

Size Effects on Sensing Properties of ZnO Nanoparticles for Detection of Isoprene

*Yunji Park, Ran Yoo, Seungryol Park, JunHo Lee, Hwaebong Jung, Wooyoung Lee**
 Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu,
 Seoul, 03722, Republic of Korea
 * E-mail: wooyoung@yonsei.ac.kr

Abstract

The sensing properties of ZnO particles have been investigated for the detection of VOCs (Volatile Organic Compounds), in particular, isoprene (C_5H_8). According to previous studies, size reduction of ZnO particles was used as one of the methods for maximizing the reactivity. Thus, we compared the reactivity of the ZnO particles, classified by average particle sizes, ~ 5 (so-called quantum dots (QDs)) and ~ 25 nm (so-called nanoparticles (NPs)), for the detection of isoprene. Evidently, from the X-ray diffraction characterizations, the ZnO particles were successfully synthesized by a wet-chemical synthesis method. According to the XPS and BET results, larger number of oxygen vacancies and specific surface area were observed in the ZnO QDs compared to the NPs. The maximum response to 1 ppm isoprene was ~ 33 at $400^\circ C$ for the QDs and ~ 5 at $500^\circ C$ for the NPs. The higher sensing response and lower optimal working temperature of the ZnO QDs can be attributed to the comparably active adsorption sites and enhanced kinetics of the surface reaction from the size effect. Furthermore, the sensing response of ZnO QDs to 1 ppm isoprene is superior to previously reported isoprene sensors that are based on semiconducting metal oxides.

Key words: gas sensor, ZnO nanoparticles, isoprene, biomarker, metal oxide semiconductors

Background and Motivation

The most common method to monitor cholesterol in blood is by an invasive blood cholesterol test. More advanced devices such as selective ion flow tube mass spectrometry (SIFT-MS) or proton transfer reaction mass spectrometry (PTR-MS) have demonstrated high sensitivity, low detection limit and sufficient selectivity for an exhaled breath [1]. However, such devices are hardly applicable in terms of convenience, cost, and efficiency.

In this work, we present a simple method to fabricate a breath analyzer using chemical resistive gas sensors with nanostructured metal oxides. These simple devices have low fabrication cost, compact size, high sensitivity, and sufficient limit of detection [2]. Metal-oxide semiconducting materials have been widely used in gas sensors because of high sensitivity, easy fabrication, and high chemical stability. Among them, ZnO has been extensively used in gas sensors owing to its high thermal and chemical stabilities, and superior sensing properties [3].

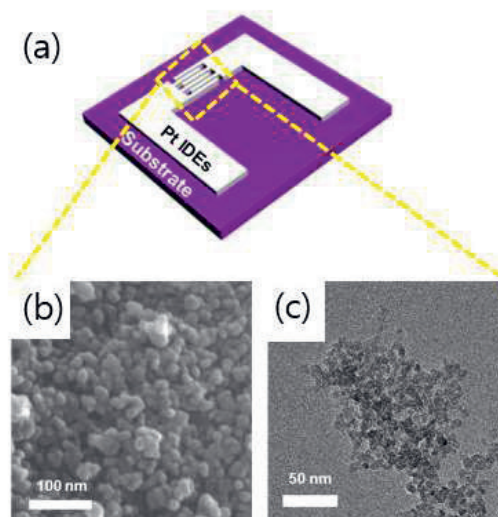


Fig. 1. (a) Schematic illustration of the sensor device; TEM images of actual (b) ZnO NPs and (c) ZnO QDs.

Results and Discussion

Figure 1(a) shows the conceptual schematic of a sensor device that measures the sensing properties. The micron-scaled Cr/Pt electrodes

were patterned on a Si/SiO₂ substrate. Figures 1(b) and 1(c) show the TEM images of the as-synthesized ZnO nanoparticles (NPs) and ZnO quantum dots (QDs), respectively. The TEM images reveal that the ZnO NPs and QDs are in a spherical structure with a diameter of ~25 nm and ~5 nm, respectively.

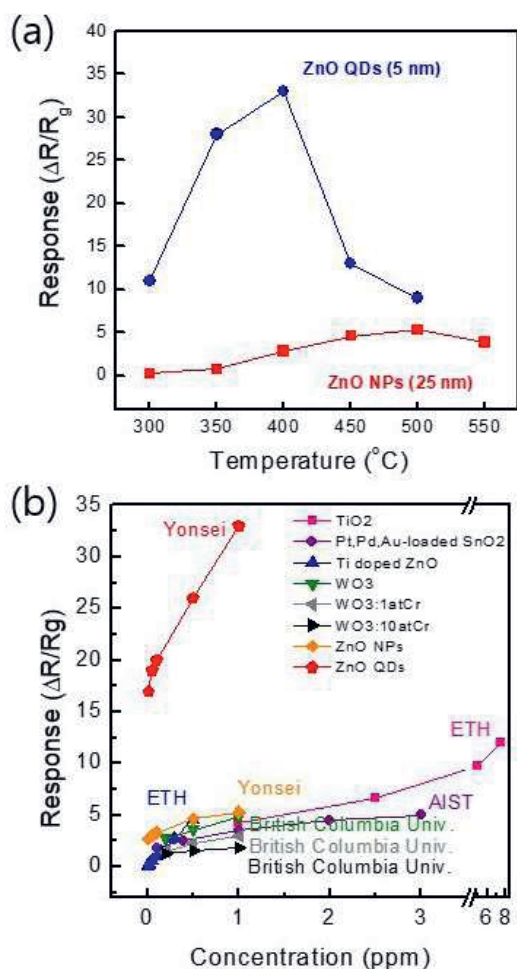


Fig. 2. (a) Maximum sensing response of the ZnO NPs and ZnO QDs toward 1 ppm of isoprene as a function of operating temperature, and (b) sensing response of ZnO NPs and ZnO QDs as a function of isoprene concentrations in the range of 0.01-1 ppm at an optimal working temperature.

The sensing properties of ZnO NPs and QDs are shown in Fig. 2. The sensing response for the isoprene gas was defined as $(R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}$ where R_{gas} and R_{air} are the resistance of the sensor in an environment containing isoprene and plane air, respectively [3]. The maximum sensing response of the samples to 1 ppm of isoprene are exhibited in Fig. 2(a). As Fig. 2(a) shows, the optimal working temperature was found to be 400°C for the ZnO QDs and 500°C for the ZnO NPs. At the optimum working temperature, the sensing response of the ZnO QDs (~33) was much higher than that of the ZnO NPs (~5). Figure 2(b) shows the response

of the ZnO NPs and QDs as a function of isoprene concentration at the optimal operating temperature. The data shows a linear increase of the response with isoprene concentration. Ultimately, the ZnO QDs exhibit superior performance with highest sensitivity value of 16.3 [1-3].

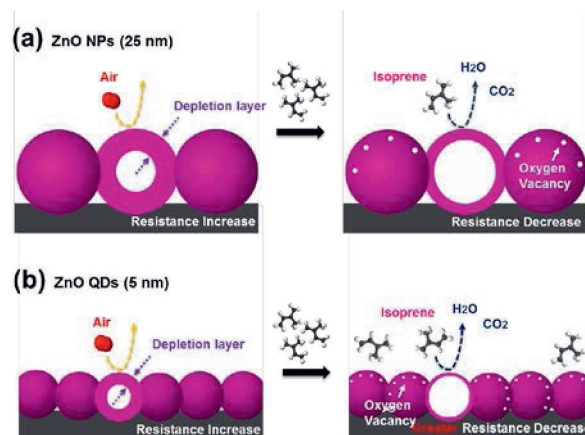


Fig. 3. Schematic diagram of the sensing reaction mechanism of (a) ZnO NPs and (b) ZnO QDs in air and isoprene.

The sensing mechanism for the isoprene detection with the ZnO NPs and the QDs is illustrated in Fig. 3. According to the sensing mechanism, the higher sensing performance is closely related to the increased number of absorbed oxygen ions. Smaller particle size of the ZnO QDs essentially implies larger surface area which consequently produces greater number of reactive sites for isoprene on the surface of the ZnO QDs. The XPS and BET results revealed that the larger number of oxygen vacancies and specific surface area were observed in the ZnO QDs compared to the NPs. Therefore, the higher sensing response and lower optimal working temperature of the ZnO QDs can be attributed to the comparably active adsorption sites and enhanced kinetics of the surface reaction from the size effect.

References

- [1] A. T. Guntner, N. J. Pineau, F. Krumeich, and S. E. Pratsinis, *Journal of Materials Chemistry B* 4, 5358-5366 (2016); doi: 10.1039/c6tb01335j
- [2] A. Teleki, S. E. Pratsinis, K. Kalyanasundaram, and P. I. Gouma, *Sensors and Actuators B* 119, 683-690 (2006); doi: 10.1016/j.snb.2006.01.027
- [3] Toshio Itoh, Daiheon Lee, Tomoyo Goto, Takafumi Akamatsu, Noriya Izu, Woosuck Shin, and Toshihiro Kasuga, *Sensors and Materials* 28, 1165-1178 (2016); doi: 10.18494/SAM.2016.1278
- [4] Ran Yoo, Dongmei Li, Sungmee Cho, and Wooyoung Lee, *Sensors and Actuators B* 254, 1242-1248 (2018); doi: 10.1016/j.snb.2017.07.084