

# Highly Sensitive C<sub>2</sub>H<sub>5</sub>OH Sensors Using Self-Assembled ZnO Hierarchical Nanostructures

Kang-Min Kim, Hyo-Joong Kim, Hae-Ryong Kim, Kwon-Il Choi and Jong-Heun Lee  
 Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea  
 jongheun@korea.ac.kr

## Abstract

Three different morphologies of ZnO nanostructures such as porous nanorods and two hierarchical structures were prepared by the reaction of mixtures of oleic-acid-dissolved ethanol solutions and aqueous dissolved Zn-precursor solutions in the presence of NaOH and their gas sensing characteristics were investigated. Ultra-high responses ( $R_a/R_g = \sim 1200$ ,  $R_a$ : resistance in air,  $R_g$ : resistance in gas) to 100 ppm C<sub>2</sub>H<sub>5</sub>OH was achieved using porous nanorods and hierarchical structures assembled from porous nanosheets. Gas sensing characteristics were discussed in relation to size, crystallinity, surface area, morphology, and nano-porosity of nanostructures.

**Key words:** ZnO, nanorods, hierarchical, self-assembly, C<sub>2</sub>H<sub>5</sub>OH, gas sensors

## Introduction

The n-type oxide semiconductors gas sensors have been used to detect trace concentration of reducing gases [1]. The properties of oxide semiconductor gas sensors determined by various parameters such as the thickness of electron depletion layer, the electron transfer, the diffusion of target gases, the oxygen adsorption/desorption, and the surface reaction [2]. Most of the key factors in gas sensing reactions, except the surface reaction, can be effectively manipulated by proper control of the size, morphology, crystallinity, and agglomerated configuration of the nanostructures [3].

The solution-based self-assembly reaction under an ambient atmosphere is a facile and cost-effective route to prepare various morphologies of ZnO nanostructures with large surface area to volume ratio. When the low-dimensional nano-building blocks, such as 1-dimensional (1D) nanorods and 2D nanosheets, are self-assembled into the higher dimensional hierarchical structures, well-defined porous morphologies can be achieved without the sacrifice of the high surface area. The rapid and effective diffusion of analyte gas onto the entire sensor surface leads to the high and fast response.

In this study, ZnO nanostructures with different morphologies and porosities are prepared by controlling the reaction of mixtures

of oleic-acid-dissolved ethanol solutions and aqueous solutions of dissolved Zn-precursors in the presence of NaOH and their gas sensing characteristics are investigated. Main focus was directed at the design of gas sensors with high gas response and linearity.

## Experimental

Zn-precursors were prepared by reaction of the mixture between an oleic-acid-dissolved ethanol solution and the Zn-precursor-dissolved aqueous solution in the presence of NaOH. The morphologies of Zn-precursors were controlled by manipulating the solvent to dissolve surfactant, the procedure of NaOH addition, and the solution temperature during the oleic-acid-based self-assembly reaction. Three different morphologies of Zn-precursors were hierarchical structures assembled from nanosheets (referred as 'H-NS' precursor); thin nanorods ('NR' precursor); and hierarchical structures assembled from thick nanorods ('H-NR' precursor). These were converted into a similar morphology of ZnO nanostructures by heat treatment at 500 °C for 1 h, which will be referred as 'H-NS', 'NR', and 'H-NR' nanostructures, respectively.

The H-NS precursors were prepared by the followings: Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.38 g, >99%, Kanto Chemical, Japan) was dissolved in deionized water (160 mL) after which ethanol (C<sub>2</sub>H<sub>5</sub>OH, 40 mL, 99%, Sigma Aldrich, USA) and oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, 1.28 g, >99%, Sigma

Aldrich, USA) were added to the solution in sequence with stirring. While ethanol and oleic acid are miscible with each other, oleic acid is insoluble in aqueous solution. Thus, water-insoluble and ethanol-soluble surfactant (oleic acid) was provided continuously and gradually by the forced stirring of the emulsion mixture of the oleic-acid-dissolved ethanol solution and the dissolved Zn-precursor aqueous solution. After 50% NaOH aqueous solution (6.4 g, Samchun Chemical Co., Korea) was instantaneously poured into the mixture, the resulting emulsion was stirred for 1 h at room temperature.

In order to prepare NR precursors, 50% NaOH aqueous solution (6.4 g) was dissolved in deionized water (160 mL). Then  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.38 g) dissolved in ethanol (40 mL) and oleic acid (1.28 g) were instantaneously poured into the solution in sequence. The solution was reacted for 1 h with continuous stirring.

The H-NR precursors were prepared by the followings:  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.38 g) was dissolved in deionized water (200 mL). After the instantaneous addition of 50% NaOH solution (9.6 g), the solution was heated at 90 °C for 1 h. The resultant products were collected by centrifugation, washed several times with deionized water and ethanol, and dried at room temperature.

## Results and Discussion

The H-NS and NR precursors were the mixtures between hexagonal ZnO and orthorhombic  $\text{Zn}(\text{OH})_2$ . The  $\text{Zn}(\text{OH})_2$  phase content was higher in NR precursors. In contrast, the H-NR precursors were identified as crystalline ZnO phase without  $\text{Zn}(\text{OH})_2$ . All the three precursors were converted into pure ZnO by heat treatment at 500 °C for 1 h.

The H-NR precursors were hierarchical structures assembled from thick nanorods (thickness: ~ 700 nm) (Fig. 1a). As-prepared NR precursors consist of 1-dimensional nanorods (length: 2 - 3  $\mu\text{m}$ , thickness: 200 - 300 nm) with clean surfaces (Fig. 1b). The H-NS precursors were hierarchical structures assembled from nanosheets (size: 3 - 5  $\mu\text{m}$ , thickness: 5 - 10 nm) (Fig. 1c). The surfaces of heat-treated H-NR nanostructures remained smooth and dense after heat treatment (Fig. 1d) while those of heat-treated NR (Fig. 1e) and H-NS (Fig. 1f) nanostructures changed into nano-porous ones due to the heat treatment. Considering the phases of H-NS ( $\text{ZnO} + \text{Zn}(\text{OH})_2$ ), NR ( $\text{ZnO} + \text{Zn}(\text{OH})_2$ ), and H-NR precursors (pure ZnO), the development of

nano-porous structures in H-NS and NR nanostructures was attributed to the dehydration of the  $\text{Zn}(\text{OH})_2$  phase during heat treatment.

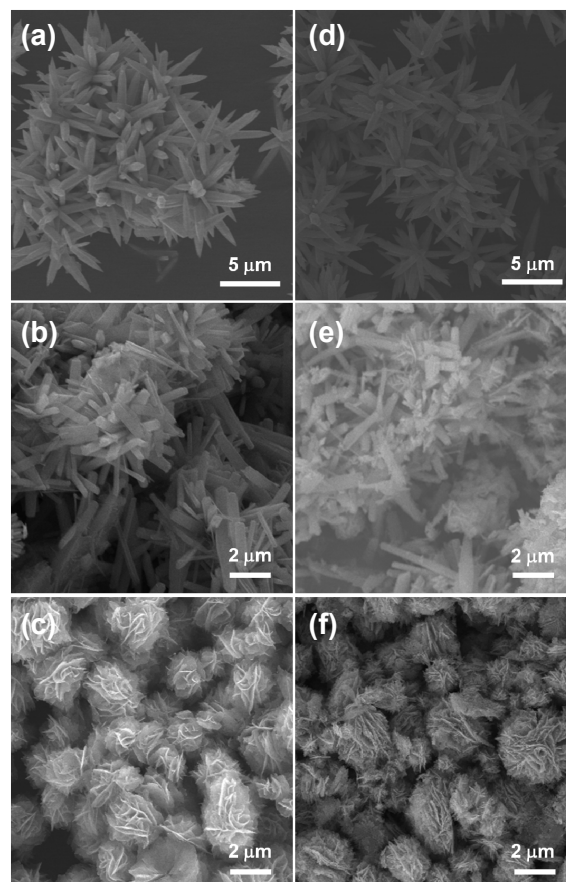


Fig. 1: SEM image of (a)H-NR, (b)NR, (c)H-NS precursors before heat treatment and (d)H-NR, (e)NR, (f)H-NS nanostructures after heat treatment at 500 °C for 1 h.

The gas responses to 100 ppm  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CH}_4$ , CO and  $\text{H}_2$  were measured at 250 – 400 °C. The response to  $\text{C}_2\text{H}_5\text{OH}$  was significantly higher than those to other gases at 250 – 400 °C. For example, the gas responses to 100 ppm  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CH}_4$ , CO, and  $\text{H}_2$  at the sensor temperature of 400 °C were shown in Fig. 2. The responses to 100 ppm  $\text{C}_2\text{H}_5\text{OH}$  of the H-NS and NR sensors were 1171.6 and 1285.1, respectively, which were significantly higher than those to  $\text{C}_3\text{H}_8$ ,  $\text{CH}_4$ , CO, and  $\text{H}_2$ . Although the response to 100 ppm  $\text{C}_2\text{H}_5\text{OH}$  of the H-NR sensor (203.0) was smaller than those of the H-NS and NR sensors, it was still sufficiently higher than its responses to other gases (1.5-2.3). Accordingly, all the sensors in the present study can be used for the selective detection of  $\text{C}_2\text{H}_5\text{OH}$  with their minimum cross-sensitivities to  $\text{C}_3\text{H}_8$ ,  $\text{CH}_4$ , CO, and  $\text{H}_2$  (Fig. 2).

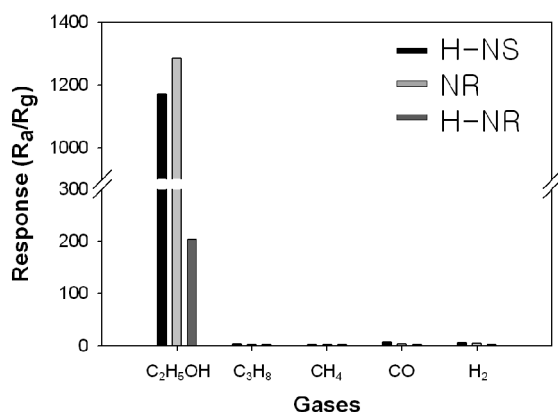


Fig. 2: Gas responses to 100 ppm  $C_2H_5OH$ ,  $C_3H_8$ ,  $CH_4$ ,  $CO$ ,  $H_2$  of H-NS, NR, and H-NR sensors at 400 °C.

The responses to 1 ppm  $C_2H_5OH$  of H-NS, NR, and H-NR sensors showed the maximum values at 340 °C (Fig. 3). However, long sensor response times were necessary to achieve steady state signal. The times to reach 90% variation in sensor resistance upon exposure to 100 ppm  $C_2H_5OH$  ( $\tau_{res}$ ) of NR, H-NS, and H-NR sensors were 1214, 866, and 500 s, respectively. Although the highest gas responses were attained at 340 °C, relatively sluggish response and recovery kinetics can limit the application of this sensor. To enhance response and recovery speed, the sensor temperature was increased to 400 °C. The  $\tau_{res}$  value of the NR sensor upon exposure to 1 ppm  $C_2H_5OH$  and air were markedly decreased to 1.8 s and the  $\tau_{res}$  values of H-NS and H-NR sensors were also decreased significantly to 8.9 and 4.5 s, respectively. Taking into account both of gas response and gas responding speed, the operation of the sensor at 400 °C is more advantageous.

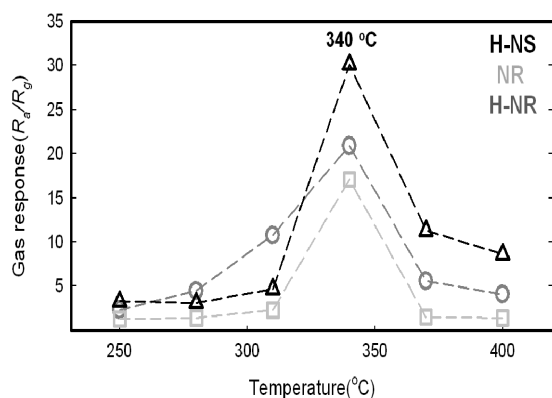


Fig. 3: Gas responses to 1 ppm  $C_2H_5OH$  of H-NS, NR, and H-NR sensors at 250–400 °C.

The responses to  $C_2H_5OH$  of the H-NS, NR and H-NR sensors at 400 °C were shown in Fig. 4. The H-NS sensor exhibited the highest responses ( $R_a/R_g$ ,  $R_a$ : resistance in air,  $R_g$ : resistance in gas) to 0.2 – 5 ppm  $C_2H_5OH$ , followed by the H-NR sensor and NR sensor. However, the order of gas responses changed as the  $C_2H_5OH$  concentration increased to 25 – 100 ppm. In the log-log plot, the gas responses of the H-NS and NR sensors abruptly increase near 5 – 25 ppm  $C_2H_5OH$ , while those of the H-NR sensors increase linearly with the entire range of concentrations. As a result, the responses to 25 – 100 ppm  $C_2H_5OH$  of the NR sensors become larger than those of the H-NR sensors. The hierarchical structures assembled from dense and crystalline nanosheets showed linear sensing behaviors. In contrast, the gas responses of porous nanorods and hierarchical structures assembled from porous nanosheets showed a deviation from the linear line above 5–10 ppm  $C_2H_5OH$  and lead to ultra-high responses to 100 ppm  $C_2H_5OH$ . This non-linearity was attributed to the additional gas sensing reaction occurring within the nanopores by the diffusion of excess analyte gas into the nanopores. The results show that not only the linear sensing but also the ultra-high gas response can be effectively designed by the control of size, morphology, and porosity of nanostructures.

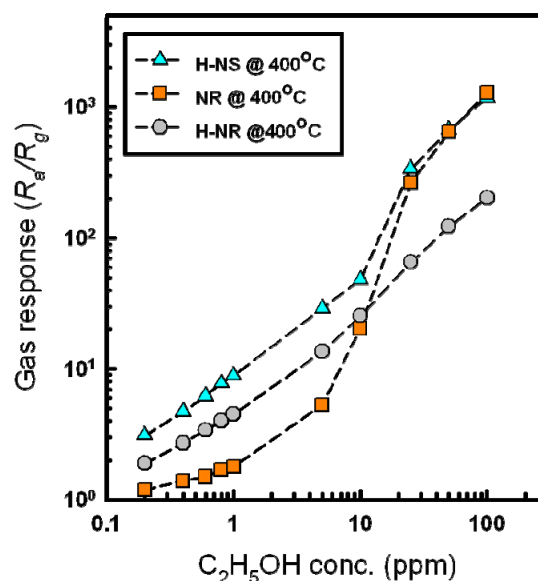


Fig. 4: Gas responses to 0.2–100 ppm  $C_2H_5OH$  of H-NS, NR, and H-NR sensors at 400 °C.

### Summary

Various ZnO nanostructures were prepared by the reaction of mixtures of oleic-acid-dissolved ethanol solutions and aqueous dissolved Zn-precursor solutions in the presence of NaOH. The hierarchical structures assembled from dense and crystalline nanorods showed linear sensing behaviors. In contrast, the gas responses of porous nanorods and hierarchical structures assembled from porous nanosheets showed a deviation from the linear line above 5–10 ppm C<sub>2</sub>H<sub>5</sub>OH and lead to ultra-high responses to 100 ppm C<sub>2</sub>H<sub>5</sub>OH. This non-linearity of gas responses at high C<sub>2</sub>H<sub>5</sub>OH concentration was attributed to the additional gas sensing reaction occurring within the nanopores by the diffusion of excess target gas into the nanopores.

### References

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