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Fabrication of microporous membranes for highly selective gas sensors

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Abstract

A major limitation of gas sensors is poor sensor, hindering the accurate detection of single target molecules in complex gas mixtures. Here, a fabrication route is presented that overcomes this limitation by combining a selective zeolite membrane with a highly sensitive Pd-doped SnO_2 sensor. While the membranes are synthesized hydrothermally, the sensors are produced in a flame aerosol process. These two processes are decoupled and therefore both membrane and sensor can be optimized individually, to match the target analyte. This is demonstrated for formaldehyde, a carcinogenic compound and potential lung cancer marker. Formaldehyde concentrations down to 30 ppb are detected, sufficiently low to identify hazardous formaldehyde levels in indoor air. Most notably, the detection was not affected by interfering analytes tested in gas mixtures, including humidity, NH_3, acetone, ethanol and isoprene at much higher concentration.

Key words: zeolite, SnO_2, formaldehyde, hydrothermal, flame spray pyrolysis

Nowadays, metal-oxide gas sensors exhibit sufficient sensitivity to detect trace analytes down to ppb-level (e.g. 5 ppb of isoprene with Ti-doped ZnO [1]). However, selective detection of a specific analyte remains a major challenge. While sufficient selectivity to some analytes has been obtained by material engineering (e.g. Si-doped MoO_3 for NH_3 [2] or Si-doped WO_3 for breath acetone [3]), no suitable match has been found for other important tracers, e.g. formaldehyde, a carcinogenic [4] pollutant and potential marker of lung cancer. Good results for formaldehyde were obtained with sensor arrays, however, these always involve statistical errors [5]. Therefore, new approaches are needed to overcome existing selectivity limitations.

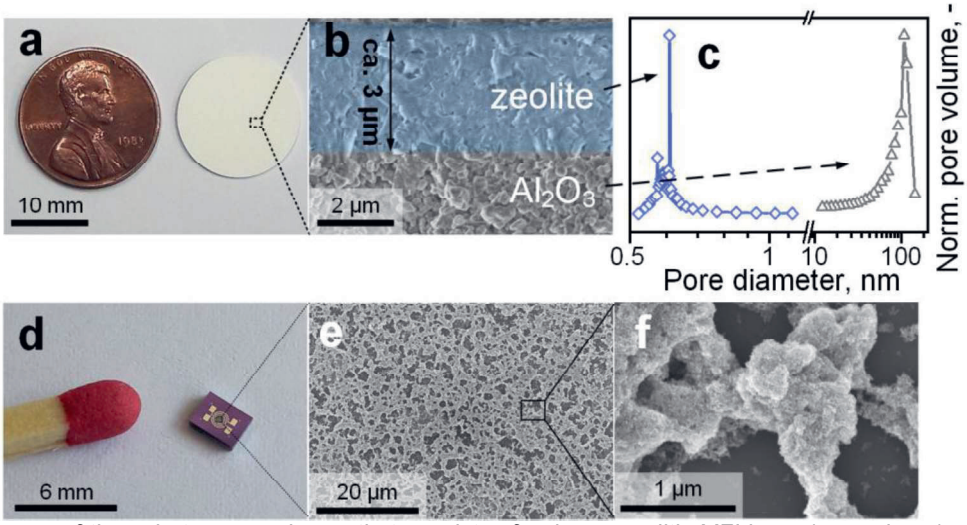

Fig.1. (a) Image of the coin-type membrane that consists of a dense zeolitic MFI layer (upper layer) supported on a macroporous Al_2O_3 (lower layer), as indicated by cross-sectional SEM (b). (c) MFI (diamonds) forms micropores in the size range of volatile molecules. (d) Compact sensor that features a highly porous sensing film, as indicated by top-view SEM in (e). (f) This film is formed by a fine network of aggregated Pd-doped SnO_2 nanoparticles providing large surface area for detection of analytes even at ppb-level. Figure adapted from [6].

Here, we propose a modular sensor system that overcomes this limitation by placing a highly selective membrane for pre-separation upstream of a highly sensitive chemo-resistive sensor [6]. The membrane consists of a supported zeolitic membrane that is hydrothermally grown in a stainless steel autoclave. Zeolites are microporous materials with a pore size comparable to the molecular dimensions of volatile compounds, thus, ideal for a pre-separation of the gas mixture.

Zeolite layer thickness and composition can be adjusted by the synthesis time and precursor composition. Therefore, the membrane can be tailored for effective separation of the target analyte. Figure 1a shows such a coin-type membrane consisting of a compact and coherent ~3 µm zeolite MFI film (Fig. 1b: upper layer) that was hydrothermally grown on a porous Al_2O_3 support (lower layer) for 8 h at 185 °C [6]. While the MFI layer (diamonds) features micropores in the range of 0.57 to 0.61 nm for effective separation, the Al_2O_3 support (triangles) has pores mostly larger than 40 nm in diameter and is required for mechanical stabilization.

As a sensor, flame spray pyrolysis (FSP)-made Pd-doped SnO_2 nanoparticles are directly deposited on sensor substrates. FSP is a versatile technique to produce various material compositions and morphologies beneficial for gas sensing. The resulting sensor is smaller than a match head (Fig. 1d) and can be combined modularly with the membrane. It features a highly porous chemoresistive sensing film (d = 500 µm) at its center (Fig. 1e,f). The open structure allows analytes to rapidly diffuse in the sensing film and interact with the large surface area enabling detection even of trace-level concentrations. In fact, such nanostructured sensors, e.g. Pd-doped SnO_2 are highly sensitive and can detect formaldehyde down to 3 ppb (at 90% RH) but without membrane they are not selective [5].

Figure 2 shows the sensor responses for 0 - 1000 ppb of formaldehyde (circles). The entire range can be measured and also levels below 100 ppb are clearly differentiated. This is important as formaldehyde in breath and indoor air occurs typically below 100 ppb, while other analytes may be present at much higher level (e.g. 833 ppb is the mean NH_3 concentration in breath). Most notably, when simulating such a situation by introducing different quantities of formaldehyde along with NH_3, acetone, isoprene and ethanol each at 1000 ppb, the calibration curve (squares) does not change even at 30 ppb of formaldehyde. This emphasizes the outstanding separation properties of the membrane that are crucial for reliable breath diagnostics and indoor air monitoring.

Finally, due to the wide flexibility and decoupled fabrication of the membrane and sensor, this concept could be extended to *other* target compounds.

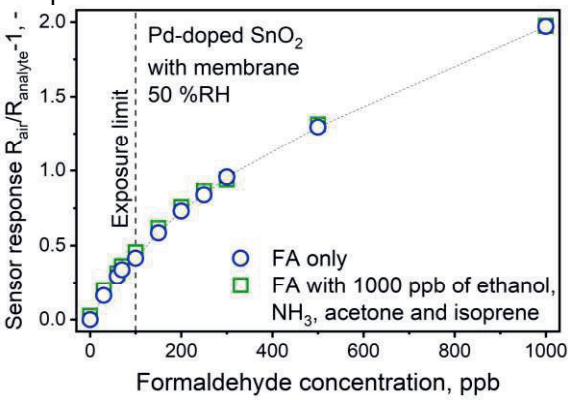

Fig. 2. Sensor calibration curve for formaldehyde in the range of 0 - 1000 ppb at 400 °C and 50% RH (circles). Interestingly, this calibration curve does not change even when introducing 1 ppm of NH_3, acetone, isoprene and EtOH, all at the same time (squares) highlighting the excellent formaldehyde selectivity of the membrane-sensor system. Figure adapted from [6].

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