Flame Made Nanoparticles for Gas Sensors

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ABSTRACT

Tin oxide nanoparticles for gas sensing application have been synthesized with an aerosol method. The particles were manufactured with the versatile Flame Spray Pyrolysis (FSP) method producing highly crystalline powders with closely controlled primary particle and crystallite size of 10 nm and 17 nm. The single crystalline particles were only slightly aggregated and directly used for thick film sensor deposition by screen printing. The flame made SnO_2 nanoparticles showed high and rapid response to reducing gases such as CO. Furthermore, the aerosol generated by the dry FSP method was directly, *in-situ* thermophoretically deposited onto interdigitated Pt-electrodes to form a porous, thick film of controlled thickness within the active sensor area. Tin oxide grain size (10 nm) and a high film porosity (98 %) was obtained These sensors exhibited high carbon monoxide (CO) sensor signals (8 for 50 ppm CO in dry air at 350°C), good reproducibility, high analytical sensitivity and a remarkably low detection limit (1 ppm CO in dry air at 350°C).

Keywords: tin dioxide, platinum, gas sensors, flame spray pyrolysis, in-situ deposition

1 INTRODUCTION

Flame aerosol technology is one of the most widely used synthesis routes in manufacturing of commercial quantities of nanoparticles [1]. The application of flame spray pyrolysis further broadens the spectrum of flame made powders and their use in various applications as there are more liquid than gaseous precursors available [2]. Even particles with pre-defined stoichiometric composition can be produced [3-5].

Metal oxides in general and SnO_2, in particular, have attracted the attention of many users and scientists interested in gas sensing under atmospheric conditions. SnO_2 sensors are the best-understood prototypes of oxide-based gas sensors [6]. The performance of metal oxide gas sensors is strongly related to the properties of the ceramic such as grain size, morphology, surface groups, etc. It has been shown that flame spray pyrolysis enables the controlled synthesis of such materials and bears the advantage of complete manufacture of nanopowder in a single high temperature process step leading to controlled microstructure and noble metal loadings if desired [7, 8]. Here, single crystalline tin oxide particles with specific averages particle sizes of 10 and 20 nm were produced using the versatile FSP technique. The particles were only slightly aggregated and were directly used for thick film sensor deposition by screen printing. The size effect has been explored for CO detection [9].

Furthermore, state-of-the-art sensors have important technical limitations that are generally related to the way in which the sensitive materials are processed. For example, the wet chemistry methods employed for both preparation and functionalization of base materials are difficult to control and as a result both the size distribution in the base material, and the amount and distribution of the noble metals additives, are rather broad. This results in significant variation of gas-sensing properties from batch to batch (30 % variation is common in the industry). The fabrication of the sensitive materials is labor and time intensive, with typical batch production times on the order of days with small batch volumes in the range of 100 g [10]. The deposition of sensing films, either by classical screen-printing or more sophisticated drop deposition techniques, is performed after the additional step of combining the sensitive material with organic carriers. This increases processing time and costs related to deposition equipment and handling. Recent advances have been made using electrospray deposition for sensor applications but limitations include processing time and the required post-processing to obtain nano-crystalline material [11]. Additionally, variations in the deposition parameters such as a new film or varying film thickness are difficult to implement and require repetition of the full process.

2 EXPERIMENTAL

2.1 Particle Production

Tin(II) 2-ethylhexanoic acid (Aldrich) was diluted in toluene to obtain a 0.5 M precursor solution. The precursor was fed into a flame spray pyrolysis (FSP) reactor by a syringe pump with a rate of x=5 or 8 ml/min and was dispersed by y=5 or 3 l/min of oxygen, respectively, into fine droplets by a gas-assist nozzle. The conditions will later be referred later as (x/y). Cooling of the reactor avoided any evaporation of the precursor within the liquid feed lines or overheating of the nozzle. The spray flame was maintained by a concentric supporting flamelet ring of premixed methane / oxygen (CH_4 = 1.5 l/min, O_2 = 3.2 l/min). In order to assure enough oxidant for complete conversion of the reactants, an additional outer oxygen flow (5 l/min) was supplied. For Pt/SnO_2 synthesis, appropriate amounts of platinum acetylacetonate ($Pt(acac)_2$, Strem, purity > 98 %) were added to the solution.

The powder was collected with the aid of a vacuum pump on a glass fiber filter (GF/D Whatman, 257 mm in diameter). During the experiment the filter was placed in a water cooled holder 400 mm above the nozzle where the off-gas temperature was maintained below 200 °C [12].

2.2 Dry depsoition

Dry aerosol synthesis applying the Flame Spray Prolysis (FSP) technique [13] has been used for direct (in-situ) deposition of pure and functionalized (doped) sensing materials which eliminates theses difficulties and functionalization of the sensing films can be realized during one proceeding step on ceramic (planar) and micro-machined substrates. The method is in principle applicable to all materials that are able to be synthesized by FSP [2]. Each sensor substrate consists of interdigitated Pt-electrodes on the front side and heater on the back side and an active sensing area of 7.0 x 3.5 mm^2. A mask was used to deposit the particles within the desired sensor area. The substrate was mounted on a water-cooled copper block equipped with a K-type thermocouple to control the substrate temperature during the deposition process. In this study, the substrate temperature was maintained at T_{sub} = 120 °C in order to avoid water condensation on the substrate. The deposition substrate was centered 200 mm above the nozzle facing it. At this position the gas temperature in front of the substrate was T_{gas} = 500 °C using the reactor settings described above. Both temperatures (T_{sub} and T_{gas}) were maintained throughout the deposition process.

2.3 Particle Characterization

X-ray diffraction patterns were recorded with a Bruker AXS D8 Advance (40 kV, 40 mA) and used to obtain the crystallite size (d_{XRD}) based on the fundamental parameter approach and the Rietveld method with the structural parameters of casserite (ICSD Coll. Code: 084576) [14, 15]. The BET powder specific surface area (SSA), was measured by nitrogen adsorption at 77 K after degassing the sample, for at least 1 hour at 150 °C in nitrogen. Assuming monodisperse spherical primary particles within an aggregate, the equivalent average primary particle diameter d_{BET} is calculated by $d_{BET} = 6 / (SSA \cdot \rho_p)$, where ρ_p is the density of SnO_2 (6.85 g/cm^3). The product powder was further analyzed by transmission electron microscopy.

2.4 Sensor Characterization

DC electrical measurements (sensor tests) were performed to monitor the sensor response to CO in dry synthetic air and in synthetic air with 50% relative humidity at 20°C. The sensing layers were fabricated by screen printing (in the case of CO sensors) on alumina substrates with interdigitated Pt-electrodes on the front side and heater on the back side [6]. After deposition, the sensors were annealed for 10 min in a belt oven at 500°C in air. For the comparison tests, commercially available SnO_2 powder (Aldrich, mesh 325, d = 330 nm) was also used for the sensor deposition [12].

The measurements were performed with a set of two identical sensors placed symmetrically in a teflon-made test chamber and operated under the same conditions. The operating temperature of the sensors was adjusted between 200 and 400°C. The sensor signal is given in the following as the resistance ratio R_{air}/R_{gas} for CO where R_{gas} and R_{air} denote sensor resistance in the presence and in the absence of CO. Gas mixing achieved using a combination of computer controlled mass flow controllers and computer controlled valves. The sensors were exposed to CO (500 and 1000 ppm) in dry and humid (50% r.h.) synthetic air. The humidity was adjusted by bubbling synthetic air through a column of water and subsequently mixing it with dry air. Defined concentration CO and were obtained in the PC controlled gas mixing bench by mixing certified CO test gas.

3 RESULTS AND DISCUSSION

Figure 1 shows a TEM image of the as prepared powders (5/5). The aggregated powder consists of highly crystalline polyhedral primary particles with size of d_{BET} = 9.9 nm and d_{XRD} = 10.7 nm (5/5) and powders which had a longer residence in the flame resulting in d_{BET} = 19.7 nm and d_{XRD} = 19.8 (8/3) (Fig. 1). The close correlation of the average primary particle and the average crystallite sizes give strong evidence that the primary particles are single crystals with a low degree of aggregation.

Similar results were obtained by Hall et al. 2002 [16] in a low pressure flat flame burner using also the tri-methyl-tin but at much lower concentrations. The authors showed

good control of the primary particle size from about 6 to 15 nm by varying the precursor concentration in the flame.

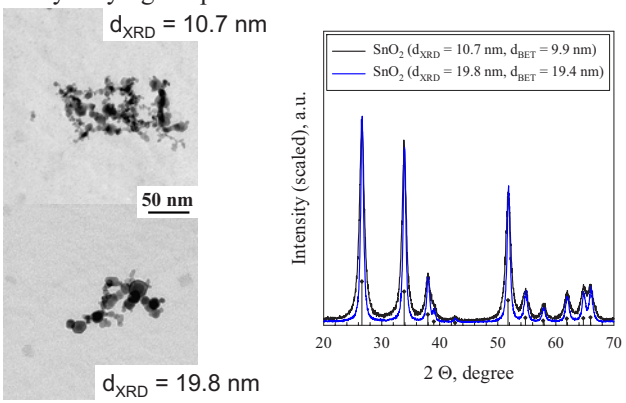

Figure 1. Increasing the precursor (solvent=toluene) flow rate from 5 to 8 ml/min increased the average primary particle size determined by BET from about 10 to 20 nm. This size increase is clearly visible in the TEM analysis. The average crystal size obtained by X-ray analysis (fundamental parameter approach and Rietveld method) resulted in nearly identical average sizes of 10 and 20 nm, respectively, indicating single crystalline particles [9].

Therefore, the tin oxide particles produced with the flame spray process are similar to the particles synthesized in the vapor flame reactor corroborating the fact that the precursor reaction and particle formation takes place within the gas phase and that all liquid precursor left the droplet environment before the formation of the tin oxide. However, the vapor flame made tin oxide powders were not tested for their sensor performance and therefore the versatile FSP technique of SnO_2 was explored.

Exposing the sensor with reducing gases (CO) decreases the resistance of the sensors which is a typical behavior for the tin dioxide as an n-type semiconductor. The measured sensor resistance in the presence of CO increases with decreasing particle size (Fig. 2). Commercial powder from Sigma Aldrich with an average size of 300 nm has two orders of magnitude lower total resistance which is an advantage in signal processing. However, the sensor signal is drastically increased for smaller (nanoscale) particles. This increase results from the higher specific surface area within the sensing layer and also from the relatively larger depletion layer size in comparison with the particle size itself.

The direct deposition from the aerosol phase resulted in fully formed functionalized sensing films. The *in-situ* prepared sensors of Pt doped SnO_2 exhibited high carbon monoxide (CO) sensor signals (8 for 50 ppm CO in dry air at 350°C), good reproducibility, high analytical sensitivity and a remarkably low detection limit (1 ppm CO in dry air at 350°C). The *in-situ* platinum doping enhanced the overall sensor performance (figure 3) [9].

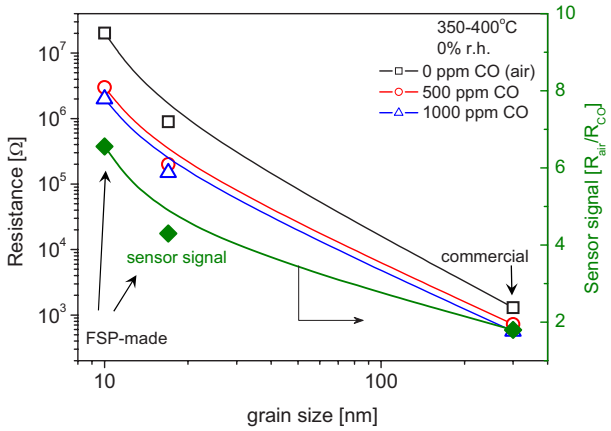

Figure 2. SnO_2 particles of different sizes (about 10 nm for 5/5, about 20 nm 8/3, and about 300 nm Sigma Aldrich, respectively) are screen printed on interdigital electrodes. The measured sensor resistance increases with decreasing particle size. The commercial powder with an average size of 300 nm has two orders of magnitude lower total resistance which is an advantage in signal processing. The sensor signal e.g. for 500 ppm (plotted on the right hand site) is drastically increased for smaller (nanoscale) particles [9].

4 CONCLUSION

In summary, we demonstrated that flame spray pyrolysis can be successfully used for the preparation of SnO_2 nanoparticles for gas-sensing applications. Single crystalline tin oxide particles with size of 10 to 20 nm were produced using the versatile FSP technique. The fabricated sensors show high sensitivity and fast response CO. Direct control of particles sizes with the FSP parameters has a promoting effect.

Nano-crystalline tin-oxide can be directly *in-situ* deposited as porous films onto alumina sensor substrates by thermophoresis. The as-obtained sensors exhibit extremely good homogeneity of the sensing film and good sensor performance. The *in-situ* prepared sensors of Pt doped SnO_2 are reproducible and have a very low detection limit for CO (down to 1 ppm) with high sensor response (up to 8).

A simple model for the sensor film growth rate by particle deposition was developed based on diffusion and thermophoresis. Its predictions were in excellent agreement with microscopic measurements of the film thickness. Control of the film thickness during the deposition process is an effective tool for tuning sensor performance besides its chemical composition. Furthermore, in principle, it is possible and simple to deposit a combination of various films having different functions (filtering, sensing) by the same deposition process, enabling direct construction of fully functional sensors in very short times using a simple and clean fabrication process.

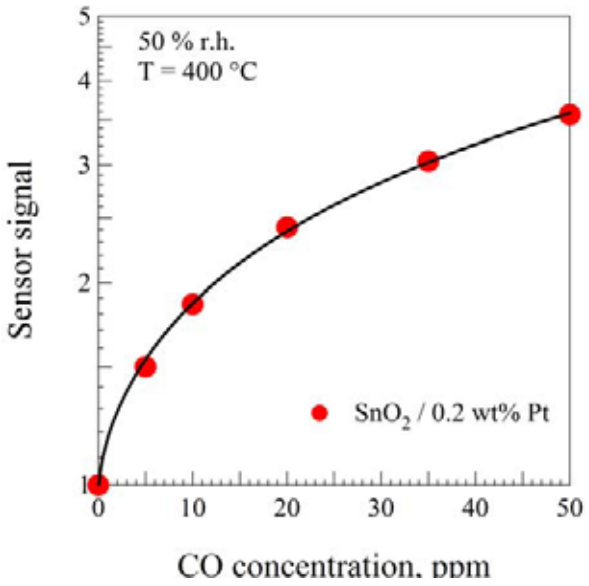

Figure 3. Sensor signal to CO for in-situ (directly) simultaneously deposited Pt-doped SnO_2 (0.2 wt% Pt) operated at 400°C in 50 % r.h. (at 20°C) air. The thickness of the sensing films is 30±3 µm (deposition time: 180 s).

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