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Nanosized tin dioxide based semiconductor materials for creation of gas sensors

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Actuallity: *Nowadays the synthesis of new oxide nanosized materials is relevant in the creation of high sensitive sensors for detection of toxic and explosive gases in air. Tin dioxide due to its chemical stability remains the most popular among oxide semiconductor materials [1]. Adsorption semiconductor sensors based on oxides in the gas sensitive layers are extensively used in gas analysis. An increase in the sensitivity of the semiconductor gas sensors based on tin dioxide can be achieved both by introducing catalytically active additives into the materials of the gas sensitive layers of the sensors [2], and by reducing the sizes of the particles of the nanomaterials [3].*

The goal of this work to *synthesize a nanosized tin dioxide and investigate it as a material of gas sensitive layer of the sensor.*

Nanosized tin dioxide for gas sensing materials

Nanosized tin dioxide was obtained by a sol-gel method using in oxalate and a 35% solution of hydrogen peroxide in water as precursors. After 2 h stirring the precursors, the resulting sol was quickly heated to decompose excess H_2O_2 and evaporate water. As a result, a transparent water-based gel was obtained, which was dried at 90 ^oC for 24 hours before turning into translucent xerogel. To obtain initial nanosized SnO_2, the xerogel was calcinated in temperature range of 20–600°C.

Nanosized SnO_2-based sensor materials have been prepared from the pastes with different quantities of SnO_2 and carboxymethylcellulose (CMC) [50 мас.% SnO_2 – 50 мас.% КМЦ (50% SnO_2), 60 мас.% SnO_2 – 40 мас.% КМЦ (60% SnO_2), 70 мас.% SnO_2 –30 мас.% КМЦ (70% SnO_2)] and formatted in air up to 620 C during 7 hours. The obtained materials were used for creating planar semiconductor sensors with a size of 2.2 x 2.2 x 0.5 mm, the design of the sensor was shown in Fig.1.

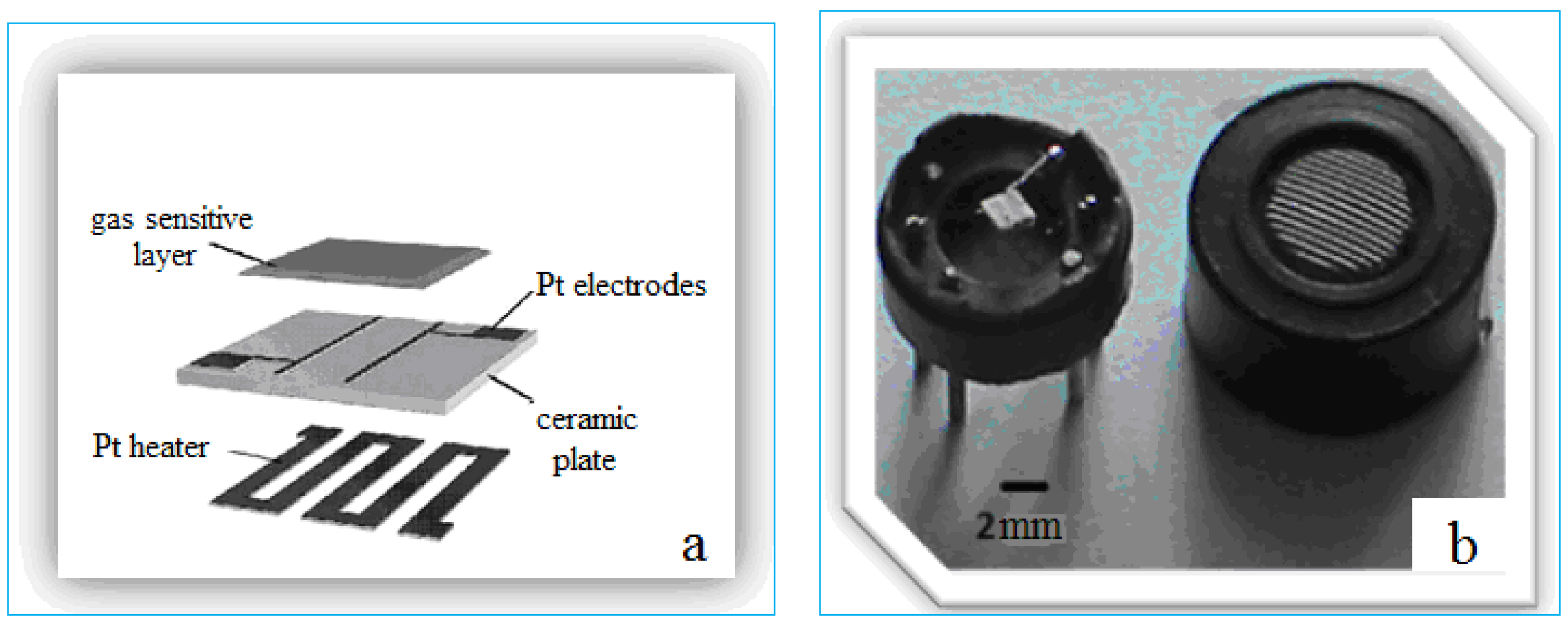

Fig.1. Schematic construction of the sensor (a) and its view in the sensor's camera (b).

The calculation of the particle sizes of these materials showed that with an increase in the heating temperature of the xerogel, the particle sizes of nanosized SnO_2 increase from 4.8 to 12.1 nm and the specific surface area (S_{sp}) decreases from 110 to 37 m^2/g (Table 1). An increase in the duration of heating also leads to a decrease in the specific surface area of nanomaterials.

Table 1

Sizes of the particles calculated by Sherrer equation and specific area of the SnO_2-based nanomaterials

Sample	*Conditions of the nanomaterial formation*		*Particle size, nm*	*S_{sp}, m^2/g*
	T, °C	*Time of the isothermal treating*		
SnO_2	*400*	*1 hour 20 min*	*4.8*	
SnO_2	*400*	*2 hours 20 min*	*5.3*	*110*
SnO_2	*450*	*1 hour 20 min*	*6.5*	*85*
SnO_2	*500*	*1 hour 20 min*	*8.3*	*60*
SnO_2	*550*	*1 hour 20 min*	*9.9*	*48*
SnO_2	*600*	*1 hour 20 min*	*12.1*	*37*

The TEM study of the material obtained by heating the xerogel at 400 ^0C for 2 h 20 min showed that it contains individual nanoparticles, the average size of which is 5 - 6 nm (Fig. 2, a). The presence of nanosized particles is confirmed by the ring electronogram (insert in Fig. 2, a). It was established that the composition of the paste with different content of tin dioxide (50% - 70% SnO_2) practically does not change the specific surface area of nanomaterials (34-39 m^2/g). Decrease in the specific surface area of sensor materials is associated with the increasing and aggregation of their particles according to TEM (Fig.2, b).

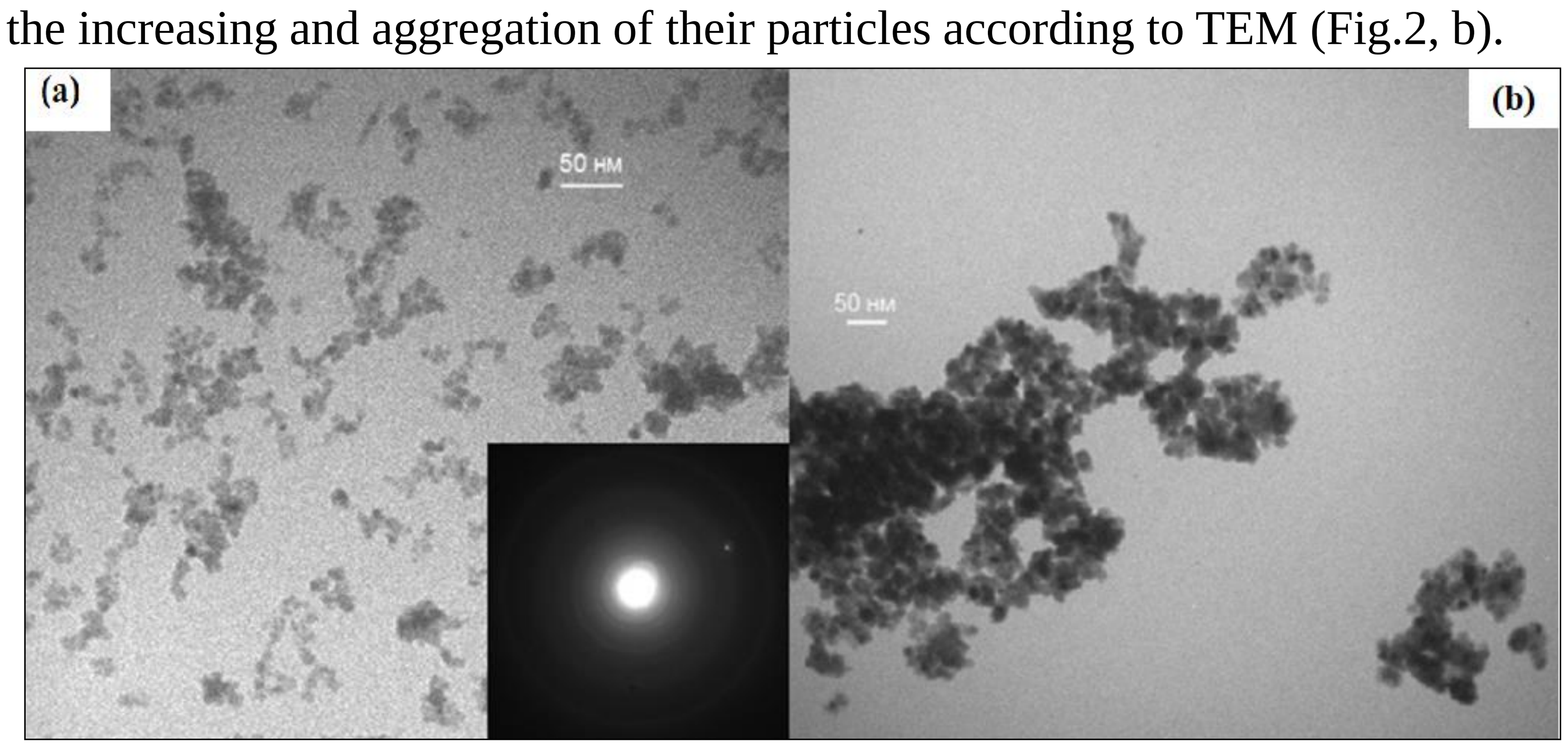

Fig. 2. TEM images: (a) material, obtained after calcination of xerogel at 400^{0}C during 2 hours 20min, (on the insert is an electronogram), (b) material of gas sensitive layer, containing 70% SnO_2.

The sensors created on the paste with 70% SnO_2 have the higher sensitivities to hydrogen (Table 2). Extreme nature of the temperature dependences of the sensitivities of the sensors based on the synthesized materials confirms the contribution of the size effect in the formation of the sensitivity.

Table 2

Sensitivity to 40 ppm H_2

T, °C	*R_0/R_g*		
	Content in gas sensitive layer of the sensor		
	50% SnO_2	*60% SnO_2*	*70% SnO_2*
225	*5.4*	*5.9*	*6.3*
260	*7.4*	*7.7*	*8.7*
295	*7.6*	*7.8*	*10.1*
325	*7.2*	*7.5*	*9.7*
350	*6.6*	*6.6*	*8.6*
380	*5.0*	*5.1*	*6.8*
405	*2.8*	*2.9*	*3.8*

Conclusion: High sensitive semiconductor sensors to hydrogen were created on the base of nanomaterial obtained by a zol-gel method. The characteristics of the sensors of different compositions are explained by necessity of the presence of a sufficient number of contacts between the particles of the sensor material, which ensure the electrical conductivity of the sensor.

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