Preparation of nanocrystalline heterostructures TiO_2-SnO_2 by modified sol-gel method

Otrzymywanie nanokrystalicznych heterostruktur TiO_2-SnO_2 modyfikowaną metodą zol-żel

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The paper presents production of TiO_2-SnO_2 nanocomposites with the use of sol-gel method combined with hydrothermal processing of the formed hydroxide gel. As proven by XRD analysis, both oxides crystallise in tetragonal systems: TiO_2–anatase, SnO_2–cassiterite. Mean sizes of the crystallites are TiO_2 ~30÷40 nm and SnO_2 ~3÷4 nm, respectively. Moreover, the produced TiO_2-SnO_2 nanocomposites are characterised by a high specific surface area (~100 m^2/g).
KEYWORDS: TiO_2-SnO_2 nanocomposites, nanopowders, sol-gel method, hydrothermal crystallisation

W pracy opisano otrzymywanie nanokompozytów TiO_2-SnO_2 metodą zol-żel połączoną z obróbką hydrotermalną otrzymanego żelu wodorotlenkowego. Analiza XRD wykazała, że obydwa tlenki krystalizują w strukturach tetragonalnych: TiO_2–anataz, SnO_2–kasyteryt. Średnie wielkości krystalitów wynoszą odpowiednio TiO_2 ~30÷40 nm, SnO_2 ~3÷4 nm. Ponadto, otrzymane nanokompozyty TiO_2-SnO_2 charakteryzują się dużym rozwinięciem powierzchni właściwej (~100 m^2/g).
SŁOWA KLUCZOWE: nanokompozyty TiO_2-SnO_2, nanoproszki, metoda zol-żel, krystalizacja hydrotermalna

There are various methods for producing nanopowders, which can be divided into nanoscale grinding (top-down) methods and atomic aggregation (bottom-up) methods [1÷3]. The most common among the methods that allow to obtain material of nanometric microstructure directly is the sol-gel method [3]. It is a method of chemical synthesis in which the precursor – metal oxide hydrolyses in water, forming sol. Next, the hydrolysed compound coagulates, forming gel, which is washed and dried. In another phase of the synthesis crystallisation of the nanoparticles occurs as a result of the gel being roasted at a high temperature or processed hydrothermally until crystalline nanoparticles are formed. The main advantage of this method is that it allows us to obtain nanopowders of uniform particle size distribution and a considerable chemical purity at a relatively low temperature [4÷6].

Materials and methods

■ **Samples preparation.** TiO_2-SnO_2 nanocomposites of varying mass fraction of SnO_2 (26.9, 44.1, 56.1, 74.0 and 77.4%) were obtained by means of a two-step sol-gel method based on hydrolysis (Fig. 1).

In the first stage of synthesis, nanocrystalline TiO_2 was produced as follows: HCl (36%) and CH_3COOH (27%) were instilled into 580 cm^3 of isopropyl alcohol until the system reached pH 3. Then, 58 cm^3 of titanium (IV) isoproxide (98%) was introduced into the prepared solution, all was mixed and added into 464 cm^3 of distilled water.

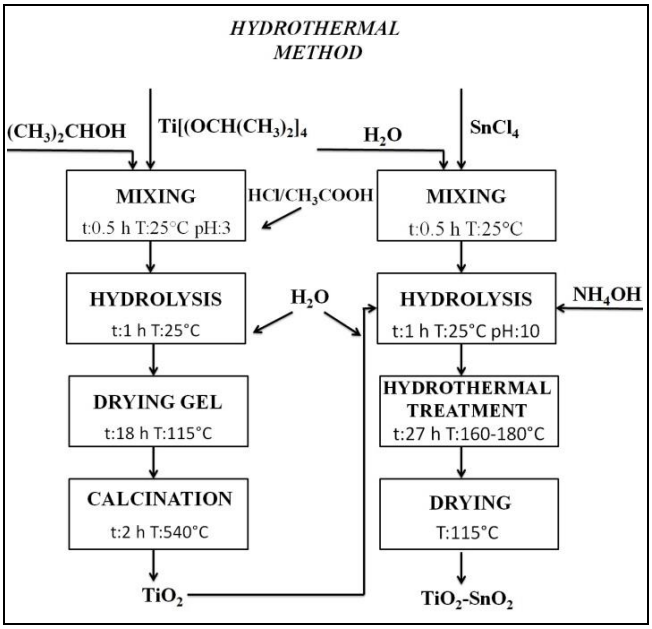

Fig. 1. The scheme of nanocomposites TiO_2-SnO_2 preparation

The obtained titanium hydroxide gel was dried and calcined. The produced TiO_2 powder was pulverised in a mortar. The second stage of the TiO_2-SnO_2 nanocomposite synthesis involved introducing SnO_2 nanoparticles. To this end, a proper amount of precursor $SnCl_4$ (99%) was each time diluted ten times in distilled water at room temperature and instilled into the colloidal solution made by 2 g of the obtained TiO_2 nanopowder dispersed with the use of an ultrasound in aqueous solution of NH_4OH [60 cm^3 NH_4OH (25%) dissolved in 160 cm^3 of distilled water] with continuous stirring. Next, the suspensions were transferred into Teflon vessels and placed in a reactor. Following the process of hydrothermal crystallisation, the suspensions were repeatedly washed with distilled water, filtered off and dried to constant weight in a laboratory dryer at 115 ºC. The dried powders were pulverised in a mortar. In the above described way TiO_2-SnO_2 nanocomposites were obtained and later characterised.

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■ **Methods of composite nanopowders characterization.** In order to determine phase composition of the produced nanopowders, the method of powder X-ray diffraction was used with PANalytical X'Pert Pro device. XRD technique was also employed for determining mean crystallite sizes basing on Scherrer equation.

The measurements of specific surface areas of the powders were performed by means of sorption method basing on Brunauer, Emmett and Teller (BET) physical adsorption isotherm measurements. The obtained physical adsorption isotherms served for determining specific surface areas. The measurements were conducted with the use of a NOVA 1200e device by Quantachrome Instruments.

In order to learn the morphology of the formed TiO_2-SnO_2 composites, the obtained nanopowders were subjected to observation with the use of a transmission electron microscope (TEM) TECNAI FEG by FEI at the accelerating voltage of 200 kV.

Results and discussion

■ **Samples characteristics.** The phase composition of the produced nanopowders was determined with the use of XRD method (Fig. 2). Titanium dioxide crystallises in a thermodynamically stable tetragonal structure of anatase. For tin dioxide, reflections only from the tetragonal structure of cassiterite are also visible. Weight fractions for both oxides and mean crystallite sizes are presented in the table.

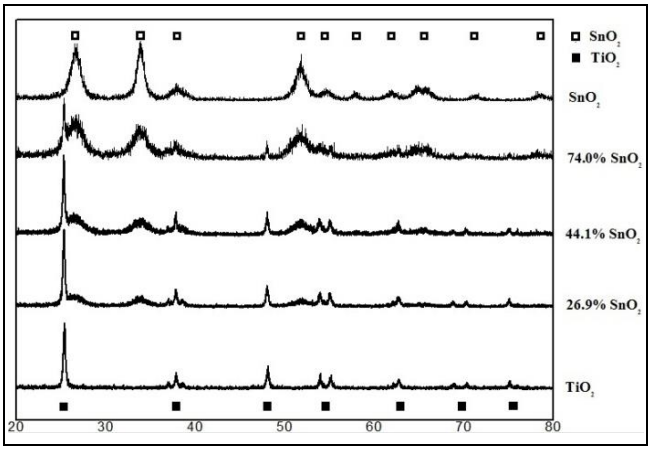

Fig. 2. XRD diffractograms of the synthesized nanopowders

TABLE. Mass fractions of dioxides, the size of crystallites specified with the use of XRD and specific surface area estimated with use of BET

Sample No.	Mass fractions (XRD), %	Average nanoparticle size (XRD) D_{hkl}, nm	Specific surface area SSA, m^2/g
1.	SnO_2 0% $TiO_2$100%	TiO_2 34.4 ± 0.2	32.2 ±5.2
2.	SnO_2 26.9% TiO_2 73.1%	TiO_2 35.0 ± 0.2 SnO_2 3.7 ± 0.2	69.5 ±5.2
3.	SnO_2 44.1% TiO_2 55.9%	TiO_2 3.2 ± 0.2 SnO_2 3.6 ± 0.2	92.1 ±5.2
4.	SnO_2 74% TiO_2 26%	TiO_2 30.2 ± 0.2 SnO_2 3.6 ± 0.2	136.3 ±5.2
5.	SnO_2 100% TiO_2 0%	SnO_2 3.0 ± 0.2	160.8 ±5.2

In the table measurements of specific surface areas conducted with the use of a standard method of analysing nitrogen vapour adsorption isotherms were also presented. The specific surface area of the TiO_2 powder produced by means of calcination at 540 ºC was the smallest, measuring 49.1 m^2/g. The specific surface area increases with the SnO_2 content in the composite as a result of growing number of smallest sized particles (with the specific surface area of SnO_2 of 160 m^2/g being the largest).

In order to learn the morphology of powders, they were subjected to microscopic observations with the use of a transmission electron microscope TEM (Fig. 3). Results obtained from the TEM analysis revealed the presence of grains varying in size. SnO_2 grains of several nanometres in diameter are located on the surface of weakly agglomerated TiO_2 grains of several tens of nanometres in size.

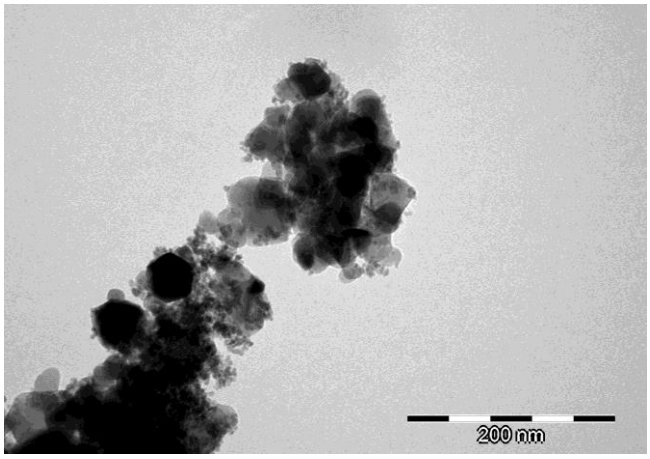

Fig. 3. TEM microphotographs of 26.9% SnO_2 powder

Conclusions

The presented method for synthesising nanopowders allows production of composites from the TiO_2-SnO_2 system not only of known and controllable chemical and phase composition, but also enables production of materials with TiO_2 and SnO_2 particles considerably varying in size.

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