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# Design and Fabrication of Highly Selective H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> at high temperatures (300 °C) in the presence of numerous interfering

gases ( $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_7\text{H}_8$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_6$ ) thus confirming the efficiency of such sensor material for hydrogen detection.

## INTRODUCTION

Hydrogen ( $\text{H}_2$ ) 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  $\text{H}_2$  engines[3] and others. However, the applications of  $\text{H}_2$  also possess some inherent problems. First of all,  $\text{H}_2$  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  $250^\circ\text{C}$ , which can cause an electrostatic discharge.[5] Finally,  $\text{H}_2$  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  $\text{H}_2$  sensors. An ideal  $\text{H}_2$  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  $\text{H}_2$  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 imidazolite 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<sub>2</sub> 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<sub>2</sub> in the presence of large gas molecules such as C<sub>6</sub>H<sub>6</sub> and C<sub>7</sub>H<sub>8</sub>. [18] Recently, Wu et al.[19], also reported an excellent selective response of H<sub>2</sub> 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  $\sim 0.8$  nm and expected pore aperture  $<0.34$  nm,[20, 21] thus having a great potential as selective barrier allowing small gases such as hydrogen ( $2.89 \text{ \AA}$ ) passing through easily, while retaining other larger gases or vapors such as  $\text{CH}_4$  ( $3.8 \text{ \AA}$ ),  $\text{C}_2\text{H}_5\text{OH}$  ( $4.5 \text{ \AA}$ ),  $\text{CH}_3\text{COCH}_3$  ( $4.6 \text{ \AA}$ ),  $\text{C}_7\text{H}_8$  ( $5.85 \text{ \AA}$ ) and  $\text{C}_6\text{H}_6$  ( $5.85 \text{ \AA}$ ) (Figure 1). The potential of the SIM-1 material as a membrane barrier for the separation of hydrogen from other gases (e.g.  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ) 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  $\text{H}_2$  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  $\text{H}_2$  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<sub>2</sub> (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<sub>2</sub> 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<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O - 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  $\text{CuK}\alpha$  radiation). Surface chemical composition was studied by X-ray Photoelectron Spectroscopy (XPS) (ESCALAB 250 Thermal Electron) with  $\text{AlK}\alpha$  (1486.6 eV). Binding energies were calibrated by using the carbon containment ( $\text{C1s} = 284.4$  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  $\text{H}_2$  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  $\text{H}_2$  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 synthesized 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 ( $2\theta = 7.3^\circ, 10.2^\circ, 12.6^\circ, 15.0^\circ, 19.5^\circ$ ) and ZnO ( $2\theta = 31.7^\circ, 34.4^\circ, 36.2^\circ$ ). 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 2p<sub>3</sub>, 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<sub>2</sub>. 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<sub>2</sub> gas, the sensor resistance decreases. Considering the fact that H<sub>2</sub> 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<sub>2</sub>, suggesting the reversible adsorption of H<sub>2</sub> 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<sub>2</sub>. Finally, increasing the H<sub>2</sub> concentration from 10 to 50 ppm, the response signal is accentuated. Indeed, for higher H<sub>2</sub> concentration, the surface reactions are enhanced due to larger surface coverage of the sensor with H<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>6</sub>H<sub>6</sub>, CH<sub>4</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COCH<sub>3</sub>. The dynamic resistances of the above compounds were compared with that of H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> molecules but lower than that of other interfering gases. Hence, only the penetration of H<sub>2</sub> molecules is theoretically possible, while the transport of other molecules should be blocked by the selective SIM-1 membrane. The small H<sub>2</sub> molecules can diffuse easily through the SIM-1 membrane network and reach the ZnO NWs surface, thus ensuring the preservation of a significant H<sub>2</sub> response. Indeed, the high adsorption capacity of

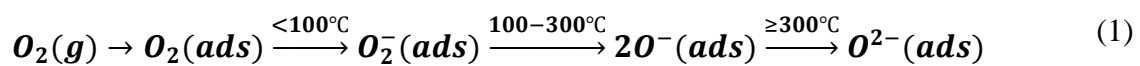
the SIM-1 structure is expected to further contribute to enhance the H<sub>2</sub> selectivity of the SIM-1 coated ZnO NWs sensor. Assuming the pore aperture of SIM-1 (<3.4Å, see Introduction) and the size of oxygen molecules characterized by their small van der Waals diameter  $d_{vdW} = 2.8\text{\AA}$ , 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>4</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>5</sub>OH and C<sub>6</sub>H<sub>6</sub> 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<sub>2</sub>. On the other hand, the pristine ZnO shows a detectable response to the interfering gases, thus leading to low H<sub>2</sub> selectivity. It must be noted that the response of SIM-1 coated ZnO NWs sensor towards H<sub>2</sub> (2.56) was slightly lower than that of pristine ZnO NWs sensor (3.17). This phenomenon is attributed to the limited H<sub>2</sub> diffusion through the SIM-1 membrane network which controls the access of H<sub>2</sub> 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

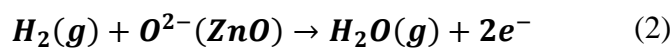
gas sensing response. In this context, the novel approach presented in this study seems very promising for an enhancement of sensor response.

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<sub>2</sub> gas with toluene (C<sub>7</sub>H<sub>8</sub>) gas and tested the sensor response towards (H<sub>2</sub>+C<sub>7</sub>H<sub>8</sub>) gas pair. As shown in Figure 8 (a), the response of SIM-1 coated ZnO NWs sensor to (H<sub>2</sub>+C<sub>7</sub>H<sub>8</sub>) mixed gases is much higher than that of C<sub>7</sub>H<sub>8</sub> single gas and is almost equal to the sensor response of sensor to H<sub>2</sub> single gas (Figure 8 (b)). In contrast, as expected, the response to C<sub>7</sub>H<sub>8</sub> single gas is negligible. This experimentally demonstrates the good selectivity of the present sensor towards H<sub>2</sub> 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<sub>2</sub>(g) results in less tedious oxygen adsorption on ZnO sensor surface. Adsorbed oxygen species O<sub>2</sub>(ads) abstracts electrons from the ZnO conduction band and accordingly, depending on the sensing temperature, converts to different oxygen species (Equation 1)[28]:



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<sub>2</sub>, the following reaction (Equation 2) can take place,[29] in which hydrogen molecules H<sub>2</sub>(g) react directly with adsorbed oxygen ions on the ZnO surface.



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<sub>2</sub>.

## 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<sub>2</sub> at 300 °C in the presence of numerous interfering gases or vapours (CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>4</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>5</sub>OH and C<sub>6</sub>H<sub>6</sub>). 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<sub>2</sub>-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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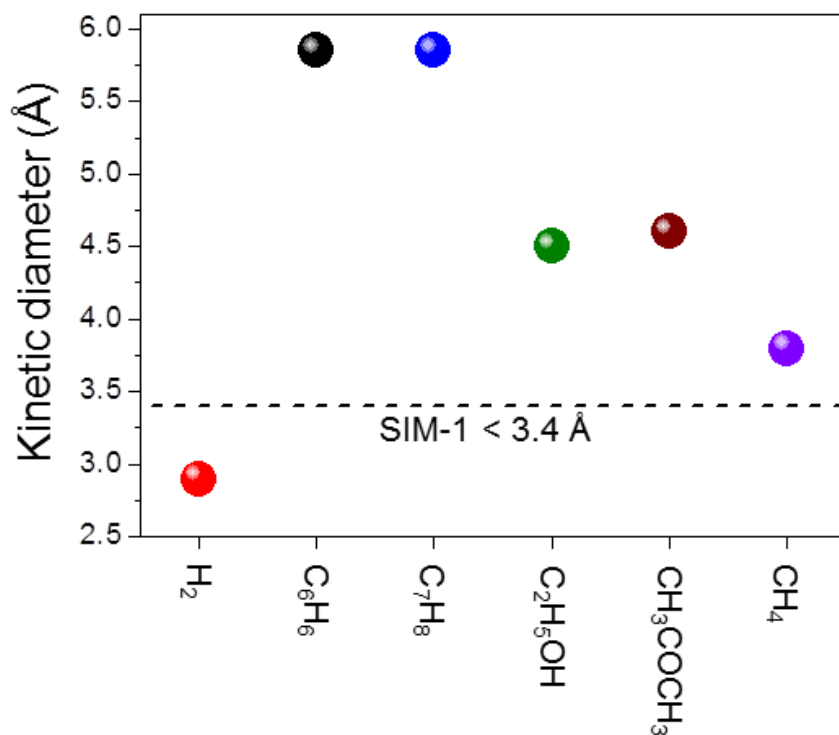
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## REFERENCES

- [1] J. Andrews, B. Shabani, Re-envisioning the role of hydrogen in a sustainable energy economy, *International Journal of Hydrogen Energy*, 37(2012) 1184-203.
- [2] G. Squadrito, L. Andaloro, M. Ferraro, V. Antonucci, 16 - Hydrogen fuel cell technology, *Advances in Hydrogen Production, Storage and Distribution*, Woodhead Publishing 2014, pp. 451-98.
- [3] H. Fayaz, R. Saidur, N. Razali, F.S. Anuar, A.R. Saleman, M.R. Islam, An overview of hydrogen as a vehicle fuel, *Renewable and Sustainable Energy Reviews*, 16(2012) 5511-28.
- [4] P. Navarro-Botella, J. García-Aguilar, Á. Berenguer-Murcia, D. Cazorla-Amorós, Pd and Cu-Pd nanoparticles supported on multiwall carbon nanotubes for H<sub>2</sub> detection, *Materials Research Bulletin*, 93(2017) 102-11.
- [5] A.S.M.I. Uddin, G.-S. Chung, A self-powered active hydrogen gas sensor with fast response at room temperature based on triboelectric effect, *Sensors and Actuators B-Chemical*, 231(2016) 601-8.
- [6] F. Falsafi, B. Hashemi, A. Mirzaei, E. Fazio, F. Neri, N. Donato, et al., Sm-doped cobalt ferrite nanoparticles: A novel sensing material for conductometric hydrogen leak sensor, *Ceramics International*, 43(2017) 1029-37.
- [7] D.-C. Nguyen, C.-C. Chu, C.-H. Lee, T. Hsu, C.-S. Chang, Fabrication and tailoring of the nano-scale textures of Pd films by selective doping for hydrogen gas sensing, *Thin Solid Films*, 616(2016) 722-7.
- [8] A. Mirzaei, K. Janghorban, B. Hashemi, M. Bonyani, S.G. Leonardi, G. Neri, Highly stable and selective ethanol sensor based on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared by Pechini sol-gel method, *Ceramics International*, 42(2016) 6136-44.
- [9] Y.J. Kwon, A. Mirzaei, S.Y. Kang, M.S. Choi, J.H. Bang, S.S. Kim, et al., Synthesis, characterization and gas sensing properties of ZnO-decorated MWCNTs, *Applied Surface Science*, 413(2017) 242-52.
- [10] G.S. Devi, P.S.P. Reddy, K. Ramya, Sol-Gel Derived ZnO: Nb<sub>2</sub>O<sub>5</sub> Nanocomposite as Selective Hydrogen (H<sub>2</sub>) Gas Sensor, *Materials Today: Proceedings*, 3(2016) 224-9.
- [11] A. Katoch, J.-H. Kim, Y.J. Kwon, H.W. Kim, S.S. Kim, Bifunctional Sensing Mechanism of SnO<sub>2</sub>-ZnO Composite Nanofibers for Drastically Enhancing the Sensing Behavior in H<sub>2</sub> Gas, *ACS Applied Materials & Interfaces*, 7(2015) 11351-8.
- [12] C. Sun-Woo, J. Sung-Hyun, K. Sang Sub, Functionalization of selectively grown networked SnO<sub>2</sub> nanowires with Pd nanodots by  $\gamma$ -ray radiolysis, *Nanotechnology*, 22(2011) 225501.
- [13] J.Y. Park, S.-W. Choi, S.S. Kim, Junction-Tuned SnO<sub>2</sub> Nanowires and Their Sensing Properties, *The Journal of Physical Chemistry C*, 115(2011) 12774-81.
- [14] G. Korotcenkov, B.K. Cho, Engineering approaches for the improvement of conductometric gas sensor parameters, *Sensors and Actuators B: Chemical*, 188(2013) 709-28.

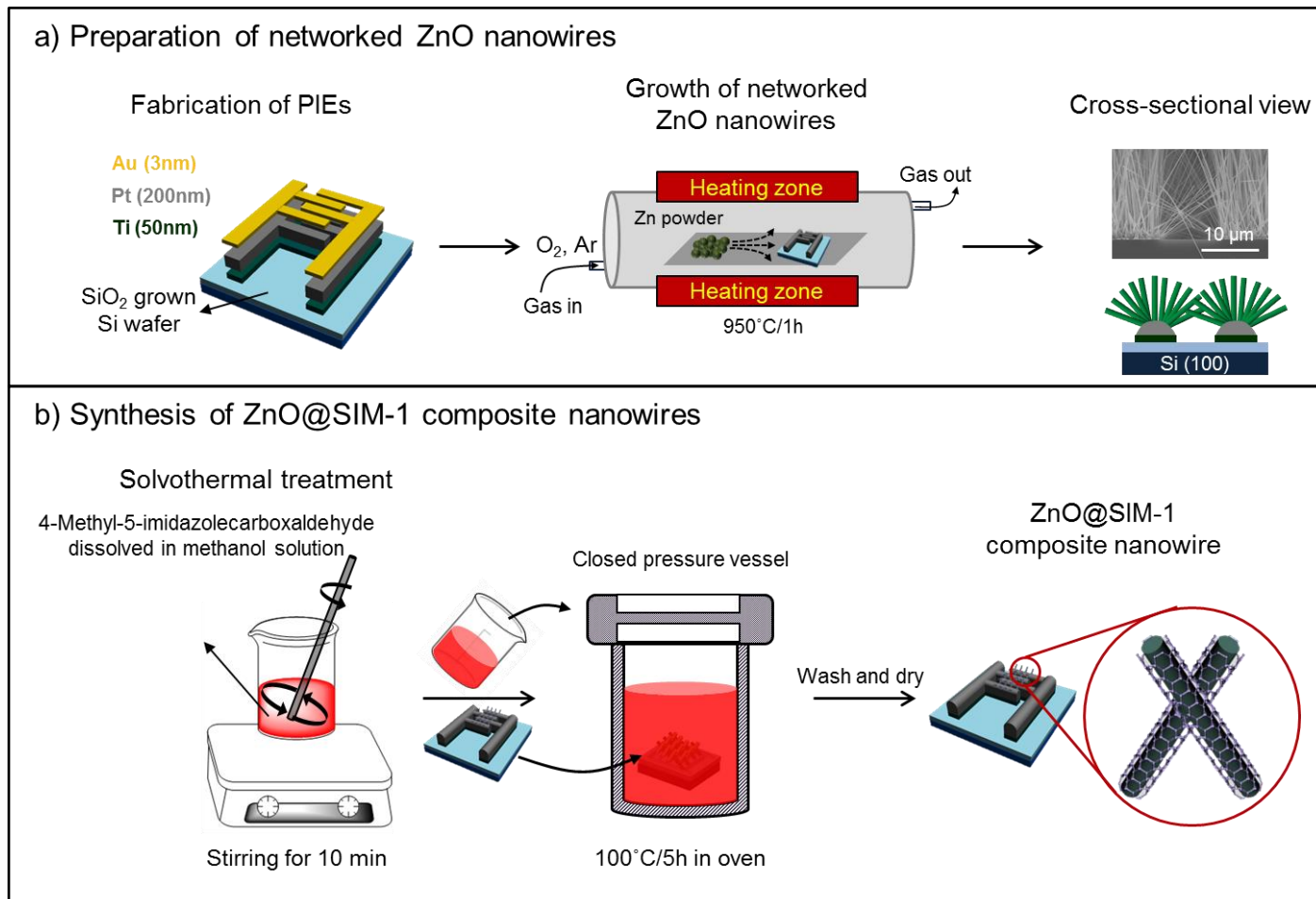
- [15] C.D. Baertsch, H.H. Funke, J.L. Falconer, R.D. Noble, Permeation of Aromatic Hydrocarbon Vapors through Silicalite–Zeolite Membranes, *The Journal of Physical Chemistry*, 100(1996) 7676-9.
- [16] C. Pijolat, J.P. Viricelle, G. Tournier, P. Montmeat, Application of membranes and filtering films for gas sensors improvements, *Thin Solid Films*, 490(2005) 7-16.
- [17] Y. Pan, B. Wang, Z. Lai, Synthesis of ceramic hollow fiber supported zeolitic imidazolate framework-8 (ZIF-8) membranes with high hydrogen permeability, *Journal of Membrane Science*, 421(2012) 292-8.
- [18] M. Drobek, J.-H. Kim, M. Bechelany, C. Vallicari, A. Julbe, S.S. Kim, MOF-Based Membrane Encapsulated ZnO Nanowires for Enhanced Gas Sensor Selectivity, *ACS Applied Materials & Interfaces*, 8(2016) 8323-8.
- [19] X. Wu, S. Xiong, Z. Mao, S. Hu, X. Long, A Designed ZnO@ZIF-8 Core–Shell Nanorod Film as a Gas Sensor with Excellent Selectivity for H<sub>2</sub> over CO, *Chemistry – A European Journal*, 23(2017) 7969-75.
- [20] S. Aguado, J. Canivet, D. Farrusseng, Facile shaping of an imidazolate-based MOF on ceramic beads for adsorption and catalytic applications, *Chemical Communications*, 46(2010) 7999-8001.
- [21] A.M. Marti, M. Van, K.J. Balkus, Tuning the crystal size and morphology of the substituted imidazole material, SIM-1, *Journal of Porous Materials*, 21(2014) 889-902.
- [22] S. Aguado, C.H. Nicolas, V. Moizan-Basle, C. Nieto, H. Amrouche, N. Bats, et al., Facile synthesis of an ultramicroporous MOF tubular membrane with selectivity towards CO<sub>2</sub>, *New Journal of Chemistry*, 35(2011) 41-4.
- [23] M. Drobek, M. Bechelany, C. Vallicari, A. Abou Chaaya, C. Charmette, C. Salvador-Levehang, et al., An innovative approach for the preparation of confined ZIF-8 membranes by conversion of ZnO ALD layers, *Journal of Membrane Science*, 475(2015) 39-46.
- [24] M. Bechelany, M. Drobek, C. Vallicari, A. Abou Chaaya, A. Julbe, P. Miele, Highly crystalline MOF-based materials grown on electrospun nanofibers, *Nanoscale*, 7(2015) 5794-802.
- [25] T.X.H. Le, R. Esmilaire, M. Drobek, M. Bechelany, C. Vallicari, D.L. Nguyen, et al., Design of a novel fuel cell-Fenton system: a smart approach to zero energy depollution, *Journal of Materials Chemistry A*, 4(2016) 17686-93.
- [26] J.-H. Kim, A. Mirzaei, H.W. Kim, S.S. Kim, Extremely sensitive and selective sub-ppm CO detection by the synergistic effect of Au nanoparticles and core–shell nanowires, *Sensors and Actuators B: Chemical*, 249(2017) 177-88.
- [27] A. Mirzaei, S. Park, G.-J. Sun, H. Kheel, C. Lee, CO gas sensing properties of In<sub>4</sub>Sn<sub>3</sub>O<sub>12</sub> and TeO<sub>2</sub> composite nanoparticle sensors, *Journal of Hazardous Materials*, 305(2016) 130-8.
- [28] A. Mirzaei, S. Park, H. Kheel, G.-J. Sun, S. Lee, C. Lee, ZnO-capped nanorod gas sensors, *Ceramics International*, 42(2016) 6187-97.
- [29] M.S. Barbosa, P.H. Suman, J.J. Kim, H.L. Tuller, J.A. Varela, M.O. Orlandi, Gas sensor properties of Ag- and Pd-decorated SnO micro-disks to NO<sub>2</sub>, H<sub>2</sub> and CO: Catalyst enhanced sensor response and selectivity, *Sensors and Actuators B: Chemical*, 239(2017) 253-61.

FIGURES

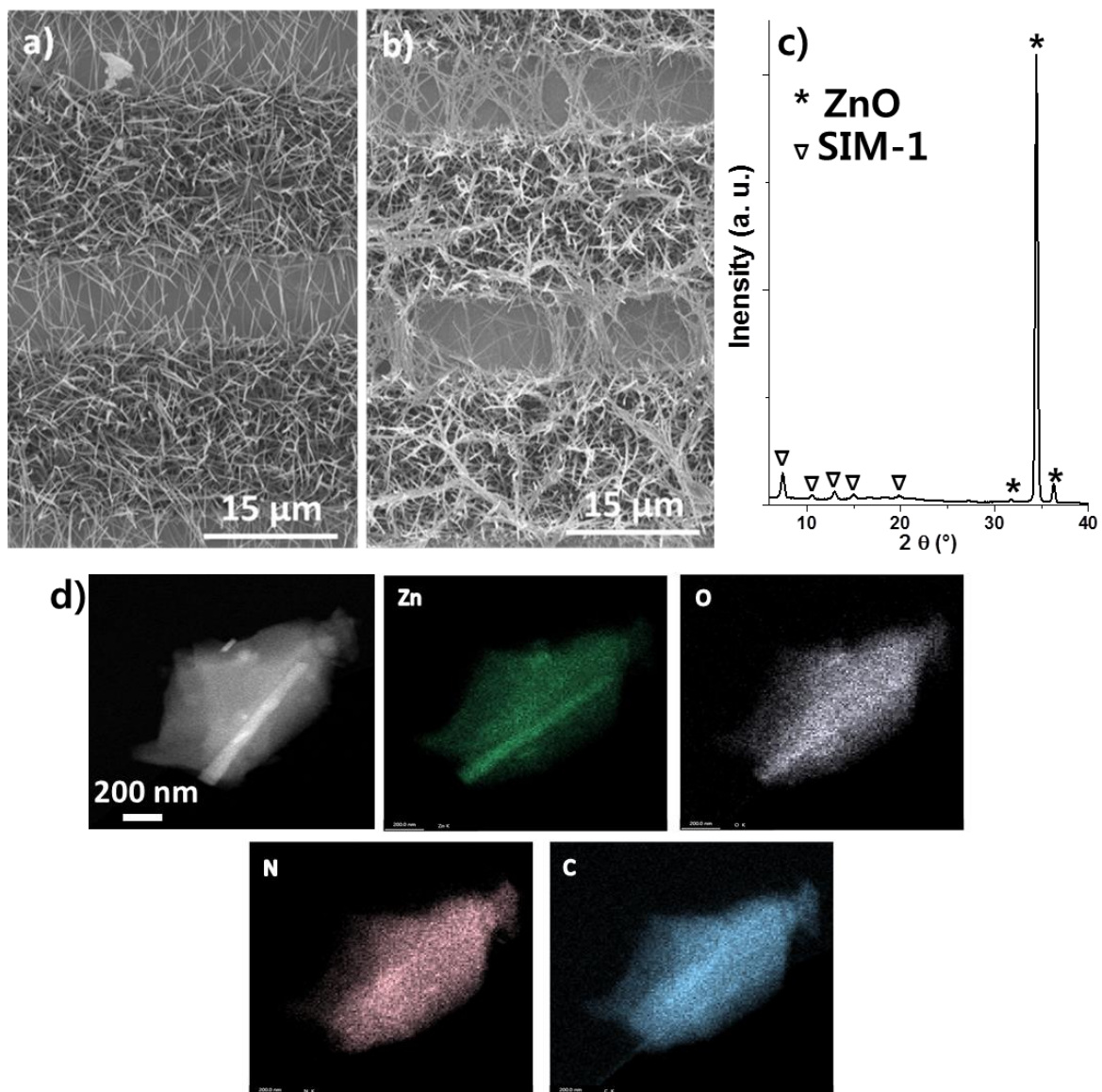


**Figure 1.** Kinetic diameters of the selected gases and vapours in relation with the estimated pore aperture of SIM-1 metal organic framework material.

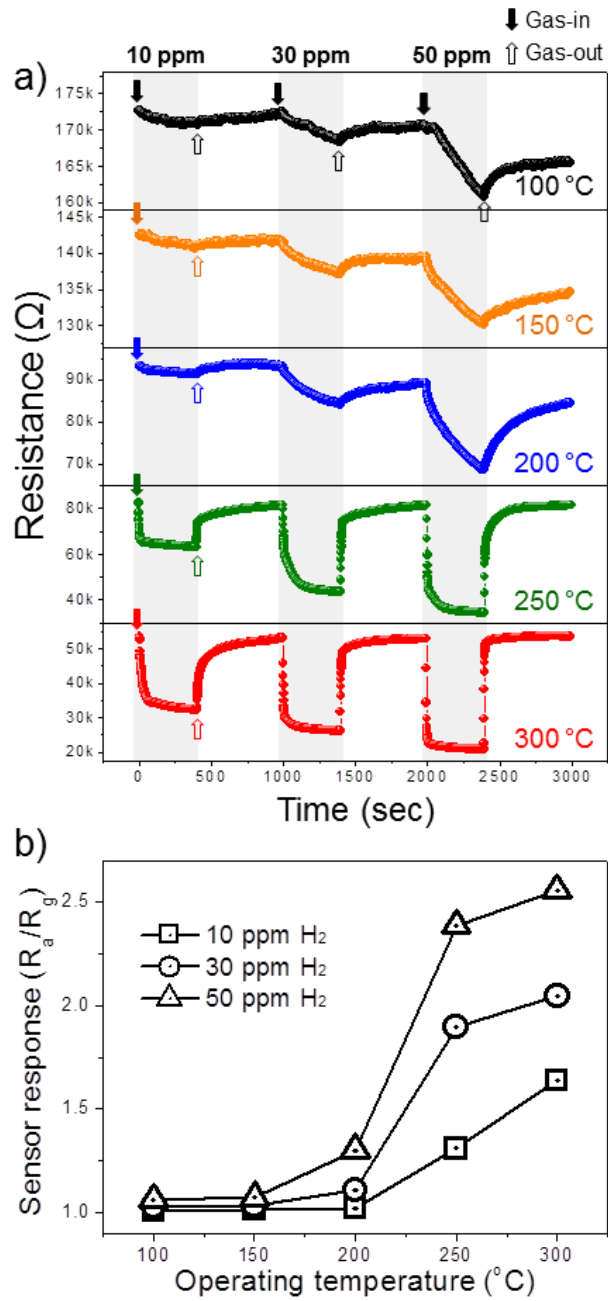




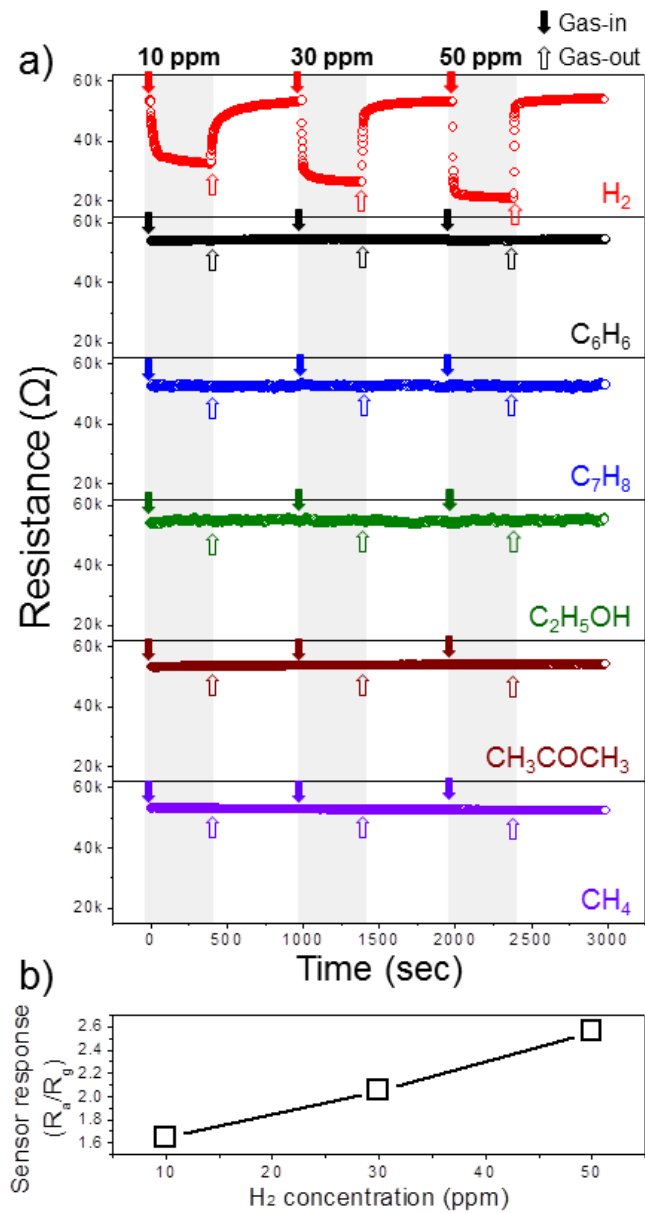
**Figure 2.** Schematic illustration of synthesis steps (a) synthesis of networked ZnO NWs (b) synthesis of SIM-1 coated ZnO NWs sensor.



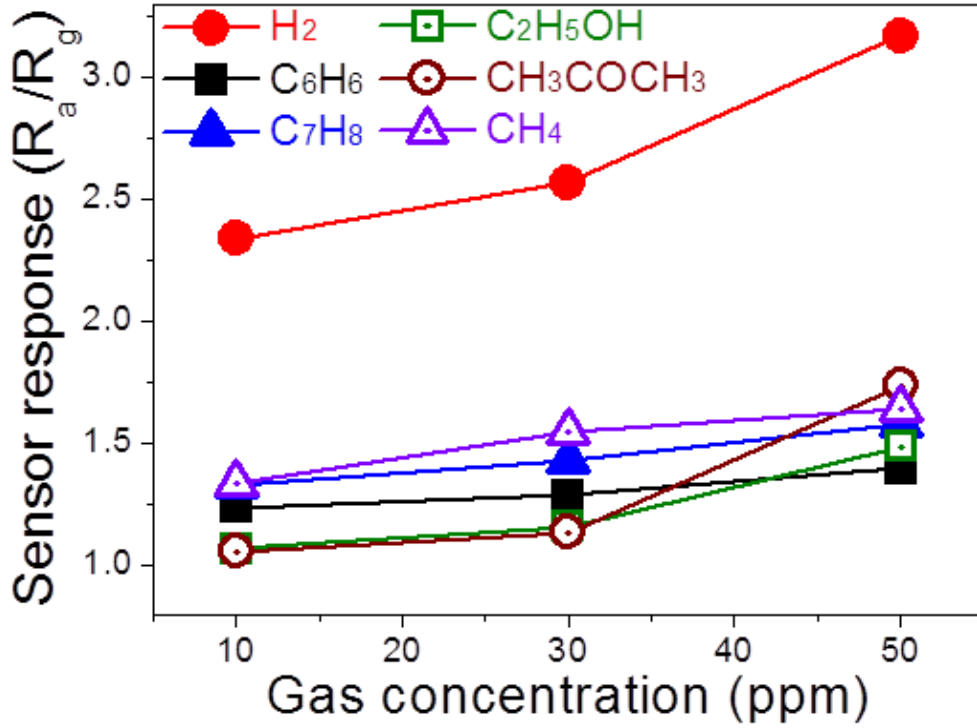
**Figure 3.** FESEM image of (a) networked ZnO nanowires, (b) SIM-1 coated ZnO nanowires; (c) XRD diffraction of SIM-1 coated ZnO nanowires; (d) TEM images of SIM-1 coated ZnO nanowires and corresponding EDX cartography analysis



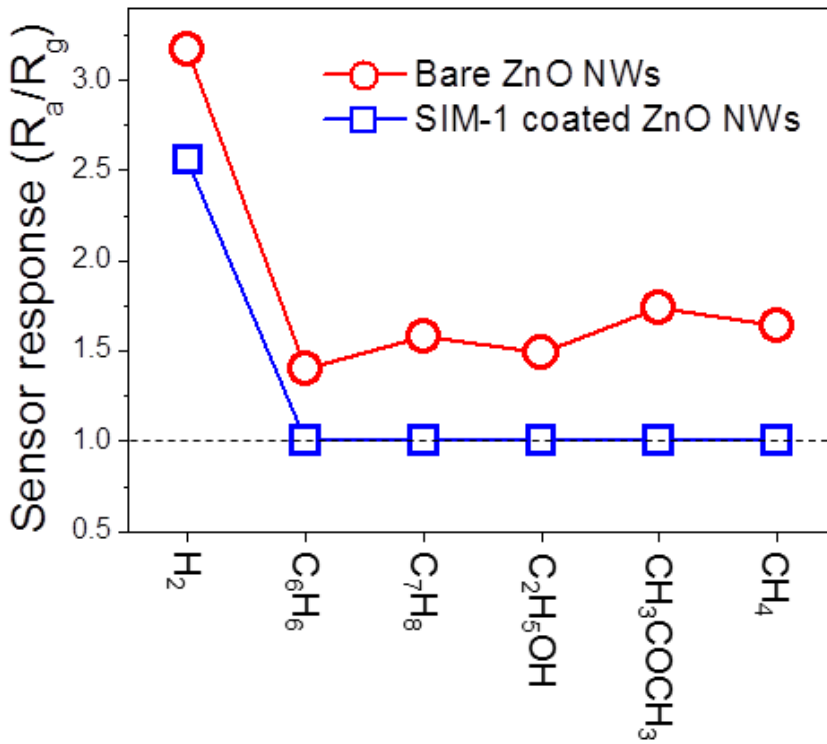
**Figure 4.** (a) Dynamic resistance curves of SIM-1 coated ZnO NWs sensor towards different concentrations of H<sub>2</sub> gas at different temperatures; (b) sensor response versus temperature.



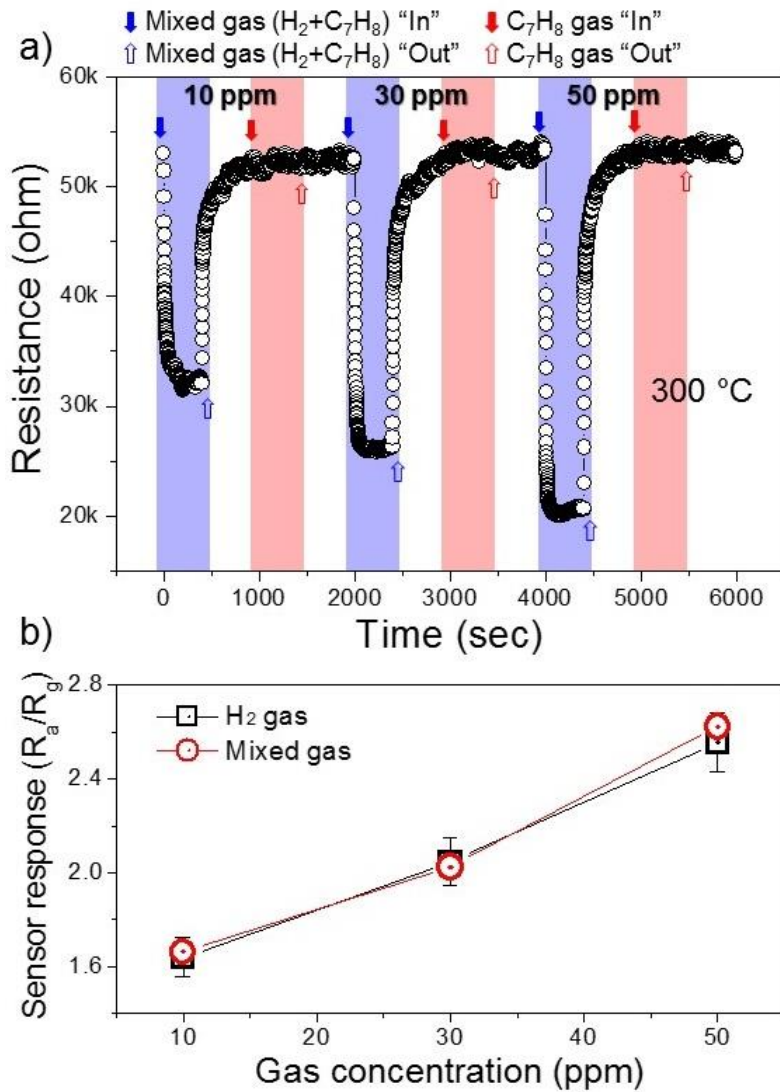
**Figure 5.** Dynamic resistance curves of SIM-1 coated ZnO NWs sensor towards 10, 30 and 50 ppm of different gases at 300°C; (b) sensor response versus  $H_2$  gas.



**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

