Amperometric sensing of H$_2$O$_2$ and glucose using wet-chemically deposited MnO$_2$ thin films

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Herein, we report that $\delta$-MnO$_2$ thin films wet-chemically deposited on electro-conductive substrates exhibited good sensing abilities toward hydrogen peroxide and glucose without the assistance of immobilized enzymes, as well as the excellent supercapacitic performance described in our previous paper. High-sensitivity values of 380 mA/(M$\cdot$cm$^2$) ($\text{H}_2\text{O}_2$) and 300 mA/(M$\cdot$cm$^2$) (glucose) were attained with low detection limits of 0.7 $\mu$mol/dm$^3$ ($\text{H}_2\text{O}_2$) and 0.6 $\mu$mol/dm$^3$ (glucose). The good sensitivities and low detection limits were attributed to the large surface area of accumulated MnO$_2$ nanosheets and their firm adhesion to the substrates. The method presented herein can be used for facile film deposition with good controllability and reproducibility.

Key-words : MnO$_2$, Thin films, Sensor, Hydrogen peroxide, Glucose

Determination of hydrogen peroxide (H$_2$O$_2$) and glucose is important in clinical applications as well as in food, pharmaceutical, and environmental analyses. Sensing of H$_2$O$_2$ and glucose is often performed amperometrically using enzyme-mediated sensors that are immobilized with either catalase or glucose oxidase. Although they exhibit high sensitivities, the enzyme-mediated sensors have shortcomings, such as limited operating conditions, short life times, instability, high cost, and frequent maintenance requirements. Recently, new types of amperometric sensors for H$_2$O$_2$ and glucose equipped with MnO$_2$ have been studied. These sensors’ detection mechanism is based on MnO$_2$ catalytic oxidization H$_2$O$_2$ into O$_2$ and protons [Eq. (1)] and oxidation of glucose into gluconolactone [Eq. (2)]. The electrons produced in those reactions are transferred through the MnO$_2$ layer and an electro-conducting substrate to the potentiogalvanostat for amperometric determination of the H$_2$O$_2$ or glucose concentration:

$$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (1)$$

$$\text{C}_6\text{H}_12\text{O}_6 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_10\text{O}_6 + \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2)$$

Although MnO$_2$-based H$_2$O$_2$/glucose sensors have shown high sensitivity and low detection limits, the reported values vary widely from report to report. The most important factor in determining sensing ability is the electrochemically active specific surface area. For this reason, sensors composed of MnO$_2$ with a high specific surface area tend to show higher sensing abilities. Some examples of previously reported sensors include sensors comprising MnO$_2$ nanorods, MnO$_2$ on carbon nanotubes, MnO$_2$ nanosheets, and MnO$_2$ nanowires. These sensors require elaborate processing, however, and they also raise other problems such as high cost.

Another key factor in enhancing sensing ability is a fast electron transfer between the MnO$_2$ layer and the conducting substrate to improve electron collection. The MnO$_2$ layers therefore must be deposited directly onto the electro-conductive substrates without the use of electrically resistive materials, such as organic binders. Techniques that have been used in sensor assembly include mainly electro-deposition or drop-coating of nano-sized MnO$_2$ suspensions followed by drying. In the latter method, the adhesion of MnO$_2$ and the substrates was achieved by mere physical contact. We have previously reported that $\delta$-MnO$_2$ thin films can be deposited onto transparent electrodes (glass slides coated with F-doped tin oxide, FTO glass) using a modified chemical bath technique, which exhibited a high specific capacity (750 F/g at 10 mV/s). This deposition technique is simple, and the adhesion between the MnO$_2$ layer and substrate is quite strong. Wet-chemically deposited $\delta$-MnO$_2$ thin films can therefore be expected to exhibit good chemical sensing capabilities.

The thin films were prepared by the methods described in detail in the literature. Briefly, a solution containing 0.010 mol/dm$^3$ of MnCl$_2$·4H$_2$O, 0.10 mol/dm$^3$ of KBr$_2$, and 0.10 mol/dm$^3$ of ethyltrimethylammonium ammonium chloride was prepared. All reagents were purchased from Kanto Chemical Co., Inc., Tokyo, Japan. A thoroughly cleaned FTO glass slide (2 cm × 3 cm) was immersed in 50 cm$^3$ of the prepared solution. The solution

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was maintained at 323 K for 6 to 14 h. During the period when the solution was kept at 323 K, MnO$_2^{2+}$ ions were slowly oxidized by BrO$_3^-$ to deposit $\delta$-MnO$_2$ on the FTO substrate, as expressed by Eq. (3). As a result, a thin film of $\delta$-MnO$_2$ was deposited on the surface of the FTO slide. Under the experimental condition used in this study, thin films with a thickness ranging from 200 to 500 nm were obtained with good reproducibility. The film thickness was controllable by changing the time and temperature of the MnO$_2$ deposition and by adjusting the ratio of the surface area of the substrate to the volume of the solution:

$$3\text{Mn}^{2+} + \text{BrO}_3^- + 3\text{H}_2\text{O} \rightarrow 3\text{MnO}_2 + \text{Br}^- + 6\text{H}^+.$$  

(3)

The surface morphology of the prepared films was observed by scanning electron microscopy (SEM, e-SEM, Shimadzu Rika Corp., Tokyo, Japan) and their thickness was measured with a surface profilometer (Dektak 3000, Veeco Instruments Inc., NY, U. S. A.). The crystalline phase was determined to be $\delta$-MnO$_2$ via X-ray diffractometry (Mini Flex, Rigaku Corp., Tokyo, Japan, data available elsewhere$^{19}$).

The sensing ability of the thin films with respect to H$_2$O$_2$ was evaluated by potentiostatic amperometry using a three-electrode cell, in which the MnO$_2$ thin film was the working electrode, and Ag/AgCl and a platinum wire were used as the reference and counter electrodes, respectively. The electrolyte comprised 200 cm$^3$ of a 0.1 mol/dm$^3$ phosphate buffer solution at pH 7.2. A constant voltage of $+0.9$ V vs. Ag/AgCl was applied to the working electrode, which was confirmed to be optimal by preliminary experimentation. To the electrolyte solution, 0.100 cm$^3$ of 0.020 mol/dm$^3$ H$_2$O$_2$ solution was added at intervals of 100 s, which increased the H$_2$O$_2$ concentration by 10 $\mu$mol/dm$^3$ every 100 s. Chronoamperograms were drawn by plotting the sensing current as a function of elapsed time, as measured with a potentio/galvanostat (VersaSTAT3, Hokuto Denko Co., Tokyo, Japan).

The sensing ability of the prepared sensors with respect to glucose was evaluated by potentiostatic amperometry using a three-electrode cell, in which the MnO$_2$ thin film was the working electrode, and Ag/AgCl and a platinum wire were used as the reference and counter electrodes, respectively. The electrolyte comprised 200 cm$^3$ of a 0.1 mol/dm$^3$ phosphate buffer solution at pH 7.2. A constant voltage of $+0.9$ V vs. Ag/AgCl was applied to the working electrode, which was confirmed to be optimal by preliminary experimentation. To the electrolyte solution, 0.100 cm$^3$ of 0.020 mol/dm$^3$ glucose solution was added at 100 s, which increased the glucose concentration by 10 $\mu$mol/dm$^3$ every 100 s. Chronoamperograms were drawn by plotting the sensing current as a function of elapsed time, as measured with a potentio/galvanostat (VersaSTAT3, Hokuto Denko Co., Tokyo, Japan).

Figure 1 shows the chronoamperogram in response to the addition of H$_2$O$_2$ measured with an optimized MnO$_2$ thin film, which was 200 nm thick and calcined at 473 K for 1 h. The current increased rapidly upon addition of H$_2$O$_2$ and promptly reached a plateau, suggesting a quick response to changes in the H$_2$O$_2$ concentration. Each increment in current corresponds to 10 $\mu$mol/dm$^3$ of H$_2$O$_2$. The current response to H$_2$O$_2$ was defined as the current averaged over 100 s after the addition of H$_2$O$_2$. From Fig. 1, the sensitivity was calculated to be 380 mA/(M·cm$^2$) with a correlation coefficient (R$^2$) of 0.999. The detection limit was calculated from the standard deviation (σ) of the current perturbation at [H$_2$O$_2$] = 0 multiplied by 3 ($\sigma$/3), moreover, and was determined to be 0.7 $\mu$mol/dm$^3$. The sensitivity of the thin films prepared in this study is higher than those in previous reports of spin-coated or electro-deposited MnO$_2$ films$^{3,7,8,20}$ whose sensitivities ranged from 50 to 270 mA/(M·cm$^2$). We speculate that, since the adherence of the MnO$_2$ layer to the substrate was very strong, Sn–O–Mn bonds likely formed at the interface between the substrate and the MnO$_2$, which probably facilitated electron transfer across the interface, to cause a high current response. Preliminary experiments indicated that the films showed slower responses with smaller increases in current as the thickness increased. Even without calcination at 473 K, the film showed a high sensitivity of 290 mA/(M·cm$^2$), suggesting that calcination may not be essential for sensor fabrication.

Figure 2 shows an SEM image of a prepared MnO$_2$ thin film. The surface morphology is sheet-like, reflecting the layered structure of $\delta$-MnO$_2$.$^{20}$ This surface morphology likely accounts for the high specific surface area, and the corresponding high sensitivity.

Figure 3 shows the chronoamperogram in response to glucose, as measured with optimized MnO$_2$ thin film with a thickness of 500 nm without calcination. Unlike the results obtained for H$_2$O$_2$, the linearity decreased with increases in the glucose concentration and the current increment.
decreased gradually as the glucose concentration rose. A similar analysis of the sensitivity and the detection limit was conducted for MnO2 film in response to glucose. The sensitivity and the detection limit were 300 mA/(M·cm²) [1.80 mA/(mol·dm³)] and 0.6 ¯mol/dm³, respectively.

In contrast to the results for H2O2, a somewhat thicker film exhibited a higher sensitivity toward glucose. Thus, the adsorption/desorption of gluconolactone, the oxidized species of glucose, likely affects the sensing performance of MnO2 thin films. Previous papers have reported sensitivity values ranging from 0.8 to 1.0 mA/(mol·dm³).11),13) The present thin film exhibited better sensitivity, which can be attributed to the surface texture and firm adhesion of the MnO2 layer to the substrate.

In conclusion, we examined the amperometric-sensing ability of wet-chemically prepared MnO2 thin films with respect to H2O2 and glucose. Optimally prepared thin films exhibited high sensitivity values and low detection limits compared to those previously reported. Wet-chemical deposition of the MnO2 thin films likely resulted in the high specific surface area of the MnO2 layer as well as its firm adhesion to the substrate, which in turn contributed to the superior sensing abilities of the prepared films.

References
1) S. Yao, J. Xu, Y. Wang, X. Chen, Y. Xu and S. Hu, Anal. Chim. Acta, 557, 78–84 (2006).
2) B. Xu, M. Ye, Y. Yu and W. Zhang, Anal. Chim. Acta, 674, 20–26 (2010).
3) F. Xiao, Y. Li, X. Zan, K. Liao, R. Xu and H. Duon, Adv. Funct. Mater., 22, 2487–2494 (2012).
4) X. Xiao, Y. Song, H. Liu, M. Xie, H. Hou, L. Wang and Z. Li, J. Mater. Sci., 48, 4843–4850 (2013).
5) M. Nakayama, A. Sato and R. Yamaguchi, Electroanal, 25, 2283–2288 (2013).
6) P. Zhang, D. Guo and Q. Li, Mater. Lett., 125, 202–205 (2014).
7) J. Oberländer, P. Kirchner, H. Boyen and M. J. Schöning, Phys. Status Solidi A, 211, 1372–1376 (2014).
8) Y. Pan, W. Yi, Z. Hou and Y. Liu, J. Sol-Gel Sci. Techn., 76, 341–348 (2015).
9) J. Lee and H. Hong, J. Appl. Electrochem., 45, 1153–1162 (2015).
10) J. Chen, W. Zhang and J. Ye, Electrochem. Commun., 10, 1268–1271 (2008).
11) S. H. Lee, J. Yang, Y. J. Han, M. Cho and Y. Lee, Sensor Actuat. B-Chem., 218, 137–144 (2015).
12) J. Yuan, Y. Cen, X. Kong, S. Wu, C. Liu, R. Yu and X. Chu, ACS Appl. Mater. Interfaces, 7, 10548–10555 (2015).
13) Y. Wang, W. Bai, F. Nie and J. Zheng, Electroanal, 27, 2399–2405 (2015).
14) L. Han, C. Shao, B. Liang and A. Liu, ACS Appl. Mater. Interfaces, 8, 13768–13776 (2016).
15) C. Guo, H. Li, X. Zhang, H. Huo and C. Xu, Sensor Actuat. B-Chem., 206, 407–414 (2015).
16) Y. Wang, S. Zhang, W. Bai and J. Zheng, Talanta, 149, 211–216 (2016).
17) X. Weina, L. Guanlin, W. Chuanshen, C. Hu and X. Wang, Electrochim. Acta, 225, 121–128 (2017).
18) K. Lin, L. Huang and S. Chen, J. Electrochem. Anal, 735, 36–42 (2014).
19) T. Kondo, Y. Matsuhashi, K. Matsuda and H. Unuma, J. Mater. Sci.-Mater. El., 27, 8001–8005 (2016).
20) S. Devaraj and N. Muniechandraiah, J. Phys. Chem. C, 112, 4406–4417 (2008).