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REGULAR ARTICLE

Electrochemical Synthesis of Zinc Oxide in the Presence of Surfactant FK 06213

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In this study investigated the electrochemical synthesis of zinc oxide (ZnO) nanoparticles using the surfactant FK 06213. This substance is a non-ionic surfactant from the group of alcohol ethoxylates. FK 06213 is a yellow liquid with a characteristic odor, with a pH value at 20 °C of 7. The density at 20 °C is 0.95 g/cm³. The class of viscosity or consistency is kinematic at 40 °C: 60 mm²/s. The synthesis was conducted through galvanostatic electrolysis, where various parameter is surfactant concentration. Other parameters of electrolysis as temperature, duration, electrolyte concentration and current density were the same in all experiments. A total of 10 experiments were conducted. The presence of FK 06213 significantly impacted on the morphology and size distribution of ZnO particles, resulting in the formation of a white precipitate. Electrochemical analysis confirmed the oxidation of zinc at the anode and hydrogen evolution at the cathode, leading to the precipitation of ZnO. All obtained powders were studied using X-ray phase and structural analysis methods. The presence of other components was not established. According to the analysis results, the crystalline structure of the obtained samples belongs to the hexagonal system (space group P63mc), in which zinc atoms have a tetrahedral coordination with oxygen atoms. The average particle thickness varies from 22.4 to 32.4 nm. For concentrations of 0.2 and 0.5 g/L, the thickness values are the smallest – 22.4 and 23.2 nm, respectively. The average particle length ranges from 196 to 444 nm, while the width ranges from 62 to 184 nm. The unfilled octahedral voids are a significant factor that can be utilized for adding elements with larger atomic radii as alloying components to improve material properties. The non-centrosymmetry of this structure is an important argument in predicting the nonlinear optical properties of the obtained material.

Keywords: Electrochemical synthesis, Nanoparticles, Zinc oxide, Crystalline structure.

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1. INTRODUCTION

The rapid development of chemistry as a science is accompanied by the emergence of new chemical compounds obtained through cutting-edge synthesis methods. The study of the optical properties of semiconductors has played an important role in the development of these novel synthesis techniques.

ZnO is a well-known luminescent material, a semiconductor with direct bandgap transitions. Zinc oxide is a technologically important material. Zinc oxide nanoparticles are used for the production of transparent conductive films, surface acoustic wave devices, and piezoelectric receivers [1].

As a semiconductor, ZnO can be used for detecting UV-A radiation (300-400 nm). When doped with magnesium, the range can be shifted to the UV-B and UV-C (200-280 nm) region. It has some other interesting properties that make it very promising for functional optoelectronic devices. Due to the high binding energy of excitons in ZnO (60 meV), effective laser generation can be achieved at room and elevated temperatures [2].

Nanoscale zinc oxide particles are used in the production of solar cells, transparent conductive films, surface acoustic wave devices, piezoelectric receivers, gas sensors, and biological sensors [3]. There are many methods for obtaining zinc oxide nanoparticles [4]. We utilize the synthesis of zinc oxide nanopowders through the electrolysis of an aqueous sodium chloride solution with a soluble zinc anode [5-9]. One of the factors that influence the properties of the synthesized particles is the addition of substances that can potentially alter particle sizes [7].

In this work, the electrolytic synthesis of zinc oxide was conducted using a surfactant with the trade name FK 06213. This substance is a non-ionic surfactant from the group of alcohol ethoxylates. FK 06213 is a yellow liquid with a characteristic odor, with a pH value at 20 °C of 7. The density at 20 °C is 0.95 g/cm³. The class of viscosity or consistency is kinematic at 40 °C: 60 mm²/s.

2. EXPERIMENTAL DETAILS

Nanometer-sized zinc oxide deposits are obtained through the electrolysis of an aqueous solution containing 1M sodium chloride and one of the surfactant FK 06213 with a concentration ranging from 0.1 to 1 g/L in

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a galvanostatic mode with two electrodes – a steel cathode with a surface area of 5 cm² and a cylindrical zinc anode at a constant temperature of 90 ºC. A magnetic stirrer was used to mix the electrolyte solution.

As a power source for the direct current, we used the B5-46 device. A constant current was passed through the electrolyte solution for 20 minutes.

For the experiments, approximately 200 ml of electrolyte solution is required. The solutions were prepared in volumetric flasks of 200 or 250 ml. To do this, we weighed 11.69 g (for 200 ml) or 14.61 g of sodium chloride (for 250 ml) and the corresponding mass of surfactant calculated from 0.1 to 1 g/L and transferred the weighed amounts into volumetric flasks, adding distilled water. The volumetric flasks were brought up to the mark in a thermostat at the experimental temperature (90 °C). The resulting solution was poured into a 400 ml beaker. The zinc electrode was weighed and immersed in the beaker along with the steel electrode. The electrodes were connected to the power source using copper wires.

The electrolyzer (a beaker with the electrolyte solution and immersed electrodes, along with contact and regular thermometers) was placed in the thermostat. After this, the magnetic stirrer, rectifier, and stopwatch were turned on.

Gas (hydrogen) was released near the cathode, the anode dissolved, and particles of white color began to form immediately around it, settling at the bottom.

After synthesis, the beaker was left to cool. A white precipitate with small gray patches remained at the bottom of the beaker. After cooling, the solution was poured off from the beaker (decanted) and filled with distilled water again. The following day, the solution from the beaker was poured off again and distilled water was added once more, and this process continued until the solution became clear and stopped foaming. Then, the precipitate at the bottom of the beaker was transferred to a Petri dish and left to dry for a day at a temperature of 50 °C, after which the obtained product was weighed. The zinc electrodes used during synthesis were air-dried and weighed. The mass of the anode decreased.

Electrolysis occurs according to the reaction:

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

The processes occurring at the electrodes are:
Anode (+): $Zn - 2e^- \rightarrow Zn^{2+}$
Cathode (–): $2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$

In total, 10 experiments were conducted, differing in the content of surfactant FK 06213 – from 0.1 to 1.0 g/L. The initial temperature varied from 89.5 °C to 90.3 °C; current strength was 2.5 A; current density was 0.5 A/cm²; electrolysis time was 20 minutes.

Table 1 – The details of experiment

No	FK 06213 content, g/l	Current, V
I1	0.1	6.0
I2	0.2	6.2
I3	0.3	5.9
I4	0.4	5.2
I5	0.5	5.0
I6	0.6	4.9
I7	0.7	4.8
I8	0.8	4.3
I9	0.9	4.8
I10	1.0	4.9

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's equation, according to which the maxima of the intensity of the diffraction pattern must satisfy the conditions:

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

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 [10]:

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

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 [8].

3. DISCUSSION

The diffractograms of nanoparticles are presented in Fig. 1-2. Reflections of all diffractograms completely coincide with the theoretical diffractogram for wurtzite-modified zinc oxide (SG $P6_3mc$).

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.

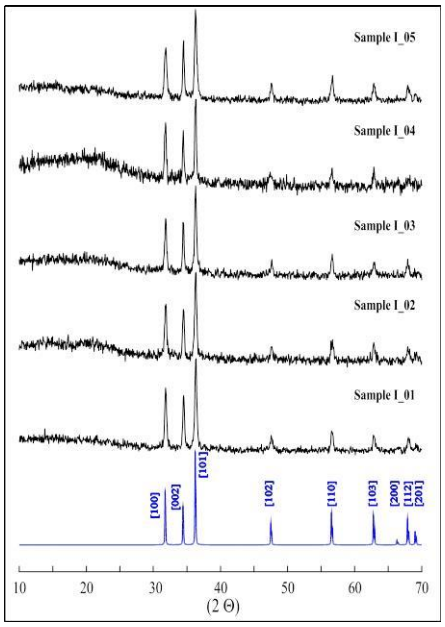


Fig. 1 – Diffractograms of volumetric precipitates obtained for samples I1-I5 at a temperature of 90 °C, time of electrolysisis 20 min, current strength of 2.5 A and different surfactant content (g/l): I1 –0.1; I2 –0.2; I3 – 0.3; I4 – 0.4; I5 – 0.5 g/l

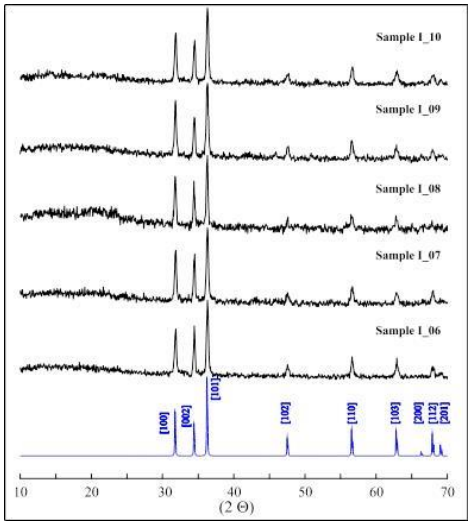


Fig. 2 – Diffractograms of volumetric precipitates obtained for samples I1-I5 at a temperature of 90 °C, time of electrolysisis 20 min, current strength of 2.5 A and different surfactant content (g/l): I6 – 0,6; I7– 0,7; I8 – 0,8; I9 – 0,9; I10 – 1,0 g/l

Table 2 – The value of the main reflection

No	Θ_1	Θ_2	$\Theta_1 - \Theta_2$	2Θ
I1	36.49	36.15	0.34	36.35
I2	36.49	36.10	0.39	36.30
I3	36.46	36.12	0.34	36.30
I4	36.42	36.12	0.30	36.35
I5	36.47	36.10	0.37	36.35
I6	36.46	36.13	0.33	36.25
I7	36.45	36.14	0.31	36.30
I8	36.39	36.12	0.27	36.30
I9	36.46	36.12	0.34	36.30
I10	36.47	36.14	0.33	36.30

After processing the diffractograms, the thickness of zincoxide 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 are given in Table 3.

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

No	Θ_1-Θ_2 (°)	β radian $\cdot 10^3$	2Θ (°)	$\cos\theta \cdot 10^2$	FK 06213 content of, g/l	D (nm)
I1	0.34	5.93	36.35	95.011	0.1	25.7
I2	0.39	6.81	36.30	95.024	0.2	22.4
I3	0.34	5.93	36.30	95.024	0.3	25.7
I4	0.30	5.24	36.35	95.011	0.4	29.2
I5	0.37	6.46	36.35	95.038	0.5	23.6
I6	0.33	5,76	36.25	95.024	0.6	26.5
I7	0.31	5.41	36.30	95.024	0.7	28.2
I8	0.27	4.71	36.30	95.024	0.8	32.4
I9	0.34	5.93	36.30	95.024	0.9	25.7
I10	0.33	5.76	36.30	95.024	1.0	26.5

The results of the calculation are presented in Fig. 3.

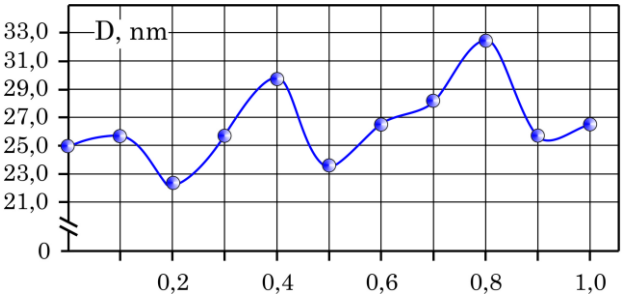
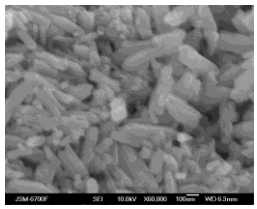
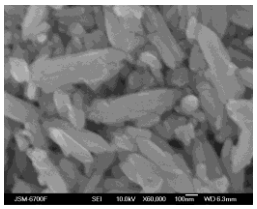


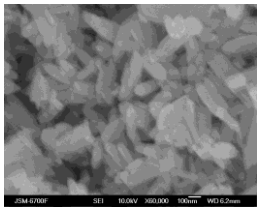
Fig. 3 – Dependence of thethickness (nm) of zinc oxide particles synthesized by electrolysis on the content of FK 06213 (g/l)



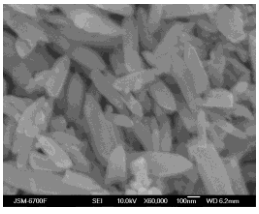
I1



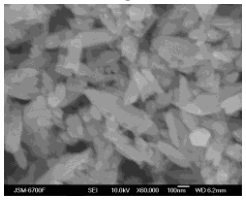
I2



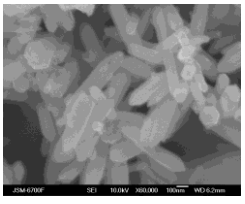
I3



I4



I5



I6

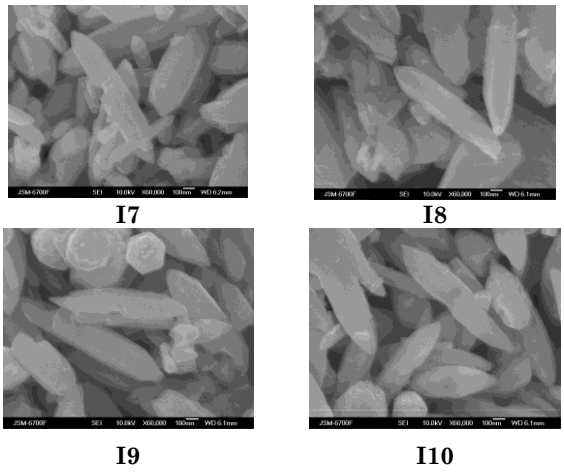


Fig.4 – SEM images of zinc oxide samples synthesized with different concentrations of surfactant FK 06213 (g/l): I1 – 0.1; I2 – 0.2; I3 – 0.3; I4 – 0.4; I5 – 0.5; I6 – 0.6; I7 – 0.7; I8 – 0.8; I9 – 0.9; I10 – 1.0.

We investigated the images and calculated the dimensions. The results of SEM analysis is presented in Fig. 4.

As can be seen in fig. 3, the influence of FK 06213 content on the average thickness of zinc oxide powder particles is insignificant. The addition of surfactant leads to a significant spread of particle thickness values. This particle size varies from 22.4 to 32.4 nm. The average value of the particle thickness is 26.6 ±2.0 nm.

After processing the results of SEM studies, the average length and width of the synthesized particles were determined (Table 4) and the distribution of the number of particles by ranges (histogram in Fig. 5).

Table 4 – The average particle size of zinc oxide when adding FK 06213

FK 06213 content of, g/l	Average length, nm	Average width, nm	Average thickness, nm
0.1	329	133	25
0.2	157	62	25.7
0.3	210	81	22.4
0.4	202	77	25.7
0.5	270	96	29.2
0.6	196	79	23.2
0.7	310	110	26.5
0.8	409	131	28.2
0.9	408	160	32.4
1.0	444	184	25.7

This dependence is more clearly observed in Fig. 5. As can be seen from the Table 4 and Fig. 5, the addition of surfactant from 0.1 to 0.6 g/l makes it possible to obtain particles smaller in average length and width compared to the sample obtained without the addition of surfactant. At other concentrations, larger particles were synthesized.

In Fig. 6 histogram of the distribution of the percentage of the number of particles by length is shown. At the content of 0.1 and 0.3 g/l of surfactant, the largest number of particles is in the range of 51÷100 nm, and at the content of 0.4, 0.6, 0.7 and 0.9 g/l, particles in the range of 301 prevail ÷400 nm. However, in the absence of surfactant and at concentrations of 0.2, 0.5 and 0.8 g/l, the largest number of particles is in the range of 101÷150 nm. Also, at a surfactant concentration of 1 g/l, the largest number of particles is in the range of 501÷600 nm.

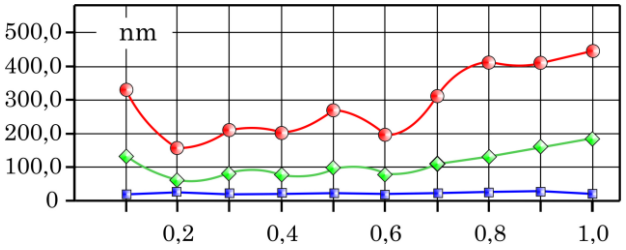


Fig. 5 – Dependence of the average linear dimensions of electrochemically synthesized zinc oxide particles on the content of FK 06213

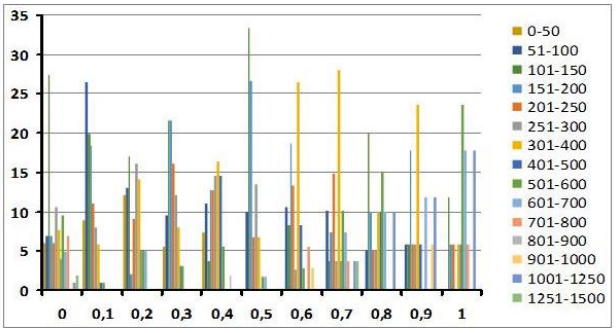


Fig. 6 – Distribution of the percentage of the number of particles by length depending on the content of FK 06213

According to the results of diffraction pattern analysis, we synthesized α-ZnO. The crystal structure of α-ZnO is presented in Fig. 7.

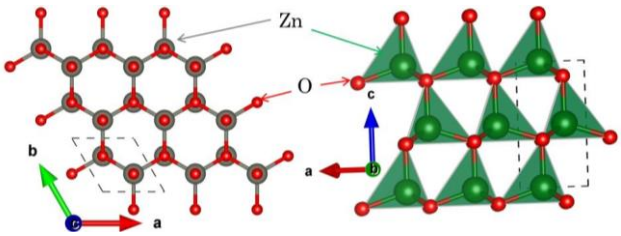


Fig. 7 – The project of a unit cell of α-ZnO (SG $P6_3mc$) and FCS (First Coordination Setting of the structure) tetrahedral of Zn atoms

As it can be seen from Fig. 7, 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.

The presence of FK 06213 does not result in significant particle reduction as it is with TERGITOL 15-S-5 in the work [11].

4. CONCLUSIONS

An electrochemical synthesis of zinc oxide was carried out by electrolysis of a 1 M aqueous solution of sodium chloride with a surfactant content of FK 06213

from 0.1 to 1 g/l with a soluble zinc anode at a constant temperature of 90 °C, electrolysis duration of 20 min, and a current density of 0.5 A/cm². The effect of surfactant content on particle size is controversial, so it cannot be considered a stabilizer of particle size, although at low concentrations, smaller particles are formed than in the sample synthesized with out the addition of surfactant.

This study highlights the potential of electrochemical methods for synthesizing ZnO nanomaterials with tailored properties through the strategic use of surfactants. Future research could explore the application of different surfactants and their effects on the electrochemical synthesis process, as well as the characterization and potential applications of the produced ZnO nanoparticles in fields such as catalysis, photovoltaics, and biomedical applications. The findings contribute to a deeper understanding of the electrochemical synthesis mechanisms and open avenues for further innovation in nanomaterial production.

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Електрохімічний синтез цинк оксиду в присутності поверхнево-активної речовини FK 06213

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У цьому дослідженні досліджено електрохімічний синтез наночастинок оксиду цинку (ZnO) з використанням поверхнево-активної речовини FK 06213. Ця речовина є неіонною поверхнево-активною речовиною з групи алкоголь етоксилатів. FK 06213 – жовта рідина з характерним запахом, зі значенням pH при 20 °C 7. Густина при 20 °C становить 0,95 г/см ³. Клас в'язкості або консистенції кінематичний при 40 °C: 60 мм²/с. Синтез проводився за допомогою гальваностатичного електролізу, де змінним параметром є концентрація поверхнево-активної речовини. Інші параметри електролізу, такі як температура, тривалість і густина струму були однаковими у всіх експериментах, змінювали лише концентрацію електроліту Всього було проведено 10 експериментів. Наявність FK 06213 справило значний вплив на морфологію і розподіл розмірів частинок ZnO. Електрохімічний аналіз підтвердив окиснення цинку на аноді та виділення водню на катоді, що призвело до осадження ZnO. Всі отримані порошки вивчалися за допомогою фазового та структурного X-променевого аналізу. Наявність інших компонентів не було встановлено. За результатами X-променевого аналізу кристалічна структура отриманих зразків належить до гексагональної системи (просторова група $P63mc$), в якій атоми цинку мають тетраедричне оточення з атомів оксигену. Середня товщина частинок варіюється від 22,4 до 32,4 нм. Для концентрацій 0,2 і 0,5 г/л значення товщини є найменшими – 22,4 і 23,2 відповідно. Середня довжина частинок є в межах 196÷444 нм, а ширина – 62÷184 нм. Незаповненість октаедричних пустот є вагомим фактором, який можна використати з метою додавання елементів з більшим атомних радіусом як легуючого компонента для покращення властивостей матеріалу. Нецентросиметричність цієї структури є важливим аргументом в прогнозуванні нелінійно-оптичних властивостей отриманого матеріалу.

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