

Functional nanomaterials based on modified titanium dioxide*

A. A. Rempel

*Institute of Metallurgy, Ural Branch of the Russian Academy of Sciences,
101 ul. Amundsena, 620016 Yekaterinburg, Russian Federation.
E-mail: rempel.imet@mail.ru*

Titanium dioxide synthesis and modification by chemical, electrochemical, and mechanochemical methods are briefly outlined. The atomistic structure, nanostructure, morphology, optical characteristics, functional properties, and peculiar features of the semiconductor material are described. Practical applications of titanium dioxide in catalysis, sorption, and biomedicine are described.

Key words: titanium dioxide, sol–gel method, anodization, high-energy milling, nanoparticles, nanotubes, photocatalysts, memristors, photosorbents.

Introduction

Titanium dioxide (TiO_2) is a nontoxic, environmentally safe, economically accessible, and effective functional material with a broad spectrum of applications.^{1–7} In the recent two decades, researchers worldwide have paid increasing attention to nanostructured TiO_2 , which is considered as promising as photocatalyst, photosorbent, and material for nanoelectronics and photonics.^{8–12} Titanium dioxide is of particular importance for green chemistry methods of synthesis of organic compounds for medicine.^{13–19} Besides, there is considerable literature on nonstoichiometric titanium dioxide (TiO_{2-x}), because it is reasonably assumed that, unlike stoichiometric TiO_2 , TiO_{2-x} absorbs visible light including most part of solar light. In this connection, it is more appropriate to use TiO_{2-x} instead of stoichiometric TiO_2 as photocatalyst and photosorbent because the latter requires hazardous UV light, which is economically unprofitable.

In this connection, in the text below we will analyze relevant publications and consider efficient methods for modification (*i.e.*, transformation) of stoichiometric TiO_2 to nonstoichiometric TiO_{2-x} with preservation of the nano state and large specific surface area.

Methods for preparation of titanium dioxide with large specific surface area

Materials with large specific surface area can be prepared using various chemical and physical nanotechnologies, which are conditionally divided into two subgroups, *viz.*, bottom–up (subgroup I) and top–down (subgroup II) methods.²⁰ This classification takes into account the key step at which a nanostructure is formed. Subgroup I methods include those where nanoparticles are formed from atoms or ions. Similar processes occur when using additive technologies. Subgroup II methods include those used to obtain nanoparticles by brittle fracture and disintegration of bulk materials, coarse grains, and powder particles. These processes are typical of mechanical processing of materials. The subgroup I and II methods are primarily based on the chemical (synthetic) and physical (mechanical) approach, respectively.

Titanium dioxide powders with large specific surface area are successfully obtained by both subgroup I and II methods including hydrothermal synthesis¹⁰ and sol–gel technique¹⁷ (subgroup I) as well as high-energy ball milling of coarse-grained TiO_2 powder (subgroup II). Electrochemical anodization of titanium foil in a specific electrolyte⁹ can also be treated as a subgroup II method because excess titanium is removed from titanium foil, although through electrochemical corrosion rather than by mechanical treatment. The process is ac-

* Dedicated to Academician of the Russian Academy of Sciences O. N. Chupakhin on the occasion of his 90th birthday.

accompanied by the oxidation of titanium up to the higher oxide; however, regions at the Ti/TiO₂ interface contain nonstoichiometric titanium dioxide and Magnéli phases.²¹

The widely used methods for large-scale preparation of titanium dioxide include, *e.g.*, various modifications of chemical vapor synthesis. For instance, Degussa TiO₂ nanopowders are obtained by combustion of titanium tetrachloride in a gas phase, and materials thus fabricated contain different amounts of nanoparticles with the rutile, anatase, and amorphous structure.^{22,23} Other practically important techniques include combustion of titanium tetrachloride in oxygen plasma,²⁴ detonation synthesis using pyrolyzed titanium tetrachloride, oxygen, and hydrogen,²⁵ synthesis of nanocrystalline titanium dioxide thin films on the surface of other phases,²⁶ synthesis of nanocrystalline TiO₂ films by atomic layer deposition using TiCl₄ and H₂O vapors on, *e.g.*, the Al₂O₃ surface.²⁷ In addition, the possibility of controlling the formation of titanium dioxide with specified structure and crystallite size on heat treatment of amorphous titanium dioxide²⁸ is of great importance.

Methods for modification of titanium dioxide

Modification (transformation) of titanium dioxide to nonstoichiometric TiO_{2-x} is primarily aimed at creating point defects in the atomistic structure of the material, *viz.*, structural vacancies in the oxygen sublattice. The emergence of oxygen vacancies causes changes not only in the atomistic structure of titanium dioxide, but also in its electron and phonon spectra, which has strong impact on the functional optical properties of the material. The appearance of additional energy levels in the TiO₂ band gap due to the effect of oxygen vacancies and Ti³⁺ ions underlies a shift of the spectral response to the visible region and to effective narrowing of the band gap.^{29–32} These changes in the electronic structure enhance

the photocatalytic activity and photosorption under irradiation with visible light, which is useful for air and water cleaning from harmful impurities, and can be used in hydrogen energetics for hydrogen generation and in medicinal chemistry for green synthesis of the available or new pharmaceuticals.

The photocatalyst and photosorbent activity depends on various parameters, such as the band gap, the specific surface area, the defect crystal structure, the concentration of active sites, and the excited-state lifetimes of electrons and holes. High performance of photocatalysts and photosorbents requires that the band gap be of at most 2–3 eV. In this case the visible light photon energy is high enough for absorption and activation of the photocatalyst. Besides, suppression of radiative transitions in the electron-hole subsystem of semiconducting TiO_{2-x} causes an increase in the catalytic and sorption capacity and an increase in the yield of the target reaction product in the case of synthesis of organic compounds. Thus, the optimal parameters of titanium dioxide nanomaterials include the specified degree of nonstoichiometry, band gap, developed surface, high concentration of active sites, long excited-state lifetimes of electrons and holes, and minimum probability of radiative transitions. Design of such materials is topical for materials science (Table 1).

High-energy ball milling in planetary mills

High-energy ball milling of coarse-grained powder of stoichiometric titanium dioxide is an efficient method for nanostructuring and modifying the material. This is a readily available technique which does not require expensive reagents. When performing high-energy ball milling, powder particles are crushed into much smaller ones that can be as small as a few nanometers in size. The number of powder particles thus increases millions of times. Fragmentation of particles and changes in their morphology

Table 1. Fields of application of coarse-grained and nanostructured stoichiometric TiO₂ as well as nanostructured modified TiO_{2-x}

Titanium dioxide	Selected characteristics of chemical compound	Fields of application
Coarse-grained TiO ₂	Pigment, with small specific surface area	Construction, paints, including zinc paints
Nanostructured TiO ₂	Nanostructured, with large specific surface area	Photocatalysis and photosorption under UV irradiation
Nanostructured TiO _{2-x}	Nanostructured, with large specific surface area and efficiently narrowed band gap	Photocatalysis and sorption under irradiation with visible light, nanoelectronics, hydrogen generation, medicinal chemistry

can be accompanied by various processes including the formation of structural defects and phase transformations. In addition, certain phases that cannot form under ambient conditions are accessible by ball milling. Co-existence of several different nanophases of titanium dioxide in a support can be used to optimize the performance of catalysts by tuning electronic and geometric effects. Thus, high-energy ball milling is actually an efficient method for preparation of mixtures of titanium dioxide nanopowders with developed surface and modified properties.

The authors of a recent study¹¹ on modification of titanium dioxide by high-energy ball milling used the following raw materials: rutile R0 (Component-Reaktiv, Russia; rutile : anatase = 96 : 4 w/w) and anatase A0 (Sigma—Aldrich; anatase : rutile = 98 : 2 w/w, purity 99.8%). A Retsch PM 200 planetary mill with jars and grinding balls made of high-strength oxide ceramics to prevent the formation of non-oxide impurities in the course of milling was used.

An analysis of experimental data for rutile showed that milling causes the particle size to decrease while the specific surface area to increase from 8 to 36 cm² g⁻¹. Milling of anatase induced phase transformations and the formation of several titanium dioxide phases (a high-pressure phase, monoclinic anatase, and rutile), as well as variation of the coherent scattering region and an increase in the specific surface area from 8 to 45 cm² g⁻¹. The introduction of defects into the system during ball milling was established and confirmed by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and Raman spectroscopy. It was also found that the defects have a positive effect on the photosorption properties of the material.

In addition, milling is accompanied by an increase in the number of grain boundaries and interfaces, which leads to an increase in the surface energy of the powder, enhancement of the adsorption properties, and stability of catalysts. The materials synthesized in this work using the simple and profitable method of high-energy ball milling possess unique properties and phase composition and can play a significant role as components of photocatalysts and photosorbents.

Electrochemical synthesis. Anodic oxidation

Nanostructured TiO₂ is often synthesized by a simple electrochemical anodization method. Ac-

cording to this method, the metal (*e.g.*, titanium) is anodized in the electrochemical system, which initiates the oxidation reaction $\text{Me} \rightarrow \text{Me}^{n+} + ne^-$.

The anodic oxidation method allows one to tune the morphology (nanotube length and the inner and outer diameters) and structure of the resulting TiO₂ nanotubes by varying the synthesis parameters, *e.g.*, the electrolyte composition, water content, medium pH, current density and voltage, anodization time and temperature, and the number of reaction steps in the overall process. Thus, at present it is possible to fabricate coatings based on titanium dioxide nanotubes of different morphology, structure, and properties⁹ for solving particular problems from photocatalysis to the design of memristor structures. The synthesized nanotubular TiO₂ has amorphous structure, the film morphology being dependent on the kinetics and conditions of the electrochemical process. By tuning the synthesis parameters one can obtain both ordered nanotubes and porous arrays and disordered nanotube bundles. An efficient method for varying the atomistic and electronic structure of TiO₂ is to induce nonstoichiometry in the material, *viz.*, to form structural vacancies in the oxygen sublattice, which leads to a shift of the spectral response to irradiation with visible light and to efficient narrowing of the band gap.

The appearance of atomic defects in the amorphous network is followed by the formation of allowed energy levels in the TiO₂ band gap, which in turn causes the absorption of visible light with $\lambda \sim 450$ nm. An analysis of the diffusion reflectance spectra using the Kubelka—Munk function showed that band gap of the nanotubular TiO₂ film is $E_g = 3.3$ eV (anodization time 120 min). In addition, the X-ray photoelectron spectrum of the synthesized amorphous nanotubular film exhibited an additional doublet corresponding to the Ti³⁺ ion.

Figure 1 presents the energy band structure of nonstoichiometric titanium dioxide. The impurity levels act as electron acceptors, the band gap of stoichiometric TiO₂ is about 3.3 eV (*cf. ca.* 2.8 eV for nonstoichiometric TiO_{2-x}). More efficient absorption of visible light owing to the presence of oxygen vacancies in the structure is due to narrowing of the band gap. This has strong effect on photocatalytic and photosorption activity of the film upon irradiation with visible light.

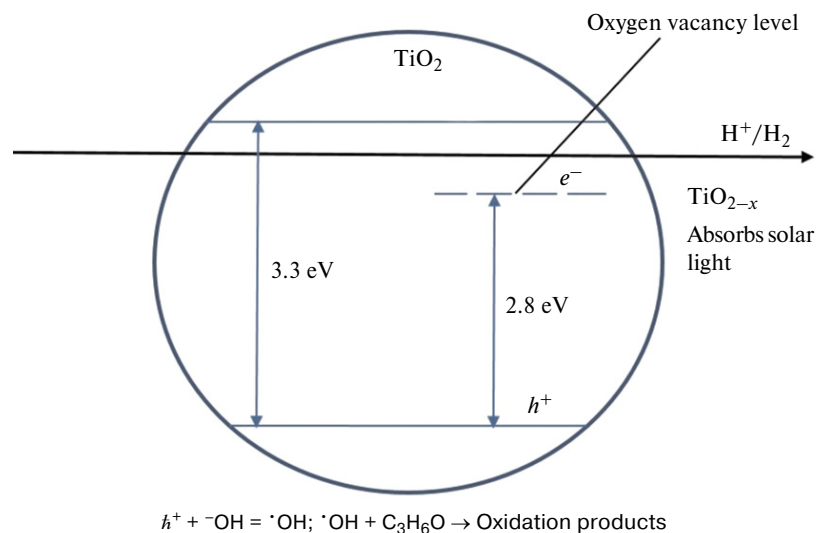


Fig. 1. Energy band structure of titanium dioxide with the oxygen vacancy defect level.

Annealing in different atmospheres

Heat treatment of nanostructured titanium dioxide is usually performed in air or in gaseous media (N₂, O₂, or an N₂–H₂ mixture). Annealing changes not only the morphology, structure, and phase composition, but also the functional properties of titanium dioxide, primarily due to the induction of nonstoichiometry. Structural vacancies formed during heat treatment have a crucial effect on the optical and photocatalytic properties of the entire material. The authors of Ref. 33 were the first who proved the deviation from stoichiometry, *viz.*, the presence of oxygen structural vacancies in the anodized nanotubular TiO₂ structures after high-temperature annealing. They reported that the oxide layer contained oxides with titanium in different charge states (Fig. 2). More recently,³⁴ an XPS examination of the composition of a TiO₂ nanotubular layer grown by anodization in an electrolyte containing water (0.3–2.4 mol L⁻¹) and NH₄F (0.015–0.17 mol L⁻¹) revealed the formation of nonstoichiometric titanium oxide TiO_{2-x} containing mainly Ti⁴⁺, a noticeable concentration of Ti³⁺, and a small amount of Ti²⁺ ions. A study of the effect of the content of H₂O and NH₄F on the morphology and properties of the barrier layer of TiO₂ nanotubes grown by potentiostatic anodization³⁵ demonstrated an increase in the concentration of Ti³⁺ and Ti²⁺ ions with increasing NH₄F concentration in the electrolyte from 0.05 to 0.2 mol L⁻¹. It was also shown that as the content of water in the electrolyte increases from 1 to 50%, the

proportion of the suboxides in the film to decreases. In addition, the chemical structure of a material depends strongly on its morphology. As the nanotube pore diameter decreases from 140 to 20 nm, the

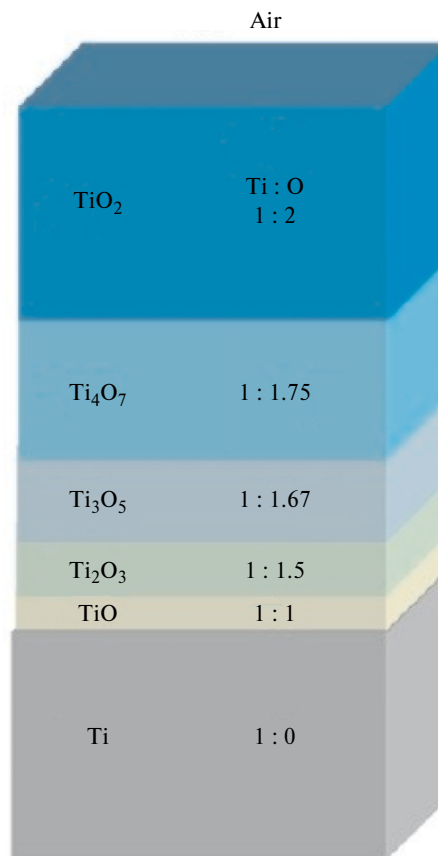


Fig. 2. Phase composition of titanium dioxide nanotubes on titanium substrate.

surface-area-to-volume ratio (and, therefore, the surface area of active sites) increases, which leads to greater dissociation of Ti^{+4} into Ti^{+3} under high-temperature annealing and thus to higher content of nonstoichiometric defects like Ti^{3+} and oxygen vacancies in the 3D TiO_2 nanotubes.³⁶

Main fields of application of modified nanostructured titanium dioxide

Modified nanostructured titanium dioxide (TiO_{2-x}) is a nontoxic, environmentally safe, economically accessible, and efficient functional material with a broad spectrum of applications. In particular, stoichiometric and nonstoichiometric titanium dioxide nanotubes have attracted increasing attention of researchers worldwide in connection with prospects for their application as photocatalysts for high-performance synthesis of organic compounds based on green chemistry principles.

Considering the rapidly developing area of medicinal chemistry, mention should be made of the design of heterogeneous catalysts for oxidation, research into new substrates, as well as search for the addition—oxidation reactions, halogen-free reactions, one-pot reactions proceeding under mild conditions, and the development of compounds for bioassays.^{8,13–19} In this connection, noteworthy are the studies headed by O. N. Chupakhin^{37–39} that are aimed, among other things, at developing new compounds for medicine.

Memristor structures are usually fabricated using advanced and expensive molecular beam epitaxy and chemical vapor deposition methods. In this connection, it seems promising to develop a nanotechnology for combining, on the atomic level, stoichiometric and nonstoichiometric (with respect to oxygen) layers of a semiconductor or dielectric sandwiched between metallic electrodes. It was reported⁹ that the memristive behavior in nanostructures of nonstoichiometric titanium dioxide (TiO_{2-x}) is usually provided by the mobility of cationic and anionic vacancies in the dielectric layer, while the thickness and defectiveness of this layer determine the electrical resistance of the structure in the low-, high-resistance, and intermediate states. The possibility to form and control the intermediate conductive states of memristor structures based on TiO_2 nanotube arrays in a wide range of changes in charge carrier mobility offers prospects for their application as a solid-state physical model

of a synapse with high plasticity. In turn, this can be used for fabrication of efficient functional media for solid-state implementations of neurocomputing systems and artificial neural networks.⁹

Modified titanium dioxide can also be used for environmental protection purposes and Cr^{VI} disposal. Hexavalent chromium is a human carcinogen which is present in, *e.g.*, industrial wastewater including waste water from metallurgical enterprises. The sorption properties of titanium dioxide depend strongly on the method of synthesis, on the specific surface area governed by the particle size, and on the particular crystalline modification. High-energy ball milling is a relatively simple one-step method for preparation of modified titanium dioxide with high sorption capacity. It was reported that high-energy ball milling of titanium dioxide improves the sorption of Cr^{VI} ions and it was established that Cr^{III} is sorbed on the ground TiO_2 much better than Cr^{VI} in a weak acidic medium (pH 4–6).¹² The presence of acetate buffer solution has positive effect on the sorption of total chromium and on the possibility to remove hexavalent chromium.

Conclusions

The functional properties of modified titanium dioxide are still far from being optimal; therefore, further studies of the mechanisms of photocatalytic reactions and photosorption are needed. Detailed studies of reaction mechanisms should be followed by targeted modification of the atomistic structure and morphology of titanium dioxide to significantly improve the functional properties of the material.

Acknowledgements

The author expresses his gratitude to Academician O. N. Chupakhin for the interest in the research into modified nanostructured titanium dioxide.

Funding

This work was financially supported by the Russian Science Foundation (Project No. 21-73-20039).

Animal Testing and Ethics

No human or animal subjects were used in this research.

Conflict of Interest

The author declares no competing interests.

References

1. X. Chen, S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891; DOI: 10.1021/cr0500535.
2. V. Augugliaro, T. Caronna, A. Paola, G. Marci, M. Pagliaro, G. Palmisano, L. Palmisano, in *Environmentally Benign Photocatalysts. Applications of Titanium Oxide-based Materials*, Eds M. Anpo and P. V. Kamat, Springer, New York, 2010, p. 623.
3. A. A. Rempel, *Russ. Chem. Bull.*, 2013, **62**, 857; DOI: 10.1007/s11172-013-0118-x.
4. K. Hashimoto, H. Irie, A. Fujishima, *J. Appl. Phys.*, 2005, **44**, 8269; DOI: 10.1143/JJAP.44.8269.
5. O. Carp, C. L. Huisman, A. Reller, *Prog. Solid State Chem.*, 2004, **32**, 33; DOI: 10.1016/j.progsolidstchem.2004.08.001.
6. S. Rossi, M. Savi, M. Mazzola, S. Pinelli, R. Alinovi, L. Gennaccaro, A. Pagliaro, V. Meraviglia, M. Galetti, O. Lozano-Garcia, A. Rossini, C. Frati, A. Falco, F. Quaini, L. Bocchi, D. Stilli, S. Lucas, M. Goldoni, E. Macchi, A. Mutti, M. Miragoli, M. Miragoli, *Part. Fibre Toxicol.*, 2019, **16**, 1; DOI: 10.1186/s12989-019-0311-7.
7. L. Zhao, Y. Zhu, Z. Chen, H. Xu, J. Zhou, S. Tang, Z. Xu, F. Kong, X. Li, Y. Zhang, X. Li, J. Hang, G. Jia, *Nanotoxicology*, 2018, **12**, 169; DOI: 10.1080/17435390.2018.1425502.
8. A. A. Rempel, A. A. Valeeva, *Russ. Chem. Bull.*, 2019, **68**, 2163; DOI: 10.1007/s11172-019-2685-y.
9. A. A. Rempel, A. A. Valeeva, A. S. Vokhmintsev, I. A. Weinstein, *Russ. Chem. Rev.*, 2021, **90**, 1397; DOI: 10.1070/rcr4991.
10. V. I. Popkov, A. K. Bachina, A. A. Valeeva, A. A. Lobinsky, E. Y. Gerasimov, A. A. Rempel, *Ceram. Int.*, 2020, **46**, 24483; DOI: 10.1016/j.ceramint.2020.06.233.
11. A. A. Valeeva, A. A. Sushnikova, A. A. Rempel, *Inorg. Chem. Commun.*, 2024, **159**, 111727; DOI: 10.1016/j.inoche.2023.111727.
12. D. P. Ordinartsev, N. V. Pechishcheva, A. A. Valeeva, P. V. Zaitseva, A. D. Korobitsyna, A. A. Belozerova, A. A. Sushnikova, S. A. Petrova, K. Yu. Shunyaev, A. A. Rempel, *Russ. J. Phys. Chem.*, 2022, **96**, 2408; DOI: 10.1134/S0036024422110231.
13. I. A. Utepova, M. A. Trestsova, O. N. Chupakhin, V. N. Charushin, A. A. Rempel, *Green Chem.*, 2015, **17**, 4401; DOI: 10.1039/C5GC00753D.
14. E. A. Kozlova, N. S. Kozhevnikova, S. V. Cherepanova, T. P. Lyubina, E. Yu. Gerasimov, V. V. Kaichev, A. V. Vorontsov, S. V. Tsybulya, A. A. Rempel, V. N. Parmon, *J. Photochem. Photobiol. A*, 2012, **250**, 10; DOI: 10.1016/j.jphotochem.2012.09.014.
15. V. P. Ananikov, L. L. Khemchyan, Yu. V. Ivanova, V. I. Bukhtiyarov, A. M. Sorokin, I. P. Prosvirin, S. Z. Vatsadze, A. V. Medved'ko, V. N. Nuriev, A. D. Dilman, V. V. Levin, I. V. Koptuyug, K. V. Kovtunov, V. V. Zhivonitko, V. A. Likholobov, A. V. Romanenko, P. A. Simonov, V. G. Nenajdenko, O. I. Shmatova, V. M. Muzalevskiy, M. S. Nechaev, A. F. Asachenko, O. S. Morozov, P. B. Dzhevakov, S. N. Osipov, D. V. Vorobyeva, M. A. Topchiy, M. A. Zotova, S. A. Ponomarenko, O. V. Borshchev, Yu. N. Luponosov, A. A. Rempel, A. A. Valeeva, A. Yu. Stakheev, O. V. Turova, I. S. Mashkovsky, S. V. Sysolyatin, V. V. Malykhin, G. A. Bukhtiyarova, A. O. Terent'ev, I. B. Krylov, *Russ. Chem. Rev.*, 2014, **83**, 885; DOI: 10.1070/RC2014v83n10ABEH004471.
16. I. A. Utepova, O. N. Chupakhin, M. A. Trestsova, A. A. Musikhina, D. A. Kucheryavaya, V. N. Charushin, A. A. Rempel, N. S. Kozhevnikova, A. A. Valeeva, A. I. Mikhaleva, B. A. Trofimov, *Russ. Chem. Bull.*, 2016, **65**, 445; DOI: 10.1007/s11172-016-1319-x.
17. A. A. Rempel, E. A. Kozlova, T. I. Gorbunova, S. V. Cherepanova, E. Yu. Gerasimov, N. S. Kozhevnikova, A. A. Valeeva, E. Yu. Korovin, V. V. Kaichev, Yu. A. Shchipunov, *Catal. Commun.*, 2015, **68**, 61; DOI: 10.1016/j.catcom.2015.04.034.
18. I. B. Dorosheva, A. A. Rempel, M. A. Trestsova, I. A. Utepova, O. N. Chupakhin, *Inorg. Mater.*, 2019, **55**, 155; DOI: 10.1134/S0020168519010047.
19. S. Higashimoto, N. Suetsugu, M. Azuma, H. Ohue, Y. Sakata, *J. Catal.*, 2010, **274**, 76; DOI: 10.1016/j.jcat.2010.06.006.
20. A. A. Rempel, *Russ. Chem. Rev.*, 2007, **76**, 435; DOI: 10.1070/RC2007v076n05ABEH003674.
21. A. Kumar, N. H. Barbhuiya, S. P. Singh, *Chemosphere*, 2022, **307**, 135878; DOI: 10.1016/j.chemosphere.2022.135878.
22. D. M. Tobaldi, R. C. Pullar, M. P. Seabra, J. A. Labrincha, *Mater. Lett.*, 2014, **122**, 345; DOI: 10.1016/j.matlet.2014.02.055.
23. M. Rahiminezhad-Soltani, K. Saberyan, A. Simchi, C. Gammer, *J. Mater. Res. Technol.*, 2019, **8**, 3024; DOI: 10.1016/j.jmrt.2018.12.027.
24. Patent RU2547490C2; *Byul. Izobr. [Invention Bull.]*, 2015, 10 (in Russian).
25. X. J. Li, X. Ouyang, H. H. Yan, G. L. Sun, F. Mo, *Adv. Mater. Res.*, 2008, **32**, 13; DOI: 10.4028/www.scientific.net/AMR.32.13.
26. R. K. Patnaik, N. Divya, *Mater. Today Proc.*, 2023, **72**, 2749; DOI: 10.1016/j.matpr.2022.10.064.
27. Patent RU1713886; *Byul. Izobr. [Invention Bull.]*, 1991 (in Russian).
28. A. K. Bachina, O. V. Almjasheva, V. I. Popkov, V. I. Nevedomskiy, V. V. Sokolov, V. V. Gusarov, *J. Crystal*

- Growth*, 2021, **576**, 126371; DOI: 10.1016/j.jcrysgro.2021.126371.
29. A. A. Valeeva, E. A. Kozlova, A. S. Vokhmintsev, R. V. Kamalov, I. B. Dorosheva, A. A. Saraev, I. A. Weinstein, A. A. Rempel, *Sci. Rep.*, 2018, **8**, 9607; DOI: 10.1038/s41598-018-28045-1.
30. A. A. Valeeva, I. B. Dorosheva, E. A. Kozlova, R. V. Kamalov, A. S. Vokhmintsev, D. S. Selishchev, A. A. Saraev, E. Yu. Gerasimov, I. A. Weinstein, A. A. Rempel, *J. Alloys Compd.*, 2019, **796**, 293; DOI: 10.1016/j.jallcom.2019.04.342.
31. V. M. Zainullina, V. P. Zhukov, M. A. Korotin, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2015, **22**, 58; DOI: 10.1016/j.jphotochemrev.2014.10.005.
32. V. P. Zhukov, M. G. Kostenko, A. A. Rempel, I. R. Shein, *Nanosyst. Phys. Chem. Math.*, 2019, **10**, 374; DOI: 10.17586/2220-8054-2019-10-3-374-382.
33. C.-C. Chen, W. C. Say, S.-J. Hsieh, E. W.-G. Diau, *Appl. Phys. A—Mater. Sci. Process.*, 2009, **95**, 889; DOI: 10.1007/s00339-009-5093-6.
34. M. Stancheva, M. Bojinov, *J. Solid State Electrochem.*, 2013, **17**, 1271; DOI: 10.1007/s10008-012-1990-2.
35. P. Acevedo-Peña, L. Lartundo-Rojas, I. González, *J. Solid State Electrochem.*, 2013, **17**, 2939; DOI: 10.1007/s10008-013-2212-2.
36. V. C. Anitha, A. N. Banerjee, G. R. Dillip, S. W. Joo, B. K. Min, *J. Phys. Chem. C*, 2016, **120**, 9569; DOI: 10.1021/acs.jpcc.6b01171.
37. O. N. Chupakhin, V. N. Charushin, *Pure Appl. Chem.*, 2017, **89**, 1195; DOI: 10.1515/pac-2017-0108.
38. O. N. Chupakhin, A. V. Shchepochkin, V. N. Charushin, *Green Chem.*, 2017, **19**, 2931; DOI: 10.1039/C7GC00789B.
39. O. N. Chupakhin, I. A. Utepova, I. S. Kovalev, V. L. Rusinov, Z. A. Starikova, *Eur. J. Org. Chem.*, 2007, **2007**, 857; DOI: 10.1002/ejoc.200600821.

Received March 6, 2024;
in revised form May 13, 2024;
accepted May 15, 2024

Publisher's Note. Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.