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Isoprene detection with Ti-doped ZnO nanoparticles

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Abstract:
Exhaled isoprene could enable non-invasive real-time monitoring of cholesterol-lowering therapies. Here, we report an isoprene-selective sensor at high relative humidity (RH). It is made of nanostructured, chemo-resistive Ti-doped ZnO nanoparticles produced by flame spray pyrolysis (FSP) and directly deposited onto sensor substrates forming highly porous films. The constituent particles consist of stable Ti-doped ZnO solid solutions for Ti levels up to 10 mol%. Ti doping strongly enhance the isoprene sensitivity (>15 times higher than pure ZnO) and turn ZnO isoprene-selective, while also improving its thermal stability. In fact, at an optimal Ti content of 2.5 mol%, this sensor shows superior isoprene responses compared to acetone, NH_3 and ethanol at 90% RH. Most notably, breath-relevant isoprene concentrations are detected accurately down to 5 ppb. As a result, an inexpensive isoprene detector has been developed that could be easily incorporated into a portable breath analyzer for non-invasive monitoring of metabolic disorders (e.g. cholesterol).

Key words: breath analysis, gas sensor, selectivity, ZnO, isoprene

Introduction

Approximately 39% of the world population has high blood cholesterol that might be responsible for a third of ischaemic heart diseases and strokes leading to over 2.6 million estimated deaths per year. Breath isoprene detection could provide a non-invasive method for easy and rapid assessment of high blood cholesterol synthesis rates and enable real-time monitoring of its therapy. In fact, the exhaled isoprene excretion in humans is decreased when treated with cholesterol-lowering lova- and atorva-statins. While healthy adults exhale isoprene concentrations typically in the range of 22 to 234 ppb, altered levels occur also in end-stage renal disease, lung cancer, liver disease patients with advanced fibrosis and during physical activity indicating the potential of this breath marker.

Several methods have demonstrated high sensitivity, low limit of detection and sufficient selectivity for breath isoprene detection, including selective ion flow tube mass spectrometry (SIFT-MS) or proton transfer reaction mass spectrometry (PTR-MS). Nevertheless, such devices are hardly applicable for daily use in widespread populations, as they are rather expensive with limited portability. In this respect, chemo-resistive gas sensors based on nanostructured metal oxides are rather promising due to their low fabrication cost, simple applicability [1] and compact size [2] that are applied readily in breath analysis (e.g. fat burn monitoring [3]) or as orthogonal sensor arrays for entrapped human sniffing [4]. However, for isoprene, no suitable materials are available that possess sufficiently low detection limit at breath-realistic, high relative humidity (RH, ~89–97%) and selectivity against other breath compounds (e.g. NH_3 and acetone).

Experimental

Ti-doped ZnO nanoparticles were produced in a FSP reactor [5]. The composition was varied to obtain Ti contents from 0 to 100 mol%. The particles were directly deposited onto the sensor substrates and subsequently *in situ* annealed by particle-free spray flames and stabilized by 5 h annealing in air at 500 °C inside an oven. Gas sensing experiments were carried out at 325 °C by powering the substrates back heater. Film resistance was measured by a multimeter. The sensing measurements were performed at a constant flow of 1 L min^{-1} synthetic air. Applied gases are 10 ppm of ethanol, ammonia, acetone and isoprene in N_2. Analytes are admixed with synthetic air at 90 % RH in a mixing setup as described elsewhere [1].

Results

Here, we present an isoprene-selective chemoresistive sensor consisting of Ti-doped ZnO. Figure 1 shows the SEM cross-sectional view of 2.5 mol% Ti-doped ZnO film. FSP-deposited nanoparticles form a highly porous film. Such fine sensing networks consist of aggregated primary particles and agglomerates.[5] The thickness of the produced films is ~5 µm and rather uniform. The additional high film porosity provides extremely large surface areas to detect even lowest ppb-level isoprene concentrations. Furthermore, the open structure enables rapid analyte diffusion into the film for fast response time.

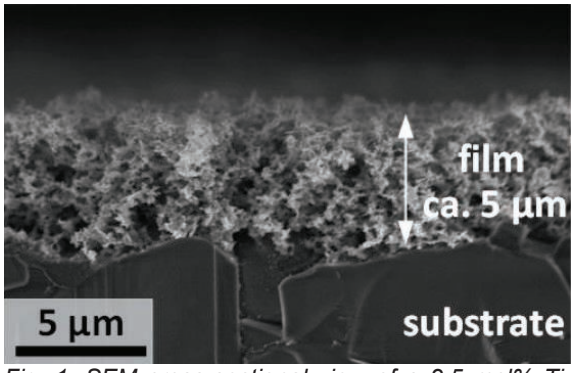

Fig. 1. SEM cross-sectional view of a 2.5 mol% Ti-doped ZnO film after annealing at 500 °C for 5 h. Deposited nanoparticles aggregate (inset) and form a fine and highly porous morphology. Such films are rather uniform with a thickness of ca. 5 mm. Figure adapted from [5]

Figure 2 presents the response as a function of Ti-content to 500 ppb of isoprene (squares), acetone (circles), ethanol (triangles), and ammonia (diamonds) at breath realistic 90 % RH. Pure ZnO can detect all these analytes and shows the strongest response to acetone. It is remarkable that Ti doping turns ZnO sensors isoprene-selective. In fact, increasing the Ti content to 2.5 mol% enhances the isoprene response more than 15 times while the response for other analytes increases only slightly.

Conclusion

As a result, flame-made Ti-doped ZnO nanoparticles were made in flames and directly deposited onto sensor substrates in a single step. The fabricated films are highly porous resulting in outstanding isoprene sensitivity. Ti-doping turns ZnO isoprene-selective and optimal responsiveness and selectivity were obtained at 2.5 mol% Ti.

These sensors can be readily incorporated into portable devices [3] so they have high potential for further development towards a simple and low-cost hand-held breath isoprene detector for monitoring cholesterol-lowering therapy. Further improvements could be achieved by adding filters (e.g. activated alumina).[6]

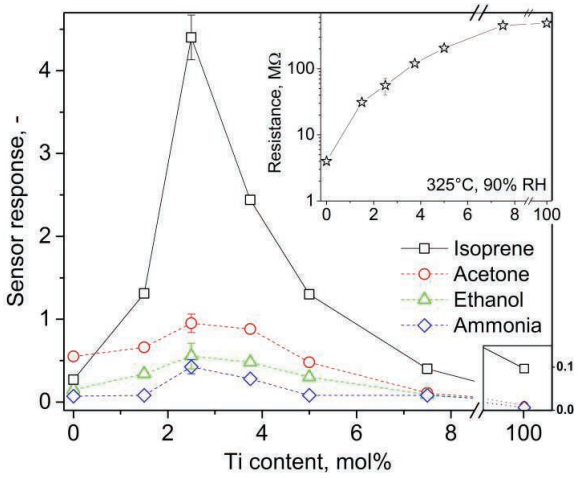

Fig. 2. Ti-doped ZnO sensor response as a function of Ti content to 500 ppb of isoprene (squares), acetone (circles), ethanol (triangles) and ammonia (diamonds) at 325 °C and 90% RH. Ti-doping turns ZnO isoprene-selective with an optimum response and selectivity at 2.5 mol% Ti. Error bars at this optimum composition indicate the variability of three identically fabricated sensors that is below ± 10%. The baseline resistance increases with increasing Ti content (inset). Figure adapted from [5]

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