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Improving Sensitivity of a Chemoresistive Hydrogen Sensor by Combining ZIF-8 and ZIF-67 Nanocrystals †

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Abstract: In the present work, nanostructures of zeolitic imidazolate frameworks (ZIF-8 and ZIF-67) were combined to obtain a novel chemoresistive sensor, improving the sensitivity of ZIF-67 and facilitating measurement of ZIF-8 by decreasing the resistivity. The sensor detected concentrations as low as 10 ppm of hydrogen increasing its resistivity about 4.5 times. The response of the sensor was compared with a similar chemoresistive sensor based exclusively on ZIF-67, and the sensitivity was around three times higher in the case of the sensor with ZIFs combination.

Keywords: chemoresisteve sensor; ZIF-8; ZIF-67; hydrogen

1. Introduction

Hydrogen is proposed as alternative to energy supply systems [1]. However, hydrogen is an odorless and colorless gas with a wide explosive range, between 4% and 75%, which suppose a safety risk if it is transported, saved or manipulated due to the possibility of leakages. Therefore, low cost sensors capable of detecting low concentrations of hydrogen in situ and in real time are urgently needed.

Aluminum silicate zeolites have been extensively used in gas adsorption, molecular sieving, catalysis, and gas detection because of its unique porous structure. However, in the last years, organic zeolites such as zeolitic imidazolate frameworks (ZIFs) have attracted major attention to detect gases because they offer two primary advantages over conventional zeolites [2]. First, they have larger porous size (about 1.6 nm for ZIF-8 and ZIF-67) and usually smaller crystal size, resulting in higher surface area. Second, many of ZIFs show a pronounced hydrophobic behaviour.

2. Materials and Methods

2.1. Synthesizing of ZIF-8 and ZIF-67

In the great ZIFs family, ZIF-8 and ZIF-67, consist of 2-methyl-imidazolate (MeIM) groups linking tetra-coordinated Zn^{2+} and Co^{2+} metal ions, respectively (Figure 1). Both ZIFs exhibit the same sodalite-like structure with pore sizes of 11.6 Å and small pore windows of 3.5 Å [2]. Nanosized ZIF-8 and ZIF-67 were synthesized as described by Yichang Pan [3], with some modifications. Then the product was collected by centrifugation (24000 rpm, 10 min), washed by DI water for three times and dried at 65 °C for one day in a drying oven.

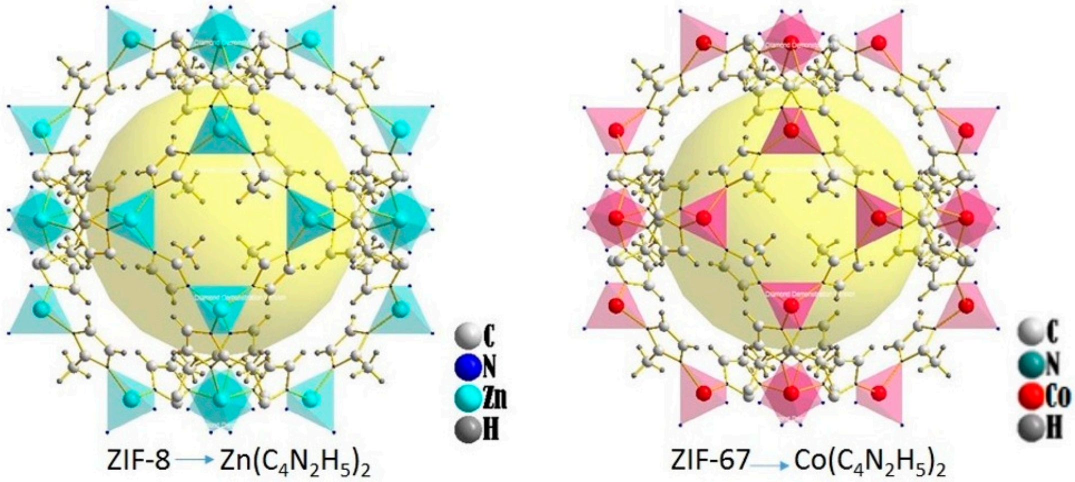


Figure 1. Representative crystal structures of ZIFs under study.

2.2. Experimental Setup

The detection system consisted of the test chamber with the sensors. A multimeter was used to acquire the resistance response of the sensors. The temperature of the sensors was kept at 180 °C. The hydrogen samples were generated from hydrogen cylinder with concentration of 100 ppm. In order to characterize the sensors with different concentrations, two mass flow controllers were used to dilute the initial concentration with synthetic air and thus keep constant the flow at 100 mL/min. The experiment control and data acquisition in real time were implemented with a PC by means of our own specialized software (Figure 2).

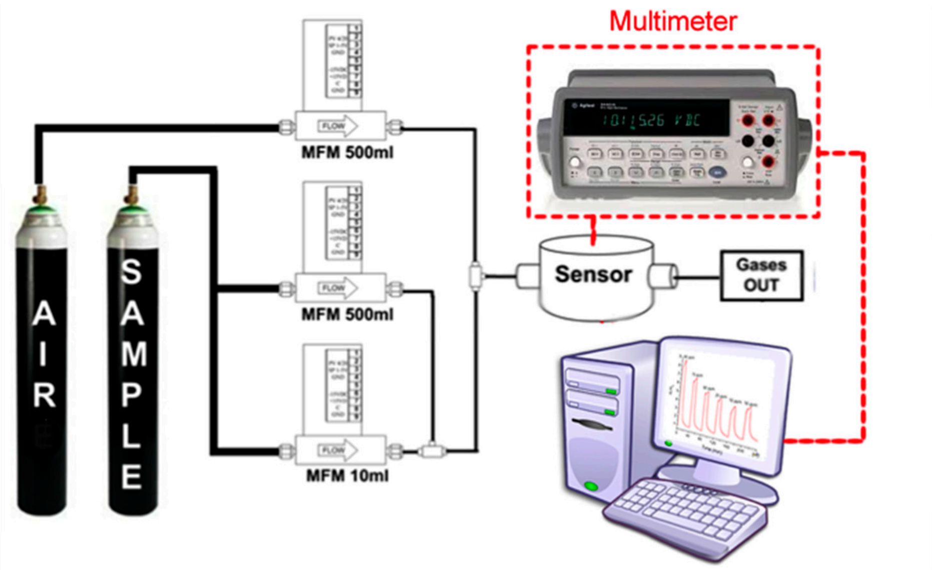


Figure 2. Experimental setup used to measure different concentrations of hydrogen in real time.

2.3. Sensor Fabrication

In order to develop the sensors the resulting ZIFs samples were sonicated for 5 min and then used to develop two sensors by drop coating of ZIFs on microfabricated electrodes (Figure 3a,b). First one consisted in a mixture of about 50% ZIF-67 and 50% ZIF-8 and the second one was developed with simple ZIF-67 solution.

3. Results

3.1. Electrical ZIFs Characterization

ZIF-8 deposited on microelectrodes had a resistivity higher than 100 MOhm at 200 °C, thus a combination of ZIF-67 and ZIF-8 was carried out to obtain reduced resistivity, and obtain a sensor capable to measure hydrogen concentrations.

3.2. Estructural and Morphological ZIFs Characterization

Both samples, ZIF-8 and ZIF-67 presented the characteristics XRD patterns and IR spectroscopy absorption bands, reported in the literature for these structures [3,4]. A particle size for ZIF-8, between 45 nm and 80 nm were revealed through TEM images (Figure 3c). Similarly the particle size for ZIF-67 ranges between 180 nm and 200 nm.

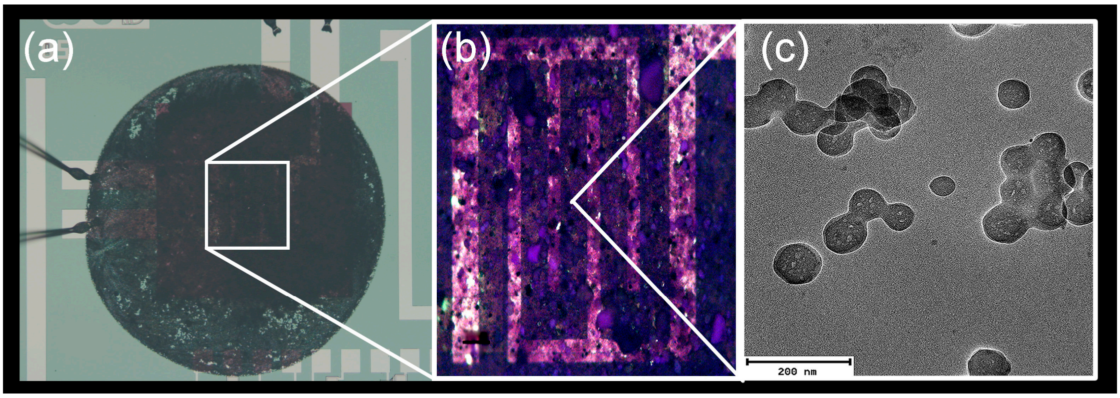
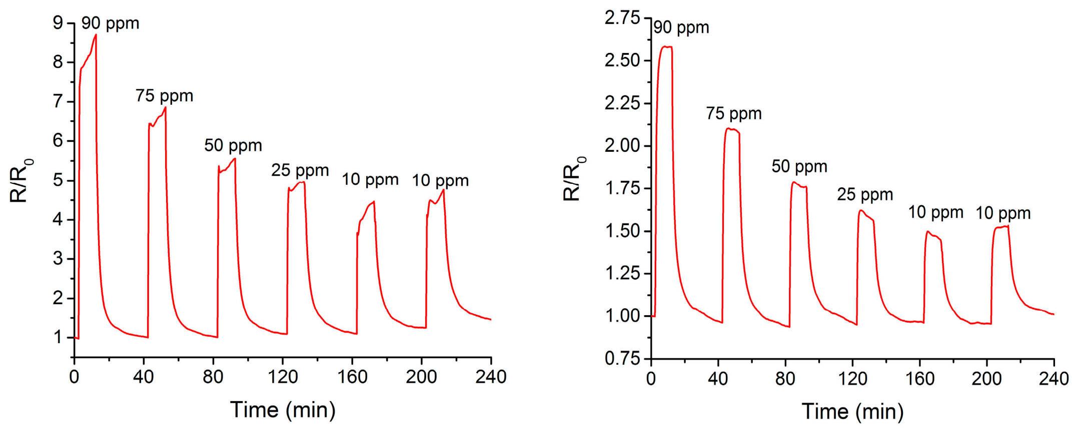


Figure 3. (**a**) Image of resulting deposition of ZIF nanocrystals solution by drop coating; (**b**) layer of ZIF deposited on microfabricated electrodes; (**c**) TEM image of ZIF-8 nanocrystal.

3.3. Hidrogen Sensor Characterization

Different hydrogen concentrations were used to characterize the sensor: 90 ppm, 75 ppm, 50 ppm, 25 ppm and 10 ppm. The sensor formed by ZIFs combination (Figure 3a) shows a better response than ZIF-67 (Figure 3b), around three times higher, increasing resistance of the sensor up to nine times with 90 ppm hydrogen detection, and a concentration as low as 10 ppm of hydrogen was detected with high response, increasing resistivity about 4.5 times with short response and recovery times.



(**a**) (**b**)

Figure 4. (**a**) Real time response of chemoresistive sensor based on (**a**) ZIF-8 and ZIF-67 combination (**b**) ZIF-67 for different concentrations of hydrogen.

4. Conclusions

Nanostructures of zeolitic imidazolate frameworks (ZIF-8 and ZIF-67) were combined in order to obtain a high sensitivity hydrogen sensor, improving the sensitivity of ZIF-67 and facilitating measurement of ZIF-8 by decreasing the resistivity. The sensor detected concentrations as low as 10 ppm of hydrogen increasing its resistivity about 4.5 times. The response of the sensor was compared with a similar chemoresistive sensor based exclusively on ZIF-67, and the sensitivity was around three times higher in the case of the sensor with ZIFs combination.

Therefore, repeatability, reversibility, accuracy, fast response and high sensitivity have been achieved for hydrogen detection with the sensor based on the combination ZIF-8 and ZIF-67 nanocrystals.

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Conflicts of Interest: The authors declare no conflict of interest.

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