

Highly Sensitive and Selective Gas Sensors Using Catalyst-Loaded SnO₂ Nanowires

In-Sung Hwang and Jong-Heun Lee⁺

Abstract

Ag- and Pd-loaded SnO₂ nanowire network sensors were prepared by the growth of SnO₂ nanowires via thermal evaporation, the coating of slurry containing SnO₂ nanowires, and dropping of a droplet containing Ag or Pd nanoparticles, and subsequent heat treatment. All the pristine, Pd-loaded and Ag-loaded SnO₂ nanowire networks showed the selective detection of C₂H₅OH with low cross-responses to CO, H₂, C₃H₈, and NH₃. However, the relative gas responses and gas selectivity depended closely on the catalyst loading. The loading of Pd enhanced the responses (R_a/R_g : R_a : resistance in air, R_g : resistance in gas) to CO and H₂ significantly, while it slightly deteriorated the response to C₂H₅OH. In contrast, a 3.1-fold enhancement was observed in the response to 100 ppm C₂H₅OH by loading of Ag onto SnO₂ nanowire networks. The role of Ag catalysts in the highly sensitive and selective detection of C₂H₅OH is discussed.

Keywords : Gas Sensor, SnO₂ Nanowires, Catalyst, Selective Detection

1. INTRODUCTION

Crystalline oxide nanowires (NWs) are promising gas sensor materials on account of their high surface area-to-volume ratio, less agglomerated configuration and good crystallinity [1, 2]. When the diameters of n-type oxide semiconductor NWs are comparable or smaller than two times the Debye length, NW gas sensors become highly sensitive due to effective electron depletion [3]. Although a single NW can be fabricated as a gas sensor using sophisticated electrode patterning technology such as e-beam lithography [4], the high cost for processing restricts its potential applications. In comparison, a networked configuration of NWs can be fabricated simply through routes such as slurry coating [5] and direct growth of NWs on catalytic layers [6]. Thus, NW networks are more practical nanoarchitectures for gas sensor applications.

High gas response, fast response speed and high selectivity are three important gas sensing characteristics. It has been known that the chemoresistive contacts between NWs enhance the gas response [5]. From this point of view, NW network sensors have an advantage over single NW sensor. Moreover, in oxide NW networks, the rapid and effective diffusion of the analyte gas over the entire sensor surface via the less agglomerated NW networks facilitates

a high gas response and fast response speed [7]. The gas response and selectivity of oxide NW sensors can be enhanced further by loading noble metal or metal oxide catalysts to promote the gas sensing reaction [8-10]. Note that the less agglomerated network configuration is advantageous for loading catalysts uniformly.

In this work, two different catalysts (Ag and Pd) are loaded onto SnO₂ NW network sensors using a solution coating and their gas sensing characteristics are investigated. The main focus of this work is directed at the design of highly sensitive and selective gas sensors and to the understanding of the role of noble metal catalysts in the gas sensing reaction.

2. EXPERIMENTAL

2.1 Preparation of SnO₂ NWs

The SnO₂ NWs were synthesized by thermal evaporation using Sn metal powder (99.999 %). An Au (30 Å)-coated Si substrate was placed downstream of the source material in a quartz tube (inner diameter: 28 mm, length: 800 mm). The pressure of the processing tube was maintained at about 10⁻² Torr by mechanical pumping to ensure a low gas pressure. NWs were grown at 750 °C for 20 min with an O₂ flow rate of 0.5 sccm.

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2.2 Sensor fabrication and the loading of Ag or Pd

The SnO₂ NWs were separated from the Si substrate by the immersion of the as-synthesized substrate in isopropylalcohol solvent and a subsequent ultrasonic treatment. After removing the solvent and drying, the SnO₂ NWs were mixed with ethyl cellulose and α -terpineol and coated on alumina substrates with two Au electrodes (on the top) and micro-heaters (on the bottom) (Fig. 1a). The sensor was heat-treated at a heater power of 500 mW for 2 h in order to remove all organic content. Ag and Pd nanoparticles with an average size of ~ 15 nm were prepared according to the procedure described by Murphy et al [11]. The Ag or Pd catalysts were loaded onto the sensor element by dropping a slurry droplet (10 μ l) containing Ag or Pd nanoparticles and subsequent heat treated at the heater power of 500 mW for 2 h.

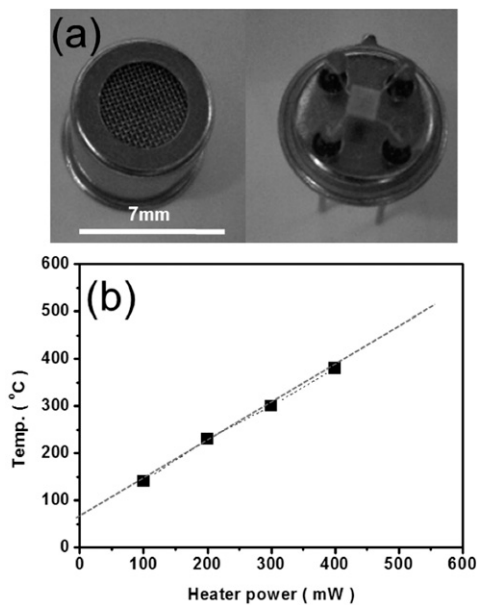


Fig. 1. (a) Sensor structure and (b) sensor temperature as a function of heater power.

2.3 Gas sensing characteristics

The sensor temperatures were controlled using the microheater underneath the substrate and were measured using an IR temperature sensor (Rayomatic 14814-2, Euroton IR tec Co.). Heater powers of 100 mW, 200 mW, 300 mW and 400 mW heated the substrates to 140 °C, 230 °C, 300 °C, and 380 °C, respectively (Fig. 1b). The gas responses ($S=R_a/R_g$, R_a : resistance in air, R_g : resistance in gas) to 200 ppm CO, H₂, C₃H₈, NH₃, and C₂H₅OH were

measured. Gas concentrations were controlled by changing the mixing ratio of the parent gases (100 ppm CO, H₂, C₃H₈, NH₃, and C₂H₅OH, all in an air balance) and dry synthetic air. The DC-2 probe resistances were measured using an electrometer interfaced with a computer.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of sensing materials

The SnO₂ NWs grown by thermal evaporation were several tens of micrometer long and 80 nm \sim 150 nm thick (Fig. 2a). From the high resolution lattice image and selected area electron diffraction, each SnO₂ NW was identified to be of a single crystalline type (not shown). The SnO₂ NWs were confirmed to have a rutile structure by X-ray diffraction measurements (Fig. 2b). The TEM images of Pd- and Ag-loaded SnO₂ NWs are shown in Fig. 3. The nanoparticles (size: ~ 15 nm) were uniformly distributed on the SnO₂ NWs, seen in Fig. 3a and Fig. 3c, were identified as Pd and Ag, respectively, by energy dispersive spectroscopy analyses (Figs. 3b and 3d). The Cu peaks in the EDS spectra of Figs. 3b and 3d emanate from the Cu grid used for the TEM analysis. The results show that slurry dropping provides a simple, effective route to load Pd or Ag nanoparticles on oxide NWs in a uniform manner.

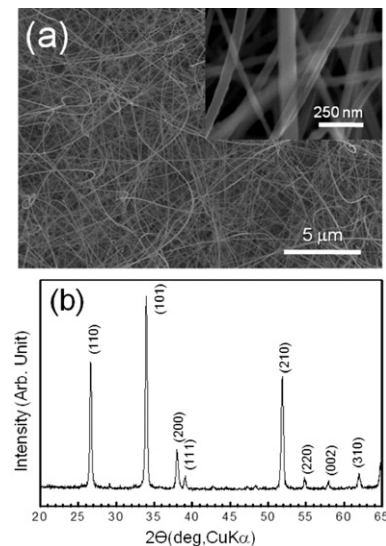


Fig. 2. (a) SEM images and (b) X-ray diffraction pattern of pristine SnO₂ nanowires.

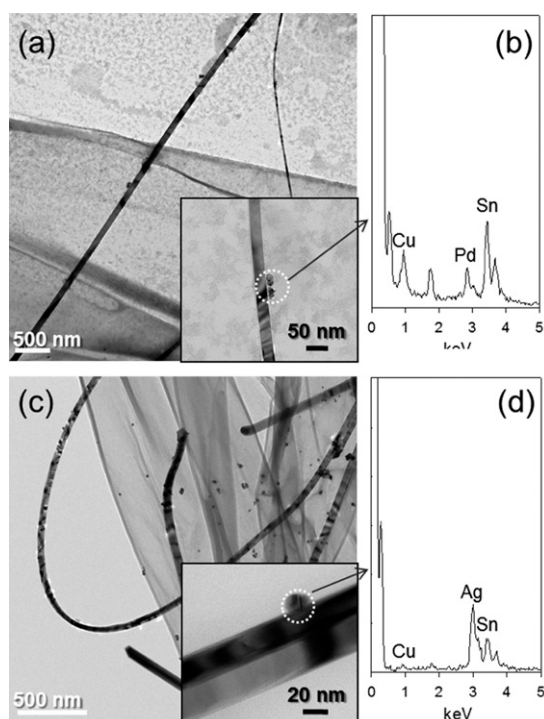


Fig. 3. TEM images and EDS results for (a,b) Pd-loaded SnO₂ nanowires and (c,d) Ag-loaded SnO₂ nanowires.

3.2 Gas sensing characteristics

Gas responses to 100 ppm CO, H₂, C₃H₈, NH₃, and C₂H₅OH of pristine, Pd-loaded and Ag-loaded SnO₂ NWs were measured at 380 °C (Fig. 4). In the pristine SnO₂ NW sensor, the response to 100 ppm C₂H₅OH ($R_d/R_g = 207.6$) is significantly higher than the responses to other gases ($R_d/R_g = 4.1 - 11.5$), indicating the selective detection of C₂H₅OH. After the loading of Pd, both the response to 100 ppm CO and H₂ increased ~ 2.7 times while the enhancement of the responses to C₃H₈ and NH₃ is relatively small. On the contrary, the response to 100 ppm C₂H₅OH was slightly decreased by the Pd loading.

In general, the loading of noble metal catalysts are known to improve gas sensing characteristics of oxide semiconductors [8]. However, the role of Pd in terms of gas response seen in various literatures has not always been consistent [12-16]. For example, Pd loading either increased or decreased gas responses according to the loading concentration [12-14] and loading method [12, 15] of the Pd catalysts as well as the optimum sensing temperature [14, 16]. In addition, the gas selectivity was also changed by Pd loading. Although the response to C₂H₅OH sensor is still markedly higher than to other gases after Pd loading, the selectivity to C₂H₅OH slightly deteriorated.

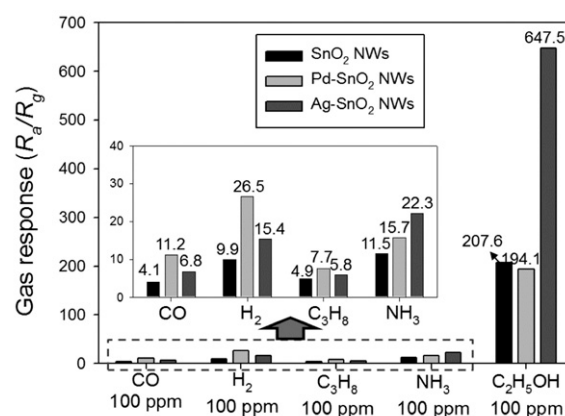


Fig. 4. Gas responses to 100 ppm CO, H₂, C₃H₈, NH₃ and C₂H₅OH of pristine SnO₂ nanowires, Pd-loaded SnO₂ nanowires and Ag-loaded SnO₂ nanowires at 380 °C.

The loading of Ag leads to different sensing behaviors. The enhancement of response to C₂H₅OH was 3.1-fold, while the responses to CO, H₂, C₃H₈, and NH₃ were increased only 1.2 times ~ 1.7 times. That is, Ag loading enhances the selectivity to C₂H₅OH to a great degree. This means that highly sensitive and selective C₂H₅OH sensors can be made using Ag-loaded SnO₂ NW networks.

The sensing transients of the Ag-SnO₂ NW network sensor to 10 ppm \sim 100 ppm C₂H₅OH are shown in Fig. 5(a). The sensor resistance decreased upon exposure to C₂H₅OH and recovered in a stable manner upon exposure to air. The responses to C₂H₅OH of pristine SnO₂ and Pd-SnO₂ NW sensors at 380 °C are compared in Fig. 5(b). The responses to 10 ppm \sim 100 ppm C₂H₅OH ranged from 42.4 to 210 in the SnO₂ NW sensor, this is significantly enhanced to 188 to 634 by loading Ag onto the sensor. The C₂H₅OH response of the Ag-SnO₂ NW sensors in the present study is higher than the Ag-loaded TiO₂ nanobelts [17], the Ag-loaded ZnO nanorods [18], and the Ag-loaded TiO₂ spherical heterostructures [19]. In particular, considering the very high response to 10 ppm C₂H₅OH ($R_d/R_g = 188$), detection of sub-ppm levels of C₂H₅OH seems to be possible using Ag-loaded SnO₂ NW networks.

‘Electronic sensitization’ and ‘chemical sensitization’ are the two main sensitization mechanisms of noble metal catalysts in the gas sensing reaction [20]. The former mechanism is explained by the extension of an electron depletion layer beneath the Ag catalyst nanoparticles and a consequent enhancement of gas response. The latter is explained by a ‘spill-over effect’ to promote the dissociation of reducing gases. At this moment, the

dominant sensitization mechanism is not clear and should be studied further. The gas responses and selectivities as a function of the morphology, size and distribution of Ag catalysts will be an effective way to elucidate the sensing mechanism. Finally, the results in Fig. 4 show the gas response and selectivity can be tuned by the proper use of noble metal catalysts and sensor data with various sensing materials will provide valuable sensing libraries for pattern recognition of multi-component chemicals.

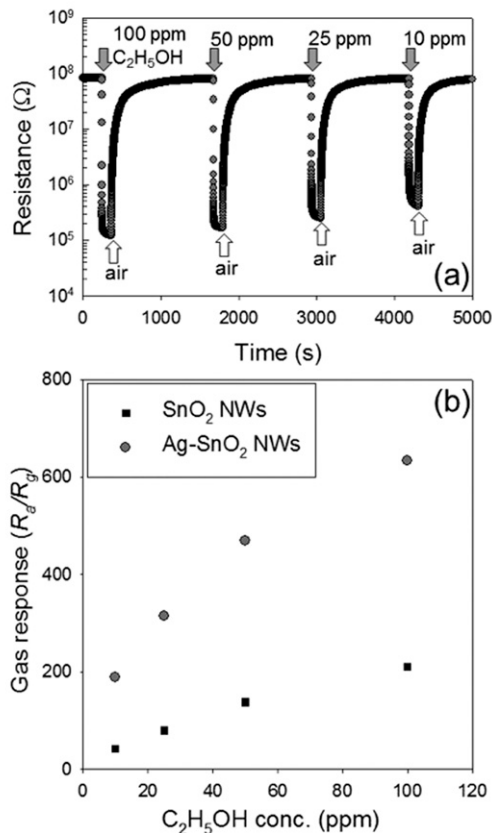


Fig. 5. (a) Gas sensing transients and (b) gas responses to 100 ppm ~ 10 ppm C₂H₅OH of the Ag-loaded SnO₂ nanowires at 380 °C.

4. CONCLUSIONS

The gas sensing characteristics of SnO₂ nanowire network sensors were modified or enhanced by Pd and Ag nanoparticles. Pristine SnO₂ nanowire networks showed the selective detection of C₂H₅OH with low cross-responses to CO, H₂, C₃H₈ and NH₃. The loading of Pd did not vary the response to C₂H₅OH but significantly increased responses to CO and H₂, which in turn deteriorated the sensor's selectivity to C₂H₅OH. The

loading of Ag induced a 3.1-fold increase in the C₂H₅OH response, which led to highly selective and sensitive detection of C₂H₅OH.

REFERENCES

- [1] A. Kolmakov and M. Moskovits, "Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures", *Annu. Rev. Mater. Res.* vol. 34, pp. 151-180, 2004.
- [2] I.-S. Hwang and J.-H. Lee, "Gas sensors using oxide nanowire networks: An overview", *J. Nanoeng. Nanomanf.*, vol. 1, pp. 4-17, 2011.
- [3] Z. Fan, D. Wang, P. C. Chang, W. Y. Tseng, and J. G. Lu, "ZnO NW field-effect transistor and oxygen sensing property", *Appl. Phys. Lett.*, vol. 85, pp. 5923-5925, 2004.
- [4] X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, "Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices", *Nature*, vol. 409, pp. 66-69, 2001.
- [5] I.-S. Hwang, Y.-S. Kim, S.-J. Kim, B.-K. Ju, and J.-H. Lee, "A facile fabrication of semiconductor nanowires gas sensor using PDMS patterning and solution deposition", *Sens. Actuators B*, vol. 136, pp. 224-229, 2009.
- [6] Y.-J. Choi, I.-S. Hwang, J.-G. Park, K.J. Choi, J.-H. Park, and J.-H. Lee, "Novel fabrication of SnO₂ nanowire gas sensor with a high sensitivity", *Nanotechnology*, vol. 19, p. 095507, 2008.
- [7] I.-S. Hwang, E.-B. Lee, S.-J. Kim, J.-K. Choi, J.-H. Cha, H.-J. Lee, B.-K. Ju, and J.-H. Lee, "Gas sensing properties of SnO₂ nanowires on micro heater", *Sens. Actuators B*, vol. 154, pp. 295-300, 2009.
- [8] A. Kolmakov, D. O. Klenov, Y. Lilach, S. Stemmer, and M. Moskovits, "Enhanced gas sensing by individual SnO₂ nanowires and nanobelts functionalized with Pd catalyst particles", *Nano Lett.*, vol. 5, pp. 667-673, 2005.
- [9] Y. Zhang, J. Xu, P. Xu, Y. Zhu, X. Chen, and W. Yu, "Decoration of ZnO nanowires with Pt nanoparticles and their improved gas sensing and photocatalytic performances", *Nanotechnology*, vol. 21, p. 285501, 2010.
- [10] I.-S. Hwang, J.-K. Choi, S.-J. Kim, K.-Y. Dong, J.-H. Kwon, B.-K. Ju, and J.-H. Lee, "Enhanced H₂S sensing characteristics of SnO₂ nanowires functionalized with CuO", *Sens. Actuators B*, vol. 142, pp. 105-110, 2009.

- [11] C.J. Murphy, T.K. Sau, A.M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi, and T. Li, "Anisotropic metal nanoparticles: synthesis, assembly and optical applications", *J. Phys. Chem. B*, vol. 109, pp. 13857-13870, 2005.
- [12] S. Matsushima, T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, "New methods for supporting palladium on a tin oxide gas sensor", *Sens. Actuators B*, vol. 9, pp. 71-78, 1992.
- [13] M. Yuasa, T. Masaki, T. Kida, K. Shimano, and N. Yamazoe, "Nano-sized PdO loaded SnO₂ nanoparticles by reverse micelle method for highly sensitive CO gas sensor", *Sens. Actuators B*, vol. 136, pp. 99-104, 2009.
- [14] J.-K. Choi, I.-S. Hwang, S.-J. Kim, J.-S. Park, S.-S. Park, U. Jeong, Y.C. Kang, and J.-H. Lee, "Design of selective gas sensors using electrospun Pd-doped SnO₂ hollow nanofibers", *Sens. Actuators B*, vol. 150, pp. 191-199, 2010.
- [15] C. -B. Lim and S. Oh, "Microstructure evolution and gas sensitivities of Pd-doped SnO₂-based sensor prepared by three different catalyst-addition process", *Sens. Actuators B*, vol. 30, pp. 223-231, 1996.
- [16] L.Liu, T. Zhang, S. Li, L. Wang, and T. Tian, "Preparation, characterization, and gas-sensing properties of Pd-doped In₂O₃ nanofibers", *Mater. Lett.*, vol. 63, pp. 1975-1977, 2009.
- [17] P. Hu, G. Du, W. Zhou, J. Cui, J. Lin, H. Liu, D. Liu, J. Wang, and S. Chen, "Enhancement of ethanol vapor sensing of TiO₂ nanobelts by surface engineering", *ACS Appl. Mater. Interfaces*, vol. 2, pp. 3263-3269, 2010.
- [18] Q. Xiang, G. Meng, Y. Zhanga, J. Xu, P. Xu, Q. Pan, and W. Yu, "Ag nanoparticle embedded-ZnO nanorods synthesized via a photochemical method and its gas-sensing properties", *Sens. Actuators B*, vol. 143, pp. 635-640, 2010.
- [19] X. Cheng, Y. Xu, S. Gao, H. Zhao, and L. Huo, "Ag-nanoparticles modified TiO₂ spherical heterostructures with enhanced gas-sensing performances", *Sens. Actuators B*, vol. 155, pp. 716-721, 2011.
- [20] N. Yamazoe, "New approaches for improving semiconductor gas sensors", *Sens. Actuators B*, vol. 5, pp. 7-19, 1991.



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