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REGULAR ARTICLE

Electrochemical Synthesis of Zinc Oxide in the Presence of Surfactant TERGITOL 15-S-5

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In this work, we present the electrochemical synthesis of zinc oxide in the presence of surfactant TERGITOL 15-S-5. A sodium chloride solution was used as the electrolyte; a zinc block as the anode, and a steel plate as the cathode; TERGITOL 15-S-5 as the surfactant. The electrolyzer consists of a power supply B5-46, which ensures constant current during electrolysis; a voltmeter and ammeter to monitor the current strength and voltage; electrodes connected to the power supply and immersed in a 1 M sodium chloride solution (58.45 g/L) or a solution with the same concentration of sodium chloride and dissolved surfactant – TERGITOL 15-S-5 (from 1 to 4 g/L). The beaker containing the electrolyte solution was stirred with a magnetic stirrer and thermostated. In the electrochemical method, the surfactant content was varied (from 1 to 4 g/L). A total of 6 experiments were conducted. Six deposits were isolated and studied. Using the *X*-ray phase analysis, we established that the deposits are pure zinc oxide in the wurtzite modification (space group $P6_3mc$) and additional phases are not observed. SEM analysis also confirmed that the material contains only nanoparticles of zinc oxide. The crystalline structure of the obtained zinc oxide indicates that it can be modified by adding atoms with a smaller atomic radius compared to zinc atoms, as all octahedral voids are free, while only 2 out of 8 tetrahedral voids are filled with zinc atoms. The structure is non-centrosymmetric, suggesting that such materials may possess nonlinear optical properties. The zinc oxide particles have a plate-like shape with a width of 30-600 nm and a length of 50-2500 nm. All obtained deposits consist of nanosized particles with a thickness in the range of 20-40 nm. The addition of the surfactant TERGITOL 15-S-5 contributes to a slight increase in particle sizes.

Keywords: Electrochemical synthesis, Nanopowder, Zink oxide, Crystalline structure.

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1. INTRODUCTION

The development of nanotechnology has opened up new opportunities for creation of materials with unique properties and applications. One such material is zinc oxide (ZnO) [1] nanoparticles, which have attracted significant attention due to their potential applications in various fields, including optoelectronics, photocatalysis, and sensors.

One of the main reasons for the change in the physical and chemical properties of small particles as their sizes decrease is the increase in the relative proportion of "surface" atoms, which are in different conditions (coordination number, symmetry of the local environment, etc.) than the atoms in the bulk phase [2, 3]. From an energetic point of view, the reduction in particle size leads to an increase in the proportion of surface energy in its chemical potential [4, 5].

In semiconductor materials science, the sizes of synthesized nanoparticles and their dispersity are of great importance. Typically, preference is given to monodisperse powders [6]. To this end, various particle size stabilizers are added to the reaction mixtures. Water-soluble polymers and surfactants (surfactants) predominantly serve as stabilizers [7, 8]. The final morphology and texture of the material deposited by the electrolysis depend on the composition of the electrolyte, temperature, electrode potential or current density, as well as the duration of the electro-deposition process [9].

Peilot and Linkot were the first to demonstrate that direct electro-deposition of high-quality zinc oxide films from aqueous solutions is possible [10]. This work sparked great interest, leading to intensive research in this field. Conventional electrolyte baths for electro-depositing zinc oxide films usually contain chlorides, nitrates, or, less commonly, acetates. The presence of various organic molecules (for example, glucose, fructose, citric acid, tartrate, polyelectrolytes, etc.) significantly affects the structure, morphology, and properties of zinc oxide films. Typically, the electrochemical deposition of zinc oxide occurs in a three-electrode electrochemical cell: a silver chloride or calomel electrode is used as a reference electrode; a platinum wire or plate, graphite rod, or zinc plate serves as the counter electrode; and the working electrode is usually glass plates coated with ITO (indium-tin oxide coating) or, rarely, stainless steel; deposition conditions are galvanostatic or potentiostatic. ZnO coatings applied at room temperature or < 333 K are unstable; quality coatings are obtained only at higher temperatures (> 333 K).

Zinc oxide is also synthesized using an

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electrochemical method, employing asymmetric alternating current and two zinc electrodes in a sodium chloride aqueous solution at high temperatures [11]. The authors [12, 13] produced zinc oxide nanoparticles through the electrolysis of sodium chloride solution with two cylindrical zinc electrodes under direct current with periodic reversal of its direction. Electrolysis was conducted for a long time (4 hours) at a temperature of 98 ºC and low constant current density. The work [14] also describes a method for obtaining zinc oxide nanoparticles through the electrolysis of an aqueous sodium chloride solution using a two-electrode method at high constant current density without current reversal.

Therefore, searching for substances for the synthesis of monodispersed powders and films is highly relevant.

This work investigates for the first time the effect of the non-ionic surfactant TERGITOL 15-S-5 on the sizes of obtained powder-like deposits via a two-electrode electrochemical method.

2. EXPERIMENTAL DETAILS

Nanometer-sized zinc oxide deposits are obtained by electrolyzing an aqueous solution containing 58.45 g/L of sodium chloride and 15-S-5 with concentrations ranging from 0 to 4 g/L, in a galvanostatic mode using two electrodes – a steel cathode with a surface area of 5 cm² and a zinc anode block with a surface area of 25 cm² at a constant temperature of 90 ºC. During the experiment, the distance between the electrodes remains constant at 5 cm. A B5-46 device was used as the power source for direct current.

A constant current was passed through the electrolyte solution for 20 minutes. Sodium chloride (analytical grade) – 58.45 g is added to a 1 L volumetric flask and diluted to the mark with distilled water (at the temperature of the experiment). This results in a sodium chloride solution with a concentration of 1 M. The obtained solution is poured into a 400 mL beaker.

The zinc electrode is immersed in the beaker along with the steel electrode. The electrodes are connected to the power supply – the B5-46 rectifier using copper wires. The electrolyzer (the beaker with the electrolyte solution and the immersed electrodes, along with contact and standard thermometers and a magnetic stirrer) is placed in a thermostat. After this, the magnetic stirrer, rectifier, and stopwatch are turned on. Gas (hydrogen) is released at the cathode, the anode dissolves, and white particles begin to form immediately near it, settling at the bottom. After synthesis, the beaker is left to cool. Once cooled, the solution is decanted from the beaker and replaced with distilled water. After one hour, the solution is again decanted from the beaker and replaced with distilled water, and this process is repeated five times. Then, the sediment at the bottom of the beaker is transferred to a Petri dish and left to dry for a day at a temperature of 50 ºC, after which the obtained product is weighed.

The electrolysis proceeds according to the reaction:

$$Zn + H_2O \rightarrow ZnO\downarrow + H_2\uparrow.$$

The processes occurring at the electrodes are:

Anode (+): $Zn - 2\ e^- = Zn^{2+}$

Cathode (–): $2H_2O + 2\ e^- = 2OH^- + H_2$

Six experiments were conducted with a 1 M sodium chloride solution, differing in the concentration of surfactant 15-S-5: 0; 1; 1.5; 2; 3; 4 g/L. Conditions of electrochemical synthesis: the temperature is 90 °C, the concentration of sodium chloride is 1 M, the duration of the synthesis is 20 min, the area of the electrode is 5 cm², current strength 2.5 A, current density 0.5 A/cm².

Table 1 – The details of experiment

No	Content of 15-S-5, g/l	Current, V
1	0	5.8
2	1	5.3
3	2	6.0
4	3	6.2
5	4	6.0
6	1.5	5.2

The powder-like bulk and cathodic deposits were studied using *X*-ray phase analysis to determine the structure and particle sizes. The basis of *X*-ray analytical methods lies in two characteristics of these rays: their ability to penetrate matter and their ability to diffract from the particles that make up the substance. *X*-ray diffraction can be viewed as the reflection of these rays from atomic planes of a crystal and can be described by the Bragg-Wulff equation, according to which the maxima of the intensity of the diffraction pattern must satisfy the conditions:

$$n\lambda = 2d\ sin\theta, \qquad (1)$$

where n is an integer (1, 2, 3...), known as the order of reflection, λ is the wavelength of the *X*-ray radiation, d is the minimum interplanar distance, and θ is the angle of reflection. Knowing the wavelength of monochromatic (characteristic) *X*-ray radiation and the angles of reflection, one can calculate the interplanar distances, parameters of the unit cell, and establish the structure and spatial arrangement of atoms in the crystal lattice.

Based on the obtained diffraction pattern, the structure of the powder-like deposits is identified. From the resulting diffractograms, in addition to identifying the structure of the substance, one can determine the average particle size.

In his first work on determining particle sizes, Paul Scherrer proposed the following formula in 1918 [15]:

$$D = K\lambda / \beta\cos\theta, \qquad (2)$$

where D is the average particle size in nm; K is a constant whose value depends on the shape of the particle, which in our case is equal to 0.941; β is defined as the full width at half maximum of the peak measured in radians; λ is the wavelength of X-ray radiation, equal to 0.15418 nm; θ is the angle of diffraction for the maximum.

Scanning electron microscopy of the synthesized samples was carried out at the Institute of Geochemistry, Mineralogy and Ore Formation of the National Academy of Sciences of Ukraine named after M. P. Semenenko.

3. DISCUSSION

In all cases, sediment accumulated at the bottom of the electrolyzer. The samples were examined by *X*-ray phase analysis.

The diffractograms of nanoparticles are presented in Fig. 1.

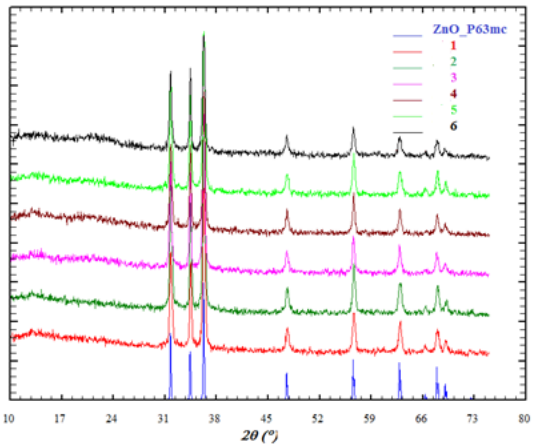

Fig. 1 – Diffractograms of precipitates obtained at 90 °C, NaCl concentration 1.0 mol/l, electrolysis time 20 min and current density 0.5 A/cm² without surfactant (sample 1) and in the presence of 15-S-5 (g/l): 1.0 (sample 2); 1.5 (sample 6); 2.0 (sample 3); 3.0 (sample 4); 4.0 (sample 5) and theoretical for zinc oxide of wurtzite modification (SG $P6_3mc$)

All powders consist only of wurtzite modified zinc oxide. Using the formula 2 calculate: the value of minimum and maximum for main reflection; half of these minimums; the value of the maximum of the highest reflection; the arithmetic mean between the value of the maximum and half the sum of the minimums; difference of values. Calculation of the parameters of the maximum reflection from the diffractogram for particles synthesized with different surfactant content at a NaCl concentration of 58.45 g/l, a current density of 0.5 A/cm² and a temperature of 90 °C is given in Table 2.

Table 2 – The value of the main reflection

No	Θ_1	Θ_2	$\Theta_1 - \Theta_2$	2Θ
1	36.48	36.13	0.35	36.28
2	36.47	36.14	0.33	36.3
3	36.42	36.1	0.32	36.25
4	36.46	36.13	0.33	36.3
5	36.46	36.14	0.32	36.3
6	36.43	36.09	0.34	36.3

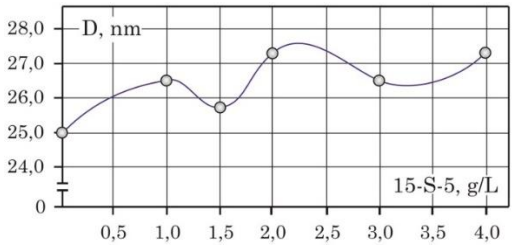

Fig. 2 – Dependence of the thickness of zinc oxide particles (nm) on the concentration of surfactant (*g/l*). Sample 1 was synthesized without surfactant, and samples 2, 3, 4, 5, and 6 were synthesized in the presence of one, respectively; 2; 3; 4; 1.5 g/L 15-S-5

After processing the diffractograms, the thickness of zinc oxide particles was calculated. The results of determinations of the half-width of the peak and the maximum of the angle θ, as well as the calculations of the average sizes for bulk and cathodic deposits obtained without surfactant and with it are given in Table 3. As can be seen from Table 3, the average thickness of the particles is in the range from 25 to 27.3 nm, i.e. their spread in thickness is insignificant. The average thickness of the particles is 26.4 nm. The obtained precipitates are nanosized.

Table 3 – The calculation of thickness with Sharrer's method

No	$\Theta_1 - \Theta_2$ (°)	B radian · 10^3	2Θ (°)	cos θ · 10^2	Content of 15-S-5 (g/L)	D (nm)
1	0.35	6.1	36.28	95.03	0	25
2	0.33	5.8	36.3	95.02	1	26.5
3	0.32	5.6	36.25	95.04	2	27.3
4	0.33	5.8	36.3	95.02	3	26.5
5	0.32	5.6	36.3	95.02	4	27.3
6	0.34	5.9	36.3	95.02	1.5	25.7

The results of the calculation are presented in Fig. 2.

In the work, SEM images were taken for samples 1-6. Images of these samples are shown in Fig. 3.

All particles are nanosized in thickness. It should also be noted that some particles have a tubular structure, that is, they are hollow inside. Such particles could be good catalysts.

The average length, width and thickness of particles in experiments 1-6 are shown in Table 4.

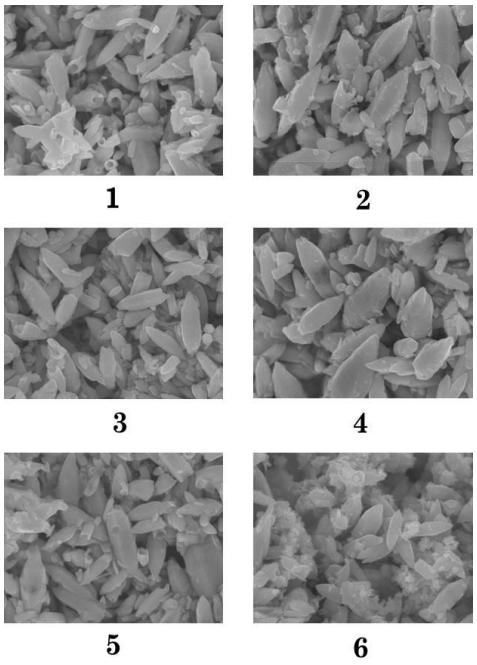

Fig. 3 – SEM images of samples 1 – 6, synthesized at a current density of 0.5 A/cm² in the presence of 15-S-5 concentration, respectively 0; 1; 2; 3; 4; 1.5 g/l

It can be seen that all particles have a lamellar structure with a width of 30 to 600 nm, a length of 50 nm to 2.5 nm, and a thickness of 20 to 40 nm. From here, we

are once again convinced that the average thickness of particles is calculated by Scherrer's method. Also, we constructed a graph based on the average particle size depending on the surfactant content (Fig. 4).

Table 4 – Dependence of the size of zinc oxide particles on the surfactant content

No	Content of 15-S-5 (g/L)	Average length, nm	Average width, nm	Average thickness, nm
1	0	329	133	25
2	1	365	160	26.5
3	2	329	137	27.3
4	3	413	181	26.5
5	4	338	146	27.3
6	1.5	314	132	25.7

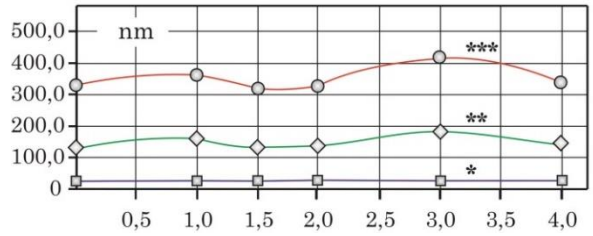

Fig. 4 – Dependence of the length, width and thickness of zinc oxide particles (nm) on the concentration of surfactant (*g/l*) (*-average length; **-average width; ***-average thickness)

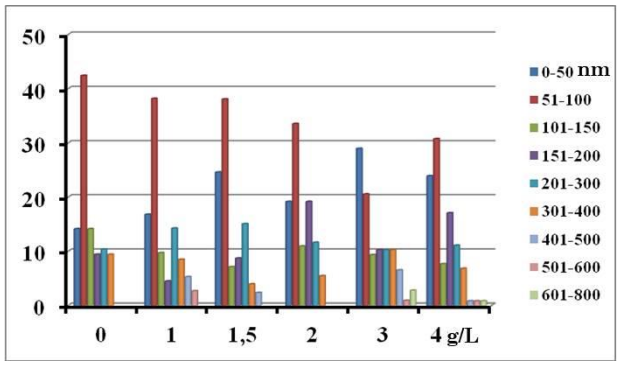

Fig. 5 – Histogram of the percentage of particles in each of the width ranges (*nm*) for zinc oxide samples depending on the surfactant content

Based on the results in Fig. 4, it can be concluded that there is no direct regularity in the dependence of the average particle size on the concentration of surfactants, however, for the length and width of the particles, a tendency towards their coarsening is visible.

Histograms of the dependence of percentages of the size range on the content of TERGITOL 15-S-5 (g/l) were created. There were a total of 9 ranges for histogram based on particle width and 11 ranges for length (Fig. 5).

As can be seen from fig. 6, in samples synthesized with a surfactant content of 0-2 *g/l* and 4 *g/l*, particles with a width of 51-100 nm prevail, and a sample with a 15-S-5 content of 3 *g/l* has more particles with a size of 0-50 nm.

According to the results of diffraction pattern analysis, we synthesized α-ZnO. The crystal structure of α-ZnO is presented in Fig. 6.

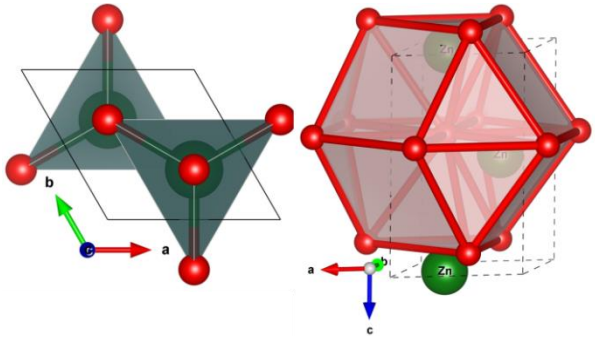

Fig. 6 – The project of a unit cell of α-ZnO (SG $P6_3mc$) and SCS (Second Coordination Setting of the structure) (cuboctahedron)

As it can be seen from Fig. 6, only two out of eight tetrahedral voids are occupied. Octahedral voids are not filled. It means that the structure may be modified by smaller atoms and in such a way to improve some physical properties, for instance, non-linear because the structure is asymmetric.

4. CONCLUSIONS

In conclusion, the powder-like deposits were synthesized for the first time by electrolyzing an aqueous solution with a constant sodium chloride content (1 M) and the surfactant TERGITOL 15-S-5 (in the range of 0 to 4 *g/L*) at a constant high current density (0.5 A/cm²) using a soluble zinc anode at a constant temperature of 90°C for a duration of 20 minutes. A total of 6 deposits were analyzed. *X*-ray phase analysis identified the formation of zinc oxide in the wurtzite modification (SG $P6_3mc$). The particle size was determined from the obtained diffractograms using the Scherrer method. The zinc oxide particles have a plate-like shape with a width of 30-600 nm and a length of 50-2500 nm. All obtained deposits consist of nanosized particles with a thickness in the range of 20-40 nm. The addition of TERGITOL 15-S-5 to the electrolyte contributes to a slight increase in the size of the powder-like deposits compared to synthesis without the surfactant.

REFERENCES

1. O.M. Yanchuk, J. Ebothé, A.M. El-Naggar, A. Albassam, L.V. Tsurkova, O.V. Marchuk, G. Lakshminarayana, S. Tkaczyk, I.V. Kityk, A.O. Fedorchuk, O.M. Vykhryst, I.V. Urubkov, *Physica E: Low-Dimensional Systems and Nanostructures.* **86**, 184 (2017).
2. Maryna Rohova, Vladyslav Kovalenko, Volodymyr Tkachenko, Inna Lych, Iryna Voloshyna. Green Biosynthesis of Zinc Nanoparticles, *ICAMS 2022 – 9th International Conference on Advanced Materials and Systems* (2022).
3. S.G. Rodrigo, *Optical Properties of Nanostructured Metallic Systems* (Springer Heidelberg Dordrecht: New York: 2012).
4. Tran X. Phuoc, Ruey-Hung Chen, *Combustion and Flame* **159** No 1, 416 (2012).
5. A. Van der Ven, Marnix Wagemaker, *Electrochem. Commun.* **11** No 4, 881 (2009).
6. Christopher B Murray, Cherie R Kagan, M.G. Bawendi,

Annual Rev. Mater. Sci. **30** No 1, 545 (2000).
7. Harish Bhardwaj, Sulekha Khute, Ram Kumar Sahu, Rajendra Kumar Jangde, *Current Nanoscience* **20** (2024).
8. S.V. Volkov, E.P. Kovalchuk, V.M. Ohenko, O.V. Reshetnyak, *Nanochemistry. Let's apply. Nanomaterials* (*K.: Naukova dumka*: 2008) [In Ukrainian].
9. G.H.A. Therese, P.V. Kamath, *Chem. Mater.* **12** No 5, 1195 (2000).
10. S. Peulon, D. Lincot, *Adv. Mater.* **8** No 2, 166 (1996).
11. Patent UA 85965 IPC C01G 9/02 C25B 1/00. V.Kh. Kozin, A.O. Omelchuk, A.V. Bliznyuk, V.D. Lytovchenko, Electrochemical synthesis of high purity zinc oxide using asymmetric alternating current. *Application* 05/29/2013, Publ. 10.12.2013, Bull. No. 23 (2013). [In Ukrainian]
12. Patent UA 92078 IPC C01G 9/00 C22B 19/00. Y.P. Lavorik, B.D. Nechiporuk, M.Yu. Novoseletskyi, O.V. Parasyuk, The method of electrolytic production of finely dispersed zinc oxide. Application 27.10.2008, Publ. 27.09.2010, Bul. No. 18 (2010). [In Ukrainian].
13. V.R. Gaevskyi, B.D. Nechiporuk, M.Yu. Novoseletskyi, B.P. Rudyk, *Ukr. Phys. J.* **58** No 4, 388 (2013).
14. A.H. Reshak, O.M. Yanchuk, D.I. Prots, *Int. J. Electrochem. Sci.* **9**, 6378 (2014).
15. P. Scherrer, *Mathematisch-Physikalische Klasse.* **2**, 98 (1918).

Електрохімічний синтез цинк оксиду в присутності поверхнево-активної речовини TERGITOL 15-S-5

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У цій роботі представлено електрохімічний синтез цинк оксиду в присутності поверхнево-активної речовини TERGITOL 15-S-5. Для електроліту використовувався розчин натрій хлориду; анодом слугував цинковий брусок, а катодом – сталевий лист; TERGITOL 15-S-5 використовувався як поверхнево-активна речовина. Електролізер складається з джерела живлення В5-46, яке забезпечує постійний струм під час електролізу; вольтметра та амперметра для моніторингу сили струму та напруги; електродів, підключених до джерела живлення та занурених у 1 М розчин натрій хлориду (58,45 г/л) або розчин з такою ж концентрацією натрій хлориду та розчиненої поверхнево-активної речовини – TERGITOL 15-S-5 (від 1 до 4 г/л). Розчин електроліту, що містився в посудині, перемішувався магнітною мішалкою та термостатувався. У електрохімічному методі вміст поверхнево-активної речовини варіювався (від 1 до 4 г/л). Було проведено всього 6 експериментів. Шість осадів були ізольовані та вивчені. Використовуючи рентгено-фазовий аналіз, встановлено, що осади є чистим цинк оксидом з модифікацією вюрциту (просторова група $P6_3mc$), і додаткові фази не спостерігаються. Аналіз SEM також підтвердив, що матеріал містить лише наночастинки цинк оксиду. Кристалічна структура отриманого цинк оксиду свідчить про те, що його можна модифікувати шляхом додавання атомів з меншим атомним радіусом порівняно з атомами цинку, оскільки всі октаедричні пустоти вільні, тоді як тільки 2 з 8 тетраедричних пустот заповнені атомами цинку. Структура є нецентросиметричною, що свідчить про те, що такі матеріали можуть володіти нелінійними оптичними властивостями. Частинки цинк оксиду мають пластинчасту форму з шириною 30-600 нм і довжиною 50-2500 нм. Усі отримані осади складаються з нанорозмірних частинок товщиною в діапазоні 20-40 нм. Додавання поверхнево-активної речовини TERGITOL 15-S-5 сприяє незначному збільшенню розмірів частинок.

Ключові слова: Електрохімічний синтез, Нанопорошок, Оксид цинку, Кристалічна структура.