Nanomaterial based on SnO_2 with Co and Sb additives - perspective material for H_2 semiconductor sensors

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Idea

Nowadays hydrogen is the most promising energy source, but at the same time H_2 can form very explosive mixture with air. Development of highly gas sensitive devices for hydrogen detection is an actual task for determination of H_2 presence in air during its using, transportation and storage. Adsorption-semiconductor sensors based on nanosized $Co/SnO_2/Sb_2O_5$ materials can be used as sensitive elements of such devices. Semiconductor sensors based on metal oxides are widely used to determine the presence of toxic and explosive gases in the ambient air. The principle of the sensor operation is based on a change of its electrical resistance in the presence of the analyzed gas. Chemical composition of the sensor sensitive layer and its morphology significantly affect the electronic processes that determine the sensitivities of the sensors to the gas. The use of the nanomaterials as gas sensitive layers of the sensors is promising for increasing the sensitivities of the sensors. Development of new nanosized materials for the sensitive layers of the sensors is necessary to increase their H_2 responses that is an actual task nowadays. Besides, significant increasing the responses of the sensors can be also achieved by introduction of catalytic active additives to the gas sensitive material of the sensor. It is known that Co_3O_4 is a promising for this goal because it is a very active catalyst of H_2 oxidation reaction.

The aim of the work was to obtain sensor materials based on $Co/SnO_2/Sb_2O_5$ by sol-gel method and by the method of co-precipitation, study their morphology, catalytic and gas sensitive properties and compare them with each other.

Preparation of microcrystalline material

Microcrystalline tin dioxide was obtained by the method of co-precipitation of hydroxides of tin and stibium obtained from their chlorides. Then hydroxides were sintered at 1000 °C. Obtained oxides were grinded.

Preparation of nanomaterials

Nanosized tin dioxide was obtained by a sol-gel method using $SnCl_4 \cdot 5H_2O$ as a precursor and ethylene glycol as a solvent

I - formation of $SnCl_4$ gel in ethylene glycol at 80 °C; evaporation of ethylene glycol; formation of a xerogel at 150 °C.
II – sintering of the xerogel at 600 °C

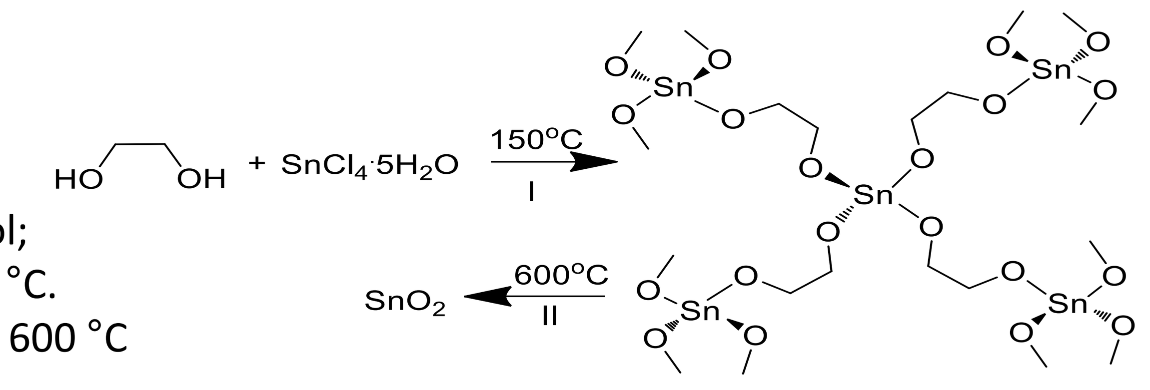

Fig.1. Scheme of SnO_2 synthesis

The materials with different Co contents were obtained on the base of the nanosized and microcrystalline tin dioxide by its impregnation with $CoCl_2$ solutions of different concentrations ($0,8\times10^{-2}$-25×10^{-2} mol/L).

Morphology of the obtained nanomaterials

The morphology of the resulting oxide materials was studied via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was established by SEM method that particle size of microcrystalline materials ranges from 1 to 30 µm (Fig 2a). It was found by TEM method that particle size of $Co/SnO_2/Sb_2O_5$ nanomaterial ranges from 5 to 25 nm; the average particle size is 12 nm (Fig.2b).

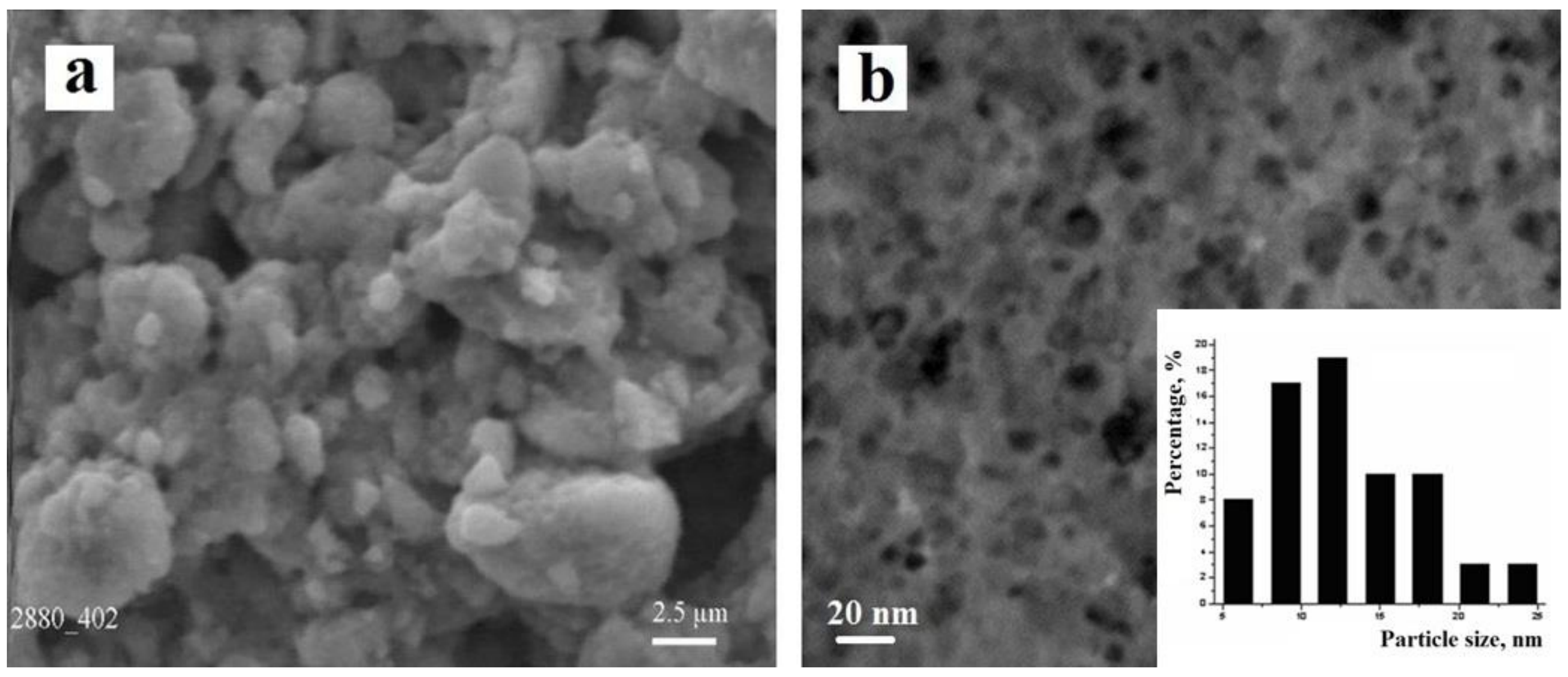

Fig.2. SEM image of microsrystalline material $Co/SnO_2/Sb_2O_5$ (a), TEM image and histogram of the size distribution of nanomaterial $Co/SnO_2/Sb_2O_5$ particles (b). ($C(CoCl_2 = 3.2\cdot10^{-2}$ mol·l^{-1}).

Structure characteristic of $Co/SnO_2/Sb_2O_5$ materials

It was found by the XRD that the both types of synthesized materials appears to be the tetragonal modification of SnO_2–cassiterite with the corresponding values of the lattice: a = 0.476 nm, c = 0.3164 nm.

Sensor preparation

To create the sensor each of the both material powders was mixed with colloid solution of carboxymethyl cellulose to form a creamy-like paste. This paste was applied on a ceramic plate of the sensor between the measuring electrodes side (fig.3). The plate with the gas-sensitive layer was dried in air at ambient temperature then heated in an oven at 90^{0}C and calcined in the temperature interval 20–620^{0}C.

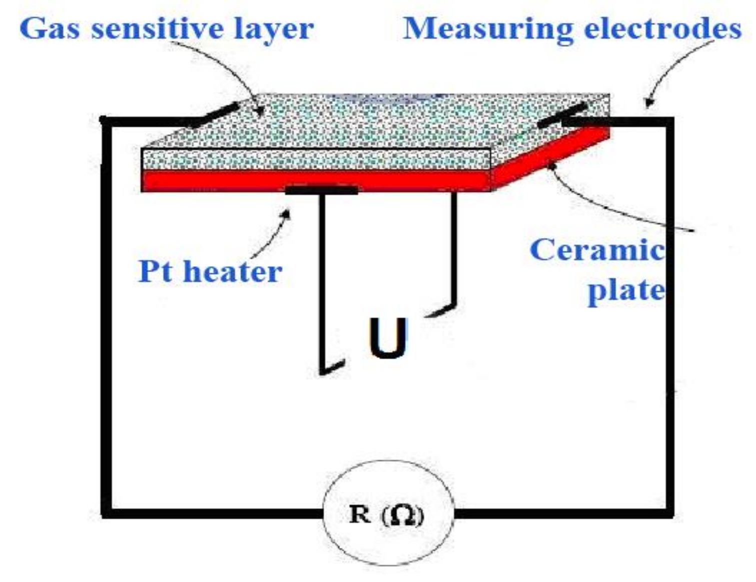

Fig. 3. Schematic structure of adsorption-semiconductor sensor

Sensor gas sensitive properties

As a measure of the sensitivity of the sensor (sensor response) was taken a ratio of the electric resistance of the sensor in air $\mathbf{R_0}$ to the electric sensor resistance in a hydrogen–air mixture (40 ppm H_2) $\mathbf{R_{H2}}$

$$\gamma = R_0/R_{H_2}$$

It was found that the sensor based on Co-containing nanomaterial was more sensitive to H_2. The response of the sensor based on the nanosized material was equal to 13.9 in the presence of 500 ppm H_2. Elecrical resistance of the sensor created on the base of microcrystalline material had changed in 6.2 times. (Fig.4a,b).

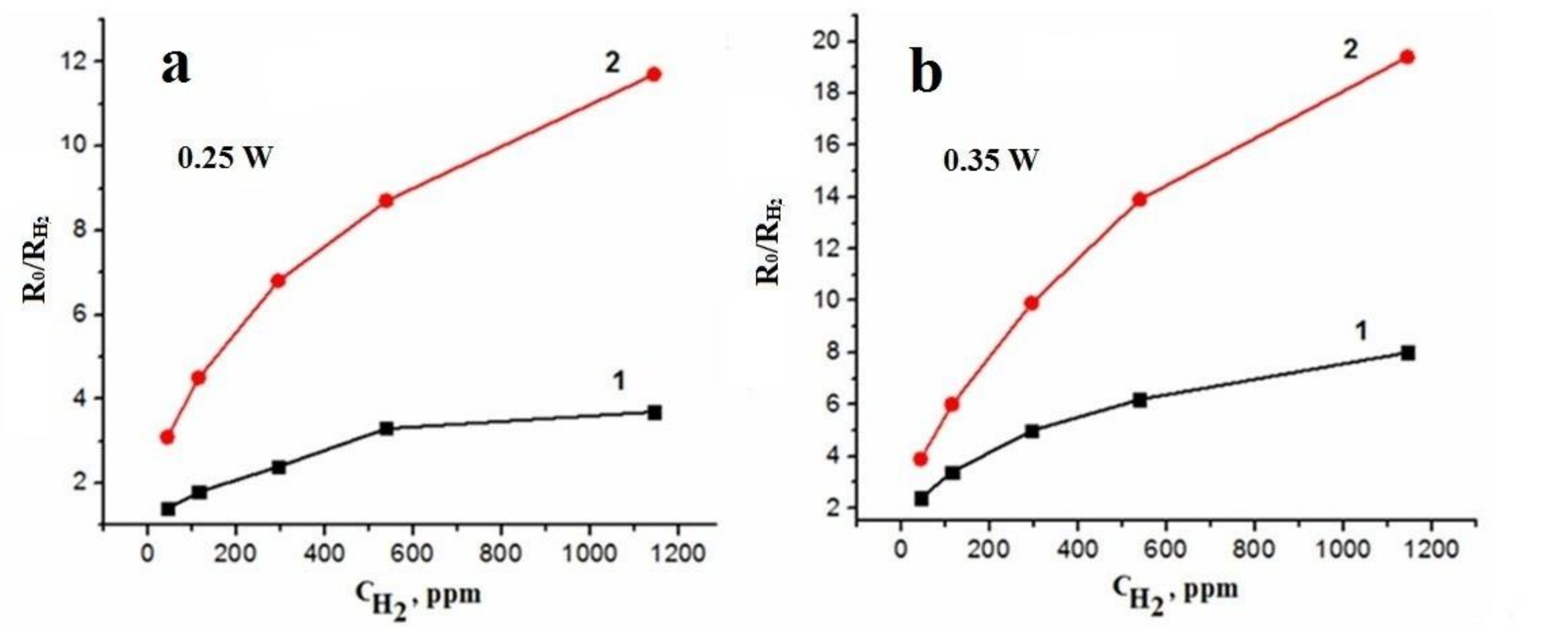

Fig.4. Dependence of sensor response (R_0/R_{H2}) on hydrogen concentration (ppm) at sensor heater power consumption 0.25 W (a) and 0.35 W (b): 1 – sensor based on microcrystalline SnO_2/Sb_2O_5 obtained by coprecipitation; 2 – sensor based on nanosized SnO_2/Sb_2O_5 obtained by sol-gel method. ($C(CoCl_2 = 3.2\cdot10^{-2}$ mol·l^{-1}).

Dynamic properties

Dynamic characteristics of the sensors were characterized by two parameters: a response time of the sensor ($t_{0,9}$) – the time when the value of the sensor signal reaches 90% of its maximum steady value when air environment is replaced by the analyzed gas; a relaxation time (τ_{rel}) – time when the value of the sensor signal returns to 10% of its initial value when the analyzed gas is replaced by air. As can be seen, the dynamic properties of the sensors based on nanosized $Co/SnO_2/Sb_2O_5$ are better at both values of the sensor heater power consumption. (Table 1)

Table 1. Dynamic properties of the sensors based on microcrystalline and nanosized $Co/SnO_2/Sb_2O_5$ in an atmosphere of 40 ppm H_2 in air at different heater power consumption. ($C(CoCl_2 = 3.2\cdot10^{-2}$ mol·l^{-1}).

Microcrystalline $Co/SnO_2/Sb_2O_5$		Nanosized $Co/SnO_2/Sb_2O_5$	
$t_{0.9}$, s	τ_{rel}, s	$t_{0.9}$, s	τ_{rel}, s
Heater power consumption, N = 0.25 W			
24	60	14	43
Heater power consumption, N = 0.35 W			
4	35	2.5	21

Summary:

The influence of cobalt additives on the properties of the sensors based on microcrystalline and nanosized $Co/SnO_2/Sb_2O_5$ materials was studied. It is shown that addition of cobalt oxide leads to increase the response of the sensors based on this both materials to hydrogen. The sensor obtained by precipitation of $3.2\cdot10^{-2}$ mol·l^{-1} $CoCl_2$ solution was found to be the most sensitive for H_2 measurement. The obtained Co-containing sensors based on the nanosized material $Co/SnO_2/Sb_2O_5$ show higher sensor responses to micro-concentration of H_2 (40 ppm) and almost twice smaller response time compared to the sensors based on the corresponding microcrystalline materials.