

Effect of Au and NiO Catalysts on the NO₂ Sensing Properties of Nanocrystalline SnO₂

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Abstract—Nanocrystalline tin dioxide has been synthesized, and its surface has been modified with Au and NiO. Their distributions in the nanocrystalline tin dioxide have been examined by X-ray diffraction and transmission electron microscopy. The NO₂ sensing properties of the materials have been studied in the range 100–1000 ppb. Both gold and nickel enhance the NO₂ response of SnO₂. Codoping with Au and NiO markedly enhances its sensing response and, in addition, lowers the peak response temperature. The observed effect of NO₂ concentration in dry air on the sensing response of the SnO₂(Au, NiO) nanocomposite can be understood in terms of the sequence of processes that take place on the SnO₂ surface upon nitrogen dioxide adsorption in the presence of chemisorbed oxygen.

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INTRODUCTION

One way of enhancing the gas-sensing performance of SnO₂-based semiconductor sensors is by doping fine-particle oxide hosts, usually with transition metals or their oxides, which are capable of influencing the electronic and catalytic properties of the surface. The use of two dopants differing in nature allows the system to be more accurately tuned to the particular chemical activity when it interacts with the gas phase.

This approach was first used by us to synthesize new gas-sensing materials based on nanocrystalline tin dioxide. One important advantage of such materials is that their properties can be tuned in wide ranges by adjusting the composition, cluster size, crystal structure, and electronic spectrum of dopants.

The objectives of this work were to synthesize nanocrystalline SnO₂, modify its surface with Au and NiO, examine the distribution of the modifiers in the nanocrystalline tin dioxide, and assess the NO₂ sensing properties of the synthesized materials in the range 100–1000 ppb, close to the level of maximum permissible concentrations (Table 1) [1, 2].

EXPERIMENTAL

SnO₂ was prepared by precipitating α-stannic acid gel from a SnCl₄ · 5H₂O solution with aqueous ammonia at 0°C. The gel was then washed repeatedly with distilled water to remove adsorbed ammonium and Cl[−] ions. Next, it was dried at 100°C for 24 h. The resultant powder was annealed at 300°C for 24 h.

SnO₂ was doped with gold and nickel by the incipient wetness impregnation method [3]. The precursors used were aqueous solutions of HAuCl₄ and Ni(NO₃)₂ · 6H₂O, respectively. After impregnation, the powders were dried at room temperature for 24 h and then annealed at 350°C for 3.5 h. In this way, we obtained composites containing gold (SnO₂(Au)), nickel (SnO₂(NiO)), or both dopants (SnO₂(Au, NiO)). The doping level in the powders was determined by laser ionization mass spectrometry (EMAL-2 instrument).

The phase composition of the samples was determined by X-ray diffraction (XRD) on DRON-3 (CoK_{α+β} radiation, λ = 1.7903 Å) and Rigaku D/MAX 2500 (CoK_α radiation, λ = 1.5406 Å) diffractometers. XRD peaks were identified using JCPDS data. The crys-

Table 1. Maximum permissible NO₂ concentration in the air [1, 2]

Workplace		Single exposure		Daily mean	
mg/m ³	ppb	mg/m ³	ppb	mg/m ³	ppb
2	1000	0.2	100	0.04	20

tallite size D_{cr} was evaluated from the width of diffraction peaks by the Scherrer formula:

$$D_{cr} = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the physical broadening of the peak. The standard used was single-crystal sapphire.

The microstructure of the samples was examined by high-resolution transmission electron microscopy (HRTEM) on a Philips CM30 SuperTwin instrument (0.19-nm resolution). The powders were deposited on graphitized copper platelets from a dilute suspension in ethanol. To reduce the agglomerate size, we used an ultrasonically agitated bath.

The specific surface area of the synthesized materials, S , was determined by low-temperature nitrogen adsorption measurements on a Micromeritics Chemisorb 2750.

The sensing response of our samples to NO₂ was assessed from in situ dc conductance measurements on thick films. The undoped and doped tin dioxide powders were mixed with a binder (ethanolic solution of terpinol), and the resultant paste was applied to microelectronic chips which incorporated platinum electrodes and heaters. The binder was removed by heat treatment at 350°C for 3 h. Conductance measurements were made in situ in a 100-ml flow cell at a controlled gas flow rate (100 ± 0.1 ml/min). The conductance was measured in a dry synthetic air atmosphere (30 min) and then in the presence of NO₂ (30 min). To prepare gas mixtures with known NO₂ concentration, a certified gas mixture containing 20 ppm of NO₂ in nitrogen was diluted with dry synthetic air using Bronkhorst gas flow controllers. The sensing response S was determined as the ratio of the difference between the resistances in the presence of NO₂ (R) and in air (R_0) to the resistance in air:

$$S = \frac{R - R_0}{R_0}. \quad (2)$$

RESULTS AND DISCUSSION

XRD examination showed that SnO₂ (cassiterite) was present in all of the samples. In addition, the SnO₂/Au and SnO₂/Au, NiO nanocomposites contained metallic gold, Au⁰ (Fig. 1, Table 2). No nickel-containing phases were detected, presumably because of the low nickel content, the formation of a SnO₂-based solid solution, or nickel oxide segregation on the surface of crystalline SnO₂ grains and the formation of a two-dimensional structure undetectable by XRD.

The microstructure of undoped SnO₂ prepared by the procedure described here was studied earlier by transmission electron microscopy [4, 5]. SnO₂ annealed at 300°C was shown to consist of agglomerated spherical particles 3–4 nm in size.

Figure 2a is a micrograph of the SnO₂/NiO nanocomposite. The sample consists of agglomerates formed by SnO₂ particles 4.5 ± 1 nm in size. In addition, there are

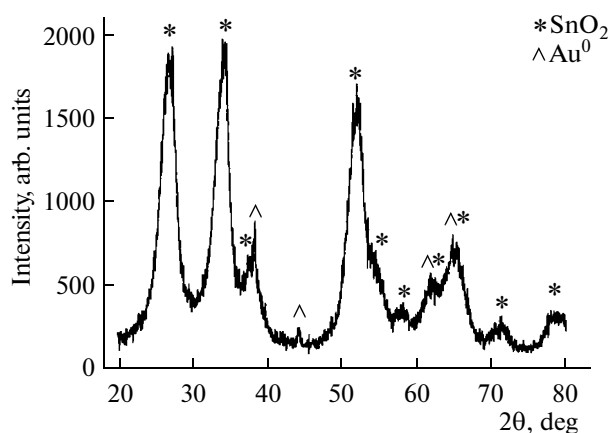


Fig. 1. XRD pattern of the SnO₂/Au, NiO nanocomposite.

nonagglomerated NiO particles 7 ± 2 nm in size, differing in contrast.

The SnO₂/Au nanocomposite consists of agglomerated SnO₂ particles and large (80–200 nm) Au⁰ particles (Fig. 2b). Tin dioxide codoped with Au and NiO contains spherical amorphous particles 5–10 nm in diameter on the surface of SnO₂ agglomerates. Their contrast in secondary electron images indicates that they consist of NiO (Fig. 2c). In addition, we observe small (1.5 ± 0.5 nm) clusters on the surface of SnO₂ particles (Fig. 2d). Their size and contrast lead us to conclude that these are Au⁰ clusters immobilized on SnO₂ surfaces. The sample was also found to contain particles of an unidentified phase, possibly a mixed oxide or a Sn_xNi_yO_z solid solution. We failed to identify this phase for lack of literature data on such compounds.

Impregnation doping reduces the specific surface S , which may be due to the additional heat-treatment step intended to decompose the salt precursors (Table 2).

In the temperature range 100 to 350°C, the presence of NO₂ increases the resistance of both undoped and doped tin dioxide (Fig. 3). This correlates with the accep-

Table 2. Phase composition and microstructural parameters of undoped and doped tin dioxide samples

Sample	Phase composition and particle size, nm		S , m ² /g
	XRD	HRTEM	
SnO ₂	SnO ₂ 3	SnO ₂ 4 ± 1	109 ± 5
SnO ₂ (NiO)	SnO ₂ 4	SnO ₂ 5 ± 1	51 ± 5
		NiO 7 ± 2	
SnO ₂ /Au	SnO ₂ 4	SnO ₂ 5 ± 1	47 ± 5
	Au 33	Au 80–200	
SnO ₂ /Au, NiO	SnO ₂ 4	SnO ₂ 5 ± 1	46 ± 5
	Au 22	Au 1.5 ± 0.5	
		50–100	
		NiO 5–10	

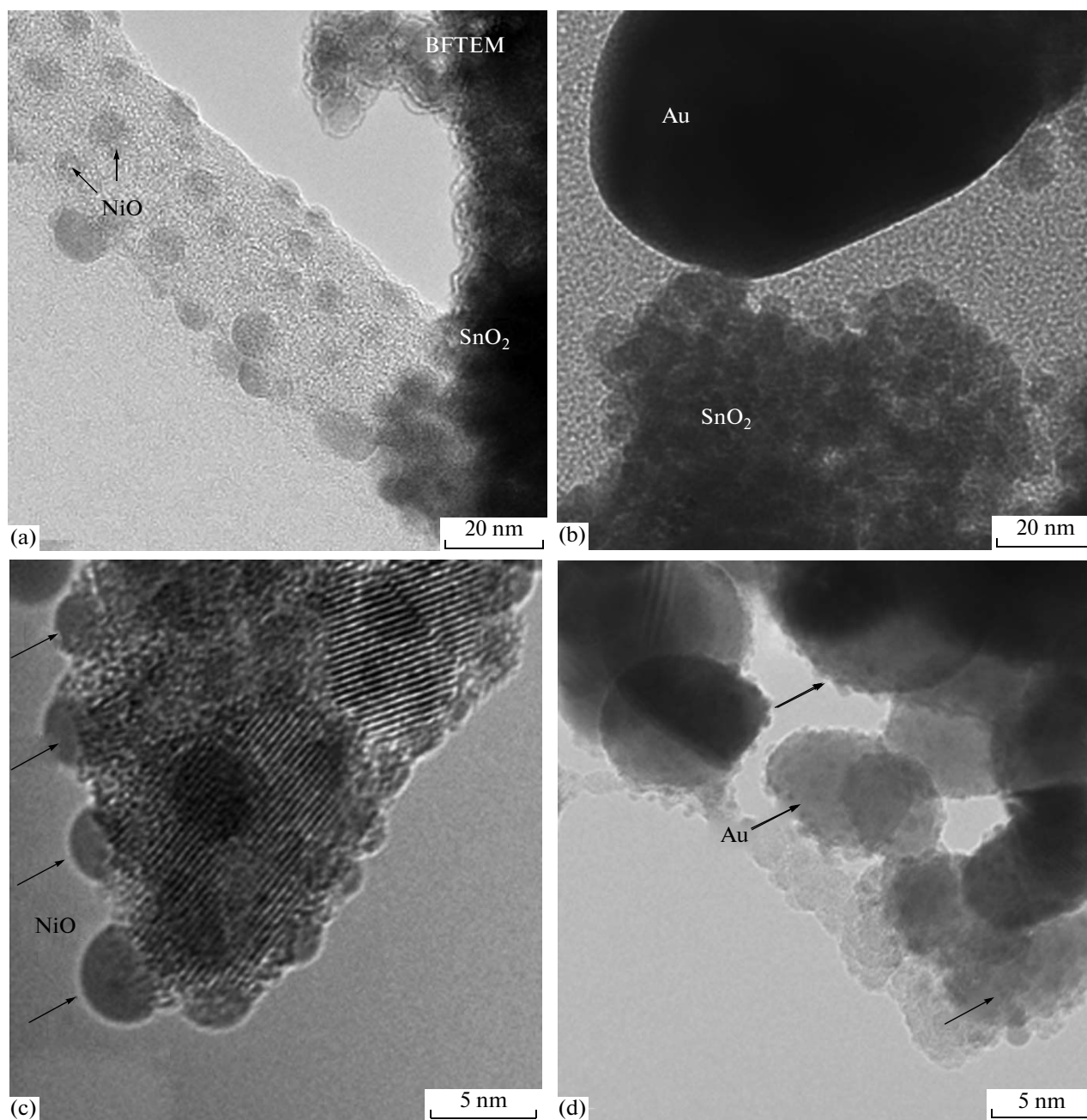


Fig. 2. HRTEM micrographs of the (a) $\text{SnO}_2\langle\text{NiO}\rangle$, (b) $\text{SnO}_2\langle\text{Au}\rangle$, and (c, d) $\text{SnO}_2\langle\text{Au, NiO}\rangle$ nanocomposites.

tor behavior of NO_2 adsorbed on the surface of an *n*-type oxide semiconductor:



where $\text{NO}_2(\text{gas})$ stands for a nitrogen dioxide molecule in the gas phase; e^- is an electron that may reach the surface, that is, possessing an energy sufficient for overcoming the barrier produced by the negatively charged surface; S is a free surface center; and $\text{NO}_2^-(\text{ads})$ is a surface nitrite ion.

Our results were used to construct the temperature dependence of the sensing response of the nanocomposites to 1000 ppb of NO_2 (Fig. 4). Doping with gold and nickel enhances the NO_2 response of SnO_2 , but these dopants influence the interaction of SnO_2 with nitrogen dioxide through different mechanisms. It is known [6] that a significant fraction of surface cations in fine-particle nickel oxide are in the oxidation state 3+. The fact that nickel doping enhances the NO_2 response of nanocrystalline tin dioxide fits well with the possibility of the $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + e^-$ transformation and electron density transfer to the oxygens of chemisorbed acceptor species.

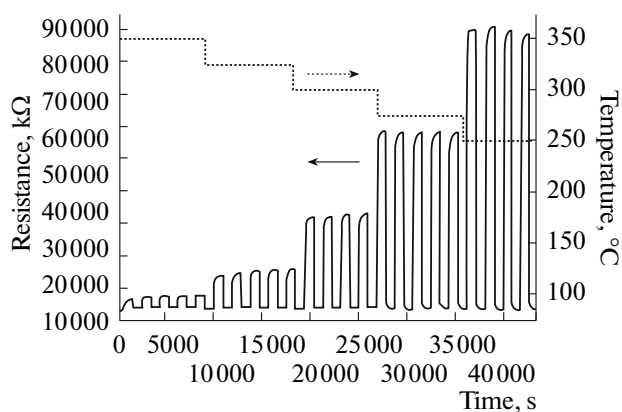


Fig. 3. Variation in the electrical conductance of the SnO₂(Au, NiO) nanocomposite in response to cyclic changes in gas phase composition (1000 ppb NO₂ in air) in the temperature range 225–350°C.

NO₂ adsorbs on gold particles without dissociation, and the heat of molecular adsorption does not exceed 71.2 kJ/mol [7]. It is reasonable to assume that, as in the case of oxygen adsorption, electron exchange between the gold particles and SnO₂ [8] promotes NO₂ adsorption, raising the nitrite ion concentration on the tin dioxide surface and markedly reducing the electrical conductance of the material.

Codoping with Au and Ni markedly enhances the sensing response and, moreover, lowers the peak response temperature. The mechanism of this synergistic effect is unclear and requires further investigation, using in situ spectroscopic characterization in NO₂-containing atmospheres. Preliminary XPS results for the Au–Ni/SiO₂ system [9] suggest that the presence of both Au⁰ and Ni²⁺ leads to partial charge removal from oxidized surface nickel atoms and increases the charge on the Au nanoparticles, as evidenced by the shift of the Au 4f level to higher binding energies. Selective adsorption on

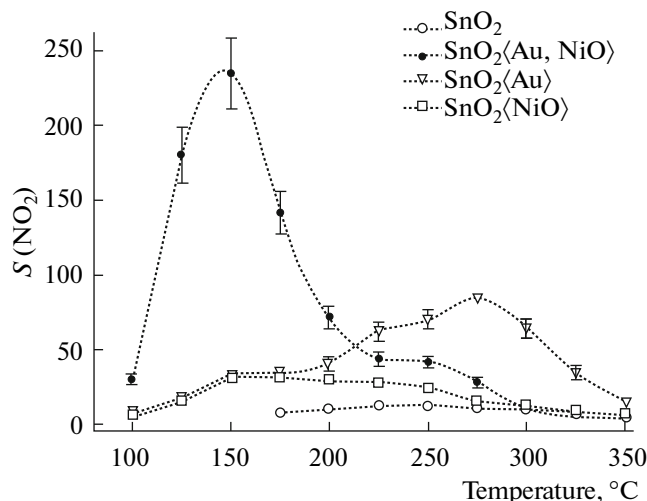


Fig. 4. Temperature dependence of the sensing response of the nanocomposites to 1000 ppb of NO₂ in air.

charged centers may have a significant effect on the electrical conductance of materials.

Figure 5 shows the sensing response of the nanocomposites as a function of NO₂ concentration in the gas phase in the range 100–1000 ppb. The measurements were performed at the peak response temperature of each material (Fig. 4). The data for the three nanocomposites are well represented by straight lines in log–log plots, indicating that the sensing response is a power-law function of NO₂ partial pressure.

It can be shown that, at a constant temperature, the electrical conductance is related to the NO₂ partial pressure in the gas phase by

$$\log \delta = \text{const} + \log \left(1 - \frac{\delta}{\delta_0} \right) - m \log p_{\text{NO}_2}, \quad (4)$$

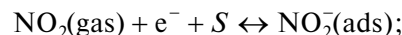
where σ is the conductance of the sample at a given NO₂ partial pressure in dry air, and σ_0 is its conductance

at $p_{\text{NO}_2} = 0$. The plots of $\log \delta - \log \left(1 - \frac{\delta}{\delta_0} \right)$ against

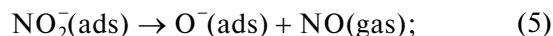
$\log p_{\text{NO}_2}$, corresponding to Eq. (4), are linear at NO₂ concentrations from 100 to 1000 ppb for the three nanocomposites (Fig. 6). The best fit m values are listed in Table 3.

To interpret the m values obtained, consider a sequence of processes (I–IV) that may take place when NO₂ adsorbs on the surface of tin dioxide in the presence of chemisorbed oxygen.

(I) Formation of surface nitrite ions (3):



(II) dissociation of the surface nitrite ions:



(III) NO₂ adsorption on the O[−](ads) chemisorbed oxygen particles formed and formation of surface nitrate ions:

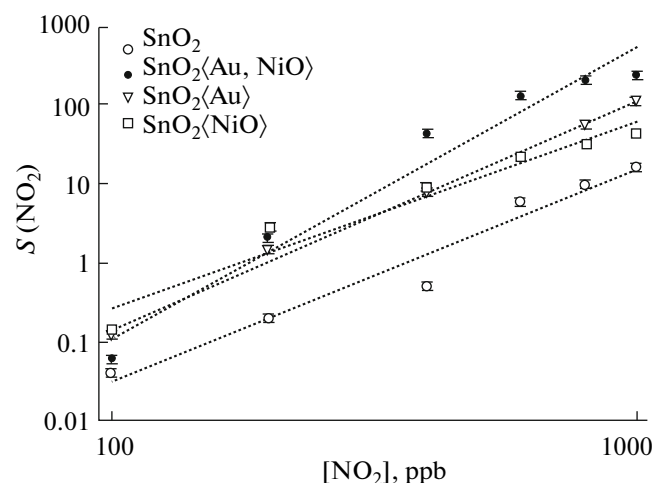
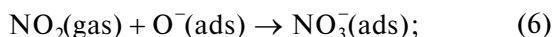


Fig. 5. Sensing response of the nanocomposites as a function of NO₂ concentration in dry air.

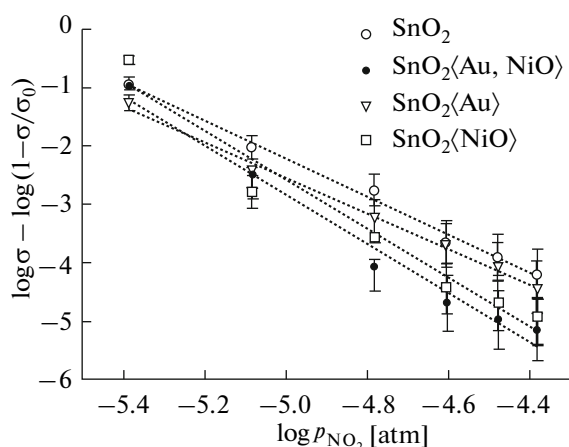
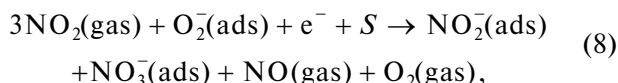


Fig. 6. Log-log plots of conductance against NO_2 partial pressure corresponding to Eq. (4).

(IV) replacement of the $\text{O}_2^-(\text{ads})$ chemisorbed oxygen by nitrite ions:



Summing up the above processes, we obtain



Therefore,

$$n_s p_{\text{NO}_2}^3 = \text{const} \frac{[\text{NO}_2^-(\text{ads})][\text{NO}_3^-(\text{ads})]p_{\text{O}_2}p_{\text{NO}}}{[\text{O}_2^-(\text{ads})]} \quad (9)$$

and

$$\log \delta = \text{const} + \log \left(1 - \frac{\delta}{\delta_0} \right) - 3 \log p_{\text{NO}_2}. \quad (10)$$

Thus, the observed effect of NO_2 concentration in dry air on the sensing response and electrical conductance of the nanocomposites is due to a sequence of processes on the SnO_2 surface upon nitrogen dioxide adsorption, which includes, in addition to reaction (3), NO_2 disproportionation [reactions (5) and (6)] and replacement of chemisorbed oxygen without changes in the number of localized electrons [reaction (7)].

The data in Table 2 leads us to assume that gold doping of tin dioxide increases the contribution of NO_2 molecular adsorption followed by nitrite ion formation. Nickel doping increases the contribution of reactions (5)–(7), which lead to the formation of nitrate ions. The m value obtained for tin dioxide codoped with gold and

nickel also attests to NO_2 dissociation and disproportionation on the surface of the nanocomposites.

CONCLUSIONS

Nanocrystalline tin dioxide and $\text{SnO}_2\langle\text{NiO}\rangle$, $\text{SnO}_2\langle\text{Au}\rangle$, and $\text{SnO}_2\langle\text{Au, NiO}\rangle$ nanocomposites were prepared by precipitation from solution followed by incipient wetness impregnation. Both gold and nickel enhance the NO_2 response of SnO_2 . Codoping with Au and NiO markedly enhances its sensing response and, in addition, lowers the peak response temperature.

The observed effect of NO_2 concentration in dry air on the sensing response of the $\text{SnO}_2\langle\text{Au, NiO}\rangle$ nanocomposite is due to a sequence of processes on the SnO_2 surface upon nitrogen dioxide adsorption, including the formation of surface nitrite ions, dissociation of the surface nitrite ions, NO_2 adsorption on $\text{O}^-(\text{ads})$ chemisorbed oxygen particles, formation of surface nitrate ions, and replacement of the $\text{O}_2^-(\text{ads})$ chemisorbed oxygen by nitrite ions without changes in the number of localized electrons.

REFERENCES

1. GN (State Standard) 2.1.6.1338-03: *Maximum Permissible Concentrations of Air Pollutants in Populated Areas*, 2003.
2. GN (State Standard) 2.2.5.1313-03: *Maximum Permissible Concentrations of Hazardous Air Pollutants in Workplaces*, 2003.
3. Zanella, R., Giorgio, S., Henry, C.R., and Louis, C., Alternative Methods for Preparation of Gold Nanoparticles Supported on TiO_2 , *J. Phys. Chem. B*, 2002, vol. 106, pp. 7634–7642.
4. Rumyantseva, M.N., Kovalenko, V.V., Gaskov, A.M., et al., Nanocomposites $\text{SnO}_2/\text{Fe}_2\text{O}_3$: Wet Chemical Synthesis and Nanostructure Characterization, *Sens. Actuators, B*, 2005, vol. 108, pp. 54–74.
5. Rumyantseva, M.N., Gaskov, A.M., Rosman, N., et al., Raman Surface Vibration Modes in Nanocrystalline SnO_2 Prepared by Wet Chemical Methods: Correlations with the Gas Sensors Performances, *Chem. Mater.*, 2005, vol. 17, pp. 893–901.
6. Bielanski, A. and Haber, J., Oxygen in Catalysis on Transition Metal Oxides, *Catal. Rev.—Sci. Eng.*, 1979, vol. 9, pp. 1–41.
7. Wickham, D.T., Banse, B.A., and Koel, B.E., Adsorption of Nitrogen Dioxide on Polycrystalline Gold, *Catal. Lett.*, 1990, vol. 6, pp. 163–172.
8. Montmeat, P., Marchand, J.-C., Lalauze, R., et al., Physico-Chemical Contribution of Gold Metallic Particles to the Action of Oxygen on Tin Dioxide Sensors, *Sens. Actuators, B*, 2003, vol. 95, pp. 83–89.
9. Nikolaev, S.A., Vasil'kov, A.Yu., Smirnov, V.V., and Tyurina, L.A., Catalytic Activity of Gold-Containing Nanoclusters in Carbon Tetrachloride Addition to Multiple Bonds, *Kinet. Katal.*, 2005, vol. 46, no. 6, pp. 915–920.

Table 3. Calculated coefficient m in Eq. (4) for undoped and doped tin dioxide samples

Sample	m
SnO_2	3.3 ± 0.1
$\text{SnO}_2\langle\text{NiO}\rangle$	4.2 ± 0.5
$\text{SnO}_2\langle\text{Au}\rangle$	3.1 ± 0.1
$\text{SnO}_2\langle\text{Au, NiO}\rangle$	4.3 ± 0.3