

**NO₂ Sensing Properties of Porous In₂O₃-based Powders Prepared by Utilizing
Ultrasonic-spray Pyrolysis Employing PMMA Microsphere Templates
: Effects of the Size of the PMMA Microspheres on their Gas-sensing Properties**

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PMMA microspheres were synthesized in distilled water by ultrasonic-assisted emulsion polymerization. The average particle size of PMMA microspheres was dependent markedly on the kind of surfactant used. Porous (pr-) In₂O₃ powders were prepared by ultrasonic-spray pyrolysis of In(NO₃)₃ aqueous solution containing the PMMA microspheres synthesized. The NO₂ response of pr-In₂O₃ was much larger than that of conventional In₂O₃ powder prepared by the similar technique employing PMMA-free In(NO₃)₃ aqueous solution. The introduction of controlled macroporous structure into the powder of the sensor material was found to be effective for improving NO₂ response properties.

Introduction

As nitrogen oxide (NO₂) is one of the most harmful gases to the human body and also a cause of air pollution, highly sensitive and selective NO₂ sensors at low cost, small size and good reliability are indispensable for the detection to low concentration of NO₂ in the atmosphere. Therefore, numerous efforts have been directed to optimizing the microstructural morphology of various gas-sensing materials with different sizes of well-developed pores to improve their gas-sensing properties, because optimization of the size and the amount of pores in the gas sensor materials are effective in controlling gas reactivity (1-6). We also have prepared mesoporous and macroporous oxides by utilizing the assembly of surfactant (several nanometers in size) and commercial polymethylmethacrylate (PMMA) microspheres (≥ 150 nm in size) as a template, respectively (7-13). However, we have not yet established a preparation method to prepare gas-sensing materials having well-developed middle-sized pores with a diameter of several nm~150 nm. Such technique is absolutely essential for optimizing the microstructural morphology of various gas-sensing materials. In this study, we have attempted to synthesize smaller PMMA microspheres with controlled particle size (several nm~150 nm in diameter) by microwave-assisted emulsion polymerization employing different surfactants. In addition, porous (pr-) In₂O₃ powders were prepared by ultrasonic-spray pyrolysis employing the synthesized PMMA microspheres, and their NO₂-sensing properties have been investigated.

Experimental

Synthesis of PMMA microsphere dispersion by ultrasonic-assisted emulsion polymerization

PMMA microspheres were synthesized in deionized water (100 cm³) by ultrasonic (19.5 kHz)-assisted emulsion polymerization (50 min) employing methylmethacrylate monomer (8 g) as a polymer source, ammonium persulfate (0.3 g) as an initiator and a surfactant (0.1 g) and subsequent stirring (400 rpm) at 60°C for 6 h. The surfactant used was sodium lauryl sulfate (SLS, CH₃(CH₂)₁₁OSO₃Na), Triton X-100 (Triton, (C₂H₄O)₁₀C₁₄H₂₂O) or P123 (EO₂₀PO₇₀EO₂₀, EO: polyethylene oxide, PO: polypropylene oxide). The PMMA microspheres in the resultant dispersions were denoted as PMMA(M) (M: surfactant employed for the synthesis of PMMA microspheres (SLS, Triton or P123)).

Preparation of porous In₂O₃-based powders by utilizing ultrasonic-spray pyrolysis employing PMMA microspheres

The PMMA microsphere dispersion (37.5 cm³) was mixed with 0.05 mol dm⁻³ In(NO₃)₃ aqueous solution (62.5 cm³) to make a precursor solution. After the precursor solution was set in a plastic container, the mist of the precursor solution was generated by ultrasonic irradiation (2.4 MHz) and then it was fed to an electric furnace at 1100°C under air flowing (1.5 dm³ min⁻¹) by using a feeding system as shown in Fig. 1 and then was directly heat-treated in the furnace. The pr-In₂O₃ powder obtained was denoted as pr-In₂O₃(M). Conventional In₂O₃ powder (c-In₂O₃) was also prepared by the similar technique employing PMMA-free precursor solution.

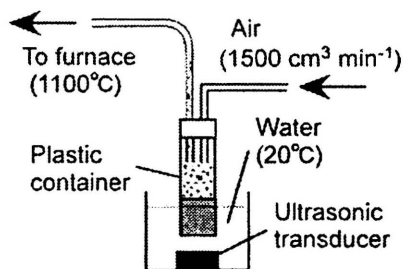


Figure 1. Schematic drawing of a feeding system of mist of precursor solution atomized by ultrasonication (2.4 MHz).

Characterization of PMMA microspheres and In₂O₃ powders

The particle size distribution of the PMMA microspheres obtained was measured by dynamic light scattering (DLS, Malvern Instrument Ltd., HPPS). The microstructure of PMMA microspheres and In₂O₃ powders was observed with scanning electron microscope (SEM: JEOL Ltd., JSM-7500F). The specific surface area (SSA) and pore size distribution of pr-In₂O₃(M) and c-In₂O₃ powders were measured by the Brunauer-Emmett-Teller (BET) and Barret-Johner-Halenda (BJH) methods, respectively, using a N₂ adsorption isotherm (Micromeritics Instrument Corp., Tristar3000).

Gas response measurement

Thick film sensors were fabricated by screen printing employing the paste of each In_2O_3 powder prepared with organic lacquer (Goo Chemical Co., Ltd., OS-4530) on an alumina substrate equipped with a pair of interdigitated Pt electrodes and subsequent heat-treatment at 550°C for 5 h. Gas response properties of these sensors were measured to 10 ppm NO_2 in air at $150\text{--}500^\circ\text{C}$. The magnitude of NO_2 response was defined as the ratio (R_g/R_a) of sensor resistance after 10 min exposure to NO_2 balanced with air (R_g) to that in air (R_a).

Results and discussions

Figures 2 and 3 show particle size distributions and SEM photographs of all PMMA microspheres synthesized by the microwave-assisted emulsion polymerization, respectively. The average particle size of PMMA microspheres was dependent markedly on the kind of the surfactant used. The particle size distribution of PMMA(SLS) was narrow, and the mean particle size of PMMA(SLS) was ca. 55.5 nm. As shown in SEM photographs, the particles of PMMA(SLS) are relatively uniform and the size was slightly smaller than that estimated by the DLS (Fig. 2). On the other hand, the particle sizes of PMMA(Triton) and PMMA(P123) were relatively large (ca. 106 nm: PMMA(Triton) and ca. 159 nm: PMMA(P123)) and their particle size distributions were broader than that of PMMA(SLS). Their SEM photographs showed that particle sizes of PMMA(Triton) and PMMA(P123) were uniform and larger than that of PMMA(SLS).

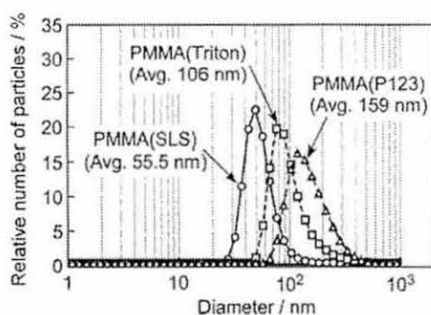


Figure 2. Particle size distributions of PMMA(M) microspheres synthesized by microwave-assisted emulsion polymerization, together with their average diameter in parentheses.

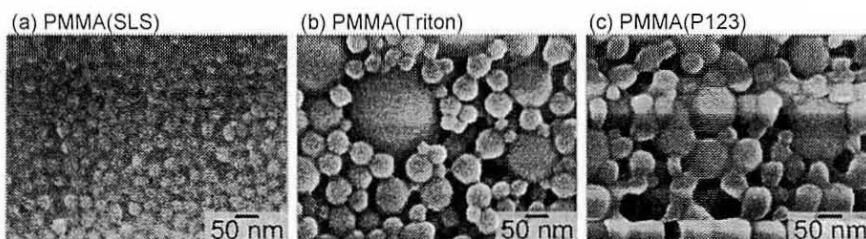


Figure 3. SEM photographs of PMMA(M) microspheres synthesized by microwave-assisted emulsion polymerization.

Figures 4 and 5 show pore size distributions together with specific surface area (SSA) and SEM photographs of pr-In₂O₃(M) and c-In₂O₃ powders, respectively. The c-In₂O₃ powder showed small SSA (3.3 m² g⁻¹) and pore volume, and its morphology was almost spherical (100~600 nm in diameter) and relatively dense. On the other hand, SSA and pore volume of the pr-In₂O₃(M) powders were larger than those of the c-In₂O₃ powder, and the SEM photographs revealed that well-developed pores were formed in the pr-In₂O₃(M) powders. However, the morphology of pores and the pore size distributions were dependent on the kind of PMMA microspheres used. Namely, the pr-In₂O₃(SLS) powder had medium pores with a centered diameter of ca. 30 nm, which was probably originated from the morphology of PMMA(SLS), as shown in Fig. 4, and small pores with a diameter less than ca. 10 nm hardly existed in the pr-In₂O₃(SLS) powder. On the other hand, pr-In₂O₃(Triton) and pr-In₂O₃(P123) powders had well-developed small pores (less than 10 nm in diameter) as well as medium pores (ca. 50 nm in centered diameter) which were confirmed from Fig. 4, along with large pores (more than 100 nm in diameter) which were confirmed from Fig. 5 (c) and (d).

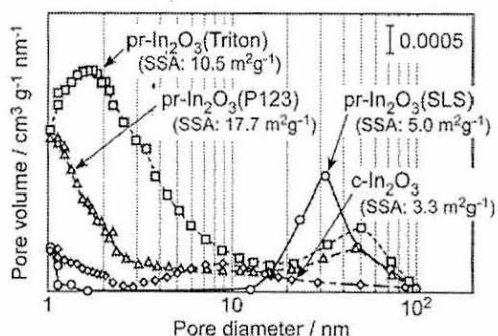


Figure 4. Pore size distribution of pr-In₂O₃(M) and c-In₂O₃ powders.

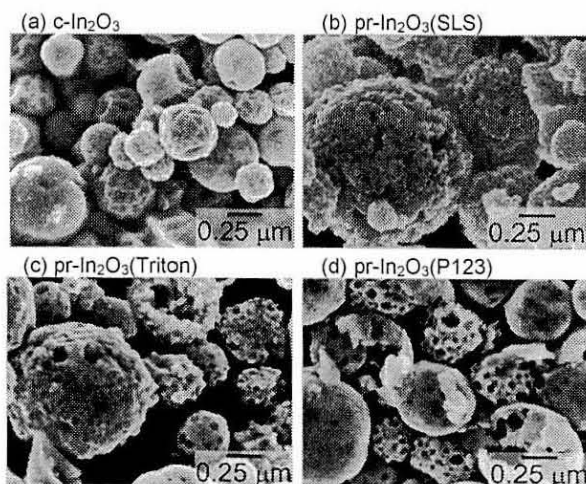


Figure 5. SEM photographs of pr-In₂O₃(M) and c-In₂O₃ powders.

Figure 6 shows response transients of all sensors to 10 ppm NO₂ in air at 400°C. The magnitude of NO₂ responses of all pr-In₂O₃(M) sensors was much larger than that of a c-In₂O₃ sensor, while the sensor resistance of all the pr-In₂O₃(M) sensors in air was much smaller than that of the c-In₂O₃ sensor. Among all the pr-In₂O₃(M) sensors, the pr-In₂O₃(SLS) sensor showed the largest response to 10 ppm NO₂ ($R_g/R_a = 36.0$) and the fastest response and recovery speeds.

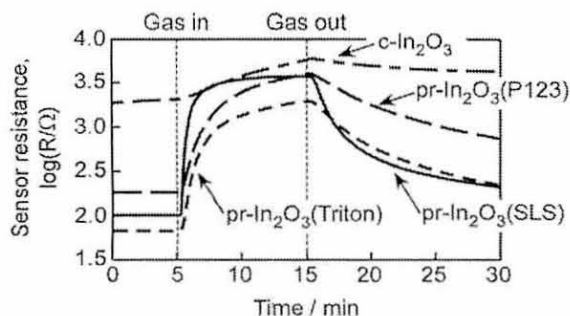


Figure 6. Response transients of all sensors to 10 ppm NO₂ in air at 400°C.

Figure 7 show operating temperature dependence of the magnitude of response (a) and 90% response time (b) of pr-In₂O₃(M) and c-In₂O₃ sensors to 10 ppm NO₂ in air. The magnitude of NO₂ responses of all the pr-In₂O₃(M) sensors was much larger than that of c-In₂O₃ sensor in the temperature range of 250–500°C. All the pr-In₂O₃(M) sensors showed the largest response at 300°C, and the response at lower temperatures ($\leq 200^\circ\text{C}$) was relatively small. On the other hand, all sensors showed extremely slow response speeds (over 8 min) at lower temperatures ($\leq 300^\circ\text{C}$). However, the response speed of pr-In₂O₃(SLS) sensors was faster than other sensors at higher temperatures ($\geq 300^\circ\text{C}$).

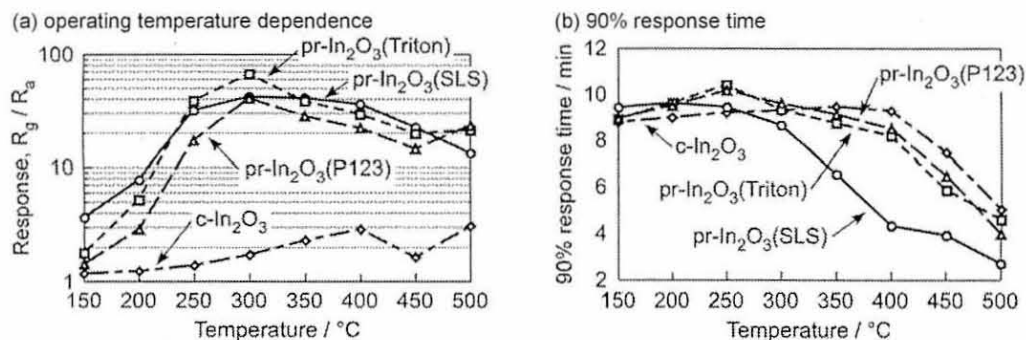


Figure 7. Operating temperature dependence of the magnitude of response (a) and 90% response time (b) of pr-In₂O₃(M) and c-In₂O₃ sensors to 10 ppm NO₂ in air.

Conclusions

PMMA microspheres with relatively-controlled particle diameter (PMMA(M)) were easily synthesized by microwave-assisted emulsion polymerization employing a typical

surfactant (M: SLS, Triton or P123). The PMMA(SLS) was the most uniform among them. pr-In₂O₃ powders were prepared by ultrasonic-spray pyrolysis employing the synthesized PMMA microspheres. The morphology of pores and the pore size distributions were dependent on the kind of PMMA microspheres used. The magnitude of NO₂ responses of all the pr-In₂O₃(M) sensors was larger than that of c-In₂O₃ sensor. The introduction of controlled macroporous structure into the powder of the sensor material was found to be effective for improving NO₂ response properties.

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