Effect of different morphologies of nanostructured SnO$_2$ and their nanocomposites on sensing behavior

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ABSTRACT. This paper reviews different methods for synthesis of SnO$_2$ and their nanocomposites with various morphologies as well as the study of sensing properties of these materials. The sensing properties of these materials depend not only upon the individual components used but also on the morphology, particle size and the interfacial characteristics. Depending on the chemical nature of the analyzed gas and the electronic structure of this metal oxide, such interactions can result in either an increase or a decrease of the sensory effect. Thus, by varying the electronic structure of this metal oxide composite sensor as well as the morphology and size of the SnO$_2$ nanoparticles, the inherent characteristics of the sensor can be changed and tailored for detection of various gases. Such findings clearly open up new opportunities for development of novel selective sensors. In this brief review, attention will be focused on changes of morphology and composition of SnO$_2$ that show dramatical effect on sensitivity of this material.

Keywords: Morphology, Nanocomposite, Sensing properties.

1. INTRODUCTION

Problems such as toxic gas emission and inflammable gas leakages provide the impetus for fundamental and applied research in environmental areas. Semiconductor gas sensors based on metal oxides have been used extensively to detect the gases for their efficiency and broad applicability [1]. However, the major problems associated with these gas sensors are their unsatisfactory selectivity and long-term stability [2]. In order to improve their properties, many efforts have been focused on the modification of semiconductor gas sensors by doping or composition with elements or metal oxide such as Pt-doped SnO$_2$, Au-doped ZnO, Sb-doped SnO$_2$, CeO$_2$ doped SnO$_2$, etc.
TiO$_2$ doped ZnO, ZnO–SnO$_2$, MoO$_3$–SnO$_2$, SnO$_2$/γ-Fe$_2$O$_3$ and In$_2$O$_3$–SnO$_2$ [3]. The addition of a second component as a surface modifier is used both as active sites for redox processes and as promoting free charge carriers that increase the electronic conductance of the oxide films. Apart from the doped and composite sensors, preparations of different morphology of SnO$_2$ have also been reported to be promising sensitive and selective gas sensors. Some reports indicate that the catalytic selectivity and sensitivity of these structures are significantly improved, compared with other shapes [4]. Thus, designing and preparing SnO$_2$ materials with novel morphology and doped/or cocomposite with other materials are of significant importance in meeting the scientific and technological applications.

As a simple review of metal oxide gas sensors, the main attention in this paper will be focused on the fabrication of SnO$_2$ sensors with different morphology and composition.

2. METHODS FOR SYNTHESIS OF SnO$_2$

A variety of methods are used for producing mixed metal oxide nanocomposites. These methods include sol-gel technique using codeposition of mixed oxides from corresponding salt solution, aerosol spraying of salt solutions with subsequent heat treatment, the deposition by reactive metal sputtering from composite targets in the presence of oxygen, and the blending of individual metaloxide nanopowders [5]. It should be noted that the structure of the nanocrystalline components in the composite may differ significantly from that of individual substances which form the base of the composite. The formation of mixed metal oxide nanocomposites may probably produce nanoparticles with high volume defects resulting mainly from the incorporation of ions of one component in the lattice of another.

There are many methods to synthesize of different morphology of this material. Ohgi et al. reported the evolution of nanoscale SnO$_2$ flakes into hierarchically structures by subsequent hydrothermal treatment. Xie and co-workers prepared 2D hierarchical SnO$_2$ flowerlike nanostructures without post-treatment of calcinations, taking advantage of slow oxidation of tin foil by the solution of KBrO$_3$ and NaOH. Mu and co-workers synthesized the flowerlike SnO$_2$ quasi-square submicrotubes by reaction between SnCl$_2$ and oxalic acid in ethanol solution, followed by calcination in air [4].

3. FACTORS INFLUENCING THE SENSITIVITY

3.1 EFFECT OF MORPHOLOGY

The sensitivity to a target gas strongly depends on the ease of diffusion of gas molecules inside the sensor. Thus, the structure and morphology of materials can be correlated with the sensor performance. Flower-like SnO$_2$ consists of numerous nanoparticles joined together into flower-like structure, resulting in much more active
exposed sites for gas chemisorptions. Thus, the realization of a high sensitivity of flower-like morphology may be explained in terms of rapid gas diffusion onto the entire sensing surface due to the specific morphology of this material [4].

3.2 EFFECT OF COMPOSITION

It is well known that materials based on the ZnO–SnO₂ composite are widely used for the production of humidity and combustible gas detection sensors. The composite ZnO-SnO₂ sensors exhibited significantly higher sensitivity than sensors constructed solely from tin dioxide or zinc oxide when tested under identical experimental conditions. Sensors based on the two components mixed together are more sensitive than the individual components alone suggesting a synergistic effect between the two components. The huge improvement in the response and selectivity of the sensor to ethanol by ZnO doping, is possibly due to the presence of Zn²⁺ species in SnO₂ that create a heterostructure containing two centers with different reductive–oxidative and acid–base properties that facilitate electronic interactions. The strong ethanol adsorption and specific surface morphology along with the smallest crystallite sizes may also contribute to the sensor selectivity (Figure 1) [5].

![Figure 1](image)

**Figure 1.** Responses of different SnO₂–ZnO nanostructured sensors as a function of operating temperature to (a) 300 ppm ethanol gas, (b) 500 ppm CO gas. Also, the MoO₃-doping to pr–SnO₂(n) improved the sensor response and selectivity towards NO₂ gas. This sensing behavior was well-correlated with the increase in
acidity of the surface of the SnO$_2$ caused by the presence of molybdenum species in the SnO$_2$ nano- and meso-porous structures (Figure 2) [6].

**Figure 2.** Temperature dependence of response of pr-SnO$_2$(5) and prmMoO$_3$–SnO$_2$(5) (m= 1, 5 and 10) thick films to 5ppm NO$_2$.

### 4. CONCLUSIONS

In summary, the gas sensing process is strongly related to the surface reactions. Different metal oxide based materials have different reaction activation to the target gases. Composite metal oxides usually show better gas response than the single component if the catalytic actions of the components complement each other. Another important structure factor is morphology. The specific morphology can provide large reaction contact area between gas sensing materials and target gases.

### REFERENCES


