing owing to their higher overpotential for oxygen reduction,\textsuperscript{14,15} accessibility, inexpensive, chemical stability, wide potential window,\textsuperscript{16} and large surface area\textsuperscript{17} compared with metal electrodes such as platinum and gold. Nowadays, the chemical modification of carbon surface has attracted great attention in various fields such as electroanalytical chemistry.\textsuperscript{18-22} Electrochemical sulfite detection may be based on direct sulfite reduction on glassy carbon\textsuperscript{23} or after electrode modification.\textsuperscript{24} Otherwise, direct sulfite oxidation may be obtained at platinum,\textsuperscript{25} gold,\textsuperscript{26} glassy carbon,\textsuperscript{27} and platinum-modified glassy carbon.\textsuperscript{28} However, there still are challenges such as problems correlated with fouling of the electrode and high positive potential for oxidation of the sulfite.\textsuperscript{25-27} As a consequence, a number of substances may interfere with the detection and measurement of the analyte.

Due to the above challenges, our group particularly focuses on the development of electrochemical modification on the carbon surface (GC electrode and CF electrode). The nitrogen-containing functional groups can form chains on the surface of GC electrode by the electro-oxidation treatment process using ammonium carbamate in aqueous medium solution at a high positive electrode potential,\textsuperscript{29} we called it aminated...
glassy carbon (AGC) electrode. In particular, it has been revealed by us that nitrogen atoms containing functional groups such as aromatic amine groups like aniline can easily be introduced to the surfaces of the glassy carbon and carbon felt electrodes by the electrode oxidation of ammonium carbamate, and the electron transfer rates of many inorganic and organic compounds are accelerated to be able to measure excellent redox waves. Our previous study reported, redox waves between hydrogen ions and hydrogen molecules (H₂) at a highly positive potential range after a long term electro-reduction of the AGC electrode in a sulfuric acid electrolyte solution. During the electrode reduction of the AGC electrode in sulfuric acid, platinum ion dissolved from platinum wire counter electrode was electrodeposited onto the surface of nitrogen-containing functional groups to which a GC electrode was introduced. We named this electrode Pt-NGC electrode, for which Pt particles are electrodeposited onto GC electrode modified with nitrogen-containing functional groups.

In the present work, a simple and environmental friendly method was used for the preparation of Pt particles electrodeposited on the nitrogen-containing functional groups for a new-type modified electrode (Pt-NGC electrode) by stepwise electrolysis. The
electrocatalytic oxidation of sulfite has been evaluated by cyclic voltammetry (CV) with comparing the Pt-NGC and various electrodes. The Pt-NGC electrode was also used for measurements of sulfite by CV and amperometry under optimized conditions. Moreover, we also evaluated the detection limit of sulfite, reproducibility, and the interference substance in an amperometric sulfite sensor.

**Experimental**

**Reagents and chemicals**

All chemicals used for the study were of analytical reagent grades. Deionized water (Millipore Milli-Q System, Japan) was used to prepare the solutions used in this investigation. Sodium sulfite (Na$_2$SO$_3$), sulfuric acid (H$_2$SO$_4$), dipotassium hydrogen phosphate (K$_2$HPO$_4$), and potassium dihydrogen phosphate (KH$_2$PO$_4$) were purchased from Fujifilm Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Ammonium carbamate was purchased from Merck KGaA (Darmstadt, Germany). The glassy carbon (GC) electrode (diameter of 3 mm) was obtained from BAS Co., Ltd. (Tokyo, Japan).
Preparation of Pt-NGC electrode

In the present work, the GC electrode was polished with 1.0 µm polishing diamond and 0.05 µm polishing alumina on the polishing micro cloth, treated with ultrasonic bath (one minute), and rinsed with deionized water.

A potential controlled electrolysis process was performed with a potentiostat/galvanostat (HA-151B, Hokuto Denko Co., Ltd., Japan). A platinum spiral wire (diameter: 0.5 mm, length: ca. 70 mm) and an Ag/AgCl (3 mol/L NaCl electrolyte) were used as a counter electrode and a reference electrode, respectively. The two step processes for Pt-NGC electrode preparation are described below. First, the GC electrode was processed in an electrode oxidation process with 0.1 mol/L ammonium carbamate aqueous solution at a constant potential of +1.1 V for 60 minutes. Next, the electro-oxidized GC electrode was electro-reduced in 1.0 mol/L sulfuric acid at -1.1 V (vs. Ag/AgCl) for 20 hours. Throughout the electrode reduction of the electro-oxidized GC electrode in sulfuric acid, platinum ion dissolved from platinum wire counter electrode was electrodeposited onto the surface of nitrogen-containing functional groups to which a GC electrode was introduced. All experiments were performed at room temperature.
**Electrochemical measurements**

The voltammetric and amperometric measurements were performed with an automatic polarization system (HZ-3000, Hokuto Denko., Ltd., Japan) with a three-electrode cell consisting of working electrode as a Pt-NGC electrode, a counter electrode as platinum wire, and an Ag/AgCl (3 mol/L NaCl electrolyte) as a reference electrode. During amperometric measurements, N₂ gas was flowed into the electrolyte. The purpose was to block oxygen molecule so that the sulfite could not oxidize to sulfate. Additionally, the Pt-NGC electrode was covered with a dialysis membrane for reducing the diffusion of sulfite from bulk to the Pt-NGC surface. According to this treatment with the dialysis membrane, the background noise current is additionally reduced during amperometric measurement of sulfite due to the reducing of electrolyte diffusion. Supporting electrolyte is 0.1 mol/L phosphate buffer solution (pH 7.0).
Results and Discussion

Electrochemical responses of 3 mM sulfite at various electrodes in 0.1 M phosphate buffer solution (pH 7.0) were evaluated by cyclic voltammetry as shown in Fig. 1. Electrocatalytic oxidation of sulfite on the AGC electrode (Fig. 1(b)) and Pt-NGC electrode (Fig. 1(d)) was seen more clearly in the presence of the sulfite oxidation peak than in the sulfite oxidation performed on bare GC electrode (Fig. 1(a)) was. The nitrogen-containing functional groups, with the AGC electrode, introduced by electrode oxidation in ammonium carbamate aqueous solution function as electron-transfer mediators for sulfite oxidation, which indicates that the AGC electrode had electrocatalytic activity and the oxidation peak potential moved to the negative direction of potential comparing with the bare GC electrode. Next, the significant oxidation peak current of sulfite was observed by using the Pt-NGC electrode. In addition, the oxidation peak potential shifted to the increasingly negative direction of potential comparing with the AGC electrode (Fig. 1(b)) and Pt-electrodeposited glassy carbon (Pt-GC) electrode (Fig. 1(c)). Hence, the Pt-NGC electrode easily promotes the electrode oxidation of sulfite. On the other hand, the above probably exhibits that the
electro-deposited Pt in collaboration with the nitrogen-containing functional groups (such as the primary amine group and other N-containing functional groups) introduced by stepwise electrolysis in ammonium carbamate solution and sulfuric acid act as active sites of the specific electrocatalytic current for sulfite. We previously exhibited that electrocatalytic activity of the Pt-NGC electrode for the electrode oxidation of hydrogen molecule did not decrease after ultrasonication performed for 5 min, which indicates that platinum particles on nitrogen-containing functional groups are securely adsorbed onto the GC surface. Based on the results in Fig. 1, it is understood that the Pt-NGC electrode is superior to the other electrodes in terms of sulfite oxidation.

Fig. 2 showed the comparison of the amperometric response of bare GC electrode (a), AGC electrode (b) and Pt-NGC electrode (c) to successive addition of 100 μM sulfite at an applied potential of +0.6 V. Current response at the Pt-NGC electrode is 4 times greater as that was obtained from the bare GC and AGC electrodes. The response time required to reach 95% of the maximum steady-state current was approximately 20 seconds. This result demonstrates fast current response for sulfite sensing at Pt-NGC electrode. The favorable catalytic sensitivity and rapid response of the Pt-NGC
electrode further demonstrates that the Pt-NGC electrode facilitates more effective electron transfer.

Relationship between the current response ($\Delta I$) and sulfite concentration is shown in Fig. 3. The oxidation current increased sharply up to 5000 $\mu$M in sulfite concentration, and achieved 95% of the maximum steady-state current within ca. 30 seconds. A favorable linear relationship ($R^2=0.9979$) was provided between the $\Delta I$ and the sulfite concentration up to 500 $\mu$M in Fig. 3 (inset). The detection limit was estimated to be 3 $\mu$M based on the criterion of signal-to-noise (S/N) ratio of 3 under optimized conditions. Based on the reproducibility of the 10 successive measurements with 80 $\mu$M of sulfite, the relative standard deviation (RSD) was calculated 8.9%. All these results demonstrated that the current response was suitable with the increase of sulfite concentration.

The selectivity of the Pt-NGC electrode has been investigated by recovery test of sulfite. Fig. 4 shows a typical amperometric response of 200 $\mu$M sulfite prepared by two different sample solutions such as test solution (0.1 M phosphate buffer) (a) and red wine sample (b). Sulfite was added in various sample solutions. Inset is recovery test
results of sulfite from real sample such as red wine. The results show that the favorable recovery of sulfite using the possible each interfering substance in real sample was obtained. In addition, we also have found that other substances such as common metal cations and anions (Na\(^+\), K\(^+\), Cl\(^-\), NO\(_3^-\), HCO\(_3^-\), H\(_2\)PO\(_4^-\), and HPO\(_4^{2-}\)), glucose, fructose, sucrose, oxalate, citric acid, also did not interfere with the determination of sulfite (data not shown). Therefore, the amperometric sulfite sensor based on the Pt-NGC electrode that we propose is a useful analytical technique since it enables simple and rapid determination of the sulfite concentration to be performed easily.

**Conclusions**

In conclusions, a new type modified glassy carbon electrode has been developed on the basis of Pt-electrodecorated on the nitrogen-containing functional groups by stepwise electrolysis. The Pt-NGC electrode exhibited a favorable electrocatalytic activity towards sulfite oxidation compared with the bare GC electrode and the AGC electrode. Electrocatalytic activity of sulfite oxidation has been applied to the amperometric sensor
of sulfite under optimized conditions. A favorable linear relationship was provided between the current response and the sulfite concentration up to 500 µM. The detection limit of sulfite was 3 µM (S/N=3) under the optimal experimental conditions. As for reproducibility, the RSD (n= 10) was 8.9% for 80 µM sulfite. The Pt-NGC electrode also showed high selectivity towards sulfite in the presence of common metal ions and other interfering substance. The good sulfite recovery test results using the possible real sample such as red wine were obtained. The Pt-NGC electrode is promising material for a wide range of applications related to sulfite measurement with high performance as a substitute for metal electrodes.
References

1. A. Isaac, J. Davis, C. Livingstone, A. J. Wain, and R. G. Compton, TrAC, Trends Anal. Chem., 2006, 25, 589.

2. T. Garcia, E. Casero, E. Lorenzo, and F. Pariente, Sens. Actuators, B., 2005, 106, 803.

3. H. Yu, X. Feng, X. Chen, S. Wang, and J. Jin, J. Electroanal. Chem., 2017, 801, 488.

4. H. J. Suh, Y. H. Cho, M. S. Chung, and B. H. Kim, J. Food Compos Anal., 2010, 20, 212.

5. S. S. M. Hassan, M. S. A. Hamza, and A. H. K. Mohamed, Anal. Chim. Acta., 2006, 570, 232.

6. D. H. Allen, Food Technol., 1985, 73, 506.

7. G. Monnier and S. Williams, Analyst, 1972, 95, 119.

8. S. Theisen, R. Hansch, L. Kothe, U. Leist, and R. Galensa, Biosens. Bioelectron, 2010, 26, 175.

9. L.J. Zhang, Z.Y. Wang, X.J. Cao, J.T. Liu, and B.X. Zhao, Sens. Actuators B., 2016, 236, 741.

10. R. Rawal and C. S. Pundir, Int. J. Biol. Macromol., 2012, 51, 449.

11. G. Jankovskiene, Z. Daunoravicius, and A. Padaraukas, J. Chromatogr. A, 2001, 934, 67.

12. L. S. T. Alamo, T. Tangkuaram, and S. Satienperakul, Talanta, 2010, 81, 1793.

13. S. Preecharueangrit, P. Thavarungkul, P. Kanatharana, and A. Numnuam, J.
14. O. Niwa, J. Jia, Y. Sato, D. kato, R. Kurita, K. Maruyama, K. Suzuki, and S. Hirono, JACS, 2006, 128, 7144.

15. A. Negishi, H. Kaneko, and K. Nozaki, DENKI KAGAKU, 1993, 61(12), 1442.

16. E. Frackowiak and F. Begun, Carbon, 2001, 39, 937.

17. N. Kishimoto and N. Matsuda, Environ. Sci. Technol., 2009, 43, 2054.

18. R. W. Murray, “Electroanalytical Chemistry and Interfacial Electrochemistry”, ed. A. J. Bard, 1984, Vol. 13, Marcel Dekker, New York, 191.

19. M. G. Heinemann, B. L. Goncalves, J. R. M. Vicenti, and D. Dias, Anal. Sci., 2019, 35, 1255.

20. J. Dang, H. Cui, X. Li, and J. Zhang, Anal. Sci., 2019, 35, 979.

21. R. Zhao, Y. Wang, Z. Zhang, Y. Hasebe, and D. Tao, Anal. Sci., 2019, 35, 733.

22. T. L. Nguyen, V. H. Cao, T. H. Y. Pham, and T. G. Le, Electroanalysis, 2019, 31, 2538.

23. A. Issac, A. J. Wain, R. G. Compton, C. Livingstone, and J. Davis, Analyst, 2005, 130, 1343.

24. R. H. O. Montes, E. M. Richter, and R. A. A. Munoz, Electrochem. Commun., 2012, 21, 26.

25. E. Gasana, P. Westbroek, E. Temmerman, H. P. Thun, and P. Kiekens, Anal. Chim. Acta, 2003, 486, 73.

26. H. Y. Li and K. Yang, Nucl. Power Eng., 2002, 23, 18.

27. T. Balduf, G. Valentin, and F. Lapicque, Can. J. Chem. Eng., 1998, 76, 790.
28. I. G. Casella and R. Marchese, *Anal. Chim. Acta*, **1995**, *311*, 199.

29. S. Uchiyama, H. Watanabe, H. Yamazaki, A. Kanazawa, H. Hamana, and Y. Okabe, *J. Electrochem. Soc.*, **2007**, *154*, F31.

30. A. Kanazawa, T. Okajima, S. Uchiyama, A. Kawauchi, and T. Osaka, *Langmuir*, **2014**, *30*, 5297.

31. X. Wang, T. Cao, Q Zuo, S. Wu, S. Uchiyama, and H. Matsuura, *Analytical Methods*, **2016**, *8*, 3445.

32. X. Wang, M. Xi, M. Guo, F. Sheng, G. Xiao, S. Wu, S. Uchiyama, and H. Matsuura, *Analyst*, **2016**, *141*, 1077.

33. H. Matsuura, T. Takahashi, S. Sakamoto, and S. Uchiyama, *Anal. Sci.*, **2017**, *33*, 703.
**Figure Captions**

Fig. 1  Cyclic voltammograms of bare GC electrode (blue line; (a)), AGC electrode (green line; (b)), Pt-GC electrode (red line; (c)) and Pt-NGC electrode (black line; (d)) containing 3 mM sulfite in 0.1 M phosphate buffer solution (pH 7.0). Scan rate is 50 mV/s.

Fig. 2. The comparison of the amperometric response of bare GC electrode ((a); blue line), AGC electrode ((b); red line) and Pt-NGC electrode ((c); green line) to successive addition of 100 µM sulfite. Supporting electrolyte: 0.1 M phosphate buffer solution (pH 7.0); the applied potential: +0.6 V; rotating speed: 550 rpm.

Fig. 3 The calibration curve of the current response (ΔI) with the different sulfite concentration. Supporting electrolyte: 0.1 M phosphate buffer solution (pH 7.0); the applied potential: +0.6 V; rotating speed: 550 rpm.

Fig. 4 Amperometric response of 200 µM sulfite in two different sample solutions such as 0.1 M phosphate buffer (pH 7.0) solution (a) and red wine sample (b). Inset is recovery test results of sulfite from real sample such as red wine.
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