Si-doped $\alpha$-MoO$_3$ sensing nanoparticles for selective breath NH$_3$ detection

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Abstract

Ammonia is an important breath marker for non-invasive detection and monitoring of end-stage renal disease (ESRD). Here, a chemo-resistive gas sensor has been developed consisting of flame-made nanostructured $\alpha$-MoO$_3$ with ribbon-like and nanoparticle/needle-like morphologies. A key novelty is the thermal stabilization of $\alpha$-MoO$_3$ by Si-doping inhibiting sintering and crystal growth at the operational conditions of such sensors. In situ XRD analysis of the MoO$_x$ phase dynamics revealed an optimal annealing temperature of 450 °C for synthesis of highly nanocrystalline $\alpha$-MoO$_3$. For selective NH$_3$ sensing, however, the optimum SiO$_2$ content was 3 wt% and the operational temperature 400 °C. This sensor showed superior NH$_3$ selectivity toward acetone, NO and CO, and accurately detected breath-relevant NH$_3$ concentrations down to 400 ppb under 90% relative humidity (RH). As a result, a stable and inexpensive sensor for NH$_3$ is presented which has the potential for further development toward a hand-held device for the early-stage diagnosis and monitoring of ESRD.

Key words: Ammonia, Breath Analysis, MoO$_3$, Thermal stabilization, Flame spray pyrolysis.

Introduction

Chronic kidney disease (CKD) is a worldwide health issue responsible for > 800 000 deaths (1.5% of all deaths worldwide) in 2012. End-stage renal disease (ESRD) negatively affects the patients’ life expectancy and quality of life while associated hemodialysis costs in the US were 88,000 $/y in 2011. Breath analysis represents a promising non-invasive, fast and cost-effective diagnostic and monitoring technique which can be used for early detection of ESRD. NH$_3$ is a promising breath marker for CKD since ESRD patients have elevated breath NH$_3$ levels (mean 4880 ppb) compared to healthy people (mean 960 ppb).

Metal-oxide (chemo-resistive) gas sensors are attractive for NH$_3$ detection since they offer simple operation, low power consumption, usability in portable devices [1] and they are applied readily in breath analysis (e.g. fat burn monitoring [2]). The $\alpha$-phase of MoO$_3$ is promising for detection of NH$_3$ down to 50 ppb at dry conditions. Due to the high operating temperatures of MoO$_3$ gas sensors (250 to 500 °C), the material must be stabilized by doping or the addition of foreign oxides. Thus, tailoring material morphology, phase composition and size enables high NH$_3$ sensing performance [3].

Experimental

Pure and Si-doped MoO$_x$ (0 – 20 wt%) nanoparticles were made by flame spray pyrolysis (FSP) and directly deposited onto Al$_2$O$_3$ sensor substrates with interdigitated Pt electrodes [3]. Subsequently, the sensor films were annealed at 450 °C for 5 h in an oven for thermal stabilization. The nanoparticles were analyzed using X-ray diffraction (XRD) patterns and the film morphology was investigated using scanning electron microscopy (SEM). The optimum sensor operating temperature was identified to be 400 °C using an experimental set-up for sensor evaluation [3].

Results

The as-prepared, pure MoO$_3$ powder shows fine crystallinity confirmed by transmission electron microscopy (TEM) (Fig. 1a) and electron diffraction (ED) patterns (Fig. 1b). By annealing the sensor substrates at 450 °C for 5 h, pure MoO$_3$ particles grow to ribbon-like structures (Fig. 1d) with large crystallites, as indicated by XRD (triangles) and the Brunauer-Emmett-Teller (BET) method (open circles) and confirmed by bright spots in ED patterns (Fig. 1c). Doping with Si reduces particle and crystal growth significantly, decreasing the crystal size from 147 nm to 65 nm and the particle size from
272 nm to 83 nm resulting in superior thermal stability. Excess Si (above 3 wt%) is not incorporated into the MoO₃ lattice, but forms amorphous SiO₂ domains, inhibiting further crystal growth, as subjected by the constant dₓRD (Fig. 1) and visible by TEM [3].

Due to those structural changes, the sensor response and selectivity depend on the SiO₂ doping content. Fig. 2 shows the response of pure and Si-doped MoO₃ sensors to 1000 ppb NH₃ (triangles), acetone (circles), NO (squares) and CO (diamonds) in dry air at 400 °C. Increasing the SiO₂ content from 0 to 3 wt% almost triples the NH₃ response from 0.22 to 0.53 while responses to the other analytes change only little (Fig. 2).

This results from the reduced sinter neck size of MoO₃ due to segregated SiO₂ domains which locally narrow the conduction channel leading to an increased electron depletion and change the morphology increasing the surface-to-volume ratio [3]. Therefore, charge carrier mobility and thus film resistance are dominated by surface phenomena increasing the sensor’s sensitivity (Fig. 2). Moreover, Si-doping (3 wt%) improved the NH₃ selectivity toward other interfering gases present in human breath achieving a response ratio to acetone (SNH₃ / Sₐ) of 3.6 and to NO of 7.9 and no sensitivity for CO (Fig. 2). Above 3 and up to 20 wt% SiO₂ content, the film resistance continuously increases (Fig. 2) due to the formation of large and inert SiO₂ domains.

In addition to the enhanced response and selectivity towards NH₃, the sensor could clearly distinguish breath-relevant NH₃ levels down to 400 ppb at realistic conditions (90% RH) [3]. Thus, it has high potential to be developed into portable device for early-stage ESRD detection and hemodialysis monitoring. This requires sensor miniaturization [4] while additional filters enhance the selectivity further [5]. Furthermore, it can be incorporated into orthogonal sensor arrays to sniff entrapped humans from their unique volatile chemical signature [6].

References


