



Cobalt location in p -CoO_x/ n -SnO₂ nanocomposites: Correlation with gas sensor performances



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ABSTRACT

Nanocomposites CoO_x/SnO₂ based on tin oxide powders with different crystallinity have been prepared by wet chemical synthesis and characterized in detail by ICP-MS, XPS, EPR, XRD, HAADF-STEM imaging and EDX-STEM mapping. It was shown that cobalt is distributed differently between the bulk and surface of SnO₂ nanocrystals, which depends on the crystallinity of the SnO₂ matrix. The measurements of gas sensor properties have been carried out during exposure to CO (10 ppm), and H₂S (2 ppm) in dry air. The decrease of sensor signal toward CO was attributed to high catalytic activity of Co₃O₄ leading to oxidation of carbon monoxide entirely on the surface of catalyst particles. The formation of a p -CoO_x/ n -SnO₂ heterojunction results in high sensitivity of nanocomposites in H₂S detection. The conductance significantly changed in the presence of H₂S, which was attributed to the formation of metallic cobalt sulfide and removal of the p – n junction.

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1. Introduction

Low selectivity is one of the principal problems of resistive type gas sensors based on semiconductor metal oxides. From materials science point of view, the solution can be found through the surface modification of highly dispersed semiconductor oxide matrix with clusters of transition metals or their oxides, which may affect the chemical properties of the surface. This method implies a directed change in the chemical state of the surface, the creation of active centers of specific chemical interaction with the target gas simultaneously with a decrease in the concentration of centers of non-selective interaction. Chemical modification leads to a sharper separation of receptor (surface) and transducer (volume) functions in a complex process of sensor signal formation. The effectiveness of this approach to increase the sensitivity and selectivity of sensor

materials has already been demonstrated in the literature [1–3].

The distribution of the modifier between the bulk and the surface of crystalline grains of the major phase is very important for the formation of functional properties of the nanocomposites [3]. This is especially important when the main phase and modifier are semiconductors of different conductivity type. The insertion of admixture atoms into the crystalline structure of the n -type semiconducting oxide results in the formation of impurity levels, the compensation effect of donor oxygen vacancies by acceptor admixture defects, and the modulation of the band relief of the semiconductor. The segregation of the modifier on the grains surface of the major phase can result in the formation of p – n junctions in the region of intergrain contacts, which also inevitably affects the electrophysical properties of the material. The distribution of the components is given by fundamental characteristics, such as the ionic radii of the corresponding metals, and by the synthesis conditions, mainly by the way of adding a modifier and annealing temperature [3,4].

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Table 1
Samples designation, composition and microstructure parameters.

Sample	Preassigned, [Co]/([Co]+[Sn]) at%	Co content, wt%		Phase composition	d_{XRD} , nm ^a	S_{BET} , m ² /g ^b
		Total	Surface			
Sn300	—	—	—	SnO ₂	7 ± 1	40 ± 5
Co1.5Sn300	1.5	0.47 ± 0.03	0.14 ± 0.01	SnO ₂	7 ± 1	40 ± 5
Co5Sn300	5	2.1 ± 0.2	0.82 ± 0.06	SnO ₂	5.5 ± 0.5	55 ± 5
Co10Sn300	10	4.8 ± 0.3	1.8 ± 0.2	SnO ₂	5.0 ± 0.5	60 ± 5
Sn750	—	—	—	SnO ₂	16 ± 1	8 ± 5
Co1.5Sn750	1.5	1.15 ± 0.09	1.05 ± 0.09	SnO ₂	16 ± 1	9 ± 5
Co5Sn750	5	1.8 ± 0.1	1.6 ± 0.1	SnO ₂	20 ± 2	9 ± 5
Co10Sn750	10	3.9 ± 0.3	3.8 ± 0.3	SnO ₂	21 ± 2	12 ± 5
				Co ₃ O ₄	10 ± 2	

^a Average crystallite size estimated using Scherrer equation.

^b Specific surface area.

In nanocomposites based on *n*-SnO₂ and cobalt oxides *p*-CoO or *p*-Co₃O₄ both electronic and chemical sensitization can be realized. Being an additive, cobalt oxides can form solid solutions with SnO₂ (cobalt is located in the volume of the SnO₂ grains) and also segregate at the surface of tin dioxide (cobalt is located on the surface of the SnO₂ crystallites). These variations in Co distribution in the SnO₂ matrix will have different influences on the electrical properties of the materials and their reactivity in the interaction with the gas phase.

The gas sensor properties of nanocrystalline materials based on cobalt-doped tin dioxide were previously investigated [5–10]. It was revealed that this doping can be accompanied by either improvement of sensor parameters at low cobalt concentration levels, or by degradation of sensor characteristics, when the cobalt concentration exceeds its solubility limit in SnO₂ [9]. In this case a part of cobalt atoms not involved in the solid solution can form crystallites of its own phase or segregate on the grain surface of the major phase (SnO₂) as a two dimensional layer, which is not detected by X-ray diffraction. Such a system is similar to supported catalysts, in which the active phase of cobalt oxide is supported over conventional supports, such as alumina or silica, or over reducible oxides, such as ceria [11]. These materials were intensively studied in the processes of low temperature oxidation of CO [11], and low temperature gas desulfurization [12,13].

Nanoheterogeneous systems based on cobalt and tin oxides in form of three-dimensional nanocomposites [14], core-shell nanospheres [15,16], microreactors [17], nanofibers with different cobalt distribution [18–22] were recently investigated as gas sensitive materials for NH₃, H₂, CO, and volatile organic compounds (VOCs) detection. The obtained results are analyzed in terms of formation of *p* – *n* junctions between oxides with different type of conductivity. The interaction of oxygen and target gases with *p* – and *n* – parts of these heterojunctions results in the modulation of potential barrier height and formation of increased sensor signal as compared with individual oxides. However, these arguments have general character, do not take into account the chemical nature of target gases, and do not explain the selectivity of the materials in the detection of NH₃ [15], methylbenzenes [16], benzene [17], ethanol [14,19], and acetone [18].

In this paper, we analyze the influence of cobalt location in CoO_x/SnO₂ nanocomposites on their microstructure parameters, electrophysical properties and sensor signal toward CO and H₂S. CO and H₂S are among the main air pollutants. The maximum permissible concentrations of these gases in the working area are 16.2 and 2 ppm, respectively. Both these gases belong to the class of reducing gases, in their presence, the electrical conductivity of *n*-type semiconductor oxides increases. However, they are characterized by different acid properties: CO does not have pronounced acidic or basic properties, while H₂S is an acidic gas. Since cobalt oxide is a catalyst for low-temperature oxidation of CO, and also

exhibits activity in the interaction with H₂S, its use for SnO₂ surface modification can provide an increase in tin dioxide selectivity in the detection of CO and H₂S. The gas sensor properties of nanocrystalline materials based on cobalt-doped tin dioxide toward CO were previously investigated [5,6,17,21,22], while gas sensor performance of CoO_x/SnO₂ nanocomposites toward H₂S were considered only in Ref. [22].

To ensure a different distribution of cobalt between the surface and the volume of tin dioxide, the semiconductor matrix was subjected to preliminary temperature treatment at 300 and 750 °C. It was shown earlier on the example of the SnO₂-Fe₂O₃ system [3] that low annealing temperature (300 °C) makes it possible to obtain solid solutions of a large extent, while the use of a temperature exceeding 700 °C, leads to the formation of two-phase oxide

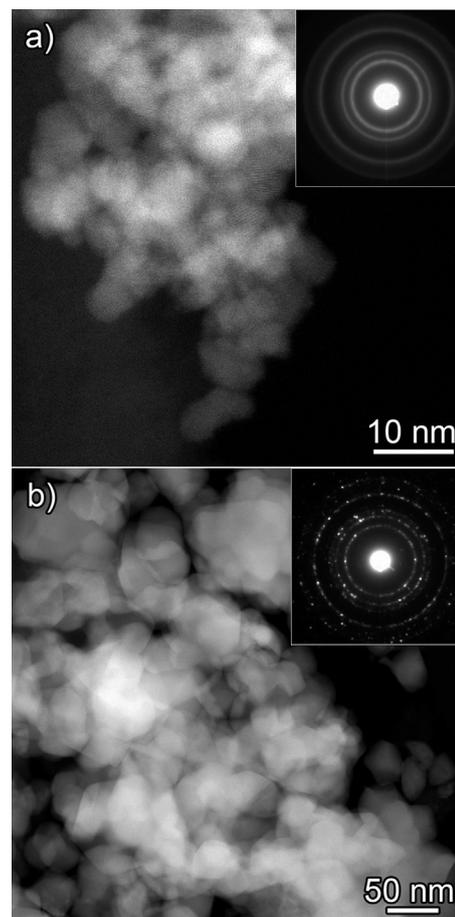


Fig. 1. HAADF-STEM images and electron diffraction patterns (insets) of (a) Co10Sn300 and (b) Co10Sn750 samples.

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