A Novel Hydrogen Peroxide Sensor Based on Specifically Interacted Silver Dispersed Sol-gel Derived Ceramic Composite Electrode

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There is an expanding demand for the fabrication of chemical sensors with highly desired analytical capabilities for the analysis of compounds of biomedical and environmental interest. The selection of the sensing material and the immobilization procedure are crucial for adequate sensors with good compatibility and performance. Recently, sol-gel derived composites have become increasingly used for the design of reproducible and robust sensors.¹⁻⁴ Moreover, the use of bi-functional sol-gel precursors would further enhance the compatibility of the sensors with possible control over the orientation and distribution of the mediator.⁴⁻⁶ Such an approach can offer promising prospects in the design of versatile sensing materials. With this idea, a metal dispersed composite electrode was constructed using (3-mercaptopropyl)trimethoxysilane (MPS) and silver. MPS is a bi-functional sol-gel precursor containing a silane and a functional thiol group. The thiol group could be used to derive catalytic sites by specific interactions with the desired catalyst, and the silane group could be used for gelation.⁵⁻⁷ The advantages of metal catalysis^{1,2,8,9} in combination with the attractive features of sol-gel, such as simple preparation, tunable porosity, low-temperature encapsulation, chemical inertness, and mechanical stability, offer great promise in the fabrication of effective electrodes with the desired characteristics. The newly designed electrode showed promising results for the electrocatalytic reduction of hydrogen peroxide (H_2O_2) at a reduced overpotential of -0.05 V with good sensitivity and stability. Most studies on H_2O_2 determination¹⁰⁻¹³ have demonstrated the electrocatalytic oxidation of H_2O_2 at relatively higher potentials, which led to possible interference from electroactive substances, such as ascorbic acid and uric acid. However, the remarkably reduced overpotential observed in the present study for the reduction of H_2O_2 favors a selective and sensitive determination. In addition, the proposed sensor has the advantages of ease of fabrication, rapid response and remarkable stability.

Experimental

MPS was purchased from Sigma (USA). $AgNO_3$, H_2O_2 (30%) and graphite powder were received from Wako Chemicals, Tokyo, Japan. All other chemicals and reagents used were of analytical grade. Ultrapure water ($\rho = 18$ M Ω) was used to

prepare all of the solutions. A 0.05 M phosphate buffer was used to adjust the pH of the electrolyte.

Electrochemical experiments were performed with a Potentiostat/Galvanostat HAB 151 connected to a recorder, and a GPIB HA 503G was interfaced with a personal computer (Hokuto Denko Ltd.). A modified composite electrode was used as the working electrode, while Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrodes, respectively. All measurements were carried out under an atmosphere of high-purity nitrogen.

The modified electrode was fabricated as follows: 2.0 ml of 0.1 M $AgNO_3$ solution was mixed with 1.5 ml of 0.1 M MPS in ethanol and sonicated for nearly 30 min; 2.0 ml of this homogenous gel was well mixed with graphite powder (200 mg) for nearly 20 min, and the mixture was allowed for gelation in a desiccator at room temperature for nearly 30 h. The resulting silver dispersed ceramic-graphite composite (Ag/CGC) was tightly packed into the cavity (3.0 mm inner diameter) of a Teflon tube with a stainless-steel base for contact, and dried in air. The surface of the Ag/CGC electrode was polished with smooth polishing paper and rinsed well in ultra-pure water. A bare composite was prepared in a similar fashion without the addition of $AgNO_3$.

Results and Discussion

When silver nitrate was added to an MPS solution, a curdy-gel mass was obtained due to the complexation of silver with the thiol group of MPS; meanwhile, the silane group initiated gelation by hydrolysis and condensation reactions. Mixing graphite powder with the gel mass resulted in a microporous composite containing dispersed silver. The graphite in the composite ensured the electrical conductivity, the cross-linked silicate network contributed to the rigidity of the composite matrix, and the silver facilitated the electrocatalysis. Figure 1 shows the cyclic voltammograms observed for the reduction of H_2O_2 with the Ag/CGC and a bare composite electrode in a 0.1 M KNO_3 solution at pH 7 adjusted with a 0.05 M phosphate buffer. The Ag/CGC electrode exhibits a redox peak with anodic and cathodic peak potentials of 0.42 and 0.14 V, corresponding to the silver redox reaction (curve c). However, no characteristic reaction was observed (curve a) in the potential range studied for the bare composite (without silver). The redox reaction of the Ag/CGC electrode was stable and reproducible for more than hundred continuous cycles in a 0.1 M KNO_3 solution. Curve b corresponds to the reduction of 8.4

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Fig. 1 Cyclic voltammograms of (a) bare, (b) 8.4×10^{-4} M H_2O_2 at bare, (c) Ag/CGC electrode, (d) 5.2×10^{-5} M, (e) 2.0×10^{-4} M, and (f) 8.4×10^{-4} M H_2O_2 at Ag/CGC electrode, respectively in a 0.1 M KNO_3 solution; pH 7 (0.05 M phosphate buffer); scan rate, 50 mV/s.

$\times 10^{-4}$ M H_2O_2 at the bare electrode. Curves d, e, and f correspond to the reduction of 5.2×10^{-5} M, 2.0×10^{-4} M, and 8.4×10^{-4} M H_2O_2 at the Ag/CGC electrode, respectively. As can be seen, the Ag/CGC electrode showed an enhanced current response for H_2O_2 reduction at a reduced potential of 0.0 V. The presence of silver in the Ag/CGC composite exerted an electrocatalytic effect for the reduction of H_2O_2 , resulting in a sensitive determination at an extremely reduced potential compared to the bare composite. The current response of the Ag/CGC electrode increased with an increase in the concentration of H_2O_2 , and was proportional to the square root of the potential scan rate in the range from 10 to 200 mV/s, indicating that the catalytic reduction of H_2O_2 is a diffusion-controlled process. Thus, the H_2O_2 has to diffuse to the surface of the Ag/CGC electrode for the electrocatalytic reduction to take place. It was observed that in the presence of H_2O_2 , the reduction peaks were shifted to more negative potentials (curves d, e and f), which is possibly due to a matrix effect of the ceramic graphite composite surface for the diffusion of the H_2O_2 to reach silver in the composite surface. However, the exact reason is uncertain at present.

It was observed that the loading of silver in the composite has a marked effect on the sensitivity of the H_2O_2 . The optimum concentrations of the silver, MPS and graphite powders were selected based on the performance of the electrode towards the sensing of H_2O_2 with good sensitivity and stability. Figure 2 shows the effect of the pH on (a) the peak potential and (b) the peak current towards the reduction of 4.0×10^{-5} M H_2O_2 . It was observed from the figure that the peak potential of the Ag/CGC electrode for the reduction of H_2O_2 shifted negatively with an increase in the pH from 2 to 12 (a). The variation of the peak current (b) with the pH showed a good response to H_2O_2 reduction in the pH range between 4 to 9. The poor response at higher pHs may be due to possible hydroxylation of the silver in the composite. Thus, a pH of 7 was maintained in amperometric studies, considering the physiological pH (7.4) condition.

Fig. 2 Effect of the pH on (a) the peak potential and (b) the peak current for the reduction of 4.0×10^{-5} M H_2O_2 at the Ag/CGC electrode; scan rate, 50 mV/s.

The hydrodynamic voltammograms (Fig. 3) registered with the Ag/CGC electrode in a stirred 0.1 M KNO_3 solution containing 5.0×10^{-5} M H_2O_2 showed a sigmoidal curve with the maximum response starting from 0.0 V (curve a). However, with a bare composite electrode, a poor current response was observed (curve b). Thus, a potential of -0.05 V was used in an amperometric determination, considering the sensitivity and selectivity. Such a reduced overpotential avoids interference, favoring the selective determination of H_2O_2 . The addition of equal molar concentrations of commonly interfering species, such as ascorbic acid and uric acid, did not affect the current response for the reduction of 5.0×10^{-4} M H_2O_2 . The absence of any interference effect was attributed to the low detection potential of the present system.

Figure 4 displays the amperometric response of the modified electrode upon the successive addition of 0.24 mM H_2O_2 in 0.1 M KNO_3 at a pH of 7. The sensor responds rapidly (< 5 s) to the concentration changes, and increases linearly with the H_2O_2 concentration in the range from 9.6×10^{-6} to 3.0×10^{-3} M with a correlation coefficient of 0.997. The detection limit was 6.8×10^{-6} M ($S/N = 3$). The relative standard deviation for ten successive determination of 5.0×10^{-5} M H_2O_2 was 2.2%. The electrode-to-electrode reproducibility was 3.2% ($n = 8$). The sensor was stable over a period of two weeks without any significant loss of sensitivity, and 93% of the response was retained for nearly one month. Moreover, it has the advantage of easy surface renewal by simple mechanical polishing of the used surface. The voltammetric characteristics and the response towards H_2O_2 sensing remained constant for repeated polishing, which indicates the remarkable renewal repeatability of the sensor. The excellent stability of the electrode is due to the combined features of the sol-gel composite and a specific interaction of silver with the MPS. The present work is a new advancement in sol-gel sensors; as in most of the sol-gel based

Fig. 3 Hydrodynamic voltammograms for the reduction of 5.0×10^{-5} M H_2O_2 at (a) an Ag/CGC electrode and (b) a bare composite in 0.1 M KNO_3 ; pH 7 (0.05 M phosphate buffer); stirring rate, 300 rpm.

Fig. 4 Current-time response of the Ag/CGC electrode for successive additions of 0.24 mM H_2O_2 to a 0.1 M KNO_3 solution; other conditions as in Fig. 3. Inset, calibration plot.

sensors, the catalysts are simply immobilized into a silicate network, which leads to a possible leakage of the catalysts in some cases. However, in the present system, stable complex formation between silver and MPS led to a remarkable increase in the stability.

In summary, the silver dispersed sol-gel composite electrode

constitutes a simple and attractive approach for the development of promising electrochemical sensors. It has been demonstrated that the MPS provides a good substance for the fabrication of a silver-dispersed composite surface. Furthermore, the favorable combination of a sol-gel composite and silver catalysis provides markedly improved sensitivity, selectivity and reproducibility for H_2O_2 monitoring. Based on the present approach, a variety of new sensing materials can be developed by utilizing different active metal ions, such as copper, platinum and iron, in addition to silver. An evaluation of the systems as a biocompatible composite by immobilizing enzymes within the composite is currently under progress in our laboratory. The versatility and the biocompatibility of the ceramic biocomposite and the specific coordination of silver with MPS favor excellent stability and effective immobilization of the enzyme. Since the potential for H_2O_2 reduction is considerably reduced, the interference from oxygen may be less. In addition, we can also utilize the system as an enzyme electrode based on the electrocatalytic oxidation of enzymatically liberated H_2O_2 .

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References

1. L. Rabinovich and O. Lev, *Electroanalysis*, **2001**, *13*, 265.
2. J. Wang, *Anal. Chim. Acta*, **1999**, *399*, 21.
3. J. Lin and C. W. Brown, *Tr. Anal. Chem.*, **1997**, *16*, 200.
4. M. M. Collinson and A. R. Howells, *Anal. Chem.*, **2000**, *72*, 702A.
5. A. Walcarius, *Electroanalysis*, **2001**, *13*, 701.
6. J. Y. Tseng, M. H. Lin, and L. K. Chau, *Colloids Surf.*, **2001**, *182*, 239.
7. G. Che and C. R. Cabrera, *J. Electroanal. Chem.*, **1996**, *417*, 155.
8. J. Wang and P. V. A. Pamidi, *Anal. Chem.*, **1997**, *69*, 4490.
9. M. C. Rodriguez and G. A. Rivas, *Anal. Lett.*, **2000**, *33*, 2373.
10. K. V. Gobi, K. Tokuda, and T. Ohsaka, *J. Electroanal. Chem.*, **1998**, *444*, 145.
11. J. Pei and X. Li, *Electroanalysis*, **1999**, *11*, 1211.
12. P. Westbroek, E. Temmerman, and P. Kiekens, *Anal. Chim. Acta*, **1999**, *385*, 423.
13. R. Garjonyte and A. Malinauskas, *Sens. Actuators B*, **1999**, *56*, 93.