Gas sensor using noble metal-loaded TiO₂ nanotubes for detection of large-sized volatile organic compounds

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Detection of volatile organic compounds (VOCs) has attracted considerable attention for indoor air quality and human breath analysis. Here, resistive-type gas sensors with porous films made of Au-loaded TiO₂ nanotubes were developed for the detection of large-sized VOCs. Well-dispersed Au nanoparticles (10 to 20 nm) were photo-chemically deposited on TiO₂ nanotubes (80 nm in diameter, 700 nm in length) prepared by a hydrothermal method. The device using the Au-loaded TiO₂ nanotubes showed improved sensor responses to ethanol and toluene (50 ppm) in air at 500°C. This suggested that Au nanoparticles deposited on the surface of TiO₂ nanotubes without aggregation. We also demonstrated that the device could be used for the detection of large-sized VOC molecule, i.e., 2,6-diisopropylphenol (propofol), an intravenously administered hypnotic drug for induction and maintenance of anesthesia. The Au-loaded TiO₂ nanotubes would offer a way to continuously monitor a change in the concentration of VOCs in exhaled air for medical diagnostics.

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1. Introduction

Extensive efforts have been devoted to the development of compact and cheap sensors that can continuously detect volatile organic compounds (VOCs).^{1)–8)} VOCs are the primary sources of indoor air pollution and cause detrimental effects on human health, and as such their detection and removal are quite important for indoor air quality. In addition, VOCs are of special concern as air pollutants that generate ozone or smog via photochemical reactions with nitrogen oxides.

VOC detection has also received considerable attention for human breath analysis. It is known that human breath contains a wide variety of compounds, including VOCs such as ethanol and acetone.^{9)–12)} Their concentrations are related to person's health conditions, and some of VOCs can potentially be utilized as breath markers for specific diseases.^{13)–16)} Thus far, several types of VOC sensors have been reported for breath analysis.^{17)–20)}

Recently, we have developed VOC sensors using porous films composed of TiO₂ nanotubes prepared by a hydrothermal method.^{21),22)} The TiO₂ nanotubular films showed high sensitivity to VOCs such as toluene and ethanol in low parts per million (ppm) concentrations at 450–550°C. We found that controlling the microstructure of TiO₂ films was important for an improvement in the sensor response to large-sized gas molecules. However, further improvement in the sensor performance is still required for practical applications.

In this study, we tried to further improve the performance of TiO₂ nanotube sensors by loading noble metal. Loading noble metal on the semiconducting oxide materials has widely been applied for improvement in the sensitivity of gas sensors such as those based on SnO₂,^{23)–25)} ZnO,^{26)–28)} WO₃,^{29)–31)} In₂O₃,^{32)–34)} and TiO₂.^{35)–37)} Here, we used Au as a promoting additive for TiO₂ nanotubes because Au loading on TiO₂ nanoparticles was found to be effective for upgrading their sensitivity to CO.³⁸⁾ Effects of noble metal loading on the gas sensing properties to ethanol and toluene were investigated. We also examined the applicability of Au-loaded TiO₂ nanotube sensors for human breath analysis, and selected propofol (2,6-diisopropylphenol) as a target compound. Propofol, which has a phenolic structure (**Fig. 1**), is intravenously administered hypnotic agent used for

Fig. 1. Chemical structure of propofol (2,6-diisopropylphenol).

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induction and maintenance of anesthesia. The analysis of propofol in breath has attracted attention, because the determination of propofol concentrations in exhaled breath makes it possible to monitor the depth of anesthesia.^{39)–42)}

2. Experimental

A TiO₂ commercial powder (P-25, Degussa) was hydrothermally treated with a NaOH solution (10 mol/L) at 230°C for 24 h in a Teflon-lined autoclave. After the treatment, the TiO₂ powder was washed with an HCl solution (0.2 mol/L) under ultrasonic irradiation for 1 h. Then, the obtained products were carefully washed with deionized (D.I.) water to remove Cl[−] ions, filtered, and dried to recover TiO₂ nanotubes. The resulting nanotubes were calcined at 600°C for 1 h, and then subjected to a ball-milling treatment using a planet-type ball-mill for 3 h.

Gold nanoparticles were deposited on TiO₂ nanotubes by a photochemical method in a manner reported elsewhere.⁴³⁾ The prepared nanotubes (1.0 g) were dispersed in D.I. water (100 mL) containing ethanol (10 mL), and then a designated amount of HAuCl₄ (0.5–2.0 wt %) was added in the suspension. Ethanol was used as an electron donor. UV light with 250 W was irradiated to the suspension for 3 h under stirring. The obtained Au-loaded TiO₂ nanotubes were washed with D.I. water, filtered, and dried to recover Au-loaded TiO₂ nanotubes, which were then calcined at 600°C for 1 h. Transmission electron microscopy (TEM) was used to observe the morphology of deposited Au particles. The loading amount of Au was tuned by changing the concentration of [AuCl₄][−] in a precursor solution and determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Sensing films were deposited on an alumina substrate (9 × 13 × 0.38 mm) by a screen-printing method. Au-loaded nanotubes were dispersed in α -terpineol (95 mass %) with ethyl cellulose (5 mass %). The obtained paste was screen-printed on an alumina substrate, in which a pair of Au electrodes (line width: 180 μ m, distance between lines: 90 μ m, sensing layer area: 64 mm²) was formed by screen printing using a commercial Au paste. The deposited sensing films were calcined at 600°C for 1 h. Their thickness was ca. 30 μ m. A schematic structure of the devices was depicted in Fig. 2.

The gas sensing properties of the films were measured in a gas-flow apparatus equipped with an electric furnace, as shown in

Fig. 3. Sample air gases containing ethanol or toluene in the ppm level were prepared by diluting standard sample gases with synthetic air. Sample gases containing propofol in air were prepared by a diffusion method using a standard gas generator (Permeator PD-1B, GASTEC). The concentration of propofol was determined by a method using a combustion catalyst and a CO₂ sensor, as reported elsewhere.⁸⁾ The total flow rate of sample gases was set to 100 mL/min using mass flow controllers. The sensing measurements were performed at 450–550°C. The sensor response was defined as $R_{\text{air}}/R_{\text{gas}}$, where R_{air} and R_{gas} are the electric resistances in air and in a test gas, respectively.

3. Results and discussion

3.1 Materials characterization

Particle size, morphology, and dispersion state of Au particles loaded on TiO₂ nanotubes were observed by TEM, as shown in Fig. 4, which confirmed their tubular structure even after calcination at 600°C. The wall thickness was estimated to be 8–10 nm, and the diameter was approximately 80 nm. The TEM images clearly indicated the presence of Au nanoparticles on TiO₂ nanotubes. An average particle size was ca. 10–20 nm for Au loading at 0.25 and 0.42 wt %, but the size increased to 20–50 nm at 0.92 wt %. Increasing the Au loading amount led to an increase in the particle size. The ICP-AES analysis revealed that about half of Au ions dissolved in a precursor solution were photo-reduced and deposited on TiO₂ nanotubes. This suggests that Au ions were not rapidly reduced on TiO₂ nanotubes through photocatalytic processes under the present conditions. It is known that Au or Pt works an electron-acceptant sink because of their

Fig. 2. Schematic structure of a sensor device.

Fig. 3. Experimental setup for measuring the sensing properties of devices. Sample gases containing propofol were prepared by a gas generator using a liquid sample. The concentration of propofol was determined using a CO₂ sensor after decomposition of propofol at the chamber where a combustion catalyst (Pt/Al₂O₃) was placed.

Fig. 4. TEM images of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %. Deposited Au nanoparticles are noted using white circles in the images.

Fig. 5. Electric resistances in air as a function of operating temperature for the thick films composed of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %.

large work function. Thus, photo-generated electrons in TiO₂ nanotubes can efficiently move to pre-deposited Au nuclei, and then react with [AuCl₄]⁻. Such a preferential photocatalytic reaction occurring over pre-deposited Au rather than over neat TiO₂ nanotubes is responsible for the observed increase in the size of Au nanoparticles in the case when the concentration of [AuCl₄]⁻ is higher in a precursor solution. This idea is supported by the reported results for Pd/TiO₂⁴⁴⁾ and Ag/TiO₂.⁴⁵⁾ Nevertheless, the TEM analysis revealed that highly-dispersed Au nanoparticles were formed on TiO₂ nanotubes by utilizing their photocatalytic activities.

3.2 Electrical resistances

Figure 5 shows the electrical resistances in air for the fabricated devices as a function of temperature ranging from 450 to 550°C. The electric resistance of all devices was decreased with increasing the operating temperature, following the typical behavior of semiconductors. The resistances of Au-loaded TiO₂

nanotubes were higher than that of neat TiO₂ nanotubes and increased with increasing the loading amount, indicating the presence of electronic interaction between Au and TiO₂. Such an increase in the electrical resistance by noble metal loading has frequently been reported for various systems.^{46)–48)} As discussed above, when Au contacts to TiO₂, the Fermi level of TiO₂ shifts to correspond to the work function of Au. Therefore Au attracts electrons from TiO₂, which would produce electron depletion layers on the surface of nanotubes, thus increasing their electrical resistance. The results confirm that Au nanoparticles were effectively loaded on TiO₂ nanotubes to induce intimate contacts between Au nanoparticles and nanotubes, as observed in TEM images. Although Au electrodes were used, its electronic interaction is small. Tamaki reported that the electronic interaction of Au electrode to metal oxide, if Au electrode of narrow gap in several ten nm was used, may become remarkable.⁴⁹⁾ But, in this study, Au electrode with large line distance (90 μm) was used, it is fitting that the electronic interaction between Au particles and TiO₂ particles is considered. Therefore the electrons, which transfer to the surface of TiO₂ particles through grain boundaries, are greatly influenced by the electronic interaction between Au particle and TiO₂. In addition, the morphology among the sensing films was compared. It was confirmed that the morphology of Au-loaded TiO₂ is almost same as that of non-loaded TiO₂, but the electric resistance of Au-loaded TiO₂ is higher than that of non-loaded TiO₂.⁵⁰⁾ From these results, it is assumed that the increase in the electric resistance is caused by the electronic interaction between Au particles and TiO₂. However, in comparison with other oxides such as SnO₂ and ZnO, the electric resistance of TiO₂ nanotubes is rather high, reaching 10⁹ Ω at lower temperatures. Thus the optimal operating temperature is judged to be higher than 500°C from a practical point of view.

3.3 Sensor responses to ethanol and toluene

Ethanol and toluene were used as probe gases to examine the VOC sensing properties of Au-loaded TiO₂ nanotubes. Figures 6 and 7 show sensor responses ($R_{\text{air}}/R_{\text{gas}}$) of the fabricated devices

Fig. 6. Sensor responses to ethanol (50 ppm) at 450–550°C for the thick films composed of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %.

Fig. 7. Sensor responses to toluene (50 ppm) at 450–550°C for the thick films composed of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %.

to ethanol (50 ppm) and toluene (50 ppm), respectively, at 450–550°C. High sensor responses were observed for the devices loaded with Au nanoparticles. However, increasing the operating temperature led to a decrease in the sensor response, and particularly at 550°C the sensor responses were almost the same as those for the device without Au loading. Enhanced catalytic activity of the sensing films at higher temperatures likely hindered the access of VOCs throughout the films because of their accelerated decomposition at the surface, thereby decreasing the sensor responses. Note that the device showed higher sensor responses to toluene than ethanol. It has been reported that toluene with an aromatic structure is less combustible than ethanol.^{51)–53)} This could facilitate the diffusion of toluene inside the sensing films. Also, we investigated the sensor responses to H₂ (500 ppm), ethanol (50 ppm), and toluene (50 ppm) gases at 500°C. H₂ ($S = 52$), ethanol ($S = 42$) and toluene ($S = 84$) gases may be regarded as having unobvious cross-sensitivity effects with H₂.

The sensor devices with different Au loading amounts showed similar sensor responses to VOCs, although the sensor responses were slightly increased by increasing the loading amount. As revealed by TEM observations, Au nanoparticles were well-dispersed on TiO₂ nanotubes, although the particle size of Au slightly increased with increasing the loading amounts. Such increase of particle size seems to depend on the preparation method. As mentioned above, it is supposed that the preferential photocatalytic reaction occurs over pre-deposited Au rather

Fig. 8. Dynamic transients of sensor resistances in response to propofol with different concentrations (30, 55, 70, and 95 ppm) at 500°C for the thick films composed of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %.

than over neat TiO₂ nanotubes. In Fig. 5, the electric resistance increased with increasing the loading amounts. This reason is guessed to be due to the difference of Au particle size. However the well-dispersion of Au particles was observed for each loading amount. It has been well accepted that highly-dispersed Au nanoparticles on metal oxides such as TiO₂ and CeO₂ show high catalytic activities for the combustion of CO^{54)–56)} and VOCs.^{57),58)} Thus, the successful deposition of well-dispersed Au nanoparticles is one of the reasons for the improved sensor response. However, we revealed that the loading of Pt nanoparticles with the same loading amounts decreased the sensor response to VOCs. This suggests that a significant improvement in the catalytic activity of the sensing films facilitated the combustion of VOCs at the surface and impeded the diffusion deep inside the films. Thus, an appropriately improved catalytic activity of the sensing films as a consequence of Au loading may account for the performance improvement.

3.4 Detection of propofol

As shown above, the Au loading significantly improved the sensor response to toluene. We next examine the applicability of Au-loaded TiO₂ nanotubes for the detection of propofol, a drug compound having an aromatic structure. The operating temperature of the device was set to 500°C to balance the electrical resistance and sensor response.

Figure 8 shows dynamic transients of resistances in response to propofol with different concentrations at 500°C for the devices with and without Au loading. Upon introduction of propofol, the resistance of the devices decreased rapidly, showing a typical behavior of resistive sensors based on n-type semiconductors. The decrease in the resistance was resulted from the reaction of surface adsorbed oxygen with propofol. The devices also showed good recovery behaviors; the resistances almost recovered to the original values upon switching the gas atmosphere from sample gases to air. This suggests that the desorption of propofol or the release of CO₂ resulting from its combustion is high enough for oxygen to re-adsorb onto TiO₂ nanotubes. The high temperature operation at 500°C likely avoided the carbon accumulation after propofol decomposition in the sensing film.

Figure 9 shows the dependence of the sensor response on propofol concentration (30–95 ppm) at 500°C. Au-loaded TiO₂ nanotubes showed much higher sensor responses than neat TiO₂

Fig. 9. Dependence of sensor responses on propofol concentration (30, 55, 70, and 95 ppm) at 500°C for the thick films composed of (a) TiO₂ nanotubes, (b) loaded with Au at 0.25 wt %, (c) 0.42 wt %, and (d) 0.92 wt %.

nanotubes in the propofol concentration range studied. The sensor responses were rather linear to the concentration of propofol. Particularly at higher concentrations, high sensor responses exceeding $S = 100$ (100 times change in resistance) were observed. Such a high sensitivity indicates the feasibility of Au-loaded TiO₂ nanotubes for on-line detection of propofol in exhaled air, although it is required to examine the sensing properties such as detection limit, selectivity, and stability under humid conditions in more detail. The porous nature of the films based on TiO₂ nanotubes enabled the easy access of large propofol molecules throughout the films. Furthermore, homogeneously distributed Au nanoparticles in the films possibly assisted in the reaction of propofol with adsorbed oxygen, thereby causing high sensor responses. Therefore the obtained results indicate the importance of the microstructure control of sensing layers in terms of grain size control, utility factor of sensing layer, and the receptor effect for optimization of sensing layers makes it possible to parts per billion (ppb) concentrations about 80 ppb.

4. Conclusion

Au nanoparticles (0.25–0.92 wt %) were deposited on TiO₂ nanotubes by a photochemical method in order to improve their sensing performance for the detection of VOCs. TEM analysis revealed that Au nanoparticles of 10 to 20 nm were homogeneously deposited on TiO₂ nanotubes without aggregation. The devices using Au-loaded TiO₂ nanotubes showed higher sensor responses to toluene and ethanol at low ppm concentrations than the device using neat TiO₂ nanotubes. The devices also showed high sensor responses to propofol, a hypnotic drug for anesthesia, with low ppm concentrations, indicating a promising applicability of the device for human breath analysis. Successful deposition of highly-dispersed Au nanoparticles in porous films made of TiO₂ nanoparticles is suggested to be critical to the observed high sensor responses to large-sized VOC molecules.

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