

Sensing of Organic Vapors by Flame-Made TiO₂ Nanoparticles

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ABSTRACT

Anatase TiO₂ nanoparticles were produced by flame spray pyrolysis (FSP) and characterized by transmission/scanning electron microscopy, X-ray diffraction and nitrogen adsorption. Thick films (30 – 50 μm) of these powders were prepared by drop-coating technique and tested for sensing of acetone, isoprene and ethanol at 500 °C in dry N₂/O₂. A high n-type sensor signal was recorded at ppm levels of these organic vapors with fast response and recovery times. Heat-treatment at 900 °C caused a nearly complete anatase to rutile transformation and a transition to p-type sensing behavior. The rutile sensor had a poor signal to all hydrocarbons tested and considerably longer recovery times.

Keywords: titanium dioxide, anatase, gas sensors, isoprene, acetone, ethanol

1 INTRODUCTION

Titanium dioxide (TiO₂) has been applied in sensors for measuring many gases including oxygen [1], carbon monoxide [2], hydrogen [3], nitrous/nitric oxide [4], water vapor [5] and hydrocarbon gases [6]. TiO₂ sensor material synthesis routes must meet the demands of close size control, large and easily accessible surface area, high crystallinity and the ability to include noble metal doping. Larger surface area materials provide high sensitivity at low gas concentrations, e.g. Gao et al. [7] found that nano-scale titania films exhibited better oxygen sensing performance than micron-sized ones. Thermal pre-treatment of sensing devices is often required to ensure sensor stability. This causes grain growth of the material, resulting in a lower surface area and poor sensor response. Moreover, in the case of TiO₂, temperatures over 600 °C lead to a crystallographic phase transition from anatase to rutile [8]. Dopants are typically added to titania either to increase its thermal stability (Si: [9]; Nb: [10]; Ta: [11]; La: [12]) or sensor sensitivity and selectivity (CuO: [13]). Nano- and micrometer TiO₂ particles for gas-sensing have been produced by sol-gel [5], oxidation of metallic titanium foil [14], laser pyrolysis [10], magnetron sputtering [3], supersonic cluster beam deposition [15] and ball milling of commercial powders [16].

Flame technology is used largely for manufacture of about 2 million tons/year pigmentary titania [17]. Size,

crystallinity and morphology of flame-made nanostructured TiO₂ can be controlled by changing the high temperature residence time of the particles in the flame [18]. Doped-TiO₂ can be readily made by co-oxidation of precursors in the flame [19, 20]. Further, flame spray pyrolysis (FSP) processes allow for the addition even of low-volatility dopant precursors (e.g. for platinum [21]).

The high and fast response of FSP-made SnO₂ [22] and Pt/SnO₂ [21] nanoparticles towards propanal, NO₂ and CO has already been demonstrated. In this study, the sensing of volatile organic compounds is explored using flame-made TiO₂ anatase nanoparticles [23]. The sensor signal to ethanol, isoprene (2-methyl-1,3-butadiene) and acetone was investigated. Acetone is a common airborne contaminant [24], isoprene can be found in human breath [25] and over forested areas [26]. Ethanol detection is required for applications such as breath analyzers, monitoring devices for food-quality [27].

2 EXPERIMENTAL

A flame spray pyrolysis (FSP) reactor [28] was used for the synthesis of TiO₂ nanoparticles. Solutions of 0.5 or 0.67 M titanium-tetra-isopropoxide (TTIP, Aldrich, purity > 97 %) in a xylene (Fluka, > 98.5 %)/acetonitrile (Fluka, > 99.5 %) mixture (11/5 by volume) were fed at 5 ml/min through the inner reactor capillary. Oxygen (Pan Gas, purity > 99%) was supplied at 5 l/min through the surrounding annulus, dispersing the precursor solution into a combustible spray. The pressure drop at the nozzle tip was held constant at 1.5 bar. The spray was ignited by a premixed methane/oxygen flame (1.5/3.2 l/min). The spray-flame could be sheathed with 40 l/min of oxygen gas and enclosed by a 40 cm long glass tube resulting in higher temperatures. Suspensions of the product powders in 1-heptanol (Acros Organics) were prepared and drop-coated onto alumina substrates with interdigitated Au electrodes (10×10 mm; Electronics Design Center, MicroFabrication Lab, Case Western Reserve University). The substrates were dried at 100 °C, at least, for 1 hour in an oven.

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 K α radiation. Anatase and rutile crystallite sizes, and phase composition were determined by the fundamental parameter approach and the Rietveld method. The BET powder-specific surface area (SSA), was measured by nitrogen adsorption at 77K

(Micromeritics Gemini 2375) after degassing the sample, at least, for 1 h at 150 °C in nitrogen. The BET equivalent average diameter (d_{BET}) was calculated as $d_{\text{BET}} = 6/(\text{SSA} \cdot \rho_p)$, where ρ_p is the weighted density of TiO_2 (4260 or 3840 kg/m^3 for rutile or anatase, respectively). The product powder morphology was analyzed by transmission electron microscopy (TEM; CM30ST microscope, FEI (Eindhoven), LaB6 cathode, operated at 300 kV, SuperTwin lens, point resolution $\sim 2\text{\AA}$). Scanning electron microscope (SEM, LEO 1530 Gemini microscope) images were prepared of the sensing films.

DC electrical measurements (sensor tests) were performed to monitor the response to acetone (1 – 7.5 ppm), isoprene (2-methyl-1,3-butadiene; 1 – 9 ppm), and ethanol (10 – 75 ppm) in a dry N_2/O_2 atmosphere (all gases Specgas, Inc.). The pulse time of the gases at each concentration was usually 180 s. For the sensor tests the substrate was placed in the center of a quartz tube (2.5 cm diameter and 60 cm length), which in turn was introduced into a tubular furnace (Lindberg/Blue). Gold wires were melted onto the sensor electrodes and externally connected to a digital multimeter (Agilent 34401) recording the sensor resistance. The furnace was heated to 500 °C in 1 hour and kept at this temperature during the sensor tests. A total gas flow rate of 1 L/min was passed through the quartz tube and controlled by mass flow controllers (1479 MKS). The measurements were done in 10 % accompanying O_2 with the balance N_2 . The sensors were allowed to stabilize for, at least, 1 hour at the sensing temperature and N_2/O_2 flow. Sensors could also be heat-treated in ambient atmosphere at 900 °C for 6 hours prior to sensing at 500 °C. The sensor signal is given in the following as the resistance ratio R_0/R_{gas} , where R_0 and R_{gas} denote the sensors' resistances in the absence and presence of the gas to be sensed, respectively. 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

Figure 1 shows TEM images of as-prepared TiO_2 nanoparticles. Sample P1 (Fig. 1a) was produced from a 0.5 M TTIP solution, while sample P2 (Fig. 1b) was produced from a 0.67 M solution with the glass tube enclosing the flame. The particles in sample P1 (Fig. 1a) are spherical and non-agglomerated of 15 nm in BET diameter consistent with Schulz et al. [28] for FSP-made TiO_2 at similar conditions. The particles in sample P2 (Fig. 1b) are larger, 43 nm BET-diameter, and polyhedral as they were made at higher temperature (in the enclosed flame) and higher TTIP concentration than those of sample P1. The phase composition in both samples is about 85 wt% anatase and the balance rutile, typical for TiO_2 formed in oxygen-rich vapor-fed [20] or spray [28] flames.

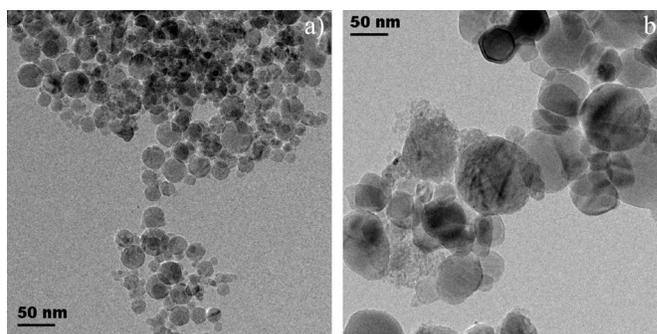


Figure 1: TEM images of FSP made TiO_2 nanoparticles. Spherical, non-agglomerated particles are visible in sample P1 (a), while particles in sample P2 (b) are polyhedral since they experienced higher temperature residence times than P1 during their flame synthesis.

The anatase crystallite size is larger in sample P2 than P1, 60 and 20 nm, respectively. In both cases the crystallite sizes are larger than the BET diameter indicating non-spherical particles, as seen in TEM images of sample P2 (Fig. 1b). The longer high temperature residence time of P2 particles than P1 enables the growth of these large, non-spherical crystals.

Sensing films S1 and S2 were prepared from samples P1 and P2, respectively. The S2 sensor was tested as-prepared and after heat-treatment. Figure 2 shows a cross-sectional SEM image of heat-treated film S2 after sensor test. The alumina substrate is also visible. The film is dense with a thickness is about 20 – 30 μm , irregularities stem from the drop-coating technique. Prior to heat-treatment more porous structures were observed and the films were 40 – 50 μm thick.

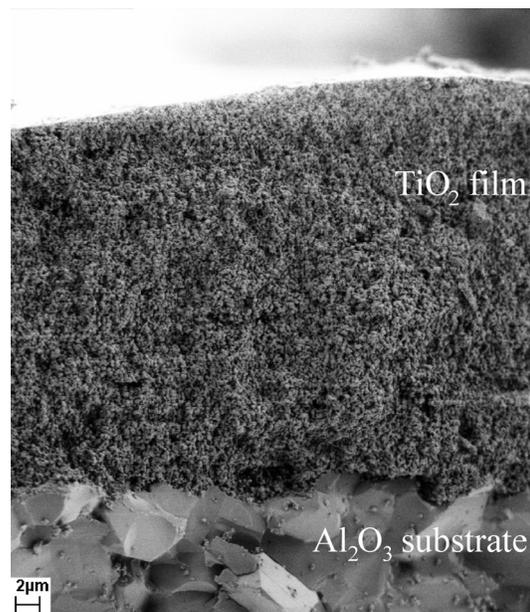


Figure 2: SEM image of TiO_2 sensing layer S2 on an alumina substrate after heat-treatment at 900 °C and sensing at 500 °C.

The phase composition of film S1 after sensor test was 87 wt% anatase consistent with the as-prepared powder P1. Also the anatase and rutile sizes were unchanged compared to as-prepared particles. Thus no anatase to rutile phase transformation or grain growth had taken place during the sensor tests indicating the high stability of flame-made particles at these conditions. A nearly complete phase transformation to rutile, however, had taken place in the heat-treated film S2 as expected at these temperatures [29]. The rutile crystallite size increased significantly to 159 nm.

3.2 Gas Sensing Properties

Sensor S1 was tested for 1 – 9 ppm of isoprene during a forward and backward cycle. The resistance decreased during the gas exposure, a typical behavior for anatase as an n-type semiconductor [6]. The sensor signal consistently increased with increasing isoprene concentration. The forward and the backward cycles nearly coincided though the signal during the backward cycle was slightly higher than the forward.

A similar signal was obtained with sensor S2 tested for acetone (triangles), isoprene (diamonds) and ethanol (rectangles) as shown in Figure 3. At 1 ppm for acetone and isoprene, the sensor first self-recovered before stabilizing at the sensor signal. The sensor signal increases rather linearly with increasing gas concentration consistent with sensor S1 and in agreement with Zhu et al. [30] for ZnO-TiO₂ thick film acetone sensors. The response curves of acetone and isoprene coincide (Fig. 3), only at 7.5 ppm acetone gives a higher signal than isoprene. The interaction of both acetone and isoprene with hydroxyl groups on the surface of TiO₂ might explain the sensor signal similarity of the two gases. Also for ethanol at 10 – 75 ppm the sensor signal increases rather linearly with increasing concentration, in agreement with ethanol sensing at higher gas concentration [27]. The signal is higher than for acetone and isoprene due to the higher ethanol vapor concentration.

The response times were within 2-3 seconds for all gases at the tested concentrations. The recovery time for acetone increased nearly linearly from 144s at 1 ppm to 302s at 7.5 ppm. The same dependence of recovery time with concentration was observed of isoprene but the sensor recovered faster than for acetone. The slower recovery after acetone exposure might stem from molecular adsorption of acetone on the surface [24]. In contrast, the recovery time decreased with increasing ethanol concentration, indicating a different sensing mechanism for ethanol. The sensing behavior of titania might not only rely on interaction of ethanol with adsorbed oxygen species, but rather on the direct adsorption at semiconductor surface sites, as was also suggested by Ferroni et al. [27].

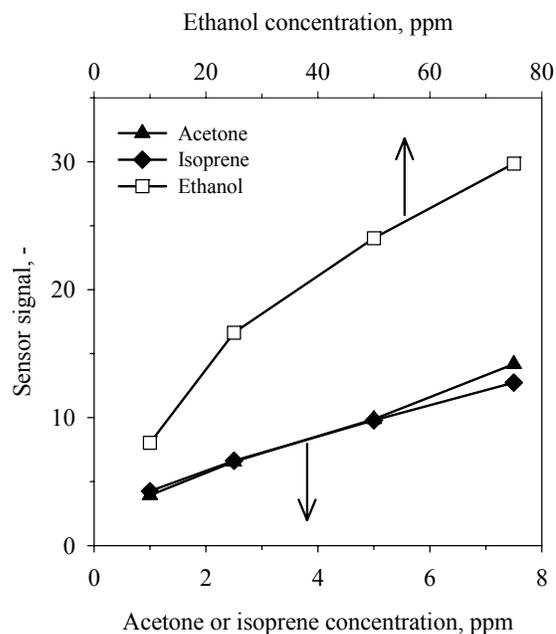


Figure 3. Sensor signal of S2 under exposure to acetone (triangles), isoprene (diamonds) and ethanol (squares) in a dry N₂/O₂ atmosphere at 500 °C.

After heat-treatment sensor S2 showed a p-type behavior towards sensing of acetone and isoprene, as an anatase to rutile transformation had taken place. However, exposing the sensor to ethanol, the response changed back to n-type. For all gases response and recovery times were slower than before the heat-treatment. This indicated that the time for heat treatment might not have been long enough to equilibrate the rutile lattice with oxygen.

4 CONCLUSIONS

TiO₂ nanoparticles were produced in a flame spray pyrolysis reactor by combustion of titanium-tetra-isopropoxide. Particles consisting mainly of anatase phase (85 wt%) with BET-equivalent particle diameters of 15 or 43 nm were prepared. These particles were drop-coated from heptanol suspensions onto alumina substrates interdigitated with gold electrodes resulting in porous films 40 – 50 μm thick. The gas sensing properties of these films were investigated for ppm levels of ethanol, acetone and isoprene vapors at 500 °C. The sensors had n-type response to these vapors with response and recovery times within a few seconds or minutes, respectively. Denser films about 30 μm thick were formed after heat-treatment at 900 °C and a complete phase transformation to rutile took place. This resulted in a n- to p-type transition and poor sensor signals.

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