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Flame-made Nb- and Cu-doped TiO_2 sensors for CO and ethanol

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Abstract

Nb- and Cu-doped TiO_2 nanoparticles were produced by flame spray pyrolysis (FSP) and tested for sensing of CO and ethanol at 400 °C in dry air. The as-prepared powders were characterized by transmission electron microscopy, X-ray diffraction, Raman spectroscopy and nitrogen adsorption. Niobium stabilized the anatase phase and retarded grain growth up to 600 °C. Copper promoted rutile formation and an anatase to rutile transformation was already observed just above 400 °C during post-synthesis calcination. This was accompanied by a segregation of large (>100 nm) CuO crystals which were initially small (<5 nm) asperities on the titania surface. Pure as well as doped TiO_2 showed an n-type signal to CO and ethanol. Both dopants improved the sensitivity towards CO over that of pure TiO_2. In contrast, for ethanol a high increase in sensitivity was observed only for Nb/TiO_2.

Keywords: Gas sensors; Flame spray pyrolysis; Aerosols; Anatase and rutile promoter

1. Introduction

Tighter emission, security and health control regulations require sensors of higher sensitivity, stability and selectivity at different environments. This poses a challenge on the efficient manufacturing of these materials. Gas phase aerosol synthesis of sensors alleviates a lot of the multiple steps of wet-chemistry processes that are currently employed in sensor manufacture.

Flame spray pyrolysis (FSP) is a promising aerosol technique for sensor material synthesis since it enables primary particle and crystal size control [1], which is important to tailor sensitivity. In FSP a spray of a combustible solvent, containing various precursor species is ignited to form a flame where precursors evaporate, decompose and react in the gas phase leading to particle formation. The FSP has been demonstrated for synthesis of a wide variety of metal ceramic and mixed-metal oxides, including ZnO [2], Au/TiO_2 [1], Pt/Al_2O_3 [3], SnO_2 [4] and Ta_2O_5/SiO_2 [5]. The produced metal-oxide powder must be deposited onto micro or macro sensor substrates. For this a powder suspension in an organic solvent is prepared which is then deposited onto the substrates [4,6]. Recently, smooth, highly porous, crack-free Pt/SnO_2 sensing films were manufactured by direct thermophoretic depostion in a single step by FSP. These films showed high sensibility by detecting CO at concentration as low as 1 ppm [7].

A high sensor signal of FSP-made anatase TiO_2 nanoparticles has already been demonstrated at ppm levels of acetone, isoprene and ethanol with fast response and recovery times [6]. Niobium is typically added to titania to inhibit the anatase to rutile transformation and hinder grain growth [8]. Further, Nb can lower the operating temperature of the sensing film [9]. Copper [10] as well as niobium [11] doping of TiO_2 by wet ball-milling or sol–gel synthesis increased the sensitivity or selectivity [12] towards CO detection. Here the potential of dry synthesis of Nb- and Cu-doped TiO_2 sensors is explored for sensing CO and ethanol and compared to that of wet-made materials.

2. Experimental

2.1. Particle and sensing film synthesis

TiO_2 nanoparticles were produced by a flame spray pyrolysis (FSP) reactor described in detail elsewhere [1,13]. Precursor solutions (0.5 M with respect to the metal atoms) were prepared from titanium-tetra-isopropoxide (TTIP, Aldrich, purity >97%), copper(II) 2-ethylhexanoate (Aldrich) and niobium 2-ethylhexanoate (Strem Chemicals) diluted in xylene (Fluka, >98.5%) resulting in pure TiO_2, Nb(4 or 10 at.%)/TiO_2 or Cu(0.5–10 at.%)/TiO_2. Pure Nb_2O_5 and pure CuO were

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prepared from their 0.025 M precursor solutions in xylene. Precursor solutions were fed at 5 ml/min through the inner reactor capillary. Through the surrounding annulus, 5 l/min of oxygen (Pan Gas, purity >99%) were fed dispersing the precursor solution into a combustible spray. The pressure drop at the FSP nozzle tip was maintained at 2 bar. The methane and oxygen flow rates in the FSP-supporting premixed flame [13] were 1.13 and 2.4 l/min, respectively.

Product particles were calcined in a furnace (Thermolyne 48000) at ambient atmosphere for 4 h at 300, 400, 500 and 600 °C. The heating rate was 10 °C/min and the samples were cooled down to room temperature at 10 °C/min.

Sensing films were prepared from FSP-made pure TiO_2, 4 at.% Nb/TiO_2, 10 at.% Nb/TiO_2, and 5 at.% Cu/TiO_2 by doctor-blading. For this a highly viscous paste was prepared by adding 2.4 wt.% ethylcellulose to α-terpineol [14] and 17 wt.% (for TiO_2 and Nb/TiO_2) or 19 wt.% (for Cu/TiO_2, adjusted for the difference in powder density) of product powder was stirred into the solution until a homogeneous paste was obtained. The paste was then deposited onto alumina substrates interdigitated with Au electrodes (10 mm × 10 mm; Electronics Design Center, MicroFabrication Lab, Case Western Reserve University) by a mechanical system with about 10 μm spacing between blade and substrate. The sensing films were heated at 0.5 °C/min sequentially to 50 and 100 °C and kept at each temperature for 1 h, then at 2 °C/min to 400 °C and kept there for another 2 h and finally cooled down to room temperature at 5 °C/min.

2.2. Particle and film characterization

X-ray diffraction (XRD) patterns of product powders and sensing films were obtained with a Bruker AXS D8 Advance diffractometer (40 kV, 40 mA, Karlsruhe, Germany) operating with Cu Kα radiation. The fundamental parameter approach and the Rietveld method [15] were applied to determine the anatase and rutile crystallite sizes, x_a and x_r, respectively, and phase composition. Raman (Renishaw InVia Raman microscope) spectra of as-prepared TiO_2, Nb/TiO_2 and Cu/TiO_2 particles were taken with a 514 nm laser with 12.5 mW power at a range of 100–990 cm^{-1} with an exposure time of 3 s. For the pure Nb_2O_5 spectrum the laser power was reduced to 1.6 mW and exposure time was set to 60 s. A 785 nm laser with 3 mW power and an exposure time of 10 s was used for the CuO sample.

The BET powder-specific surface area (SSA) was measured by nitrogen adsorption at 77 K (Micromeritics TriStar) after sample degassing, at least, for 1 h at 150 °C in nitrogen. The product powder was deposited onto a holey carbon foil supported on a copper grid for further analysis by transmission electron microscopy (TEM; CM30ST microscope, FEI, LaB6 cathode, operated at 300 kV, SuperTwin lens, point resolution ∼2 Å). Elemental maps of Ti, scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray (EDX) analysis were recorded as described in detail elsewhere [16]. The sensing films were investigated with a scanning electron microscope (SEM, LEO 1530 Gemini microscope).

2.3. Gas sensing characterization

The change in sensor resistance upon exposure to ethanol vapor (10–300 ppm) and CO (50–750 ppm) in dry air (79% N_2/21% O_2, all gases PanGas) was measured as described in detail elsewhere [6]. The sensor was placed in the center of a quartz tube (3.5 cm diameter and 90 cm length) which in turn was introduced into a tubular furnace (Nabertherm). The tube was filled with silicon carbide (1 mm grains) upstream the sensor position to homogenize the flow. Gold wires were gap welded to the sensor electrodes and externally connected to a digital multimeter (Keithley 2700 multimeter) recording the sensor resistance. A Ni-CrNi thermocouple (MDW GmbH, DIN IEC 584 Type K) was positioned right above the sensor to monitor the temperature. The furnace was heated at 15 °C/min to reach 400 °C at the sensor and kept there during all tests. A total gas flow rate of 1 L/min was passed through the quartz tube and controlled by mass flow controllers (Bronkhorst). The sensors were allowed to stabilize at 400 °C and dry air flow until a stable baseline was obtained. A mass spectrometer (MS; Thermo Star, Pfeiffer Vacuum) analyzed effluent gases from the quartz tube. The sensor signal is given as the resistance ratio R_0/R_{gas} where R_0 and R_{gas} denote the sensors' resistance in the absence and presence, respectively, of the gas to be sensed. The sensor response is defined as the time required until 90% of the response signal is reached. The recovery time denotes the time needed until 90% of the original baseline signal is recovered.

3. Results and discussion

3.1. Particle and sensing film properties

Fig. 1 shows TEM images of as-prepared 10 at.% Nb/TiO_2 (a and c) and 10 at.% Cu/TiO_2 (b and d) nanoparticles by FSP. The Nb-doped titania particles (Fig. 1a) are mostly spherical with a SSA of 103 m^2/g similar to FSP-made pure TiO_2 [6]. At higher TEM magnification (Fig. 1c) the crystal lattice fringes are visible, however no segregated regions of Nb or Ti can be discerned. EDX analysis over large sample areas as well as on single particles verified the presence of both Nb and Ti and thus indicates the formation of a mixed oxide and/or a thin layer (<1 nm) or small domains of niobia on the titania particles not detectable by TEM at this resolution. The SSA is independent of Nb content (Table 1), in agreement with Jehng and Wachs [17] for wet-impregnated Nb_2O_5 on TiO_2 and similar to flame-made 10 wt.% V_2O_5/TiO_2 [18] where V_2O_5 had coated TiO_2 particles.

The Cu-doped titania particles also appear spherical in TEM images (Fig. 1b) but at higher magnification (Fig. 1d) small spherical asperities (<5 nm) evenly distributed over the particle surface can be seen. The optical appearance of the powders changed from white for pure titania to greenish with increasing copper content. Pure copper oxide had a very dark, rather black, appearing colour. Chiang et al. [19] reported that Degussa P25 changed from white to greyish while depositing CuO on TiO_2 particles by wet photodeposition. The presence of Cu and Ti in the FSP-made sample was verified by EDX analysis, however