Preparation of WO$_3$ nanoplatelet-based microspheres and their NO$_2$ gas-sensing properties

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Microspheres consisting of WO$_3$ nanoplatelets were prepared by a simple polyol process using tungsten chloride, poly(vinylpyrrolidone) (PVP), and ethylene glycol. The microsphere sizes could be easily controlled by the appropriate adjustment of the molecular weight of the added PVP from 3500 to 1300000. The microspheres prepared by using PVP with a molecular weight of 1300000 had average diameters of about 877 nm and consisted of nanoplatelets that were ~500 nm long by 30 nm wide. The gas-sensing properties of the WO$_3$ microspheres were investigated by exposure to 50 ppb to 1 ppm NO$_2$. The sensor element constructed with microspheres composed of the PVP with a molecular weight of 1300000 showed a higher sensor response to NO$_2$ gas than the others, because the nanoplatelets had smaller particle sizes and larger specific surface areas.

Key-words : Chemical synthesis, Tungsten oxide, Microsphere, NO$_2$, Gas sensor

1. Introduction

Effective and inexpensive systems for the detection and quantification of environmentally hazardous gases are required for the protection of human health. NO$_2$, in particular, is highly neurotoxic as well as damaging to respiratory organs. Its threshold exposure limit, which is defined as the maximum concentration of a chemical allowable for repeated exposure without producing adverse health effects, is regulated by the American Conference of Governmental Industrial Hygienists.¹ Thus, high-response detection is desirable for air quality monitoring. Standard air pollution measurements are still based on time-consuming and expensive analytical techniques such as optical spectroscopy and gas chromatography.²⁻⁵ Gas sensors have been considered as promising candidates for the measurement of environmental pollution levels because of their low cost, high sensitivity, fast responses, and direct electronic interfaces.

Among the metal oxide semiconductors, n-type semiconductors (specifically those based on WO$_3$, which exhibit high sensitivity) hold great promise for use in the detection of NO$_2$.⁶⁻⁸ Although the semiconductor-based gas sensors can be classified into two types, based on thick/thin films or nanoparticles, the latter are considered as more promising for gas-sensing applications due to their large specific surface areas.⁹ Therefore, the sizes and morphologies of the nanoparticles are considered to influence the gas-sensing properties. Recently, Z. Liu et al. reported the assembly of tungsten oxide nanorods into microspheres by a hydrothermal process, and the resultant microsphere-based gas sensor showed good NO$_2$ gas-sensing properties due to its three-dimensional pore network.¹⁰ Our research group previously reported that monodispersed nanoparticles of the hybrid material cerium oxide/poly(vinylpyrrolidone) (PVP) could be prepared by a simple polyol method.¹¹,¹² The nanoparticles have core–shell type structures (cerium oxide cores with PVP shells) and are easily dispersed in water or organic solvent due to the PVP-coated particle structure around the cerium oxide. The size of the nanoparticles could be easily controlled by changing the molecular weight of the PVP: the nanoparticle size decreased with increasing PVP molecular weight.¹² In a semiconductor oxide-based gas sensor, the gas-sensing layer is usually prepared by dispersing a paste, slurry, or ink containing the semiconductor oxide particles. The core–shell type nanoparticle-based gas-sensing layer is considered to have an effective three-dimensional pore network without the agglomeration seen in the semiconductor oxide pastes.

In the present work, WO$_3$ microspheres consisting of nanoplatelet assemblies were prepared by a polyol method, varying the molecular weight of the added PVP in order to obtain small WO$_3$ nanoparticles. The NO$_2$ gas-sensing properties of sensor elements that used these WO$_3$ nanoparticles were also examined.

2. Experimental procedure

Tungsten(VI) chloride (3.0 g, Wako Pure Chemical Industries, Ltd.) and PVP (3.5 g, with average molecular weights of 3500, 10000, 55000, 360000, and 1300000, Sigma-Aldrich), were dissolved in ethylene glycol (70 mL, Wako). Then, 1 M HNO$_3$ (10 mL) was added. The solution was stirred and heated under reflux at 190°C for 1 h, yielding a mixture of dispersed particles. The particles were recovered from the unreacted starting material and excess PVP using centrifugation at 18000 rpm, followed by washing with ethanol and drying at 90°C.

X-ray diffraction analysis (XRD) was performed to identify the crystalline phase of the samples. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out at a heating rate of 10°C/min under air. The morphologies of the samples were observed by field emission scanning electron microscope (FE-SEM). The average size and standard deviation of the microspheres were assessed through the SEM images.

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Each sample was mixed with an ethyl cellulose-type organic vehicle (10 wt% ethyl cellulose and 90 wt% terpineol) to obtain a paste suitable for air dispensing. The weight ratios of the particles and the organic vehicle were 1:16. The paste was dispensed on a surface-oxidized Si substrate, consisting of 2.5 × 4 mm² platinum interdigital electrodes with a line and space definition of 15 μm each. The substrate was annealed at 400°C for 2 h in air to obtain the sensor elements.

To investigate NO₂ gas-sensing properties, a sensor element was placed into a test chamber heated to 200°C in an electrical tube furnace. Air was introduced into the chamber for 15 min, and then, a mixture of NO₂ in air was injected for 15 min at a flow rate of 200 mL/min. The mixed gas flow was then halted and replaced by air injected at a flow rate of 200 mL/min. The concentration of NO₂ was controlled at values of 0, 0.05, 0.1, 0.5, and 1 ppm in air. The resistance between the electrodes of the element in various gaseous atmospheres was measured by the two-probe method with a K2700 digital multimeter (Keithley) at 10 s intervals. We defined the sensor response value (S) in accord with the equation: 

\[ S = \frac{R_g}{R_a} \]

where \( R_g \) denotes the resistance of the sensor element after NO₂ gas exposure for 15 min and \( R_a \) denotes the resistance in air.

3. Results and discussion

3.1 Characterization of nanoparticles

When the tungsten chloride and PVP were mixed in ethylene glycol, the viscosity of the colorless, transparent solution increased with the increasing molecular weight of the PVP. This occurs because, as the PVP molecular weight increases in a solution, a larger force is needed to propel the PVP, and the solution viscosity becomes higher. When the ethylene glycol solutions of tungsten chloride and PVP were heated at 190°C for 1 h, the solutions became yellow-green and turbid, and yellow-green particles were obtained after washing. In our preliminary experiment, when an ethylene glycol solution of tungsten chloride without PVP was heated at 190°C for 1 h, no change in the solution was observed and no particles were obtained. Since the solution without PVP was unsaturated, no precipitation of particles from the solution was expected.

Figure 1 shows the SEM images of the particles prepared by heating at 190°C for 1 h with various molecular weights of PVP: 3,500, 10,000, 55,000, 360,000, and 1,300,000. For the reaction that used the lowest molecular weight PVP, bulky blockish particles that were several tens of micrometers in size and consisted of 30-nm-wide platelets, were observed in the SEM image. In the SEM photos of the particles prepared using higher molecular weight PVPs (10,000, 55,000, 360,000, and 1,300,000), no bulky blocks could be seen; instead, microspheres with uniform sizes consisting of nanoplatelets were observed. Figure 2 shows the relationship between the PVP molecular weight and average microsphere size. The size of the particles obtained using the PVP with a molecular weight of 3,500 was omitted, because these particles were not microspheres. The average microsphere size and standard deviation decreased with the increasing molecular weight of the PVP. The average microsphere size with the PVP with a molecular weight of 1,300,000 was estimated to be 877 nm. The average microsphere sizes prepared by using PVP with molecular weights from 10,000 to 1,300,000 were 877–2,137 nm, and were smaller than those in earlier reports.10),13)

Figure 3 shows the XRD patterns of particles prepared by heating at 190°C for 1 h with the highest molecular weight PVP before and after annealing at 200, 300, 400, and 500°C for 2 h. Although the peaks in Figs. 3(a) and 3(b) did not match well
with any cards of the Joint Committee on Powder Diffraction Standards (JCPDS), we suspect that the unknown peaks are due to tungsten-containing compounds. It was reported that WO₃·0.33H₂O or WO₃·xH₂O particles were precipitated by a hydrothermal process: WO₃ easily forms a layered structure with interlayered water. Since ethylene glycol was used in our polyol process, particles were expected to form layered structures with ethylene glycol. The broad peaks at 2θ = 22°–26° and 32°–36° observed in Fig. 3(c) gradually separated and increased in intensity with the annealing temperature. The peaks in Figs. 3(c) to 3(e) matched well with monoclinic WO₃ (JCPDS card no. 43-1035), indicating that the particles were completely converted to monoclinic WO₃ after annealing at 300 to 500°C for 2 h. No difference among the XRD patterns of particles obtained using PVP molecular weights of 3500, 10000, 55000, 360000, and 1300000 was confirmed.

Figure 4 shows the DTA-TG curves of particles prepared by heating at 190°C for 1 h with a PVP molecular weight of 1300000. The peaks in Figs. 3(c) to 3(e) matched well with monoclinic WO₃ (JCPDS card no. 43-1035), indicating that the particles were completely converted to monoclinic WO₃ after annealing at 300 to 500°C for 2 h. No difference among the XRD patterns of particles obtained using PVP molecular weight of 3500, 10000, 55000, 360000, and 1300000 was confirmed.

Figure 6 shows SEM images of the sensor element surfaces prepared from particles with PVP molecular weights of 3500, 55000, and 1300000. Although the edges of the platelet particles are slightly rounded by annealing at 400°C, the platelets on the microsphere surfaces can be clearly seen. These microstructures are very helpful in the formation of the porous sensing layer. The thickness of WO₃ films prepared from particles with PVP molecular weights of 3500, 55000, and 1300000 was in the range of 7–10µm. In the case of particles with a PVP molecular weight of 3500, the sensor element surface was rough because the particles before annealing were large, bulky, and blockish.

Figure 7 shows the responses of the sensor elements that used particles with PVP molecular weights of 3500, 55000, and
exposed sensor element reached the saturation within 60 min for air exposure and the sensor element showed a good repeatability of NO2 gas sensing. The sensor responses toward NO2 exposure for the samples prepared using PVPs of molecular weights 3500, 55000, and 1300000 were estimated to be 24.1, 30.8, and 68.9, respectively. No difference on the thickness and crystallinity of the WO3 films among particles with PVP molecular weights of 3500, 55000, and 1300000 was shown. The sensor element containing the highest molecular weight PVP-based particles showed a relatively higher sensor response to NO2 than the others because the nanoplatelets had smaller particle sizes and the particles had larger specific surface areas. These sensor responses are much larger than that of the sensor element comprising commercial WO3 particles, measured under the same conditions (S = 19.2 for 1 ppm NO2 exposure at 200°C) or that of a sensor element with WO3·H2O-based microspheres (S ≈ 30 for 1 ppm NO2 exposure at 200°C).7) Since the obtained particles consist of nanoplatelets, the specific surface areas of the samples are expected to be larger than those of commercial WO3 or WO3·H2O-based microspheres. These results suggest that the sensing layer of the sensor element employing these particles has an effective microstructure for NO2 gas sensing. However, Choi et al. reported that a sensor element using lamellar WO3 particles showed a high response of about 130 for 1 ppm NO2 exposure at 200°C.8) Although the responses of our obtained particles are not sufficiently large at this stage, we expect that they can be improved after optimizing the microsphere and nanoplatelet sizes by varying the synthesis conditions (temperature, time, and PVP concentration).

4. Conclusions

In this paper, microspheres consisting of tungsten oxide nanoplatelets were prepared by a simple polyol process. We succeeded in controlling the microsphere size by changing the molecular weight of the PVP. When the microspheres were annealed at temperatures higher than 300°C, the tungsten-containing compound was converted to monoclinic WO3 while preserving the nanoplatelet-based microsphere morphology. The NO2 gas-sensing properties of sensor elements prepared with the various microstructures based on PVP molecular weights were investigated by exposure to NO2 (50 ppb to 1 ppm in air). The sensor element containing the molecular weight 1300000 PVP exhibited a higher sensor response to NO2 than the others because the nanoplatelets had smaller particle sizes and larger specific surface areas. In future, we plan to prepare smaller microspheres of tungsten oxide with a very narrow size distribution, to fabricate NO2 gas sensors with high sensor responses.

References

1) American Conference of Governmental Industrial Hygienists. Available online: http://www.acgih.org (accessed on 22 August 2013).
2) J. Saito, K. Inoue, A. Sugawara, M. Yoshikawa, K. Watanabe, T. Ishida, Y. Ohtsuka and M. Munakata, J. Allergy Clin. Immunol., 114, 512–516 (2004).
3) J. A. Giannovario, R. L. Grob and P. W. Rulon, J. Chromatogr. A, 121, 285–294 (1976).
4) M. Akiyama, J. Tamaki, N. Miura and N. Yamazoe, Chem. Lett., 20, 1611–1614 (1991).
5) J. Tamaki, T. Hashihin, Y. Uno, D. V. Dao and S. Sugiyama, Sens. Actuators, B, 132, 234–238 (2008).
6) C. Zhang, M. Debluyay, A. Boudiba, H. Liao and C. Coddet, Sens. Actuators, B, 144, 280–288 (2010).
7) T. Akamatsu, T. Itoh, N. Izu and W. Shin, Sensors, 13, 12467–
12481 (2013).
8) Y. G. Choi, G. Sakai, K. Shimane, Y. Teraoka, N. Miura and N. Yamazoe, *Sens. Actuators, B*, 93, 486–494 (2003).
9) J. Tamaki, C. Xu, N. Miura and N. Yamazoe, *Sens. Actuators, B*, 3, 147–155 (1991).
10) Z. Liu, M. Miyauchi, T. Yamazaki and Y. Shen, *Sens. Actuators, B*, 140, 514–519 (2009).
11) N. Izu, T. Itoh, M. Nishibori, W. Shin and I. Matsubara, *J. Ceram. Soc. Japan*, 117, 773–776 (2009).
12) N. Izu, I. Matsubara, T. Itoh, W. Shin and M. Nishibori, *Bull. Chem. Soc. Jpn.*, 81, 761–766 (2008).
13) J. Huang, X. Xu, C. Gu, G. Fu, W. Wang and J. Liu, *Mater. Res. Bull.*, 47, 3224–3232 (2012).
14) T. Itoh, N. Izu, I. Matsubara, W. Shin and M. Nishibori, *Chem. Lett.*, 37, 1116–1117 (2008).