JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **17** No 1, 01015(5pp) (2025)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **17** № 1, 01015(5cc) (2025)

OPEN ACCESS

REGULAR ARTICLE

Electrochemical Synthesis of Zinc Oxide in the Presence of Surfactant FARMACOAT

O.V. Smitiukh[1,*], O.M. Yanchuk[1,2], O.V. Marchuk[1], Ju.O. Khmaruk[1], M.M. Yatsyshyn[3], Oleksii A. Vyshnevskyi[4], I.I. Velymchanitsa[1]

[1] *Lesya Ukrainka Volyn National University, 43025 Lutsk, Ukraine*
[2] *Volyn Medical Institute, 43016 Lutsk, Ukraine*
[3] *Ivan Franko National University of Lviv, 79000 Lviv, Ukraine*
[4] *M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation NAS of Ukraine, 03142 Kyiv, Ukraine*

(Received 06 January 2025; revised manuscript received 20 February 2025; published online 27 February 2025)

In this work, we present the electrochemical synthesis of zinc oxide in the presence of the surfactant FARMACOAT from a sodium chloride solution and the corresponding surfactant concentration (in the range of 0 to 2.0 g/L). A total of 10 experiments were conducted, and X-ray phase analysis was performed on the synthesized samples. All powders do not contain impurity phases. The crystalline structure of the formed nanoparticles belongs to the hexagonal crystal system (Space group $P6_3mc$) and is non-centrosymmetric. According to the second coordination environment, the formed cuboctahedron contains three zinc atoms located in tetrahedral positions, which accounts for 3/8 of all tetrahedral voids. While the octahedral voids are empty, allowing for doping with such substances as transition metal atoms that have a tetrahedral environment and are characterized by small atomic radii (e.g., iron, nickel, cobalt). The obtained nanoparticles were also analyzed using SEM. From the obtained images, information regarding the width, length, and thickness of the particles was gathered. It is important to note that the width and length of the particles are quite significant; however, the thickness of the particles ranges from 25 to 29 nm. Overall, the largest number of particles (by width) is found in the range of 51 to 100 nm for surfactant concentrations from 0.2 to 1.4 g/L. With an increase in concentration, the number of particles shifts to the range of 151 to 200 nm. In terms of length, the smallest particles are in the range of 30 to 50 nm, while the largest reach up to 1.5, and occasionally even 2.5 μm. For samples synthesized in the presence of the lowest surfactant content, particles sized from 50 to 200 nm quantitatively prevail, whereas in the case of samples with the maximum surfactant content, particles range from 300 to 400 nm. Thus, at low surfactant concentrations, particle parameters are smaller, while with increasing surfactant concentration, both thickness and length significantly increase.

Keywords: Electrochemical synthesis, Nanoparticles, Zinc oxide, Crystallography project.

DOI: 10.21272/jnep.17(1).01015 PACS numbers: 61.46. + w, 82.45.Aa

1. INTRODUCTION

The development of fundamental and applied concepts regarding nanomaterials and nanotechnology in the coming years may lead to radical changes in many areas of human activity: materials science [1], energy, electronics, computer science, machine engineering [2], medicine [3], agriculture [4], and ecology [5]. Alongside computer-information technologies and biotechnology, nanotechnology serves as the foundation for the scientific and technological revolution in the 21st century. New optical properties of semiconductor-based nanoparticles have been discovered. It has been demonstrated that they are key components in the production of nanodevices. It has been proven that the properties of nanostructured materials change with the size and shape of the particles [6-8].

In semiconductor materials science, the size of synthesized nanoparticles and their dispersibility are of significant importance. Naturally, a preference is given to monodisperse powders. To this end, various particle size stabilizers are added to the reaction mixtures. Primarily, water-soluble polymers and surfactants serve as stabilizers [9-11]. Therefore, the search for such substances for the synthesis of monodisperse nanosized powders and films is relevant.

In this work, we investigate the effect of methylhydroxypropylcellulose (trademark Farmacoat) on the sizes of the obtained powdery precipitates using a two-electrode electrochemical method for the first time. We have been using this synthesis method for a long time due to its obvious advantages over others [10-15].

Farmacoat is methylhydroxypropylcellulose (where propylene oxide is used instead of ethylene oxide for molecular substitution). The aforementioned product has methoxy (DS) and hydroxypropoxy (MS) substitutions of 29 % and 9 %, respectively. The particle size is 50-70 microns. It is a good film-forming agent.

2. EXPERIMENTAL DETAILS

Nanosized zinc oxide deposits are obtained through the electrolysis of an aqueous solution containing 1 M sodium chloride and Farmacoat at a concentration of 0.2

* Correspondence e-mail: Smitiukh.Oleksandr@vnu.edu.ua

Cite this article as: O.V. Smitiukh et al., *J. Nano- Electron. Phys.* 17 No 1, 01015 (2025) https://doi.org/10.21272/jnep.17(1).01015

to 2.0 g/L in a galvanostatic mode with two electrodes – a steel cathode with a surface area of 5 cm^2 and a zinc cylindrical anode at a constant temperature of 90 °C. A magnetic stirrer was used to mix the electrolyte solution. The DC power source used was the B5-46 device. For 20 minutes, a constant current of 2.5 A was passed through the electrolyte solution. The numbering of samples, the content of surfactants, and the voltage during electrolysis are presented in Table 1.

Table 1 – The numbering of samples, the content of surfactants, and the voltage during electrolysis

No	Content of surfactant, g/l	Current, V
F1	0.2	5.0
F2	0.4	5.4
F3	0.6	5.4
F4	0.8	5.4
F5	1.0	5.4
F6	1.2	5.4
F7	1.4	4.8
F8	1.6	5.2
F9	1.8	5.6
F10	2.0	6.0

The extraction of synthesized nanopowders and the mechanism of electrolytic formation of zinc oxide are described in [10-15].

X-ray phase analysis has established that all samples are pure zinc oxide in the wurtzite modification. The peaks in all diffractograms completely coincide with the theoretical diffractogram for zinc oxide in the wurtzite modification (SG $P6_3mc$.) (Fig. 1a) and b).

The crystalline structure of the synthesized nanooxide can be described as a hexagonal close packing (Fig. 2c), in which zinc atoms are located in the tetrahedral voids.

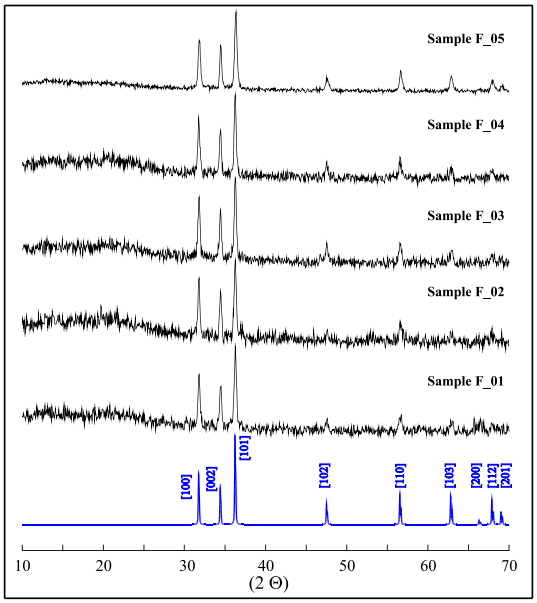

Fig. 1(a) – The diffractograms of the deposits obtained for samples F1-F5 at a temperature of 90 °C, an electrolysis time of 20 minutes, a current strength of 2.5 A, and different surfactant concentrations (g/L): F1 – 0.2; F2 – 0.4; F3 – 0.6; F4 – 0.8; F5 – 1.0"

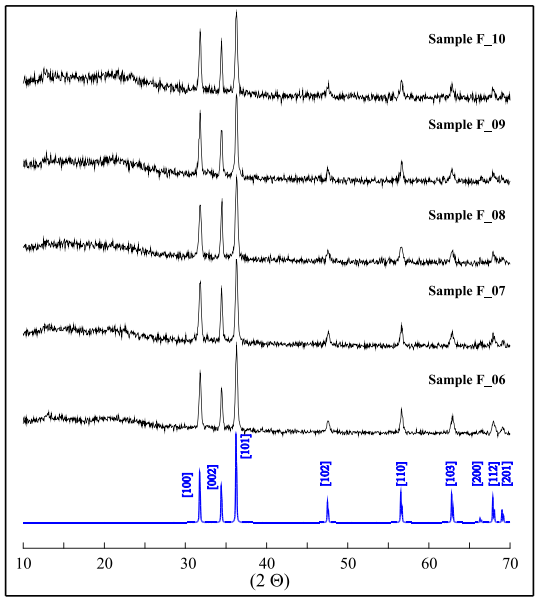

Fig. 1(b) – The diffractograms of the deposits obtained for samples F1-F5 at a temperature of 90 °C, an electrolysis time of 20 minutes, a current strength of 2.5 A, and different surfactant concentrations (g/L): F6 – 1.2; F7 – 1.4; F8 – 1.6; F9 – 1.8; F10 – 2.0"

The structure exhibits two types of interatomic distances: δ(Zn-O) = 1.9598 Å and δ(Zn-O) = 2.042 Å (Fig. 2a). Overall, the crystalline structure is characterized by a low packing coefficient of the unit cell. This indicates that, based on the second coordination environment (Fig. 2b), we see that 3/8 of the tetrahedral voids are filled with zinc atoms, while all octahedral voids remain unoccupied. Such a material can be doped with various elements, particularly iron or cobalt atoms, which can enhance the magnetic component, among other properties.

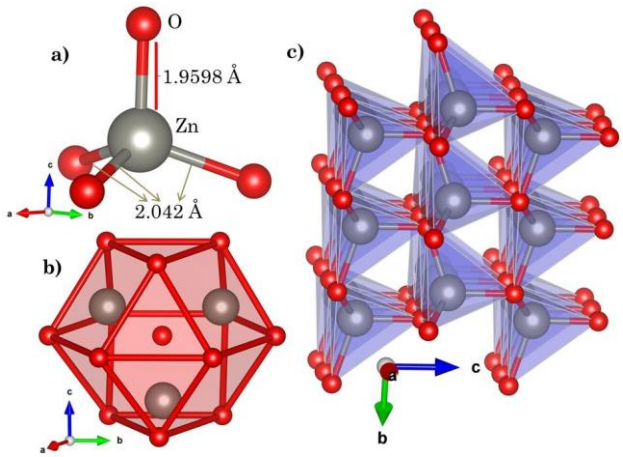

Fig. 2 – Projection of the crystalline structure of synthesized ZnO nanoparticles: a) tetrahedron $[ZnO_4]^{6-}$; b) second coordination environment; c) arrangement of tetrahedra $[ZnO_4]^{6-}$

The structure is non-centrosymmetric, indicating the potential for nonlinear optical properties to manifest. Considering all of the above, it is clear that the synthesized material has promising significance for materials science in the field of creating materials with controlled properties.

Using the Scherrer method [16], the average thickness of the obtained particles was determined from the maximum peaks of the diffractogram. It turned out that the thickness of the particles calculated by this method is in the range of 24 to 29 nm. The average particle thickness is 27 ± 2 nm. There is a trend toward an increase in thickness with an increase in surfactant content. This indicates that the particles are nanosized in terms of thickness.

In addition, the synthesized zinc oxide powders were studied using scanning electron microscopy (SEM). The obtained photographs for all samples and for the sample synthesized without surfactants are shown in Fig. 3.

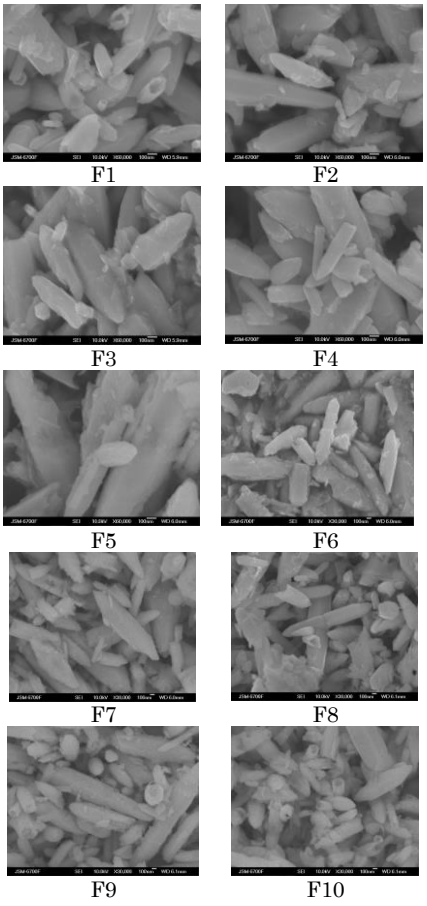

Fig. 3 – SEM images of samples synthesized at a current density of 0.5 A/cm² with FARMACOAT content of 0.2; 0.4; 0.6; 0.8; 1.0; 1.2; 1.4; 1.6; 1.8; 2.0 g/L

As can be seen from Fig. 3, all particles predominantly have paddle-like, shovel-like, singular tubular, and singularly destructured shapes.

To obtain information about the average particle sizes and the distribution of the number of particles by size in each photograph, all available particles were numbered and their linear dimensions were determined. The number of particles in each photograph varied. All particles were distributed into 16 ranges: 0-50; 51-100; 101-150; 151-200; 201-250; 251-300; 301-400; 401-500; 501-600; 601-700; 701-800; 801-900; 901-1000; 1001-1250; 1251-1500; 1501-2500 nm. Based on the sizes of individual particles, the average length and width of the particles for each synthesized sample were determined. The average sizes of the particles synthesized in the presence of surfactants were compared with the sample K1, synthesized without surfactants [11], and presented in Table 2.

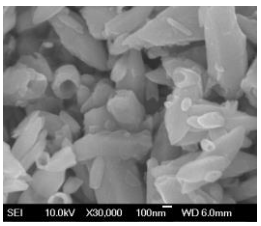

Fig. 4 – SEM image of sample K1 synthesized at a current density of 0.5 A/cm² without FARMACOAT content

Table 2 – Dependence of average zinc oxide particle size on FARMACOAT content

Content of Farmacoat, g/L	Length, nm	Width, nm	Thickness, nm
0	329	133	25.0
0,2	298	126	26.5
0,4	303	132	26.5
0,6	334	143	25.7
0,8	414	170	29.2
1,0	398	149	27.3
1,2	552	195	28.2
1,4	583	220	26.5
1,6	526	214	24.3
1,8	525	205	28.2
2,0	539	233	29.2

As can be seen from Table 2, the average particle sizes in terms of length range from 300 to 600 nm, and in terms of width, from 150 to 230 nm. This dependence is more clearly observed in Fig. 4. As indicated in Table 2 and Fig. 4, the addition of surfactants at concentrations of 0.2 to 0.4 g/L allows for the production of particles that are slightly smaller in average width and length compared to the sample obtained without the addition of surfactants. At other concentrations, larger particles are synthesized.

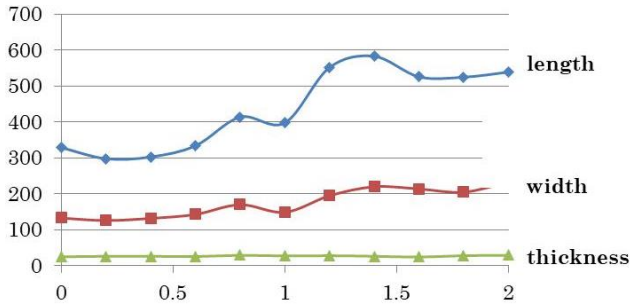

Fig. 5 – Dependence of the average linear dimensions of electrochemically synthesized zinc oxide particles on the FARMACOAT content

It should be noted that a significant dispersion of particle sizes was observed in each synthesized sample. In particular, the smallest particles were found to be between 30 and 50 nm, while the largest measured up to 1.5, and in some cases even 2.5 μm. The percentages of the number of particles falling into different size ranges were calculated. For the samples synthesized in the presence of the lowest surfactant content, particles sized between 50 and 200 nm predominated, whereas for the samples with the highest

surfactant content, particles sized between 300 and 400 nm were more common (Table 3 and Fig. 6).

Table 3 – Dependence of average zinc oxide particle size on FARMACOAT content

Sample	К1	F1	F2	F3	F4	F5
Content of Farmacoat, g/L	**0**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Range						
0-50	5.9	14.3	8.3	6.5	3.2	3.7
51-100	6.9	2.4	11.1	16.1	3.2	22.2
101-150	27.4	11.9	19.4	16.1	9.7	18.6
151-200	6.9	14.3	8.3	22.6	9.7	7.4
201-250	5.9	14.3	11.1	0	9.7	0
251-300	10.6	9.5	11.1	3.2	3.2	7.4
301-400	7.6	7.1	8.3	6.5	19.4	11.1
401-500	4	7.1	2.8	0	12.9	11.1
501-600	9.4	9.5	0	3.2	6.5	0
601-700	4.9	2.4	5.6	12.9	3.2	0
701-800	6.9	0	5.6	9.7	9.7	3.7
801-900	0	4.8	5.6	0	3.2	0
901-1000	0.9	2.4	0	0	3.2	0
1001-1250	0.9	0	2.8	3.2	0	7.4
1251-1500	1.8	0	0	0	3.2	0
1501-2500	0	0	0	0	0	7.4
Sample	**F6**	**F7**	**F8**	**F9**	**F10**	
Content of Farmacoat, g/L	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**	
Range						
0-50	2.5	0	0	0	0	
51-100	2.5	5	0	4	0	
101-150	17.5	2.5	10	6	0	
151-200	12.5	7.5	7.5	6	6.1	
201-250	0	5	12.5	12	6.1	
251-300	7.5	10	7.5	10	6.1	
301-400	7.5	7.5	17.5	18	24.3	
401-500	2.5	15	5	12	15.1	
501-600	5	7.5	5	8	18.1	
601-700	7.5	13	10	4	9	
701-800	12.5	10	12.5	8	0	
801-900	0	0	0	2	3	
901-1000	2.5	2.5	2.5	0	0	
1001-1250	7.5	5	5	2	6.1	
1251-1500	12.5	5	0	2	6.1	
1501-2500	0	5	5	6	0	

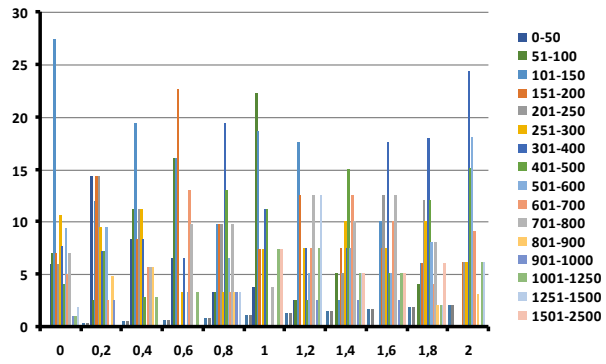

Fig. 6 – Histogram of the distribution of the percentage of the number of particles by length depending on the Farmacoat content

In Table 4 and Fig. 7, the distribution of the percentage of the number of particles by width is presented. As seen from Fig. 7 and Table 4, at a surfactant content ranging from 0.2 to 1.4 g/L, the largest number of particles falls within the range of 51 to 100 nm, while at a surfactant content of 1.6 to 1.8 g/L, particles in the range of 151 to 200 nm predominated. At a surfactant concentration of 2 g/L, the highest number of particles is found in the range of 251 to 300 nm. A significant dispersion of particle width is observed, ranging from 20 to 600 nm.

Table 4 – Distribution of the percentage of particle number by width by ranges

Sample	К1	F1	F2	F3	F4	F5
Content of Farmacoat, g/L	**0**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Range						
0-50	14.3	21.4	11.1	19.3	3.2	25.9
51-100	42.6	33.4	38.9	22.6	25.6	33.4
101-150	14.3	14.3	19.4	19.3	22.6	11.1
151-200	9.4	11.9	13.9	6.5	22.6	0
201-250	4	7.1	5.6	16.1	6.5	11.1
251-300	6.9	4.8	2.8	9.7	6.5	0
301-400	7.6	7.1	8.3	6.5	6.5	7.4
401-500	0	0	0	0	6.5	11.1
501-600	0.9	0	0	0	0	0
Sample	**F6**	**F7**	**F8**	**F9**	**F10**	
Content of Farmacoat, g/L	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**	
Range						
0-50	5	2.5	2.5	0	0	
51-100	32.5	25	15	18	6.1	
101-150	5	7.5	15	16	15.1	
151-200	17.5	18	22.5	20	21.3	
201-250	7.5	13	10	14	15.1	
251-300	15	10	10	18	24.3	
301-400	7.5	13	20	8	15.1	
401-500	7.5	10	5	6	0	
501-600	2.5	2.5	0	0	3	

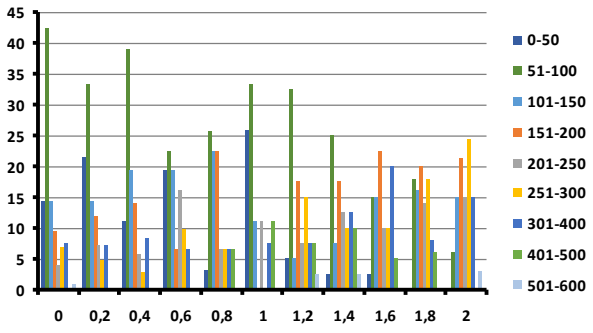

Fig. 7 – Histogram of the distribution of the percentage of the number of particles by width depending on the FARMACOAT content

Increasing the surfactant content contributes to an increase in the average length, width, and thickness of the particles.

3. 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 FARMACOAT (in the range of 0 to 2 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 10 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 133-233 nm and a length of 329-539 nm. All obtained deposits consist of nanosized particles with a thickness in the range of 25-29 nm.

REFERENCES

1. Bawoke Mekuye, Birhanu Abera, *Nanoselect* **4** No 8, 486 (2023).
2. Taha Basheer Taha, Azeez Abdullah Barzinjy, Faiq Hama Seaeed Hussain, Togzhan Nurtayeva, *Memories – Materials, Devices, Circuits and Systems* **2**, 100011 (2022).
3. Abid Haleem, Mohd Javaid, Ravi Pratap Singh, Shanay Rab, Rajiv Suman, *Global Health J.* **7** No 2, 70 (2023).
4. K. Neme, A. Nafady, S. Uddin, Y.B. Tola, *Heliyon* **7** No 12, e08539 (2021).
5. A. Aghababai Beni, H. Jabbari, *Res. Eng.* **15**, 100467 (2022).
6. Ashutosh Sharma, Goldie Oza, *Nanochemistry: Synthesis, Characterization and Applications, 1st Ed.* (*CRC Press*: 2023).
7. Kenneth J. Klabunde, Ryan M. Richards, *Nanoscale 2nd Ed.* (New Jersey: Published by John Wiley & Sons, Inc.: Hoboken: 2009).
8. Geoffrey A. Ozin, André C. Arsenault, *Nanochemistry: A Chemical Approach to Nanomaterials* (Cambridge: RSC Publishing: 2005).
9. S.V. Volkov, Ye.P. Kovalchuk, V.M. Ohenko, O.V. Reshetniak, *Nanokhimiia. Nanosystemy. Nanomaterialy* (K.: *Naukova dumka*: 2008) [In Ukrainian].
10. R.V. Korol, O.M. Yanchuk, O.V. Marchuk, V.F. Orlov, I. Moroz, O.L. Vyshnevskyi, *Phys. Chem. Solid State* **22** No 2, 380 (2021).
11. O.V. Smitiukh, O.M. Yanchuk, O.V. Marchuk et al., *J. Nano- Electron. Phys.* **16** No 5, 05032 (2024).
12. O.V. Smitiukh, O.V. Marchuk at al., *J. Nano- Electron. Phys.* **16** No 6, 06016 (2024).
13. A.H. Reshak, O.M. Yanchuk, D.I. Prots et al., *Int. J. Electrochem. Sci.* **9** No 11, 6378 (2014).
14. O.M. Yanchuk, J. Ebothe, A.M. El-Naggar et al., *Physica E* **86**, 184 (2017).
15. O.V. Smitiukh, O.M. Yanchuk, O.V. Marchuk et al., *J. Nano- Electron. Phys.* **16** No 1, 01024 (2024).
16. P. Scherrer, *Nachrichten von der Gesellschaft der Wissenschaften, Göttingen, Mathematisch-Physikalische Klasse* **2**, 98 (1918).

Електрохімічний синтез цинк оксиду в присутності поверхнево-активної речовини FARMACOAT

О.В. Смітюх[1], О.М. Янчук[1,2], О.В. Марчук[1], Ю.О. Хмарук[1], М.М. Яцишин[3], О.А. Вишневський[4], І.І. Велимчаниця[3]

[1] *Волинський національний університет імені Лесі Українки, 43025 Луцьк, Україна*
[2] *Волинський медичний інститут, 43016 Луцьк, Україна*
[3] *Львівський національний університет імені Івана Франка, 79000 Львів, Україна*
[4] *Інститут геохімії, мінералогії та рудоутворення ім. М.П. Семененка, 03142 Київ, Україна*

У роботі представлено електрохімічний синтез цинк оксиду в присутності поверхнево-активної речовини (ПАР) FARMACOAT з розчину натрій хлориду і відповідної концентрації ПАР (в діапазоні 0÷2,0 г/л). Було проведено 10 експериментів та для синтезованих зразків виконано Х-променевий фазовий аналіз. Усі порошки не містять домішкових фаз. Кристалічна структура утворених наночастинок належить до гексагональної сингонії (Пр.гр. $P6_3mc$) і є нецентросиметричною. Згідно з другим координаційним оточенням, утворений кубооктаедр містить три атоми цинку, які розташовані в тетраедричних позиціях, що становить 3/8 усіх тетраедричних пустот. В той час як октаедичні пустоти є порожніми, що дозволяє проводити допування таких речовин атомами перехідних металів, що мають тетраедричне оточення і характеризуються невеликими атомними радіусами (н-д залізо, нікол, кобальт). Також отримані наночастинки аналізували за допомогою СЕМ. З отриманих зображень отримали інформацію щодо ширини, довжини та товщини частинок. Важливо зазначити, що ширина і довжина частинок є досить значною, проте товщина частинок перебуває в межах 25-29 нм. В цілому найбільше число частинок (за шириною) міститься в діапазоні 51÷100 нм для 0,2 до 1,4 г/л ПАР. При збільшенні концентрації число частинок зміщуються в діапазон 151÷200 нм. За довжиною можна помітити найдрібніші частинки частинки 30÷50 нм, а найбільші 1,5, а подекуди і 2,5 мкм. Для зразків, синтезованих у присутності найменшого вмісту ПАР кількісно переважають частинки з розмірами від 50 до 200 нм, а у випадку зразків з максимальним умістом ПАР – від 300 до 400 нм. Таким чином, за невеликих концентрацій ПАР параметри частинок менші, а при збільшенні концентрації ПАР і товщина, і довжина суттєво зростають.

Ключові слова: Електрохімічний синтез, Наночастинки, Оксид цинку, Криталографічна проекція.