

This paper reports a study the into processes of plasma-electrolyte formation of heterooxidic coatings on titanium alloys for the photocatalytic destruction of natural and man-made toxicants. The synthesis of coatings was carried out from aqueous solutions of diphosphates under a galvanostatic mode. For a quantitative description of photocatalytic reactions, the constants of the reaction rate k_f from the linearized dependences $\ln(C_t/C_0)$, where C_t is the current, C_0 is the initial concentration of the reagent, were calculated. The morphology of the coating surface was investigated by atomic force microscopy, and the results were visualized by reconstruction of the relief in the form of 2D and 3D topographic maps. Morphological features of coatings made of titanium oxide (IV) and heterooxidic composites containing oxides of transition metals were analyzed. It is shown that the specific surface area remains an effective factor in regulating the photocatalytic activity of coatings. The establishment of the morphology of heterooxidic composites, as well as methods for controlling this parameter of the target product, is a constant component of the systematic study of such materials in determining their functional properties. It has been established that compared to oxide-titanium coatings whose surface layers are characterized by a toroidal mesostructure, heterooxidic compositions have a more developed surface, which has a positive effect on their functional properties. Subsequent heat treatment similarly affects the properties of the coating. The speed constants of the photocatalytic decomposition of the methyl yellow-hot azo dye were used to rank coatings of different composition according to their functional properties. Coatings from $\text{TiO}_2\text{-ZnO}$ showed the highest catalytic activity among the materials studied – k_f is $5.26 \cdot 10^{-3} \text{ min}^{-1}$, which is several times higher than the corresponding value for TiO_2

Keywords: plasma-electrolyte oxidation, titanium heterooxides, heterooxidic photocatalyst, photocatalyst morphology, azo dye, dopant

UDC 621.35
DOI: 10.15587/1729-4061.2022.269942

PATTERNS IN THE ELECTROCHEMICAL SYNTHESIS OF THIN-FILM PHOTOCATALYTIC MATERIALS BASED ON TITANIUM HETEROOXIDE COMPOUNDS

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Received date 10.10.2022
Accepted date 13.12.2022
Published date 30.12.2022

How to Cite: Sakhnenko, M., Stepanova, I., Korogodskaya, A., Karakurkchi, A., Skrypnyk, O., Dzhenuk, A., Halak, O. (2022). Patterns in the electrochemical synthesis of thin-film photocatalytic materials based on titanium heterooxide compounds. *Eastern-European Journal of Enterprise Technologies*, 6 (12 (120)), 30–39. doi: <https://doi.org/10.15587/1729-4061.2022.269942>

1. Introduction

Among the numerous problems that have worsened in Ukraine as a result of martial law, environmental problems occupy a prominent place. This situation is caused by numerous destructions of industrial facilities, leaks of tech-

nogenic oxides from destroyed enterprises of the industrial complex and housing and communal infrastructure, etc. A significant number of these problems can be solved by the widespread introduction of highly effective technologies for the conversion of natural and man-made toxicants using chemical, physical and physical-chemical methods based on

nanosynthesis, nanocatalysis [1, 2], etc. The chain of such technologies includes reagent-free methods for neutralizing chemically hazardous substances of natural and man-made origin, means of reducing toxic emissions from transport engines, etc. [3, 4]. In such circumstances, the problem of ensuring the functioning of life support services, as well as mobile means of military and civilian use, is among the most relevant. Filter-ventilation systems for the arrangement of stationary facilities and mobile vehicles need improved technologies, too [5]. Therefore, research aimed at creating the scientific foundations of controlled synthesis of functional materials for the catalytic neutralization of natural, synthetic, and man-made toxicants is becoming important and, undoubtedly, relevant.

2. Literature review and problem statement

Among the methods of destruction of natural and man-made toxicants, the leading role is played by methods of heterogeneous catalysis [6], although by the nature of the processes taking place, they are costly and involve the use of various reactants. Household photocatalytic devices for surface disinfection [7] and air conditioning have become widespread due to their unpretentiousness and ease of use. Methods of purification of liquid media are based on the same basis [8, 9], which is also due to their very attractive features, but the processes of creating materials for their implementation are either costly or require quite expensive equipment. As photocatalysts, first of all, such semiconductor materials as TiO_2 [10], ZnO [11], etc. are considered. To improve the functional characteristics of materials, they are modified by various elements both in the volume of Fe_2O_3 [12] and on the surface [13]. A separate group consists of composites based on semiconductor compounds [14], although it is not as numerous as the previous ones. However, despite the positive results of testing such photocatalysts in model reactions and in the decomposition of individual toxicants, the informativeness of the results is very limited by the lack of consistency and ranking of the studied systems. Although among the listed photocatalysts, titanium oxide (IV) (TiO_2) is considered the most attractive due to its chemical inertness and non-toxicity [15], however, complex two-component oxide systems can exhibit significantly higher activity [16]. At the same time, it is highly expected to increase their selectivity [17], as is practically proven in the case of multicomponent synergistic alloys [18]. However, only individual photocatalytic systems were tested, which significantly limits the spectrum of materials suitable for practical use. The reason for this is the lack of a comparative analysis of their properties by ranking by photocatalytic activity.

Practical application of photocatalytic systems based on semiconductor structures [19] involves the formation of a developed surface and a decrease in the width of the band gap. To do this, it is necessary to modify them either due to surface and volumetric doping, or to create composites based on them [20, 21]. In the latter case, this requires detailed research due to the lack of effective empirical approaches. There are three main opinions about the mechanism of modification of TiO_2 , doped with non-metals, and the nature of synergism, which are explained: narrowing the width of the band gap (a), the energy level of impurities (b), oxygen vacancies (c):

a) Narrowing the width of the restricted area. In [22], $2p$ hybridization of nitrogen states and $2p$ hybridization of oxygen states in nitrogen-doped TiO_2 anatase was revealed since their energies are very close. Due to this, the width of the forbidden zone N- TiO_2 is narrowed and capable of absorbing visible light.

b) Energy level of impurity. It has been established [23] that oxygen nodes in the structure of TiO_2 , replaced by nitrogen atoms, form isolated impurity energy levels above the valence zone. UV light irradiation excites electrons both at the energy level of the valence zone and at the impurity energy level, while exposure to visible light excites electrons only at the impurity energy level.

c) Oxygen vacancies. The authors of [24] concluded that areas with oxygen deficiency formed at the grain boundaries are important for the manifestation of viscosity activity and doping with nitrogen in some areas with oxygen deficiency is important as a re-oxidation blocker.

Thus, the analysis of the information field on the problem of synthesis of effective materials for photocatalysis allows us to conclude on promising directions for improving the efficiency of the photocatalytic process. The working hypothesis underlying the study is based on the possibility of realizing a better charge distribution and expanding the active light range [25, 26] by creating composites (including heterostructures) based on two or more semiconductors. However, the implementation of the proposed solutions involves the use of nanotechnology, which currently significantly limits the possibilities of their implementation. A comprehensive solution to this problem is seen in the development of scientific foundations for controlled synthesis of coatings with heterooxidic and/or doped titanium oxides (IV) on the surface of metal carriers. At the same time, the priority is the use of titanium alloys as carriers, and the synthesis process should be implemented using electrochemical technologies [27], which was the object of the study. It is on such principles that the study should be carried out, the result of which will be the technological basis for the production of effective photocatalytic materials and coatings for the needs of the industrial complex. The result will be the solution of a number of environmental problems and the creation of safe conditions for the functioning of the population in areas of destruction of infrastructure facilities.

3. The aim and objectives of the study

The aim of this study is to identify patterns of controlled electrochemical synthesis of coatings with heterooxidic and/or doped titanium oxides (IV) on the surface of metal platforms, in the role of which the priority is the use of titanium alloys. This will provide an opportunity to create high-performance photocatalytic materials with a wide range of applications.

To accomplish the aim, the following tasks have been set:

- to develop an effective basis for the electrochemical formation of heterooxidic coatings based on titanium oxides (IV);
- to investigate the morphology of heterooxidic coatings depending on their elemental composition and modes of formation;
- to establish the kinetic parameters of the reaction of photocatalytic decomposition of model toxicants in the presence of heterooxidic coatings of different composition and to rank them.

4. The study materials and methods

Heterooxidic coatings based on titanium (IV) were synthesized by plasma-electrolyte oxidation on substrates made of alloy VT1-0 [28] from aqueous solutions. The solutions were prepared on the basis of $1.0 \text{ mol/dm}^3 \text{ K}_4\text{P}_2\text{O}_7$, to which dopant compounds were injected either as soluble salts (Co, Cu, Mn, Sn, Mo, W) or phase oxides (ZnO , ZrO_2). The plasma-electrolyte oxidation (PEO) process was carried out by direct current j , varying the current density in the range of $2.0\text{--}8.0 \text{ A/dm}^2$ with support of the forming voltage in the range of $110\text{--}180 \text{ V}$ for 30 min. Electrolysis was carried out with forced cooling to a temperature of a little more than 30°C . Heat treatment of some samples after applying the oxide coating was carried out for 20 minutes in a muffle furnace with free aeration at 500°C .

The composition and morphology of the surface of the mixed oxide layers was investigated using a raster electron microscope (SEM) ZEISS EVO 40XVP. The images were obtained by registering secondary electrons by scanning with an electron beam, which made it possible to study topography with high resolution and contrast. The error in measuring the content of the components was $\pm 1 \text{ wt } \%$.

The topography of the coating surface was analyzed according to the results of atomic force microscopy (AFM), using the NT-206 microscope. The scanning was performed by the contact sensor CSC-37 (lateral and vertical resolution of 2 and 0.2 nm, respectively; sensor-cantilever B , tip radius 10 nm), and the visualization of the results was carried out using 2D and 3D topographic maps.

The photocatalytic properties of the coatings were tested in the model oxidation reaction of the methyl yellow-hot (MYH) azo dye. The studies were carried out in a thermostatic photocatalytic reactor at temperature of 25°C and constant stirring; the initial concentration of the azo dye varied in the range of $(0.02\text{--}2.0) \cdot 10^{-4} \text{ mol/dm}^3$. A solution of MYH with submerged carrier plates, on the surface of which photocatalytic coatings with TiO_2 monoxide were formed, as well as heterooxidic compositions, was irradiated using an EBT-01 mercury lamp emitting soft ultraviolet light. Previously, all solutions with submerged catalysts were kept in the dark for 60 minutes to establish adsorption equilibrium. The content of the MYH dye in the reactor was determined at regular intervals by the photocolometric method. In parallel, the process of oxidation of MYH without UV irradiation and in the absence of a photocatalyst was investigated. For a quantitative description of photocatalytic reactions, the reaction rate constants were determined from linearized dependences $\ln(C_t/C_0)$, where C_t is the current concentration of the azo dye, C_0 is the initial concentration of the reagent [29].

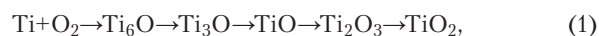
5. Results of studies of titanium-based heterooxidic composites as thin-film photocatalytic materials

5.1. Electrochemical formation of heterooxidic coatings based on titanium (IV) oxides

The latest electrochemical technologies are implemented with the involvement of large databases, cloud, and Internet technologies, artificial intelligence, and other means of organizing electrochemical systems and industrial production, that is, on the basis of Industry 4.0 [30]. When creating high-tech products, which include innovative technologies of electrochemical synthesis of the above materials, priority

is given to the functional properties of the latter – electro- and photocatalytic, chemical resistance, etc. At the same time, they take into account the possibility of controlling the morphology of sediments to create a predetermined degree of surface development and crystallinity, fractality, texture, porosity, and other important parameters. If we limit the range of issues considered only to the problems of electrochemical materials science, then we can define the meaning of solving the problem as surface treatment of highly doped materials, which include high-alloyed titanium alloys. Such alloys are the starting material for creating the main matrix of heterooxidic composites by forming an appropriate morphology of catalytic cover carriers. The conjugate process is the incorporation into the surface oxide layers of the alloying components, resulting in the creation of appropriate electrical and photocatalytic systems. The complexity of the problem in this case is due to the high chemical resistance of these materials and the heteroresistivity of the treated surface, which significantly complicates the use of electrochemical technologies, as the least costly, to solve surface engineering problems. However, one of the most effective ways to overcome these obstacles is to homogenize the treated surfaces by parallelizing anode processes in order to dissolve the alloying elements from the surface layers and simultaneously oxidize the main alloy matrix. For the implementation of this method of processing high-alloyed alloys, in particular titanium alloys of various composition and nature, the method of plasma-electrolyte oxidation (PEO) is very attractive [31, 32].

At the same time, titanium oxidation, compared to the oxidation of other valve metals (aluminum, niobium, tantalum), is the most difficult process. The reason for this is due to the possibility of the formation of TiO_x titanium oxides of different composition ($0.75 < x < 1.3$), as well as Ti_2O_3 and TiO_2 , which differ in structure, chemical and physical properties. The sequence of stages of titanium oxidation is reflected in the scheme:



which takes into account the probability of interaction under certain conditions of TiO_2 with metallic titanium and the formation of lower oxides and solid solutions. At the same time with the formation of the oxide layer on titanium, its dissolution also occurs, and the course of competing reactions causes a general instability of the formation process. The reasons for the latter are the formation of oxides with different resistivity (1), a decrease in the resistance of titanium dioxide with increasing temperature in the discharge zone and a spark breakdown of the oxide film. It is also possible to reduce TiO_2 metallic titanium to oxides with a lower valence, which, due to their semiconductor or metallic nature, also have a lower resistance. But even taking into account the above-mentioned complexities of PEO titanium alloys, it allows you to create highly efficient variable processes for the synthesis of functional covers for various purposes, in particular photocatalytic.

The synthesis of oxide compositions of different composition and structure on the surface of the carrier from the valve metal or its alloy took place in PEO modes. The driving force of the synthesis was the course of the anode reaction of oxidation of the carrier metal under conditions when the temperature in the discharge zone can reach 2000°C . Addition to the electrolyte of compounds containing metal

in the composition of oxygen-containing anions (oxo anions) provides an increased content of metal oxides in the composition of coatings and increases the specific surface area, which predictably should contribute to the growth of catalytic activity of the synthesized materials. Coatings synthesized in PEO mode, from electrolytes with different ratios of ingredients, as well as at different current densities (Table 1), are distinguished by a strong adhesion bond with the substrate and specific morphology. The composition of the electrolyte and the density of direct current affect both the sparking voltages U_s and the formation of U_f (Table 1), as well as the content of the elements and the relief of the surface oxide layers.

Table 1
Conditions for the synthesis of heterooxidic coatings in the PEO mode

Sample No.	Electrolyte composition, mol/dm ³	PEO parameters	
		Current density j , A/dm ²	Voltage U_s/U_f , V
1	K ₄ P ₂ O ₇ -1.0	7.0	60/120
	ZnO-0.4		
2	K ₄ P ₂ O ₇ -1.0	7.0	60/110
	ZnO-0.1		
	CuSO ₄ -0.08		
3	K ₄ P ₂ O ₇ -1.0	8.0	80/140
	ZnO-0.1		
	CuSO ₄ -0.08		
4	K ₄ P ₂ O ₇ -0.5	4.0	120/180
	Na ₃ Cit-0.1		
	ZnO-0.1		
5	K ₄ P ₂ O ₇ -0.5	4.0	80/120
	Na ₂ WO ₄ -0.1		
	ZnO-0.1		
6	K ₄ P ₂ O ₇ -0.5	2.0	100/130
	Na ₂ WO ₄ -0.05		
	CoSO ₄ -0.05		
7	K ₄ P ₂ O ₇ -0.5	2.0	70/120
	ZnO-0.1		
	CoSO ₄ -0.1		
8	K ₄ P ₂ O ₇ -0.5	5.0	120/260
	Na ₂ MoO ₄ -0.1		
	ZnO-0.1		
9	K ₄ P ₂ O ₇ -0.5	3.0	60/200
	ZrO ₂ -0.15		
10	K ₄ P ₂ O ₇ -0.5	4.0	60/110
	SnSO ₄ -0.2		

The composition and topography of the surface layers of PEO are due to oxidation processes with the formation of local channels of thermal and/or electrical destruction of the oxide film. In the vicinity of these zones, the surface of juvenile titanium is oxidized, as well as the formation of gas bubbles that play the role of polarized electrodes, and high-temperature melting of electrolyte components.

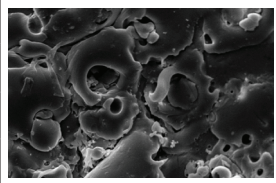
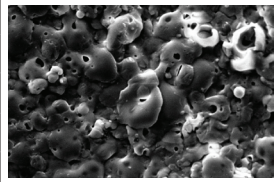
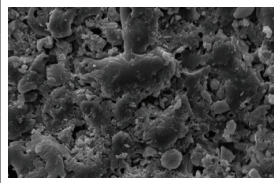
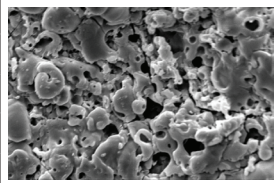
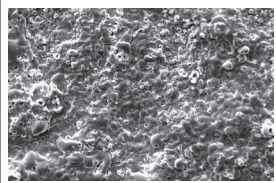
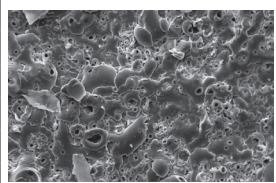
Chronograms of voltage in the process of forming heterooxidic coatings on titanium in diphosphate electrolytes have a traditionally classical form, which reflects the presence of three sections [28]. The initial is the pre-charge section of a

linear shape, which corresponds to the growth of the thickness of the oxide layer. For all electrolytes under study, the time to reach the sparking voltage is 10–60 s. The exception is an electrolyte containing ions MoO₄²⁻, for which this period increases to 150–200 s.

5. 2. Study of morphology of heterooxidic coatings depending on their elemental composition and modes of formation

When analyzing the topography of coatings formed in the PEO mode, one can note a well-developed surface of mixed zinc-containing oxides TiO₂-ZnO, applied at $j=7$ A/dm² (sample 1, Table 2). The images position the toroidal structures over fairly deep rounded pores, the size of which ranges from 1 to 5 microns. In addition, the coating includes melting of electrolyte components, in particular phosphorus oxide (V).

Table 2
Composition and surface morphology of heterooxidic coatings formed in the PEO mode on titanium alloy VT1-0

Sample number	The composition of the surface layer, mol. %	Surface image, magnification ×2000
1. TiO ₂ -ZnO	Ti-16.1	
	O-67.1	
	P-14.8	
	Zn-2.0	
2. TiO ₂ -ZnO-CuO	Ti-16.0	
	O-65.9	
	P-15.8	
	Zn-1.5	
3. TiO ₂ -ZnO-CuO	Ti-13.7	
	O-65.3	
	P-16.9	
	Zn-0.3	
4. TiO ₂ -ZnO-CuO	Ti-22.4	
	O-65.0	
	P-9.6	
	Zn-0.2	
5. TiO ₂ -ZnO-WO ₃	Ti-21.44	
	O-46.30	
	P-23.75	
	Zn-4.67	
6. TiO ₂ -CoO-WO ₃	W-3.83	
	Ti-16.51	
	O-59.68	
	P-15.72	
	W-1.26	
Co-1.30		
K-5.53		

The introduction of copper (II) sulfate into the electrolyte naturally contributes to the inclusion of CuO in the surface layer (sample 2, Table 2). Moreover, when the ZnO/Cu²⁺ molar ratio in the electrolyte is ~1:1, the metals are included in the coating in a ratio of 2:1 at the same current density. The sparking and forming voltages practically do not change, which reflects the effect of zinc oxide on surface morphology and the electrical resistivity of mixed oxide coatings. It should also be noted that the surface becomes more evenly developed and globular, the size of the globules is reduced to 1–2 microns, and the pores – to 100–500 nm compared to sample 1.

As the current density increases to 8.0 A/dm², the surface morphology changes significantly and becomes more spherical, and the content of metals included in the TiO₂ matrix changes and is 1:12 with respect to Zn/Cu (Example 3, Table 2). At the same time, the sparking and molding voltages increase by almost 20 V.

The addition of a citrate ion as a ligand, while reducing the concentration of diphosphate, makes it possible to achieve the appearance of a microarc in the PEO mode at a lower current density of 4 A/dm². However, at the same time, the values of the voltages *U_s* and *U_f* increase by almost 40 V (sample 4, Table 2), the coating is enriched with copper, and the multicomponent oxide TiO₂·ZnO·CuO becomes more porous.

Thus, by varying the composition of electrolytes and PEO modes, it is possible not only to introduce additional

oxides into the main matrix of titanium oxide but also to control the morphology of the surface.

In coatings formed from electrolytes containing Co²⁺ and WO₄²⁻ ions (sample 6 in Table 2), significantly fewer tungsten compounds were found compared to the coating of TiO₂·ZnO·WO₃ (sample 5 in Table 2). At the same time, the morphology of the surface of the samples changes in the direction of a more developed relief with an uneven distribution of structural elements. Analyzing the elemental composition of coatings TiO₂·CoO·WO₃, it should be noted that the content of the elements is almost the same on the surface of craters and in the valleys.

The results of SEM are well consistent with atomic force microscopy data. In a detailed study of the topography of the synthesized coatings, it was found that in comparison with the original structure of TiO₂ (Fig. 1), heterooxidic coatings of TiO₂·ZnO (Fig. 2) have a more developed surface. Over time, the surface grows and during heat treatment acquires a uniform distribution of globular structures and micropores (Fig. 3).

Thus, it should be noted that the heat treatment of heterooxidic coatings can improve at least two factors of the photocatalytic process. Firstly, titanium oxide (IV) presumably turns into a more active form – anatase, and, secondly, the specific surface area of the coating increases. Presumably, it is the combination of both factors, as expected, that will increase the efficiency of photocatalytic transformations involving heterooxidic composites.

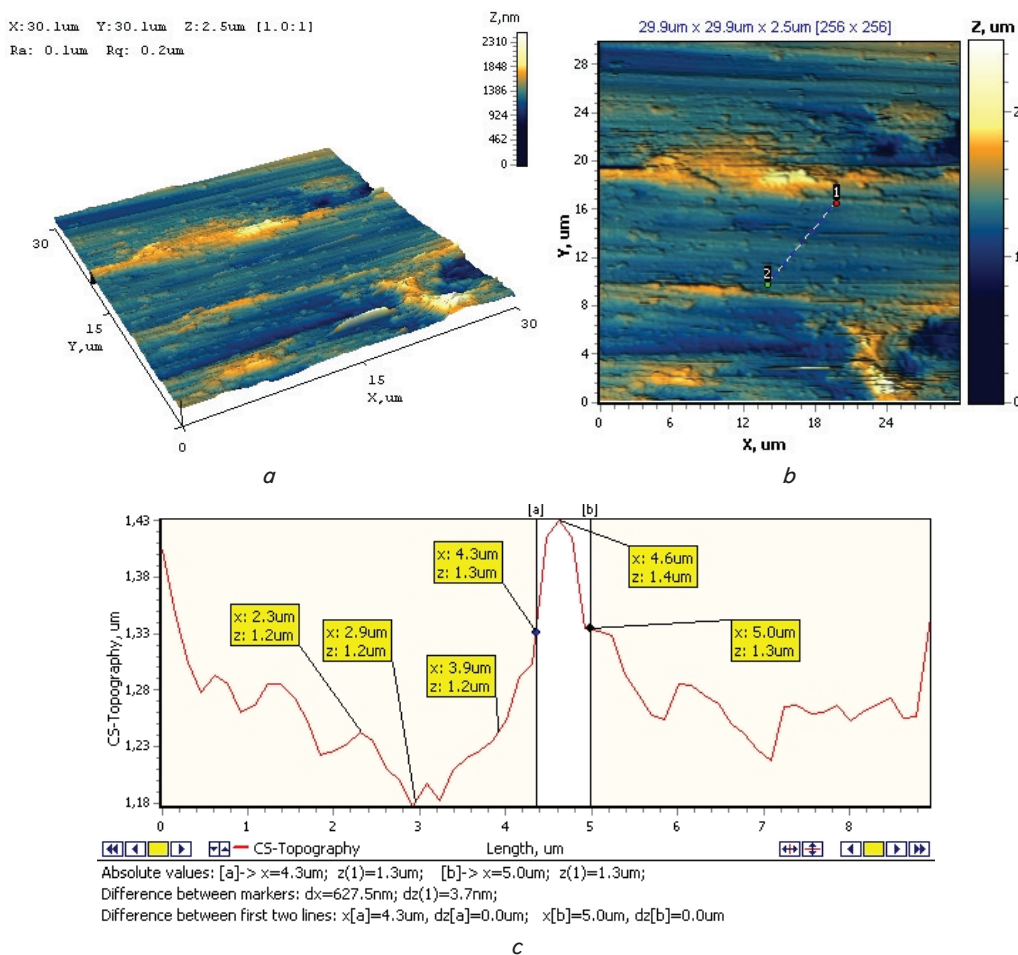


Fig. 1. Atomic force microscopy results for coating from TiO₂ oxide: a – 2D map; b – 3D-map (scanning area 30×30 microns); c – surface profile between markers 1 – 2

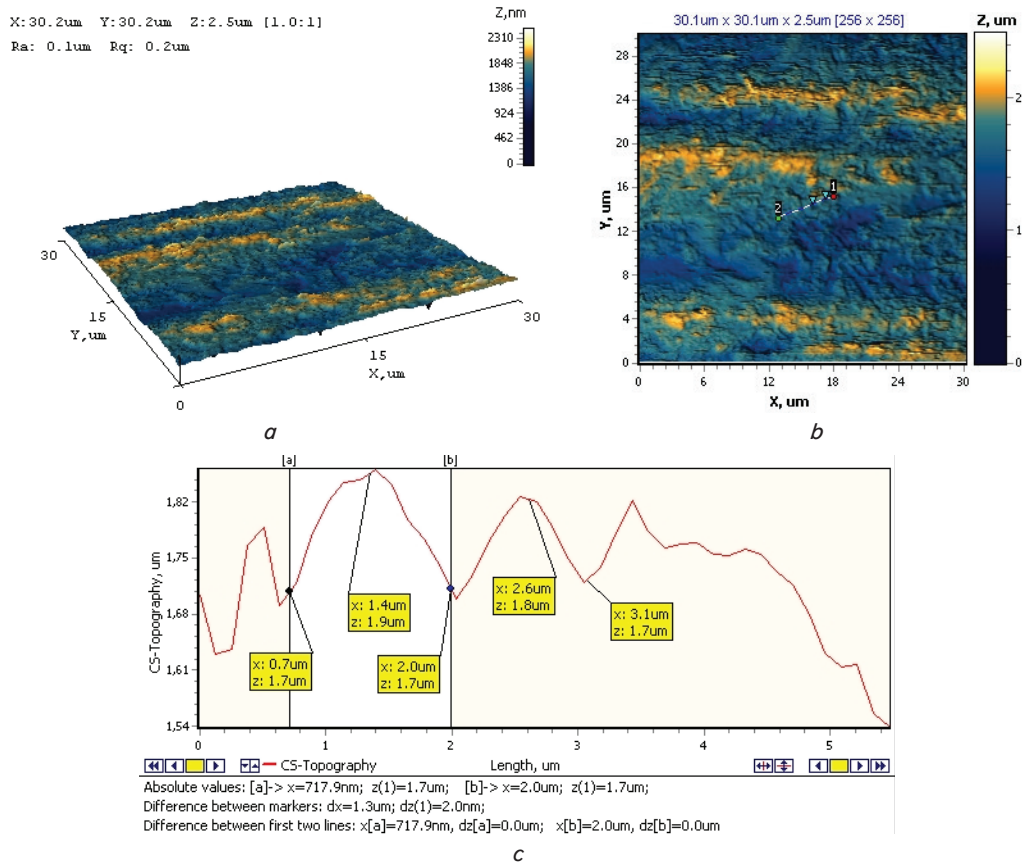


Fig. 2. Atomic force microscopy results for coating $\text{TiO}_2\text{-ZnO}$ heterooxide before calcination: *a* – 2D map; *b* – 3D-map (scanning area 30×30 microns); *c* – surface profile between markers 1–2

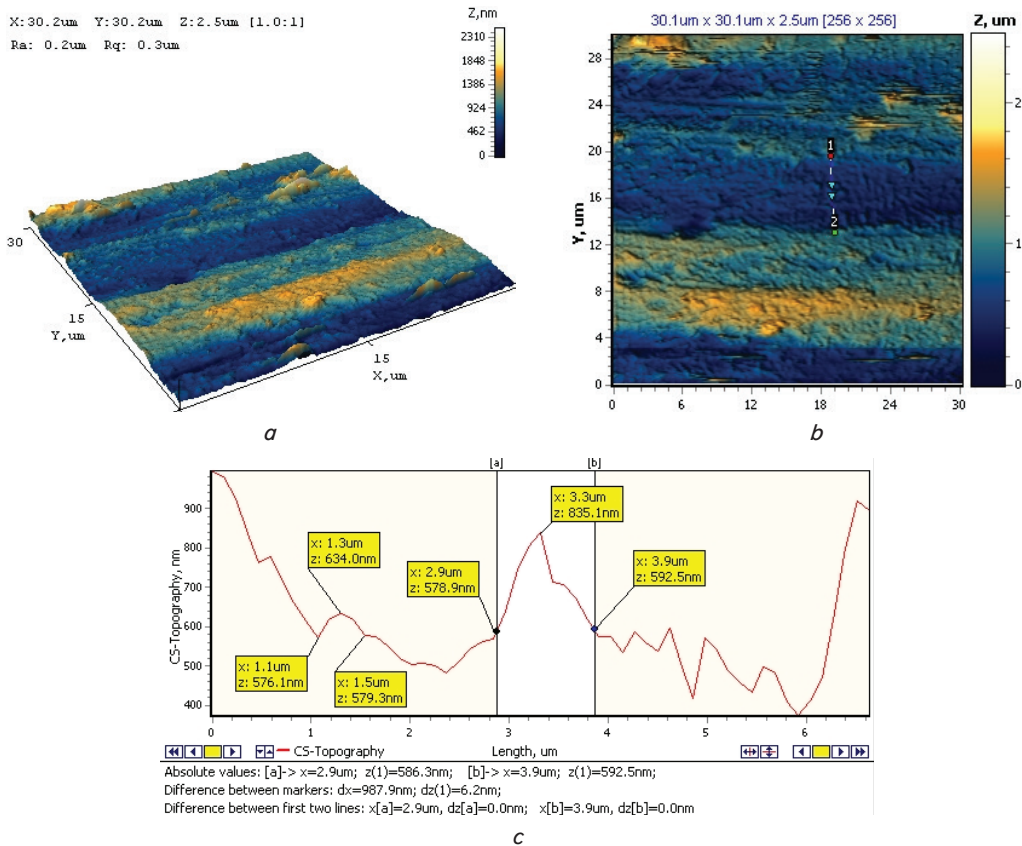
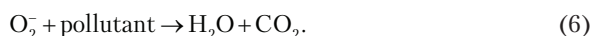
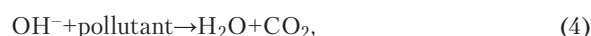


Fig. 3. Atomic force microscopy results for coating $\text{TiO}_2\text{-ZnO}$ heterooxide after calcination: *a* – 2D map; *b* – 3D-map (scanning area 30×30 microns); *c* – surface profile between markers 1–2

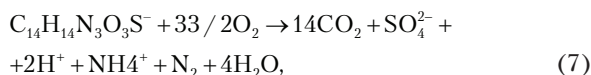
5. 3. Investigation of photocatalytic decomposition of methyl yellow-hot azo dye in the presence of heterooxidic coatings and their ranking

The photocatalytic activity of the catalyst is due to the formation of holes in the valence zone h_{vb}^+ and electrons in the conduction zone e_{cb}^- due to the absorption of photon energy by reaction (2). In this case, the energy level should exceed or equal to the width of the band gap of the semiconductor [33].

Under such conditions, holes contribute to the formation of hydroxide radicals and the oxidation of organic compounds by reactions (3), (4), and electrons contribute to the formation of superoxide radicals by reactions (5), (6), as well as decomposition and oxidation reactions [34]:



Since photocatalytic activity undoubtedly depends on the composition and morphology of the surface of the coatings, as well as on the concentration of reagents, the content of MYH in the test solution varied. When analyzing the data obtained, they took into account the fact that the consequence of the photocatalytic process is a change in the pH of the solution. So, in accordance with the gross reaction of oxidation and complete mineralization of MYH:



it is possible to predict a decrease in the pH of the solution during photooxidation. However, pH chronograms indicate that acidification of the solution occurs up to a pH of 6.65 only during the first 10–12 minutes of irradiation.

The photocatalytic properties of mono- and heterooxidic coatings were evaluated by chronograms of changes in the content of MYH in aqueous solutions due to the decomposition of the azo dye. In this way, composite materials were ranked according to functional properties, albeit with some limitations. $C(t)$ chronograms have a typical character, which reflects the dependence of changes in the concentration of azo dyes under the influence of UV irradiation in the presence of catalytically active material.

The main factors affecting the rate of photocatalytic reactions are the nature of reactants (μ_p), including oxidizer (μ_{OX}), and their initial concentrations (c_i), the nature of dopants (μ_M) and their content (ω_M) in the photocatalyst. It is also necessary to take into account the temperature (T) and pressure (p) of the reaction mixture, the specific surface area of the catalyst (S_k) and exposure intensity ($h\nu$). It is in the factor space of these variables that a heterogeneous photocatalytic process is realized, the efficiency of which, at a fixed time of transformation t , can be given by the operator

$$X = f(\mu_p, c_i, \mu_M, \omega_M, T, p, S_k, h\nu \dots). \quad (8)$$

From the analysis of dependences $C(t)$ it follows that the kinetics of decomposition of MYH is determined not only by the nature of the catalytic material and its content but also by the concentration of MYH and other factors. Investigation of the kinetics of azo dye decomposition in the presence of synthesized photocatalytic materials by linearization of kinetic chronograms in coordinates $\ln(C_t/C_0) - t$ proved the first order of reaction (Fig. 4).

Calculated from the indicated linearized dependences, the reaction rate constants k_f (Fig. 5) made it possible to conduct a comparative analysis of the effect of heterooxidic photocatalytic coating on the process of destruction of the azo dye.

Comparison of the properties of heterooxidic systems by photocatalytic activity with the coating of unalloyed TiO_2 (Fig. 4, 5) showed the expected fact of a significant influence of d -element doping on the increase in the functional properties of the monoxide matrix [34]. Thus, in the presence of titanium monoxide, the value of the reaction rate constant k_f is $2.8 \cdot 10^{-3} \text{ min}^{-1}$, whereas under the same conditions for heterooxidic coating $\text{TiO}_2\text{-ZnO}$ increases to $5.26 \cdot 10^{-3} \text{ min}^{-1}$. In addition, it can be argued quite proven that according to the geometry and nature of the formative PEO dependences, it is possible to predict the behavior of heterooxidic systems in the reactions of photocatalytic decomposition of certain groups of toxicants [33]. Presumably, this dependence should exist in relation to heterogeneous catalysis in general, and in particular electrocatalysis, although these observations must be proven by the results of extensive experimental testing.

Very interesting and important were the results of the assessment of the effect of the subsequent PEO heat treatment of heterooxidic composites on their photocatalytic activity. Thus, the catalytic activity of $\text{TiO}_2\text{-ZnO-CuO}$ heterooxide, the composition of which corresponds to sample 2 of Table 2, significantly depends on the concentration of MYH in solution and heat treatment (Fig. 6).

Obviously, the long-term activity of such a system increases after heat treatment (curves 1 and 2 in Fig. 6) and allows you to achieve a conversion of 24.6 % in 60 minutes. In addition, the three-component oxide layer works better at lower concentrations of MYH (dependence 3 in Fig. 6).

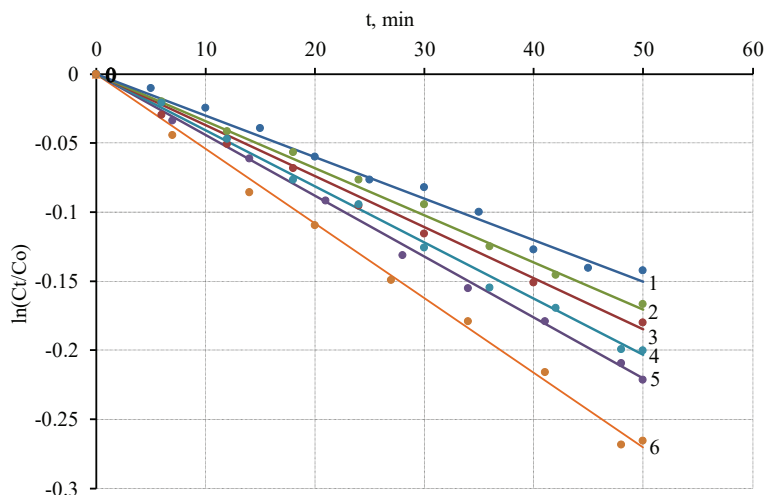


Fig. 4. Influence of heterooxidic systems composition on the degree of decomposition of methyl yellow-hot azo dye under ultraviolet irradiation: 1 – Ti/TiO_2 ; 2 – $\text{ZnO-WO}_3/\text{TiO}_2$; 3 – $\text{ZnO-MoO}_3/\text{TiO}_2$; 4 – $\text{ZnO-Co}_3\text{O}_4/\text{TiO}_2$; 5 – CuO/TiO_2 ; 6 – ZnO/TiO_2

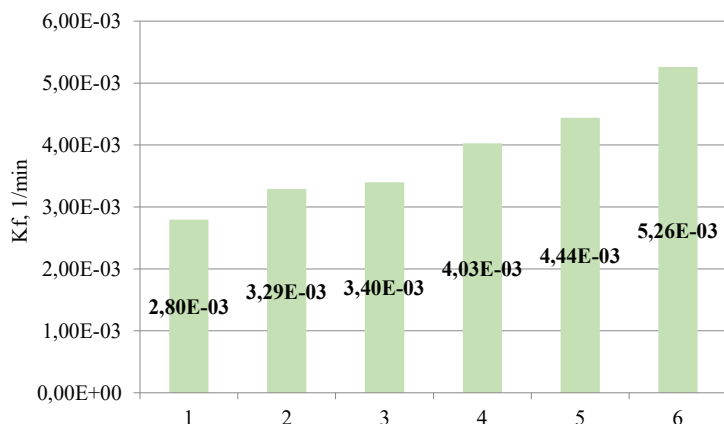


Fig. 5. Constants of the decomposition rate of methyl yellow-hot azo dye during ultraviolet irradiation in contact with coatings of the following composition: 1 – Ti/TiO₂; 2 – ZnO-WO₃/TiO₂; 3 – ZnO-MoO₃/TiO₂; 4 – ZnO-Co₃O₄/TiO₂; 5 – CuO/TiO₂; 6 – ZnO/TiO₂

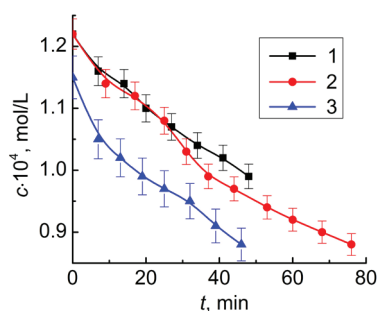


Fig. 6. Photo destruction of methyl yellow-hot azo dye on TiO₂-ZnO-CuO coatings: 1 – without heat treatment; 2, 3 – with heat treatment, 1, 2 – concentration of methyl yellow-hot azo dye, $1.22 \cdot 10^{-4}$ mol/l; 3 – concentration of methyl yellow-hot azo dye, $1.15 \cdot 10^{-4}$ mol/l

The obtained results from the evaluation of the photocatalytic activity of heterooxidic composites of variable composition, synthesized on a platform from titanium alloys, became the basis for ranking the materials obtained according to their functional purpose. It is these results that make it possible to determine the most promising materials for practical application in photocatalytic purification systems of liquid and gaseous media from toxicants.

6. Discussion of results of the study of titanium-based heterooxidic composites as thin-film photocatalytic materials

The results of our authentic research into the development, studying the morphology, and testing the photocatalytic materials clearly indicate in favor of the use of the electrochemical method of PEO to create heterooxidic composites based on titanium. As follows from the analysis of the results given in Tables 1, 2, coatings synthesized in the PEO mode from electrolytes when varying the ratio of ingredients at different current densities (Table 1) are distinguished by a specific morphology. Thus, in comparison with the original structure of TiO₂ (Fig. 1), heterooxidic coatings of TiO₂-ZnO (Fig. 2) have a more developed surface. Over time, the surface grows and during heat treatment acquires a uniform distribution of globular structures and micropores (Fig. 3). One of the characteristic features of PEO technology was the ability to

form heterooxidic coatings, which include compounds of alloying elements. The quantitative content of the latter can be varied by changing the composition of electrolytes and electrolysis modes, as well as creating a controlled surface morphology.

Comparison of photocatalytic activity of heterooxidic systems compared to coatings of unalloyed TiO₂ (Fig. 4, 5) showed the expected fact of increasing the functional properties of the monoxide matrix due to the doping of *d*-elements using PEO technology.

The materials created in this way have a predetermined composition and controlled morphology, and therefore a specific surface area, which, unlike [19], is the basis for their use as thin-film photocatalytic materials. Variation of the modes of formation of heterooxidic composites makes it possible to change the structure and composition of surface layers within wide limits and determine the most effective systems for functional purpose.

The main reason for increasing the efficiency of heterooxidic compositions with respect to TiO₂ monoxide is the effect of using dopants, the conditions for the implementation of which are laid down in the PEO technology. This allows you to create high-performance film photocatalytic converters.

Determining the role of dopants in the composition of heterooxidic compositions is quite natural for the exhaustive characteristics of the photocatalytic coating. However, such a procedure should be carried out only with a stable content of oxides, which limits the variability of the technology, since the content of titanium oxides and dopants in heterooxidic compositions can vary several times (Table 2). It is important to note that, depending on the conditions of synthesis, the content of individual compounds in the heterooxidic coating can vary within fairly wide limits, which, on the one hand, is definitely a positive factor, but complicates the search for optimum. It is this fact that imposes restrictions on the technological aspects of the implementation of the results obtained when creating effective photocatalytic materials.

The dependence of the degree of photocatalytic destruction of the man-made emitter *X* on the example of the MYH azo dye in solutions of variable concentration on the content of dopant *M* in the photocatalyst $X=f(M)$ (8) is multifactorial, and therefore nonlinear. Therefore, the establishment of its appearance, taking into account the quantitatively justified discrimination of dopants, is the cornerstone of the synthesis of the latest photocatalytic materials.

It is important to note that the obtained results regarding the ranking of heterooxidic systems according to the degree of decomposition of the methyl yellow-hot azo dye under ultraviolet irradiation make it possible to formalize the task of finding the most effective heterooxidic composites in terms of functional purpose. Thus, the quantitative characteristics of the photocatalytic process, such as the velocity constants k_f , the adsorption interaction *K*, the synergistic factor *R*, etc. are derivatives of the listed array of variables. Separately, we outline the influence of the geometric factor, which is one of the most significant for heterogeneous transformations. In this case, the specified factor, the contribution of which to (8) is reproduced by parameter S_k , can be stabilized, since individual series of photocatalytic materials are created using PEO technology. In general, establishing the shape of operator (8) is too difficult, so we will use the analysis of the influence of individual factors. With a high degree of probability, it can be assumed that

the rate of photocatalytic transformation is specific to each type of catalytic material, as well as the initial level X_0 , from which the contribution of the dopant acquires significance in accelerating the photocatalytic process or increasing its effectiveness. If we fix the values of individual factors of vector (8) at a predetermined level ($T, p, c_{OX}, S_k, h\nu, t$), then under such limitations, its analysis allows us to formulate a number of methodological provisions:

– first, the dependence of the degree of photo destruction on the nature of the dopant reflects the selectivity of the material with respect to individual catalytic transformations;

– second, the limits of variation of the dopant content in the catalytic material are limited by the peculiarities of the technology, therefore, the dependence of the degree of photo destruction on the content of the dopant in the catalytic composition will reflect the concentration interval, the limit values of which will vary depending on the nature of the dopant, the composition of the applied solutions and the technological parameters of the synthesis process;

– third, an increase in the dopant content in the composition of the catalytically active material will accelerate the reaction of photo destruction of reactants, as a result of which the degree of their photo destruction will change symbiotically;

– fourth, the degree of photo destruction depends on the nature of the reactant, the increase in the concentration of which will lead to a decrease in the degree of photocatalytic destruction at the same values of the dopant content, which is fully consistent with the basic physicochemical laws of catalytic reactions.

The listed methodological provisions may become the basis for the further development of research into the search for new highly efficient thin-film photocatalytic materials. Thus, according to plasma-electrolyte technology, it is possible to form heterooxidic coatings on titanium alloys with a variable content of components for the needs of photocatalytic decomposition of natural and man-made toxicants.

7. Conclusions

1. According to the results of the research, the expediency of forming heterooxidic photocatalytically active coatings on titanium alloys using the method of plasma-electrolyte oxidation in diphosphate solutions in galvanostatic mode in the current density range of 2–8 A/dm² was established. A number of transition metals – zinc, copper, cobalt, tungsten, molybdenum, tin, and zirconium – were investigated in the

role of titanium oxide dopants, in the presence of which heterooxidic coatings were synthesized.

2. The determination of the morphological features of the coating structure according to atomic force microscopy proved that compared to titanium oxide, as a material of a photocatalytic platform, heterooxidic coatings have a more developed surface, the specific area of which increases with processing time. Varying the density of the oxidation current allows you to change the content of the individual components of the heterooxidic coating and, thus, manage their composition. The use of subsequent heat treatment of coatings contributes to a more even distribution of globular forms and micropores.

3. Testing of synthesized materials was carried out in a model reaction of photocatalytic decomposition of methyl yellow-hot azo dye. Determined under identical conditions of implementation, the velocity constants of the photocatalytic reaction were used to rank coatings of different composition according to their functional properties. It was found that the addition of titanium oxide (IU) with the above-mentioned transition metals contributes to an increase in the rate of photocatalytic destruction of the azo dye. Thus, in the presence of titanium monoxide, the value of the reaction rate constant k_f is $2.8 \cdot 10^{-3} \text{ min}^{-1}$, for coating ZnO–MoO₃/TiO₂ – $3.4 \cdot 10^{-3} \text{ min}^{-1}$, and, under the same conditions for heterooxidic coating TiO₂:ZnO, it increases to $5.26 \cdot 10^{-3} \text{ min}^{-1}$.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

Funding

The research was funded by the Ministry of Education and Science of Ukraine within the framework of the project “Physical-chemical bases of metal oxide nanocomposite technology for high-efficiency dual-purpose catalytic converters” (registration number 0121U109542).

Data availability

All data are available in the main text of the manuscript.

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