**BRIEF
COMMUNICATIONS**

Synthesis and Properties of SnO Prepared from Ammoniacal and Carbonate Suspensions of Tin(II) Hydroxy Compound under Microwave Radiation

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Abstract—SnO powder was prepared by microwave treatment of ammoniacal and carbonate $Sn_6O_4(OH)_4$ suspensions. It was shown that the type of the precipitant (aqueous ammonia and sodium carbonate) for Sn(II) hydroxy compound affects the surface properties of the resulting oxide. It is found that SnO powders prepared by homogeneous precipitation of tin(II) hydroxy compound with sodium carbonate, followed by the microwave treatment, have the smaller specific surface area ($\sim$0.4 m^2 g^{-1}) and contain agglomerates of the larger size ($\sim$50 μm) joint together into a "flower."

Tin(II) oxide of the tetragonal system attracts much attention of researchers, because materials on its basis are used as electrodes in lithium-ion batteries [1, 2], solar cells [3] and photocatalysts [4]. Tin(II) oxide is synthesized by thermal or microwave decomposition of tin(II) hydroxide and tin(II) oxyhydroxide [5–8]. Analysis of the literature data shows that the method of decomposition and the type of a precipitant used for tin(II) hydroxyl compound in synthesis of SnO from tin(II) salts affect the surface morphology of SnO [9–12].

It was shown [8] that the use of strong bases (NaOH and KOH), which fast precipitants for hydroxides, leads to the formation of SnO platelet-shape crystals with the sizes from 30 nm to 2 μm. At the same time, in synthesis of SnO in the presence of KOH, square massive plates of SnO particles with the sizes from 100 to 150 nm are formed [12]. Using homogeneous [13] precipitant Na_2CO_3, the authors of [14] have separated SnO whiskers of the tetragonal structure with a diameter of 10–40 nm and a length of 100–400 nm. From the above, it follows that data on the influence of a precipitant on the surface morphology are contradictory.

In the study, a comparative analysis was performed of the properties and morphology of the surface of SnO obtained by microwave processing of tin(II) oxyhydroxide in the presence of the precipitants (aqueous ammonia and sodium carbonate).
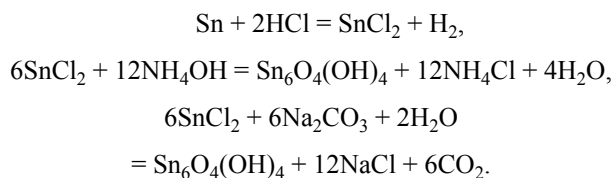
EXPERIMENTAL

Samples of tin(II) oxide were prepared from ammoniacal and carbonate tin(II) oxyhydroxide suspensions by dissolving metallic tin in concentrated hydrochloric acid, followed by tin(II) precipitation with 25% aqueous ammonia or solid sodium carbonate at a pH 8–10.

The obtained ammoniacal or carbonate tin(II) suspensions were subjected to microwave treatment in a 539-W oven (2450 MHz) for 15 min. The sediments were separated by centrifugation, exhaustively washed in distilled water, and dried in a desiccator at 90°C.

The composition of sediments was determined by the X-ray phase analysis (XPA) on a Rigaku Miniflex 600 diffractometer (CuK_α radiation, $2\theta = 10°-90°$, scan step 0.02°, scan rate 5 deg min^{-1}). JCPDS data were used to index diffraction peaks and calculate regions of coherent scattering. The specific surface area of the obtained SnO samples was determined by BET analysis

of low-temperature nitrogen sorption isotherms obtained using a TriStarII automated gas adsorption analyzer. Surface morphology was examined on a Hitachi TM3000 scanning electron microscope operated at an accelerating voltage of 15 kV with surface charge elimination (electron gun: 5×10^2 Pa, sample chamber, 30–50 Pa) equipped with a QUANTAX 70 energy dispersive spectrometer. IR spectra of the samples were recorded with an Agilent Technologies Cary 600 Series FTIR spectrophotometer in the frequency range 1000–4000 cm^{-1}.

According to XPA, the solid phase in the suspensions obtained using both aqueous ammonia and sodium carbonate as a precipitant, is tin(II) hydroxy compound of the composition $Sn_6O_4(OH)_4$ (Fig. 1), formed by the following reactions:

$$Sn + 2HCl = SnCl_2 + H_2,$$

$$6SnCl_2 + 12NH_4OH = Sn_6O_4(OH)_4 + 12NH_4Cl + 4H_2O,$$

$$6SnCl_2 + 6Na_2CO_3 + 2H_2O$$

$$= Sn_6O_4(OH)_4 + 12NaCl + 6CO_2.$$

$Sn_6O_4(OH)_4$ is crystallized in the tetragonal crystal system with the lattice parameters $a = b = 7.9622$ nm, $c = 9.1427$ nm and coherent scattering regions (CSRs) 22 and 14 nm in the [101] and [002] crystal growth directions, respectively.

Microwave processing of the obtained solutions of ammonium and carbonate $Sn_6O_4(OH)_4$ suspensions at a radiation power of 539 W for 15 min yields a single-phase product, which was identified as tetragonal SnO (P4/nmm) (Fig. 2).

However, tin(II) oxide synthesized with ammoniacal prehistory has the lattice parameters: $a = b = 3.8035$ nm and $c = 4.836$ nm and CSR 49.3 nm in the crystal growth direction in an hkl plane (002) (Fig. 2, pattern 1). In the case of SnO, synthesized with sodium carbonate, the lattice parameters are slightly larger: $a = b = 3.8125$ nm, $c = 4.8396$ nm. The size of the CSR in the growth direction in an hkl plane (002) is lesser (40.5 nm). As seen from diffraction patterns, the intensity of reflections corresponding to the growth of the SnO crystals along the z axis [in an hkl plane (001, 002)] increases, as NH_4OH is replaced for Na_2CO_3.

The above-said shows that in the presence of Na_2CO_3 the SnO crystallites grow predominantly along the z axis [in an hkl plane (001, 002)] after nucleation. For these samples, the anisotropy coefficient, calculated as
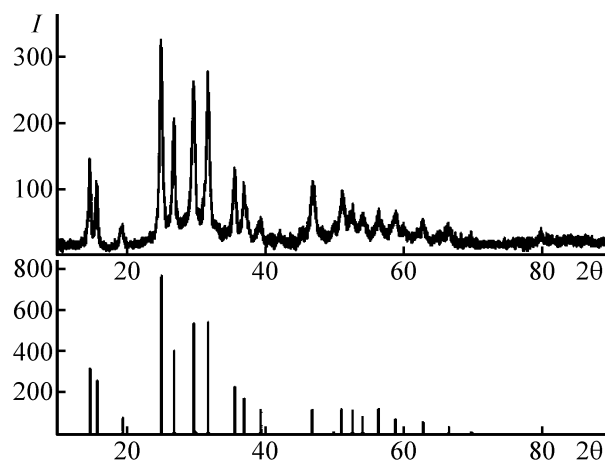

Fig. 1. XPA pattern of the solid phase of the suspension. (I) Intensity (rel. units.) and (2θ) Bragg angle (deg); the same for Fig. 2.

the ratio of the RCS size in the (002) plane to that in the (101) plane, is 0.84. The anisotropy coefficient of SnO obtained by fast precipitation of tin (II) oxyhydroxide with aqueous ammonia is 1.00.

Analysis of the SEM data shows that the resulting tin(II) oxide has the form of tetragonal plates in both cases. SnO particles synthesized in the presence of NH_4OH are irregularly shaped fragments 3–15 μm in size (Fig. 3a).

In the case of synthesis with a Na_2CO_3 precipitant, irregular SnO agglomerates of larger size (up to 50 μm), a minority of particles with the size 2–5 μm, and flowers
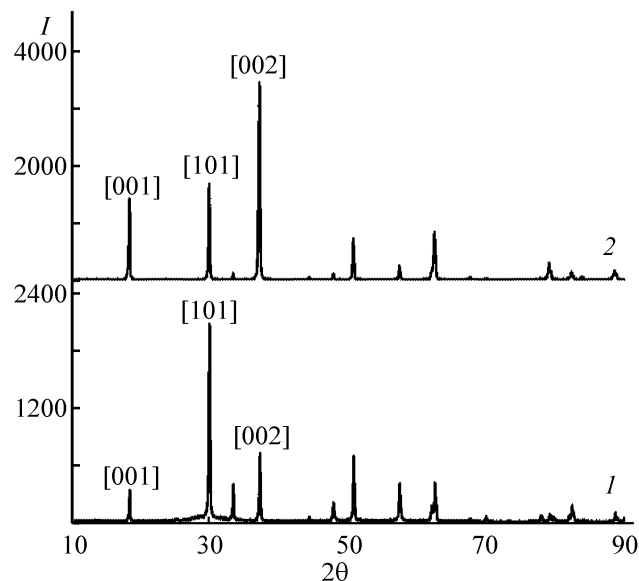

Fig. 2. XPA patterns of the SnO samples prepared by microwave processing with (1) NH_4OH and (2) Na_2CO_3 precipitants.
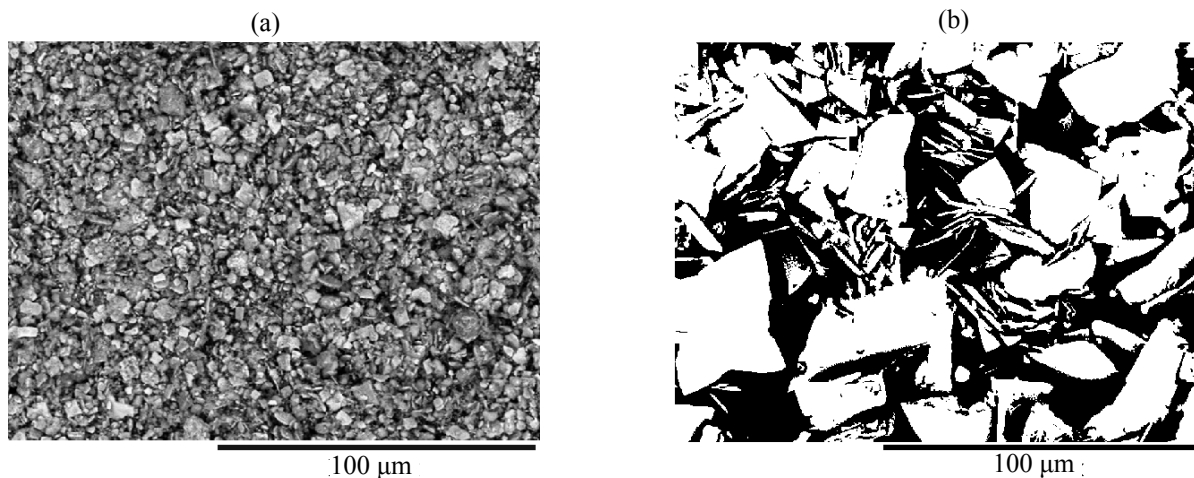
(a) (b)

Fig. 3. Photomicrographs of the SnO samples prepared by microwave processing in the presence of (a) NH_4OH and (b) Na_2CO_3 as precipitant.
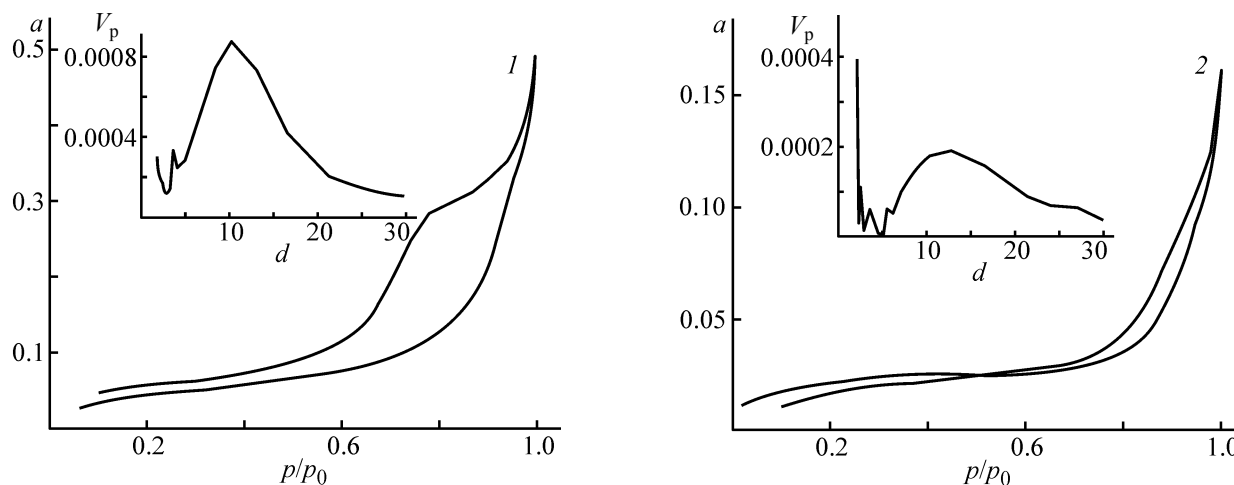

Fig. 4. Nitrogen adsorption-desorption isotherms and differential pore size distribution for SnO obtained by microwave processing in the presence of (*1*) NH_4OH and (*2*) Na_2CO_3 as precipitant. Adsorption (mmol g^{-1}), (V_p) pore volume ($cm^3 g^{-1} nm^{-1}$), (*d*) pore diameter (nm), and (p/p_0) relative pressure.

of particles, each plate having size up to 30–50 μm, are formed, with coherent scattering region however lesser (Fig. 3b). The increase in the agglomerate size decreases the specific surface area of SnO. The results of the low-temperature adsorption of nitrogen vapor indicate that the specific surface area of tin(II) oxide prepared with ammoniacal prehistory is nearly an order of magnitude higher than for SnO prepared with carbonate (3.0 and 0.4 $m^2 g^{-1}$, respectively).

Figure 4 shows the adsorption-desorption isotherms of the samples studied, which correspond to type H3 in the IUPAC classification and are typical of adsorbents with plate-like particles (slit-shaped pores) [15].

Analysis of the differential pore size distribution shows that the synthesized SnO powders have mesopore structure with incorporation of micropores. However, the SnO sample prepared by precipitation of $Sn_6O_4(OH)_4$ with NH_4OH is characterized by a larger hysteresis area on the adsorption-desorption curve, pore volume of 0.0008 $cm^3 g^{-1} nm^{-1}$ and contains pores from 5 to 20 nm in diameter (Fig. 4, curve *1*). SnO sample prepared with a Na_2CO_3 precipitant has a narrow hysteresis, pore volume of 0.0002 $cm^3 g^{-1} nm^{-1}$, and the same pore size distribution (Fig. 4, curve *2*). Comparative analysis of the adsorption-desorption isotherms of the above oxides indicates on the different interaction between
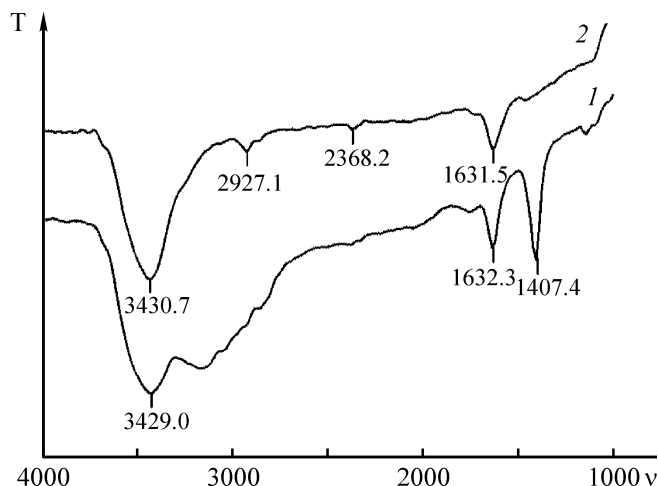
Fig. 5. IR spectra of SnO obtained under microwave conditions in the presence of (*1*) NH$_4$OH and (*2*) Na$_2$CO$_3$ as precipitant. (T) Transmission and (v) wave number (cm^{-1}).

the adsorbate and the adsorbent, which may be due to different pore volumes. SnO samples with different porosity have different surface properties.

According to the IR spectroscopic analysis, adsorbed water molecules are present on the surface of all SnO samples kept in air at room temperature (Fig. 5). The absorption bands in the region 3450–2355 and 1650–1620 cm^{-1} correspond to stretching and deformation vibrations of OH groups of the H$_2$O molecules adsorbed from the air [16]. The IR spectrum of the SnO sample obtained from Sn$_6$O$_4$(OH)$_4$ in the presence of NH$_4$OH in air at room temperature contains additional absorption band at 1407.4 cm^{-1}, which also corresponds to deformation vibrations of OH groups of water molecules [16]. For samples kept in a vacuum, the intensity of all the above bands decreases up to zero value. The above-said shows that the given tin(II) oxide has the larger amount of coordinatively unsaturated Sn^{n+} ($n < 2$) centers, which may be adsorbing sites on the SnO surface.

CONCLUSIONS

It is found that the properties of SnO obtained under the exposure to microwave radiation, depend on type of the tin (II) hydroxide precipitant, which is the precursor in oxide synthesis. Tin(II) oxide with larger size of agglomerates and smaller specific surface area is synthesized in the presence of a homogeneous precipitant Na$_2$CO$_3$.

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