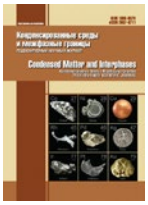


ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2021.23/3677

Synthesis and properties of nanosized ZnO/wood composite

E. V. Tomina[1,2]✉, A. A. Pavlenko[2], A. I. Dmitrenkov[1], S. A. Neminushchaya[1]

[1]Voronezh State University of Forestry and Technologies named after G. F. Morozov, 8 Timiryazeva ul., Voronezh 394087, Russian Federation

[2]Voronezh State University, 1 Universitetskaya pl., Voronezh 394018, Russian Federation

Abstract

The aim of the study was to synthesise a ZnO/silver birch wood (*Bétula péndula*) nanocomposite and evaluate its physical and mechanical properties in comparison with an unmodified natural polymer.

Using the sol-gel method, we synthesised almost spherical impurity-free zinc oxide nanoparticles with a predominant particle size of about 20 nm. Amorphous hydrated $Zn(OH)_2$ was impregnated into the wood material at the gel formation stage. It resulted in the reaction of zinc hydroxide decomposition with the formation of ZnO nanoparticles in the wood as a nanoreactor.

The hydrophobic properties of the surface of ZnO/silver birch wood nanocomposite improved significantly (the contact angle of wetting doubled). Its moisture and water resistance decreased (2-5 times and 30%, respectively). The nanocomposite also showed less swelling in the radial (8-10 times) and tangential (2.6-10 times) directions in comparison with natural wood.

Keywords: Zinc oxide, Sol-gel synthesis, Nanoparticles, Silver birch wood (*Bétula péndula*), Impregnation, Modification

Acknowledgements: the research results were partially obtained using the equipment of the Centre for Collective Use of Scientific Equipment of Voronezh State University. URL: http://ckp.vsu.ru.

For citation: Tomina E. V., Pavlenko A. A., Dmitrenkov A. I, Neminushchaya S. A. Synthesis and properties of nanosized ZnO/wood composite. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23(4): 578–584. https://doi.org/10.17308/kcmf.2021.23/3677

Для цитирования: Томина Е. В., Павленко А. А., Дмитренков А. И, Неминущая С. А. Синтез и свойства композита наноразмерный ZnO/древесина. *Конденсированные среды и межфазные границы*. 2021;23(4): 578–584. https://doi.org/10.17308/kcmf.2021.23/3677

✉ Elena V. Tomina, e-mail: tomina-e-v@yandex.ru

1. Introduction

Nanocomposites containing nanosized ZnO are currently a large group of in-demand materials for a variety of applications. This is due to the unique combination of their properties, the availability of raw materials, and the possibility of creating economical and environmentally friendly industries [1]. The synthesis and study of the properties of nanocomposites based on polymers is one of the priority areas due to the wide variety of functional properties of such nanomaterials. There are two main ways to synthesise polymer nanocomposites: via physical mixing of polymers and nanostructured materials by mechanical milling and diffusion in liquid or gas using ultrasonic treatment, etc. [2, 3], and by the synthesis of nanoparticles in a polymer matrix as a result of chemical reactions [4].

Nanosized zinc oxide is used as a sulphur vulcanisation activator for natural and synthetic rubbers, and as a vulcanising agent for some elastomers containing functional groups such as -Cl, -COOH, etc. [5, 6]. Compared to bulk material of the same composition, zinc oxide nanoparticles increase the rate of vulcanisation and improve the mechanical properties of the samples. When synthesising composites, it is important to establish a correlation between the synthesis conditions, the content of the composite, and its physico-chemical and performance characteristics [7].

Wood is a renewable, natural polymer material. Currently, scientists are working on improving the properties of wood by impregnating it with various compositions that are combustible, toxic (carcinogenic), change the colour of wood, or have a pungent and persistent odour, a limited lifetime, flammable, etc. There is also a promising alternative approach: the synthesis of nature-like nanocomposites with improved functional properties based on low-value wood. The capillary-porous structure of wood can act as an excellent matrix for the impregnation of nanoparticles or their synthesis in wood as in a nanoreactor. Modifying natural wood with nanosized zinc, titanium, or magnesium oxide particles gives the wood surface super-hydrophobic properties and increases its bio-resistance [8–11].

The aim of the work was to synthesise a ZnO/silver birch nanocomposite and to evaluate its physical and mechanical properties compared to the unmodified wood.

2. Experimental

To synthesise zinc oxide, we used one of the "soft chemistry" methods, the sol-gel method. It allowed us to produce nanomaterials with a narrow particle-size distribution at relatively low temperatures. As a precursor, we used zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$ (chemically pure grade, GOST 5106-77). A 20% NaOH solution (GOST R 55064-2012) was used as the precipitant. First, a 0.5 M solution of $Zn(NO_3)_2$ was introduced drop by drop to the boiling water. After the salt had been added, we boiled the mixture for a few more minutes until a sol was formed. The resulting sol was cooled to room temperature, then a solution of sodium hydroxide was added in the amount necessary for complete precipitation of Zn^{2+} cations. The resulting gel was stirred for some time.

To characterise the zinc oxide nanoparticles, the gel was separated using a vacuum filter, washed with distilled water, and dried at room temperature until a stable weight. The gel was then annealed in air at 240 °C for 2 h. To study the phase composition of the powder, we used X-ray diffraction (XRD, Empyrean B.V. X-ray diffractometer with a Cu anode (λ = 1.54060 nm)). The scanning was performed within a range of angles 2θ = 0–80° with a step of 0.1. The size of the coherent scattering regions (CSRs) in zinc oxide samples was calculated based on the XRD data using the Scherrer formula (1):

$$D_{hkl} = \frac{k \cdot \lambda}{\beta_{hkl} \cdot \cos\theta} \quad (1)$$

where D_{hkl} is the average particle size, Å, k is the correction factor (k = 0.9 for spherical particles), λ is the X-ray tube wavelength, θ is the position of the peak maximum in degrees, and β_{hkl} is the intrinsic physical broadening of the diffraction maximum in radians.

The size and morphology of the synthesised powder particles were determined by transmission electron microscopy (TEM, CarlZeiss Libra-120 transmission electron microscope).

To study the effect of zinc oxide nanoparticles on the properties of a natural polymer material,

we chose samples of silver birch wood (*Bétula péndula*) from the experimental forestry of Voronezh State University of Forestry and Technologies named after G. F. Morozov. This birch is one of the most common hardwoods growing in the Russian Federation. For the synthesis of the ZnO/wood nanocomposite, silver birch (*Bétula péndula*) samples, pre-dried at 103 °C, were placed in the gel for 30 min, then dried in a desiccator for 6 h at 110 °C.

To determine their moisture absorption qualities, the nanocomposite samples were dried to an absolutely dry state according to the requirements of GOST 16483.7-71 and weighed with an error of not more than 0.001 g on ACZET CY-64 analytical scales. Distilled water was poured on the bottom of the desiccator, the samples were placed on the desiccator platform on their sides so that they did not touch each other and the walls of the desiccator. The samples were kept in a closed desiccator at 20±2 °C. The first weighing of the samples was performed one day after placing them in the desiccator, subsequent measurements were performed after 2, 3, 6, 9, 13, 20, and 30 days. The percentage of moisture absorbed (*W*) was calculated with an accuracy of 0.1 % using formula (2).

$$W = \frac{m_n - m_1}{m_1} \cdot 100\,\%, \quad (2)$$

where m_1 is the weight of the absolutely dry sample in grams; and m_n is the weight of the sample weighed after *n* days from the time when it was first placed in the desiccator in grams.

To determine their water absorption, the nanocomposite samples were dried at 103 °C in weighing bottles until absolutely dry and placed to the bottom of the desiccator with distilled water, so that the samples were completely covered with water. The amount of water absorbed was calculated using formula (2). The samples were weighed after 1, 3, 10, and 30 days.

The samples used to determine water absorption were removed from the desiccator after a certain period of time. Their parameters were measured in the tangential and radial directions using a micrometer with an accuracy of 0.01 mm. Then, the radial and tangential swelling values were determined by formulas (3 and 4).

$$a_t = \frac{L_{t\max} - L_{t\min}}{L_{t\min}} \times 100\,\%, \quad (3)$$

$$a_R = \frac{L_{R\max} - L_{R\min}}{L_{R\min}} \cdot 100\,\%, \quad (4)$$

where $L_{t\,\max}$, $L_{R\,\max}$ are the dimensions of the sample in the tangential and radial directions respectively after soaking in water for 1, 3, 10, and 30 days; $L_{t\,\min}$, $L_{R\,\min}$ are the dimensions of the absolutely dry sample in the tangential and radial directions respectively.

The contact angle of wetting of the ZnO/silver birch wood (*Bétula péndula*) nanocomposite samples with distilled water was measured by the sessile drop method using a goniometer and the HIview 10 software. The liquid was applied to the wood surface using a 0.01 ml microsyringe. Images were made with a handheld camera of the Digital Microscope (Ruihoge, China) and recorded for 1, 30, and 60 seconds.

3. Results and discussion

According to [12, 13], zinc oxide powders synthesised in neutral or weak acid media (pH = 6, 7) are amorphous, which is probably due to the suppression of zinc nitrate hydrolysis under these conditions. As we know from [14], the sol-gel synthesis of ZnO nanopowder at pH = 9 promotes the formation of crystalline samples. Indeed, the X-ray pattern (JCPDS, card 36-1451) showed the narrow high intensity reflections corresponding to zinc oxide. They indicate the synthesis of ZnO nanocrystals (Fig. 1). A noticeable background level may be due to the presence of a certain fraction of the amorphous phase of zinc oxide. The average CSR value of zinc oxide particles, calculated by the Scherrer formula, is 22±2 nm (Table 1).

Table 1. The average CSR of the synthesised ZnO sample

The CSR diameter of the particles, nm	D_1	D_2	D_3	D_{cp}
ZnO	19±3	20±2	26±1	22±2

The TEM results are consistent with the XRD data (Fig. 2). TEM images show that the zinc oxide particles synthesised by the sol-gel method are almost spherical. The particle size of the predominant fraction does not exceed 20

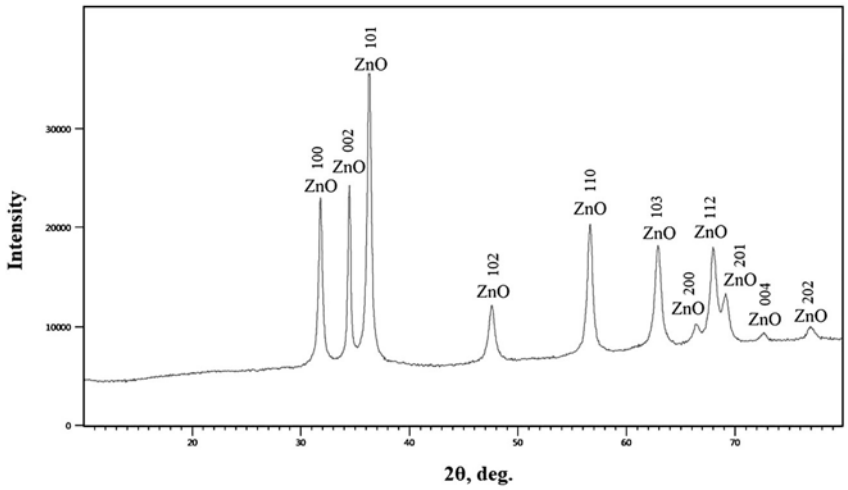
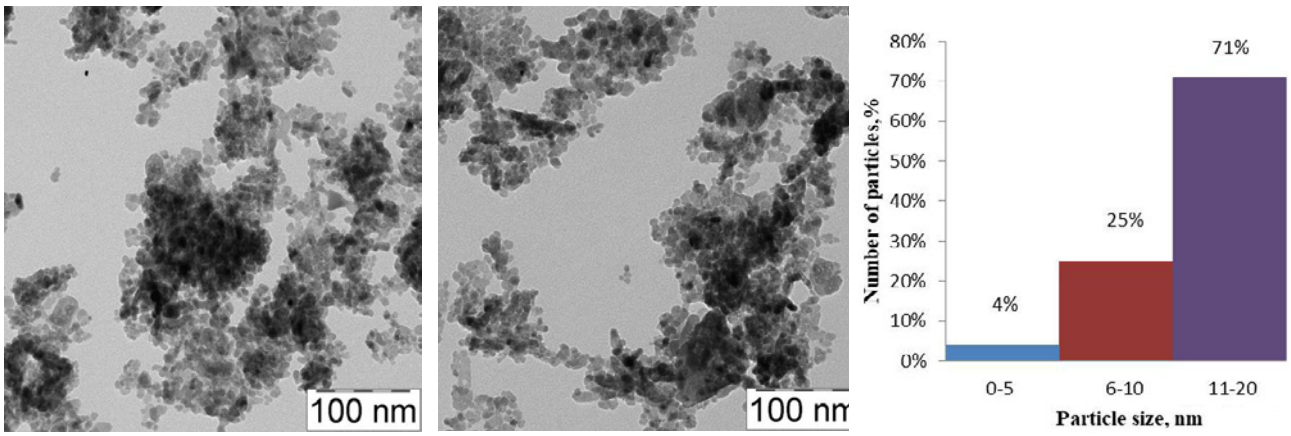


Fig. 1. Diffraction pattern of the ZnO sample synthesised via sol-gel method using NaOH as a precipitant



a b c

Fig. 2. TEM images of ZnO in the gel layer – a), b), and c) – ZnO particle size distribution histogram

nm, the degree of agglomeration is low, and the size of agglomerates is less than 150 nm. The sizes and morphological features of zinc oxide nanoparticles suggest their free penetration into silver birch (*Bétula péndula*) samples through the conductive elements of wood, vessels (diameter from 0.02 to 0.5 mm).

The gel formed after the introduction of a precipitant during the synthesis of ZnO is a loose amorphous zinc hydroxide with a variable water content. This gel enters the wood through conducting vessels. The presence of water molecules facilitates the penetration of $Zn(OH)_2$ into the cavities of the wood, as wood is highly hydrophilic. When heated to 373 K and higher, zinc hydroxide begins to lose water, which is accompanied by decomposition into zinc oxide [15]. A number of studies on the synthesis of zinc oxide nanoforms confirm this temperature range of hydroxide decomposition [16, 17]. Thus, the size and morphological features of zinc oxide nanoparticles are largely determined by the size and shape of the silver birch wood cavities (*Bétula péndula*) filled with hydrated $Zn(OH)_2$ gel. The retention of heated ZnO nanoparticles in wood vessels and capillaries is facilitated by the interaction of the polar reactive O-ZnO surface with functional groups of wood components (e.g., OH-groups of cellulose). This interaction results in the formation of hydrogen bonds [18].

Analysis of the values of the contact angle of water on the surfaces of natural birch and the ZnO/silver birch wood (*Bétula péndula*) nanocomposite (Table 2) showed that the introduction of zinc oxide nanoparticles into the wood vessels significantly increased the hydrophobic properties of the surface (the contact angle increased more than twofold).

Table 2. The contact angle of birch wood and ZnO/wood nanocomposite

Sample composition	The contact angle after 20 seconds, deg.
Birch wood	30
ZnO/wood nanocomposite	75

Filling the wood cavities with nanosized zinc oxide significantly reduced moisture and water absorption in the birch wood. After 1 day of the experiment, the moisture absorption (Fig. 3A) of the ZnO/silver birch wood (*Bétula péndula*) nanocomposite was 2.5 %, compared with 12.1 % for natural birch wood. After 30 days this parameter increases to 12.5 % for the composite and to 26 % for natural birch wood. Thus, impregnating zinc oxide nanoparticles in the natural polymer reduced its moisture absorption by almost 5 times after 1 day of testing. This effect decreased over time, but was still pronounced (the moisture absorption of the nanocomposite was half that of birch wood). The water absorption (Fig. 3B) of silver birch wood (*Bétula péndula*) doped with nanosized zinc oxide was 30 % less after one day of testing compared to natural wood (diagram 1). After 30 days of testing, the effectiveness of ZnO hardly diminished and the water absorption of the composite remained 30% lower than that of untreated birch wood (*Bétula péndula*).

Doping birch wood with zinc oxide nanoparticles reduced the swelling in both the radial (Fig. 3C) and tangential (Fig. 3D) directions. After 1 day in water, the swelling of ZnO/silver birch wood (*Bétula péndula*) nanocomposite was practically 10 times lower in both radial and tangential directions compared to untreated birch wood. After 30 days of testing for water resistance, the swelling improvement of the doped wood decreased slightly and reached 8 times in the tangential direction and 2.6 times in the radial direction.

4. Conclusions

Using the sol-gel method with sodium hydroxide as precipitant, we synthesised zinc oxide nanoparticles with predominant size of about 20 nm and almost spherical shape (TEM data) at relatively low temperatures. Amorphous hydrated $Zn(OH)_2$ was impregnated into the wood material at the gel formation stage. It resulted in the reaction of zinc hydroxide decomposition with the formation of ZnO nanoparticles in the wood as a nanoreactor. The hydrophobic properties of the surface of ZnO/silver birch (*Bétula péndula*) wood nanocomposite improved significantly (the contact angle doubled). Its moisture and water resistance decreased (2–5 times and 30 %, respectively). The nanocomposite also showed less swelling in the radial (8-10 times) and tangential (2.6–10 times) directions in comparison with natural wood.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

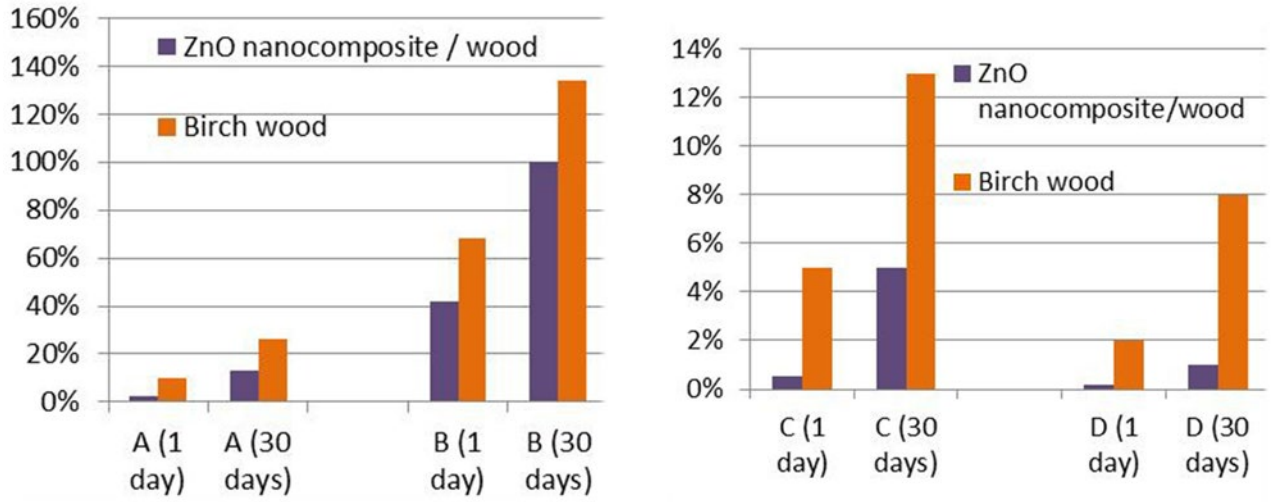


Fig. 3. Moisture absorption (A), water absorption (B), swelling in the radial (C) and tangential (D) directions of birch wood after 1 and 30 days of testing (%)

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Sunandan B., Joydeep D. Hydrothermal growth of ZnO nanostructures. *Science and Technology of Advanced Materials*. 2009;10(1): 1–18. https://doi.org/10.1088/1468-6996/10/1/013001

2. Yang Y., Li Y.-Q., Fu S.-Y., Xiao H.-M. Transparent and light-emitting epoxy nanocomposites containing ZnO quantum dots as encapsulating materials for solid state lighting. *Journal of Physical Chemistry C*. 2008; 112 (28): 10553–10558. https://doi.org/10.1021/jp802111q

3. Dong Y., Chaudhary D., Ploumis C., Lau K. T. Correlation of mechanical performance and morphological structures of epoxy micro/nanoparticulate composites. *Composites Part A: Applied Science and Manufacturing*. 2011;42(10): 1483–1492. https://doi.org/10.1016/j.compositesa.2011.06.015

4. Nebukina E. G., Khokhlov E. M., Zaporozhets M. A., Vitukhnovskii A. G., Gubin S. P. A comparative study of the structural and spectral characteristics of ZnO nanoparticles dispersed in isopropanol and polyethylene. *Inorganic Materials*. 2011;47(2): 143–147. https://doi.org/10.1134/S0020168511020117

5. Demir M. M., Koynov K., Akbey Ü., Bubeck C., Park I., Lieberwirth I., Wegner G. Optical properties of composites of PMMA and surface-modified zincite nanoparticles. *Macromolecules*. 2007;40(4): 1089–1100. https://doi.org/10.1021/ma062184t

6. Galimova E. M., Dorozhkin V. P., Kochnev A. M. Vliyanie mekhanoaktivirovannykh oksida tsinka i difenilguanidina na kinetiku sernoi vulkanizatsii izoprenovogo kauchuka [Influence of mechanically activated zinc oxide and diphenylguanidine on the kinetics of sulphur vulcanisation of isoprene rubber]. *Bulletin of Kazan Technological University*. 2011; (19): 144–147. Available at: https://www.elibrary.ru/item.asp?id=17062989 (In Russ.)

7. Tsang S., Avdeeva A. V., Muradova A. G., Yurtov E. V. Poluchenie nanosterzhnei oksida tsinka khimicheskimi zhidkofaznymi metodami [Preparation of zinc oxide nanorods by chemical liquid-phase methods]. *Khimicheskaya Tekhnologiya*. 2014;15(12): 715–722. Available at: https://www.elibrary.ru/item.asp?id=22662585 (In Russ.)

8. Lulu X., Ye X., Baokang D., Zhangning Ye., Chunde J., Qingfeng S., Xiaohong Yu. Insitu anchoring of Fe_3O_4/ZIF-67 dodecahedrons in highly compressible wood aerogel with excellent microwave absorption properties. *Materials & Design*. 2019;182(15): 108006. https://doi.org/10.1016/j.matdes.2019.108006

9. Cai T., Shen X., Huang E., Yan Y., Shen X., Wang, F., … Sun Q. Ag nanoparticles supported on MgAl-LDH decorated wood veneer with enhanced flame retardancy, water repellency and antimicrobial activity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2020;598(5): 124878. https://doi.org/10.1016/j.colsurfa.2020.124878

10. Holy S., Temiz A., Köse Demirel G., Aslan M., Mohamad Amini M. H. Physical properties, thermal and fungal resistance of Scots pine wood treated with nano-clay and several metal-oxides nanoparticles. *Wood Material Science and Engineering*. 2020;16(1): 1–10. https://doi.org/10.1080/17480272.2020.1836023

11. Qiu Z., Xiao Z., Gao L., Li J., Wang H., Wang Y., Xie Y. Transparent wood bearing a shielding effect to infrared heat and ultraviolet via incorporation of modified antimony-doped tin oxide nanoparticles. *Composites Science and Technology*. 2019;172(1): 43–48. https://doi.org/10.1016/j.compscitech.2019.01.005

12. Alias S. S., Ismail A. B., Mohamad A. A. Effect of pH on ZnO nanoparticle properties synthesized by sol–gel centrifugation. *Journal of Alloys and Compounds*. 2010;499(2): 231–237. https://doi.org/10.1016/j.jallcom.2010.03.174

13. Rani S., Suri P., Shishodia P. K., Mehra R. M. Synthesis of nanocrystalline ZnO powder via sol-gel route for dye-sensitized solar cells. *Solar Energy Materials & Solar Cells*. 2008;92(12): 1639–1645. https://doi.org/10.1016/j.solmat.2008.07.015

14. Karpova S. S., Moshnikov V. A., Myakin S. V., Kolovangina E. S. Surface functional composition and sensor properties of ZnO, Fe_2O_3, and $ZnFe_2O_4$. *Semiconductors*. 2013;47(3): 392–395. https://doi.org/10.1134/S1063782613030123

15. Lidin R. A., Molochko V. A., Andreeva L. L. *Khimicheskie svoistva neorganicheskikh veshchestv*

[Chemical properties of inorganic substances]. Moscow: Koloss Publ.; 2006. 480 p. (In Russ.)

16. Qu X., Jia D. Synthesis of octahedral ZnO mesoscale superstructures via thermal decomposing octahedral zinc hydroxide precursors. *Journal of Crystal Growth.* 2009;311(4): 1223–1228. https://doi.org/10.1016/j.jcrysgro.2008.11.079

17. Zhu Y., Zhou Y. Preparation of pure ZnO nanoparticles by a simple solid-state reaction method. *Applied Physics A*. 2008; 92 (2): 275–278. https://doi.org/10.1007/s00339-008-4533-z

18. Vrublevskaya V. I., Matusevich V. O., Kuznetsova V. V. Substantiation of the interaction mechanism of wood components and water. *Bulletin of Higher Educational Institutions. Lesnoi Zhurnal (Forestry Journal)*. 2017;3(357): 152–163. https://doi.org/10.17238/issn0536-1036.2017.3.152

Information about the authors

Elena V. Tomina, DSc in Chemistry, Associate Professor, Head of the Department of Chemistry, Morozov Voronezh State University of Forestry and Technologies, Voronezh, Russian Federation; e-mail: tomina-e-v@yandex.ru. ORCID iD: https://orcid.org/0000-0002-5222-0756.

Anna A. Pavlenko, 1st year master's degree student, Voronezh State University, Voronezh, Russian Federation; e-mail: pavlenko-a-a@mail.ru. ORCID iD: https://orcid.org/0000-0003-4899-609X.

Aleksandr I. Dmitrenkov, PhD in Technical Sciences, Morozov Voronezh State University of Forestry and Technologies, Voronezh, Russian Federation; e-mail: dmitrenkov2109@mail.ru. ORCID: https://orcid.org/0000-0001-9296-1762.

Sofiya A. Neminushchaya, student, Morozov Voronezh State University of Forestry and Technologies, Voronezh, Russian Federation; e-mail: nem.sofi@bk.ru ORCID: https://orcid.org/0000-0003-2203-3324.

Received August 23, 2021; approved after reviewing September 3, 2021; accepted for publication November 15, 2021; published online December 25, 2021.

Translated by Anastasiia Ananeva
Edited and proofread by Simon Cox