Fabrication of ZnO@ZIF-8 gas sensors for selective gas detection

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Abstract
In this paper, zinc oxide nanorods encapsulated with a representative of the zeolithic imidazole based metal organic framework family (ZIF–8) is used as gas sensor material for the detection of hydrogen gas and benzene vapour. The material properties of this ZnO@ZIF-8 hybrid material was investigated by XRD, electron microscopy, Fourier transform infrared spectroscopy and gas sensing experiments. Selectivity and sensitivity of these thin films to various gases H2 and C6H6 were also studied. The ZnO@ZIF–8 sensor with the nanostructure showed a remarkable selective response to hydrogen gas compared to the pristine ZnO nanorods sensor, while the ZnO sensor shows high sensitivity to H2 and C6H6. The ZnO@ZIF–8 sensor exhibits a significant selective response to hydrogen compared to the original ZnO nanorod sensor. This behavior can be attributed to the small pore aperture of ZIF–8, where H2 molecules can easily spread through the ZIF–8 network and reach the ZnO surface. This result indicate that the selectivity of ZnO gas sensor can be regulated by surface ZIF–8 coating.

1. Introduction

The fabrication of metal oxide gas sensors (MOGs) has several advantages as compared with other sensors such as easy construction, low cost and simple measuring performance. The mechanism of sensing involves the gas adsorption on the sensor material surface which causes a change in electrical conductivity of the sensor [1 and 2]. The sensor characteristics, including (i) sensitivity, (ii) selectivity, (iii) response and recovery times [3 and 4] are influenced by several parameters such as environmental conditions (temperature, humidity), doping of the sensor material [5] and thin film morphology (grain size and roughness). [6] Increasing the sensor selectivity is one of the most challenging tasks in the field of metal oxide gas sensor development. To improve the selectivity of a metal oxide gas sensor the metal oxide can be chemically functionalized e.g. with catalytically active additives, including noble metals such as gold [7], platinum [8] or palladium, [9] or by other oxides such as the doping of a SnO2-based sensor material with ZnO [10]. Recently a combination of metal oxide-based sensors with the metal-organic frameworks (MOF) has been reported [11–17].

The method involves the deposition of a representative of the Zeolitic Imidazole Framework (ZIF) family, ZIF–8, on ZnO nanorods. The nanorods were produced by a two-step process: first ZnO seeds were deposited on an interdigitated Pt electrode (IDE), then a hydrothermal growth of ZnO nanorod was initiated [18]. The coating of the ZnO with ZIF–8 was carried out by a sacrificial support method [19–21]. Due to their highly porous structures MOFs can be used for many fields of application such as catalysis [22], gas separation [23] and storage [24] or nonlinear optics [25]. Recently, there has been an increased interest in the application of MOFs in the field of selective gas sensing [26]. As an example the sensing properties of zinc oxide and zinc oxide coated with ZIF–8 were studied in the presence of hydrogen and methane gas [27]. The development of hybrid material-based sensors combining the gas filtering effect of MOFs with the sensitivity of metal oxide materials might increase the selectivity for a specific gas within a gas mixture. In particular toxic or dangerous gases must be detected selectively to avoid any unwanted exposure, e.g. by inhalation (organic solvent vapors) or accidents (explosive gases). The sensing properties of semiconductors and the gas filtering effect of MOFs makes it attractive to combine both functionalities to develop sensors with a high selectivity for a specific gas.
In this work, the selectivity of the gas sensors consisting of ZnO nanorods either with or without ZIF-8-based coating were used as sensing material to investigate two representatives of the before mentioned gas classes:

(1) Although hydrogen is an efficient and promising gas as source of renewable energies e.g. in terms of fuel cells, it requires a high level of safety standards during production, storage, transportation and application \cite{28, 29}. Accordingly, the effective detection of gas leakages of hydrogen containing tubes or tanks is extremely important.

(2) The second sample gas used for the sensing experiments described in this work is benzene, which represents a toxic and carcinogenic solvent. In this context ZnO based sensors without and with ZIF-8 coating were used and compared in terms of sensor selectivity, sensitivity, response and recover time. We demonstrate that the gas selectivity for H$_2$ gas increased with a ZIF-8 coating applied to the ZnO-based sensor material.

2. Experimental

2.1. Synthesis of ZIF-8

The ZIF-8 thin film was prepared by the solvothermal method on a porous Al$_2$O$_3$ substrate by dissolving 0.538 g (3.95 mmol) of zinc chloride ($\geq$99%, Merck), 0.486 g (5.92 mmol) of 2-methylimidazole (2-MIM) ($\geq$99% Sigma-Aldrich) and 0.268 g (3.94 mmol) of sodium formate ($\geq$99% Sigma-Aldrich) solved by ultrasonic treatment in 80 ml methanol (99.9%, Roth). The substrate is placed horizontally in the 45 ml autoclave with the polished finish up. The solution is heated up to 100 °C for 27 h. The autoclave is then cooled to room temperature. Then, the substrate is removed and rinsed three times with methanol to remove solvents from the surface. After that, it is immersed in methanol for 12 h to exchange the solvent with the channels of ZIF-8. Finally dry the substrate at 60 °C for 24 h. Using the solvothermal method to produce the ZIF-8 on the porous aluminum oxide as shown in figure 1.

2.2. Synthesis of ZnO coated by ZIF-8 (ZnO@ZIF-8)

2.2.1. Growth ZnO seeds

For the preparation of the ZnO seeds, which are required for the following growth of the ZnO nanorods 10 ml of a 0.05 mol/L ethanolic solution of zinc acetate dihydrate (≥99% Sigma-Aldrich) [Zn(OOCCH$_3$)$_2$·2H$_2$O] were mixed in a 50 ml beaker. A 30 μl solution was applied to a thin-film platinum interdigital electrode (Pt-IDE) microstructured on an Al$_2$O$_3$ substrate ($7 \times 7$mm$^2$) with a microstructured heater at the reverse side \cite{30} by spin coating (Laurell WS-400-STFW-FULL) at a rate of 2000 rmp for 30 s and then rinsed with clean ethanol. For later this process was repeated 10 times to increase the layer thickness. The thickness of the zincacetate layer can be controlled by the number of spin coating runs. The ZnO seed layers were pre-heated at 200 °C for 10 min by using a hot plate and allowed to cool naturally to the room temperature by switching the hot plate off. The coated substrates were dried at room temperature and annealed in the oven at 150 °C for 30 min \cite{31}.

2.2.2. Growth ZnO nanorods

The ZnO nanorods growth was carried out by the chemical bath deposition (CBD) technique. The ZnO seed sample was immersed in a solution of 0.15 g of zinc nitrate hexahydrate (≥99% Sigma-Aldrich) and 0.035 g hexamine (≥99% Sigma-Aldrich) [(CH$_2$)$_3$N$_4$] in 20 ml of deionized water and 4 ml aqueous ammonia (≥99.98% Sigma-Aldrich) to vary the pH at room temperature. The ammonia was added to raise the pH to 9 and to initiate the growth of the ZnO nanorods. The solution and substrate were placed horizontally into a 45 ml Teflon-lined autoclave with the seeded/smooth surface facing upward. The growth temperature was kept at...
140 °C for 6 h. As a next step the substrate was rinsed with deionized water and dried with nitrogen gas (99.99%). The ZnO nanorods were annealed at 300 °C for 30 min in the oven [31].

2.2.3. Preparation ZnO@ZIF-8
For the sacrificial growth of the ZIF-8, the substrate with the grown ZnO nanorods was immersed in a solution which contains powder of (0.3 g) 2-methylimidazole (2-MIM) dissolved in 4: 16 ml of mixture of water and dimethylformamide (DMF, ≥99.98% Sigma-Aldrich) in a teflon container of an autoclave. The autoclave was heated in an oven to 100 °C for 24 h and then cooled down to room temperature. The ZnO@ZIF-8 composite was washed several times with methanol and dried at 70 °C for 2 h [21]. Figure 1 shows a synthesis and mechanism diagram of ZnO@ZIF-8 sensor.

2.3. Sample characterization
An x-ray diffractometer (Bruker D5000) was used to characterize the crystalline property of the films. Electron microscopy was carried out with a Philips XL 30 Field Emission Gun Environmental Scanning Electron Microscope (FEG-ESEM) from FEI. The FTIR measurement was carried out with a Bruker Vertex 80 system.

2.4. Gas sensing experiments
The resistance of the films that were sequentially exposed to H2 and C6H6 gases at 50 °C–375 °C was determined by measuring the conductance inside the home-made gas sensing set-up equipped with a small hot plate for heating the samples and a power supply for bias voltages up to 5 volts (Hiltex 40531, 10-Amp 30-Volt DC Digital Power Supply Conductance measurements were carried out in the dark, so that photon excitation of the semiconductor material did not influence the results. The gas flows (100 ml min$^{-1}$) were controlled by two calibrated flow meters (acrylic panel mounts, gas flow meter, Drahor Inc.), and the gas was fed into an injection point located below the sample holder. After the introduction of hydrogen and methane gas at a concentration of 50 ppm each to the examination chamber, the resistance of the thin film is measured with time and at different temperatures. After that, the amount of the sensitivity, which represents the susceptibility of the sensor to respond to the concentration of available gas, is calculated. The sensitivity is calculated by the following relationship: $S = (R_s - R_a)/R_s \times 100$, where $R_s$ and $R_a$ are the resistances of the sensor layer in synthetic air and target gas in synthetic air, respectively. Before and after the gas is passed and achieves saturation [32].

3. Results and discussion
This behaviour can be attributed to the small pore aperture of the ZIF-8 cavity (3.4 Å)

3.1. X-ray diffraction
Figure 2 illustrates the XRD pattern for ZnO nanorods coated with ZIF-8 (ZnO@ZIF-8) on a porous Al$_2$O$_3$ substrate. This figure shows that XRD peaks at 2θ values of 7.349°, 10.386°, 12.66°, 14.695°, 16.459°, 18.044° and 25.629° corresponding to ZIF-8 (011), (002), (112), (022), (013), (222) and (224) respectively [19–21]. The reflections at the 2θ values of 31.9°, 34.4°, and 36.2° correspond to the (100), (002) and (101) directions of the ZnO, respectively [1, 6]. All XRD patterns match the Wurtize hexagonal phase of ZnO (ICSD 01-074-0534). The dominant diffraction (002) peak can be assigned to the ZnO grown nanorods, which indicates that the aligned ZnO nanorods were fabricated along the c-axis of the hexagonal Wurtzite structure. These results are in agreement with the results published by [1, 6, 7, 27, 33].

3.2. SEM measurements
Representative SEM images of the ZnO@ ZIF-8 thin films are shown in figure 3. In figure 3(a) the homogenous and uniform coating over the entire substrate is observed. Figures 3(a)–(d) shows that the ZIF-8 coating, consists of particulate, platelet-like structures. Figures 3(e) and (f) show cross-sections of ZnO films, before and after the coating with ZIF-8 respectively. The length of the ZnO nanorods has been determined to about 7 ± 0.5 μm.

3.3. FTIR measurements
Figure 4 shows the FTIR spectra in the range of 500–3500 cm$^{-1}$ for the ZIF-8, ZnO@ZIF-8 and 2MIM (2-methylimidazole) deposited on the porous Al$_2$O$_3$ substrate. The absorption peaks for ZIF-8 at 2956 cm$^{-1}$ and 3136 cm$^{-1}$ can be assigned to the aromatic and aliphatic C–H stretching vibrations of the imidazole, respectively, while the band at 1587 cm$^{-1}$ belongs to the C=N stretching mode. The bands in the range 1100–1400 cm$^{-1}$ region can be assigned to the C–N stretching vibrations. The results agree well with published values [21 and 27]. When the ZnO is coated with ZIF-8 a new broad peak appears in the range between 690 and 870 cm$^{-1}$ which related to
Figure 2. XRD pattern of ZnO@ZIF-8 deposited on porous Al₂O₃ as gas sensor.

Figure 3. SEM top view (a)–(d) of ZnO@ZIF-8 and cross section view (e) and (f) of ZnO and ZnO@ZIF-8 respectively.
the Zn–O stretching vibrations. Comparing the infrared spectra of 2-methylimidazole with that of ZIF-8 at 950 cm$^{-1}$, a redshifted stretching vibrations peak is confirmed$^{[33]}$.

3.4. Gas sensing experiments

To investigate the gas-sensing performance of the ZnO@ZIF-8 thin film and to compare it with the raw ZnO nanorod film, we fabricated a ZnO@ZIF-8 core–shell nanorod sensor and a raw ZnO nanorod sensor. The fabricated ZnO and ZnO@ZIF-8 based sensors were tested for two gases: H$_2$ and C$_6$H$_6$.

Figure 5(a) shows that the sensitivity of a ZnO-based sensor for both gases increases with increasing operation temperature and reaches the maximum value at 275 °C which can be considered as the optimal temperature for the operation of the fabricated sensors$^{[32]}$. Figure 5(b) shows the sensitivity of the ZnO@ZIF-8 sensor for H$_2$ and C$_6$H$_6$ as a function of different operation temperatures. While the sensitivity of the sensor to H$_2$ is clearly visible, it nearly vanishes in the case of the C$_6$H$_6$ gas. In the case of H$_2$, again the temperature of 275 °C is optimal, which is comparable with the results from the ZnO-based material shown in figure 5. The sensitivity of gas sensor depends on the changed in the resistance of the ZnO and ZnO@ZIF-8 thin films$^{[30, 32]}$.

The gas response time is defined as the time span between the moment of gas exposure until the moment when the resistance of the sensor is decreased to 90% of its original value before gas exposure. The recovery time was the time which is needed by the sensor to get back to 90% of the original resistance$^{[32]}$. The ZnO sensor response as a function of time for H$_2$ and C$_6$H$_6$ gases at the operation temperature of 275 °C is shown in figure 6(a). It is observed that the response and recovery times were 25.3 s and 50 s, for H$_2$ and 26 s and 53 s for C$_6$H$_6$, respectively.

Figure 6(b) shows the gas response of the sensor as a function of time before and after gas exposure for the case of a ZnO@ZIF-8 based sensor material at an operation temperature of 275 °C. From this data response and recovery times for H$_2$ of 50 s and 130 s, respectively, are obtained. In contrast to the pure ZnO-based sensor material no sensor response can be detected for benzene in the case of the ZIF-8 coated sensor material. This behaviour can be attributed to the small pore aperture of the ZIF-8 cavity (kinetic diameter 3.4 Å), which avoids
the diffusion of the C₆H₆ gas molecules (kinetic diameters 5.27 Å) to the interface with ZnO [19, 23, 24, 33]. On the other hand, H₂ molecules (kinetic diameter 2.89 Å), can diffuse easily through the ZIF-8 network and reach the ZnO surface [24, 29, 31]. Moreover, it must be noted that in spite of the excellent H₂ selectivity of ZnO@ZIF-8 nanorod sensors, its response and recovery times remain quite low, or significantly higher, respectively, compared to the situation where ZnO without ZIF-8 coating was used. This can be explained by the following arguments: (1) as a consequence of the fact that the ZIF-8 coating is hindering the free access of the H₂ molecules to the ZnO, the average number of H₂ molecules per time unit reaching the ZnO interface is reduced compared to the ZnO material without ZIF-8 coating. This additional transport limitation of the target gas to the ZnO/ZIF-8—interface will not only reduce the sensitivity, but also increase the time until an equilibrium state is reached which is reflected by a stable sensor signal for the sensor sensitivity. (2) The high absorption capacity of the MOF structures for H₂ is expected to increase the recovery time even when the sample gas support is interrupted as the stored hydrogen can diffuse to the ZnO@ZIF-8 interface. The H₂ molecules adsorbed inside the MOF pores can diffuse to and interact with the ZnO interface. This result clearly indicates that H₂ is selectively detectable when using the ZnO@ZIF-8 gas sensor [24, 34, 35]. Wu et al have reported that gas sensitivity and selectivity increased for ZnO gas sensor after coated by ZIF-8 for H₂ over CO gases [21]. Nair et al, have reported that the gas sensing behaviour towards propene and ethene has been studied under non-humid and humid atmosphere conditions. The structural and morphological analysis supported the formation of core-shell heterostructures with a functional ZnO core and a porous ZIF-8 shell and good material stability under the
given experimental conditions. Gas sensing tests yielded an increased sensitivity towards propene compared to that of ethene, a general increase of conductance after deposition of ZIF-8 and a typical sensitivity of both, the ZnO- and the ZnO@ZIF-8 layer to water vapour when exposed to synthetic air \[36\].

4. Conclusion

A chemical bath deposition method was used to produce ZnO-based nanorods on a Pt IDE as a gas sensitive material for hydrogen and benzene sample gases with significantly different kinetic diameters. By the additional coating of the ZnO nanorods with the metal-organic framework ZIF-8, using a solvothermal deposition method, we could show that the ZIF-8 coating acts as a molecular sieve, hindering diffusion through the pores to the ZnO interface of the larger benzene molecules compared to the smaller H$_2$. For both the ZnO and ZnO@ZIF-8–based material the highest sensitivity was achieved at a temperature of 275 °C for both gas components.

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