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Design and Fabrication of Highly Selective H_2 Sensors Based on SIM-1 Nanomembrane-Coated ZnO Nanowires

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ABSTRACT

High quality hydrogen sensors are of an utmost importance in many industrial applications to efficiently address the safety issues concerning the production, delivering, storage and use of H_2 gas. Recently a special effort has been devoted to modification of semiconductor metal oxides in order to improve their gas sensing characteristics. In this context here we report on the preparation of a novel ZnO-based semiconductor sensor modified by a thin SIM-1 hydrogen selective membrane serving as an efficient molecular sieving layer. Compared to pristine ZnO sensors, the optimized SIM-1 coated ZnO nanowires showed remarkable selectivity towards H_2 at high temperatures (300 °C) in the presence of numerous interfering

gases (CH_3COCH_3, CH_4, C_7H_8, C_2H_5OH and C_6H_6) thus confirming the efficiency of such sensor material for hydrogen detection.

INTRODUCTION

Hydrogen (H_2) gas is a promising source of energy that might address the challenge of irreversible climate change, uncertain oil supply, and rising pollution.[1] Accordingly, it is used in a wide range of fields, such as fuel cells,[2] cars with H_2 engines[3] and others. However, the applications of H_2 also possess some inherent problems. First of all, H_2 is extremely dangerous as it is both flammable and explosive at concentrations of >4 vol.% and 15-59 vol.%, respectively.[4] In addition it has low sparking energy of 0.017 mJ, and ignition temperature of 250°C, which can cause an electrostatic discharge.[5] Finally, H_2 is an odourless and colourless gas with high diffusivity making it one of the most challenging gases to be detected.[6] Safety issues concerning its production, delivery, storage and use must be therefore always considered, and secured e.g. by the presence of efficient H_2 sensors. An ideal H_2 gas sensor should be highly sensitive, selective, and stable.[7] The most popular example in this area are metal oxide-based gas sensors because of their numerous advantages for gas sensing such as enhanced sensitivity, portability, simple design, on-line operation, rapid response time, stability and, last but not least, low cost.[8] Among different metal oxide-based sensors, ZnO as a dexterous n-type metal oxide is considered as a unique material in gas detection. In particular, it has excellent sensing properties due to high mobility of electron carriers and large band gap (3.37 eV).[9] Accordingly, numerous studies have been reported in the literature about H_2 sensing with ZnO.[10, 11] Moreover, this oxide can be easily synthesized in a variety of relevant morphologies such as networked nanowires (NWs),[12] yielding faster response and superior sensitivity to the target gas in comparison with other NWs configurations.[13] Nevertheless networked ZnO NWs often suffer from poor selectivity, which is defined as the ability of a sensor to respond to a specific gas in the presence of a gas

mixture.[8] Different strategies have been reported to overcome low selectivity of metal oxides such as control of sensing temperature, electrode configuration, thickness of the sensing layer, application of sensor arrays, use of filters, etc.[14] In this context, the use of filters is an attractive approach for improving the gas sensors selectivity; selective charcoal adsorbers have been applied commercially for CO sensors to avoid the interfering effects of hydrocarbon compounds.[15] Another strategy for the implementation of filter materials is based on the application of either permselective barriers (membranes) or catalytic films on the sensor surface. Indeed, permselective barriers can physically retain interfering gases as a function of their kinetic diameter (molecular sieving effect), while catalytic films may transform interfering molecules into inactive species.[16] In the case of molecular sieves, ultramicroporous materials with mesh sizes smaller than 0.7 nm are of a particular interest[16] because such pore apertures fit the kinetic diameters of the most common gases.

In this respect, metal organic frameworks (MOFs) have attracted significant attention due to ultrahigh porosity, structural tunability, composition flexibility and huge equivalent internal surface areas. A special attention has been recently devoted to zeolitic imidazolat frameworks, e.g. ZIF-8, as an attractive ultramicroporous material with good thermal and chemical stability. It has a relatively rigid but open crystalline framework with a huge potential for the extraction of H_2 from gas mixtures.[17] In the area of gas sensing, the zeolitic imidazolate frameworks materials are expected to increase both sensors response sensitivity (preconcentration effect by enhanced species uptake) and selectivity (size/shape exclusion effect by molecular sieving). The high potential of such materials has been recently demonstrated by our research group for a ZIF-8 coated ZnO NWs sensor exhibiting a high selectivity towards H_2 in the presence of large gas molecules such as C_6H_6 and C_7H_8.[18] Recently, Wu et al.[19], also reported an excellent selective response of H_2 in the presence of CO using ZIF-8 coated ZnO nanorods gas sensors. In order to further improve the gas sensing selectivity towards hydrogen, in this work we report on a novel nanocomposite sensor composed of ZnO NWs homogeneously

coated with a SIM-1 (substituted Imidazolate material-1) membrane layer. SIM-1 is an isostructural material with ZIF-8 with a cage size ~ 0.8 nm and expected pore aperture <0.34 nm,[20, 21] thus having a great potential as selective barrier allowing small gases such as hydrogen (2.89 Å) passing through easily, while retaining other larger gases or vapors such as CH_4 (3.8 Å), C_2H_5OH (4.5Å), CH_3COCH_3 (4.6 Å), C_7H_8 (5.85 Å) and C_6H_6 (5.85Å) (Figure 1). The potential of the SIM-1 material as a membrane barrier for the separation of hydrogen from other gases (e.g. CO_2, N_2, CH_4) has been demonstrated elsewhere.[22]

To the best of our knowledge, in the area of gas sensors, the SIM-1 coated ZnO NWs for a selective detection of hydrogen has never been reported yet. Gas sensing experiments evidenced that, in contrast with pristine ZnO NWs sensor, its counterpart coated with SIM-1 thin layer exhibits an excellent selectivity towards H_2 in the presence of a number of interfering gases thanks to the unique molecular sieving potential of SIM-1 membrane homogeneously covering the ZnO nanowires.

MATERIALS AND METHODS

The overall fabrication process of SIM-1 coated ZnO nanowires (ZnO NWs) sensor is schematically shown in Figure 2. It results from a combination of the authors' expertise in the areas of both semiconductor metal oxides (SMOs)-based sensors and synthesis of MOF-based membranes. The synthesis of SIM-1 coated ZnO NWs sensor in the present work involved two key steps: i) growth of ZnO NWs on the sensor substrate; and ii) controlled solvothermal conversion of the ZnO NWs top-surface, in order to grow an ultrathin SIM-1 molecular sieve membrane covering the ZnO NWs. The synthesis procedure was optimized in such way to get a maximal selectivity in gas sensing response for H_2 in the presence of other interfering gases.

1. Synthesis of ZnO nanowires.

ZnO NWs were grown on a patterned interdigital electrode (PIDE) that had been fabricated on SiO_2 (200 nm thick)-grown Si (100) substrates using a lithography technique. The PIDE consisted of tri-layers of Au (3 nm)/Pt (200 nm)/Ti (50 nm) films which were deposited sequentially using sputtering. Both ZnO powders (in alumina boat) and the wafer with as-fabricated PIDE were put in a horizontal-type tube furnace. The temperature was maintained at 950 °C for 1 hour while flowing Ar and O_2 through the tube furnace at rates of 800 and 50 sccm respectively. At high temperatures, ZnO NWs were grown selectively on the Au catalytic layer and formed a 3-dimensional network.

2. Synthesis of SIM-1 coated ZnO NWs sensor

The ZnO NWs were introduced in a closed pressure vessel (Teflon®-lined stainless-steel autoclave – 45 ml) and submitted to a solvothermal treatment in a solution containing 4-methyl-5-imidazolecarboxaldehyde ($C_5H_6N_2O$ - Sigma Aldrich -99%) dissolved in methanol (1 wt.%). The autoclave was heated in conventional oven at 100° C for 5h and cooled down to room temperature. The resulting SIM-1 coated ZnO NWs sensor was then washed several times with methanol and dried at 70°C for 2h to remove the solvent. This protocol, based on MOFs grow using only ZnO as the metal source, has been adapted from a synthesis strategy of ZIF-8 membranes and films already published by the authors [23-25]. The washing procedure using methanol has been adopted from a protocol published elsewhere [21].

3. Characterizations

The characteristics of both virgin ZnO and SIM-1 coated ZnO NWs sensor were studied at different locations on the gas sensor support, using a high resolution scanning electron microscope (FESEM, Hitachi S-4800). Samples have been studied by transmission electron microscopy (HR-TEM, FEI Tecnai F20) using different analyses including TEM imaging. The phase and crystallinity of synthesized products were studied using grazing incidence X-

ray diffraction (GIXRD, Bruker D5000 with CuKα radiation). Surface chemical composition was studied by X-ray Photoelectron Spectroscopy (XPS) (ESCALAB 250 Thermal Electron) with AlKα (1486.6 eV). Binding energies were calibrated by using the carbon containment (C1s = 284.4 eV). Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT 2960, under air atmosphere in the temperature range 25-600°C - at heating rate of 5°C/min.

4. Gas sensing measurements

The gas sensing performance of the pristine and SIM-1 coated ZnO NWs sensors was studied by exposing the sensors to different gases at various temperatures. The main target was a selective detection of H_2 and it was tested with interfering gases and vapours, in order to evaluate the sensors selectivity. The gas concentrations were controlled by changing the mixing ratio of dry air and dry air-balanced target gas using mass flow controllers. The gas sensing system used in this study was similar to that in our previous works.[11, 26] The sensors resistances in the presence of air (R_a) and target gas/vapour (R_g) were carefully recorded and the sensors response (R) was defined as R_a/R_g.

RESULTS AND DISCUSSION

The preparation of highly selective hydrogen gas sensors based on SIM-1 coated ZnO NWs has been based on a controlled functionalization of ZnO NWs by their partial conversion to a SIM-1 selective barrier homogeneously covering the ZnO nanowires (Figure 2). The synthesis protocol has been optimized in order to get a maximal selectivity in gas sensing response to H_2 in the presence of methane, ethanol, acetone, benzene, and toluene. The as-prepared materials have been characterized through a comparison of both pristine ZnO NWs and derived SIM-1 coated ZnO.

1. Synthesis of SIM-1 coated ZnO sensors

The typical microstructure of the ZnO nanowires 3-dimensional network connecting neighboring electrode pads on the gas sensor support can be observed in Figure 3a. This nanowire–nanowire junction provides the electrical pathway whose resistance changes as a function of both concentration and nature of the molecules getting into a contact with the sensor. The SIM-1 coated ZnO NWs have been synthetized by solvothermal conversion of pristine ZnO nanowires exposed to a methanolic solution of 4-methyl-5-imidazolecarboxaldehyde ($C_5H_6N_2O$; 1 wt.%) at 100°C for 5h. The above reaction conditions were selected after a series of experiments examining the extent of ZnO NWs conversion to SIM-1. In fact the conversion degree of the metal oxide has to be sufficient to ensure a uniform coverage of the ZnO NWs with a continuous SIM-1 layer, while leaving a sufficient quantity of ZnO core in the wire in order to maintain the nanowire–nanowire junction. Under solvothermal conditions, the $C_5H_6N_2O$ ligand reacts with the ZnO NW surface and coordinates with Zn^{2+} ions to grow the SIM-1 material on the ZnO NW surface. Considering the low dissociation rate of ZnO to Zn^{2+} under the mild applied reaction conditions (1wt.% $C_5H_6N_2O$ in methanol, 100°C, 5h), relatively slow growth rates were expected, with only a partial ZnO conversion to SIM-1, thus maintaining the initial gas sensor architecture. FESEM observations of the ZnO nanowires after the solvothermal treatment (Figure 3b) clearly confirms a preservation of the three-dimensional interwoven nanofibers mat architecture on the sensor support. Closer comparison of the SIM-1 coated ZnO NWs with the pristine ZnO nanowires allows to conclude that after the synthesis the initially individual nanowires (Figure 3a) are more stacked together (Figure 3b), thus forming larger bridge connections between the electrode pads. The HRTEM analysis (TEM imagery) confirmed that the sensor support is well composed of ZnO nanowires whose core is coated with a SIM-1 nanomembrane shell which covers homogeneously the entire nanowire surface. This uniform shell is expected to serve as an effective selective membrane that it does not contain any undesirable defects, i.e.

non-selective preferential pathways for gas transport. In fact, the STEM X-ray maps (Figure 3d) showed that the shell covering the ZnO NWs is composed of Zn, C, N and O, as expected for a SIM-1 material. In addition, STEM/EDX line scan (Figure S1) confirmed the presence of ZnO at the centre of the nanofibers (high quantity of Zn and O atoms), surrounded by N, O, C and Zn-based material corresponding to SIM-1. The presence of both ZnO and SIM-1 in the final composite material has been further attested by GIXRD measurements (Figure 3c and Figure S2), detecting the principal diffraction lines of both SIM-1 (2θ= 7.3°, 10.2°, 12.6°, 15.0°,19.5°) and ZnO (2θ = 31.7°, 34.4°, 36.2°). Finally, the coexistence of both SIM-1 and ZnO has been also verified by XPS measurements (Figure S3). The XPS spectra shows that all the expected features were observed: the binding energies C 1s, O 1s, Zn 2p3, and N 1s at 284.87, 398.90, 530.85 and 1021.33 eV respectively, thus confirming the formation of SIM-1 coated ZnO NWs.

2. Sensing studies and gas sensing mechanism

Sensing temperature is one of the most important parameters which determines the gas sensitivity of sensors. Indeed, adsorption, desorption, diffusion and reaction phenomena strongly depends on the operating temperature, which ultimately affects the sensor performance.**[27]** Therefore, the first step is to determine the optimal working temperature of the sensor. Figure 4a shows the dynamic resistance curves of the SIM-1 coated ZnO NWs sensor at different temperatures in the range 100-300°C towards various concentrations of H_2. The maximum temperature was set at 300°C, since TGA of an equivalent SIM-1/ZnO composite powders (Figure S4), confirmed that the material was stable till 350°C.

As evidenced in Figure 4a, upon exposure to H_2 gas, the sensor resistance decreases. Considering the fact that H_2 is a reducing gas, this observation confirms the n-type behaviour of the fabricated sensor which does not change the original semiconducting property of ZnO by its coverage with SIM-1. Moreover, the signal returns to its initial baseline value after

stoppage of H_2, suggesting the reversible adsorption of H_2 on the sensor surface. This phenomenon is very important from a practical point of view since in real gas sensing applications, sensors are often exposed to either air or H_2. Finally, increasing the H_2 concentration from 10 to 50 ppm, the response signal is accentuated. Indeed, for higher H_2 concentration, the surface reactions are enhanced due to larger surface coverage of the sensor with H_2, thus resulting in a more pronounced signal change. Figure 4b shows the variations of the sensors response at different temperatures. At low temperatures (up to 200°C), the H_2 molecules do not have enough energy to overcome the energy barrier for an adsorption on the sensor surface. Hence, the sensor response values are very low, e.g. only 1.011, 1.012 and 1.019 at 100, 150 and 200°C, respectively for 10 ppm H_2 concentration. Contrary, at higher temperatures, the sensors sensitivity increases significantly with a maximum response ~1.64 obtained at 300°C. Considering both the good thermal stability of the sensor and its high sensing response, all the other tests were performed at this temperature.

For the sake of testing the sensor selectivity towards various gases, the as-prepared SIM-1 coated ZnO NWs sensor was exposed to different interfering gases and vapours such as C_6H_6, CH_4, C_7H_8, C_2H_5OH and CH_3COCH_3. The dynamic resistances of the above compounds were compared with that of H_2 at the optimal working temperature (300°C) (Figure 5). It can be seen that there is almost no change in the sensor resistance thus suggesting no interfering effect of the tested gas. However, in a comparative view, the response to H_2 is noticeable. This finding clearly demonstrates the effectiveness of SIM-1 membrane as a molecular sieve barrier. In fact, as presented in the introduction part, SIM-1 pore aperture is larger than the kinetic diameter of H_2 molecules but lower than that of other interfering gases. Hence, only the penetration of H_2 molecules is theoretically possible, while the transport of other molecules should be blocked by the selective SIM-1 membrane. The small H_2 molecules can diffuse easily through the SIM-1 membrane network and reach the ZnO NWs surface, thus ensuring the preservation of a significant H_2 response. Indeed, the high adsorption capacity of

the SIM-1 structure is expected to further contribute to enhance the H_2 selectivity of the SIM-1 coated ZnO NWs sensor. Assuming the pore aperture of SIM-1 (<3.4Å, see Introduction) and the size of oxygen molecules characterized by their small van der Waals diameter d_{vdW} = 2.8Å, the oxygen from air could potentially pass through the membrane and reach the sensor surface during the recovery period.

In order to compare the sensing performance of SIM-1 coated ZnO NWs sensor with those of the pristine ZnO NWs sensor, the latter was exposed to both H_2 and other gases at 300°C. The dynamic resistance curves are shown in Figure S5. In contrast to a SIM-1 coated ZnO NWs sensor, the pristine ZnO NWs sensor shows high response to both H_2 (main gas) and interfering gases. For an easier comparison, Figure 6 represents the calibration curves of ZnO NWs sensor response to different gases as a function of their concentration. For example, the response to 50 ppm of H_2, CH_3COCH_3, CH_4, C_7H_8, C_2H_5OH and C_6H_6 are 3.17, 1.74, 1.64, 1.58, 1.49 and 1.4 respectively, demonstrating clearly the effectiveness of the SIM-1 membrane for blocking the transport of interfering gases. A simple graphical representation of the gas response/selectivity for both pristine and SIM-1 coated ZnO NWs sensor is depicted in Figure 7. It can be seen that for interfering gases, the SIM-1 coated ZnO NWs sensor shows no response, thus proving an excellent selectivity towards H_2. On the other hand, the pristine ZnO shows a detectable response to the interfering gases, thus leading to low H_2 selectivity. It must be noted that the response of SIM-1 coated ZnO NWs sensor towards H_2 (2.56) was slightly lower than that of pristine ZnO NWs sensor (3.17). This phenomenon is attributed to the limited H_2 diffusion through the SIM-1 membrane network which controls the access of H_2 to the surface of ZnO NWs. It should be emphasized that such a lower response does not present any drawback for gas detection as in real applications a low response can be effectively amplified by an electrical circuit. Indeed, the most important parameter in gas detection is the selectivity which needs to be as high as possible in order to provide efficient

gas sensing response. In this context, the novel approach presented in this study seems very promising for an enhancement of sensor response.

Since in real applications two or more interfering gases may be present in the environment, we have also performed gas sensing tests in the presence of a gas mixture. In this respect, we mixed H_2 gas with toluene (C_7H_8) gas and tested the sensor response towards (H_2+C_7H_8) gas pair. As shown in Figure 8 (a), the response of SIM-1 coated ZnO NWs sensor to (H_2+C_7H_8) mixed gases is much higher than that of C_7H_8 single gas and is almost equal to the sensor response of sensor to H_2 single gas (Figure 8 (b)). In contrast, as expected, the response to C_7H_8 single gas is negligible. This experimentally demonstrates the good selectivity of the present sensor towards H_2 in a gas mixture environment.

It must be noted that the gas sensing mechanism in metal oxide based gas sensors like ZnO is based on the change of electrical resistance during gas injection/removal cycles. In air, the large electronegativity of oxygen molecules O_2(g) results in less tedious oxygen adsorption on ZnO sensor surface. Adsorbed oxygen species O_2(ads) abstracts electrons from the ZnO conduction band and accordingly, depending on the sensing temperature, converts to different oxygen species (Equation 1)**[28]**:

$$\boldsymbol{O_2(g) \rightarrow O_2(ads) \xrightarrow{<100℃} O_2^-(ads) \xrightarrow{100-300℃} 2O^-(ads) \xrightarrow{\geq 300℃} O^{2-}(ads)} \qquad (1)$$

Electron transfer from the ZnO surface to the chemisorbed oxygen results in a decrease of the electron concentration forming a so-called depletion layer on the outer surface of ZnO NWs. When the ZnO NWs sensor is exposed to H_2, the following reaction (Equation 2) can take place,**[29]** in which hydrogen molecules H_2(g) react directly with adsorbed oxygen ions on the ZnO surface.

$$\boldsymbol{H_2(g) + O^{2-}(ZnO) \rightarrow H_2O(g) + 2e^-} \qquad (2)$$

The released electrons diminish the thickness depletion layer. Thus a high modulation in the sensor electrical resistance results in the observation of an intense sensor response. Since

SIM-1 membrane has not any semiconducting properties and acts only as a molecular sieve for blocking the transport of interfering gases, ZnO semiconducting NWs can play the role as electron transport channels, selectively adsorbing and desorbing H_2.

CONCLUSION

In this work we present a highly selective hydrogen sensor based on SIM-1 nanomembranes grown on semiconductor metal oxide (ZnO) surface. The strategy is based on the encapsulation of ZnO NWs with a thin SIM-1 permselective membrane having a complex three dimensional architecture, high specific surface area and molecular sieving properties. In comparison with the pristine ZnO NWs sensor, the SIM-1 coated ZnO NWs sensor showed remarkable selectivity towards H_2 at 300 °C in the presence of numerous interfering gases or vapours (CH_3COCH_3, CH_4, C_7H_8, C_2H_5OH and C_6H_6). It must be emphasized that this approach is very flexible since the same experimental procedure can be used to prepare gas sensors from different materials (both metal oxides and MOFs) in order to tune the selectivity to a specific gas. High quality H_2-selective sensors are urgently required for answering the safety issues associated to hydrogen production, delivering, storage and applications. The present SIM-1 coated ZnO NWs sensors represent an attractive tool for hydrogen detection in all these areas and associated systems both at small domestic scale and large industrial scale.

SUPPORTING INFORMATION. Additional TEM images, STEM/EDX line scan, XPS, XRD, TGA analyses and Dynamic resistance curves of ZnO NWs sensor towards different concentrations of various gases at 300°C are available as supporting information.

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FIGURES

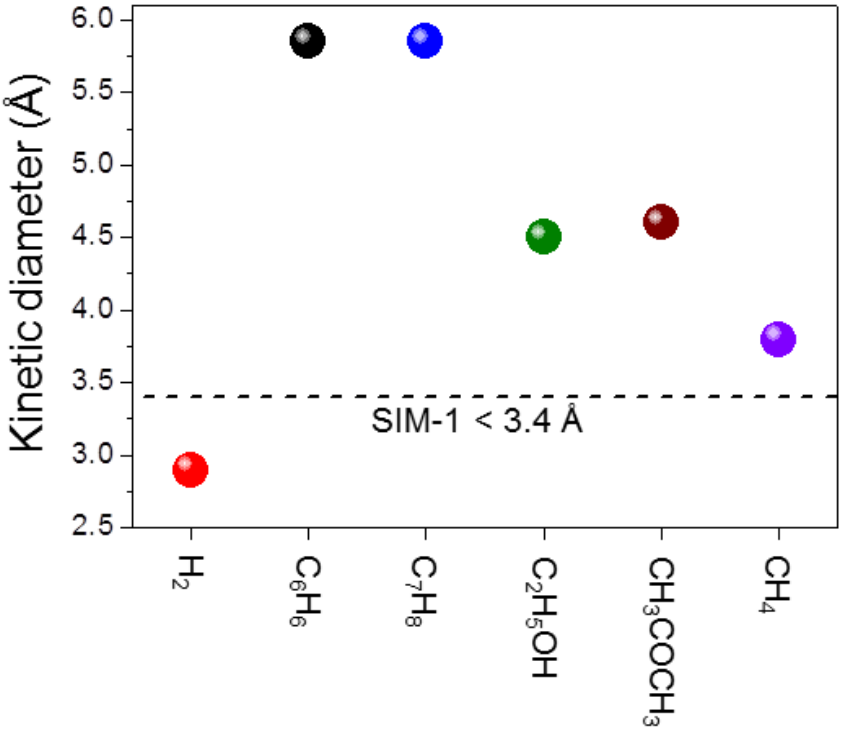

Figure 1. Kinetic diameters of the selected gases and vapours in relation with the estimated pore aperture of SIM-1 metal organic framework material.

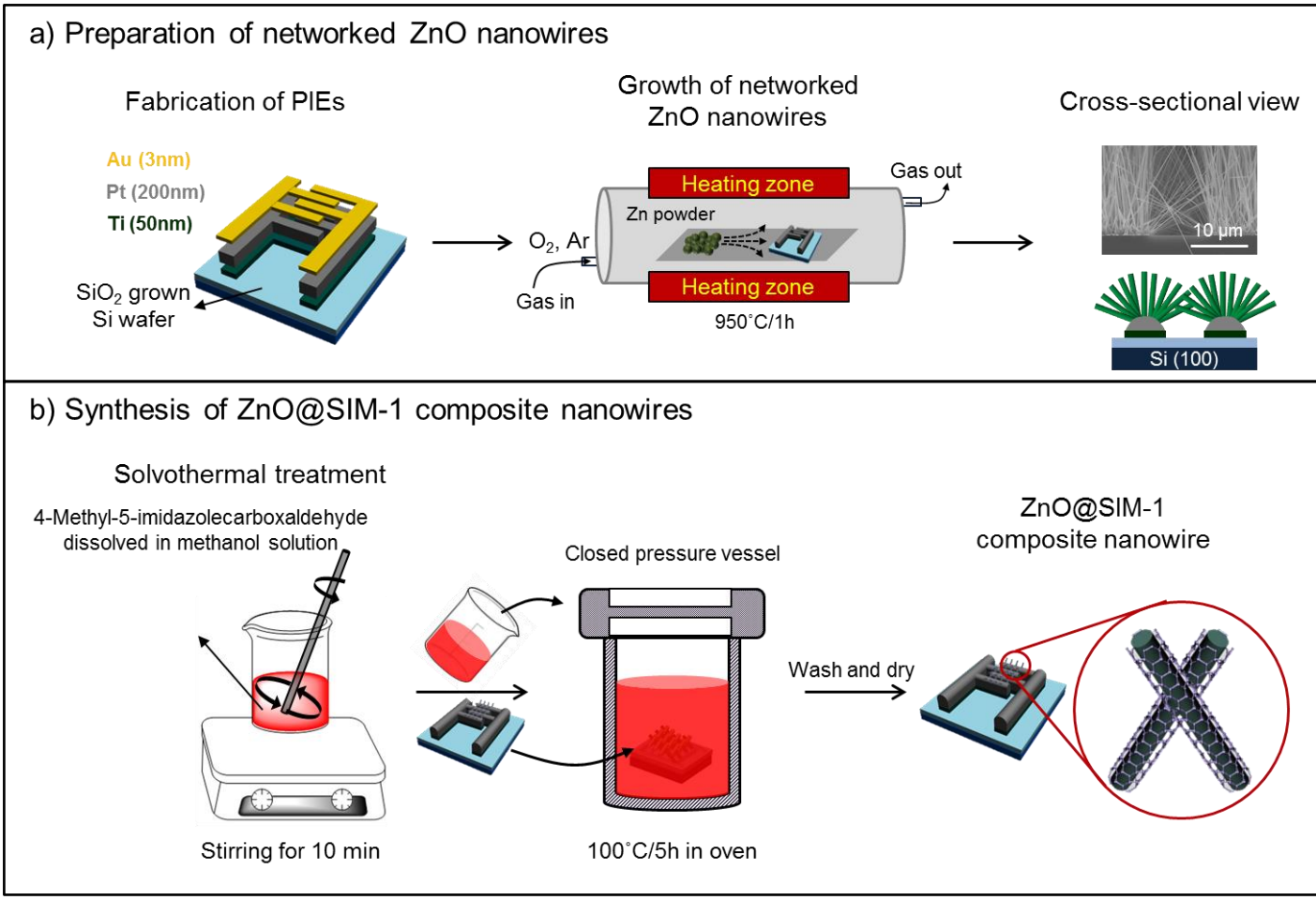

Figure 2. Schematic illustration of synthesis steps (a) synthesis of networked ZnO NWs (b) synthesis of SIM-1 coated ZnO NWs sensor.

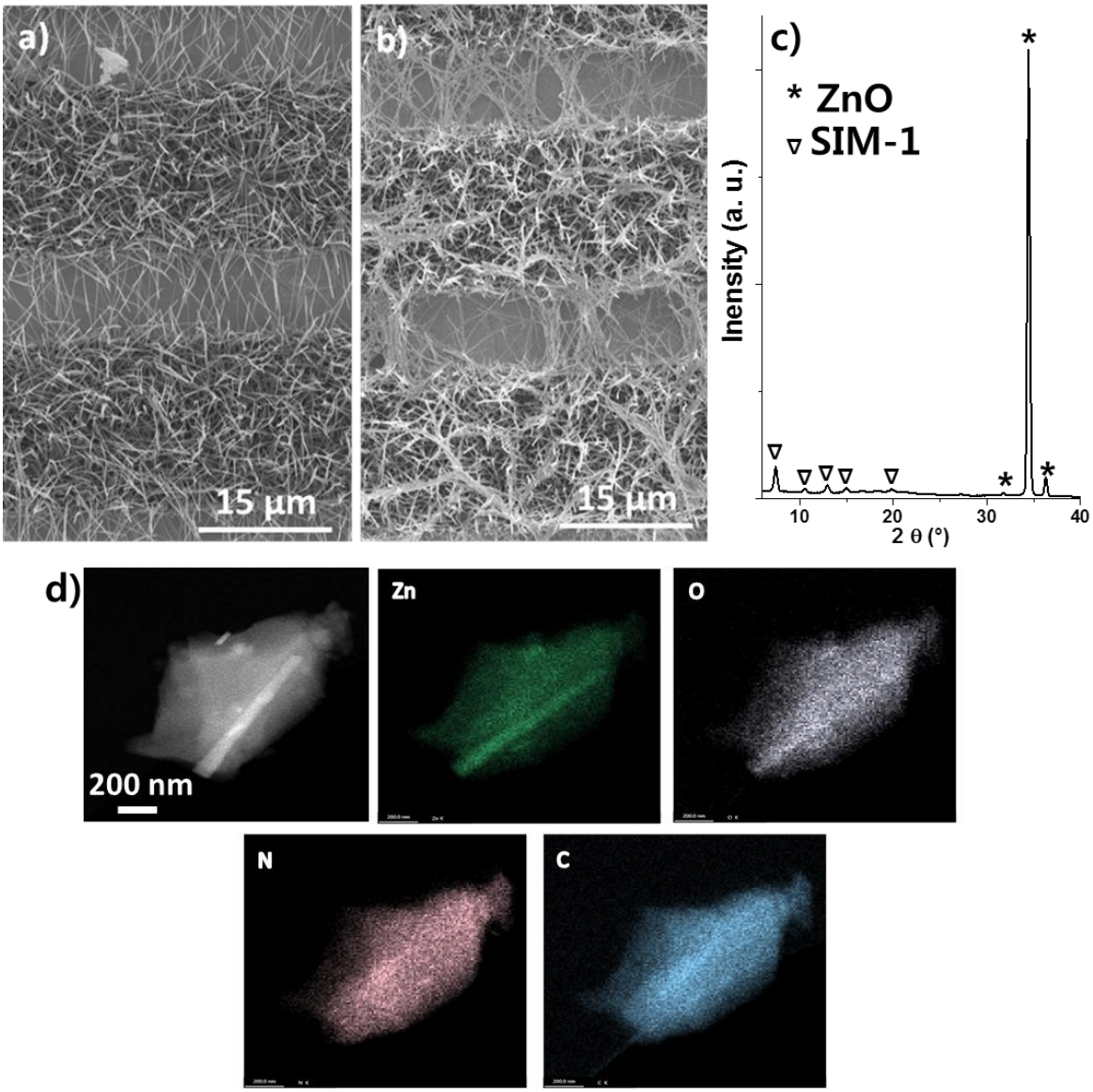

Figure 3. FESEM image of (a) networked ZnO nanowires, (b) SIM-1 coated ZnO nanowires; (c) XRD diffraction of SIM-1 coated ZnO nanowires; (d) TEM images of SIM-1 coated ZnO nanowires and corresponding EDX cartography analysis

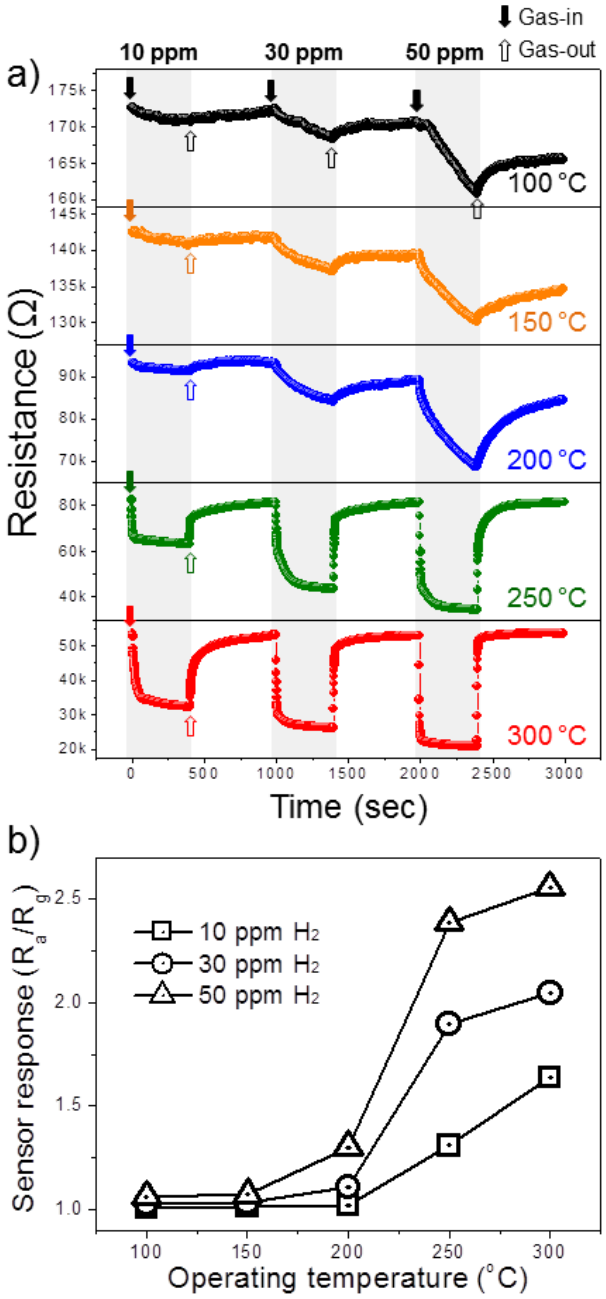

Figure 4. (a) Dynamic resistance curves of SIM-1 coated ZnO NWs sensor towards different concentrations of H_2 gas at different temperatures; (b) sensor response versus temperature.

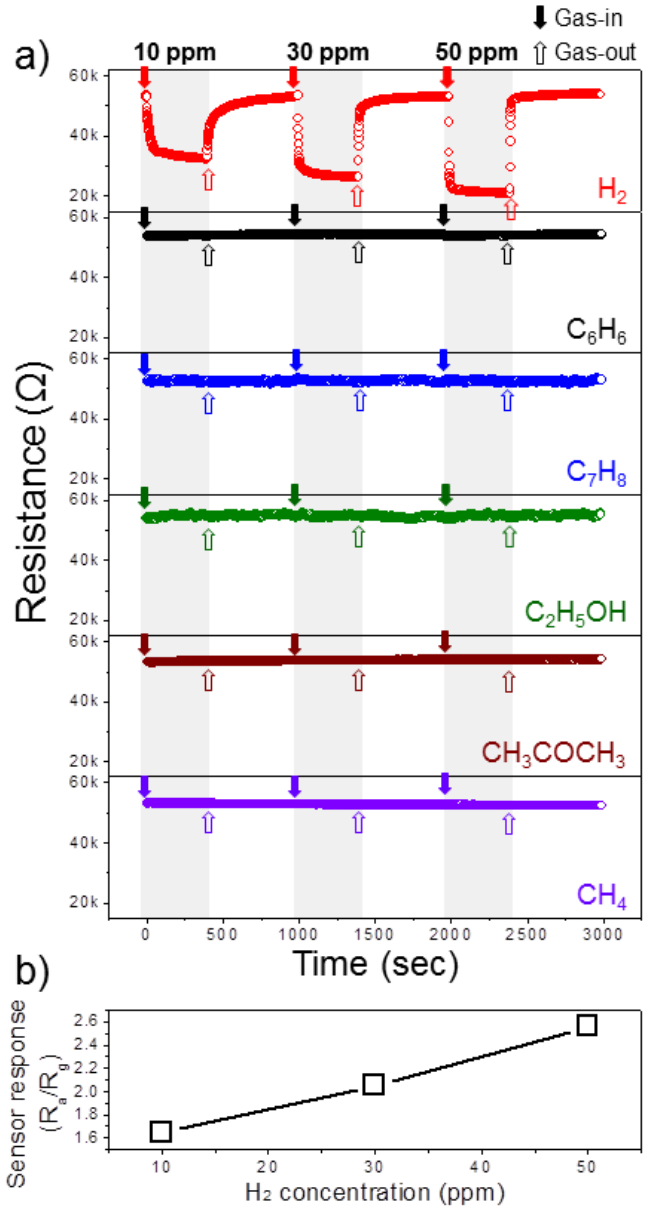

Figure 5. Dynamic resistance curves of SIM-1 coated ZnO NWs sensor towards 10, 30 and 50 ppm of different gases at 300°C; (b) sensor response versus H_2 gas.

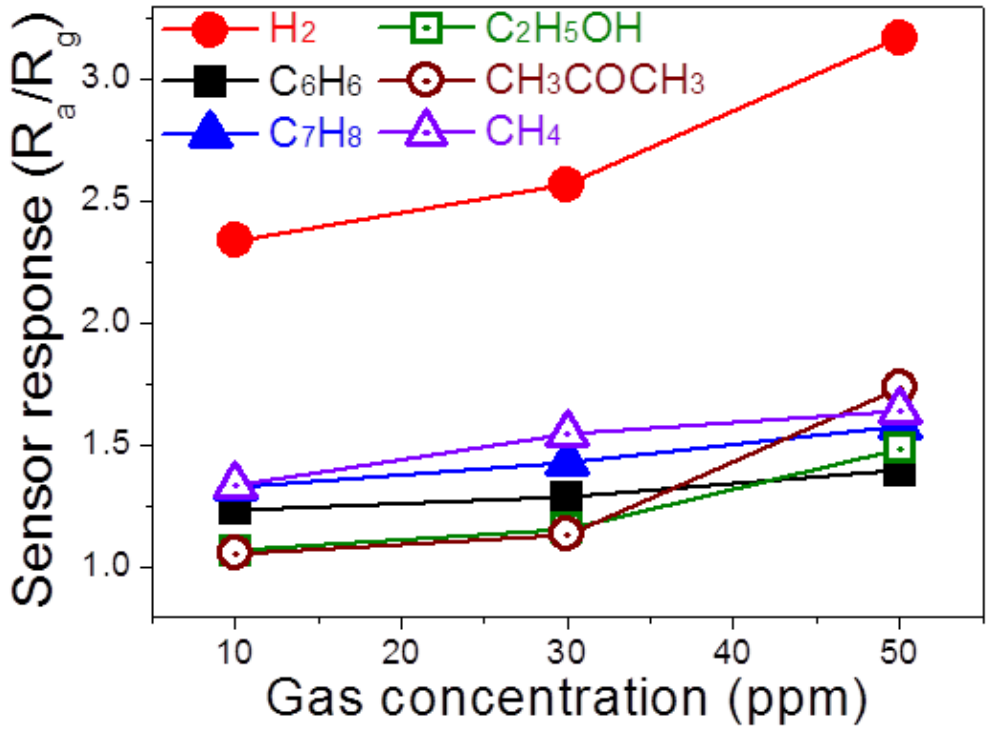

Figure 6. Calibration curves of ZnO NWs sensor towards different concentrations of various gases at 300°C.

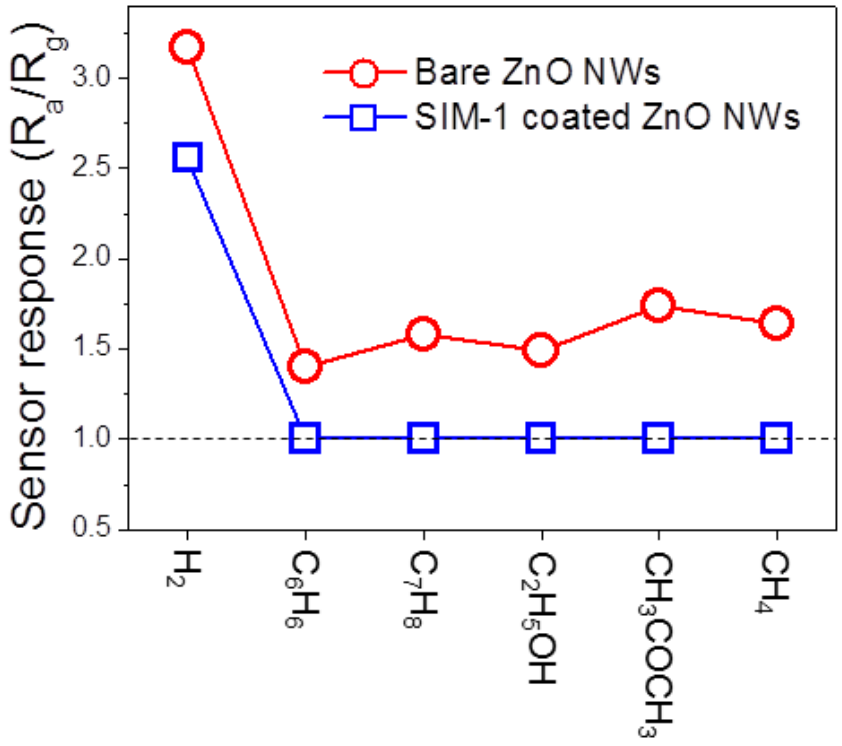

Figure 7. Selectivity histogram ZnO NWs sensor and SIM-1 coated ZnO NWs sensor towards 10 ppm of different gases at 300°C.

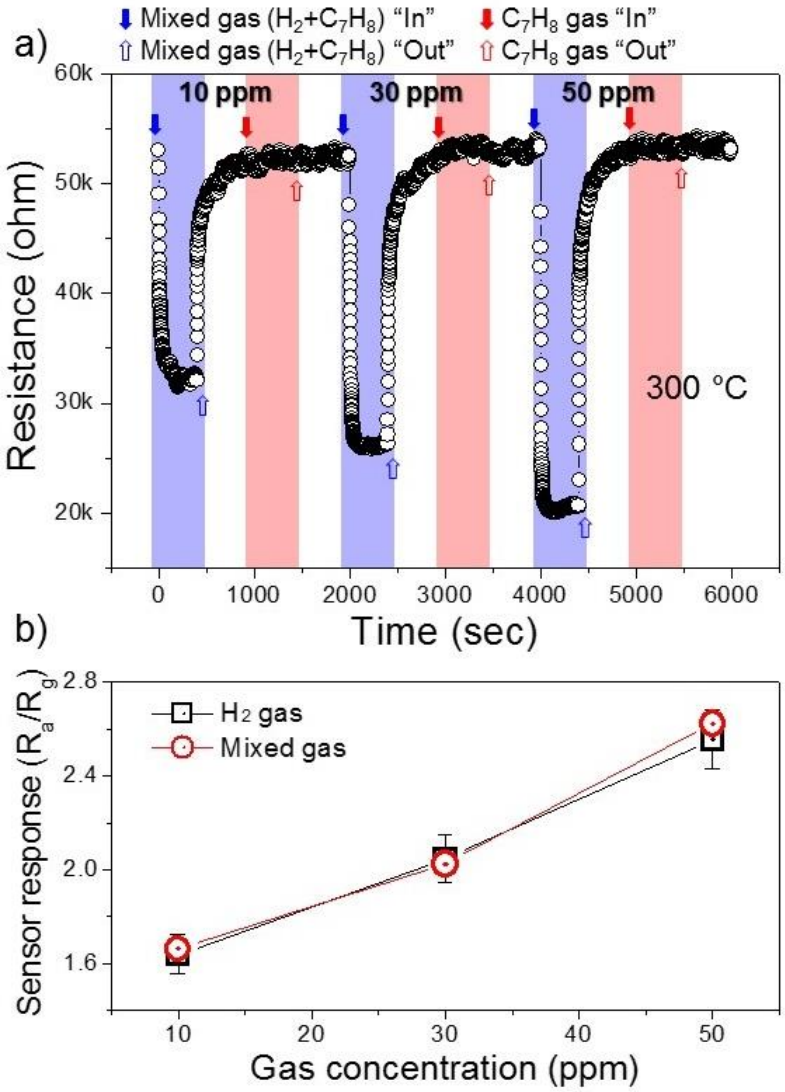

Figure 8. Dynamic resistance curves of SIM-1 coated ZnO NWs sensor towards 10, 30 and 50 ppm of (H_2+C_7H_8) gas mixture and C_7H_8 single gas at 300°C; (b) comparison between the sensor response to 10 ppm (H_2+C_7H_8) gas mixture and 10 ppm H_2 single gas at 300°C.

GRAPHICAL ABSTRACT