Effects of Additives on the DMMP Sensing Behavior of SnO₂ Nanoparticles Synthesized by Hydrothermal Method

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Abstract

SnO₂ nanoparticles were synthesized by a hydrothermal method and gas sensors were fabricated using nanoparticles to detect dimethyl methylphosphonate(DMMP) gas. The prepared SnO₂ nanoparticles exhibited a high response(72 at 500 °C) to 5 ppm DMMP gas compared to commercial SnO₂ nanopowders, but their recovery was relatively poor. Various metals(Ni, Sb, Nb) were added to the SnO₂ nanoparticles to improve their recovery properties. The focus of this study was to investigate the effects of metal oxide additives on DMMP sensing behavior in SnO₂ nanoparticles.

Keywords : SnO₂, Sensor, DMMP, Recovery, Additive

1. INTRODUCTION

Among the various kinds of oxide semiconductor materials for gas sensors, SnO₂ has attracted much attention for its ability to detect hydrogen gas and other environmental gases such as CO, H₂S, NOx, and VOCs[1-6]. Recently, semiconductor metal oxides including SnO₂ and WO₃ have also been used in detection of chemical warfare agents(CWAs) or simulant gases[7, 8]. There are many well-known organophosphorus(OP) compounds such as tabun(GA), distilled mustard(HD), sarin(GB). Sarin is a representative nerve agent and Dimethyl methylphosphonate(DMMP) can be used as a good substitute for sarin gas because it has a similar functional group to sarin. To date, much research on the detection of DMMP have been published[9-11].

Semiconductor metal oxide gas sensors for detecting DMMP simulant gas have many advantages, such as their cost, small size, and high sensitivity, when compared to other type sensors including quartz crystal microbalance(QCM)[12, 13], microcantilever(MCL)[14, 15], surface acoustic wave(SAW)[16, 17]. However, semiconductor metal oxide sensors for DMMP exhibit a poisoning effect due to the irreversible reaction between surface atoms of the metal oxides and phosphorus atom of the DMMP molecules[18, 19]. To solve this problem, various metal oxides have been added to the SnO₂ particles[20, 21].

In this study, we synthesized crystalline SnO₂ nanoparticles using a simple hydrothermal method. The prepared SnO₂ nanoparticles exhibited a high response to DMMP gas compared to commercial SnO₂ nanopowders, but response time was very slow and their recovery was poor. To compensate for this poor recovery, the SnO₂ nanoparticles were doped with various metals(M: Ni, Sb, Nb) and their DMMP sensing behaviors were investigated.

2. EXPERIMENTAL

2.1 Preparation of SnO₂ nanoparticles with additives

SnO₂ nanoparticles and M (M: Ni, Sb, Nb)-doped SnO₂ nanoparticles were synthesized using a hydrothermal method. 3.47 g of tin chloride pentahydrate(SnCl₄·5H₂O, GR, Kanto Chemical Co., Inc., Japan) was first dissolved in 10 mL distilled water, and the solution was mixed with 1 M of ammonium bicarbonate(NH₄HCO₃, ≥ 95 %, Junsei Chemical Co., Ltd., Japan) aqueous solution under vigorous magnetic stirring. The resulting white precipitates were washed by centrifuge 5 times with distilled water. The precipitates were dispersed in 55 mL ammonia solution(pH 10.5) and transferred to Teflon-lined
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autoclaves and hydrothermally treated at 200 °C for 3 h. This hydrothermal treatment resulted in a clear and homogeneous SnO2 sol. In addition, 5 wt% of nickel (II) chloride hexahydrate(NiCl2 · 6H2O, 98 %, Kanto Chemical Co., Inc., Japan), antimony(III) chloride(SbCl3, cica-reagent, Kanto Chemical Co., Inc., Japan), and niobium (V) chloride(NbCl5, 99 %, Sigma-Aldrich Co., Germany) was mixed with the prepared SnO2 sol to obtain Ni-, Sb-, and Nb-doped SnO2 nanoparticles, respectively. After heat-treatment at 600 °C for 1 h, each sol was transformed into undoped-, Ni-, Sb-, and Nb-doped SnO2 nanoparticles.

2.2. Characterization of SnO2 nanoparticles with additives

The prepared SnO2 nanoparticles were examined by X-ray diffraction(XRD, D8- Advance, BRUKER MILLER Co.) for phase identification and field emission scanning electron microscopy(SEM, JSM-7401F, JEOL) for morphology. The added elements and their chemical states were confirmed by XPS analysis(AXIS-His, KRATOS).

2.3. Measurements of DMMP sensing performance

To prepare the gas sensors, SiO2/Si wafers were used as substrates and they were cleaned successively with acetone, ethanol, and deionized water. Platinum interdigitated electrodes were deposited on the cleaned SiO2/Si substrates, and they were annealed at 600 °C for 1 h. SnO2 nanoparticles were deposited on the platinum interdigitated SiO2/Si substrates by dropping the prepared SnO2 sols on the surface. After drying, the SnO2 nanoparticle sensors were annealed at 600 °C for 1 h.

The SnO2 nanoparticle sensors were loaded into a quartz tube located in an electrical furnace to investigate their gas sensing properties. Au lead wires were attached to the platinum electrode pairs using silver paste in order to measure the resistance of the SnO2 nanoparticle films. The resistance of the sensing films was recorded using a Keithley Multimeter 2002.

For measuring their DMMP sensing properties, DMMP vapor was prepared using the bubbling method. Liquid DMMP was kept in a canister at 30 °C, and dry air gas was passed through the canister. Vapor concentrations were calculated using the Antoine Equation, and the concentrated DMMP vapor was diluted by additional air to obtain a 5 ppm DMMP gas/air mixture. The DMMP vapor and dry air gases were alternatively injected into the gas sensors. The DMMP sensing performance of the synthesized SnO2 nanoparticles and the M (M: Ni, Sb, Nb)-doped SnO2 nanoparticles were examined at various operating temperatures for 5 ppm DMMP gas. The DMMP response was defined as the ratio of the resistance in air(Rair) to that in the target gas(Rgas). In addition, the DMMP sensing behavior of commercial SnO2 nanopowders was also measured for comparison with that of the synthesized SnO2 nanoparticles.

3. RESULTS AND DISCUSSION

![Fig. 1. XRD patterns of synthesized SnO2 nanoparticles (a) as-prepared (b) after annealing at 600 °C.](image)

![Fig. 2. SEM images of undoped SnO2 nanoparticles (a) as-prepared (b) after annealing at 600 °C, (c) Ni-, (d) Sb-, (e) Nb-doped SnO2 nanoparticles, and (f) commercial SnO2 nanopowder.](image)