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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Mechanochemical Synthesis of Nanosize Tin Dioxide Powders

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Abstract—Structural parameters, dispersity, morphology, and magnetic properties of a tin dioxide–magnetite nanosize composite material mechanochemically synthesized from salt systems were studied. The possibility of using the composite nanopowder as a sorbent for nucleic acids was analyzed.

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Selective sorbents based on oxide powders are widely used for isolation of the genetic material of DNA (RNA) and other biological substances necessary for rapid, precise, and high-sensitivity diagnostics [1]. It is known that the role of such a sorbent can be played by a dispersed tin dioxide powder with an average particle size of 1 μm, produced by oxidation of a metallic tin powder [1]. It is expectable that diminishing particles to nanosize (<20 μm) and introducing a magnetic component should markedly raise the adsorption capacity of the tin dioxide powder for nucleic acids and accelerate the sorption process.

A promising way to produce nanosize powders, including those of composite nature, is mechanochemical synthesis from salt systems in the presence of an inert diluent [2–5]. In the course of mechanochemical activation (MA), chemical reactions occur at the continuously regenerated phase boundaries that appear as a result of crushing of the starting reagents, e.g., metal chlorides and carbonates. The heat released in a reaction is dissipated in the inert diluent, and the final product of the process are nanoparticles dispersed in a soluble inert matrix.

The aim of this study was to examine physicochemical properties of nanosize tin dioxide (SnO_2) particles produced by mechanochemical synthesis from salt systems in the presence of an inert diluent, sodium chloride.

EXPERIMENTAL

Tin dioxide was synthesized by the reaction:

$$SnCl_2 + Na_2CO_3 + 0.5O_2 = SnO_2 + 2NaCl + CO_2.$$

A mixture of reagents with an inert diluent, NaCl, was hermetically sealed in steel drums containing ShKh15 steel balls 5 mm in diameter. The mechanochemical synthesis was performed in an MPV (60 g) water-cooled planetary mill. A prescribed content of the magnetic phase was obtained by abrasive-reactive wear of balls, followed by thermal treatment.

The product obtained upon MA was washed on a filter with distilled water and dried at room temperature. For separation into fractions, the product was treated with ultrasound and centrifuged (UZDN-2T and Bekman J2-21).

The content of iron in the composite powders synthesized, $SnO_2 + Fe_3O_4$, was determined by complexonometry in the presence of sulfosalicylic acid.

The phase composition, morphology, and dispersity of the product were determined by X-ray diffraction analysis (Shimadzu-XRD-6000, CuKα radiation) and transmission electron microscopy (EM-125). The specific surface area of the tin dioxide powder was measured by

the BET method on a SORBI®N.4.1 instrument, with nitrogen used as adsorbate gas. Preliminarily, the powder was subjected to thermal aging at 200°C for 1 h.

The method of synchronous thermal analysis (STA 449 C Jupiter) was used to measure heat effects and changes in the sample mass under heating in the atmosphere of argon.

IR spectroscopy of the nanosize composite material $SnO_2 + Fe_3O_4$ was carried out on a Nicolet 5700 IR Fourier spectrometer (wave number range 4000–400 cm^{-1}) with a diffuse-reflection attachment.

According to the results of an electron-microscopic analysis, nanosize tin dioxide particles can be divided into two structural levels. To the first level belong spherical 3–20-nm particles, the so-called light fraction, whose content in the sample is approximately 40 wt % (Figs. 1a, 1b). To the second structural level belong weakly aggregated spherical particles 40–80 nm in size. In addition, separate 100–120-nm particles and aggregates with sizes of up to 200 nm are seen.

The X-ray diffraction analysis demonstrated that the main phase formed in MA is SnO_2 with a tetragonal lattice (Fig. 2). Also observed was a SnO_2 phase with an orthorhombic lattice, the high-pressure phase, which is characteristic, as first noted by Cukrov et al. [5], of particles with sizes of several nanometers. According to the results of an X-ray structural analysis, processed using POWDER CELL 2.5 full-profile analysis software, the lattice constant of the synthesized tin dioxide is a = 0.4738 nm, the size of coherent-scattering regions (SCR) lies within the range 9–16 nm, and the magnitude of microdistortions is large and varies within the range (6–8) $\times 10^{-3}$. In this case, the larger the average particle size, the smaller microdistortions, in good agreement with the known published data.

The average sizes of SnO_2 nanoparticles were determined by electron microscopy and X-ray diffraction analysis and found from the results of measurements of the specific surface area calculated by the formula

$$D = \frac{6 \times 10^{-4}}{\gamma S},$$

where S is the specific surface area ($m^2\ g^{-1}$); γ, density ($g\ cm^{-3}$); and D, particle diameter (cm). The particle sizes found in different ways are well correlated (see table).

A study of the effect of temperature on the size of tin dioxide powder nanoparticles demonstrated that, upon calcination of a SnO_2 powder at 300 and 600°C for 1 h,

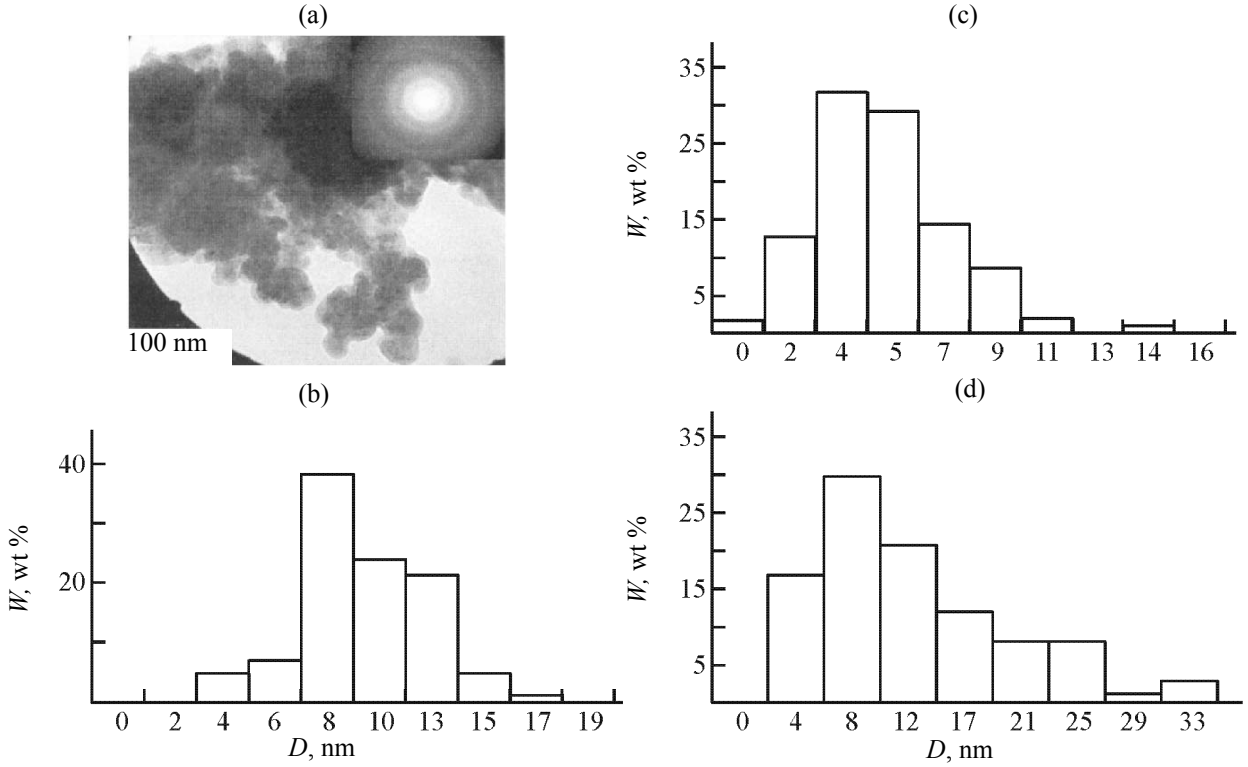

Fig. 1. (a) Electron micrograph and (c–d) particle size distribution histograms of tin dioxide powder. (b) Powder dried at T = 25°C; (c) Tanneal = 300°C, τ = 60 min; and (d) Tanneal = 600°C, τ = 60 min. (W) Particle content and (D) particle diameter.

the particle size changes only slightly (Figs. 1c, 1d), but treatment at $T = 900°C$ yields a film with a nanocrystalline structure.

According to the results of a thermal analysis, the loss of water occurs in two stages at 140.2 and 350.1°C (Fig. 3). The observed temperature ranges of dehydration agree with published data and correspond to decomposition of crystal hydrates of α- and β-modifications [6].

Thermal analysis shows that dehydration processes are observed in calcination up to 600°C, after which particles start to merge into a nanocrystalline film. Presumably, presence of water hinders coarsening of particles in annealing of the tin dioxide powder at 300 and 600°C.

According to IR spectroscopic data, the absorption bands at 649.3 and 570.3 cm^{-1} in the spectrum of the tin dioxide–magnetite composite material correspond to vibrations of the Sn–O bond in nanosize tin dioxide power. However, the shift of these bands to longer wavelengths may indicate that, in the course of mechanosynthesis, iron penetrates into voids in the crystal lattice of tin dioxide to give a solid solution (Fig. 4; spectra *1, 2*). Also present are absorption bands at 602.9, 549.0, 510.0, 439.9, and 401.1 cm^{-1}, which are characteristic of magnetite Fe_3O_4 [7]. In addition, an absorption band is observed at 420.9 cm^{-1}. This band is characteristic of vibrations of the Fe–O bond in iron oxide FeO (Fig. 4; spectra 1, 3), i.e., iron(II) oxide is present on the surface of particles of the composite nanopowder.

Structural parameters of nanosize tin dioxide

Phase	S, $m^2 g^{-1}$	Average particle size, nm, according to measurements			$\Delta d/d \times 10^3$
		specific surface area	electron microscopy	X-ray diffraction analysis	
Tetragonal	130.0	8.5	10.0	9.5	6.8
Orthorhombic				8.7	7.7

Inasmuch as an abrasive-reactive wear of steel balls occurs in the process of MA and a tin dioxide–magnetite composite material is formed, the magnetic properties of

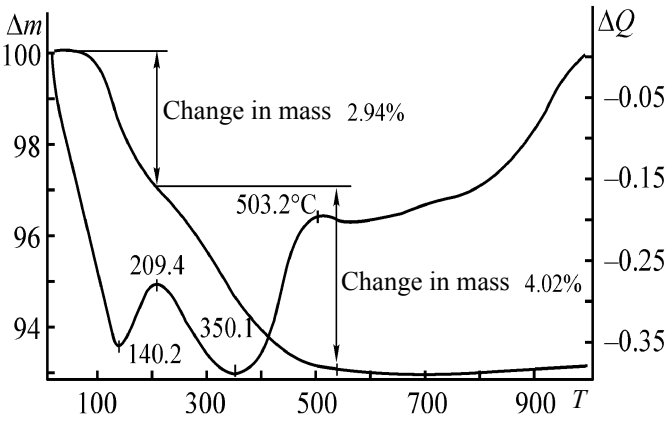

Fig. 3. Data furnished by thermographic analysis and scanning calorimetry of the $SnO_2 + Fe_3O_4$ composite nanopowder. (Δ*Q*) heat effect, mW mg^{-1}; (Δ*m*) relative change in mass, %; (*T*) temperature , °C.

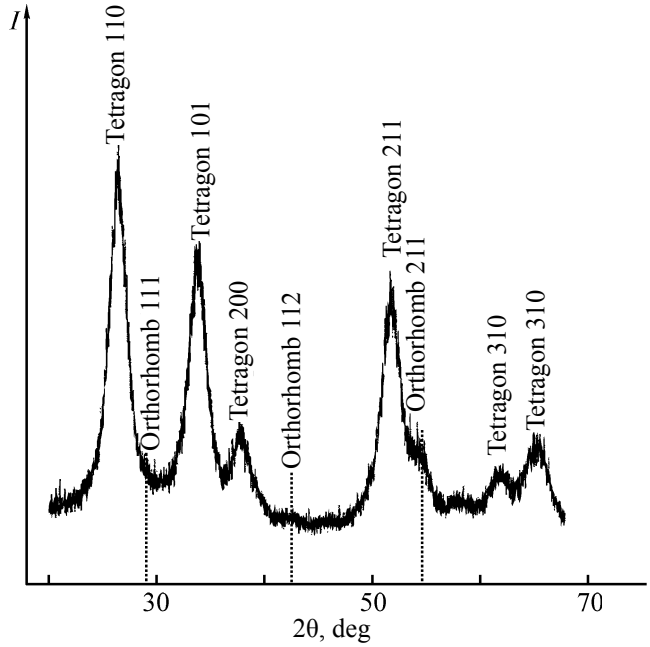

Fig. 2. X-ray diffraction pattern of SnO_2 nanopowder. (*I*) Intensity and (2θ) Brag angle.

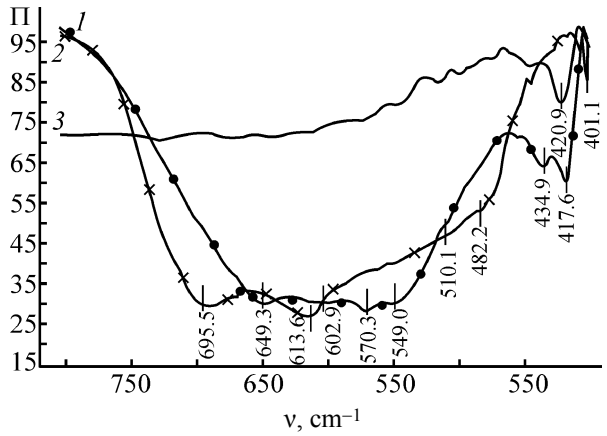

Fig. 4. IR spectroscopic data for (*1*) composite nanopowder dried in air at $T = 25°C$, (*2*) SnO_2 of analytically pure grade, and (*3*) electroexplosive FeO nanopowder. (Π) Transmission and (ν) wave number.

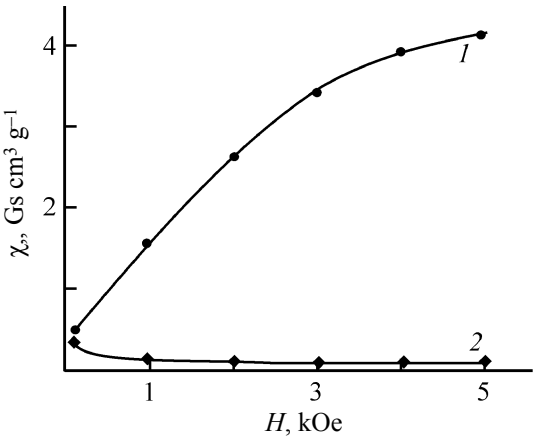

Fig. 5. Specific magnetization χ of composite powders vs. the magnetic field strength H. (*1*) $SnO_2 + Fe_3O_4$ dried in air and (*2*) $SnO_2 + Fe_2O_3$ annealed in air at 600°C for 1 h.

the powder obtained were studied. Figure 5 shows how the specific magnetization of a SnO_2 powder containing 18 wt % magnetite Fe_3O_4 depends on the magnetic field strength. A powder dried in air exhibits pronounced magnetic properties (Fig. 5, curve *1*), whereas that calcined in a muffle furnace at 600°C for 1 h almost completely loses its magnetic properties (Fig. 5, curve *2*) because Fe_3O_4 is converted to Fe_2O_3 when the powder is heated in air [6].

A study of the sorption activity of tin dioxide nanoparticles toward nucleic acid demonstrated a high adsorption activity toward nucleic acids and, in particular, DNA, whose parameters exceed those of the existing sorbents (diatomaceous earth, Silica) [8, 9]. An estimate of the buffer capacity (nanocomposite/DNA) of the nanomaterial demonstrated that the amount of bound DNA molecules nonlinearly depends on the amount of the nanopowder in the suspension. An increase in the amount of the nanocomposite does not lead to any significant rise in the adsorption efficiency. The buffer capacity of tin dioxide is 1 : 20.

A study of the possible inhibiting properties of the composite nanomaterial under consideration with respect to enzymatic reactions demonstrated that the efficiency of the polymerase chain reaction (PCR) does not decrease upon addition of the tin dioxide nanopowder to the reaction mixture. It was found, in addition, that the PCR efficiency increases and the yield of the amplificate becomes higher, which may be due to the stabilizing effect of nanopowders on nucleic acid synthesis enzymes.

CONCLUSIONS

(1) A powdered tin dioxide–magnetite nanosize composite with an average particle size in the range 3–20 nm was produced by mechanochemical synthesis, and its phase composition, structural parameters, and magnetic properties were determined.

(2) It was found that the powder synthesized can be used as a sorbent for nucleic acids and, in particular, DNA.

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