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Determination of hydrogen peroxide based on a metal dispersed sol-gel derived ceramic-graphite composite electrode

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Abstract A new copper dispersed ceramic-graphite composite electrode was fabricated by the initial mixing of copper nitrate and (3-mercaptopropyl)trimethoxy silane (MPS) followed by stirring with graphite powder. The combination of the metal catalysis and the advantages of the ceramic composite favored the electrocatalytic reduction of hydrogen peroxide (H_2O_2) at a reduced overpotential of -0.2 V with good sensitivity, stability and reproducibility. The sensor showed a good linear response to H_2O_2 in the range from 8.3×10^{-6} M to 2.0×10^{-3} M with a correlation coefficient of 0.9989 and the detection limit was 6.2×10^{-6} M ($S/N = 3$).

Keywords Ceramic composite · Copper dispersion · Sol-gel · Electrocatalysis · Hydrogen peroxide

Introduction

In recent years, sol-gel technology has enjoyed extensive popularity in the fabrication of electrochemical sensors for a wide variety of applications [1, 2]. In particular, sol-gel derived composite electrodes have received wide-spread interest owing to their exciting features such as ease of preparation, low temperature synthesis, tunable porosity, controllable hydrophobicity and mechanical stability [1, 2, 3, 4]. These interesting features were further enhanced by the use of bi-functional sol-gel precursors. The feasibility of the specific interaction of the mediators with the functional sol-gel precursors provides a promising means for the development of new amperometric sensors with the possible control over the distribution and orientation of the catalytic sites. Moreover, due to the specific attachment of the mediators to the functional sol-gel precursor, the leaching of the mediators from the composite was

avoided, leading to improved stability. With this idea, a metal dispersed ceramic-graphite composite electrode was fabricated using copper and (3-mercaptopropyl)trimethoxy silane (MPS). MPS is a bifunctional sol-gel precursor containing SH group, which was utilized for the specific interaction with copper, meanwhile, the silane group of MPS was utilized in deriving the silicate network through sol-gel process [5, 6]. The favorable combination of high catalytic activity of the copper [7, 8, 9, 10, 11] and the advantages of the ceramic composite resulted in a sensor with highly desired properties for the electrochemical reduction of H_2O_2 at a reduced potential with good sensitivity and selectivity. H_2O_2 is a compound of great importance in chemical, biological, environmental and industrial analysis. Despite the number of reports on the determination of H_2O_2 [12, 13, 14], the present sensor has the advantages of high sensitivity, excellent stability and remarkable reproducibility.

Experimental

Reagents and apparatus. MPS was purchased from sigma (USA). $\text{Cu}(\text{NO}_3)_2$, 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 ($\rho = 18 \text{ M}\Omega$) was used to prepare all 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 GPIB HA 503G interfaced with a personal computer (Hokuto Denko Ltd.). The modified composite electrode was used as the working electrode, while Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrode, respectively. All measurements were carried out under an atmosphere of highly pure nitrogen. The XPS measurements were taken with a Physical Electronics ESCA 5600 spectrometer with a monochromatic Al K α x-ray source operated at a power of 400 W.

Fabrication of the modified electrode. The modified electrode was fabricated by the initial mixing of 1.8 ml of 0.1 M $\text{Cu}(\text{NO}_3)_2$ with 1 ml of 0.1 M MPS in ethanol for 20 minutes and then with graphite powder (220 mg) for nearly 20 minutes and the mixture was allowed to gel for nearly 30 hours. The resulting copper dispersed ceramic-graphite composite (Cu/CGC) was packed tightly into the cavity (3.0 mm inner diameter) of a Teflon tube with a

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stainless steel base for contact and dried in air. The surface of the Cu/CGC electrode was polished with a smooth polishing paper and rinsed well in ultra-pure water. A bare composite was prepared in a similar fashion without the addition of $\text{Cu}(\text{NO}_3)_2$.

Results and discussion

When $\text{Cu}(\text{NO}_3)_2$ solution was mixed with MPS, the copper ion will specifically interact with the thiol moiety of the MPS resulting in a curd-like gel mass. Meantime, the silane moiety of the MPS starts gelation by hydrolysis and condensation reactions. Mixing of graphite powder with this gel-mass results in the dispersion of graphite within the silica gel and ensures electrical conductivity. The ceramic composite was very stable and robust and does not require any organic binder because the compactness is ensured by the silicate continuum. The interaction of copper and sulfur was indicated from the XPS data shown in Fig. 1. The peak for copper ($\text{Cu } 2p_{3/2}$) at the binding energy of 932.3 eV and the shift in the binding energy of the sulfur ($\text{S } 2p_{3/2}$) from 163.8 to 162.6 eV indicates the formation of a copper sulfide complex.

The Cu/CGC electrode showed very stable voltammetric peaks corresponding to the copper redox reaction (Fig. 2). The curves (a) and (c) corresponds to bare and Cu/CGC electrode respectively. The Cu/CGC electrode exhibits two cathodic peaks at 0.0 V and -0.25 V corresponds to $\text{Cu}^{2+/+}$ and $\text{Cu}^{+/0}$ reaction, respectively and a single anodic peak at 0.15 V corresponds to $\text{Cu}^{0/2+}$. The redox peaks are well defined at lower scan rates and were highly stable during continuous cycles in 0.1 M KNO_3 solution for more than 100 cycles. The bare composite does not show any characteristic reaction in the potential range studied. The curves d, e and f correspond to the reduction of 3.4×10^{-4} M, 9.0×10^{-4} M and 1.3×10^{-3} M H_2O_2 , respectively at the Cu/CGC electrode. Curve b corresponds to the reduction of 1.3×10^{-3} M H_2O_2 at the bare composite. As

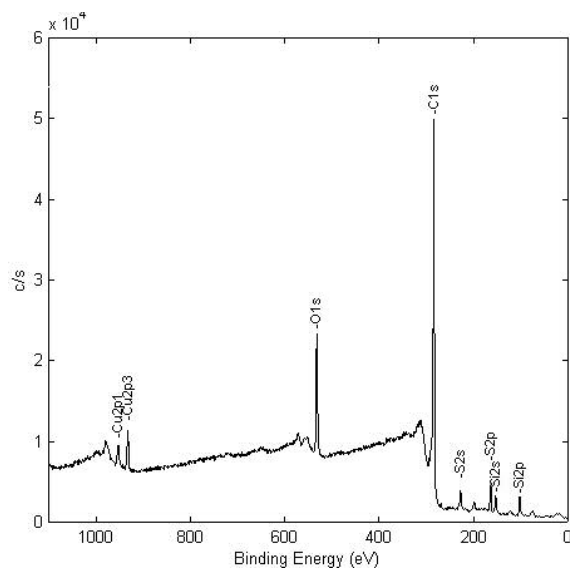


Fig. 1 XPS spectrum of the Cu/CGC electrode surface

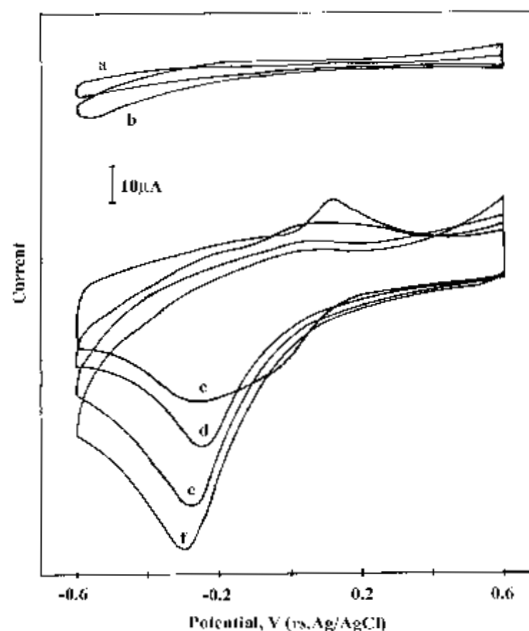
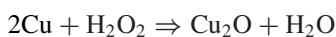


Fig. 2 Cyclic voltammograms of (a) bare composite, (b) 1.3×10^{-3} M H_2O_2 at the bare composite, (c) Cu/CGC composite, (d) 3.4×10^{-4} M, (e) 9.0×10^{-4} M and (f) 1.3×10^{-3} M H_2O_2 at the Cu/CGC electrode respectively; Electrolyte: 0.1 M KNO_3 ; pH 7 (0.05 M phosphate buffer); Scan rate 50 mV/s

can be seen, in the presence of H_2O_2 , no distinct current response was observed at the bare composite electrode, whereas a well-defined reduction peak at a potential of around -0.2 to -0.3 V was observed at the Cu/CGC electrode. Thus the over potential for the reduction of H_2O_2 was significantly reduced at the Cu/CGC electrode with a remarkable current enhancement in comparison to the bare composite. The cathodic current response increase with the increase in the concentration of H_2O_2 with a corresponding decrease in the anodic current and the catalytic current was linear with the square root of the potential scan rate in the range from 10 to 200 mV/s, indicating the diffusion controlled electrocatalytic reaction.

The sensitivity of the electrode towards the H_2O_2 reduction was influenced with the loading of copper in the composite. The optimum concentration of the copper was selected based on the best performance of the electrode towards the H_2O_2 sensing with good stability and sensitivity. Figure 3 shows the effect of pH on the peak current (a) and peak potential (b) for the reduction of 3.0×10^{-4} M H_2O_2 at the Cu/CGC electrode. As can be seen, good current response was observed in the pH range from 3 to 9 with a maximum response from pH 6 to 8 (Fig. 3a). The poor response at higher pHs may be due to the hydroxylation of copper in the composite. The peak potential for the H_2O_2 reduction was also influenced by the pH, which shifts negatively with the increase in pH of the medium (Fig. 3b). Based on the results, the possible mechanism for H_2O_2 reduction at the Cu/CGC electrode may be written as [8]:



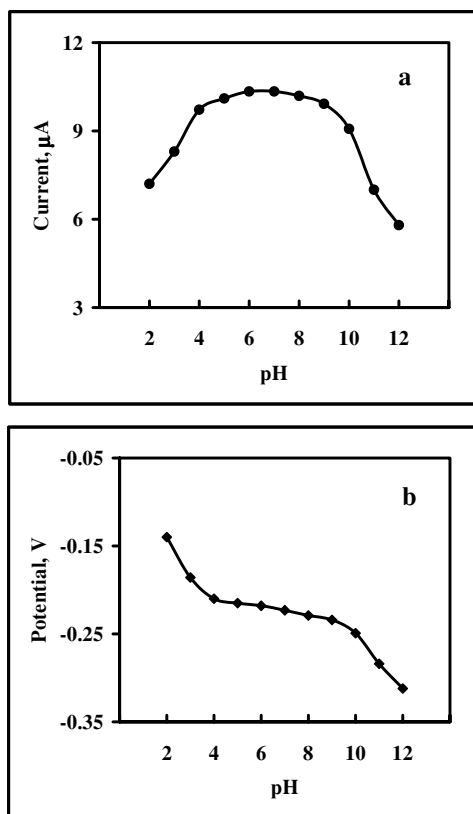


Fig. 3 Effect of pH on **a** peak current and **b** peak potential for the reduction of 3.0×10^{-4} M H_2O_2 at the Cu/CGC electrode in 0.1 M KNO_3 ; Scan rate: 50 mV/s

at the electrode,

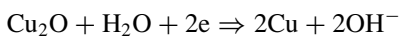


Figure 4 shows the hydrodynamic voltammograms registered by measuring the current response for the reduction of 5.5×10^{-4} M H_2O_2 in a stirring solution of 0.1 M KNO_3 at an interval of 50 mV. The electrocatalytic activity of the Cu/CGC electrode permitted the convenient detection of H_2O_2 at lower potentials with high sensitivity (curve a). In the presence of H_2O_2 , the current response started increasing from 0.2 V, reaching a limiting value at -0.2 V with a sigmoidal shape. In contrast, the bare composite showed the detection of H_2O_2 only at very higher potentials with poor sensitivity (curve b). Thus a potential of -0.2 V was applied during the amperometric studies of the sensitivity and selectivity. The influence of possible interfering substances such as ascorbic acid (AA) and uric acid (UA) on the response of the H_2O_2 reduction was studied. Figure 5 shows the effect considering the addition of 1.0 mM AA and 1.0 mM UA during the amperometric determination of 4×10^{-4} M H_2O_2 with the Cu/CGC electrode at -0.2 V. As can be seen, both AA and UA did not show any significant current response indicating the absence of interference effect from these compounds, this being due to the low detection potential applied in the present system.

The amperometric response of the Cu/CGC electrode at -0.2 V to successive addition of $125 \mu\text{M}$ H_2O_2 is shown

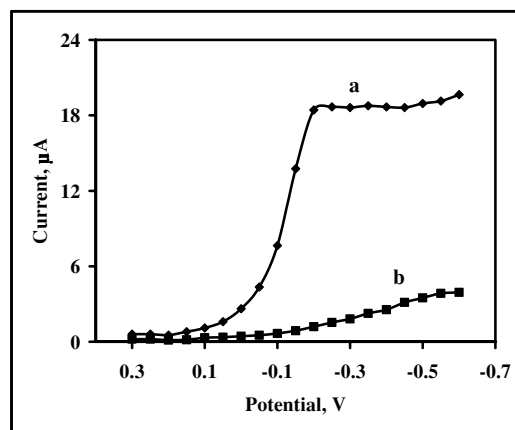


Fig. 4 Hydrodynamic voltammograms for the reduction of 5.5×10^{-4} M H_2O_2 at the (a) Cu/CGC and (b) bare composite electrode in 0.1 M KNO_3 ; pH 7 (0.05 M phosphate buffer); Stirring rate: 300 rpm

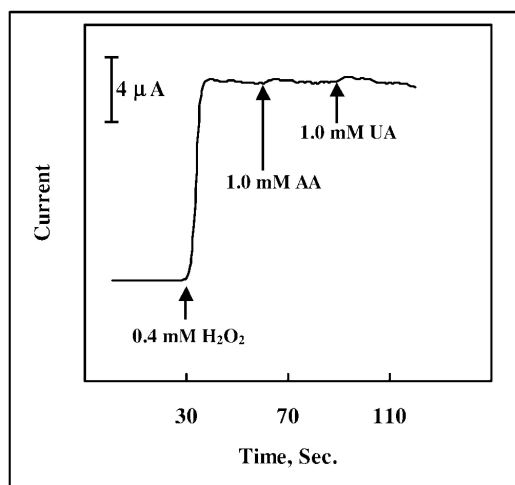


Fig. 5 Interference effect of 1.0 mM ascorbic acid and uric acid on the determination of 4.0×10^{-4} M H_2O_2 with Cu/CGC electrode in 0.1 M KNO_3 ; pH 7 (0.05 M phosphate buffer); Stirring rate: 300 rpm; Potential: -0.2 V

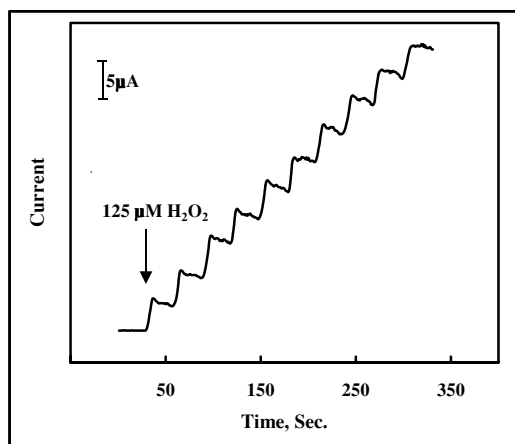


Fig. 6 Amperometric response of the Cu/CGC for the successive additions of $125 \mu\text{M}$ H_2O_2 to 0.1 M KNO_3 ; Other conditions as in Fig. 5

in Fig. 6. The electrode showed rapid response (<6 s) to the concentration changes. Under the selected experimental conditions, a good linear relationship was observed between the peak current and the H_2O_2 concentration over the range of 8.3×10^{-6} M to 2.0×10^{-3} M with a correlation coefficient of 0.9989. The detection limit was 6.2×10^{-6} M (S/N = 3). The precision of the method was evaluated for 10 successive measurements of 1×10^{-4} M H_2O_2 and the related standard deviation (RSD) was found to be 1.90%. The RSD for the electrode-to-electrode reproducibility was 3.4% ($n = 8$). The Cu/CGC electrode retained its initial response for three weeks and 92% of the response was retained for nearly two months. The excellent stability was due to the specific interaction of copper with the MPS as well as the stable nature of the ceramic-composite. The surface renewal was easily achieved by simply polishing the used surface. Five successively regenerated Cu/CGC electrode surface yielded a RSD of 4.2% for the sensing of 3.0×10^{-4} M H_2O_2 , which indicates that the copper is uniformly distributed in the bulk of the composite matrix. It is advisable to regenerate a new surface by polishing after continuously using for 18 to 25 days to retain the good and original response of the sensor.

Conclusion

A new Cu/CGC electrode exhibited highly desirable characteristics for the reduction of H_2O_2 at a reduced overpotential over a broader pH range. The simplicity, sensitivity

and stability of the present sensor suggest the new and promising alternative for H_2O_2 determination. The utility of the proposed system in the fabrication of biocomposites by incorporating enzymes within the composite is currently under investigation.

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References

1. Wang J (1999) *Anal Chim Acta* 399:21–27
2. Lin J, Brown CW (1997) *Trends Anal Chem* 16:200
3. Tsionsky M, Gun G, Glezer V, Lev O (1994) *Anal Chem* 66:1747
4. Wang P, Wang X, Ren C, Zhu G (2000) *J Mater Chem* 10:2863
5. Walcarius A (1998) *Electroanalysis* 10:1217
6. Che G, Cabrera CR (1996) *J. Electroanal Chem* 417:155
7. Rodriguez MC, Rivas GA (2001) *Electroanalysis* 13:1179
8. Somasundrum M, Kirtikara K, Tanticharoen M (1996) *Anal Chim Acta* 319:59
9. Gao Z, Ivaska A, Li P, Lui K, Yang J (1992) *Anal Chim Acta* 259:211
10. Sugiyama K, Aoki K (1989) *J Electroanal Chem* 262:211
11. Toniolo R, Comisso N, Bontempelli G, Schiavon G (1996) *Electroanalysis* 8:151
12. Cai LT, Chen HY (1999) *Sens Actuators B* 55:14
13. Gobi KV, Tokuda K, Ohsaka T (1998) *J Electroanal Chem* 444:145
14. Garjonyte R, Malinauskas A (1998) *Sens Actuators B* 46:236