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Selective C_2H_2 detection with high sensitivity using SnO_2 nanorod based gas sensors integrated with a gas chromatography

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ABSTRACT

We report on the sensitive and selective sensing properties of SnO_2 nanorods (NRs) based gas sensors coupled with a miniature gas chromatography (mini-GC) system for the detection of acetylene. The SnO_2 NRs were fabricated by a glancing angle deposition (GLAD) method and their average height and diameter were ~200 nm and ~30 nm, respectively. In order to overcome a selectivity issue of metal oxide semiconductor gas sensors, we integrated our SnO_2 NRs based sensors with a packed column. The device accurately and selectively detected acetylene within 2 min (~120 s). We found that loading a thin layer (5 nm) of metal catalysts such as Au, Pt or Pd increases the sensing abilities of the SnO_2 NRs sensors. Among the tested sensors, the Pd-coated SnO_2 NRs sensor (Pd-SnO_2 NRs) exhibited the best sensing performance for the detection of 10 ppm of acetylene and the lower detection limit of 0.01 ppm. The superior sensing properties of Pd-SnO_2 NRs are due to the large amount of oxygen deficiencies on the surface of Pd-SnO_2 NRs, which acts as reactive sites. More importantly, the mini-GC device can be used to selectively detect 10 ppm of acetylene from other gases such as H_2. Our findings demonstrate that Pd-SnO_2 NRs integrated with a mini-GC device can be utilized to monitor the dissolved acetylene gas in transformer oil in real time.

1. Introduction

Transformers are used worldwide to lower voltages and distribute electricity to individual houses. In order to decrease the internal temperature of transformers and to insulate currents, oils are being used in transformers. Since transformers have a long lifetime, there is a high risk for oils in older devices to degrade and damage the transformer [1–3]. This is because defects such as fractures, or discharges inside the transformer can cause the oil or cellulose to decompose and release various gases inside the transformer. These gases may include hydrogen (H_2), hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6) and carbon oxides (CO, CO_2) [1]. Of these gases, acetylene, C_2H_2, holds some serious potential risks. An accumulation of only small amounts of C_2H_2 (5–7 ppm) may cause arcing inside the transformer, which can lead to extremely dangerous situations such as explosions [2]. Hence, monitoring the concentration of C_2H_2 during operation is a critical issue for the operation of transformers.

Various devices are currently being used to examine fault gases inside transformer oils [3–7]. These methods can be divided into two groups: off-line and on-line techniques. In an off-line analysis, transformer oils are extracted from sampling valves of transformers and transferred to separate laboratories for analysis. To analyze the gas, dissolved gas analysis (DGA) or gas chromatography (GC) are usually utilized [3–5]. However, because of the time gap between the extraction and the analysis, the dissolved gases can diffuse to the atmosphere, leading to inaccurate results. On the contrary, using an on-line method, membranes are directly attached to transformer oils to separate gases from them [3,8]. This system is, however, quite expensive and complex to install in all transformers. Therefore, it is necessary to develop an economical device, which can perform real-time monitoring of gases dissolved in transformer oils with high sensitivity and selectivity.

In order to develop a sensitive device, it is crucial to find an efficient

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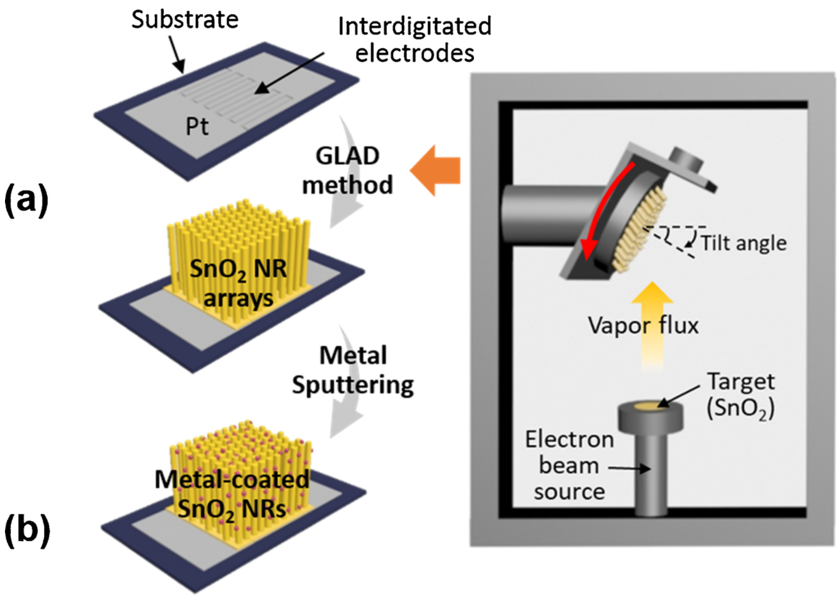

Fig. 1. An illustration of the fabrication of (a) the bare SnO_2 NRs using a glancing angle deposition (GLAD) method via e-beam evaporation and (b) the resulting metal-coated SnO_2 NRs.

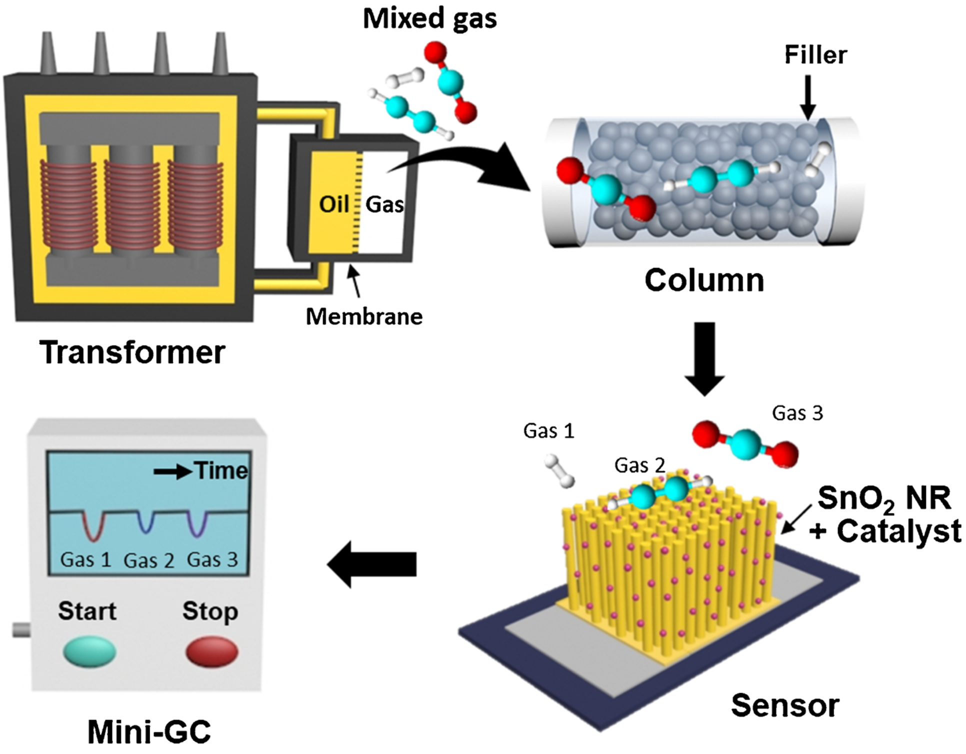

Fig. 2. Scheme of the concept of the selective gas sensing process of fault gases in transformer oils using the mini-GC system with an integrated Pd-coated SnO_2 NR sensor. The fault gases are separated from the transformer oil by membranes and then injected into the mini-GC, after which the sensor selectively detects each gas component.

sensing material for C_2H_2. Extensive researches have been carried out to fabricate gas sensors based on metal oxide semiconductors (MOS) for the detection of C_2H_2 [9–19]. Especially, SnO_2 has been widely used as a sensor material for detecting various kinds of gases due to its wide bandgap (~3.7 eV), high chemical and physical stability, and good sensitivity [10–14,18–23]. In order to improve the sensing performance, an increase in the specific surface area of the sensing material is generally employed by construing a nanostructure. There are many reports on the preparation of various types of nanostructures in SnO_2 [22]. In addition, decoration of noble metals, such as Au, Pt, and Pd, could be added to further enhance the sensing properties because the metals serve as sensitizers or promoters. Most of the study presented that the metal-loaded SnO_2 exhibited a higher sensing response than pure SnO_2.

In this context, we have recently demonstrated that Pd-coated SnO_2 nanorod arrays (NRs) synthesized by glancing angle deposition (GLAD) via e-beam evaporation possess notable sensing properties towards H_2 [24]. The Pd-coated SnO_2 NRs exhibited a superior sensing response compared to other SnO_2 based sensors with a detection limit of 0.2 ppm at room temperature. With this excellent performance as a gas sensor,

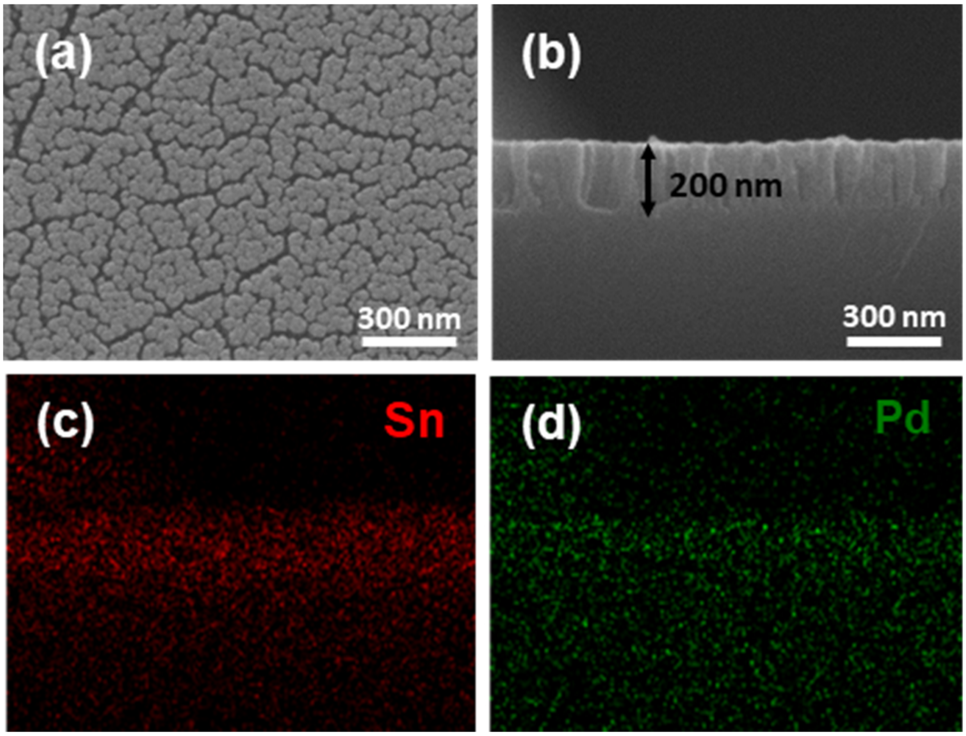

Fig. 3. SEM images of the (a) top and (b) cross-sectional views of Pd-coated SnO_2 NRs and elemental color mapping images for (c) Sn and (d) Pd using energy dispersive X-ray spectroscopy (EDS).

we decided to investigate its sensing characteristics to C_2H_2, because MOS based gas sensors usually have high responses for various types of gases. Furthermore, since production of H_2 is accompanied by that of C_2H_2, it is necessary for a H_2 gas sensor to overcome a selectivity issue, a common obstacle for MOS sensors. Introducing a column for GC to a gas sensing device would help overcome this problem by separating two gases.

In this work, we investigated the sensing properties of the bare and noble metal (Au, Pt and Pd) coated SnO_2 NRs to C_2H_2. We found that a noble metal on the surface of SnO_2 NRs significantly enhanced their sensing properties. This was owing to the spill-over effect of the noble metals by creating a higher proportion of oxygen defect sites. We demonstrated that the Pd-coated SnO_2 NRs sensor integrated with a GC column can sensitively and selectively detect acetylene in a mixed gas within 2 min.

2. Materials and methods

2.1. Synthesis and characterization of SnO_2 nanorod arrays

SnO_2 nanorod arrays (SnO_2 NRs) were fabricated on Al_2O_3 substrate (0.5 × 0.25 mm^2) supplied with Pt interdigited electrodes and heating components by glancing angle deposition (GLAD) via e-beam evaporation (Fig. 1(a)). Commercial SnO_2 granules (4 N purity, Kojundo Chemical Laboratory Co., Ltd.) were used as SnO_2 source inside a 7cc-crucible and all conditions for the experiment were mentioned in a previous report [24,25]. The incident angle for the deposition was 80° with respect to the vapor flux and the substrate was rotating at a speed of 15 rpm. The growth rate was maintained at 1 Å/s and the process was initiated at an pressure of 5.0×10^{-6} torr. The process was conducted at room temperature and sensors were heat treated at 550 °C for 2 h afterwards.

Thin metal films (Au, Pt, Pd) were deposited on the top of the SnO_2 NRs using an ultra-high vacuum DC sputtering system (SNTEK Co., Ltd; Fig. 1(b)). The deposition was conducted at a pressure of 3.4×10^{-7} torr and 34 sccm of Ar was injected for initiation. The deposition rates of Au, Pt, and Pd were 0.67 nm/s, 0.28 nm/s, and 0.31 nm/s, at working powers of 30 W, 20 W, and 30 W, respectively.

The microstructures and the crystallinity of the fabricated SnO_2 NRs were investigated by field emission-scanning electron microscopy (FE-SEM, JSM-7100 F) equipped with an energy-dispersive X-ray spectroscope (EDS). Surface elemental analysis was conducted by X-ray photoelectron spectroscopy (XPS, K-alpha Thermo U. K.) using Al Kα radiation.

2.2. Sensor characterization

The mini-GC system previous reported in detail [26,27] was used for all gas sensing experiments. In brief, it was equipped with a sensor based on SnO_2 NR, a packed gas chromatography column (GC column), a sampling loop, a mini-sized pump and three solenoid valves. The actual dimensions of the device were 8 × 13 × 16 cm^3 and the length and the inner radius of the column were 90 cm and 0.1 cm, respectively. The column was filled with Porapak Q (Restek), and both ends of fillers were sealed by piles of glass wool.

The selective detection procedure of the mini-GC device integrated with the SnO_2 NR based sensor is described in Fig. 2. We operated the mini-GC device with an integrated SnO_2 NR based sensor by first injecting 1 mL of target gas (C_2H_2) mixed with interfering gases in ambient air at room temperature into the sampling loop by mini-pump without pre-concentration. Consequently, the mixed gas was divided into each component after passing the packed column because the strength of interaction between each gas molecule and the column filler was different. The gases with non-polarity (e.g. H_2) and smaller size are

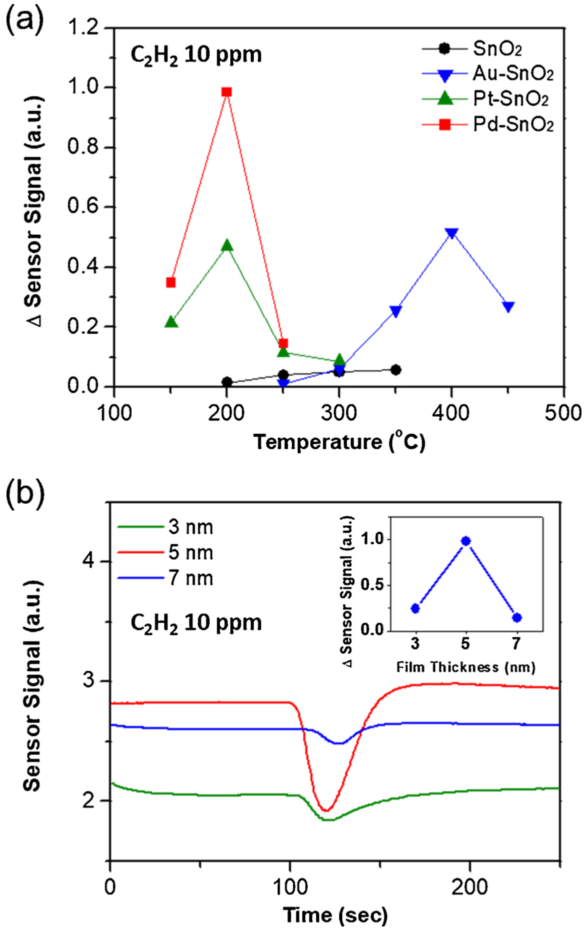

Fig. 4. (a) Sensor response (Δ sensor signal) of the device integrated with bare SnO_2 NRs and the Au-, Pt-, and Pd-SnO_2 NRs (5 nm) for an acetylene concentration of 10 ppm as a function of operating temperatures. (b) Variation of the sensor signal as a function of time for different Pd thicknesses (3, 5, and 7 nm). The inset presents the sensor response of Pd-coated SnO_2 NRs prepared with different Pd thickness at 200 °C.

released from the column faster than others because of the weak polarity of the stationary phase coated on the column filler. Thereafter, the target gas was separately detected within 3 min by the SnO_2 NRs based sensors. The operating temperature of sensors were varied for the different sensing materials based on their optimal working temperature, but that of the column was set to 25 °C.

In the mini-GC system, response of a sensor was defined as follows [26,27]:

$$\Delta SensorSignal = \log(Resistance)_{max} - \log(Resistance)_{min}$$

where *log(Resistance)max* and *log(Resistance)min* represent the resistance of the sensor when exposed to ambient air and the target gas, respectively. These values were derived from the peak height in the gas chromatograms corresponding to the relative response of the sensing material.

3. Results and discussion

In order to investigate the microstructure and the elemental distribution of the as-synthesized catalyst-coated SnO_2 NRs, we carried out FE-SEM and EDS analysis. Fig. 3(a) and (b) shows the SEM images of the top and cross-sectional views of the Pd-coated SnO_2 NRs fabricated on Al_2O_3 substrate, respectively. The nanorods were randomly distributed on the entire surface in clusters and the distance between the clusters was about 5–20 nm (Fig. 3(a)). Since the size of a single grain inside the cluster was about 30 nm in diameter, we concluded that the average diameter of a single nanorod was ~30 nm. The nanorods were vertically attached to the surface of the substrate and the average height of the nanorods was ~200 nm as depicted in the cross-sectional view of the Pd-coated SnO_2 NRs (Fig. 3(b)). EDS elemental color mapping images on the cross-sectional view of the sample (Fig. 3(c) and (d)) confirmed that the Pd nanoparticles were evenly deposited on the surface of the SnO_2 NRs.

In order to optimize the sensing performance of the SnO_2 NRs toward acetylene, we first examined the optimal working temperature and thickness of the metal catalysts of the as-synthesized SnO_2 NRs. We determined the optimal working temperature by measuring the peak heights (Δ Sensor Signal) of the bare and the different catalyst-coated SnO_2 NRs upon exposure to 10 ppm of C_2H_2 at increasing temperatures (Fig. 4(a)). The optimal working temperatures for the bare and the Au-, Pt-, and Pd-coated SnO_2 NRs (5 nm) were 350 °C, 400 °C, 200 °C, and 200 °C, respectively. Since SnO_2 NRs sensors can degrade at a temperature above 350 °C in long-term use, however, the optimal temperature for the Au-coated SnO_2 NRs was set to 350 °C, instead of 400 °C. To optimize the thickness of the catalyst coating, we used the Pd-coated SnO_2 NRs because they showed the highest sensing response in the previous test. By investigating coating thickness of 3, 5, and 7 nm, we found that depositing 5 nm of Pd led to the best sensing performance (Fig. 4(b)). We used the same thickness for the other metal coatings as well.

To evaluate the acetylene sensing performances of the as-synthesized bare and Au-, Pt-, and Pd-coated SnO_2 NRs integrated in the mini-GC system, we analyzed the changes in the sensor signal over time. The sensor signals of the samples were measured at their respective optimal working temperature at different C_2H_2 concentrations in the range of 0.01–50 ppm in dry air (Fig. 5). All SnO_2 NRs showed single peaks indicating the presence of C_2H_2 at around 120 s. Among the tested sensors, the bare SnO_2 NRs exhibited the lowest sensing properties and the metal-coating improved their responses.

To evaluate the sensing abilities of the SnO_2 NR sensors to acetylene, we estimated the sensing response (Δ Sensor Signal) from the sensor signal curves at the various C_2H_2 concentrations. Fig. 6(a) shows Δ Sensor Signal against concentration curves (both in log scales) for all fabricated SnO_2 NRs. All curves exhibited linearity and this was mainly due to an exponential relationship between sensor response and concentration [28]. The Pd-coated SnO_2 NRs, exhibited the best sensing performance at 10 ppm or lower concentrations of acetylene. At 10 ppm C_2H_2, the sensing response was ~0.06, ~0.52, ~0.47, and ~0.99 for the bare SnO_2 NRs and the Au-, Pt-, and Pd-coated SnO_2 NRs, respectively (Fig. 6(b)). Similarly, the detection limit was the lowest for the Pd-coated SnO_2 NRs (0.01 ppm) compared to the bare (1 ppm) and the Au- (0.1 ppm), and Pt-coated SnO_2 NRs (0.05 ppm; Fig. 6(b)), respectively. Accordingly, we found that the metal-coated SnO_2 NRs had significantly improved sensing abilities compared to the bare SnO_2 NRs. Therefore, it could be inferred that metal nanoparticles improved overall properties of sensors dramatically. As a result, the Pd-coated SnO_2 NRs had the best sensing performance, such as highest sensing response at C_2H_2 concentration below 10 ppm, the lowest detection limit, and the lowest optimal working temperature compared to other samples. Detecting C_2H_2 at concentrations of less than 10 ppm is crucial to prevent malfunction inside a transformer. Therefore, the Pd-coated SnO_2 NRs seem to be the best option among our investigated samples for the use in a gas analyzer of dissolved C_2H_2 in transformer oil.

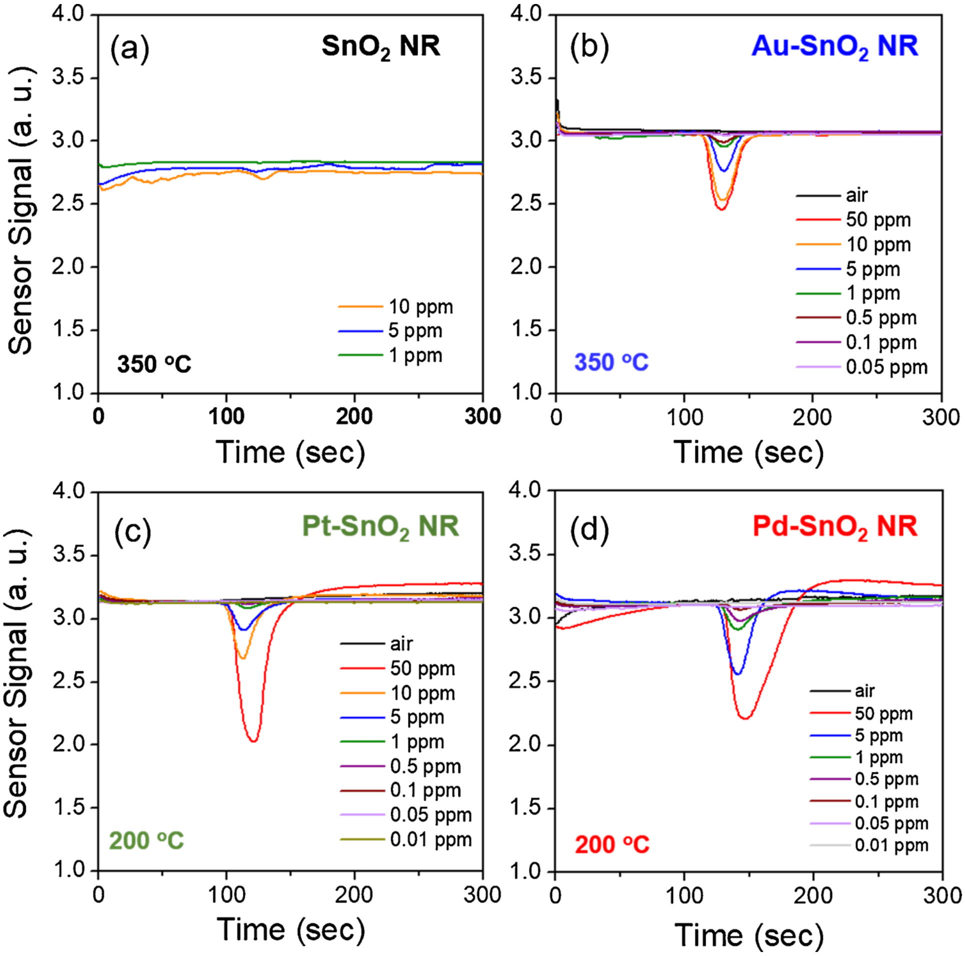

Fig. 5. Sensor signal of (a) bare, (b) Au-coated, (c) Pt-coated, and (d) Pd-coated SnO_2 NRs as a function of time for various C_2H_2 concentrations at their respective operating temperatures.

To analyze the chemical composition and oxidation states of elements in sensing materials, we performed XPS analysis (Fig. 7(a)–(d)). From XPS results, we found that all samples showed the peaks for Sn 3d (~500 eV), Sn $3p^1$ (~760 eV), and O 1s (~530 eV) [29] confirming the successful fabrication of the SnO_2 NRs. Additionally, XPS peaks for Au (e.g. Au 4f (~100 eV), Au $4d^5$ (~340 eV), Au $4d^3$ (~360 eV) and others), Pt (e.g. Pt 4f, Pt $4d^5$, Pt $4d^3$ and others), and Pd (e.g. Pd 4p, Pd 3d, Pd $3p^1$) were observed in the Au-, Pt-, and Pd-coated SnO_2 NRs, respectively. This indicates the presence of metal nanoparticles in each sample and as a consequence, successful deposition of each metal [30,31].

To investigate the cause for the differing sensing performances of the various metal coated NRs, we assessed the ratio of the oxygen vacancies in different samples. For this, we deconvoluted the O1s peaks in the XPS results of the bare, Au-, and Pt-coated SnO_2 NRs into three individual Gaussian peaks at about 530 eV (blue), 531.5 eV (green), and 532 eV (pink) (Fig. 7(e)–(g)). The peaks correspond to O^{2-} ions in SnO— bonds of SnO_2 structure, oxygen deficient sites (oxygen vacancies, and oxygen interstices), and oxygen atoms chemisorbed on the surface of SnO_2, respectively. For the Pd-coated SnO_2 NRs, we used six different peaks to deconvolute the peak at ~528 eV–540 eV because the Pd 3p peaks occurred in the same region [30] (Fig. 7(h)). The ratio of the peak assigned to oxygen vacancies varied from 19.31% in the bare SnO_2 NRs to, 25.29% in the Au-, 29.42% in the Pt-, and 32.28% in the Pd-coated SnO_2 NRs. The great increase of deficient oxygen in the metal-coated SnO_2 NRs compared to the bare NRs can be attributed to the spill-over effect of the noble metal [28]. Because this tendency correlates that of the sensing performance, the density of oxygen deficient sites such as oxygen vacancies could be related to the sensing performance of the NRs. This is corroborated by a previous study reporting that oxygen vacancies were responsible for the sensitivity of n-type MOS gas sensors [32].

Based on our findings, we propose the following sensing mechanism of Pd-coated SnO_2 NRs (illustrated in Fig. 8). In ambient air, a thicker electron depletion layer is formed inside them compared to the bare SnO_2 NRs (Fig. 8, left). This is because the work function of Pd metal is higher than that of the SnO_2 semiconductor, so that more electrons belonging to SnO_2 are transferred to Pd [33,34]. Therefore, the dissociation of the oxygen molecules into oxygen ion species at the surface of the Pd nanoparticles is enhanced. Consequently, due to the spill-over effect of Pd, the large number of oxygen ion species easily diffuses to the surface of the SnO_2 NRs [33,34], resulting in the more reactive sites for the detection of the target gas. Further, the thicker electron depletion layer limits the conduction paths of electrons inside the SnO_2 NRs, and consequently increases the resistance. As the sensor is exposed to a C_2H_2 environment, C_2H_2 molecules react with the oxygen ion species

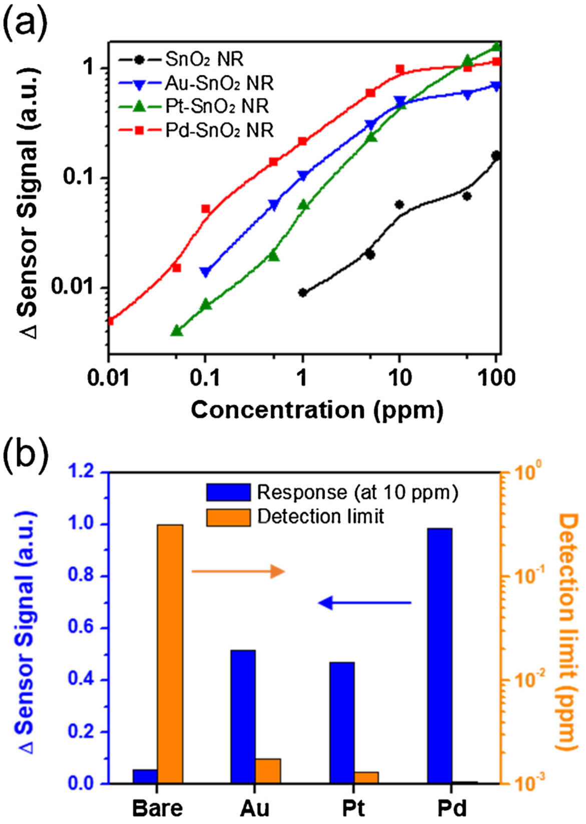

Fig. 6. (a) The sensor response of the different SnO_2 NR based sensors as a function of C_2H_2 concentration in log scales. (b) Columnar diagrams of both Δ Sensor Signal (blue, left y-axis) and detection limit (orange, right y-axis) of all sensors (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

and produce CO_2 and H_2O (Fig. 8, right). During these reactions, electrons are released back to the conduction band of the SnO_2 NRs. This leads to a decrease in the depth of depletion layers, resulting in a decrement of resistance. Pd nanoparticles might also acted as active sites for the activation of target gas molecules, thus catalyzing sensing reactions. Therefore, change of resistances for SnO_2 NRs based sensors in air and C_2H_2 environment made the detection possible.

Finally, in order to verify selectivity, we tested the selective C_2H_2 detection of Pd-coated SnO_2 NRs with a mixture gas of 10 ppm C_2H_2 and 100 ppm H_2 at an operating temperature of 200 °C. To compare the signals, air, 100 ppm H_2, and 10 ppm C_2H_2 were also separately injected and evaluated (Fig. 9). H_2 was chosen as an interfering gas since it is another main default gas frequently evolved from transformer oil. As a result, when 100 ppm H_2 and 10 ppm C_2H_2 were singly injected, a single peak was observed at 20 s and 120 s, respectively. For the gas mixture of H_2 and C_2H_2, we could detect both peaks clearly separated indicating the high acetylene sensing selectivity of the Pd-coated SnO_2 NRs. This characteristic implies that the selectivity can be achieved from gas sensors based on metal oxide semiconductor by integrating with a GC column. We believe that this device would be applicable to an on-line sensing system for diffused gases from transformer oils filtered by membrane filters, thus enabling a real-time monitoring system for transformers.

4. Conclusion

In conclusion, we report on a miniaturized gas chromatography (GC) device equipped with a SnO_2 NR-based sensor for accurate and selective detection of C_2H_2, a critical fault gas dissolved in transformer oils. We found that Au-, Pt-, and Pd-coated SnO_2 NRs exhibited an improved sensing performance compared to the bare SnO_2 NRs. In particular, Pd-coated SnO_2 NRs with a coating thickness of 5 nm showed the best sensing response to 10 ppm C_2H_2 at the lowest optimal working temperature of 200 °C. Pd-coated SnO_2 NRs were able to detect 0.01 ppm C_2H_2 within 120 s and to selectively detect C_2H_2 in a mixture with H_2 (10 ppm C_2H_2/100 ppm H_2). The dramatically improved performance of the Pd-coated compared to the bare SnO_2 NRs was mainly attributed to an increase of oxygen deficient sites on the surface of the metal-coated SnO_2 NRs owing to the spill-over effect of the noble metal nanoparticles. In conclusion, we successfully demonstrate that by integrating Pd-coated SnO_2 NRs into a GC column, the selectivity issue of acetylene sensors can be overcome. We anticipate that the device can be utilized for real-time monitoring of evolved gases from transformer oils.

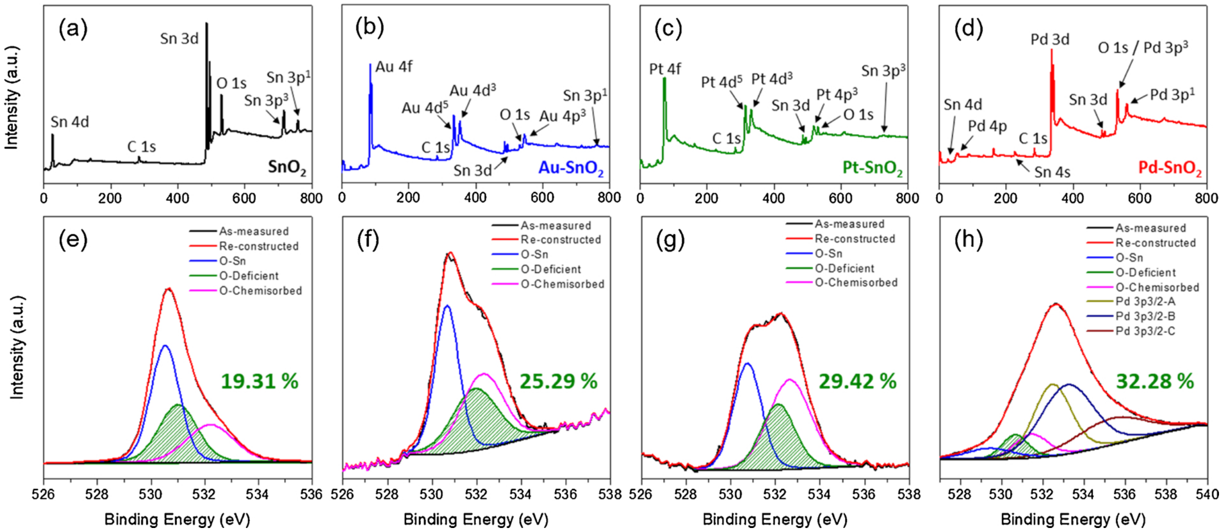

Fig. 7. Full XPS spectra of (a) bare SnO_2 NRs, (b) Au-SnO_2 NRs, (c) Pt-SnO_2 NRs, and (d) Pd-SnO_2 NRs. (e–h) Deconvolution of the O 1s peak at 525 eV–540 eV for each sensor (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

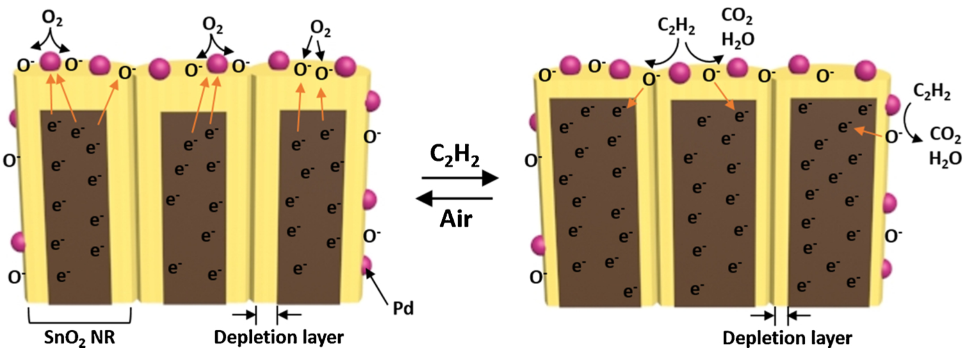

Fig. 8. Sensing mechanism of Pd-coated SnO_2 NRs. In ambient air condition (left), electrons react with oxygen molecules to form oxygen species on the surface the of SnO_2 NRs as well as thick electron depletion layers. Pd nanoparticles (pink) catalyze the reaction owing to a spill-over effect. When exposed to C_2H_2 (right), the C_2H_2 molecules react with the oxygen species and produce CO_2, H_2O, and electrons. Electrons move back to SnO_2 NRs and decrease electron depletion layers. The resistance of Pd-coated SnO_2 NRs decreases during the process (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

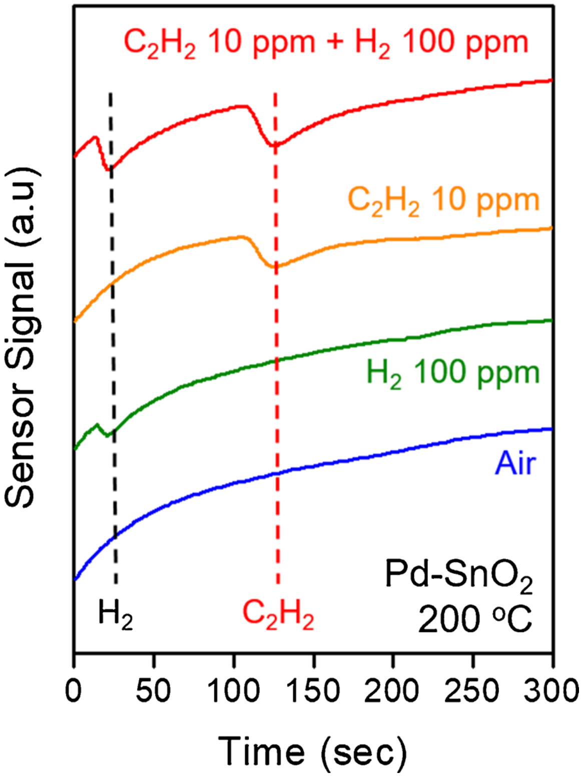

Fig. 9. The sensor signal of the mini-GC device integrated with Pd-SnO_2 NRs when exposed to air, 100 ppm H_2, 10 ppm C_2H_2, and a gas mixture of 100 ppm H_2 and 10 ppm C_2H_2 at 200 °C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] M. Duval, A review of faults detectable by gas-in-oil analysis in transformers, IEEE Electr. Insul. Mag. 18 (2002) 8–17.

[2] M. Wang, A.J. Vandermaar, K.D. Srivastava, Review of condition assessment of power transformers in service, IEEE Electr. Insul. Mag. 18 (2002) 12–25.

[3] H. He, X. Xu, Study on transformer oil dissolved gas online monitoring and fault diagnosis method, 2012 IEEE International Conference on Condition Monitoring and Diagnosis, IEEE, 2012, pp. 593–596.

[4] M. Duval, Dissolved gas analysis: it can save your transformer, IEEE Electr. Insul. Mag. 5 (1989) 22–27.

[5] J. Faiz, M. Soleimani, Dissolved gas analysis evaluation in electric power transformers using conventional methods a review, IEEE Trans. Dielectr. Electr. Insul. 24 (2017) 1239–1248.

[6] K. Nagapriya, S. Sinha, R. Prashanth, S. Poonacha, G. Chaudhry, A. Bhattacharya, et al., Laser calorimetry spectroscopy for ppm-level dissolved gas detection and analysis, Sci. Rep. 7 (2017) 42917.

[7] F. Wan, Q. Zhou, J. Zou, Z. Gu, W. Chen, C. Wang, Using a sensitive optical system to analyze gases dissolved in samples extracted from transformer oil, IEEE Electr. Insul. Mag. 30 (2014) 15–22.

[8] L. Tong, G. Wu, J. Sheng, J. Zhang, L. Zhou, Oil-gas separation mechanism of polymer membranes applied to online transformer dissolved gases monitoring, Conference Record of the 2004 IEEE International Symposium on Electrical Insulation, IEEE, 2004, pp. 97–100.

[9] X. Wang, M. Zhao, F. Liu, J. Jia, X. Li, L. Cao, C_2H_2 gas sensor based on Ni-doped ZnO electrospun nanofibers, Ceram. Int. 39 (2013) 2883–2887.

[10] Q. Zhou, C. Tang, S. Zhu, W. Chen, J. Li, Synthesis, characterisation and sensing properties of Sm_2O_3 doped SnO_2 nanorods to C_2H_2 gas extracted from power transformer oil, Mater. Technol. 31 (2016) 364–370.

[11] W. Chen, Q. Zhou, X. Su, L. Xu, S. Peng, Morphology control of tin oxide nanostructures and sensing performances for acetylene detection, Sens. Transducers 154 (2013) 195.

[12] C. Jiang, D. Zhang, N. Yin, Y. Yao, T. Shaymurat, X. Zhou, Acetylene gas-sensing properties of layer-by-layer self-assembled Ag-decorated tin dioxide/graphene nanocomposite film, Nanomaterials 7 (2017) 278.

[13] L. Jin, W. Chen, Q. Zhou, G. Xiao, C. Yu, Detection of acetylene dissolved in transformer oil using SnO_2/rGO nanocomposite gas sensor, 2016 IEEE International Conference on Power System Technology (POWERCON), IEEE, 2016, pp. 1–4.

[14] F. Li, H. Yang, R. Wang, T. Zhang, Au-loaded Sm/SnO_2 microfibers-based acetylene gas sensor with high response and selectivity, Sens. Lett. 13 (2015) 371–375.

[15] Y. Lin, C. Li, W. Wei, Y. Li, S. Wen, D. Sun, et al., A new type of acetylene gas sensor based on a hollow heterostructure, RSC Adv. 5 (2015) 61521–61527.

[16] N. Tamaekong, C. Liewhiran, A. Wisitsoraat, S. Phanichphant, Acetylene sensor based on Pt/ZnO thick films as prepared by flame spray pyrolysis, Sens. Actuators B Chem. 152 (2011) 155–161.

[17] H. Zhang, W. Chen, L. Jin, F. Cui, Hierarchically porous WO_3 microstructures with networks for acetylene sensing application, Mater. Lett. 214 (2018) 198–201.

[18] Q. Zhou, M. Cao, W. Li, C. Tang, S. Zhu, Research on acetylene sensing properties and mechanism of SnO_2 based chemical gas sensor decorated with Sm_2O_3, J. Nanotechnol. 2015 (2015).

[19] Q. Zhou, H. Liu, C. Hong, L. Xu, W. Chen, Fabrication and enhanced acetylene sensing properties of PdO-decorated SnO_2 composites chemical sensor, Sens. Lett. 14 (2016) 1144–1149.

[20] R. Malik, V.K. Tomer, V. Chaudhary, M.S. Dahiya, A. Sharma, S. Nehra, et al., An excellent humidity sensor based on In–SnO_2 loaded mesoporous graphitic carbon nitride, J. Mater. Chem. A 5 (2017) 14134–14143.

[21] V.K. Tomer, S. Duhan, A facile nanocasting synthesis of mesoporous Ag-doped SnO_2 nanostructures with enhanced humidity sensing performance, Sens. Actuators B Chem. 223 (2016) 750–760.

[22] V.K. Tomer, S. Duhan, Ordered mesoporous Ag-doped TiO_2/SnO_2 nanocomposite based highly sensitive and selective VOC sensors, J. Mater. Chem. A 4 (2016) 1033–1043.
[23] J. Fan, F. Wang, Q. Sun, H. Ye, Q. Jiang, Application of polycrystalline SnO2 sensor chromatographic system to detect dissolved gases in transformer oil, Sens. Actuators B Chem. 267 (2018) 636–646.
[24] M.H. Kim, B. Jang, W. Kim, W. Lee, Enhanced hydrogen sensing properties of Pd-coated SnO_2 nanorod arrays in nitrogen and transformer oil, Sens. Actuators B Chem. 283 (2019) 890–896.
[25] S.D. Han, M.-S. Noh, S. Kim, Y.-S. Shim, Y.G. Song, K. Lee, et al., Versatile approaches to tune a nanocolumnar structure for optimized electrical properties of In_2O_3 based gas sensor, Sens. Actuators B Chem. 248 (2017) 894–901.
[26] J.H. Lee, H. Jung, R. Yoo, Y. Park, H. Lee, Y.-S. Choe, et al., Real-time selective detection of 2-chloroethyl ethyl sulfide (2-CEES) using an Al-doped ZnO quantum dot sensor coupled with a packed column for gas chromatography, Sens. Actuators B Chem. 284 (2019) 444–450.
[27] H. Jung, W. Cho, R. Yoo, H. Lee, Y.-S. Choe, J.Y. Jeon, et al., Highly selective real-time detection of breath acetone by using ZnO quantum dots with a miniaturized gas chromatographic column, Sens. Actuators B Chem. 274 (2018) 527–532.
[28] R.W. Scott, S. Yang, G. Chabanis, N. Coombs, D. Williams, G. Ozin, Tin dioxide opals and inverted opals: near-ideal microstructures for gas sensors, Adv. Mater. 13 (2001) 1468–1472.
[29] M. Sun, Q. Zhao, C. Du, Z. Liu, Enhanced visible light photocatalytic activity in BiOCl/SnO 2: heterojunction of two wide band-gap semiconductors, RSC Adv. 5 (2015) 22740–22752.
[30] J. Kappler, N. Barsan, U. Weimar, A. Dieguez, J.L. Alay, A. Romano-Rodriguez, et al., Correlation between XPS, Raman and TEM measurements and the gas sensitivity of Pt and Pd doped SnO_2 based gas sensors, Fresenius J. Anal. Chem. 361 (1998) 110–114.
[31] P. Manjula, S. Arunkumar, S.V. Manorama, Au/SnO_2 an excellent material for room temperature carbon monoxide sensing, Sens. Actuators B Chem. 152 (2011) 168–175.
[32] R. Yoo, D. Lee, S. Cho, W. Lee, Doping effect on the sensing properties of ZnO nanoparticles for detection of 2-chloroethyl ethylsulfide as a mustard simulant, Sens. Actuators B Chem. 254 (2018) 1242–1248.
[33] A. Koo, R. Yoo, S.P. Woo, H.-S. Lee, W. Lee, Enhanced acetone-sensing properties of pt-decorated al-doped ZnO nanoparticles, Sens. Actuators B Chem. 280 (2019) 109–119.
[34] A.A. Daryakenari, A. Apostoluk, J.J. Delaunay, Effect of Pt decoration on the gas response of ZnO nanoparticles, Phys. Status Solidi (c) 10 (2013) 1297–1300.

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