Si-doped α-MoO₃ sensing nanoparticles for selective breath NH₃ 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 α-MoO₃ with ribbon-like and nanoparticle/needle-like morphologies. A key novelty is the thermal stabilization of α-MoO₃ 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 α-MoO₃. For selective NH₃ sensing, however, the optimum SiO_2 content was 3 wt% and the operational temperature 400 °C. This sensor showed superior NH₃ selectivity toward acetone, NO and CO, and accurately detected breath-relevant NH₃ concentrations down to 400 ppb under 90% relative humidity (RH). As a result, a stable and inexpensive sensor for NH₃ 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, MoO₃, 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. NH₃ is a promising breath marker for CKD since ESRD patients have elevated breath NH₃ levels (mean 4880 ppb) compared to healthy people (mean 960 ppb).

Metal-oxide (chemo-resistive) gas sensors are attractive for NH₃ 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 α-phase of MoO₃ is promising for detection of NH₃ down to 50 ppb at dry conditions. Due to the high operating temperatures of MoO₃ 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 NH₃ 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_2O_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 MoO₃ 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_x 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 MoO_3 lattice, but forms amorphous SiO_2 domains, inhibiting further crystal growth, as subjected by the constant d_{XRD} (Fig. 1) and visible by TEM [3].
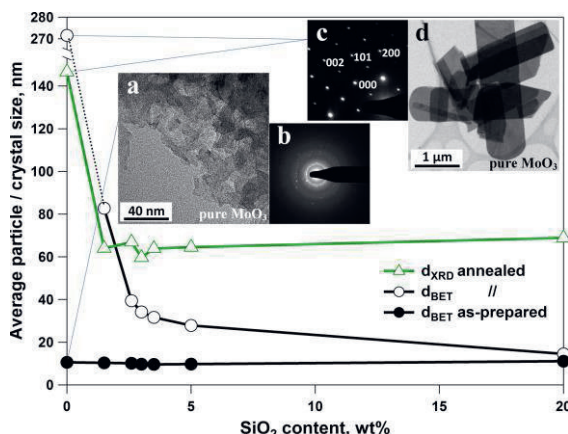

Fig. 1. *Average particle (d_{BET}, circles) and crystal sizes (d_{XRD}, triangles) as function of SiO_2 content for as-prepared (filled symbols) and annealed (open symbols) powders at 450 °C for 5 h. As-prepared consists of particles with ultrafine crystallinity (a) for pure MoO_x. During annealing, particles grow to large, ribbon-like MoO_3 structures (d). Doping with Si strongly reduces the particle and crystal sizes.* [3]

Due to those structural changes, the sensor response and selectivity depend on the SiO_2 doping content. Fig. 2 shows the response of pure and Si-doped MoO_3 sensors to 1000 ppb NH_3 (triangles), acetone (circles), NO (squares) and CO (diamonds) in dry air at 400 °C. Increasing the SiO_2 content from 0 to 3 wt% almost triples the NH_3 response from 0.22 to 0.53 while responses to the other analytes change only little (Fig. 2).
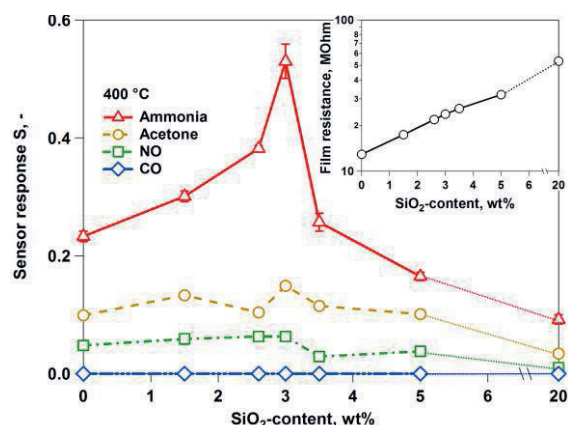

Fig. 2. *Average sensor response as a function of SiO_2 content to 1000 ppb ammonia (triangles), acetone (circles), NO (squares) and CO (diamonds) in dry air at 400 °C. The baseline film resistance increases with increasing SiO_2 content (inset).* [3]

This results from the reduced sinter neck size of MoO_3 due to segregated SiO_2 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 NH_3 selectivity toward other interfering gases present in human breath achieving a response ratio to acetone (S_{NH3} / S_A) of 3.6 and to NO of 7.9 and no sensitivity for CO (Fig. 2). Above 3 and up to 20 wt% SiO_2 content, the film resistance continuously increases (Fig. 2) due to the formation of large and inert SiO_2 domains.

In addition to the enhanced response and selectivity towards NH_3, the sensor could clearly distinguish breath-relevant NH_3 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].

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