ADVANCES IN CHEMICAL PHYSICS, 2025, Vol. 44, No. 1, pp. 78–82

CHEMICAL PHYSICS OF NANOMATERIALS

STRUCTURE, CONDUCTIVITY AND SENSOR PROPERTIES OF NiO–In_2O_3 COMPOSITES SYNTHESIS BY DIFFERENT METHODS

© 2025 M. I. Ikim[a]*, A. R. Erofeeva[a], E. Y. Spiridonova[a], B. F. Gromov[a], G. N. Gerasimov[a], and L. I. Trakhtenberg[a, b]

[a] *Semenov Federal Research Center of Chemical Physics, Russian Academy of Sciences, Moscow, Russia*

[b] *Lomonosov Moscow State University, Moscow, Russia*

**e-mail: ikimmary1104@gmail.com*

Received November 03, 2023

Revised November 15, 2023

Accepted November 20, 2023

Abstract. The effect of the synthesis method of NiO–In_2O_3 composites on their structural, conductive and sensory characteristics when detecting hydrogen was studied. Impregnation of indium oxide nanoparticles with a nickel nitrate salt and a hydrothermal method with aqueous solutions of the corresponding salts were used. It has been shown that during the impregnation process, nickel oxide is formed in the form of amorphous nanoparticles on the surface of indium oxide, and during hydrothermal treatment, nickel ions are introduced into In_2O_3 structures. In impregnated composites, the particle size of indium oxide does not depend on the composition and is 60 nm, while in hydrothermal composites it decreases from 35 to 30 nm with increasing nickel content. With an increase in nickel content from 0 to 3 wt.% for both synthesis methods, the conductivity decreases, and the resistance for hydrothermal samples is an order of magnitude higher than for impregnated ones. The sensory response was almost twice as high.

Keywords: *composite, hydrothermal method, impregnation method, indium oxide, conductivity, sensory response, hydrogen*

DOI: 10.31857/S0207401X250110e7

1. INTRODUCTION

The continuous growth of toxic and explosive gas emissions into the atmosphere leads to the need to develop sensors for their detection. Semiconductor sensors are of interest due to their commercial availability, ease of fabrication, good stability and prospects for modernization. The n-type metal oxides In_2O_3, ZnO, SnO_2, CeO_2 have been widely used in gas detection systems (see, for example, [1–4]). In binary sensors, the use of In_2O_3 is associated with a high concentration of electrons in the conduction zone [5–8].

Indium oxide crystallizes in two polymorphic modifications: cubic and rhombohedral, the properties of which affect the conductive and sensory characteristics. The conductivity of the rhombohedral phase of indium oxide is 8–12 times higher and the sensory response 1.5–2 times higher than that of its cubic phase [6]. Addition of catalytically active oxide to indium oxide leads to increased sensitivity in detection of various gaseous substances [9]. Doping In_2O_3 with ions of different valence also improves selectivity and sensitivity in the detection of hazardous gases [4].

One of the most promising *p*-type semiconductors as an additive for gas sensors is nickel oxide due to its chemical and thermal stability and high catalytic activity. Such an additive helps to reduce the operating temperature and response/recovery time [10]. The doping of indium oxide with 5 mol% NiO contributes to increase in the sensory response compared to pure In_2O_3 for the detection of 200 ppm CH_4 at a relatively low operating temperature [11]. The incorporation of 2 mol% Ni into In_2O_3 leads to a 12-fold increase in the response to 10 ppm NO_2compared to pure In_2O_3, at an operating temperature of 200 °C [12]. In addition, the sensor showed a low detection limit of 5 ppb of nitric oxide.

In this work, the influence of the synthesis method on the structural characteristics, conductivity, and sensory properties of layers based on nanoscale NiO-In_2O_3 composites for hydrogen detection in a wide temperature range was investigated. The composites were prepared by impregnation of indium oxide nanopowder with nickel nitrate salt with its subsequent transformation into oxide and by hydrothermal method using nitrate aqueous solutions of nickel and indium.

2. EXPERIMENTAL PART

NiO-In_2O_3 composites containing 0 to 3 wt.% nickel oxide were synthesized by two methods: hydrothermal [13] and impregnation [14]. Commercial In_2O_3 powder (AnalaR grade, 99.5%, BDH/Merck Ltd., Lutterworth, Leicestershire, UK) and chemically pure (CP) nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (GOST 5106–77) were used to obtain impregnated composites. Indium oxide powder was placed in an aqueous solution of nickel nitrate and incubated at room temperature for 24–48 hours. Further removal of water was carried out at a temperature of about 70–80 °C, then heated the samples for several hours to 500 °C to obtain impregnated composites.

Indium nitrate $In(NO_3)_3 \cdot 4H2O$ ($\geqslant$99.5%) and nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ ($\geqslant$99%) were used as precursors for hydrothermal synthesis. To obtain indium oxide, 2 mmol of indium nitrate and 18 mmol of urea were dissolved in 80 mL of distilled water. To form the composites, the required amounts of nickel nitrate were added to the above composition. The synthesized solutions were incubated in an ultrasonic bath for 1 hour at 30 °C. Then they were placed in a 100 mL Teflon-coated autoclave for hydrothermal treatment for 3 hours at 160 °C. The resulting hydroxides were separated by centrifugation for 5 min at 4500 rpm and then washed with distilled water and annealed in air at 500 °C.

The phase composition, structure and morphology of the obtained composites were studied by X-ray diffraction (XRD) on a Rigaku Smartlab SE diffractometer using Cu($K\alpha$)-radiation with a wavelength of 1.5406 Å and transmission electron microscopy (TEM) on a Tecnai Osiris FEI instrument equipped with an energy dispersive analysis system.

To determine the conductivity and sensory properties, the synthesized composites were mixed with distilled water, and the resulting paste was applied to a special chip equipped with a heater and contacts. Further, the temperature was gradually increased up to 550 °C until a constant resistance of the obtained film was achieved.

The sensor response to H_2 was investigated using the developed setup in the temperature range from 300 to 550 °C. The chip with the applied sensing layer was placed in a special chamber with a volume of about 1 cm^3, into which purified air or a gas mixture containing 0.9% H_2 was supplied. The pumping rate of gases through the chamber was 200 ml/min, and the accuracy of temperature maintenance was within 1 °C. The response was defined as $S = R_0/R_g$, where R_0 is the initial sensor resistance (before the analyzed mixture was introduced) and R_g is the minimum value of the sensor resistance after the analyzed gas was introduced. The change in sensor resistance was recorded using a Keysight digital multimeter, the signal from which was transmitted to a computer.

3. DISCUSSION OF RESULTS

The data of X-ray phase analysis showed that regardless of the synthesis technique, when adding different concentrations of NiO to the composite, only peaks corresponding to the cubic phase of indium oxide with preferential orientation (222) are registered. The absence of nickel or its compounds may be due to the dissolution of nickel ions in the In_2O_3 lattice, the formation of an X-ray amorphous phase, or a small amount of Ni O.

With increasing nickel content in composites synthesized by the hydrothermal method, there is a shift of the diffraction angle towards higher values, while in impregnated composites the shift of peaks is insignificant. The ionic radius of Ni^{2+} is 0.75 Å, which is smaller than this value for In^{3+} – 0.81 Å. Consequently, the introduction of nickel ions into the In_2O_3 crystal lattice leads to a shift of the diffraction peaks of indium oxide towards larger angles.

As NiO is introduced into the composites obtained by the hydrothermal method, the lattice parameter decreases due to the difference in ionic radii, while in impregnated samples the lattice parameter is practically independent of the nickel oxide content in the composite (Fig. 1a). That is it can be assumed that for hydrothermal samples nickel is embedded in the structure of indium oxide, and in impregnated samples X-ray amorphous nickel oxide is formed on the surface of In_2O_3.

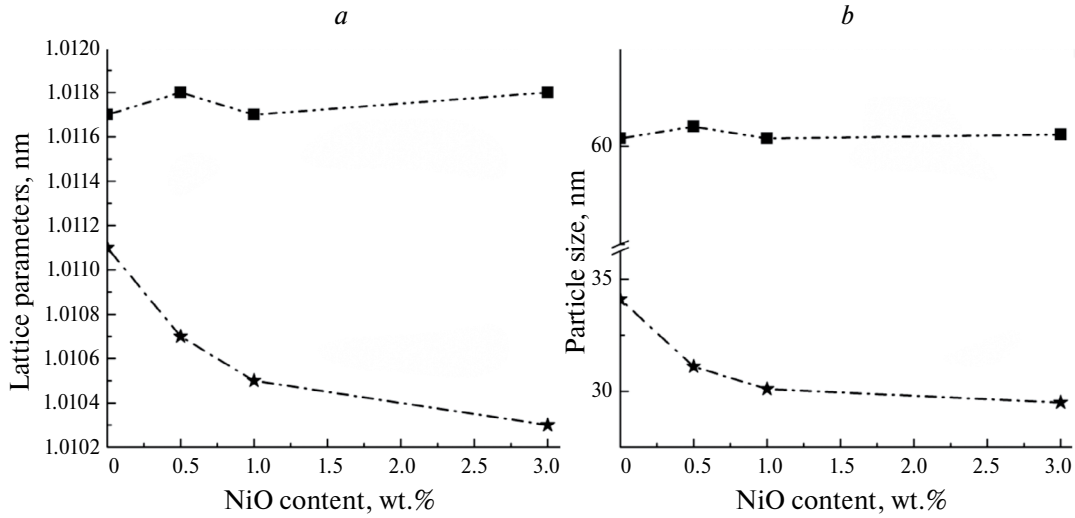

Fig. 1. Dependence of lattice parameter (*a*) and particle size (*b*) of In_2O_3 on NiO content in composites obtained by different methods

The particle sizes were calculated from X-ray phase analysis data, using the Debye-Scherrer equation by the peak width at its half-height and amounted to about 60 nm in the case of impregnated samples and 35–30 nm for composites obtained by the hydrothermal method (Fig. 1b). The increase in the concentration of nickel oxide in hydrothermal composites is accompanied by a decrease in the particle size from 35 to 30 nm, which is associated with the occurrence of deformation due to indium substitution in the crystal lattice. The introduction of nickel ions into the In_2O_3 structure prevents crystal growth. In the case of impregnated samples, unlike hydrothermal samples, the addition of nickel oxide does not significantly affect the particle size (Fig. 1b).

According to TEM data of impregnated NiO-In_2O_3 nanocomposites, spherical particles up to 20 nm are formed on the porous surface of indium oxide (particle size up to 100 nm) after impregnation with nickel nitrate and further heat treatment. In the case of hydrothermal samples, the particles have a cubic shape with a size of about 30 nm, which agrees with the XRD data. The results of energy dispersive analysis showed that in the hydrothermal composites, nickel ions are uniformly distributed in the indium oxide particles. While in impregnated composites, particles containing only nickel ions are observed on the surface of indium oxide. At the same time, some amount of nickel is distributed in the surface layer of indium oxide particles. The data of TEM, energy dispersive and X-ray diffraction analyses are in good agreement with each other.

For NiO-In_2O_3 composites obtained by impregnation and hydrothermal method, conductivity and sensory properties were investigated in the temperature range from 300 to 550 °C. Regardless of the synthesis method, an increase in conductivity with increasing temperature was observed, which is characteristic of *n-type* semiconductors. The dependence of resistance on nickel content for impregnated and hydrothermal composites is shown in Fig. 2a. It can be seen that the resistivity increases with increasing nickel content for both synthesis methods.

Since the electron yield work of NiO (5.5 eV) is larger than that of In_2O_3 (4.3 eV), electron transfer occurs from nanoparticles In_2O_3 to NiO nanoparticles, which leads to an increase in the resistance of composites due to a decrease in the concentration of electrons in the well-conducting indium oxide particles. During the hydrothermal synthesis process, nickel ions (Ni^{2+}) are introduced into the In_2O_3lattice, replacing In^{3+}) ions. Simultaneously, positively charged oxygen vacancies V^{+}_{O} are formed, which provides a balance of positive and negative charges during substitution. A similar process was observed during the formation of hydrothermal composites ZnO-In_2O_3 containing up to 20 wt.% of zinc oxide [15].

Note that the resistance of hydrothermal samples is an order of magnitude higher than impregnated composites. This may be due to the fact that the number of In^{3+} ions substituted by Ni^{2+} ions during hydrothermal synthesis of composites is greater than during impregnation, when the composite

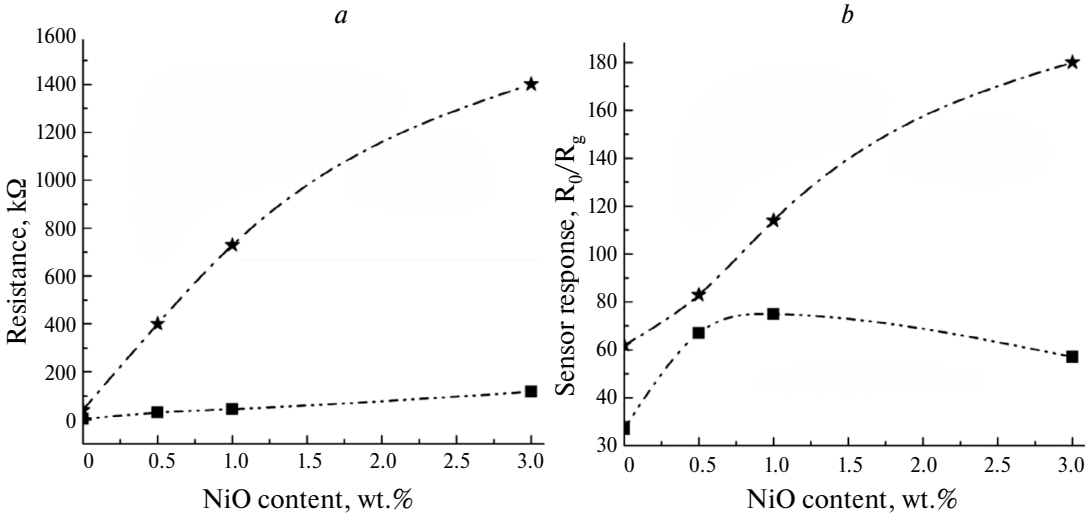

Fig. 2. Concentration dependence of resistance (*a*) and sensory response in detection of 0.9% H_2 (*b*) composites prepared by different methods

formation is concentrated mainly in the surface layers of nanocrystals.

In NiO – In_2O_3 composites, regardless of the method of their synthesis, the temperature dependence of the sensor response has a typical for semiconductor sensors curve with a maximum S_{max} at certain temperature T_{max}. Increasing the content of nickel oxide leads to a decrease in the operating temperature in hydrothermal samples by 60 °C, and in impregnated samples by 20 °C. This decrease may be due to the high catalytic activity of Ni O. For example, the operating temperature of composites obtained by solvothermal method was reduced by 60 °C in methane detection [16]. The sensory response of hydrothermal composites at hydrogen detection for all compositions is almost two times higher than that of the samples obtained by the impregnation method (Fig. 2b). The reason for this may be the small size of indium oxide nanoparticles, as the bond strength in their lattice is weakened, which leads to a significant decrease in the vacancy formation energy. The increase in the concentration of oxygen vacancies, which are the centers of chemisorption of oxygen and analyzed gas, contributes to the increase in the sensory activity of hydrothermal composites.

The method of synthesis of NiO-In_2O_3 composites significantly affects the character of change of their sensory response depending on the concentration of nickel oxide (Fig. 2b). For impregnated samples a maximum is observed at 1% NiO, further introduction of nickel oxide into the composite leads to a slight drop in the sensory response in contrast to hydrothermal composites where 3% NiO causes a sharp increase in sensory sensitivity. This is due to the interaction between the components: in hydrothermal composites, nickel ions are embedded in the lattice of indium oxide, while in composites synthesized by impregnation, nickel oxide nanoparticles are formed on the surface of In_2O_3 nanoparticles [17].

4. CONCLUSION

Studies of properties of NiO – In_2O_3 composites demonstrate a significant influence of the method of their synthesis on structural characteristics, conductivity and sensitivity at hydrogen detection. In the case of sample synthesis by impregnation method, X-ray amorphous NiO is formed on the surface of large indium oxide particles of the order of 60 nm. The formation of nickel oxide nanoparticles does not lead to a change in the structural characteristics and particle size of indium oxide. On the contrary, in hydrothermal samples nickel ions are uniformly distributed over the volume of In_2O_3 nanoparticles, the size of which decreases from 35 to 30 nm with increasing nickel concentration.

The conductivity of the samples, regardless of the method of synthesis, monotonically decreases with increasing concentration of nickel oxide in the composite. This change in the case of impregnated samples is associated with electron transfer between nanoparticles forming the composite, and in hydrothermal samples by modification of the electronic structure of In_2O_3. At the same time, the values of resistance and sensory response

to hydrogen of hydrothermal composites at all nickel concentrations are higher than those of impregnated ones.

The detailed study of the properties of NiO-In_2O_3 composites performed in this work indicates the essential role of the interaction between the metal-oxide components, which will allow further consideration of the mechanisms of such interaction in the sensing process.

FUNDING

The research was supported by the Russian Science Foundation grant No. 22–19–00037; https://rscf.ru/project/22–19–00037/.

REFERENCES

1. *Li Q., Zeng W., Li Y.* // Sens. Actuators B. 2022. Vol. 359. P. 131579.
2. *Zhang C., Xu K., Liu K., Xu J., Zheng Z.* // Coord. Chem. Rev. 2022. Vol. 472. P. 214758.
3. *Krishna K. G., Parne S., Pothukanuri N., Kathirvelu V., Gandi S., Joshi D.* // Sens. Actuators A. 2022. Vol. 341. P. 113578
4. *Trakhtenberg L. I., Ikim M. I., Ilegbusi O. J., Gromov V. F., Gerasimov G. N.* // Chemosens. 2023. Vol. 11(6). P. 320.
5. *Yan S., Song W., Wu D., Jin S., Dong S., Hao H., Gao W.* // J. *Alloys Compd*. Alloys Compd. 2022. Vol. 896. P. 162887.
6. *Ikim M. I., Spiridonova E. Yu., Gromov V. F., Gerasimov G. N., Trakhtenberg L. I.* // Chemical Physics. 2023. Vol. 42. No. 5. P. 71.
7. *Jimenez L. C., Mendez H. A., Paez B. A., Ramırez M. E., Rodrıguez H.* // Braz. J. Phys. 2006. Vol. 36. P. 1017.
8. *Prathap P., Gowri D. G., Subbaiah Y. P. V., Ramakrishna R. K. T., Ganesan V.* // Current Appl. Phys. Phys. 2008. Vol. 8. P. 120
9. *Gerasimov G. N., Gromov V. F., Ikim M. I., Trakhtenberg L. I.* // Chemical Physics. 2021. Vol. 40. No. 11. P. 65.
10. *Fan X., Xu Y., He, W.* // RSC advances. 2021. Vol. 11(19). P. 11215.
11. *Zhang Y., Cao J., Wang Y.* // Vacuum. 2022. Vol. 202. P. 111149.
12. *Jin Z., Wang C., Wu L., Song H., Yao X., Liu J., Wang F.* // Sens. Actuators B. 2023. Vol. 377. P. 133058.
13. *Ikim M. I., Spiridonova E. Yu., Gromov V. F., Gerasimov G. N., Trakhtenberg L. I.* // Chemical Physics. 2022. Vol. 41. No. 12. P. 79.
14. *Gromov V. F., Ikim M. I., Gerasimov G. N., Trakhtenberg L. I.* // Chemical Physics. 2021. Vol. 40. No. 12. P. 76.
15. *Ikim M. I., Spiridonova E. Yu., Gromov V. F., Gerasimov G. N., Trakhtenberg L. I.* // Russ. J. Phys. Chem. Vol. 18, 283 (2024).
16. *Wang Y., Yao M., Guan R., Zhang Z., Cao J.* // J. Alloys Compd. Alloys Compd. 2021. Vol. 854. P. 157169.
17. *Ikim M. I., Gromov V. F., Gerasimov G. N., Spiridonova E. Y., Erofeeva A. R., Kurmangaleev K. S., Polunin K. S., Ilegbusi O. J., Trakhtenberg L. I.* // Micromachines. 2023. Vol. 14(9). P. 1685.