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# THE TEMPLATE SOL-GEL METHOD FOR SYNTHESIS OF TIN (IV) OXIDE NANOPARTICLES

**Background.** It is known that the presence of templates greatly affects on physical and chemical properties of the synthesized powders. Therefore, investigation of powders synthesis $SnO_2$ in the presence and absence of templates by sol-gel method are scientific and practical interest.
**Objective.** The purpose this paper was synthesis of $SnO_2$ nanoparticles in absence and presence of template non-ionic type (ethylene glycol and PEG) by sol-gel method and characterization of obtained powders.
**Methods.** In paper synthesized the tin (IV) oxide powders by sol-gel method with and without the use of templates. The ethylene glycol and polyethylene glycol with a molecular weight of 6000 (PEG 6000) was used as templates.
**Results.** The minimum temperature for crystallization of hydrated tin (IV) oxide powders is defined by thermal analysis. It is found that the heat treatment under these conditions leads to the formation of the polycrystalline powders pure rutile modification with a low degree of crystallinity and with a structure approximated to amorphous state. It is shown that the sol-gel method produces nanocrystalline (0.8–3.5 nm) and nanoparticulate (10–15 nm) powders of tin oxide (IV), and the use of template-PEG 6000 2–4 times reduces the size of crystallites. It is shown that the increase in mass of content template PEG-6000 from 1 to 10–75 % results in a slight distortion of the crystal lattice of tin oxide (IV). The calculated value of the bandgap for $SnO_2$ is equal to 3,69 eV. This value is in good agreement with literature data.
**Conclusions.** The use of sol-gel method allows to obtain of nanoparticle $SnO_2$ powders, and template – significantly smaller crystallite size $SnO_2$ (to 0.8 nm). It is shown that minimum temperature for receiving of crystalline $SnO_2$ is 350 °C.
**Keywords:** Tin (IV) Oxide; nanoparticles; sol-gel method; template.

## Introduction

The tin (IV) oxide ($SnO_2$) is an important n-type semiconductor with wide bandgap (3.6 eV), high electrical conductivity, optical transparency, sensitivity to adsorbed molecules. $SnO_2$ used widely as a sensing layer in metaloxide gas sensors and other applications (lithium-ion batteries, sensitized solar cells, and catalysts). However, sensors based on tin (IV) oxide have low sensitivity. In order to increase of sensitivity the $SnO_2$ particle size necessary reduce to nanometer range. For this, successfully different methods of $SnO_2$ synthesis are used: hydrothermal synthesis [1, 2], sol-gel [3, 4] and template [4] methods and chemical vapor deposition (CVD) [5, 6]. Among them sol-gel technology is most popular due to achieving high homogeneity of materials. In addition, in recent years the template method becomes more and more popularity through the possibility of obtaining nano-objects with different morphologies. In this way zero-dimensional and one-dimensional nanostructures are obtained [7]. The different anionic, cationic and nonionic surfactants are used as a template. Among them non-ionic surfactants are most popular, for example, polyethylene glycol (PEG). But there are questions about choice of temperature for decomposition of hydrated tin (IV) oxide to its oxide and remove of PEG residual. Therefore, investigation the tin (IV) oxide synthesis in presence and absence of templates by sol-gel method is actual and it is interesting from the point view of obtaining nanosized oxide powder.

## Formulation of the problem

The purpose this paper was synthesis of $SnO_2$ nanoparticles in absence and presence of template non-ionic type (ethylene glycol and PEG) by sol-gel method and characterization of obtained powders.

## Materials and methods

The reagents tin (IV) chloride (chemically pure), ammonia 25 % w/w (chemically pure), polyethylene glycol (PEG-6000), ethylene glycol were used.

Synthesis of $SnO_2$ sample without template carried out as follows. Solution of tin (IV) chloride was prepared with a concentration 0.05 mol/dm$^3$. Then solution was heated to 50 °C and in obtained solution with vigorous stirring aqueous ammonia was added dropwise to pH 7.8 (Fig. 1). The resulting gel was kept at 50 °C for 2 hours and at room temperature for 12 hours. Then gel was washed with distilled water and dried at 100 °C for 2 hours

and calcined at a temperature of 350 °C in air for 1 hour.

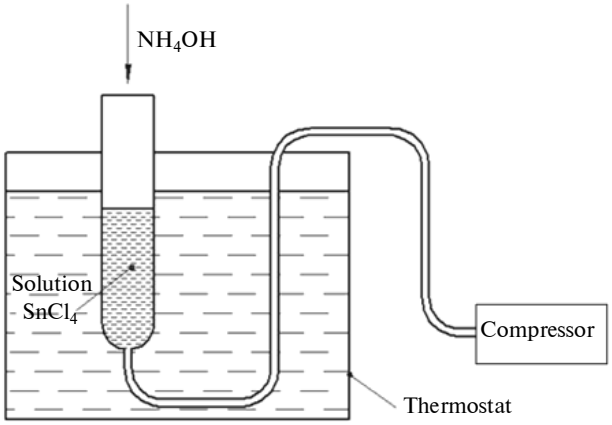



Fig. 1. The scheme of $SnO_2$ obtaining

In the synthesis of $SnO_2$ samples in presence template to solution of tin (II) chloride with vigorous stirring ethylene glycol or PEG were added, then obtained solution was heated and added dropwise concentrated solution of ammonia to the formation of a white gel. Then obtained gel was washed, dried and calcined by the above conditions.

Thus 7 samples were obtained: sample 1 – without template, sample 2 – with ethylene glycol (1 % w/w), sample 3 – with PEG-6000 (1 % w/w), sample 4 – 5 – with PEG-6000 (25 % w/w), sample 6 – with PEG-6000 (50 % w/w), sample 7 – with PEG-6000 (75 % w/w).

The particle sizes of obtained samples were determined with a transmission electron microscope ПЕМ 100-01.

XRD (X-ray diffraction) measurements were conducted using X-ray diffractometer Ultima IV Rigaku with CuKa radiation.

The thermal analysis of obtained samples was carried out in air with thermoanalyzer Derivatigraf Q-1500 (MOM, Hungary) in a small platinum crucible using calcined $Al_2O_3$ as a standard at heating rate of 10 deg/min.

Bandgap of $SnO_2$ samples was determined by measuring the optical absorption of $SnO_2$ films. Measurements were performed on a spectrophotometer UV-5800 PC.

**Results and discussion**

On Fig. 2 presents thermograms of synthesized gels in the presence of templates: *1* – in presence of ethylene glycol, *2* – in presence of PEG-6000. As seen from Fig. 2 in both samples at temperature of 110–150 °C there is a great loss of water (about 16 % wt.). Then two small exothermic effects are fixed, which there are not clear due to the simultaneous crystallization of $SnO_2$ and combustion residues of ethylene glycol and PEG-6000. Nevertheless, the beginning of crystallization and remove residual template already is fixed at 300, the end there is at 500 °C (for ethylene glycol), and at 800–900 °C (for PEG). And in case used PEG-6000 the exothermic effects and weight loss are larger. This is due to the great calorific value of PEG-6000. Based on the obtained thermograms heat treatment temperature of gels were selected 350 °C.

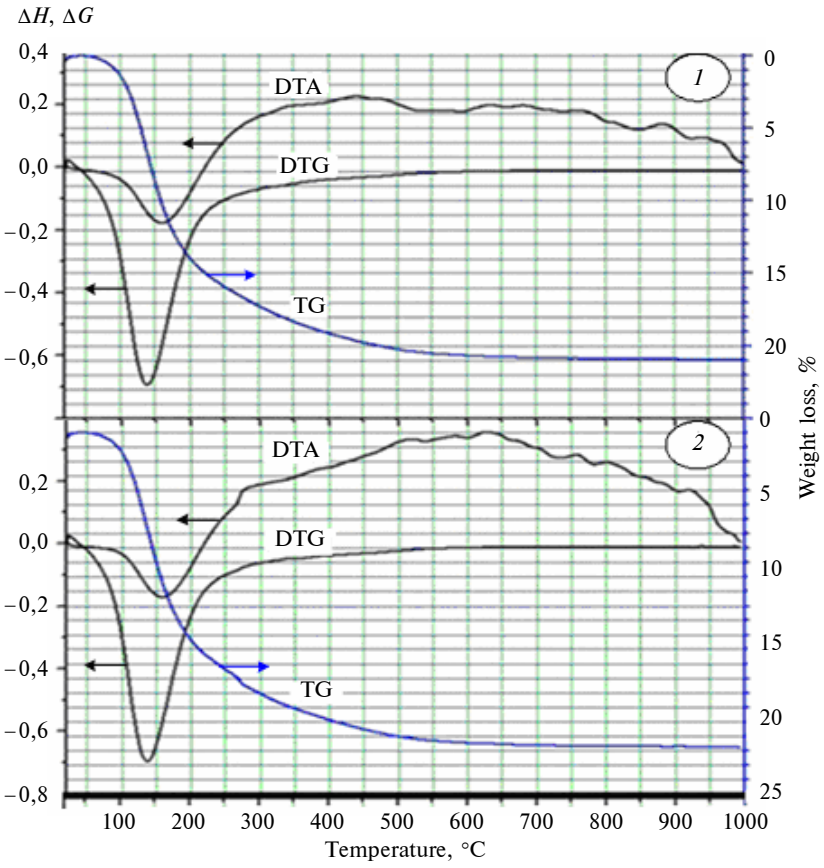



Fig. 2. The thermogram of $SnO_2 \cdot xH_2O$ gels: *1* – in presence of ethylene glycol (sample 2), *2* – in presence of PEG-6000 (sample 3)

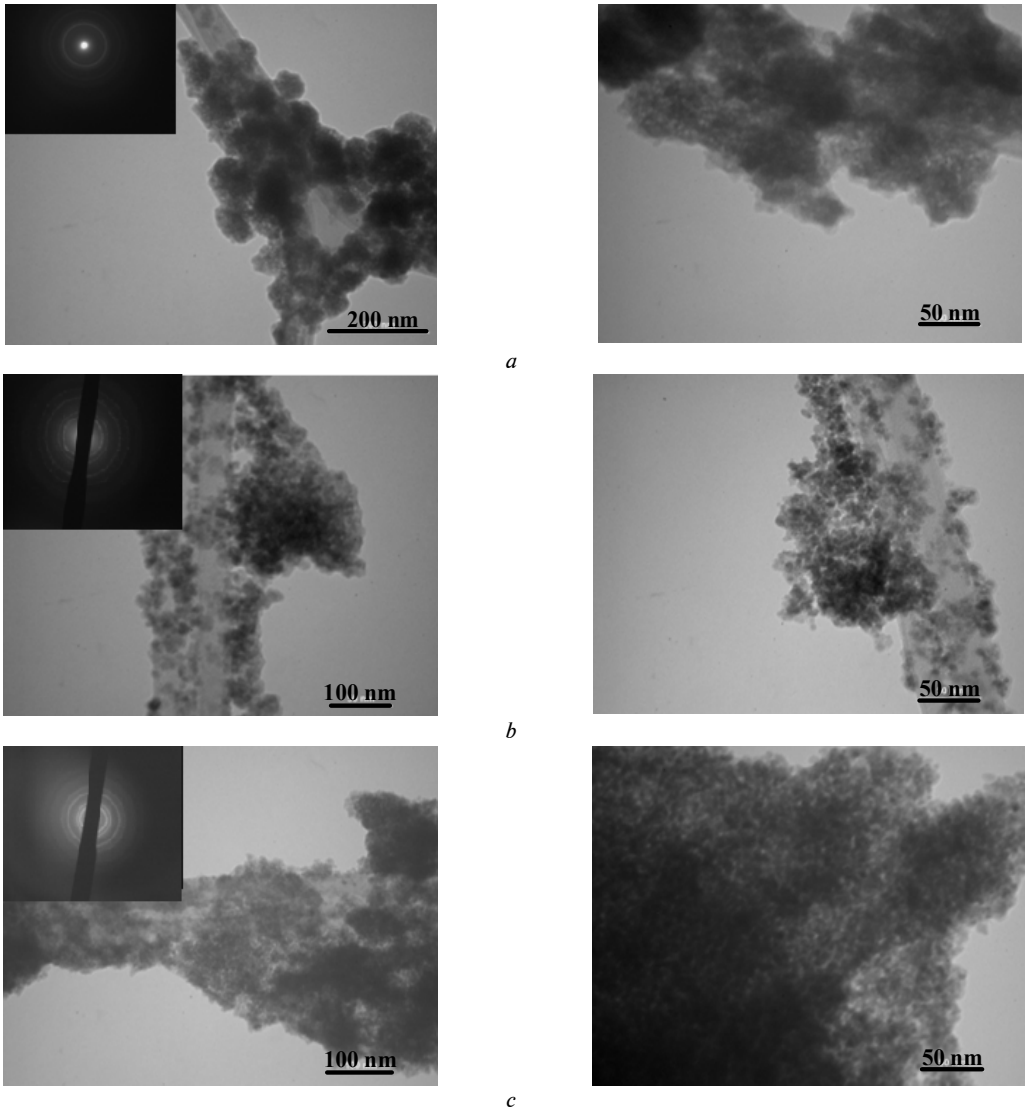



Fig. 3. TEM images of $SnO_2$ samples and corresponding SAED patterns: *a* – sample 1; *b* – sample 2; *c* – sample 3

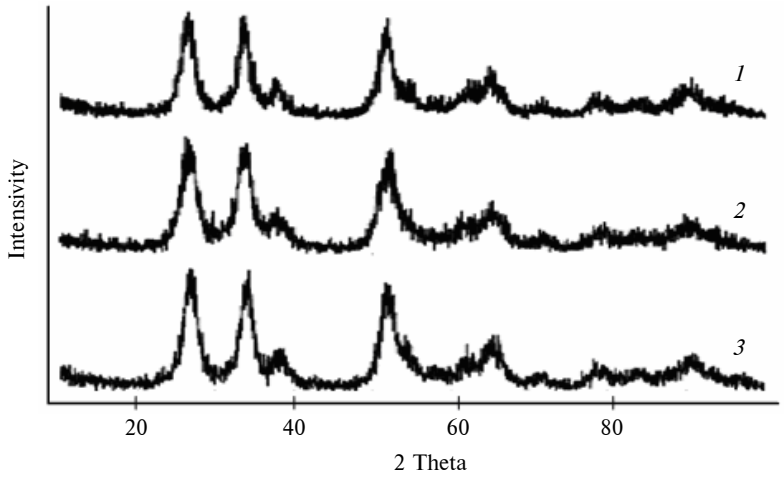



Fig. 4. The XRD patterns of $SnO_2$: *1* – sample 1; *2* – sample 2; *3* – sample 3

TEM images of synthesized $SnO_2$ powders (samples 1–3) are shown in Fig. 3. As seen from the TEM images, the all samples particle are enough small size (less than 10 nm) and globular-spongy structure that resembles of amorphous materials. For a crystal structure is necessary to increase the duration and/or time of thermal processing. So used sol-gel method provides a nanoparticle powder $SnO_2$. The template effects on the structure and size of the $SnO_2$ particles were not found.

Fig. 4 shows XRD patterns of obtained samples $SnO_2$ (samples 1–3). The structural parameters of $SnO_2$ presented in Table 1.

Most distinct peaks on XRD patterns correspond to (110), (101) and (211) crystal faces (according card № 1000062, USER (COD)). All diffraction lines can be indexed to the tetragonal rutile phase. The comparison of the defined lattice constants for the samples 1–3 with their standard values ($a$ = 0.476, $c$ = 0.318) shows that the crystalline lattice of $SnO_2$ in samples well-nigh was not deformed. All samples have little values of coherent scattering region (CSR), so the particles structure closer to the amorphous state. The crystallite size decreases from sample 1 (3.5 nm) to sample 3 (1.8 nm).

Fig. 4 presents TEM images of obtained $SnO_2$ samples (samples 4–7). According to the TEM images $SnO_2$ samples 3–7 there are more amorphous. The resulting diffraction patterns for these samples indicate what pure $SnO_2$ of rutile modification are obtained. The structural parameters of $SnO_2$ samples 3–7 presented in Table 1.

The comparison of the defined lattice constants for the samples 4–7 with their standard values shows some deformation in $SnO_2$ samples. All samples have even less crystallite size than samples 1–3, so the structure of particles still closer to the amorphous state. The crystallite sizes are in the region of 1 nm in all cases.

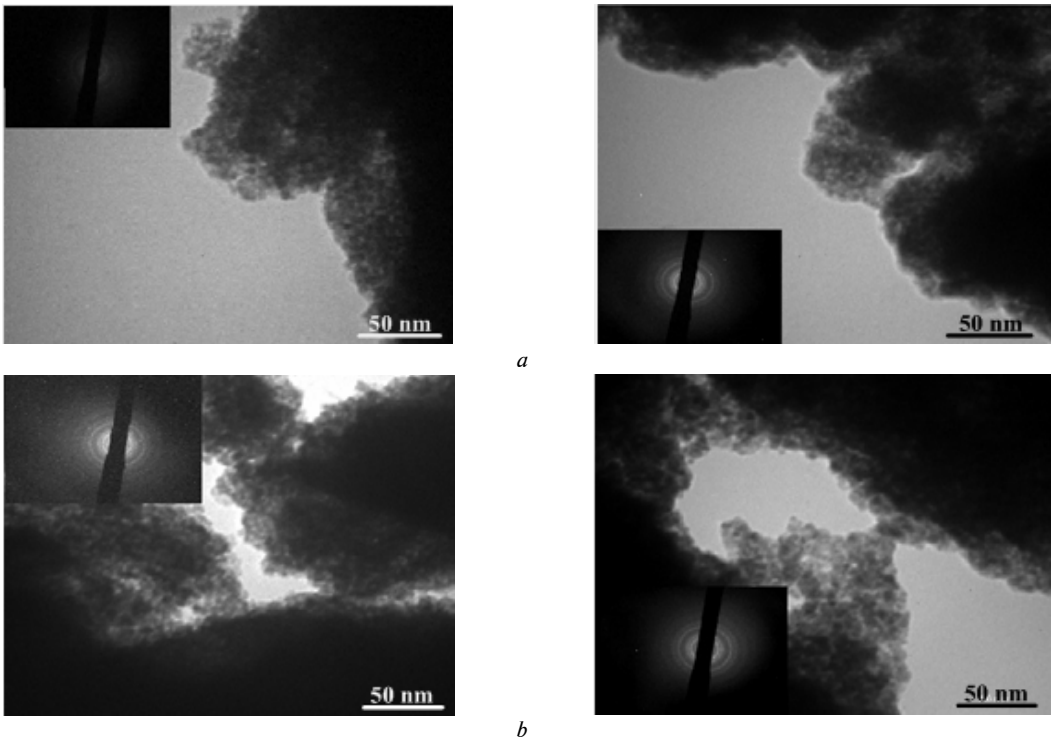
***Table* 1.** The structural parameters of $SnO_2$ samples 1–3

| Sample | hkl | 2θ, deg. | Crystalline size, nm | Lattice constant, nm | |
|---|---|---|---|---|---|
| | | | | *a* | *c* |
| 1 | 110 | 26.88 | 3.5 | 0.473 | 0.319 |
| | 101 | 33.77 | | | |
| | 211 | 52.09 | | | |
| 2 | 110 | 26.88 | 2.53 | 0.470 | 0.318 |
| | 101 | 33.77 | | | |
| | 211 | 52.09 | | | |
| 3 | 110 | 26.88 | 1.8 | 0.476 | 0.323 |
| | 101 | 33.77 | | | |
| | 211 | 52.09 | | | |

***Table* 2.** The structural parameters of $SnO_2$ samples 4–7

| Sample | Crystalline size, nm | Lattice constant, nm | |
|---|---|---|---|
| | | *a* | *c* |
| 4 | 0.93 | 0.471 | 0.328 |
| 5 | 0.83 | 0.473 | 0.323 |
| 6 | 1.0 | 0.479 | 0.312 |
| 7 | 1.3 | 0.476 | 0.318 |

Fig. 6 shows dependence of the absorption coefficient on wavelength for sample 3. Limit wavelength value determined from the obtained diagrams is 337 nm. The bandgap was calculated by the formula:




*a*

*b*

Fig. 5. TEM images of $SnO_2$ samples and corresponding SAED patterns: *a* – sample 4; *b* – sample 5; *c* – sample 6; *d* – sample 7

$$\Delta E = \frac{h \cdot c}{\lambda_{\lim it}},$$

where $h$ – Planck constant; $c$ – speed of light.

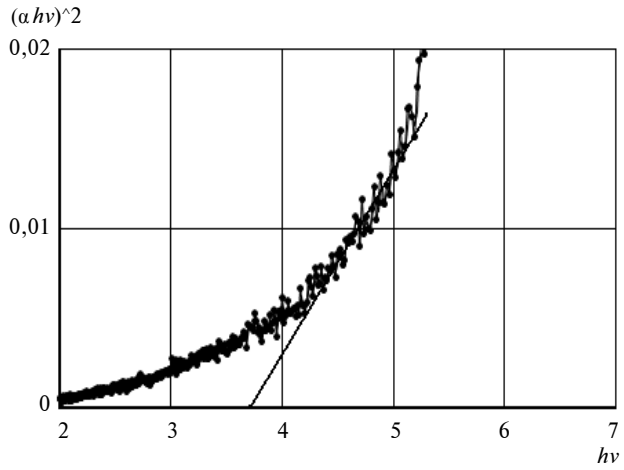



Fig. 6. Dependence of the absorption coefficient on wavelength

The value of the bandgap for sample 3 is equal to 3,69 eV. This value is in good agreement with literature data.

## Conclusions

The use of sol-gel method allows to obtain of nanoparticle $SnO_2$ powders, and template – significantly smaller crystallite size $SnO_2$ (to 0.8 nm). It is shown that minimum temperature for receiving of crystalline $SnO_2$ is 350 °C. The temperature and duration of calcination process desirable to increase for a better crystallization and more complete remove of residual template. The calculated value of the bandgap for $SnO_2$ is equal to 3,69 eV. This value is in good agreement with literature data.

In future the effect of temperature and duration of heat treatment on crystallite size and degree of crystallinity of $SnO_2$ will be investigated.

## List of literature

1. *Preparation* and characterization of $SnO_2$ nanoparticles by hydrothermal route / E.P. Ganesh, D.K. Dnyaneshwar, B.G. Vishwas et al. // Int. Nano Lett. – 2012 – № 2. – P. 1–5.
2. *Hydrothermal* synthesis of various hierarchical ZnO. Nanostructures and their methane sensing properties / Q. Zhou, W. Chen, L. Xu et al. // Sensors. – 2013. – № 13. – P. 6171–6182.
3. *Stabilization* of nanoscale Tin (IV) Oxide on the surface of Carbon nanotubes / T. Dontsova, I. Ivanenko, I. Astrelin et al. // J. Electrical Engineering. – 2014. – **2**(1). – P. 34–38.
4. *Fabrication* and characterization of wire-like $SnO_2$ / C.M. Liu, X.T. Zu, Q.M. Wei et al. // J. Physics. – 2006. – **39**. – P. 2494–2497.
5. *Нагірняк С.В., Донцова Т.А., Астрелін І.М.* Синтез та характеристика нанодисперсних порошків оксиду стануму (IV) з оксалату стануму (II) // Наукові вісті НТУУ "КПІ". – 2012. – № 2. – С. 151–155.
6. *Synthesis* and properties of Tin (IV) Oxide obtained by CVD method / S.V. Nagirnyak, V.A. Lutz, T.A. Dontsova at al. // Nanoscale Res. Lett. – 2015 (accepted for publication).
7. *Wang H., Rogach A.L.* Hierarchical $SnO_2$ Nanostructures: Recent Advances in Design // Chem. Mater. – 2014. – **26**, no. 1. – P. 123–133.

## References

1. E.P. Ganesh *et al.*, "Preparation and characterization of $SnO_2$ nanoparticles by hydrothermal route", *Int. Nano Lett.*, no. 2, pp. 1–5, 2012. doi:10.1186/2228-5326-2-17
2. Q. Zhou *et al.*, "Hydrothermal synthesis of various hierarchical ZnO. Nanostructures and their methane sensing properties", *Sensors*, no. 13, pp. 6171–6182, 2013. doi:10.3390/s130506171
3. T. Dontsova *et al.*, "Stabilization of nanoscale Tin (IV) Oxide on the surface of Carbon nanotubes", *J. Electrical Engineering*, vol. 2(1), pp. 34–38, 2014.
4. C.M. Liu *et al.*, "Fabrication and characterization of wire-like $SnO_2$", *J. Physics*, vol. 39, pp. 2494–2497, 2006. doi:10.1088/0022-3727/39/12/004
5. S.V. Nagirnyak *et al.*, "Synthesis and characterization of nanoscale powders tin (IV) oxide with Stanum (II) oxalate", *Naukovi Visti NTUU KPI*, no. 2, pp. 151–155, 2012 (in Ukrainian).

6. S.V. Nagirnyak *et al.*, "Synthesis and properties of tin (IV) oxide obtained by CVD method", *Nanoscale Res. Lett.*, 2015, vol. 10.
7. H. Wang *et al.*, "Hierarchical $SnO_2$ Nanostructures: Recent Advances in Design", *Chem. Mater.*, vol. 26, no. 1, pp. 123–133, 2014. doi: 10.1021/cm4018248

Т.А. Донцова

ВИКОРИСТАННЯ ТЕМПЛАТНОГО ЗОЛЬ-ГЕЛЬ МЕТОДУ ДЛЯ ОТРИМАННЯ НАНОЧАСТИНОК СТАНУМУ (IV) ОКСИДУ

**Проблематика.** Відомо, що наявність темплатів значно впливає на фізико-хімічні характеристики порошків, що синтезуються. Тому дослідження отримання порошків $SnO_2$ за наявності та відсутності темплатів відомим золь-гель методом становить науково-практичний інтерес.

**Мета дослідження.** Метою роботи є синтез наночастинок $SnO_2$ темплатним золь-гель методом з подальшою характеризацією отриманих порошків.

**Методика реалізації.** В роботі проведено синтез порошків стануму (IV) оксиду золь-гель методом з та без використання темплатів. Як темплати застосовували етиленгліколь та поліетиленгліколь з молекулярною масою 6000 (ПЕГ-6000).

**Результати дослідження.** Термічним аналізом було визначено мінімальну температуру для кристалізації гідратованих порошків стануму (IV) оксиду. Встановлено, що за заданих умов прожарювання утворюються полікристалічні порошки чистої рутильної модифікації з невисоким ступенем кристалічності та зі структурою, що наближена до аморфного стану. Показано, що золь-гель метод дає змогу отримувати нанокристалічні (0,8–3,5 нм) та нанодисперсні (10–15 нм) порошки стануму (IV) оксиду, а використання темплату ПЕГ-6000 у 2–4 рази знижує розмір кристалітів. Показано, що збільшення масового вмісту темплату ПЕГ-6000 з 1 до 10–75 % призводить до незначних спотворень кристалічної решітки стануму (IV) оксиду. Розрахована ширина забороненої зони за оптичними спектрами становить 3,69 еВ, що досить добре узгоджується з літературними даними.

**Висновки.** Використання золь-гель методу дає змогу отримати частинки $SnO_2$ в нанодіпазоні. Наявність темплату приводить до одержання стануму (IV) оксиду зі значно меншим розміром кристалітів (до 0,8 нм). Мінімальна температура для отримання кристалічного $SnO_2$ становить 350 °С.

**Ключові слова:** стануму (IV) оксид; наночастинки; золь-гель метод; темплат.

Т.А. Донцова

ИСПОЛЬЗОВАНИЕ ТЕМПЛАТНОГО ЗОЛЬ-ГЕЛЬ МЕТОДА ДЛЯ ПОЛУЧЕНИЯ НАНОЧАСТИЦ ОКСИДА ОЛОВА (IV)

**Проблематика.** Известно, что наличие темплатов значительно влияет на физико-химические характеристики синтезируемых порошков. Поэтому исследования по получению порошков $SnO_2$ в присутствии и отсутствии темплатов золь-гель методом представляет научно-практический интерес.

**Цель исследования.** Целью работы является синтез наночастиц $SnO_2$ темплатным золь-гель методом с последующей характеризацией полученных порошков.

**Методика реализации.** В работе синтезированы порошки оксида олова (IV) золь-гель методом с и без использования темплатов. В качестве темплатов применяли этиленгликоль и полиэтиленгликоль с молекулярной массой 6000 (ПЭГ-6000).

**Результаты исследования.** Термическим анализом определена минимальная температура для кристаллизации гидратированных порошков оксида олова (IV). Установлено, что при данных условиях термообработки образуются поликристаллические порошки чистой рутильной модификации с невысокой степенью кристалличности и со структурой, приближенной к аморфному состоянию. Показано, что золь-гель метод позволяет получать нанокристаллические (0,8–3,5 нм) и нанодисперсные (10–15 нм) порошки оксида олова (IV), а использование темплата ПЭГ-6000 в 2–4 раза снижает размер кристаллитов. Показано, что увеличение массового содержания темплата ПЭГ-6000 с 1 до 10–75 % приводит к незначительным искажениям кристаллической решетки оксида олова (IV). Рассчитанная по оптическим спектрам ширина запрещенной зоны составляет 3,69 эВ, которая хорошо согласуется с литературными данными.

**Выводы.** Использование золь-гель метода позволяет получить частицы $SnO_2$ в нанодипазоне. Наличие темплата приводит к получению оксида олова (IV) со значительно меньшим размером кристаллитов (до 0,8 нм). Минимальная температура для получения кристаллического $SnO_2$ составляет 350 °С.

**Ключевые слова:** оксид олова (IV); наночастицы; золь-гель метод; темплат.

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