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STUDY OF ANTIBACTERIAL PROPERTIES OF MODIFIED TITANIUM OXIDE NANOFILMS SYNTHESIZED BY ATOMIC AND MOLECULAR LAYER DEPOSITION TECHNIQUES

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Abstract. This work presents the results of the study of the antibacterial properties of samples of TiO_2, TiON, TiN, TiAlN, TiO_2:V_2O_5 ultrathin films synthesized by Atomic and Molecular Layer Deposition (ALD/MLD) techniques. The studies were conducted on the colonies of the E. coli and S.aureus bacteria. It was found that samples of TiON films exhibit the greatest antibacterial activity. After an hour of exposure of the TiON samples under UV light with 365 nm wave length in presence of colonies of E. coli bacteria, the activity was 93.32%, and under normal daylight it was 74.60%, which is higher than for undoped TiO_2 samples with activity of 53.80% in UV light and 21.1% in daylight. Similar results were obtained with colonies of S.aureus bacteria, where the efficiency values were slightly lower due to the higher viability of these bacteria.

Keywords: *atomic layer deposition, molecular layer deposition, films, antibacterial, E. coli, S.aureus.*

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1. Introduction

The development of science led to the widespread use of technologies for modifying the surface of materials and the formation of thin nanofilms with a unique structure and different properties. The use of thin films and nanocoatings in medicine is relevant. Preventing bacterial colonization of medical surfaces is an important condition for limiting the spread of infections. Thin films can impart desired surface functions without affecting bulk mechanical properties. Antibacterial coatings have become a very active area of research, which is largely due to the growing urgency of identifying alternatives to the traditional use of antibiotics. As the analysis shows, the market of antibacterial coatings in 2024 will exceed 7.4 billion US dollars (*https://www.gminsights.com/pressrelease/antimicrobial-coatings-market*). The US Centers for Disease Control and Prevention in 2016 allocated fourteen million dollars in grants to thirty-four research groups to create a protective coating against antibiotic-resistant bacteria (Centers for Disease Control and Prevention).

The use of photocatalytic effects of nanothin TiO_2 films is a promising technology to reduce bacterial contamination. However, the band gap of titanium dioxide is 3.0–3.2 eV, which means that it can only be excited by ultraviolet radiation with a wavelength

<380 nm, which is only 5% of the solar spectrum. One of the ways to solve this problem is doping of TiO_2 nanofilms with elements capable of increasing its photocatalytic properties in the visible spectra. It will allow to shift a band gap below 3.0 eV, which would support photoactivity in the visible solar spectra.

In this work atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques have been applied to synthesize a series of modified TiO_2 film samples for antibacterial testing. ALD/MLD techniques allow to uniformly dope materials with various elements to obtain desired properties without any segregation of dopants (Abdulagatov *et al.* 2013; Kalkofen *et al.*, 2013; Gao *et al.*, 2018; Black *et al.*, 2018; Malek *et al.*, 2014, Illiberi *et al.*, 2014). ALD and MLD are novel thin film deposition techniques which are based on sequential self-limiting surface reactions (Jhonson *et al.*, 2014). If ALD allows to synthesize only inorganic coatings, with MLD it is possible to use organic molecules, thus giving hybrid organic-inorganic thin films. The unique features of these techniques are the ability to control the thickness and composition of nanofilms at the atomic level, high uniformity and a high level of film homogeneity when applied to membranes and nanoparticles. Numerous methods for doping TiO_2 with different elements are known in the literature (Carneiro *et al.*, 2005; Li & Li, 2001; Wu & Chen, 2004; Treschev *et al.*, 2008). In this work, we used ALD and MLD methods for the synthesis of visible light photoactive nanofilms of TiO_2 doped with nitrogen, vanadium, and aluminum.

The application of thin films on the surface can improve a variety of properties of implantable medical devices, including strength, wear resistance and slipperiness of surgical and dental equipment, coronary and urinary tract stents, wear resistance of devices designed to clean the coronary arteries and urinary tract, corrosion resistance, optical properties, antibacterial, electrical and thermal properties etc.

1.1 Antibacterial effect of TiO_2 based materials

The antibacterial effect of TiO_2 is based on the photocatalytic properties. When exposed to UV irradiation on the surface of TiO_2, electrons obtaining energy (hv) which equals or more than band gap energy (E_g) move from valence band to conduction band thereby leaving holes behind, which serve as oxidants (h^+) and electrons itself serve as reducers (e^-) of possible pollutants on the surface of TiO_2. It leads to the formation of highly activehydroxyl radicals ($OH^{\cdot}$) (Fig. 1), which destroy microorganisms on the surface of the particles. In many research papers (Menard *et al.*, 2011), the toxicity of various TiO_2 nanoparticles with respect to *E. coli* was studied. Many studies associate the toxicity of TiO_2 nanoparticles with their small particle size and crystal structure (Treschev *et al.*, 2008). It is usually considered that anatase TiO_2 is more toxic than rutile TiO_2, causing more oxidative stress (De Matteis *et al.*, 2016). Planchon et al (2013) reported 30% reduction in the growth of E.coli (Planchon *et al.*, 2013). It was also reported 72% reduction by 5 g/L TiO_2 and 44% of reduction in the growth of E.coli by 1 g/L TiO_2 nanoparticles (Adams *et al.*, 2006). In other work it was reported 70% reduction in the growth of E.coli by 10 mg/L TiO_2 (Adams *et al.*, 2006). However, the mechanism by which TiO_2 and TiO_2 based materials induce bacterial death and the effects that they have on bacteria are not well understood. Kubacka et al. (2014) conducted a complicated research trying to understand the impact of TiO_2-UV treatment on bacterial cells on the genetic level (Kubacka *et al*., 2014). Particularly TiO_2-UV treatment selectively affects cell structure components which leads to the overexpression of encoding enzymes responsible for the metabolism of lipids essential for cell membrane structure. After intervention cells experience significant deficiencies in the cell wall components, responding to it by activating the set of genes and proteins which produce lipids of cell membrane. Cells react to destructive effect of TiO_2-UV treatment by activating detoxification and repair mechanisms. TiO_2-UV treatment also effects the set of respiratory components of the cell by overexpression of NAD(P)1/NADH oxidoreductases, cytochrome c terminal oxidase components.

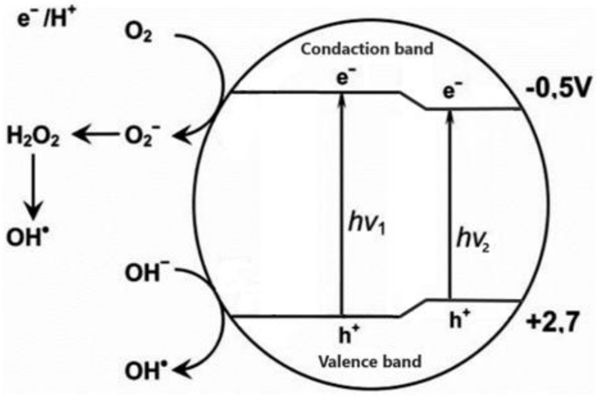

Figure 1. Mechanism of TiO_2photocatalysis: hv_1: pure TiO_2; hv_2: metal-doped and nonmetal TiO2

Many researches had been targeted on enhancing antibacterial and photocatalytic activity of TiO_2 in visible light spectra ((λ > 400 nm) by doping it with metal elements (Ag, Cu, Fe, Nb, W, Ce, Eu, La, Y) (Boonyod *et al.*, 2011; Xing *et al.,* 2009; Song *et al.,* 2008; Gartner *et al.,* 2005; Tobaldi et al., 2013) and nonmental elements (N, S, C, B, P, I, F) (Ohno *et al.,* 2003; Liu *et al.,* 2005; Yu *et al*., 2003) which would lead to narrowing band gap of TiO_2 and consequently less energy is needed for e^- to shift to conduction band (Fig.1.). The phenomenon of band-gap narrowing of doped TiO_2 has been reported in the literatures (Lin *et al.*, 2007; Akpan & Hameed, (2010)). In the case of Cu and Ag dopants, a direct increase in photocatalytic and antibacterial activity was observed with a concentration increase of the dopant, which apparently due the own antibacterial properties of Cu, Ag. In each of the cases of Fe^{3+}, Nb, Eu, La, Y there was the enhancement of antibacterial activity in visible spectra. However, the need for high-temperature annealing in the case of doping with metal atoms is a significant drawback.

2. Material and method

ALD and MLD films of TiO_2:V_2O_5, TiAlN, TiON, TiN, TiO_2, and Vanticone were synthesized in hot-wall, viscous-flow ALD reactor of “ASO Nanotech” company (Makhachkala, Russia). A detailed procedure for the synthesis of samples is described in previous works of the authors (Abdulagatov *et al.*, 2018; Abdulagatov, 2012). The determination of the antibacterial efficiency of film samples was carried out according to the methodological guidelines (Monitoring bacteria resistance to disinfectants in medical organizations, Federal Clinical Recommendations of Russia. M., 2014; Methods of laboratory research and testing of disinfectants to assess their effectiveness and safety, 2010).

a) Preparation of solutions of microbiological cultures of S. aureus and E. coli

Solutions of microbiological cultures with a concentration of 104 CFU / ml were prepared by diluting the initial solution with a concentration of 10^9 CFU / ml. For this, a 1 ml aliquot of the initial solution was taken with a dispenser and the total volume of the solution was adjusted to 10 ml with physiological saline. This procedure was repeated for new solutions to achieve a concentration of 104 CFU / ml. The concentration of CFU in the solution unit was estimated in Gorjaev's chamber.

b) The method for determining the antibacterial efficiency of film samples

For antibacterial efficiency determination, film samples of TiO_2, TiON, TiN, TiAlN, TiO_2: V_2O_5 and Vanticone were used. All film samples were sterilized first with ethyl alcohol, then with UV irradiation for 1 hour. The sterilized film samples were placed in a Petri dish and the nutrient medium, which was served as dried nutrient agar, was applied to them. 100 μl of bacterial culture of E. coli sanitary indicative microorganisms was carefully placedon samples with the nutritional medium. Samples were exposed to a UV (26 watts) with major wave length of 365 nm at a distance of 10 cm. Samples without UV exposure were used as a control, as well as samples of the tested cultures irradiated but deposited on undoped TiO_2. After 24 hours of incubation at 37° C, colonies were selected with an inoculation needle, diluted in physiological saline, 100 μl were taken out and sown on dense nutrient media with further dilution and 24 h incubation period. All studies were performed in 3 repetitions. Antibacterial activity of the investigated films was calculated by qualitative and quantitative methods. In parallel, the same manipulations were performed using S. aureus bacterial colonies. Studies were also performed in the presence of natural (room) light.

Qualitative assessment is comparing the growth of bacterial culture in Petri dishes. The antibacterial activity of the studied samples is judged by a statistically significant reduction in the number of colony-forming units (CFU), in the experiment compared with the control.

3. Results and Discussion

Nutrient agar mixed with saline solution in petri dishes was used as a breeding ground for bacteria. Fig. 2 and Fig. 3 show E. coli and S. aureus bacteria solutions after 24 h of incubation for different film samples. As can be seen, the lowest number of bacterial cultures after the incubation period was in the case of the TiON, TiAlN and V_2O_5 + TiO_2 samples, which indicate their highest antibacterial activity.

The samples of TiN film showed relatively high activity. In the case of undoped TiO_2, the lowest activity was observed compared with other samples, which confirms the absence of antibacterial activity 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 to conclude that TiO_2 acquires antibacterial properties in the visible light spectrum, which makes it potentially suitable for medical applications without the use of special sources of UV light. The results of studies of antibacterial efficiency of film samples of microorganisms E.coli and S.aureus are presented in the form of diagrams in Fig. 4 and Fig. 5.

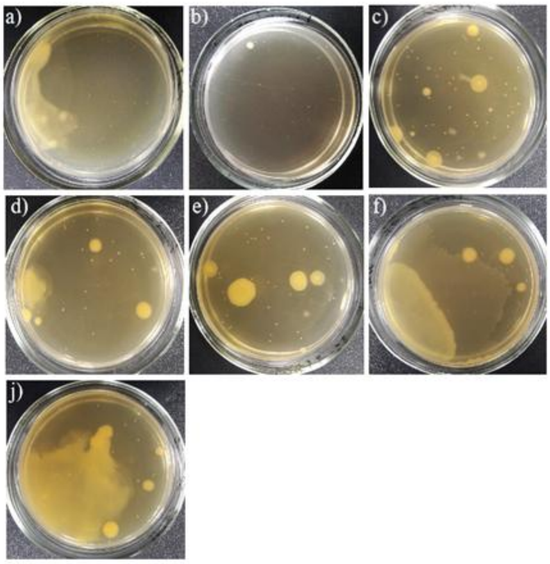

Figure 2. Solutions of bacterial cultures of E.coli after sowing on nutrient media and dilution in saline. a) TiO_2, b) TiON, c) TiN, d) TiAlN, e) V_2O_5: TiO_2, f) Vanticone, j) control

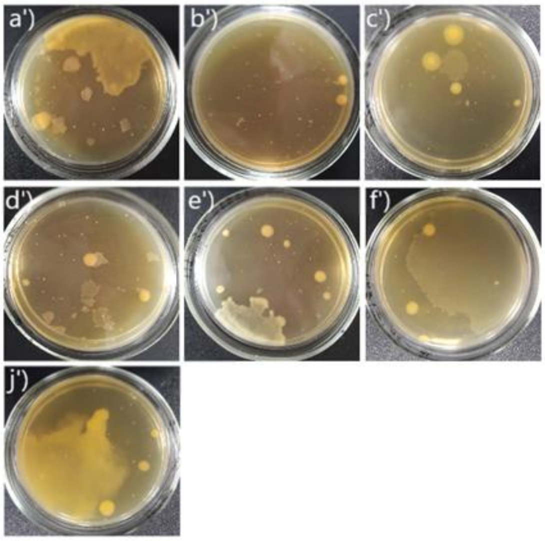

Figure 3. Solutions of bacterial cultures of S.aureus after sowing on nutrient media and dilution in saline. a') TiO_2, b') TiON, c') TiN, d') TiAlN, e') V_2O_5: TiO_2, f') Vanticone, j) control

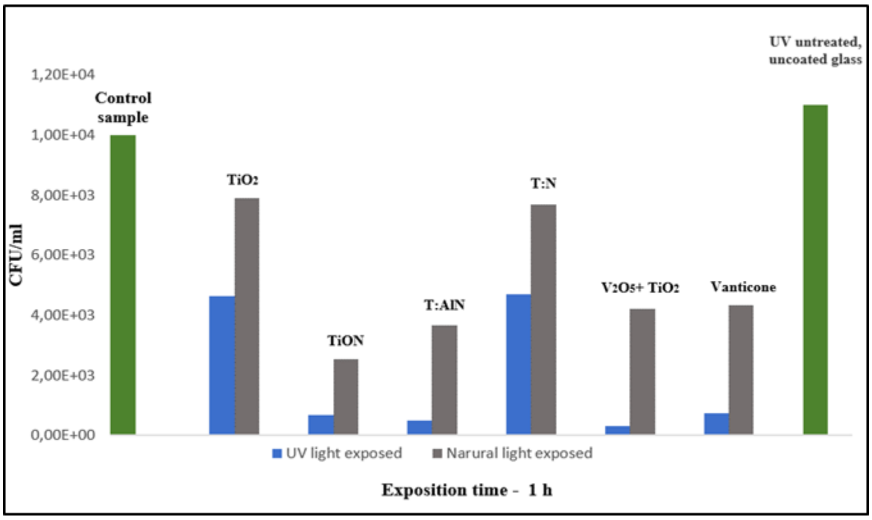

Figure 4. Results of the determination of the antibacterial activity of experimental samples in relation to E.coli.

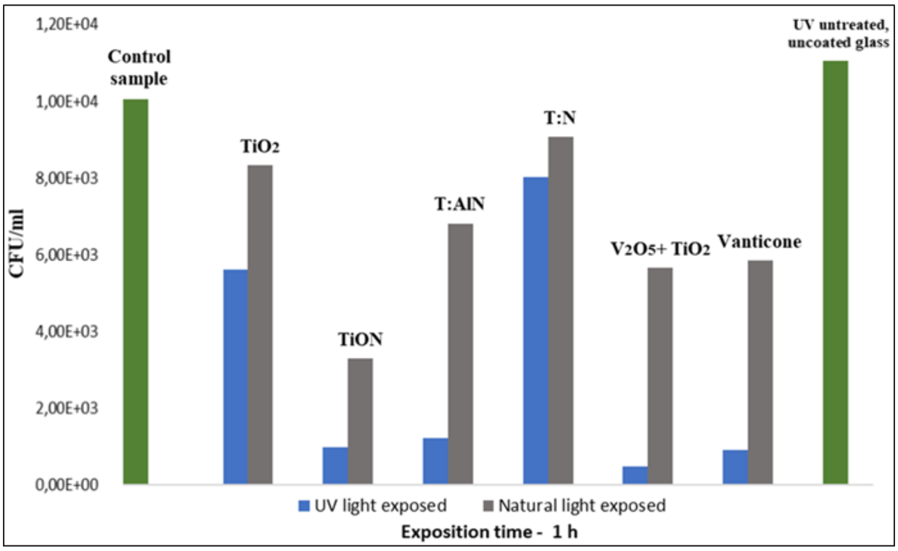

Figure 5. Results of the determination of the antibacterial activity of experimental samples in relation to S.aureus.

The significant difference in the results of antibacterial activity in the case of UV light source and natural light, which can be seen in the diagrams presented, is mainly due to the activity of TiO_2 itself in UV region. 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. The results of studies of antibacterial properties of samples with colony of bacteria S.aureus are illustrated in Fig.4. The main results of the determination of the antibacterial activity of the experimental samples are presented in Table 1.

Table 1. The results of the determination of the antibacterial activity of experimental samples

Samples	Exposition time	Antibacterial efficiency, %			
		Natural light exposition	UV light exposition	Natural light exposition	UV light exposition
	1 hour	E. coli	E. coli	S.aureus	S.aureus
TiO_2		21.10	53.80	17. 12	41.44
TiON		74.60	93.32	67.25	90.17
T:AlN		36.50	94.97	32.15	87.78
T:N		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
Untreated and uncoated glass samples		-	-	-	-

These results are in a very good agreement with previous works. Kim et al (2012) reported that the survival rate of *E. coli* in case of TiO_2:V_2O_5 nanoparticles after 50 min of illumination under fluorescent light source was 3.3-fold less than in case of pure TiO_2 nanoparticles (Kim *et al*., 2012) which is similar to death rate of *E. coli* reported in this work (TiO_2 - 21,1%, TiO_2:V_2O_5 - 57,83%).

In other work (He *et al*., 2013) it was reported that after 2 h of irradiating sample of N-doped TiO_2 in natural light the survival rate of *E. coli* was 8,75 %. According to the work (Vymětalová *et al*., 2016) antibacterial efficiency was 89% for N-doped TiO_2 and 59% for pure TiO_2 in case of bacteria colony of *E. coli* under mercury lamp which is similar to experimental results of our work where TiO_xN_y efficiency after UV-treatment was 93,32% and for TiO_2 - 53,80%.

4. Conclusions

According to obtained results, TiON,TiO_2:V_2O_5,TiAlN thin films exhibit the highest antibacterial activity in relation to the class of bacteriological cultures of E.coli and S. aureus, both under natural light and UV lamp. Vanticone thin films performed high activity in case of S.aureus under exposure of UV lamp (95.28% and 90.94%, respectively). It was found that the tested samples of thin films synthesized by ALD and MLD, have high antibacterial activity against bacterial cultures of sanitary indicative microorganisms S.aureus and E.coli. This study demonstrated a novel approach for the efficient utilization of visible light in killing bacteria through doping TiO_2 with various elements by atomic layer deposition and molecular layer deposition techniques. Understanding the processes of increasing photocatalytic, and as a result, the antibacterial activity of the synthesized thin films will allow in the future creating materials with predetermined parameters and functionality.

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