Amperometric Sensor Consisting of Gold-Nanoparticle-Dispersed Carbon Fiber Electrodes for Blister Agent Detection

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An amperometric sensor consisting of gold (Au)-nanoparticle-dispersed carbon fiber (Au-NDCF) electrodes was developed for detecting a blister agent, i.e., sulfur mustard (HD) gas. A Au-NDCF electrode was prepared by casting hexane solution containing gold nanoparticles onto a carbon fiber substrate. Field-emission scanning electron microscopy (FE-SEM) images showed that the Au particles were highly dispersed on the carbon fiber substrate. The diameter of the Au particles varied between 2 and 10 nm. By using the Au-NDCF electrode, no significant response was observed even with the introduction of atmospheric species, such as NO, NO_2, SO_2, O_3, NH_3 and CO, into the environment. The Au-NDCF electrode exhibited a relatively high sensitivity to HD, and the signal-to-noise (S/N) ratio of the proposed sensor depended on the amount of Au nanoparticles on the carbon fiber and the potential applied to the Au-NDCF electrode. Thus, the resulting electrode could be used for HD ($1–20$ mg/m^3) detection without the error caused by atmospheric interferences. An HD detection limit ($S/N = 3$) of 1.5 mg/m^3 was obtained, which is the required concentration for an on-site HD monitoring system.

1. Introduction

Chemical warfare agents (CWAs) are extremely toxic to the human body and can be classified into blister agents, nerve agents, choking agents, blood agents, vomit agents, tear gases, and incapacitating agents.[1,2] They are utilized to injure or incapacitate an enemy in warfare and related military operations. CWAs have been intermittently used in both warfare and acts of terrorism, such as the recent Japanese subway attacks.[3] In

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crisis and the consequent management of terrorism using CWAs, the on-site monitoring of CWAs is necessary to protect against terrorism and also minimize terrorism damage.

Commercially available chemical detection devices, such as the ion mobility spectrometry (IMS) system, that are widely used as portable systems for CWA measurement with high sensitivity are very costly[4–6] since IMS generally requires a highly radioactive Ni-63 source. To date, a simple and inexpensive on-site monitoring of CWAs remains to be developed. Therefore, it is essential to develop other simple and highly sensitive methods of CWA detection for use in scenes of terrorist attacks.

Electrochemical sensing techniques can realize very simple and inexpensive systems compared with other sensing methods. Therefore, these techniques can be used more widely than other detection methods, such as the use of transducers in commercially available chemical sensors.[7] In an amperometric sensing system, the analyte is oxidized or reduced at the electrode, and the resulting current can be directly measured. For this reason, the amperometric sensing system has been used in detecting various gases.[8–10] However, a new approach based on amperometric sensing techniques is necessary to improve the sensitivity and detection limit.

Highly dispersed nanoscale metal particles have been attracting increasing interest because of their unique physical and chemical properties and also their high potential for wide applications.[11–17] Gold or platinum nanoparticles are widely used for electrochemical detection since they have high electrocatalytic activity and good stability compared with other bulk materials.[18] Hence, numerous works have dealt with the use of gold or platinum nanoparticles in electroanalysis.[19–24] However, very few studies have focused on the electrochemical detection of CWAs using these nanoparticles.[25,26]

In this work, we report the preparation of a gold-nanoparticle-dispersed carbon fiber (Au-NDCF) electrode to develop an amperometric gas sensor for detecting a blister agent, i.e., sulfur mustard. We characterized the Au-NDCF electrode using field-emission scanning electron microscopy (FE-SEM). The electrochemical properties of the 9.5 µg Au-NDCF electrode were studied to evaluate it as an amperometric sensor for sulfur mustard detection. Sulfur mustard, commonly known as mustard gas, is an alkylating agent capable of causing short- and long-term morbidities upon skin contact. Since it has a mustardlike odor, it was called sulfur mustard or mustard gas.

2.   Experimental Procedure

2.1   *Materials*

Sulfuric acid (H_2SO_4; Kokusan Chemical Co., Ltd., Tokyo, Japan) was used as received. A carbon fiber substrate was obtained from Tsukuba Materials Information Laboratory Ltd. (Tsukuba, Japan). A porous expanded PTFE (denoted as e-PTFE; thickness, 0.2 mm) membrane was purchased from Sumitomo Electric Co., Ltd. (Osaka, Japan). Sulfur mustard (2,2'-dichlorodiethylsulfide) gas (HD) was synthesized at the National Research Institute of Police Science (NRIPS) under special license. Ozone gas was prepared using an ozone generator (model ED-OG-L1, Eco Design, Inc., Saitama, Japan). The concentration of ozone gas produced was confirmed using an ozone monitor (model 450, Advanced Pollution Instrumentation, Inc., San Diego, CA). The

other standard gases (NO, NO$_2$, SO$_2$, NH$_3$ and CO) used were of analytical grade (Taiyo Nippon Sanso Co., Ltd., Tokyo, Japan).

2.2   *Preparation of nanoscale gold particles and gold nanoparticle-dispersed carbon fiber electrodes*

Nanoscale gold particles capped with a decanethiolate monolayer shell (DT-Au) in hexane were synthesized by Schiffrin's two-phase synthesis protocol.[27]

Gold-nanoparticle-dispersed carbon fiber (Au-NDCF) electrodes were prepared as follows. A carbon fiber surface was treated with a plasma etching system (model FA-1, SAMCO, Japan). A 150-µL aliquot of gold nanoparticles in hexane was cast onto the carbon fiber, followed by natural evaporation at room temperature. To remove the decanethiolate monolayer encapsulate from the gold nanoparticles, the carbon fiber modified with DT-Au nanoparticles was heated at 300°C for 2 h.

2.3   *Apparatus*

The diameter of the gold nanoparticles was determined by FE-SEM (JSM-7600F, JEOL, Ltd., Tokyo, Japan). We used an acceleration voltage of 2.0 kV for the FE-SEM.

All electrochemical measurements were performed with a potentiostat (model 1112; Husou Electrochemical System, Kanagawa, Japan). The response of the gas sensor was recorded with a digital recorder (GR-3500, KEYENCE, Tokyo, Japan). A typical schematic diagram of the gas sensor is shown in Fig. 1. An amperometric sensor was constructed as a conventional three-electrode cell system with 3 ml of 9 mol/dm^3 H$_2$SO$_4$ aqueous solution. The Au-NDCF working electrode (WE) was attached to a porous e-PTFE membrane. The diameter of the working electrode was 28 mm for the sensors. The reference electrode (RE) and counter electrode (CE) in the sensor were gold-black-
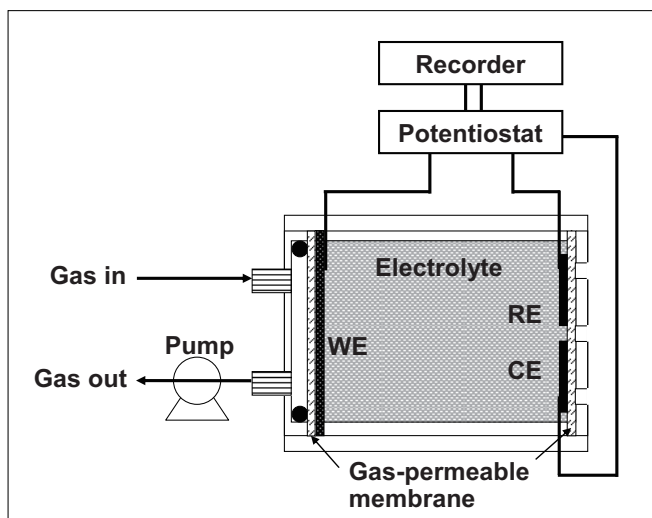

Fig. 1.   Schematic diagram of amperometric sensor and gas sensing system.

screen-printed on a porous e-PTFE membrane. The reference and counter electrodes were those generally used by Riken Keiki Co., Ltd. (Tokyo, Japan) as sensors of toxic gases, such as SiH_4 and SO_2. The flow rate of the sample gases was 0.3 dm^3/min. All potentials were reported versus the gold-black-screen-printed reference electrode at room temperature. For amperometric measurement to detect HD by the Au-NDCF electrode, the electrode potential was set at 0.2 V. The electrode potential of the reference electrode in the sensor was estimated to be 0.75 V against a Ag/AgCl (saturated KCl) electrode.

3.   Results and Discussion

3.1   *Electrode structure*

   Figure 2 shows a FE-SEM image of the Au-NDCF electrode. The light spots correspond to Au nanoparticles. The Au particles are highly dispersed on the carbon fiber. The size of the Au particles varies between 2 and 10 nm. Moreover, about 80% of the Au particles are in the diameter range from 4 to 7 nm in this photograph. The average diameter of the Au particles ($n = 180$) is 5.6 nm.

3.2   *Effect of amount of gold nanoparticles on carbon electrode*

   To achieve HD detection with a high signal-to-noise (S/N) ratio, we investigated the effect of the amount of gold nanoparticles on the carbon electrode. Figure 3 shows the relationship between the amount of gold nanoparticles on the carbon electrode and the S/N ratio for the detection of 48 mg/m^3 HD. The S/N ratio increased with increasing amount of gold nanoparticles from 2.4 to 9.5 µg. This indicates that the oxidation current of HD (HD signal) increased with the amount of gold nanoparticles on the carbon electrode. On the other hand, the S/N ratio decreased sharply when the amount of gold nanoparticles was higher than 9.5 µg. With such an amount of gold nanoparticles, the baseline drift also increased. That is, the oxidation current of HD and the baseline drift increased simultaneously, which resulted in a low S/N ratio. The optimum S/N ratio
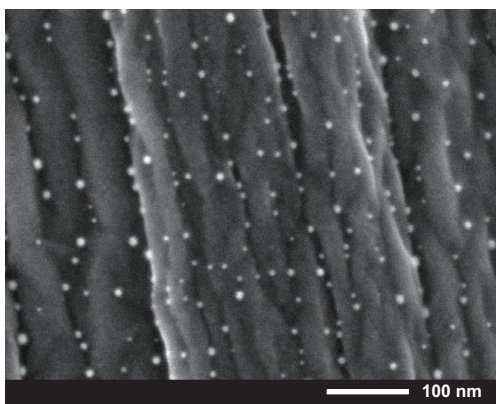

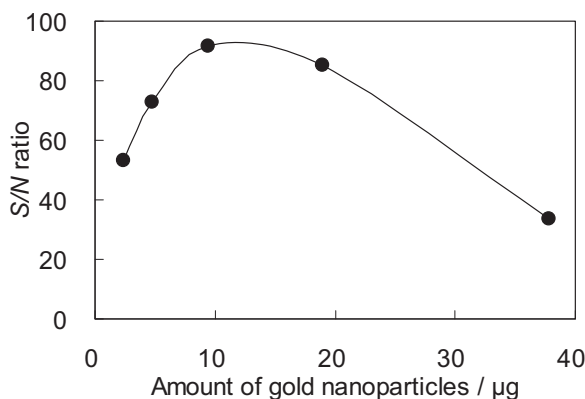Fig. 2.   FE-SEM image of Au-NDCF electrode.

Fig. 3.   Effect of modified amount of gold nanoparticles on *S/N* ratio of carbon electrode.

was achieved at 9.5 µg of gold nanoparticles. Therefore, this amount was used in the following measurements owing to the possible realization of the lowest detection limit for HD.

3.3   *Sensing performance*

Our preliminary examination showed that we chose the electrode potential of 0.2 V as the optimum condition of the HD detection due to the high *S/N* ratio. A typical current response curve of the sensor for 10 mg/m³ of HD is shown in Fig. 4. Residual current with air flowing through the sensor was measured. When HD was introduced into the sensor, oxidation current increased immediately. The electrode reaction of HD by this sensor type has been expected as eq. (1).

$$(CH_2CH_2Cl)_2S + H_2O \rightarrow (CH_2CH_2Cl)_2S{=}O + 2H^+ + 2e^- \tag{1}$$

Oxidation current showed a maximum of ca. 0.9 µA after 50 s, which then decreased gradually. The initial residual oxidation current was recovered after nearly 10 min, when air was introduced again into the sensor. This current profile was mainly explained by the change in HD concentration. It takes approximately 20 s to reach 80% of the maximum oxidation current for the response under these experimental conditions. In the case of a bare carbon electrode, no response for HD was obtained. These results suggest the high electrocatalytic activity of the gold nanoparticles on the carbon electrode.

Figure 5 shows a calibration curve for HD on the Au-NDCF electrode obtained using an amperometric measurement. The sensor current in Fig. 5 was estimated from the maximum value of the current profile. The sensor response current was proportional to HD concentration in the range from 1 to 20 mg/m³ with a good correlation coefficient of 0.998. The detection limit (*S/N* = 3) calculated from Fig. 4 is 1.5 mg/m³. The obtained detection limit is equivalent to the required concentration of 1.5 mg/m³ for HD detection using an on-site monitoring system.[28] The relative standard deviation of three measurements of 10 mg/m³ HD was 2.1%.
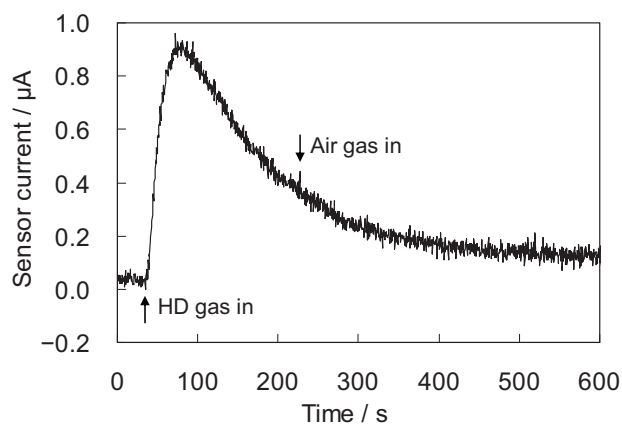
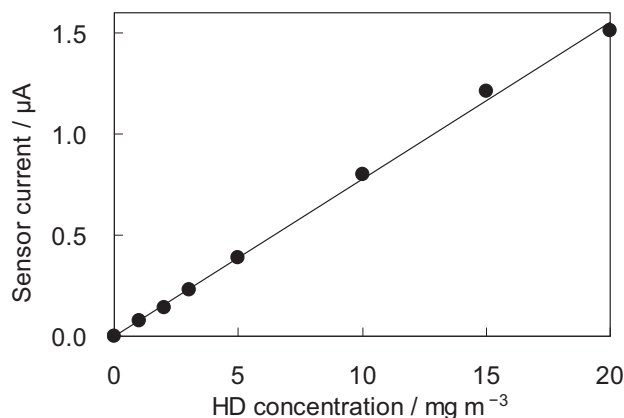Fig. 4.   Typical current response obtained by amperometric sensor with Au-NDCF electrode. [HD] = 10 mg/m³.

Fig. 5.   Calibration curve for HD on Au-NDCF electrode in amperometric measurement.

The interference currents (ΔI) for our sensor from other gases expected to coexist in the environment are shown in Table 1. The current sensitivity (J) is calculated using eq. (2), where Cg is the volume concentration of the measured gas in ppm. Selectivity (S) is obtained using eq. (3) as the ratio of the sensitivity of each gas to that against HD, where J(HD) is the sensitivity for HD.

$$J = \Delta I / Cg \qquad\qquad (2)$$

$$S = J/J(\text{HD}) \qquad\qquad (3)$$

The concentration of the test gas used is higher than that of each gas in the atmosphere. No significant response was observed by introducing atmospheric species, such as NO,

Table 1
Sensor currents (ΔI), sensitivities (J) and selectivities (S) for proposed sensor.

Gas	Concentration/ppm	$\Delta I/\mu A$	$J/\mu A\ ppm^{-1}$	S
mustard (HD)	1.4^*	7.8×10^{-1}	5.6×10^{-1}	1.0
NO	10	3.3×10^{-3}	3.3×10^{-4}	5.9×10^{-4}
NO_2	1.0	1.2×10^{-2}	1.2×10^{-3}	2.1×10^{-3}
SO_2	1.0	3.2×10^{-2}	3.2×10^{-2}	5.7×10^{-2}
O_3	0.21	1.3×10^{-2}	6.2×10^{-2}	1.1×10^{-1}
NH_3	20	5.0×10^{-3}	2.5×10^{-4}	4.5×10^{-4}
CO	1.0×10^{2}	1.0×10^{-2}	1.0×10^{-4}	1.8×10^{-4}

*HD concentration: 1.4 ppm $\cong 10$ mg/m^3

NO_2, SO_2, O_3, NH_3 and CO, into the environment. This indicates that the selectivity of our sensor is high against environmental interferences owing to the good electrocatalytic property of the nanoscale gold particles on the carbon electrode. From these results, our proposed sensor is promising for HD detection in practical applications.

4.   Conclusions

We have developed an on-site amperometric HD gas sensor consisting of Au-NDCF electrodes. The electrodes could be used for HD (1–20 mg/m^3) detection without error caused by atmospheric interferences. A detection limit ($S/N = 3$) of 1.5 mg/m^3 can be obtained for HD, which is the required concentration for an on-site HD monitoring system. The proposed sensor is applicable to the rapid, highly sensitive, selective and accurate detection of HD. The Au-NDCF electrode proved to be suitable for detecting trace levels of CWAs.

Acknowledgement

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