

Novel Nanostructures for Solid State Alcohol Breath Analyzers

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ABSTRACT

Nanostructured mixed tin - titanium oxide particles were made by atmospheric flame spray pyrolysis, directly deposited onto sensing electrodes and *in situ* stabilized by rapid flame annealing. Pure solid solutions up to 80% Ti were obtained without segregation from SnO₂. These particles had a rutile structure with tunable lattice constants. At higher Ti - contents, part of TiO₂ was segregated in its anatase phase. Even then, the presence of Sn strongly inhibited the formation of anatase. At low Ti - contents, Ti cations substitutionally reduced the size of the rutile cell with small deviation from Vegard's law but the change in physical and chemical properties was not linear. The UV - vis absorption indicated a drastic red shift already at 5.5% Ti where the band gap reached almost the value of pure TiO₂ rutile. Also, the adsorption of terminal and rooted OH groups due to water vapor dissociation was drastically reduced already at low Ti - content ($\leq 9\%$) showing similar IR - spectra (4000 - 500 cm⁻¹) to that of pure TiO₂ particles. As a consequence the cross - sensitivity to humidity decreased rapidly with increasing Ti - content. Nevertheless, the sensor signal had a maximum at low Ti - content and further increasing the Ti - content reduced remarkably its response to EtOH.

1 INTRODUCTION

Solid state alcohol breath analyzers are commonly used by the law enforcement authorities, due to high sensitivity toward ethanol, their portability and fair response and recovery times.^[1] Common materials for the synthesis of the sensitive element are SnO₂ nanoparticles with an average size below 15 nm.^[2] The main drawback of the exploitation of SnO₂ as sensing material is its high cross-sensitivity to humidity, which requires expensive and elaborated systems for preparation of the gas probe.^[3] The cross-sensitivity issue can be solved in some extent by utilizing other oxides such as TiO₂.^[4] Nevertheless, such semiconductors have from less sensitivity to EtOH than SnO₂ and may have some stability problems. In fact, it has been reported that flame-made TiO₂ nanoparticles undergo crystallographic phase transition from anatase to rutile while heated at sufficient temperatures thus drastically reducing sensitivity.^[4]

Tin oxide^[5] and TiO₂^[4] nanoparticles can be readily made in flame reactors leading to small size and thus high sensitivity. These nanoparticles can also be deposited directly from the hot aerosol on a target substrate placed above the flame reducing process times.^[6] Here, synthesis of novel SnO₂-TiO₂ nanostructures with drastically reduced cross-sensitivity to humidity and high sensitivity to ethanol have been obtained by flame spray pyrolysis. The solid solution properties, such as the band gap, crystal size and morphology, are correlated to the sensing performance. In particular, the cross-sensitivity to humidity during EtOH detection is investigated at different relative humidity and compared to real operating conditions.

2 RESULT AND DISCUSSION

First a liquid precursor containing tin (II) ethylhexanoate and titanium-tetra-isopropoxide is combusted and evaporated forming a super saturation of the target oxides. Nucleation, condensation and coagulation lead to formation of a solid solution of SnO₂/TiO₂ nanocrystals (Fig. 1) with a predominant rutile phase.

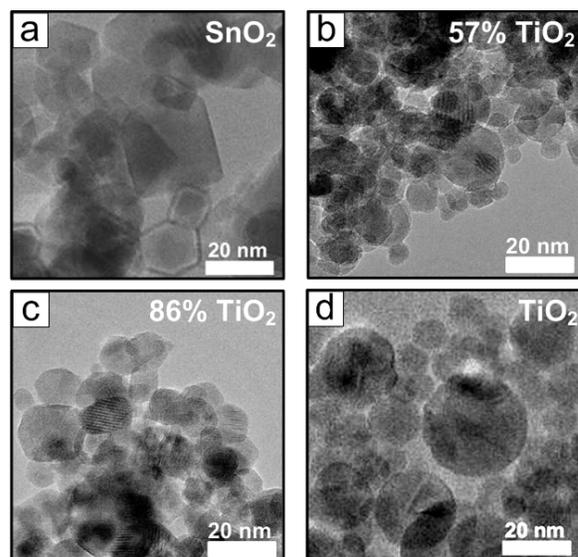


Figure 1: TEM images of pure SnO₂ and TiO₂ and SnO₂/TiO₂ nanoparticles as a function of the TiO₂ content.

The lattice constants *a* and *c* (Fig. 2) of the rutile cell monotonously decrease with increasing Ti - content in

agreement with the smaller ionic radii of Ti (0.61 Å) than Sn (0.71 Å).^[7] Nevertheless, such a reduction is slightly not linear confirming that Vegard's law (Fig. 3 continuous line) is not applying to SnO₂ - TiO₂ solid solution.^[8] Deviation from Vegard's law which resulted in larger lattice constants were observed also in low - pressure premixed flames.^[9] At 81.5% Ti the lattice constant a reaches 4.61 Å (Fig. 3a) while c is 2.97 Å (Fig. 3b). Just above 81.5% Ti - content, both lattice constants are slightly increased. This is attributed to the nucleation of the anatase phase which may change the Ti - content of nearby rutile crystals.

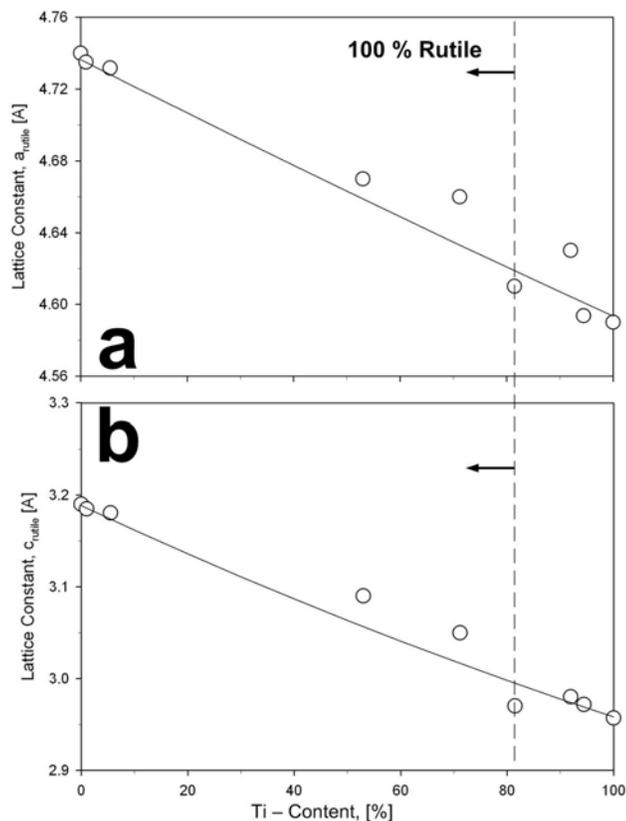


Figure 2: Lattice constants a (a) and c (b) of the rutile primitive cell as a function of the Ti - content. The values decrease from the ones of pure SnO₂ to the ones of pure TiO₂, but do not follow Vegard's law (continuous line).

3 CONCLUSIONS

Substitutional solid solutions of tin - titanium - oxides with rutile phase and crystal size below 10 nm were obtained by atmospheric flame spray pyrolysis. These Sn - and Ti - cations were dispersed homogeneously without detectable segregated regions of SnO₂ or TiO₂. Above a critical Sn/Ti ratio, a segregated anatase phase was formed doubling the grain size. This was attributed to the 3 times larger anatase size than rutile. Nevertheless, the anatase phase content was effectively inhibited below 25 wt% by Sn - cations up to 95% Ti - content. In comparison, for

pure TiO₂ the anatase content was 95 wt%. In conclusion, the SnO₂/TiO₂ nanostructures with tunable lattice constants are a highly performing material for alcohol breath analyzers with the potential of strongly reducing the cost of such devices.

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