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Synthesis and antibacterial properties of modified thin films of TiO_2

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Objective: determination of the antibacterial properties of modified TiO_2 films on the colonies of *Staphylococcus aureus* and *Escherichia coli* bacteria. Comparison of antibacterial properties of samples of TiO_2 films doped with different elements.
Materials and methods. Synthesis and modification of TiO_2 films were carried out by atomic / molecular-layer deposition in a hot-wall reactor. The antibacterial properties of the films were determined by comparing the concentrations of bacterial cultures of *S. aureus* and *E. coli* irradiated with UV and natural light in the presence of TiO_2 films with the control.
Results. The lowest concentration of bacterial cultures after the incubation period was in the case of the TiON and TiAlN samples, which indicates that they are the most effective. The samples of TiN and V_2O_5: TiO_2 films showed relatively high activity. In the case of undoped TiO_2, the lowest activity was observed compared to other samples, which confirms the absence of antibacterial properties for TiO_2 in the visible spectra.
Cunclusion. The tested samples of TiO_2-based thin films (doped with N, C and vanadium), obtained by Atomic and Molecular Layer Deposition Techniques, have high antibacterial activity against bacterial cultures of sanitary indicative microorganisms *Staphylococcus aureus* and *Escherichia coli*.

Keywords:
antibacterial properties, nanofilms, colonies, atomic layer deposition, molecular layer deposition

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As analysis shows, the antibacterial coating market in 2024 will exceed 7.4 billion US dollars [1]. In 2016, the US Centers for Disease Control and Prevention allocated fourteen million dollars in grants to thirty-four research groups to build a protective coating against antibiotic-resistant bacteria [2]. Interest in antibacterial coatings is also growing in the food industry (aluminum food packaging) [3, 33-37].

Aluminum (Al) is widely used in the food industry because it is a lightweight recyclable material that protects the stored liquid from various external factors, such as humidity, microbiological contamination, etc. Nevertheless, some internal factors, such as chemical processes initiated by the stored liquid, can lead to degradation of the aluminum surface, which leads to corrosion and metal migration [34–37]. CO_2-containing beverages, such as beer and carbonated drinks, contain acidity and chlorides and, when packed in aluminum cans, can contribute to the corrosion process by coming into contact with aluminum material. To minimize this problem, the inner surfaces of commercial aluminum cans are coated by spraying, usually with natural or synthetic epoxy resins, the purpose of which is to protect the aluminum surface from direct contact with the beverage. However, when the resin is not applied correctly or when Al may be subjected to mechanical stress or elevated temperatures, this leads to local corrosion. The development of simple, inexpensive and effective antibacterial coatings is very important, because damage from harmful and resistant microorganisms becomes a serious social problem.

The use of the photocatalytic effects of nanosized TiO_2 is a conceptually simple and promising technology for reducing bacterial contamination. However, the band gap of titanium dioxide is 3.0–3.2 eV, which means that it can be excited by ultraviolet radiation with a wavelength of <380 nm, which makes up only 5% of the solar spectrum. One way to solve this problem is to dope TiO_2 nanofilms with carbon or nitrogen. This makes it possible to create a material with a band gap of less than 3.0 eV, which would support photoactivity in low light conditions (close to daylight). Numerous methods for producing coatings doped with nitrogen or carbon are known in the literature. In this work, we used methods for the synthesis of photoactive nanofilms of titanium dioxide doped with nitrogen, vanadium, and aluminum based on atomic and molecular layered deposition (ALD and MLD). If ALD allows only inorganic coatings to be applied using MLD, organic and hybrid organo-inorganic thin films can be applied. The unique features of these techniques include the ability to control the thickness and composition of nanofilms at the atomic level and a high level of film uniformity when applied to membranes and nanoparticles.

Bacterial infection on the surface of implanted medical devices is a serious problem in the field of biomedicine. Approximately 11,200 (4.3%) of orthopedic implants introduced annually into the human body in the United States were infected in 2.6 million patients. Bacterial infections not only cause serious pain and suffering for patients, but also increase medical costs. For example, due to the removal of prostheses, repeated operations are necessary, which leads to additional costs and causes discomfort for patients. Infections associated with the implant are the result of adhesion of bacteria, concomitant colonization and the formation of a biofilm on its surface. Therefore, it becomes necessary to incorporate functional agents into the surface of the implant in order to inhibit bacterial adhesion. Inhibiting bacterial adhesion is an important step in preventing implant-related infections.

Each year, millions of patients improve their quality of life with surgical procedures that include the implantation of medical devices that replace or act as part or all of a biological structure. Implants are used in many different parts of the body for various applications, such as orthopedics, pacemakers, cardiovascular stents, defibrillators, neural prosthetics or a drug delivery system. The growth of strains of mutant microbes resistant to antibiotics is also of concern. Today's estimates show that 90% of people over 40 suffer from degenerative joint diseases. In 2000, the total number of hip replacement operations was about 152,000, which is 33% more than the number of operations in 1990, as well as about half of the estimated number of operations by 2030. Cardiovascular disease is another example. Over the past two decades, coronary stents have become the new standard in the procedure of angioplasty. In 2004, the number of implanted drug-eluting stents exceeded two million. Restenosis in the stent (pestenosis) is almost entirely a consequence of tissue hyperplasia, which occurs mainly around the points at which the stent stands are in contact with the artery wall. Less common, but very unpleasant, is subacute thrombosis, a complication that is not completely eliminated with the help of modern methods of deployment of the wall and antiplatelet agents. Due to the application of functional nanocoatings or drugs aimed at locally thrombotic or hyperplastic reactions, drug-coated stents are one of the possible solutions to the above problems. Medical devices are currently an integral part of modern medical care for patients. The development of medicine, from the point of view of implantable devices, has led to serious changes in people's lives (cosmetic, dental, facial and cardiological devices, etc.). Medical devices have expanded the ability of doctors to diagnose and treat diseases, making a great contribution to the health and quality of life of patients. Functional nanocoatings (encapsulation) on implantable medical devices can solve many problems, such as barrier coatings (release of toxic materials into the body), implantation of bio-sensors, etc.

About one sixth of the world's population does not have access to safe drinking water, which leads to the deaths of millions of people, especially children [18]. Many types of bacteria and organic pollutants can lead to serious and even fatal infections for humans [19]. Therefore, the development of an effective technology for cleaning water sources from various types of microorganisms and dyes is becoming an urgent problem.

The development of science at present has led to the widespread use of technology to modify the surface of materials and the formation of thin nanofilms with a unique structure and set of properties. Topical is the use of thin films and nanocoatings in medicine. Spreading thin films on the surface can improve a wide variety of properties of implantable medical devices, including strength, wear resistance and slippage of surgical and dental equipment, stents of the coronary and urinary tract, wear resistance of devices designed to clean the coronary arteries and urinary tract , corrosion resistance, optical properties, antibacterial, electrical and thermal properties.

Antibacterial properties of TiO_2

When titanium dioxide (TiO_2) is irradiated with light close to ultraviolet, this semiconductor exhibits strong bactericidal activity. Under ultraviolet light (<380 nm), TiO_2 can decompose various organic compounds and generate reactive oxygen species, products of redox reactions (ROS), such as superoxide O_2^-, hydroxyl radical (OH) and hydrogen peroxide (H_2O_2). The mechanism of these reactions is as follows.

$$\mathbf{TiO_2 + 2hv \rightarrow 2e^- + 2H^+}$$

$$\mathbf{H_2O + 2hv + \rightarrow (1/2)O_2 + 2H^+}$$

$$\mathbf{2H^+ + 2e^- \rightarrow H_2}$$

or general reaction

$$\mathbf{H_2O + 2hv \rightarrow (1/2)\ O_2 + H_2}.$$

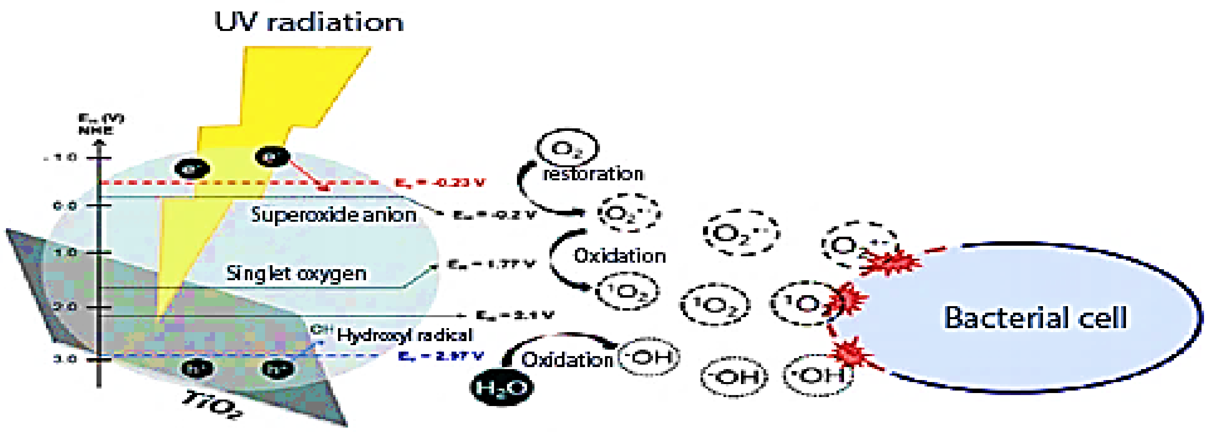

Figure 1. Schematic representation of the antibacterial mechanism of atomic layered deposition TiO_2 by means of redox reaction products under the influence of ultraviolet light [17].

These decomposition products can kill bacteria because they oxidize the external membrane of bacteria, thereby causing their death. A simplified mechanism for the destruction of bacteria by products of redox reactions under the influence of ultraviolet light is shown in Figure 1.

When excited by ultraviolet light, the photon energy hv excites valence electrons and generates pairs of electrons and holes that diffuse and are captured on or near the TiO2 surface. These excited electrons and holes have a strong reducing and oxidizing activity and react with atmospheric water and oxygen to form reactive oxygen species such as hydroxyl radicals (˙OH) and superoxide anions O_2^-. Electron holes are extremely active in contact with organic compounds. TiO_2-based photocatalysts, when doped with anion, are activated by irradiation with visible light. TiO_2 films work only under ultraviolet light (<380 nm), while films doped with TiO_2-xNx nitrogen, TiO_2-xCx carbon (x is the mole fraction of concentration) and some other elements can work on the border of visible light (in red light), i.e. at wavelengths of approximately 565 and 425 nm, respectively [4]. Water is one of the main resources of the planet. Monitoring water quality is a task of paramount importance to humans. Although the land contains a variety of bodies of water, including oceans and rivers, freshwater resources are very limited. In recent years, due to increased industrialization and the introduction of agricultural technologies, the quality of drinking water has been threatened. The main obstacles to the safety of drinking water are the presence of new pollutants, including pesticides, drugs and dyes [28, 29]. In addition, there are also concerns about the possibility of biological hazards, such as harmful microorganisms, which often lead to epidemic outbreaks [30]. There is a wide range of bacteria, viruses, algae, fungi and protozoa that pose a direct and indirect risk to water quality, and therefore, to humans. It has been proven that toxic bacteria, such as *Escherichia coli*, secrete toxins, which enter the body through water intake. The intensity of microbial pollution in water bodies is influenced by various factors, including seasonal weather, flow patterns, water temperature, distance from the source of pollution, livestock management practices, waste water and rainfall. Fortunately, many microbes can be naturally sanitized by sunlight. Therefore, it is possible to use the sun to effectively destroy microbes (solar disinfection). However, the effectiveness of such natural methods is very limited in large-scale applications. In addition, traditional chemical disinfection methods such as ozone and chlorine are very ineffective. In addition, they tend to form harmful by-products.

Electrons and holes formed during the photocatalysis process of oxide-based semiconductors are involved in redox reactions. To date, many types of semiconductor materials, such as zinc oxide (ZnO), titanium oxide (TiO_2), wolfram oxide (WO_3), etc., have been used for such applications. Among all the photocatalytic semiconductor materials, TiO_2 is most often used to develop new functional materials with antibacterial properties. However, due to some known shortcomings of TiO_2 (for example, high recombination and low sensitivity to solar energy), various types of modifications of TiO_2 nanofilms have been developed. Photo-catalysis of TiO_2 is promising, as for the degradation of pollutants and their disinfection. Thus, this may turn out to be a key process for the complete purification of water [32]. Since significant changes have occurred in the field of TiO_2-based disinfection methods for water pollutants, this allows us to study their applicability to microbial de-infection. Since water purification requires not only the removal of chemical pollutants, but also the disinfection of undesirable biological components, TiO_2-based catalysis technology performs this dual role with high efficiency. Photocatalytic solar disinfection is certainly an effective way to treat wastewater. The use of photocatalysts induced by visible light for antimicrobial studies is one of the most effective approaches for solving and deep understanding of the disinfection process. To solve the problem of water pollution, semiconductor photocatalysis is of particular importance due to the decomposition of bacteria and pollutants [17-23].

Earlier, many authors obtained a number of TiO_2-based photocatalysts that were successfully used for photocatalytic disinfection of *E. coli* and degradation of pollutants [24]. However, pure TiO_2 photocatalyst can be activated only in the ultraviolet (UV) region of the light, which greatly complicates its practical application [25–27]. From the point of view of the efficient use of renewable solar energy, it is desirable to prepare highly efficient photocatalysts by modifying (doping) TiO_2, which function under visible light, which can have practical applications in restoring the environment.

The use of titanium dioxide for these purposes as bactericidal coatings is a very promising direction. Doping with carbon and nitrogen atoms is one of the most common ways to improve the antibacterial indices of TiO_2 [5–7, 31]. The introduction of these elements into the TiO_2 structure promotes a shift in the absorption spectrum into the visible region of the solar spectrum and, as a result, enhances bactericidal properties and photocatalytic activity with respect to visible light. Previously, the antibacterial activity of titanium dioxide films [8] was demonstrated on bacterial colonies of *Streptococcus mutans* (*S. mutans*) under the influence of UV light. Upon UV irradiation for 60 minutes, the concentration of S mutans colonies decreased from 4.8×10^6 colony forming units (CFU) to 4×10^3 CFU, which indicates an almost thousand-fold decrease in their concentration.

Physicochemical fundamentals of atomic and molecular layer deposition

ALD is a thin-film deposition method based on sequential, self-limiting surface reactions. The ALD process itself can be represented in the form of four schematically depicted stages in Figure 2 [9]. At the first stage, the dosage of the first reagent X and its interaction with surface functional groups occur.

In the second stage, reaction products and unreacted reagents are purged. In a third step, a second reagent Y is metered. In a fourth step, a purge step is repeated. In the first and third stages, surface reactions of the dosed reagent with functional groups on the film surface occur. These two stages are one cycle. By varying the number of cycles, it is possible to adjust the film thickness. MLD is a relatively new method that relies on the principles of ALD. While ALD was developed exclusively for the deposition of inorganic thin films, MLD is based on self-limiting surface reactions, where one or two reagents are organic molecules.

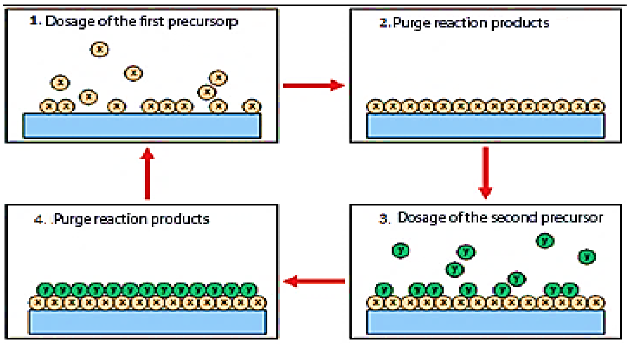

Figure 2. The mechanism of the synthesis of films by atomic layered deposition.

This provides additional opportunities for spraying organic or organo-inorganic thin films.

Methods of ALD and MLD can find many other applications in medicine: this is an increase in the degree of visualization of biopsy needles [10], an increase in the wear resistance of implants, obtaining biocompatible coatings [11], the creation of separation materials [12], etc.

Experimental part

Samples of TiO_2 films: V_2O_5, TiAlN, TiON, TiN, TiO_2 were synthesized by atomic and molecular-layered deposition using ALD Nanotech equipment (Makhachkala, Russia). A detailed procedure for the synthesis of samples is described in previous works of the authors [13, 14]. Determination of the bactericidal activity of the film samples was carried out according to the guidelines [15, 16]:

a) preparation of solutions of bacteriological cultures of *S. aureus* and *E. coli*. Solutions of bacteriological cultures with a concentration of 10^4 CFU / ml were prepared by diluting the stock solution with a concentration of 10^9 CFU / ml. For this, an aliquot of the stock solution with a volume of 1 ml was selected with a dispenser and the total solution volume was adjusted to 10 ml with physiological saline. This procedure was repeated for new solutions until a concentration of 10^4 CFU / ml was reached.

The concentration of CFU in a solution unit was determined by visual colorimetry;

b) the methodology for determining the antibacterial activity of film samples. In this work, we used *E. coli* and *S. aureus* as model bacteria to study the antibacterial properties of the TiO_2-based nanomaterials we obtained. Among all the microbes, bacteria have been identified as an effective indicator of water pollution. For example, among a wide range of bacteria, E. coli is recognized as an indicator of unhygienic water, as their presence usually reflects fecal contamination of water.

To determine the bactericidal activity, samples of ALD films of TiO_2, TiON, TiN, TiAlN, TiO_2: V_2O_5, Vanticone were taken. All film samples were sterilized first with ethanol, then UV irradiation for 1 hour. Sterilized film samples were placed in a Petri dish and a nutrient medium, which served as endoagar, was applied to them. 100 μl of bacterial culture of sanitary-indicative microorganisms *E. coli* were applied to samples of films with nutrient medium. The experimental samples were exposed to a halogen lamp (50 watts) as a simulator of sunlight at a distance of 10 cm; samples without exposure to ultraviolet radiation, as well as samples of the tested cultures irradiated but applied to undoped TiO_2 were used as control. After 24 hours of incubation at 37 °C, the colonies were selected with a bacteriological loop, diluted in physiological saline, 100 μl were taken and plated on solid nutrient media with further dilution in equal amounts of physiological saline. All studies were performed in 3 repetitions. The antibacterial activity of the studied films was calculated by qualitative and quantitative methods. In parallel, the same manipulations were carried out using bacterial colonies of *S. aureus*. Studies were also carried out in the presence of (room) light. A qualitative assessment is to compare the growth of bacterial culture in Petri dishes. The antibacterial activity of the test samples is judged by a statistically significant decrease in the number of CFU in the experiment compared with the control.

Results and discussion

Meat-peptone agar has a fuchsin dye, so bacterial solutions with a nutrient medium are red in color. Figure 3 shows the solutions of *E. coli* bacteria after 24 hours of incubation for different film samples.

As can be seen, the smallest number of bacterial cultures after the incubation period was in the case of samples of TiON and TiAlN, which indicates their greatest antibacterial activity.

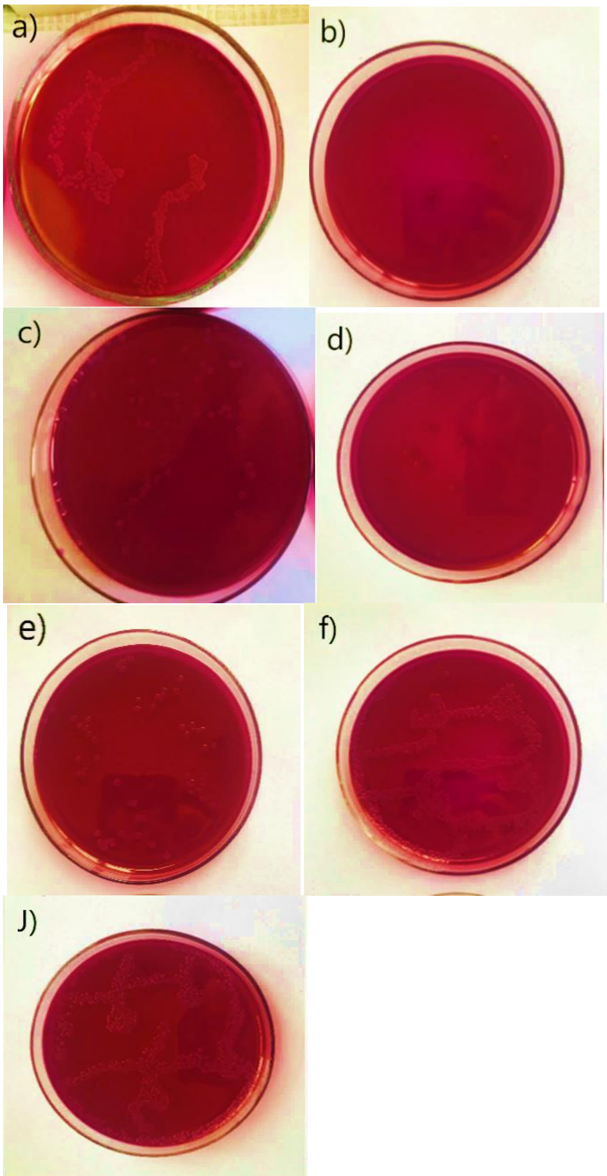

Figure 3. Solutions of bacterial cultures of *E. coli* after plating on nutrient media and dilution in saline after exposure to halogen light. a) TiO_2, b) TiON, c) TiN, d) TiAlN, e) V_2O_5: TiO_2, f) Vanticone, j) activity control. Relatively high activity was exhibited by samples of TiN and V_2O_5: TiO_2 films.

In the case of undoped TiO_2, the lowest activity was observed in comparison with other samples, which confirms the absence of antibacterial properties for TiO_2 in the visible region of sunlight. For control samples (f, J), continuous growth of colonial cultures was observed. This comparative analysis allows us to conclude that TiO_2 acquires antibacterial properties in the visible spectrum of light, which makes it potentially suitable for medical applications without the use of special UV light sources. The results of studies of the antibacterial activity of film samples for the class of microorganisms *E. coli* and *S. aureus* are presented in the form of diagrams in Figures 4 and 5.

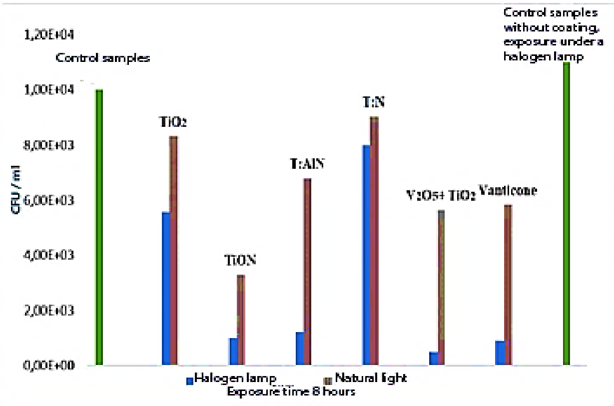

Figure 4. The results of determining the antibacterial activity of prototypes by in relation to the class of microorganisms *E. coli*.

A significant difference in the results of antibacterial activity in the case of exposure under a halogen lamp and in natural light, which can be observed in the presented diagrams, is mainly due to the high intensity of the halogen lamp. In the case of a control sample coated with dark matter, continuous growth of bacterial cultures was observed. A relatively low change in the concentration (21.1%) of bacteria in the case of undoped samples of TiO_2 films in natural light can be noted.

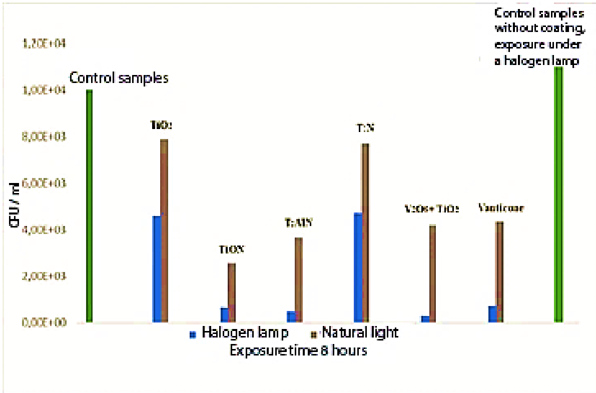

Figure 5. The results of determining the bactericidal activity of the test samples in relation to the class of microorganisms *S. aureus*.

The results of studies of the antibacterial properties of samples with microorganisms of *S. aureus* are shown in Figure 2. Due to the greater stability of the colonies of bacteria S. aureus compared to *E. coli*, the concentration of bacteria for *S. aureus* is slightly higher after 8 hours of irradiation.

The main results of determining the antibacterial activity of the test samples are shown in table 1.

Table 1. The results of determining the antibacterial activity of the test samples

Prototypes	Exposure time	Antibacterial activity, %			
		Natural light	Exposure under the halogen lamp	Natural light	Exposure under the halogen lamp
		E. coli	*E. coli*	*S. aureus*	*S. aureus*
TiO_2	8 hours	21.1	53.80	17.12	41.44
TiON		74.60	93.32	67.25	90.17
TiAlN		36.50	94.97	32.15	87.78
TiN		23.12	53.17	9.77	20.17
$V_2O_5 + TiO_2$		57.83	96.82	43.65	95.28
VANTICONE		43.65	92.70	20.17	90.94
Control samples without coating		-	-	-	-

Thus, thin films of TiON exhibit the highest bactericidal activity in relation to the class of bacteriological cultures of *E. coli* and *S. aureus* both in natural light and in the case of exposure under a halogen lamp. Thin films of V_2O_5 + TiO_2 and

VANTICONE showed high activity with respect to the class of bacteriological cultures of *S. aureus* in the case of exposure under a halogen lamp (95.28% and 90.94%, respectively). Each sample showed activity in the visible region of the world. Studies of structural and chemical surface modifications to achieve the optimal band gap and the search for new photocatalysts with a low band gap are still ongoing.

Conclusion

Thus, it was found that the tested samples of thin films based on TiO_2 (doped with nitrogen, carbon and vanadium) obtained by the ALD and MLD methods have high antibacterial activity against bacterial cultures of sanitary indicative microorganisms *S. aureus* and *E. coli*. Understanding the processes of increasing the photocatalytic, and, as a consequence, antibacterial activity of synthesized thin films will allow in the future to create materials with predetermined parameters and functionality.

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The authors declare the absence of obvious and potential conflicts of interest related to the publication of this article.

This study was conducted at the personal expense of members of the team of authors.

The participation of the authors: the concept and design of the study - Abdulagatov A.I., Abdulagatov I.M.; collection and processing of materials - Amashayev R.R., Maxumova A.M.; analysis of the obtained data, writing the text - Ashurbekova K.N., Aliev A.A.; text editing - Isaeva R.Kh., Rabadanov M.Kh.

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