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HAL Id: hal-01677978
https://hal.umontpellier.fr/hal-01677978v1

Submitted on 7 Jul 2021

MOF-based membrane encapsulated ZnO nanowires for enhanced gas sensor selectivity

Martin Drobek[1±], Jae-Hun Kim[2±], Mikhael Bechelany[1], Cyril Vallicari[1], Anne Julbe[1], Sang Sub Kim*[2]*

[1]*Institut Européen des Membranes, UMR 5635, Université de Montpellier, ENSCM, CNRS, Place Eugène Bataillon, F-34095 Montpellier cedex 5, France*

[2]*Department of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea*

[±] These 2 authors participated to this work equally

<u>*corresponding authors:</u>

Mikhael Bechelany: mikhael.bechelany@univ-montp2.fr,
phone: +33467149167, Fax: +33467149119

Sang Sub Kim:sangsub@inha.ac.kr ,
phone: +82328607546, Fax: +82328625546

KEYWORDS. ZnO, nanowires, ZIF-8 membrane, encapsulation, gas sensing

ABSTRACT

Gas sensors are of a great interest for applications including toxic or explosive gases detection in both in-house and industrial environments, air quality monitoring, medical diagnostics or control of food/cosmetic properties. In the area of semiconductor metal oxides (SMOs)-based sensors, a lot of effort has been devoted to improve the sensing characteristics. In this work, we report on a general methodology for improving the selectivity of SMOx nanowires sensors, based on the coverage of ZnO nanowires with a thin ZIF-8 molecular sieve membrane. The optimized ZnO@ZIF-8-based nanocomposite sensor shows markedly selective response to H_2 in comparison with the pristine ZnO nanowires sensor, while

showing the negligible sensing response to C_7H_8 and C_6H_6. This original MOF-membrane encapsulation strategy applied to nanowires sensor architecture pave the way for other complex 3D-architectures and various types of applications requiring either gas or ion selectivity, such as biosensors, photo(catalysts) and electrodes.

Gas sensors represent a huge market that nowadays exceeds 2.5 billion dollars, in which semiconductor oxide materials contribute for more than 20%.[1] The driving applications include detection of toxic or explosive gases in industrial environments, in-house measurements of dangerous gases, air quality and greenhouse gas monitoring[2], alongside with emerging applications in medical diagnostics[3] and food/cosmetic quality control[4]. The sensing mechanism involves the adsorption of gases on the surface of the functional oxide material that causes a change of its electrical conductivity.[5] In addition to the measurement of electrical conductivity variation, gas sensing could be realized by measuring the change in capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interactions. Acoustic and calorimetric methods are also possible options.[6] Indeed, the sensors surface characteristics such as composition, crystalline structure, morphology, and microstructure (roughness, porosity, grain size, etc…) are crucial parameters for optimal sensing response. These parameters impact on sensor properties: *i)* sensitivity, *ii)* selectivity, *iii)* response and recovery times but also on the stability of the sensing material over time.

For semiconductor metal oxides (SMOs)-based sensors, the selectivity is intrinsically scarce and strong efforts were recently devoted to improve both sensor response and selectivity[7-9]. Typical approaches for improving sensitivity include the development of nanostructured materials with high effective surface areas, aiming to increase the number of gas adsorption sites.[10] On the other hand, functionalization of sensor materials with special catalytic elements including noble metals or metal oxides is often used to improve the selectivity. Composing

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"sensor arrays" with zones providing different functional properties and whose response can be treated comparatively is a potential option to achieve the required selectivity in gas mixture atmosphere. Only rare examples of attractive gas sensing properties have been reported for organic inorganic-hybrid layers. Original nanoporous organotin hybrid thin film has been recently developed by self-assembling, providing unexpected selectivity for H_2 gas sensing at moderate temperature[11]. The best selectivity to H_2 was observed at 150°C with films that do not display any response to CO.[12]

In the area of novel functional materials, our research group recently developed an innovative approach for the synthesis of ZIF-8-based nanocomposite membranes applying so called "reactive seeding" approach.[13] The method involves the Atomic Layer Deposition (ALD) of ZnO thin films and their subsequent conversion to ZIF-8 using a 2-methylimidazole/methanol solution under solvothermal conditions. ZIFs structures (Zeolitic Imidazolate Frameworks) represent a sub-family of Metal-Organic Frameworks (MOFs) which feature ultrahigh porosity, structural and chemical tunability together with structural flexibility and huge equivalent internal surface areas. The unique attributes of MOFs can be advantageously exploited for a large variety of applications including catalysis, gas separation and storage, nonlinear optics, light-harvesting, drug delivery, and more recently sensory applications[14] and the protection of sensing devices with MOF-based selective barriers.[14-15] Indeed the highly porous structures of MOFs enhance species uptake (pre-concentration) and the well-defined pore structures of MOFs provides molecular sieving.[13] These two effects are expected to enhance both sensor response sensitivity (preconcentration effect) and selectivity (size/shape exclusion effect). Taking advantage of the unique properties of ZIF-8 material, we proposed in this work a very promising synthesis strategy for improving the selectivity of SMOx nanowire gas sensors. In order to reach the objective, an original design of the functional material composed of ZnO nanowires (ZnO NWs) homogeneously encapsulated in

a crystalline ZIF-8 selective layer has been achieved. The method relies on the utilization of ZnO NWs as a unique source of zinc which is subsequently used for growing a thin ZIF-8 layer on the nanowires surface. In fact, this method enables homogeneous coverage of ZnO NWs with a ZIF-8 selective barrier (membrane) with high equivalent specific surface area and molecular sieving properties. Application of such an approach, targeting enhanced gas sensing selectivity thanks to a synergic effect of ZnO and ZIF-8 in the specifically designed nanocomposite ZnO@ZIF-8 material has never been reported in the literature, yet. As shown, thanks to the molecular sieving effect of the thin ZIF-8 membrane, the ZIF-8 encapsulated ZnO nanowires-based sensor exhibits greatly improved selectivity for H_2 in comparison with the pristine ZnO NWs sensor. Because H_2 is a clean, efficient promising candidate for renewable energy sources, its production, transportation and storage are key processing steps which must be performed safely. Accordingly, the accurate detection of H_2 gas leaks is crucial and the novel approach developed in this work could be relevant for such strategic applications.

The present approach for improving the gas sensing selectivity of ZnO NWs by a controlled encapsulation of ZnO NWs with a MOF-based membrane involves two key steps: (i) growth of ZnO NWs on the sensor support; and (ii) controlled conversion of the ZnO NWs surface, in order to grow a thin ZIF-8 selective barrier covering the ZnO NWs. (Figure 1 and Supporting information S1)
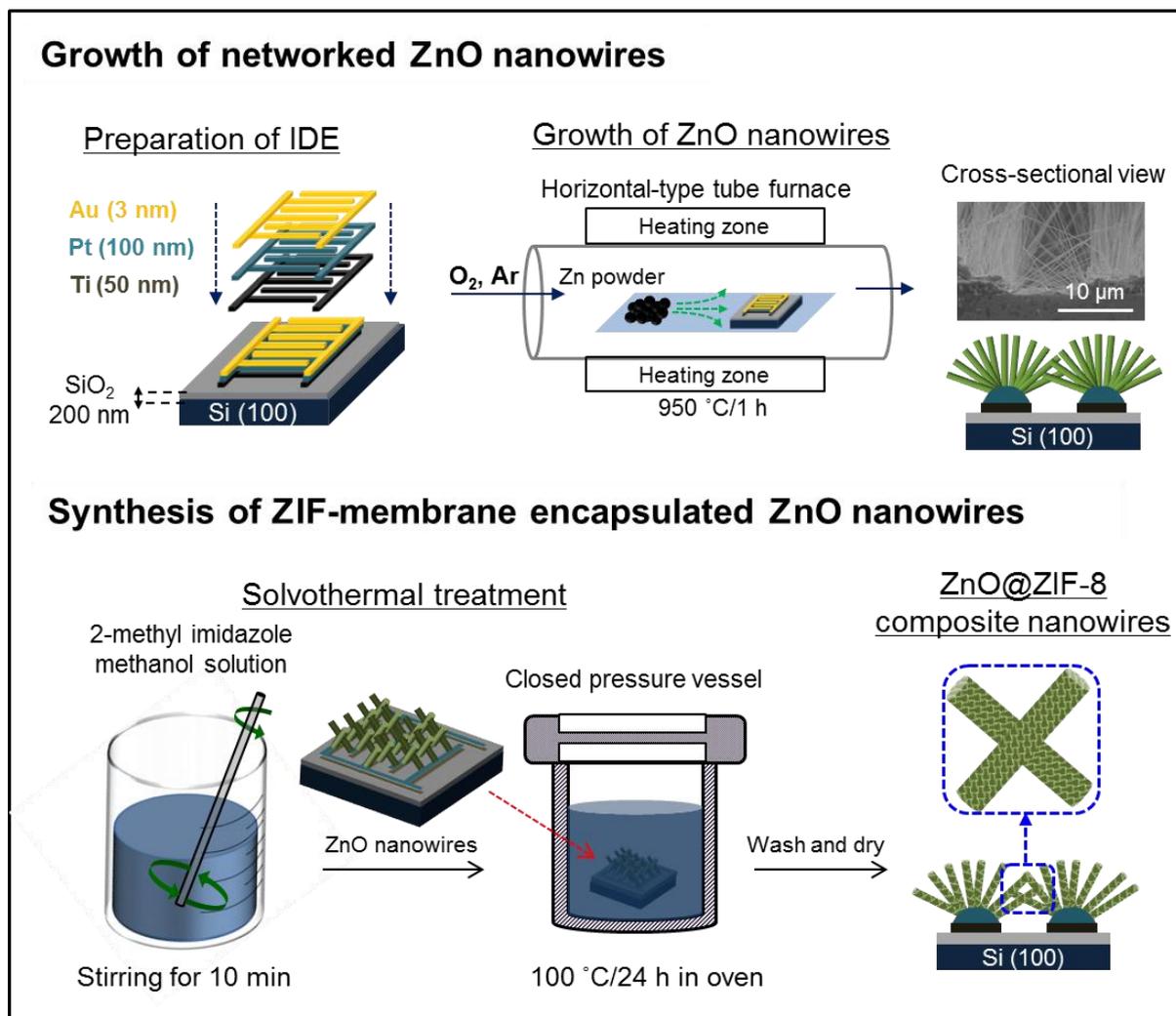
Figure 1. Schematic of the synthesis steps yielding the ZIF-membrane encapsulated ZnO nanowires (ZnO@ZIF-8 NWs).

The synthesis protocol has been optimized in order to get a maximal selectivity in gas sensing response for H_2 in the presence of C_6H_6 and C_7H_8. The characteristics of both pristine ZnO NWs and the derived ZnO@ZIF-8 nanocomposites have been investigated. Gas sensing experiments have been performed with C_6H_6, C_7H_8 and H_2 single gases.

Figure 2a (typical plane-view FESEM image) clearly shows the microstructure of the ZnO NWs 3-D network connecting neighboring electrode pads on the gas sensor support. This

nanowire–nanowire junction provides the electrical pathway whose resistance changes as a function of the concentration and type of surrounding molecules. The high resolution SEM image shown in the Figure 1 reveals the networking design of the ZnO nanowires more evidently. The typical diameter of the ZnO NWs was ~85 nm, with the length reaching up to 25 µm.

The encapsulated ZnO@ZIF-8 NWs have been prepared by conversion of the pristine ZnO NWs surface in contact with a methanolic solution of 2-methylimidazole (2-mim) at 100 °C for 24 h. Different concentrations of the organic linker in the reaction solution have been tested in order to examine the impact on the ZnO NWs conversion degree. The goal was to grow a continuous ZIF-8 layer on the ZnO NWs while maintain the interconnected ZnO network on the sensor support. Indeed, under optimal reaction conditions with 2-mim concentration of 10 wt%, a ZIF-8 layer was grown on the ZnO nanowires, covering their entire surface. ZnO conversion to ZIF-8 occurs via a coordination reaction between Zn^{2+} cations (ZnO top-surface) and imidazolium anions (mim^-) in the solution. Assuming a right balance between the dissolution and coordination rate of Zn^{2+}, no metal loss by leaching is expected during the solvothermal synthesis. Considering the low dissociation rate of ZnO into Zn^{2+} under the gentle solvothermal conditions applied, relatively slow conversion rates were involved with a limited (only top-surface) conversion of ZnO to ZIF-8. These optimized conditions allow conserving the initial gas sensor architecture, with the interconnected ZnO NWs deposited on the sensor support. Both ZIF-8 and ZnO crystalline phases were found to co-exist in the ZnO@ZIF-8 samples, as confirmed in Figure S1 by the characteristic GIXRD lines of both ZIF-8 (2Θ = 7.3° (011), 10.4° (200), 12.7° (112), 18.0° (222)) and ZnO (2Θ = 31.7° (100), 34.4° (002), 36.2° (101)). The success of the partial conversion of ZnO NWs to ZnO@ZIF-8 composite materials has been attested as well by XPS analysis (Table S1). Indeed the binding energies of C1s, O1s, Zn2p3, and N1s peaks observed at 283.12, 530,

1020.05 and 397.18 eV confirm the presence of both ZIF-8 and ZnO in the samples. The global EDX mapping measurements of the whole gas sensor surface revealed uniform distribution of nitrogen and carbon on the ZnO NWs, confirming the formation of ZIF-8 material (Figure S2 and Table S2). This observation is in line with our parallel investigations of ZIF-8 growth on PAN electrospun nanofibers covered by ALD of ZnO thin films.[14] This previous work demonstrated the feasibility and robustness of the proposed synthesis strategy for growing MOF-based materials from a metal oxide surface used as the sole metal source.[16] FESEM images of the ZnO NWs after the solvothermal treatment in the presence of 2-mim (Figure 2b) clearly confirms the preservation of the 3D interwoven nanofibers mat architecture on the sensor support. Due to the small size of ZnO nanofibers before and after the solvothermal treatment, it was very tricky to determine the characteristics (thickness, mean crystal size…) of the grown encapsulating ZIF-8 layer by using a classical SEM apparatus. From a closer examination of the composite material it could be concluded that, after the solvothermal treatment, the ZnO NWs seem to be more stacked together in a form of plait-like structures (Figure 2b), making bridge connections between the electrode pads.

In order to get a further insight into the ZnO@ZIF-8 NWs microstructure, HRTEM observations have been conducted on the as-prepared samples. The HRTEM analysis (TEM imaging and STEM/EDX analysis) confirmed that the nanowires scratched out from the sensor support are composed of a ZnO fiber core encapsulated in a ZIF-8 nanomembrane shell. In fact the STEM/EDX mapping shown in Figure 2c clearly evidences the distribution of elements in the sample, confirming a high quantity of ZnO (Zn and O atoms) in the center of the nanofibers, surrounded with a N, C and Zn-containing compound which corresponds to ZIF-8 material (See Figure S3: line scan). Even if sample observation was relatively tricky, the ZIF-8 layer grown on the ZnO surface was found to cover the entire fiber surface. The thickness of the covering layer was in the range 50-250 nm. Some large ZIF-8 crystals (500

nm in size) with very angular shapes were also detected on few nanowires. An encapsulation of a large majority of ZnO NWs by the molecular sieving membrane (i.e. without non-selective preferential pathways) is a required condition for controlling the access of gas species to the ZnO sensing material and obtaining efficient sensor response improvements. Due to both small dimensions of the gas sensor support and extremely low quantity of the deposited ZnO@ZIF-8 NWs composite materials (thin layer of ZIF-8 covering ZnO NWs) it was not feasible to perform any direct measurement of their specific surface area. In parallel experiments with other types of supports providing much higher available surfaces (PolyAcryloNitrile fibrous mats), the specific surface area of ZnO@ZIF-8 materials, prepared by conversion of an ALD ZnO layer on PAN fibers, has been found to reach $S_{BET} = 1760 \pm 260$ m^2/g. Because of the negligible contribution of PAN mat and significantly low surface area of ZnO ALD layer ($S_{BET}(ZnO) \sim 10$ m^2/g), the high S_{BET} value of the composite system was principally attributed to ZIF-8 contribution.[16]
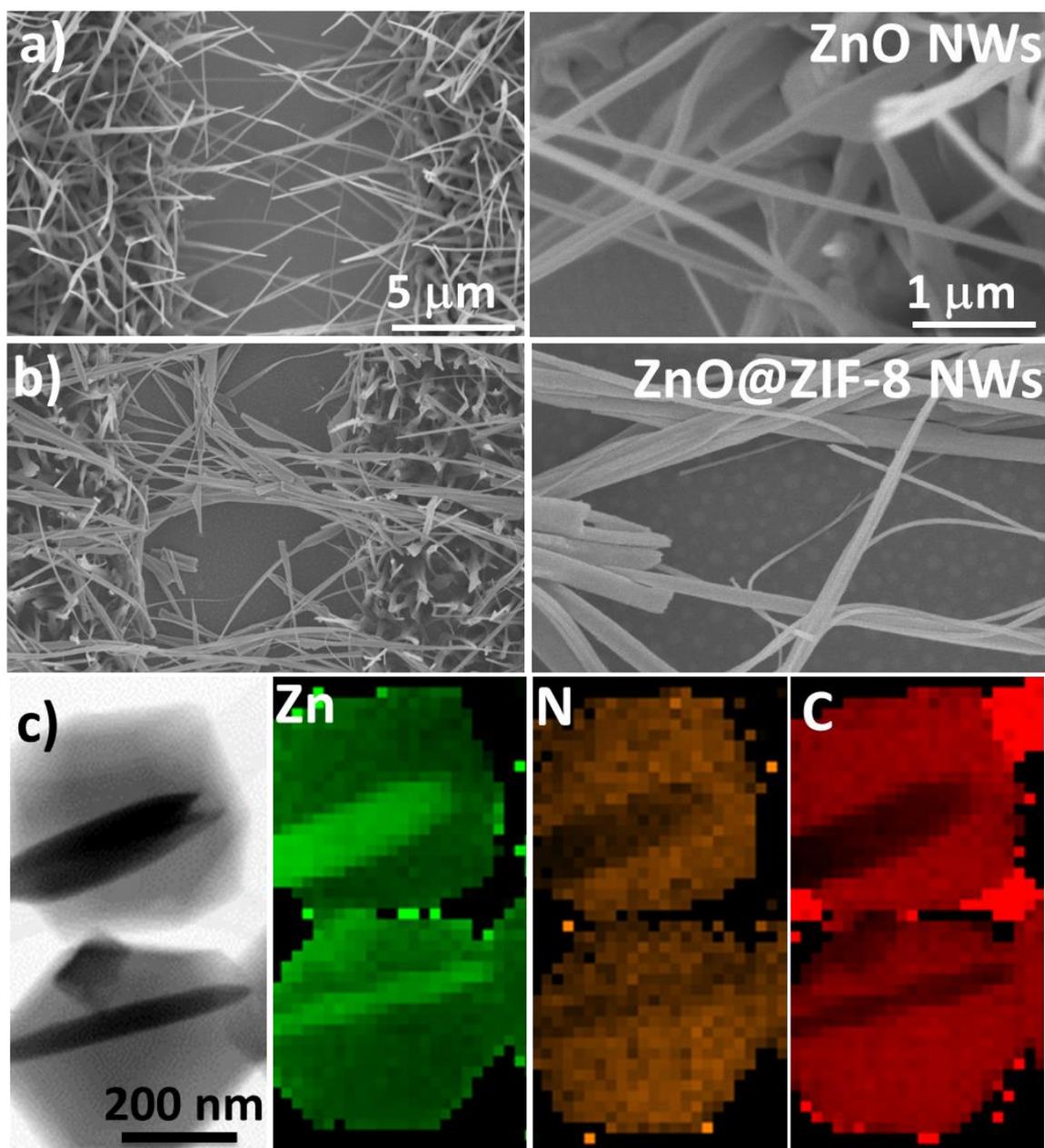
Figure 2. a) plane-view FESEM image of networked ZnO nanowires, b) ZnO@ZIF-8 composite nanowires and c) TEM images of ZnO@ZIF-8 composite nanowires and the corresponding STEM/EDX cartography for Zn, N and C elements.

The dynamic resistance curves of the ZnO NWs and ZnO@ZIF-8 NWs were obtained for various kinds of reducing gases, such as H_2, C_6H_6 and C_7H_8 with concentrations in the range

of 10 to 50 ppm. Results are compared in Figure 3. For the pristine ZnO NWs, the typical n-type sensing behavior is observed; the sensor resistance decreases with the introduction of the tested reducing gases, whereas it reversibly recovers the original resistance value when the supply of the reducing gases is stopped and dry air is supplied. In ambient air, oxygen species adsorbed to the surface of the ZnO NWs extract electrons from the ZnO conduction band, forming an electron-depletion layer underneath of the nanowire surface.[17] This suppresses the conduction channel of the nanowire along the radial direction, determining the overall resistance of the pristine ZnO NWs sensor. The reducing gases supplied interact with the preadsorbed oxygen species, creating volatile molecules, thereby returning the captured electrons back to the conduction band of ZnO. This thins the electron-depletion layer, namely, the radial modulation of the conduction channel takes place. This consequently decreases the sensor resistance.

In Figure 3, a dramatic change in sensor response can be observed in the presence of ZIF-8 membrane grown on the ZnO NWs surface. For H_2 sensing characteristics (Figure 3a), the response values of the pristine ZnO NWs that correspond to 2.34, 2.47 and 2.62 for 10, 30 and 50 ppm H_2 respectively, are found to decrease to 1.17, 1.34 and 1.44, respectively for the optimized ZnO@ZIF-8 NWs composite sensor. In sharp contrast, the responses of the composite ZnO@ZIF-8 NWs for C_7H_8 (Figure 3b) and C_6H_6 (Figure 3c) are almost vanished, approaching 1.0. Note that the response value of "1.0" means no resistance change before and after the gas supply, indicating zero gas sensing response. As expected and as a result of size exclusion effect by the small portal size of ZIF-8 cavities (3.4 Å) the molecular sieving capability of the ZIF-8 membrane layer prevents C_7H_8 and C_6H_6 gas molecules (kinetic diameters 5.92 Å and 5.27 Å, respectively) from accessing the ZnO NWs surface, thus resulting in virtually zero gas sensing response. On the other hand, H_2 molecules, featuring smaller kinetic diameter (2.89 Å), can diffuse easily through the ZIF-8 membrane network

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and can thus access the ZnO NWs surface, ensuring preservation of a significant H_2 response. However, at the same time, the sensor sensitivity is limited by the diffusion of H_2 through the ZIF-8 membrane network which controls the access of H_2 to the ZnO NWs surface and thus its detection rate. The high adsorption capacity of MOF structures (concentration effect) is also expected to further contribute to increase the sensor response sensitivity towards the diffusing species. This finding clearly indicates the enhanced selective detectability of H_2 when using the optimized ZnO@ZIF-8 composite NWs sensor. The thermal stability of ZnO@ZIF-8 composites has been first evaluated both by TGA analysis (Figure S4) and the in-situ X-ray thermodiffraction study (Figure S5), while the stability of ZnO@ZIF-8 NWs has been assessed directly during gas sensing experiments. The above analytical techniques confirmed an excellent material steadiness up to 400°C, thus making it sufficiently stable for long-term gas sensing experiments performed at 300°C. The sample was maintained at the operating temperature of 300°C for durations as long as 72 h and its H_2-sensing properties were measured at different time intervals. The results are summarized in Figure S6. As evidenced, the response curves to 10, 30 and 50 ppm H_2 track well the supply and cutoff of H_2 gas, even after 72 h at 300°C. Such experiment demonstrates not only that the composite ZnO@ZIF-8 NWs sensor was very stable at the operating temperature of 300°C, but was also excellent in response repeatability. Additionally, in Figure S7, the H_2 sensing properties measured at 250°C of the composite ZnO@ZIF-8 NWs sensor are shown. As is evident, the sensor clearly tracks the presence of H_2, demonstrating its stable sensing performance at that operating temperature. Moreover, it must be noted that in spite of the excellent H_2 selectivity of the ZnO@ZIF-8 NWs sensor, its response remains quite low. In sensor applications, a low response might be amplified by a simple electrical circuit, although selectivity cannot. Selectivity is thus a more important sensor characteristic that needs to be as high as possible

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for real sensor applications. In this sense, the novel approach attempted in this study has a considerable significance.
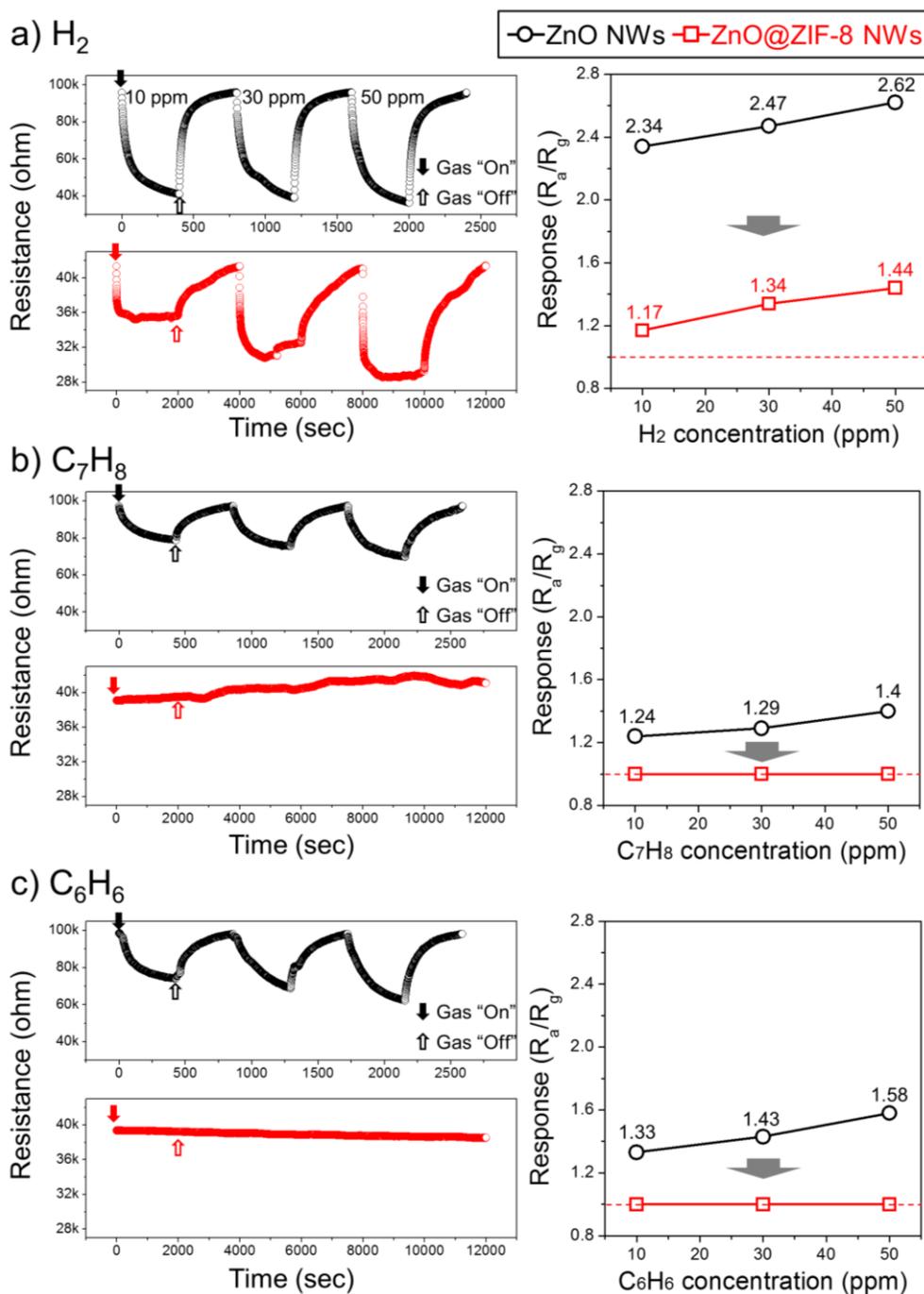
Figure 3: Responses of the pristine ZnO nanowires and ZnO@ZIF-8 composite nanowires in contact with 10, 30 and 50 ppm single gas concentration: H_2 (a); C_7H_8 (b) and C_6H_6 (c).

In summary, we have established a very promising strategy for improving the selectivity of SMOx sensors with NWs morphology. This approach involves the preparation of an original design of the functional material based on the encapsulation of ZnO nanowires with a thin ZIF-8 selective nanomembrane exhibiting both high equivalent specific surface area and molecular sieving properties. The ZnO@ZIF-8 NWs sensors show greatly enhanced selectivity at 300°C for H_2 over C_7H_8 and C_6H_6 in comparison to the pristine ZnO nanowires sensor.

This new approach is highly versatile because it can be used to prepare sensors in which the oxide composition[18] and derived molecular sieve (oxide conversion to different MOF families) [16] can be tuned accurately in order to improve the selectivity of SMOx sensors to different gas mixtures. This strategy opens the door as well to the potential development of a large class of nanomaterials with more complex three-dimensional architectures, adapted for applications where either gas[19] or ion[20] selectivity is required such as biosensors,[21] catalysts,[22-23] photocatalysts,[24] electrodes and membrane reactors.

SUPPORTING INFORMATION. An experimental section (sensors synthesis, gas sensing measuremets), additional EDX measurement during SEM and TEM observation, XRD, XPS, TGA analyses and gas sensing at 250°C and long-term stability are supplied as Supporting Information.

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