NO₂ sensing properties of WO₃-decorated In₂O₃ nanorods and In₂O₃-decorated WO₃ nanorods

Bumhee Nam, Tae-Kyoung Ko, Soong-Keun Hyun* and Chongmu Lee*

Abstract
In₂O₃ nanoparticle (NP)-decorated WO₃ nanorods (NRs) were prepared using sol–gel and hydrothermal methods. The In₂O₃ NRs and WO₃ NPs were crystalline. WO₃ NP-decorated In₂O₃ NRs were also prepared using thermal evaporation and hydrothermal methods. The NO₂ sensing performance of the In₂O₃ NP-decorated WO₃ NR sensor toward NO₂ was compared to that of the WO₃ NP-decorated In₂O₃ NR sensor. The former showed a high response to NO₂ due to a significant reduction of the conduction channel width upon exposure to NO₂. In contrast, the latter showed a far less pronounced response due to limited reduction of the conduction channel width upon exposure to NO₂. When the sensors were exposed to a reducing gas instead of an oxidizing gas (NO₂), the situation was reversed, i.e., the WO₃ NP-decorated In₂O₃ NR exhibited a stronger response to the reducing gas than the In₂O₃ NP-decorated WO₃ NR sensor. Thus, a semiconducting metal oxide (SMO) with a smaller work function must be used as the decorating material in decorated heterostructured SMO sensors for detection of oxidizing gases. The In₂O₃ NP-decorated WO₃ NR sensor showed higher selectivity for NO₂ compared to other gases, including reducing gases and other oxidizing gases, as well as showed high sensitivity to NO₂.

Keywords: Gas sensor, Heterostructure, WO₃, In₂O₃, NO₂

1 Introduction
Despite the numerous merits of semiconducting metal oxides (SMOs) as sensor materials there are still certain limitations, such as their relatively low response to gases at room temperature and dissatisfactory selectivity [1]. To address the dissatisfactory sensing properties, various strategies have been attempted, including noble metal catalyst doping, heterojunction formation, and radiation-assisted treatment with energetic particles including ion beams, electrons, and ultraviolet (UV) lights [2–4]. Of these techniques, heterostructure formation is plausibly most widely studied and is used for the fabrication of chemiresistive nanostructured gas sensors. There are several types of heterostructures including p-n, n–n and p–p heterostructures. Generally, p–p heterostructures are less commonly utilized because of their inferior sensing properties, whereas n–n heterostructures are as widely utilized as the p–n counterparts because of their superior sensing properties [5]. However, strangely, n–n heterostructures have not been studied as intensively as the p–n congeners. The enhanced sensing properties of n–n heterostructures are mainly due to the resistance modulation at the n–n heterojunctions in n–n heterostructures. Various heterostructure combinations are known, such as a simple mixture of two different types of n-SMOs [6], bi-layer type n–n nanostructures [7], n–n core–shell structures [8], a single type of n-SMO nanostructure decorated with another type of n-SMO nanoparticles (NPs) [9], etc.

This study focuses on, decorated n–n heterostructures. WO₃ and In₂O₃ are chosen as sensor materials for detecting a typical oxidizing gas, NO₂. The sensing properties
of In$_2$O$_3$ NP-decorated WO$_3$ nanorods (NRs), WO$_3$ NP-decorated In$_2$O$_3$ NRs, pristine WO$_3$ NRs, and pristine In$_2$O$_3$ NRs are compared and the differences in the sensing properties of these four nanostructures are analyzed and the origin of the differences is discussed in detail.

2 Methods

2.1 Preparation of In$_2$O$_3$ nanoparticles-decorated WO$_3$ nanorods

High purity In$_2$O$_3$ NPs were synthesized using a sol–gel method [10]. Indium acetate ([In(C$_2$H$_3$O$_2$)$_2$·H$_2$O]; 0.6695 g) was dissolved in diethylene glycol and stirred for 5 min. The solution was homogenized by heating to 130 °C and 3 mL of 3 N-nitric acid was added to the solution and stirred well. The solution was heated at 180 °C for 5 h, and pure yellowish In$_2$O$_3$ NPs were precipitated. The In$_2$O$_3$ NPs were dried at 400 °C for 2 h and then calcined at 500 °C for 1 h to obtain the pure In$_2$O$_3$ NPs. The WO$_3$ NRs were synthesized by using a low-temperature hydrothermal method [11]. Sodium tungstate (1.956 mL) and oxalic acid (1.512 mL) were dissolved in distilled water (50 mL). The solution was acidified to PH 0.7–0.9 by mixing with 3 mol/L HCl solution. A transparent precursor solution was formed and 3 g of K$_2$SO$_4$ was added to the solution. The mixed solution was maintained in an autoclave at 100 °C for 24 h, cooled to room temperature, and was centrifuged to collect the green product. The product was rinsed with ethanol and dried at 60 °C for 1 h to obtain pure WO$_3$ NRs. The substrate on which the WO$_3$ NRs were synthesized was placed on a spin coater and then rotated at 500 rpm. The In$_2$O$_3$ NPs synthesized via the sol–gel method were dispersed in ethanol with a micropipette and the ethanolic dispersion of In$_2$O$_3$ NPs was dropped on the rotating WO$_3$ NR substrate.

2.2 Preparation of WO$_3$ nanoparticles-decorated In$_2$O$_3$ nanorods

In$_2$O$_3$ NRs were synthesized using a thermal evaporation method [12]. A 3 mm thick gold film—coated p-type Si (100) substrate was placed on the top of an alumina boat containing a mixture of In$_2$O$_3$ powders and positioned at the center of a horizontal quartz tube furnace. The furnace was heated to 900 °C and maintained at that temperature for 30 min under argon gas at a constant flow rate of 200 cm$^3$/min. The WO$_3$ NPs were synthesized using a hydrothermal method [13]. WO$_3$ powders (2 mL) were dissolved in 48 mL of hydrochloric acid in sonicator. The pH of the solution was controlled at 7 using sodium hydroxide. After sonication of the solution for 6 h the precipitated powders were collected by removing the liquid, leaving the powders behind. The powders were placed into a hydrothermal synthesizer containing ethanol and the synthesizer was placed in an oven and heated at 180 °C for 12 h. WO$_3$ NPs were synthesized in the hydrothermal synthesizer. The substrate on which the In$_2$O$_3$ NRs were synthesized by the thermal evaporation method was placed in a beaker containing ethanol and then ultrasonicated to separate the In$_2$O$_3$ NRs from the substrate. Meanwhile, the WO$_3$ NPs synthesized by the hydrothermal method were dispersed in ethanol. The two solutions (In$_2$O$_3$ NRs dispersed in ethanol and the WO$_3$ NPs dispersed in ethanol) were mixed and the mixed solution was exposed to UV (254 nm) irradiation for 12 h using a UV lamp. The mixed solution was then annealed under argon atmosphere at 400 °C for 1 h in an annealing furnace.

2.3 Fabrication of chemiresistive sensors

The In$_2$O$_3$ NP-decorated WO$_3$ NRs and WO$_3$ NP-decorated In$_2$O$_3$ NRs grown on the Si substrate were dispersed ultrasonically in isopropyl alcohol. A multiple-networked chemiresistive sensor was fabricated by pouring the solution containing the precursors of the two different nanostructures onto SiO$_2$/Si substrates with a patterned interdigital electrode with a double layer comprising separate layers of Ti (10 nm) and Au (100 nm): the assembly was dried at 150 °C for 1 min. For comparison of the sensing properties, pristine In$_2$O$_3$ and WO$_3$ NR sensors were also fabricated in a similar manner.

2.4 Characterization

The microstructures and phases of the synthesized NR samples were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The microstructures and phases of the samples were examined further by transmission electron microscopy (TEM).

2.5 Gas sensing tests

The NO$_2$ sensing performances of the fabricated sensors were examined using a custom-made gas sensing system. The concentration of NO$_2$ gas was controlled precisely in the concentration range of 5–200 ppm by mixing NO$_2$ with dry synthetic air using the mass flow controllers. Electrical measurements to examine the sensing properties of the sensors were conducted at room temperature under 50% relative humidity. The detailed sensing test procedure is described elsewhere [14]. The response of the sensors to NO$_2$ was evaluated by using the $R_g/R_a$ ratio, where $R_g$ and $R_a$ are the resistances of the sensor measured in the presence of air and NO$_2$, respectively. The response and recovery times were determined by measuring the times required to reach 90% of the total
change in the resistance of the sensor after exposure of the sensor to the analyte gas and ambient air, respectively.

3 Results and discussion

Figure 1a, b show low-magnification TEM images of the pristine and In$_2$O$_3$ NPs-decorated WO$_3$ NRs, respectively. The average diameter of the WO$_3$ NRs was ~50 nm and the length of the WO$_3$ NRs ranged from 200 to 1100 nm. The average diameter of the In$_2$O$_3$ NPs on the WO$_3$ NRs was 20 nm. The SEM images of the pristine and WO$_3$ NP-decorated In$_2$O$_3$ NRs are exhibited in Fig. 1c, d. The average diameter of the In$_2$O$_3$ NRs was 250 nm and the lengths of the In$_2$O$_3$ NRs ranged from 1 to 10 μm. The average diameter of the WO$_3$ NPs on the In$_2$O$_3$ NRs was 140 nm. Hence, the average diameter of the WO$_3$ NPs on the In$_2$O$_3$ NRs was ~7 times larger than that of the In$_2$O$_3$ NPs on the WO$_3$ NRs. The difference in size might be due to the different preparation methods (sol–gel versus hydrothermal methods).

Figure 2a, b show the XRD patterns of the In$_2$O$_3$ NP-decorated WO$_3$ NRs and WO$_3$ NP-decorated In$_2$O$_3$ NRs, respectively. In the former pattern, the WO$_3$ NRs exhibited relatively sharp and intense reflection peaks, assigned to the primitive tetragonal structured WO$_3$ (JCPDS card No. 89-4481, $a$ = 0.5275 nm, $c$ = 0.7846 nm). In contrast, the In$_2$O$_3$ NPs exhibited relatively less sharp and less intense reflection peaks, assigned to body-centered cubic In$_2$O$_3$ with a lattice constant of $a$ = 1.011 nm (JCPDS No. 89-4595). The lower intensity peaks for In$_2$O$_3$ compared to WO$_3$ might be due to the smaller volume of the In$_2$O$_3$ NPs relative to that of the WO$_3$ NRs. In contrast, in the latter pattern (Fig. 2b), In$_2$O$_3$ peaks were
taller and sharper than WO₃ peaks, which might be due to the larger volume of In₂O₃ NRs than those of the WO₃ NPs.

Figure 3a, b present the high-resolution TEM image and corresponding selected area electron diffraction (SAED) pattern of the In₂O₃ NP-decorated WO₃ NRs. The regularly aligned fringes in both the WO₃ and In₂O₃ regions suggest that the WO₃ and In₂O₃ nanostructures are both crystalline. The corresponding spotty electron diffraction (ED) pattern in Fig. 3b reveals that the WO₃ and In₂O₃ nanostructures are single crystals.

The temperature-dependent responses of all four different sensor materials to NO₂ are presented in Fig. 4. The responses of all the four sensor materials to NO₂ tended to increase with increasing temperature up to 300 °C, and then to decrease with further increases in the temperature. This result suggests that 300 °C is the optimal operating temperature of the sensors in detecting the NO₂. All the sensing tests hereafter were conducted at 300 °C. At too low operating temperature (250 °C or lower), the NO₂ molecules may not have enough energy to overcome the energy barrier of adsorption, and fail to be adsorbed on the surface of the sensor materials, WO₃ and In₂O₃. However, at too high operating temperature (350 °C or higher), adsorption failure might also occur because the rate of desorption may outweigh that of adsorption [15].

Figure 5a–d present the dynamic response curves of the four different sensors toward NO₂. All the sensors showed stable and reversible response and recovery behavior. The resistances of the sensors increased when an oxidizing gas (NO₂) was supplied, and recovered to the initial value when the NO₂ supply was stopped and the sensors were exposed to ambient air. This response toward the oxidizing gas is in accord with the sensing behavior of n-type semiconductors. As is well known, both WO₃ and In₂O₃ are n-type semiconductors. The resistance changes increased as the NO₂ concentration was increased. The starting resistances of the pristine and WO₃ NP-decorated In₂O₃ NRs was markedly lower than the pristine and In₂O₃ NPs-decorated WO₃ NRs, respectively, which might be due to the much lower resistivity of In₂O₃ than that of WO₃.

Figure 6 shows the responses of the four different sensors to NO₂ as a function of the NO₂ concentration. The response of the In₂O₃ NP-decorated WO₃ NRs to NO₂ far exceeded those of the other three sensors over the entire NO₂ concentration range. The more pronounced response of the In₂O₃ NP-decorated WO₃ NR sensor to NO₂ than that of the pristine WO₃ NRs and the greater response of the WO₃ NPs-decorated In₂O₃ NRs sensor to NO₂ than that of the pristine In₂O₃ NRs is plausibly due to the resistance modulation at the WO₃–In₂O₃ heterojunction formation [16]. Contrarily, the much stronger response of the In₂O₃ NP-decorated WO₃ NR sensor to NO₂ than that of the WO₃ NP-decorated In₂O₃ NR sensor is very interesting. The origin of this difference in the response of the heterostructured sensors with inverse configuration is discussed in detail in the next section.

Figure 7a, b show the response and recovery times of the four different sensors toward NO₂ as a function of the NO₂ concentration. As expected, the response and recovery times of the In₂O₃ NP-decorated WO₃ NR sensor were shorter than those of the pristine WO₃ NRs. In contrast, the response and recovery times of the WO₃ NP-decorated In₂O₃ NR sensor were longer than those of the pristine In₂O₃ NR sensor. Comparison of the response
and recovery times of the In₂O₃ NP-decorated WO₃ NR sensor with those of the WO₃ NP-decorated In₂O₃ NR sensor, interestingly, shows shorter response and recovery times for the former in the higher NO₂ concentration range, whereas longer response and recovery times for the lower NO₂ concentration range than the latter. Shorter response and recovery times are commonly associated with a higher response for gas sensors.

The response of the In₂O₃ NP-decorated WO₃ NR sensor to various gases is shown in Fig. 8. The sensor showed a much stronger response to NO₂ than to the other oxidizing gases such as O₃ and SO₂ or reducing gases such as CO, CH₄ and H₂S, demonstrating the selectivity and sensitivity of the In₂O₃ NP-decorated WO₃ NR sensor toward NO₂. The selectivity of the sensor toward NO₂ against other gases might be related to the different optimal operating temperatures of the sensor for different target gases. The response of a sensor material to a certain gas might depend on many factors such as solid solubility of the gas in the material, the decomposition rate of the adsorbed molecule at the material surface, the charge carrier concentration in the material, the Debye length in the material, the catalytic activity of the material, the orbital energy of the gas molecule, etc. The dissociation (or reduction) rate of an oxidizing gas such as NO₂ is determined by these factors. Therefore, each gas has the characteristic optimal dissociation temperature at which its dissociation rate is maximized. The In₂O₃-decorated WO₃ nanorod sensor fabricated in this study showed higher response fortunately to NO₂ than other gases at 300 °C because of the higher dissociation rate of NO₂ at the surface of In₂O₃ and WO₃ at the temperature, but it might show higher responses to other gases than NO₂ at different temperatures [17–22].

Figure 9a–d illustrate the sensing mechanism of the In₂O₃ NP-decorated WO₃ NR sensor toward NO₂. Earlier studies reported that the response of a base sensor material could be enhanced by decoration with another type of SMO NPs, mainly because of the greater modulation of the width of the depletion layer or the conduction channel, resulting in the greater modulation of the sensor resistance [23–25]. n-Type WO₃ has a larger work function ($q\Phi$) than n-type In₂O₃ (Fig. 9a). Accordingly, if WO₃ and In₂O₃ are in contact, even under vacuum, electron transfer from In₂O₃ (with a larger work function) to WO₃ (with a smaller work function) tends to
occur until electronic equilibrium is attained between WO$_3$ and In$_2$O$_3$, as shown in Fig. 9a. Consequently, electron-accumulation and electron-depletion layers are formed in the WO$_3$ and In$_2$O$_3$ regions, respectively. The schematic shows the In$_2$O$_3$ NP-decorated WO$_3$ NRs with an accumulation layer with a width of $W_{11}$, formed by electron transfer from the In$_2$O$_3$ NPs to the WO$_3$ NRs (Fig. 9b). In ambient air, the surfaces of the WO$_3$ NR and In$_2$O$_3$ NP adsorb oxygen molecules and the adsorbed oxygen molecules are ionized by the capture of the free electrons in the WO$_3$ and In$_2$O$_3$ surface regions (Fig. 9c). Consequently, a depletion layer with a width of $W_{12}$ is formed in the surface region of WO$_3$. The schematic shows a decorated WO$_3$ NR with a depletion layer formed via ionization of adsorbed oxygen molecules and an accumulation layer formed by electron transfer from the In$_2$O$_3$ to the WO$_3$ (Fig. 9c). When NO$_2$ gas is supplied, NO$_2$ and O$_2$ molecules are both adsorbed by the In$_2$O$_3$ and WO$_3$ surfaces. The adsorbed NO$_2$ molecules are converted into NO$_2^-$ or NO [26, 27] and the adsorbed oxygen molecules are converted into oxygen ions by capturing electrons from the WO$_3$ and In$_2$O$_3$ surface regions. Consequently, a thicker depletion layer (with a width of $W_{22}$) (Fig. 9d) is formed than that formed in ambient air. The schematic shows a WO$_3$ NR with a depletion layer with a width of $W_{22}$ as well as the accumulation layer with a width of $W_{21}$ formed by the electron transfer from the In$_2$O$_3$ to the WO$_3$ (Fig. 9d).

The sensing mechanism of the WO$_3$ NP-decorated In$_2$O$_3$ NR sensor toward NO$_2$ is illustrated in Fig. 9e, f.
As discussed above, electron-accumulation and depletion layers are formed in the WO$_3$ and In$_2$O$_3$ regions, respectively. Thus, a depletion layer with a width of $W_{31}$ forms on the In$_2$O$_3$ side of the WO$_3$–In$_2$O$_3$ interface (Fig. 9e). In ambient air, oxygen molecules are adsorbed by the In$_2$O$_3$ NR surface and ionized by accepting the electrons from the In$_2$O$_3$ and WO$_3$ surface regions. Consequently, a depletion layer with a width of $W_{32}$ is formed in the In$_2$O$_3$ surface region. A WO$_3$ NP-decorated In$_2$O$_3$ NR with a depletion layer formed due to the ionization of adsorbed oxygen molecules and a depletion layer formed by electron transfer from the WO$_3$ NP is shown in Fig. 9e. Under NO$_2$ atmosphere, a thicker depletion layer (with a width of $W_{42}$) than that generated in ambient air is formed due to the adsorption and ionization of both NO$_2$ and O$_2$ molecules (Fig. 9f). Note that no electron-accumulation layer is formed in the In$_2$O$_3$ NR throughout the on–off cycling of the NO$_2$ gas supply.

Under ambient air and NO$_2$, there was no big difference in the basic response of the In$_2$O$_3$ NPs-decorated WO$_3$ NRs versus that of the WO$_3$ NPs-decorated In$_2$O$_3$ NRs. A relatively thin depletion layer is formed in both samples upon exposure to air and a thick depletion layer is generated upon exposure to NO$_2$. Consequently, the width of the conduction channel of the In$_2$O$_3$ NP-decorated WO$_3$ NRs formed upon exposure to NO$_2$ is much smaller than that of the WO$_3$ NP-decorated In$_2$O$_3$ NRs formed in ambient air. The conduction channel of the In$_2$O$_3$ NP-decorated WO$_3$ NRs has a room for substantial reduction upon exposure to NO$_2$ because the conductive channel width has already been expanded due to the formation of an accumulation layer by the transfer of electrons from the In$_2$O$_3$ NP to the WO$_3$ NR. In contrast, the conduction channel of the WO$_3$ NPs-decorated In$_2$O$_3$ NRs was already shrunk due to the formation of the electron-depletion layer via electron transfer from the In$_2$O$_3$ NR to the WO$_3$ NP. Accordingly, the conduction channel of the In$_2$O$_3$ NR has little room for further reduction upon exposure to NO$_2$ [28].

The response, $S$ is defined as $R_g/R_a$, for the oxidizing gas NO$_2$ and $S$ is proportional to $A_g/A_a$ because the resistance $R = \rho l/A$, where $\rho$, $l$ and $A$ are the density, length and cross-sectional area of the conductor (channel, here) [29]. $S$ can be expressed as the ratio of the conduction channel width for an analyte gas to that for air, $S = W_g^2/W_a^2$ because $A = \pi W^2$, where $W$ is the conduction channel width. Therefore, the In$_2$O$_3$ NP-decorated WO$_3$ NR sensor has a higher response, $S$ to NO$_2$ because of the far smaller conduction channel width, $W_g$ in NO$_2$ atmosphere. In contrast, the WO$_3$ NP-decorated In$_2$O$_3$ NR sensor has a lower response, $S$ because
Fig. 9 Energy band diagrams of a WO$_3$-In$_2$O$_3$ couple a before and b after contact. Energy band diagrams and schematics of In$_2$O$_3$ NPs-decorated WO$_3$ NRs: c in air and d in NO$_2$, and of WO$_3$ NPs-decorated In$_2$O$_3$ NRs: e in air and f in NO$_2$. 
of the lower contraction of the conduction channel width, $W_g$, in NO₂ atmosphere.

4 Conclusions
The sensing properties of the In₂O₃ NP-decorated WO₃ NR sensor toward NO₂ were compared to those of the WO₃ NP-decorated In₂O₃ NR sensor. The response of the former sensor to NO₂ was more pronounced than that of the latter due to the significant reduction of the conduction channel width of the former sensor upon exposure to NO₂. The conduction channel of the In₂O₃ NP-decorated WO₃ NR sensor had room for sufficient reduction as it was already expanded by electron transfer from the In₂O₃ NPs to the WO₃ NRs. In contrast, the WO₃ NP-decorated In₂O₃ NR sensor showed a lower response due to insufficient reduction of the conduction channel width upon exposure to NO₂. The conduction channel of the WO₃ NP-decorated In₂O₃ NR sensor had little room for further reduction due to prior shrinkage associated with electron transfer from the In₂O₃ NRs to the WO₃ NPs. For the detection of a reducing gas instead of an oxidizing gas, the magnitude of the sensor response would be reversed. Therefore, choosing a proper decorating material in fabricating n-SMO NR sensors decorated with n-SMO NPs is important in obtaining high sensitivity. An SMO with a smaller work function must be chosen as a decorating material in a decorated heterostructured sensor for oxidizing gas detection. In contrast, an SMO with a larger work function must be chosen as the decorating material for heterostructured sensors geared toward the detection of a reducing gas.

Competing interests
The authors declare that they have no competing interests.

References
1. A.C. Romain, J. Nicolas, Long term stability of metal oxide-based gas sensors for e-nose environmental applications: an overview. Sens. Actuators B Chem. 146, 502–506 (2010)
2. G. Lu, L.E. Ocola, Room-temperature gas sensing based on electron transfer between discrete tin oxide nanocrystals and multiwalled carbon nanotubes. Adv. Mater. 21, 2487 (2009)
3. D.R. Miller, S.A. Akbar, P.A. Morris, Nanoscale metal oxide-based heterojunctions for gas sensing: a review. Sens. Actuators B 204, 250–272 (2014)
4. D.S. Dhaivale, R.R. Salunkhe, V.J. Fulari, M.C. Rath, S.N. Saviant, C.D. Lokhande, Liquefied petroleum gas (LPG) sensing performance of electron beam irradiated chemically deposited TiO₂ thin films. Sens. Actuators B 141, 58–64 (2009)
5. H.J. Kim, J.H. Lee, Highly sensitive and selective gas sensors using P-type semiconductors: Overview. Sens. Actuators B 192, 607–627 (2014)
6. D. Shaposhnik, R. Pavelko, E. Llobet, F. Gispert-Guirado, X. Vilano, Hydrogen sensors on the basis of SnO₂–TiO₂ systems. Proc. Eng. 25, 1133–1136 (2011)
7. R. Vasilev, M. Rumyantsseva, Effect of interdiffusion on electrical and gas sensor properties of CuO/SnO₂ heterostructure. Mater. Sci. 57, 241–246 (1999)
8. S. Park, S. Kim, H. Hee, C. Lee, Oxidizing gas sensing properties of the n-ZnO/Co₃O₄ composite nanoparticle network sensor. Sens. Actuators B Chem. 222, 1193–1200 (2015)
9. U. Shaislamov, B.L. Yang, CdS sensitized single-crystalline TiO₂ nanorods and polycrystalline nanotubes for solar hydrogen generation. J. Mater. Sci. 48, 418–423 (2012)
10. J. Poullier, J.C. Blanpain, I.P. Texier, J.M. Cattin, J.A. Darr, Gas sensing with nano-indium oxides (In₂O₃) prepared via continuous hydrothermal flow synthesis. Langmuir 28, 1879–1885 (2012)
11. Y. Yan, L. Chou, Competitive growth of In₂O₃ nanorods with rectangular cross sections. Appl. Phys. A 92, 401–405 (2008)
12. J.K. Lee, W.S. Lee, W.I. Lee, S.B. Choi, S.K. Hyun, C.M. Lee, Selective detection of a reducing gas using WO₃-decorated ZnO nanorod-based sensor in the presence of oxidizing gases. Phys. Status Solidi A 215, 170929 (2018)
13. M. Shibuya, M. Mayauchi, Site-selective deposition of metal nanoparticles on aligned WO₃ nanotrees for super-hydrophilic thin films. Adv. Mater. 21, 1373–1376 (2009)
14. S.H. Kim, S.H. Park, S.Y. Park, C.M. Lee, Acetone sensing of Au and Pd-decorated WO₃ nanorod sensors. Sens. Actuators B 209, 180–185 (2015)
15. G.J. Sun, J.K. Lee, S.B. Choi, W.I. Lee, H.W. Kim, C.M. Lee, Selective oxidizing gas sensing and dominant sensing mechanism of n-CaO-Degraded n-ZnO nanorod sensors. ACS Appl. Mater. Interfaces 9, 9975–9985 (2017)
16. W. Wang, Z. Li, W. Zheng, H. Huang, C. Wang, J. Sun, Cr2O3-sensitized ZnO electrospun nanofibers based on ethanol detectors. Sens. Actuators B 215, 734–758 (2015)
17. K. Parray, P. Santhanam, J. Mangos, B. Rambabu, Electrocalytic performance of In₂O₃-supported Pt/C nanoparticles for ethanol electro-oxidation in direct ethanol fuel cells. Int. J. Electrochem. Sci. 5, 1342–1354 (2010)
18. K.J. Choi, H.R. Kim, K.M. Kim, D. Liu, G. Cao, J.H. Lee, C₂H₅OH sensing characteristics of various Co₃O₄ nanostructures prepared by solvothermal reaction. Sens. Actuators B Chem. 146, 183–189 (2010)
19. Y.L. Li, Y. Xu, J. Chao, D. Chen, S. Ouyang, J. Ye, G. Shen, High-aspect-ratio single-crystalline porous In₂O₃ nanobelts with enhanced gas sensing properties. J. Mater. Chem. 21, 12852–12857 (2011)
20. Z. Wen, L. Tianmo, Gas-sensing properties of SnO₂-TiO₂-based sensor for volatile organic compound gas and its sensing mechanism. Phys. B 405, 1345–1348 (2010)
21. C. Feng, W. Li, C. Li, L. Zha, H. Zhang, Y. Zhang, S. Ruan, W. Chen, L. Yu, Highly efficient rapid ethanol sensing based on In₂O₃-NiO nanofibers. Sens. Actuators B Chem. 166–167, 83–88 (2012)
22. S. Park, S. Kim, G. Sun, C. Lee, Synthesis, structure, and ethanol gas sensing properties of In$_2$O$_3$ nanorods decorated with Bi$_2$O$_3$ nanoparticles. ACS Appl. Mater. Interfaces 7, 8138–8146 (2015)

23. K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. 79, 7983–7990 (1996)

24. H.S. Woo, C.W. Na, I.D. Kim, J.H. Lee, Highly sensitive and selective trimethylamine sensor using one-dimensional ZnO–Cr$_2$O$_3$ heterostructures. Nanotechnology 23, 24550123 (2012)

25. M. Mashock, K. Yu, S. Cui, S. Mao, G. Lu, J. Chen, Modulating gas sensing properties of CuO nanowires through creation of discrete nanosized p–n junctions on their surfaces. ACS Appl. Mater. Interfaces 4, 4192–4199 (2012)

26. T.V. Belysheva, L.P. Bogovtseva, E.A. Kazachkov, N.V. Serebryakova, Gas-sensing properties of doped In$_2$O$_3$ films as sensors for NO$_2$ in air. J. Anal. Chem. 58, 583–587 (2003)

27. R. Ferro, J.A. Rodríguez, P. Bertrand, Peculiarities of nitrogen dioxide detection with sprayed undoped and indium-doped zinc oxide thin films. Thin Solid Films 516, 2225–2230 (2008)

28. S.W. Choi, A. Katochi, J.H. Kim, S.S. Kim, Striking sensing improvement of n-type oxide nanowires by electronic sensitization based on work function difference. J. Mater. Chem. C 3, 1521–1527 (2015)

29. E. S. Yang, Fundamentals of Semiconductor Device (McGraw-Hill Inc., New York, 1978). ISBN 10: 0070722366 ISBN 13: 9780070722361

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.