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Selective Formaldehyde Detection at low ppb Level with Microporous Membranes and SnO_2 Sensors

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Abstract

A major challenge in gas sensing (e.g. air quality and breath analysis) is the selective detection of trace-level pollutants. While many gas sensors exhibit sufficient lower detection limit down to ppb, they lack selectivity. Here, we present a novel concept that combines (1) a membrane taking over the selectivity task by pre-separating the gas mixture with (2) a chemoresistive gas sensor detecting the analyte. The membrane is decoupled from the sensors to allow individual fabrication and independent operation. It consists of a zeolitic molecular sieve featuring adjustable separation properties to match the analyte. As proof-of-concept, a compact zeolite MFI/Al_2O_3 membrane is placed before a non-specific Pd-doped SnO_2 sensor. In fact, this system exhibits excellent selectivity (even in gas mixtures) to carcinogenic formaldehyde over ethanol, ammonia, acetone and isoprene (all > 100) at 50% relative humidity, superior to existing sensors. This novel concept can be extended to other tracers and it could facilitate a new class of selective and portable gas detectors.

Key words: selectivity, zeolite, SnO_2, hydrothermal, formaldehyde

Modern chemical gas sensors (e.g. semiconductive metal-oxides [1]) can detect analytes at the parts-per-billion (ppb) level. By featuring also a compact design, such sensors are attractive for small indoor air quality monitors or portable breath analyzers [2]. However, a major challenge remains their lack of selectivity to the target analyte. Despite extensive research in the last decades, only a few selective chemoresistive sensing materials have been developed (e.g. Ti-doped ZnO for isoprene [3] Si-doped MoO_3 for NH_3 [4]). Exploring these requires time-consuming in-depth material engineering and for many gases, such might not even exist. What is truly needed are novel strategies that complement chemoresistive sensing.

Additional filters can enhance the selectivity of a gas sensor by pre-separating the gas mixture. Zeolite molecular sieves - already intensively used in gas separation and catalysis - are particularly promising due to their widely tunable separation properties to be matched to the target analyte. In specific, zeolites are aluminosilicates that form three-dimensional frameworks with well-defined pore size in the range of volatile molecules. In principle, their separation properties are mainly governed by their pore size (tunable by framework selection) and chemical composition (e.g. tunable by Al/Si-ratio and incorporation of foreign metals) to filter gas molecules based on their kinetic diameter, sorption and diffusion characteristics.

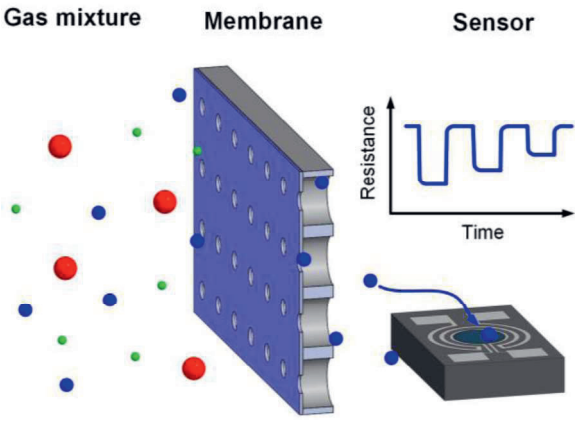

Fig. 1. Concept of the membrane-sensor assembly for selective analyte detection. A microporous membrane pre-separates gas mixtures and ideally allows only a target analyte (blue) to permeate through. A chemoresistive sensor placed downstream detects the analyte resulting in an electrical signal correlated to its concentration. Figure adapted from [5].

Here, we present a novel approach for selective gas detectors by combining (1) a zeolitic membrane for gas mixture pre-separation with

(2) a chemoresistive gas sensor for analyte detection (Figure 1) [5]. Ideally, only a single target analyte (blue) can permeate through the membrane while other interfering gases (red & green) are held back. Since the membrane and sensor are decoupled and modular, they can be fabricated individually to match the analyte and operated independently. To demonstrate the concept's immediate relevance and impact, we place a zeolite MFI/Al_2O_3 membrane upstream of a highly sensitive and nanostructured Pd-doped SnO_2 sensor for selective sensing of formaldehyde, a carcinogenic [6] pollutant and possible tracer for lung cancer.

Figure 2a shows the sensor response of Pd-doped SnO_2 without membrane upon exposure to 1 ppm of individual analytes in air with 50% RH. Without membrane, the sensor interacts with all analytes, demonstrating the non-specific character of the Pd-doped SnO_2 sensor alone. In other words, this sensor cannot detect formaldehyde selectively in a gas mixture since it is not possible to distinguish it from other gases consistent with literature.

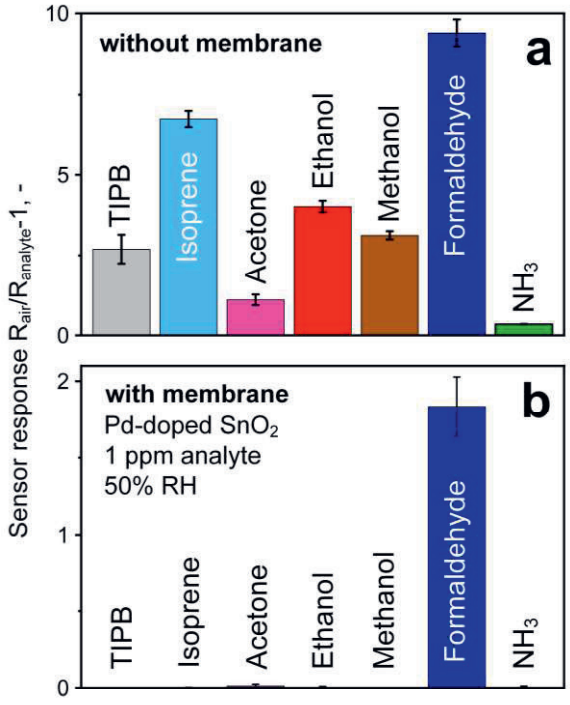

Fig. 2. (a) Sensor response of a Pd-doped SnO_2 sensor (without membrane) upon exposure to 1 ppm of 1,3,5-triisopropylbenzene (grey), isoprene (light blue), acetone (purple), ethanol (red), methanol (brown), formaldehyde (blue) and NH_3 (green) at 50% RH. (b) Introducing the MFI/Al_2O_3 membrane turns the device formaldehyde-selective. Figure adapted from [5].

Now, when installing the MFI/Al_2O_3 membrane and exposing the device to the individual analytes again, only formaldehyde is detected (Fig. 2b). More specifically, the response to formaldehyde is decreased to 1.85 while the responses to all other analytes are suppressed almost completely. That way, the formaldehyde selectivity to acetone is improved to more than 100 and that to NH_3, isoprene, ethanol, methanol and 1,3,5-triisopropylbenzene (TIPB) is even more than 1000, much higher than without membrane and considerably better than state-of-the-art formaldehyde detectors. Actually, TIPB should be separated due to its larger molecular size compared to the distinct MFI pore diameter range. This *size cut-off* is rather important for indoor air monitoring and breath analysis since both gas mixtures contain a myriad of such larger molecules potentially interfering with the sensor and the MFI layer should filter out all of them similarly efficient as TIPB.

Finally, this concept could be extended to other target compounds. Since membrane and sensor are decoupled, they can be engineered independently to match the target analyte. For the membrane, a variety of zeolitic and metal-organic frameworks are available with widely tunable separation properties while suitable MOx sensors can detect the tracer at the ppb level. So we anticipate that this novel approach will facilitates a new class of highly selective and portable gas detectors.

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