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Ultraselective and ultrasensitive detection of trimethylamine using MoO_3 nanoplates prepared by ultrasonic spray pyrolysis

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ABSTRACT

An ultraselective and ultrasensitive trimethylamine (TMA) sensor was achieved using MoO_3 nanoplates-prepared by ultrasonic spray pyrolysis followed by a heat treatment at 450 °C. The small and thin MoO_3 nanoplates with gas-accessible structures showed an unusually high response to 5 ppm TMA (ratio of resistance to air and gas = 373.74) at 300 °C with detection limit as low as 45 ppb. Moreover, the ratios of the cross-responses to interfering gases (i.e., 5 ppm C_2H_5OH, CO, CH_4, C_3H_8, H_2, and NO_2) to the response to 5 ppm TMA were extremely low (0.008–0.016). The source of the ultraselective and highly sensitive detection of TMA with negligible interference from other gases is discussed with respect to the acid/base properties, size, and morphology of the MoO_3 sensing materials.

1. Introduction

Trimethylamine (TMA) is secreted during the decomposition of trimethylamine *N*-oxide (TMAO) in dead fish and sea creatures [1,2], and induces skin burns, headaches, nausea, and irritation of the eye and respiratory system. The concentration of TMA increases with the decay of the dead fish and marine products: The fish is regarded as "decayed" when the concentration of TMA is greater than 10 ppm [3]. However, the TMA concentration is dependent upon the sensing conditions (e.g., distance from fish or marine products and number of decaying fish). Thus, the ability to sense TMA concentrations of less than 10 ppm is also necessary to estimate the degree of decay of fish or for highly sensitive instantaneous screening of decaying marine products. The National Institute for Occupational Safety and Health, USA, specifies permissible exposure limits of 10 ppm for 10 h for long-term exposure and 15 ppm for 15 min for short-term exposure [4]. Accordingly, detection of ppm levels of TMA is important to estimate fish freshness and identify harmful environments.

The chemiresistive variation of n-type oxide semiconductors such as SnO_2 [5], ZnO [6], TiO_2 [7], In_2O_3 [8], Fe_2O_3 [9], WO_3 [10], and MoO_3 [11] is used to detect trace concentrations of reducing gases. Simple sensor structure, high sensitivity, facile integration, and cost-efficiency are major strengths of oxide semiconductor gas sensors. However, the negatively charged oxygen adsorbed on the surface can react with a range of reducing gases, which often renders the discrimination of different gases difficult. To date, various oxide semiconductors have been explored to achieve selective and sensitive detection of TMA; these include ZnO doped with Al_2O_3, TiO_2, and V_2O_5 [12], WO_3 [13], Ru-doped SnO_2 [14], $LaFeO_3$ [15], ZnO–In_2O_3 composites [16], Cr_2O_3-decorated ZnO [17], and CdO–Fe_2O_3 [18]. Among these, WO_3 hollow spheres, which were prepared by the present authors, exhibited very high selectivity and responses to TMA [13]. Although, the selectivity of the WO_3 hollow spheres to TMA was among the highest of the reported oxide semiconductor gas sensors, the cross-responses to 5 ppm NH_3 (R_a/R_g = 12.3, R_a: resistance in air, R_g: resistance in gas) and 5 ppm C_2H_5OH (R_a/R_g = 4.8) were 21.6% and 8.4%, respectively, of that to 5 ppm TMA (R_a/R_g = 56.9), which impedes the ultraselective detection of TMA.

Selective detection of a specific gas can be achieved by manipulating the sensing temperature [19], loading catalytic materials to promote the sensing reaction of a specific gas [20,21], compositional control of sensing materials with different acidities and basicities [22], and employment of a catalytic filtering layer [23]. The selective detection of TMA by WO_3 hollow spheres occurred via the strong interaction between basic TMA gas and acidic WO_3 [13]. MoO_3 is also an acidic oxide [24] and has the same orthorhombic crystal structures as WO_3. From this perspective, MoO_3 is potentially a good candidate material for the selective detection of TMA

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gases. However, thus far, most studies using MoO_3 nanostructures have mainly focused on sensing C_2H_5OH [11,25], NH_3 [26–30], NO_2 [31–34], CO [32,35–37], H_2 [38], and H_2S [39]. Although TMA sensors using MoO_3 microrods were investigated [40], the selectivity to TMA and the cross-responses to several ppm-level interfering gases were not investigated.

Because of the low melting point of MoO_3 (795 °C), significant particle growth and densification of MoO_3 occur during the heat treatment even at moderate temperatures (~600 °C) [41,42], which could impair the design of highly sensitive gas sensors. In this contribution, Mo-containing hollow precursors with thin shells were prepared by ultrasonic spray pyrolysis and successfully converted into MoO_3 nanoplates with small crystallites and gas-accessible nanostructures by the heat treatment. The resultant MoO_3 nanoplates showed extremely high selectivity and sensitivity toward TMA with negligibly low cross-responses to possible interfering gases. The reasons for the ultrahigh selectivity and sensitivity are explained with respect to the acid/base interactions between the sensing materials and analyte gas and the morphology and crystallinity of the MoO_3 nanostructures.

2. Experimental

Hexaammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, Junsei, 99%) (3.5310 g) and citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$, Sigma-Aldrich, 99%) (2.1014 g) were dissolved in 1 L of distilled water and stirred for 3 h. The solution was used to obtain particles via spray pyrolysis. Citric acid was added to induce the hollow morphology of the spheres during spray pyrolysis [43]. The spray pyrolysis system consists of a droplet generator, quartz-tube reactor, and particle-collecting chamber. Six ultrasonic generators (resonant frequency: 1.7 MHz) were used to generate a plethora of droplets. The droplets were carried into the high-temperature quartz-tube reactor (inner diameter: 55 mm) by a carrier gas (air, 40 L/min). Mo-containing precursor spheres were prepared through the pyrolysis of droplets containing molybdenum precursors and collected on a Teflon bag filter in the particle-collecting chamber. The temperature of the chamber was held at ~250 °C to prevent water condensation. Details of the experimental setup were previously reported [44]. The reactor temperature was maintained at 700 °C. As-prepared precursor particles were heated at 450 °C for 2 h, washed five times with distilled water, and dried in air at 70 °C for 24 h. For simplicity, the specimen prepared by spray pyrolysis and subsequent heat treatment is referred to as "Mo-SP."

For comparison, the following three specimens were also prepared. For the first specimen, 5 g of $(NH_4)_6Mo_7O_{24}$ $4H_2O$ was heat-treated at 450 °C for 2 h, washed five times with distilled water, and dried in air at 70 °C for 24 h to prepare MoO_3 powders (referred to as "Mo-HT"). For the second specimen, MoO_3 powders were prepared using the method reported by Dhage et al. [45]: $(NH_4)_6Mo_7O_{24}$ $4H_2O$ (6 g), urea (NH_2CONH_2, Junsei, 99%) (1.2 g), and sodium dodecyl sulfate ($C_{12}H_{15}O_4S{\cdot}Na$, Sigma-Aldrich, 99%) (0.12 g) were dissolved in 200 mL of distilled water. The solution was titrated with nitric acid (HNO_3, Samchun, 60.0%) to a pH of 3.0. The precursor powders were prepared by ultrasonic transduction of the solution for 30 min. The MoO_3 specimens (referred to as "Mo-UT") were then heat-treated at 450 °C for 2 h, washed five times with distilled water, and dried in air at 70 °C for 24 h. For the third specimen, 5 g of commercial molybdenum(VI) oxide powder (MoO_3, Sigma-Aldrich, 99.5%) was heat-treated at 450 °C for 2 h, washed five times with distilled water, and dried in air at 70 °C for 24 h. This specimen is referred to as "Mo-CS."

The phases and crystal structures of the particles were analyzed by X-ray diffraction (XRD, Rigaku D/MAX-2500V/PC) using Cu $K\alpha$ radiation. The morphology of the particles was observed using field-emission scanning electron microscopy (FE–SEM, S-4800, Hitachi Co. Ltd., Japan). The surface areas were measured using the Brunauer–Emmett–Teller method (BET, Tristar 3000, Micrometrics Co. Ltd, USA).

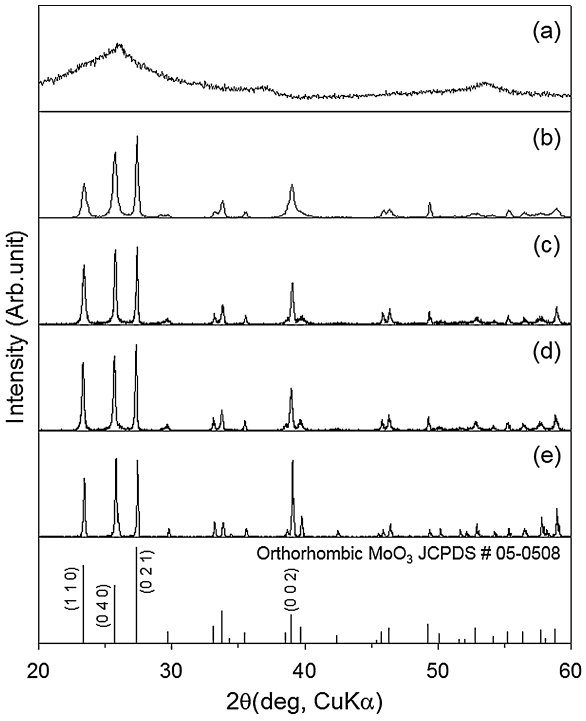

Fig. 1. X-ray diffraction patterns of (a) precursor particles prepared by spray pyrolysis (Mo-SP precursor), (b) Mo-SP powders, (c) Mo-HT powders, (d) Mo-UT powders, and (e) Mo-CS powders.

Small amounts of MoO_3 powders (0.01 g) were ultrasonically dispersed in distilled water (2 mL), and 0.2 μL aliquots of this slurry were dropped five times onto an alumina substrate (1.5 mm × 1.5 mm × 0.25 mm) with two Au electrodes. The substrate was dried at 60 °C for 20 min between the additions of each droplet. The sensor was heat-treated at 400 °C for 3 h to remove any moisture. A flow-through technique with a constant flow rate of 500 cm^3/min was used, and a four-way valve was employed to switch the gas atmospheres. The responses of the sensors to 5 ppm TMA, C_2H_5OH, H_2, CO, NH_3, NO_2, and toluene were measured at 300–400 °C by switching between the mixture gases (i.e., 5 ppm TMA, C_2H_5OH, H_2, CO, NH_3, NO_2, and toluene, all in air balance) and dry synthetic air. The R_a/R_g (R_a: resistance in air, R_g: resistance in gas) and R_g/R_a values were used as the gas responses to reducing (TMA, C_2H_5OH, H_2, CO, NH_3, and toluene) and oxidizing (NO_2) gases, respectively. The dc-2 probe resistance of the sensor was measured using as electrometer interfaced with a computer.

3. Results and discussion

The as-prepared Mo-containing precursors showed weakly crystalline peaks in the X-ray diffraction patterns (Fig. 1a). After the heat treatment at 450 °C for 2 h, the compound converted into a crystalline orthorhombic MoO_3 (α-MoO_3) phase (JCPDS no. 05-0508) (Fig. 1b). The Mo-HT, Mo-UT, and Mo-CS powders after heat treatment also showed crystalline α-MoO_3 phases (Fig. 1c–e). The low crystallinity of the as-prepared Mo-precursors despite the high reaction temperature (700 °C) is likely due to the short residence time (~3 s) of the droplets in the reactor during spray pyrolysis. The increase in crystallinity caused by the heat treatment at a