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Influence of grain size on gas sensing properties of TiO₂ nanopowders

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Abstract

The aim of this research is to study size – dependent effects and gas sensing properties of TiO₂ nanomaterials prepared on the base of nanopowders obtained by Flame Spray Synthesis, FSS. The specific surface area (SSA) and the resulting particle sizes of the prepared powders are controlled by the flow rate of the precursor. The results concerning morphological properties of nanomaterials investigated by BET, adsorption isotherms, X – ray Diffraction, XRD, Scanning Electron Microscopy, SEM are discussed. Electrical resistivity of gas sensing tablets is measured as a function of hydrogen concentration within the range of 50 – 3000 ppm at constant temperature of 200 °C – 400 °C. Dynamic changes in the electrical resistivity upon interaction with hydrogen are large and reproducible. The sensor response increases systematically with the decrease in the temperature of operation down to 250°C. Smaller grain size results in a higher electrical conductivity suggesting the predominant influence of intergrain contacts.

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1. Introduction

An increasing interest in nanomaterials for gas sensing has its beginning in 1990s when it was demonstrated that nanocrystalline SnO₂ reveals improved gas sensing performance [1]. Since that time we can observe a growing research concerning different nano-sized metal oxides, among others TiO₂, for gas detection. There is a wide range of publications undertaking the issue of TiO₂ in a form of nanotubes [2], nanofibers [3], nanowires [4], nanopowders [5] that exhibit well – promising gas sensing features. Nanocrystalline TiO₂ reveals improved conductivity [6] and decreased operating temperature [7] when compared with micro-sized counterparts.

Previous investigations carried out by our research group concentrated on TiO₂ doped with Cr nanopowders for H₂ sensing [7] with the aim to determine the influence of both controllable doping and grain size on gas sensing properties. The objective of this work is to study the impact of grain diameter intentionally changed by means of adjusting synthesis parameters on electrical and hydrogen sensing behaviour of undoped TiO₂ nanopowders.

Theoretical approach to size – dependent effects takes into consideration the relationship between grain size d and Debye length λ_D which determines the width of near surface depletion layer, defined as:

$$\lambda_D = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{q^2 n_b}} \quad (1)$$

where ϵ and ϵ_0 denote relative permittivity of the material and vacuum permittivity, respectively, k_B is Boltzmann constant, T denotes temperature, q and n_b represent the charge of an electron and density of ionic defects, respectively. Simulation of Debye length based on eq. (1) for TiO₂ of various concentrations of charges indicates that λ_D is of the order of 20 nm at room temperature because of high value of dielectric constant ϵ . It is therefore more probable to obtain the limit of small grains $d \leq \lambda_D$ as opposed to SnO₂ where the Debye length is of the order of 3 - 5 nm. In this work the threshold for size effect in terms of the minimum particle or grain size is sought for in the case of TiO₂ which differs significantly from SnO₂.

2. Experimental

Nanopowders of TiO₂ were obtained by Flame Spray Synthesis, FSS, as described in detail in [6]. Titanium – 2.4 – pentanedionate (C₁₆H₂₈O₆Ti) dissolved in ethanol was used as metal – organic precursor. Specific Surface Area, SSA, of synthesized TiO₂ nanopowders was intentionally changed by means of adjusting flow rate. In order to measure SSA, BET (Brunauer – Emmett - Teller) adsorption isotherms obtained with a Beckman - Coulter SA3100 were used. Grain size of nanopowders was determined from the SSA data while the dimensions of crystallites were analysed on the basis of XRD patterns recorded with the help of X'Pert MPD Philips diffractometer. Morphology of the prepared nanomaterials was studied by means of Scanning Electron Microscopy SEM performed with Hitachi SU-70 apparatus.

Dynamic changes in the electrical resistance upon hydrogen exposure have been detected over low-to-medium concentration range of 50-3000 ppm at 200 - 400°C [7]. Tablets subject to gas sensing experiments have been prepared by pressing the nanopowder at the pressure of 25 MPa and heating up to 400°C. Sensor response S was defined as the relative change in the electrical resistance value upon interaction with hydrogen.

3. Results

Flame Spray Synthesis, FSS, technique was applied to obtain TiO₂ nanopowders with the specific surface area, SSA, from about 37 m²/g to 121 m²/g. Fig. 1 presents SEM image of TiO₂ sensing tablet

characterized with the smallest SSA = 37.5 m²/g together with the corresponding grain size distribution. As it can be seen, FSS method provided spherical morphology and narrow size distribution of synthesized nanomaterials.

Fig. 2 demonstrates XRD patterns of the samples. TiO₂ nanopowders reveal high degree of crystallinity and predominance of anatase polymorphic phase. Table 1 contains detailed results of BET and XRD analysis. The contribution from rutile is small and amounts to about 5 - 6 wt.%. The corresponding anatase and rutile crystal sizes vary between 27 and 12 nm for anatase and 14 to 10 nm in the case of rutile.

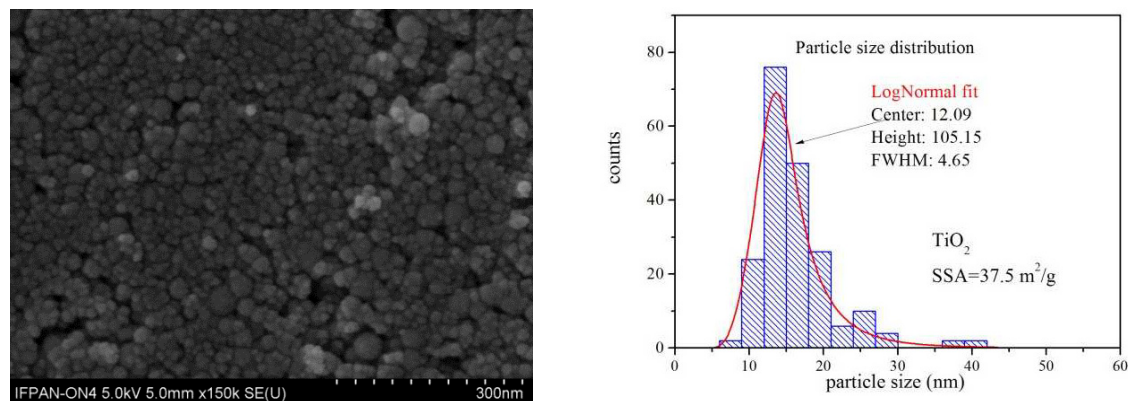


Fig. 1 SEM image and grain size distribution for TiO₂ sensing tablet with SSA=37.5 m²/g

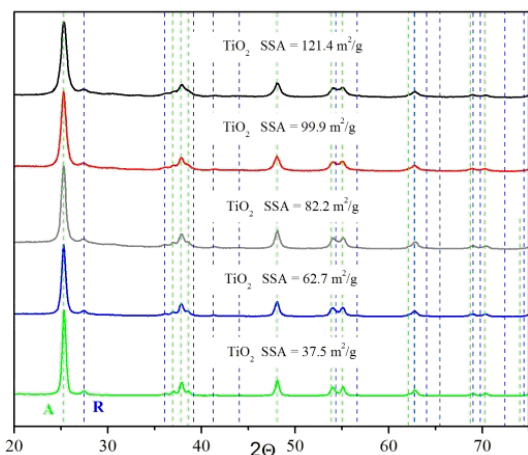


Fig. 2 XRD patterns for TiO₂ sensing tablets made of FSS nanopowders with different SSA

Table 1. Basic parameters of TiO₂-based nanopowders obtained by FSS

Specific surface area SSA (m ² /g)	Grain size (nm)	Phase composition; f _A – weight percentage of anatase	Crystal size (nm) from XRD	
			anatase	rutile
121.4	12.6	93.6 wt. %	12.2	10.3
99.9	15.4	95.5 wt. %	15.1	12.1
82.2	18.7	94.1 wt. %	16.6	13.0
62.7	24.5	95.0 wt. %	19.9	15.9
37.5	41.5	94.0 wt. %	26.8	13.6

Fig. 3 shows the sensor response *S* as a function of the operating temperature for two TiO₂ sensing tablets with SSA values equal to: 54.3 and 121.4 m²/g upon interaction with 500 and 3000 ppm H₂. The sensor performance clearly improves with a decrease in the operating temperature which is a well – promising feature in terms of decreasing power consumption.

Temperature dependence of the electrical conductivity σ(T) with its activation energy E_a in air is shown in Fig.4. Systematic increase in σ with the increased SSA and decreased particle size indicates the predominant role of the contacts between conducting grains.

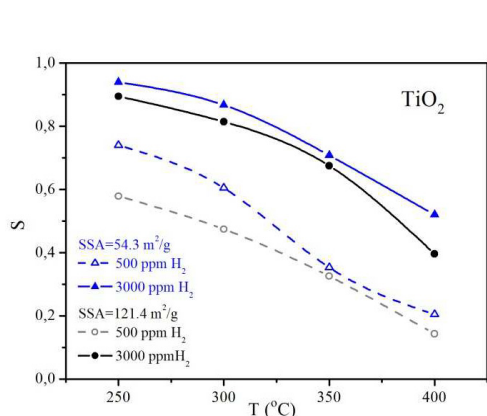


Fig. 3 Temperature dependence of electrical resistivity responses S upon 500 and 3000 ppm H_2 for sensing tablets made of FSS TiO_2 nanopowders with different SSA

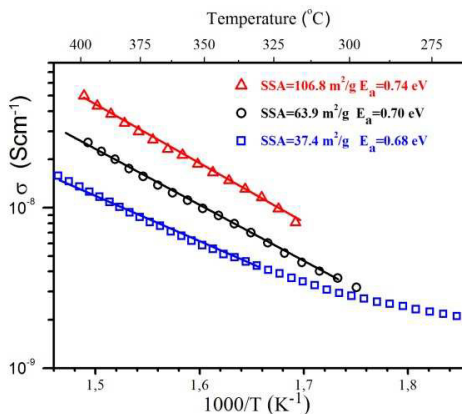


Fig. 4 Temperature dependence of the electrical conductivity σ for TiO_2 with different SSA; E_a is the activation energy

4. Conclusions

Well-crystallized TiO_2 nanopowders with the specific surface area, SSA, from about $37 \text{ m}^2/\text{g}$ to $121 \text{ m}^2/\text{g}$ and anatase form in majority have been successfully synthesized from metal-organic precursor by means of Flame Spray Synthesis FSS. The positive influence of decreasing particle diameter manifests itself in the increase of electrical conductivity and sensor response while lowering operating temperature.

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