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Studies on the effect of the stabilizer activity on the structure and properties of titania-based hybrid films

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Macroscopically ordered mesostructured films were prepared by the dip-coating method using a sol-gel technology. Stabilizers of different nature, such as poly(ethyloxazoline), diethylamine, poly(ethylene imine), octylamine, and dodecylamine, were used as modifying additives. The effect of activity of functional amino groups containing primary, secondary, and tertiary amines on the physicochemical properties of films was investigated. The film compositions were studied by X-ray powder diffraction; the film morphologies, by atomic force microscopy and small-angle X-ray scattering. IR spectroscopy was used to suggest a scheme for the chemical reactions. It was shown that the change in activity of a stabilizer considerably affects the composition and properties of the final product and can also lead to high self-organization of the surface formed not only on the nano but also on the micro scales. Comparative characterization of photoactivity and the nature of stabilizers was undertaken.

Key words: titanium dioxide, film structure, stabilizer, coordinating activity, sol—gel technology, template synthesis.

In the last decade, synthesis of complex materials with high spatial organization underwent significant changes.[1,2] An area of expertise known as "organized matter chemistry"[3] suggests the use of organic templates (surfactants, polymers, microspheres) in combination with hydrolysis by a sol—gel technology. This allows one to obtain ordered coatings, which, depending on the nature of modifying additive, form mesostructures of a given shape.[4] The use of hydrolysis stabilizers and variations in conditions of the synthesis (pH, temperature, molar ratio), as a rule, lead to the structuring of materials on the micro level, that is attributed to the coordinating activity of functional groups and specificities of the phase separation during the drying process. It is also known that the basicity and ability of coordination compounds to form stable bonds with ions of polyvalent metals decrease in the series of amines with the increase in the length of aliphatic moiety.[5] At the same time, an increase in the number of electron-donating nitrogen atoms in amines allows one to increase stability of coordination compounds due to the formation of chelate and polychelate complexes.[5] Thus, the presence of coordination-active groups in the structures of organic templates, assisting the molecule in performing the role of stabilizer, and the presence of hydrophilic and hydrophobic chains in its structure can lead to the formation of stable hierarchical superstructures with a narrow pore size distribution in the nano and micro regions.[6—9] The advantage of such materials is defined by an increased surface area and a high degree of hydroxylation. For example, the sol—gel synthesis of porous TiO_2 allows one to modify the surface of a macropore by incorporation of heterocyclic compounds, which promote increase in the yield of free charge carriers on exposure to the sunlight, without changes in the structure of the anatase crystal lattice.

The use of the above-mentioned materials with highly developed porosity is especially promising in such fields as photocatalysis, electronics, optics, sensor devices, and biomedical agents.[1,10—13] Application of mesostructured coatings with macropores allows one to increase the efficiency of molecule delivery to the site of its reaction with larger bacterium or cell.

Earlier,[14—18] effects of the synthesis conditions on the morphology of a macroporous film based on TiO_2—PEG (PEG is poly(ethylene glycol)) have been studied and it was found that the macro regions are formed if solidification of inorganic phase occurs after the phases were separated, which is caused by a strong interaction between an inorganic oligomer and an organic polymer present in the solvent. This leads to the formation of micron-sized drops, which are the virtual pore templates. For the rearrangement of nanostructuring particles to be rapid, a high enough film fluidity is also required: it is necessary to

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avoid rapid drying in order to provide high mobility of oligomers and prevent the formation of aggregates. These details of the control of small pore structures are similar to the control of formation of mesoporous coatings with allowance for the processes of self-organization and solvent evaporation.[7,19] However, despite a growing number of publications in the field of studies on the principles of formation of TiO_2 films on the nano and micro scales, special attention should be paid to the effects of the surface structure on the value of photoresponse, which is the most versatile index for the comparison of the film photoactivities. Here, the elucidation of relationship between the photoresponse and the nature of modifying additive is also a very relevant problem.[20]

The purpose of this work is to study effects of activity of different amino groups in the structure of an organic template on the properties and structure of the titania-based film materials obtained in the course of sol—gel synthesis.

Experimental

Preparation of solutions for the film deposition. Structure-forming additives (0.5 g) were added to isopropanol (reagent grade) (80 mL) with constant stirring. The nature of materials was different: poly(ethyloxazoline) (PEOz, Aldrich, 99.5%, M_n ~500.000), nonionic polymer; poly(ethylene imine) (PEI, Aldrich 99.8%, M_n ~10.000), polyelectrolyte; diethylamine (DEA, Fluka, 99.0%), octylamine (OA Aldrich, 99.5%), dodecylamine (DDA, Aldrich, ≥99%), nonionogenic surfactants. For the effects of activity of molecules on physicochemical properties of the obtained films to be compared, poly(ethylene glycol) monooleate (PEG MO, Aldrich, 99.98%, M_n ~460) was also used, which possesses weak coordinating activity and serves as an organic template in the template sol—gel synthesis. The thus obtained solution was heated to 70 °C and stirred for 4 h. Titanium isopropylate (Aldrich, 98%) (10 g) was added dropwise to the solution obtained. The final solution was stirred for 5 h at 70 °C. A part of the solution was hydrolyzed with water present in ethanol (15 mL) to obtain a sol, which was dried at 60 °C until white or light yellow powder was obtained.

Preparation of TiO_2 films. A part of the solution was used for depositing films on the glass surface by dip-coating. The lifting speed was 4 mm s^{-1} ($T = 21$ °C, $W = 55\%$) needed for efficient proceeding of hydrolysis upon exposure to atmospheric moisture and polycondensation reactions in the process of solvent evaporation. The glass surface was preliminary purified with ethanol and dried in air at 80 °C. After deposition, the films were dried in air for 1 h. The thus obtained films were subjected to thermofixation at $T = 300$ °C for 1 h. During calcination, the heating zone was continuously blown through with atmospheric oxygen for more complete removal of the organic phase in the combustion process.

Characterization of materials. Phase transition temperatures and the total loss in weight of the samples during heating process were determined by thermal analysis on a Q1000 (MOM) derivatograph, the temperature range was 20—800 °C, the heating rate was 10 °C min^{-1}, the weight of the analyzed sample was 100 mg.

The obtained powder of TiO_2 was studied by X-ray powder diffraction on a Dron-2 diffractometer (Cu-Kα radiation). To calculate the crystallite sizes obtained by thermal treatment at 350 °C and storage for 1 h, the Scherrer equation was used $d = B\lambda/(\beta\cos\theta)$, where d is the average crystallite size, B is the Scherrer constant (0.94), λ is the wavelength of X-ray beam, θ is the diffraction angle of the phase under study, β is the peak width at half height.

IR spectra were recorded on an Avatar 360 FTIR ESP spectrometer.

The small-angle X-ray scattering data and the Wulf—Bragg equation were used for the calculation of correlation radii and estimation of the presence of ordering in the samples.

Analysis of the surface of the film ~0.5 μm thick was performed on a SPM Solver P47H-PRO Microscope scanning probe microscope with a 1×1 μm frame size.

Results and Discussion

It is well known that titanium alkoxides readily react with water (Scheme 1, reactions (1)—(3)); however, in the present work hydrolysis was carried out in the presence of different stabilizers.

Scheme 1

$$\equiv Ti{-}OR + H_2O \longrightarrow \equiv Ti{-}OH + ROH \qquad (1)$$

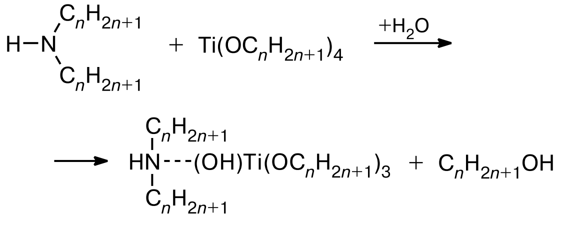
$$\equiv Ti{-}OH + RO{-}Ti \longrightarrow \equiv Ti{-}O{-}Ti\equiv + ROH \qquad (2)$$

$$\equiv Ti{-}OH + OH{-}Ti \longrightarrow \equiv Ti{-}O{-}Ti\equiv + H_2O \qquad (3)$$

The changes in the course of chemical reactions with the use of various amines were analyzed based on the IR spectroscopic data. Figure 1 shows examples of the spectra for the secondary amine (diethylamine) used as the stabilizer.

When the spectra for the pure DEA sample and its hybrid are compared, it is seen that the intensity of the N—H vibrations (3312 cm^{-1}) decreases, whereas the C—N vibrations are shifted (from 1129 to 1090 cm^{-1}) indicating the reaction between DEA and $Ti(OPr)_4$, which, apparently, occurs with the formation of hydrogen (ionic) bonds with respect to the OH—Ti≡ hydroxyl groups formed in the process of hydrolytic polycondensation of titanium isopropylate (Scheme 2).

Scheme 2



$$HN(C_nH_{2n+1})_2 + Ti(OC_nH_{2n+1})_4 \xrightarrow{+H_2O} (C_nH_{2n+1})_2HN\cdots(OH)Ti(OC_nH_{2n+1})_3 + C_nH_{2n+1}OH$$

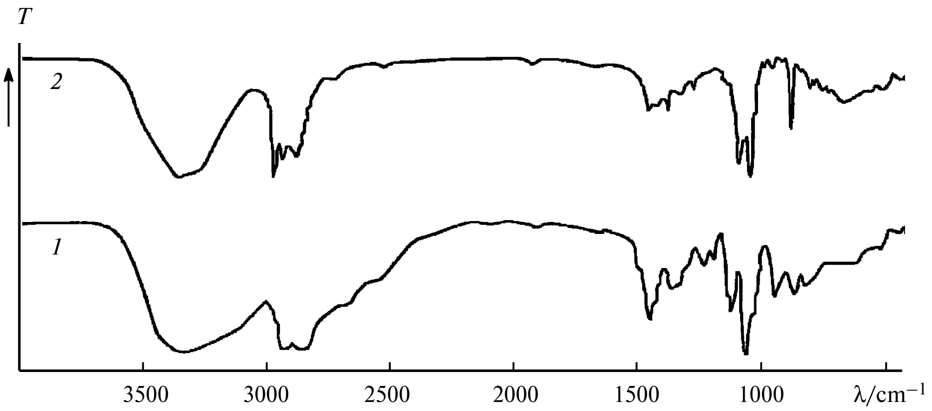
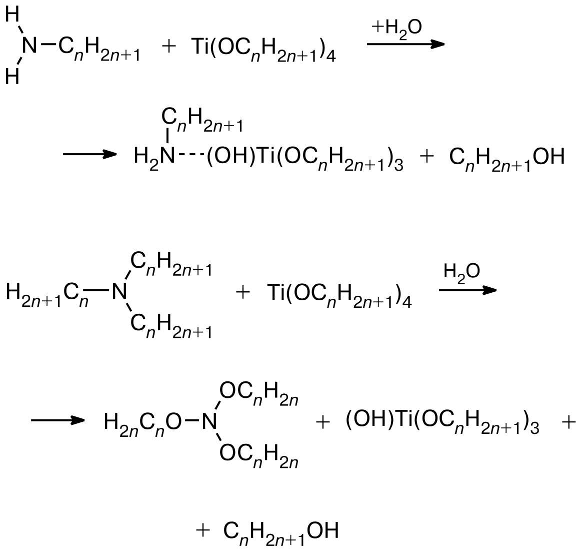


Fig. 1. The IR spectra of DEA (*1*) and $\mathrm{Ti(OPr)_4}$ + PrOH + DEA (*2*) samples.

Morphology of the $\mathrm{TiO_2}$ film is mainly determined[15—18] by the decrease in fluidity in the course of polycondensation and phase separation between the adsorbed polymer and the solvent. Smooth coatings can be obtained by acceleration of polycondensation.[16] Therefore, the use of stabilizers with high coordinating activity is the most efficient. Complex-forming activity of primary amines (octylamine, dodecylamine) is not high enough to considerably slow down the hydrolysis and polycondensation reactions, that leads to the formation of macropores with a broad size distribution. For the films formed with the use of tertiary amines, the planar structure is observed, that indicates low activity of the stabilizer with the OH—Ti≡ hydroxo groups. To sum up, the chemical reactions for the formation of hybrid materials have the form shown in Scheme 3.

For the films obtained by hydrolysis of isopropylate in the presence of poly(ethyloxazoline), the separate formation of coarse agglomerates of hydrated titanium dioxide and planar structures of the polymer, poly(ethyloxazoline), were observed (Fig. 2). Due to this, one can suggest that in the process of thermal treatment the anatase-type crystal structures will be the least defective.

Scheme 3



$$\mathrm{H_2N{-}C_nH_{2n+1}} + \mathrm{Ti(OC_nH_{2n+1})_4} \xrightarrow{+\mathrm{H_2O}} \mathrm{H_2\overset{C_nH_{2n+1}}{N}\cdots(OH)Ti(OC_nH_{2n+1})_3} + \mathrm{C_nH_{2n+1}OH}$$

$$\mathrm{H_{2n+1}C_n{-}N(C_nH_{2n+1})_2} + \mathrm{Ti(OC_nH_{2n+1})_4} \xrightarrow{\mathrm{H_2O}} \mathrm{H_{2n}C_nO{-}N(OC_nH_{2n})_2} + \mathrm{(OH)Ti(OC_nH_{2n+1})_3} + \mathrm{C_nH_{2n+1}OH}$$

The use of secondary amines leads to a high self-organization on the micro level. As it is shown in Figure 3, the

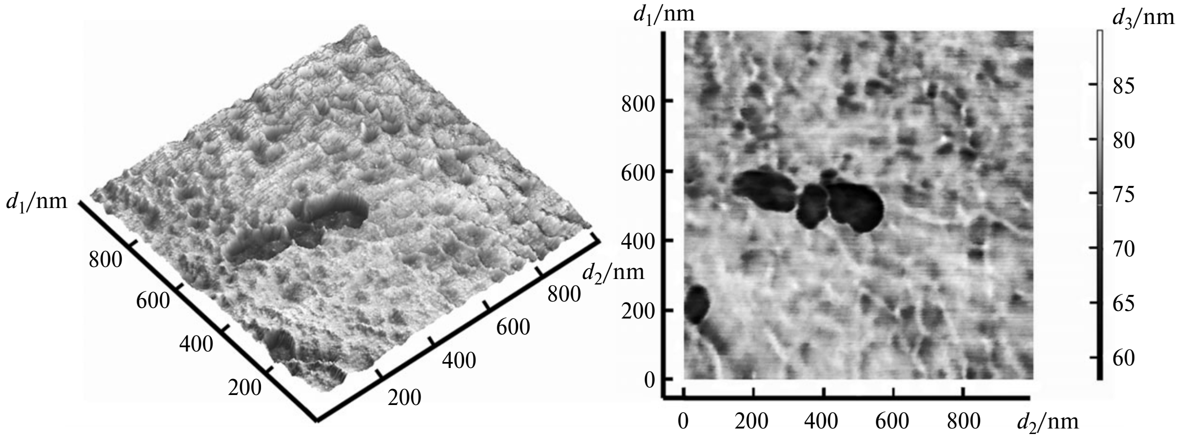


Fig. 2. The morphology of the noncalcined film obtained by hydrolysis of titanium isopropylate in the presence of poly(ethyloxazoline).

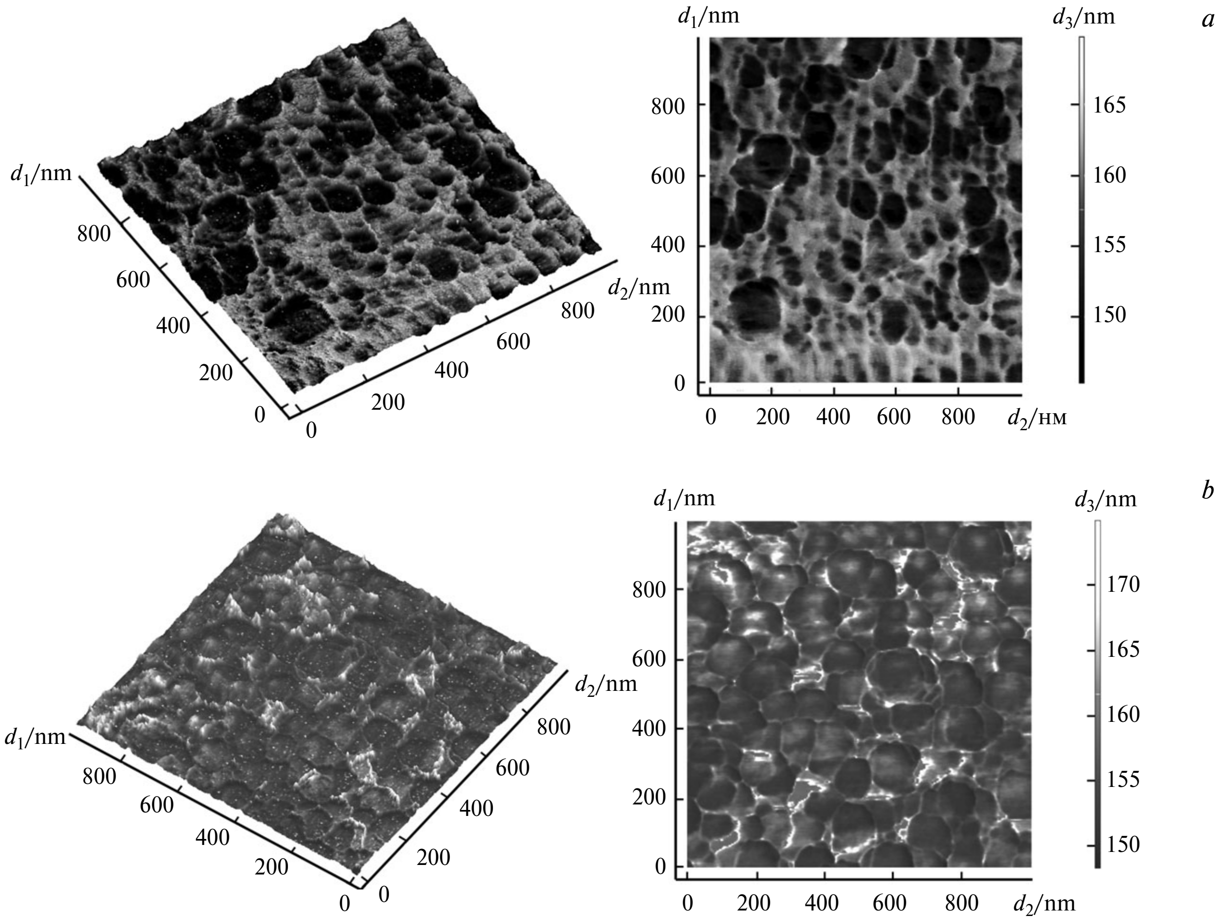


Fig. 3. The morphology of the noncalcined film obtained by hydrolysis of titanium isopropylate in the presence of diethylamine (*a*) and poly(ethylene imine) (*b*).

surface of TiO_2 film modified with poly(ethylene imine) and diethylamine is characterized by the formation of macropores with a narrow size distribution: for PEI, 105 nm, whereas for DEA, 86 nm.

For the films modified with primary amines, self-organization with the formation of spherical macropores of a wide range is observed: for octylamine, from 120 to 200 nm, for dodecylamine, from 20 to 60 nm (Fig. 4).

Structure formation in the process of thermal treatment. It is known that the morphology of a mesostructured film formed in the step of drying undergoes considerable changes during the calcination to remove organic templates.[21] In the first place, this is caused by transition of material from amorphous to crystalline state, which is accompanied by growth of crystallites and, possibly, coalescence of pores. The indicated processes are significantly affected by the nature of modifying additive and solvent, the environment, the heating rate, *etc.*[10] At the present time, there are plenty of approaches to the analysis of the problem under consideration. However, effects of the process of thermal treatment on the structural transitions of coatings possessing high organization on the nano and micro scales are not studied enough.

To study phase transitions and stepwise decomposition in the process of thermal treatment,we measured the DTA—DTG curves. Three weight loss steps were observed: below 120 °C (~15%), 110—180 °C (~10%), and 200—300 °C (~23%). The first weight loss step in all the samples corresponds to the removal of isopropanol and adsorbed water. In the second step, consolidation of the earlier formed ≡Ti—OH groups is observed. The exothermic peak, which, according to the DTA data, appears in the temperature region 270—320 °C, corresponds to the beginning of crystallization of amorphous TiO_2. The total weight losses of the samples are shown in Table 1. The results of thermal analysis show that the complete removal of the organic phase occurs at 350 °C. The samples TiO_2—PEI, TiO_2—OA, and TiO_2—DDA show displacement of the region of the anatase crystalline phase formation toward higher temperatures.

Note that the hybrid film containing in the structure chemically bound modifying additive is characterized by

Table 1. Thermal analysis data

Sample	$T_{tr}{}^{a}$/°C	Weight loss (%)	$T_{comb}{}^{b}$/°C
TiO_2 + PEOz	270	43	290
TiO_2 + PEI	300	40	350
TiO_2 + DEA	290	35	330
TiO_2 + OA	320	45	340
TiO_2 + DDA	310	44	320

[a] Temperature of the amorphous titanium dioxide—anatase phase transition.

[b] Temperature of complete combustion of the organic phase.

a high flexibility. Thermal treatment allows one to remove an organic template and finish the processes of rearrangement of inorganic frameworks, which results in the change of the initially formed structures, that, in turn, leads to the formation of a photoactive crystal modification.

Formation of mesostructured materials. The data given above indicate that primary and secondary amines are in the chemically bound state with Ti^{4+}. Due to this, we studied a possibility of application of stabilizers as organic templates for the formation of mesophases. So far, an example of existence of the secondary structure was considered only for PEG, which is a weak stabilizer because of very low coordinating activity.[14]

We used small-angle X-ray scattering to identify the presence of mesostructured regions in the structure of the materials obtained. Simultaneously, we carried out qualitative and quantitative analysis of the phase composition and crystallite sizes of the samples calcined at different temperatures.

As it follows from the X-ray powder diffraction data (Fig. 5), the hybrid TiO_2 film modified with poly(ethyloxazoline) does not give small-angle reflections, which are characteristic of mesostructures, that confirms the suggestion made earlier on the absence of chemical binding between the tertiary amino group and the OH—Ti≡ group.

Poly(ethylene imine) molecules belong to the class of polyelectrolytes. The presence of ionogenic groups repeat-

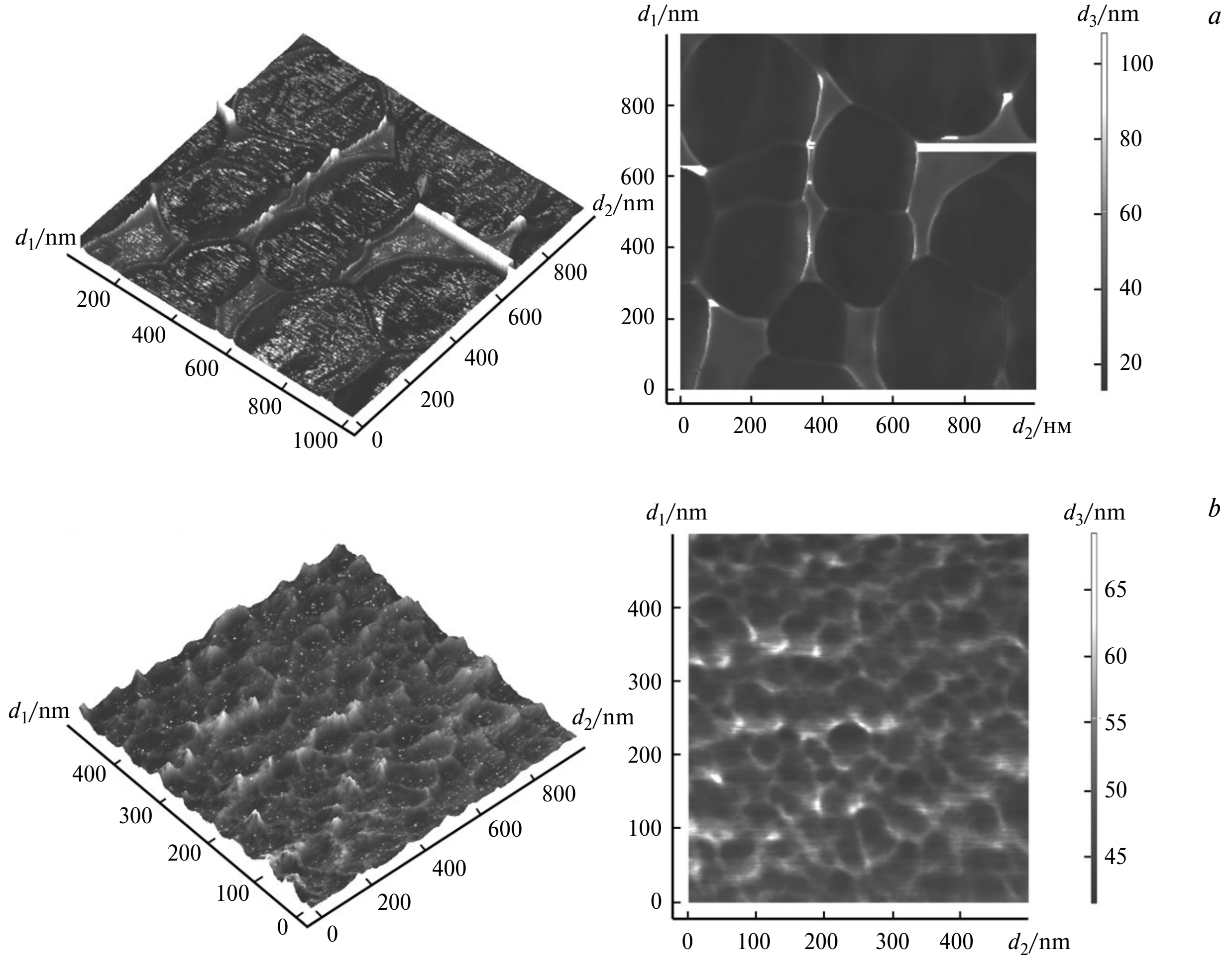


Fig. 4. The morphology of the noncalcined film obtained by hydrolysis of titanium isopropylate in the presence of octylamine (*a*) and dodecylamine (*b*).

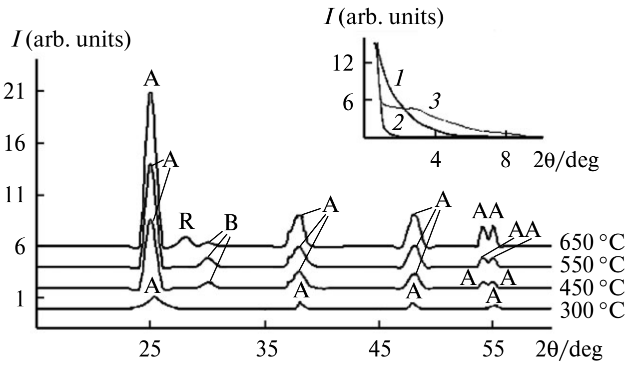


Fig. 5. The X-ray diffraction pattern of materials obtained in the presence of poly(ethyloxazoline); in the insertion, the data for TiO_2 calcined at 300 (*1*) and 200 °C (*2*), as well as for the noncalcined sample (*3*).

ed along the macromolecule chain affects ability to adopt conformations and other properties of high-molecular-weight compounds in solutions. Electrostatic interaction in polyions leads to a considerable deformation of flexible chains. Due to the repulsion between groups with like charges, polyions occupy a much greater volume than the corresponding electroneutral macromolecules, with the degree of asymmetrization in them being also much higher. The conditions created in the step of their synthesis promote "unfolding" of the poly(ethylene imine) molecule and formation of stable bonds with the precursor, with the bonds between the secondary amino group and OH—Ti≡ being the most stable.[22] As it is shown in the X-ray diffraction pattern (Fig. 6), the PEI molecule assists in the self-organization with the formation of mesostructures, playing the role of a polymeric template.

Diethylamine also possesses high coordinating activity; however, because of the absence of coarse hydrophobic moieties, it cannot be used as an organic template for the mesophase formation. The presence of a reflection for noncalcined samples indicates the formation of spherical particles, and the coherent scattering region corresponds to the average distance between the formed particles (Fig. 7). The calcination process is accompanied by agglomeration of particles, leading to the coarse aggregates.

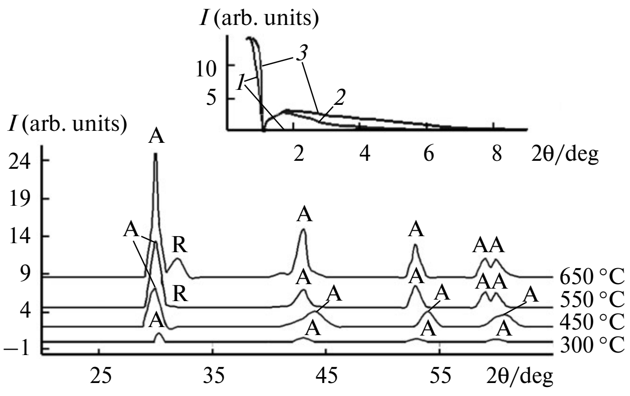


Fig. 6. The X-ray diffraction pattern of materials obtained in the presence of poly(ethylene imine); in the insertion, the data for TiO_2 calcined at 500 (*1*) and 300 °C (*2*), as well as for the noncalcined sample (*3*).

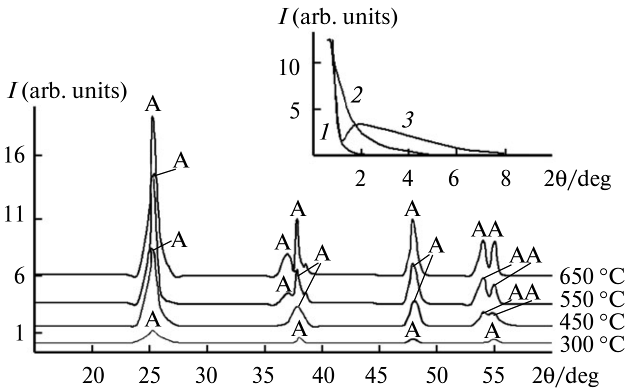


Fig. 7. The X-ray diffraction pattern of materials obtained in the presence of diethylamine; in the insertion, the data for TiO_2 calcined at 500 (*1*) and 300 °C (*2*), as well as for the noncalcined sample (*3*).

Dodecylamine and octylamine molecules form micellar templates in polar solutions, whose functional amino groups react with hydroxo groups at the titanium atom to form "wormhole-like" mesopores evenly distributed throughout the material.[4] According to the small-angle X-ray diffraction data (Fig. 8), the coherent scattering region for the calcined film samples obtained in the presence of dodecylamine is 5.5 nm, whereas in the presence of octylamine, 4.2 nm. The difference in these values is explained by the elongation of the hydrocarbon chain by four methyl groups.

To sum up, the use of coordination-active groups in the structure of templates promotes self-organization not only on the micro, but also on the nano scales. It was shown that the nature of modifying additive significantly affects the phase composition of the film.

Studies of film photoactivities. Spectroscopic studies of photochemical reactions on the surface of materials based on TiO_2 allow one to only partially describe the processes of charge transfer and effects of the internal structure on photoactivity of films as a whole. The greatest difficulties emerge when structural impurities are included into a crystal lattice, as well as when there is present a large structured surface of materials, which are subjected to the strong thermal treatment for the formation of photoactive crystal modification (Fig. 9). As a result of these processes, all the films have an "island" structure formed of aggregates of different shape.

To evaluate photoactivity of the materials obtained, we used the method of photopolarization measurements in combination with the electric conductivity data. Photo-

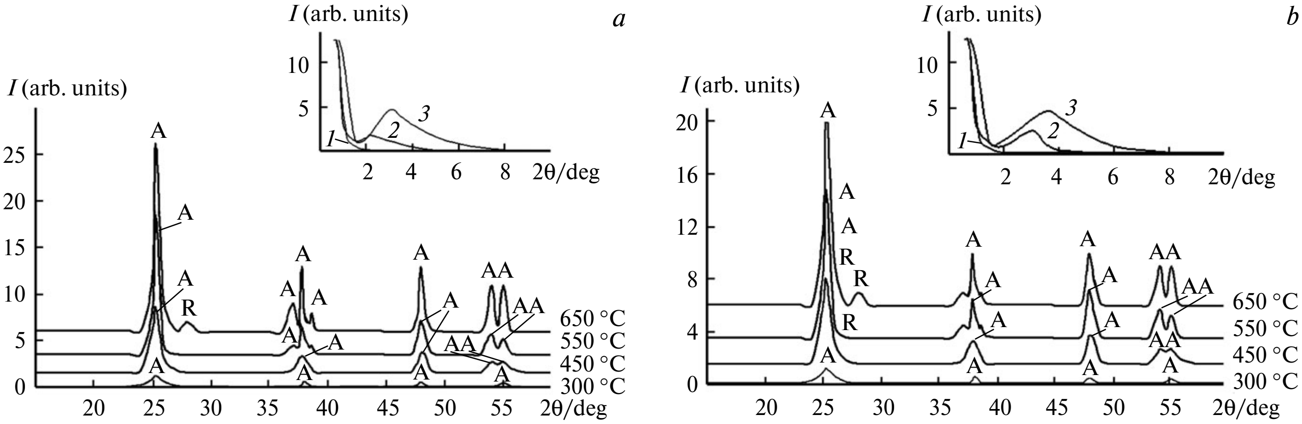


Fig. 8. The X-ray diffraction pattern of materials obtained in the presence of dodecylamine (*a*) and octylamine (*b*); in the insertions, the data for the samples calcined at 500 (*1*) and 300 °C (*2*), as well as for the noncalcined sample (*3*).

activity of films was evaluated based the photo-emf data upon a short-time irradiation with a UV lamp (250 W); Pt gauze was the second electrode. The data obtained are given in Table 2.

Since crystallization process has specific features, the products were obtained with different physicochemical properties. Calcination of hybrid films leads to the increase in photo-emf by several dozen times, which is due to the formation of crystalline phase in the film. It is known that TiO_2 is an indirect-gap semiconductor characterized by the n-type conductivity, and such a mechanism of the charge transfer suggests the formation of vacancies O^{2-} in the crystal lattice, whereas two neighboring Ti^{4+} ions acquire the charge 3+. This leads to the formation of one weakly bound electron in the outer electron level each, which is responsible for the type of conductivity. The pres-

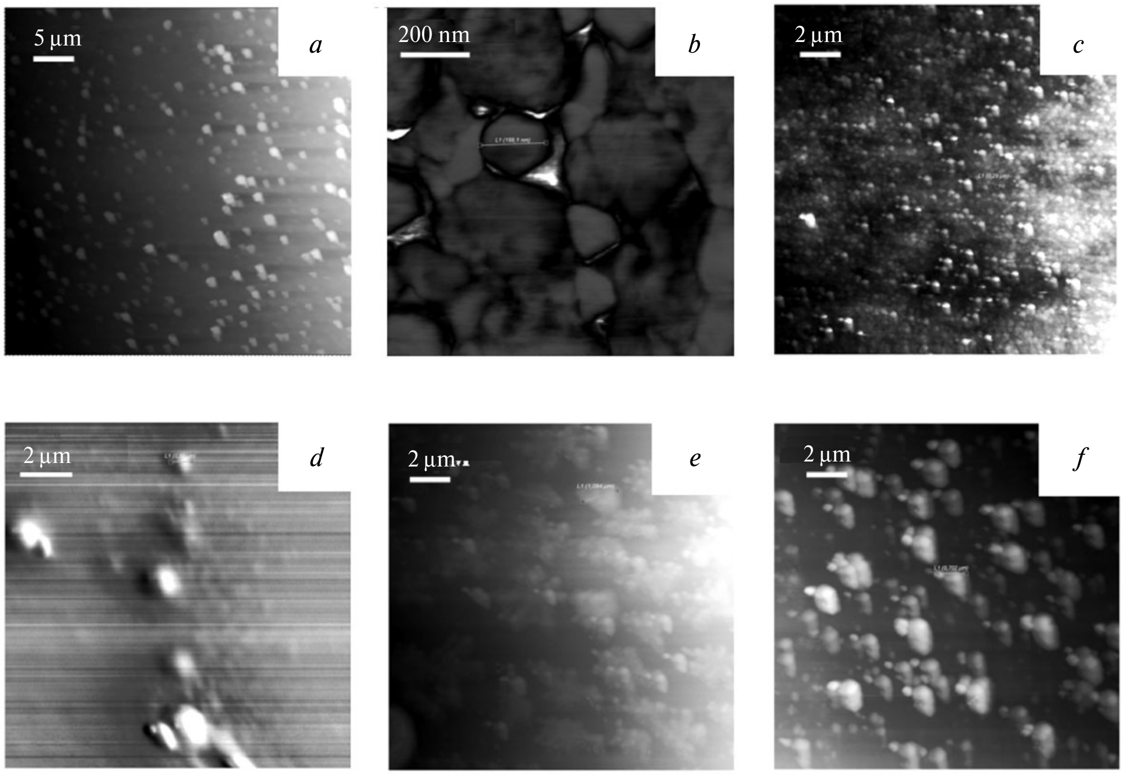


Fig. 9. The surface of films calcined at 300 °C modified with diethylamine (*a*), poly(ethylene glycol) monooleate (*b*), poly(ethylene imine) (*c*), dodecylamine (*d*), octylamine (*e*), and poly(ethyloxazoline) (*f*).

Table 2. Physicochemical and structural properties of modified TiO_2 films 0.5±0.1 mm thick

Modifier	Average crystallite size/μm	Content of n-type additive after annealing 300 °C (wt.%)	R_{cor} of calcined sample	Conductivity type	Photo-emf /mV
Poly(ethyloxazoline)	2.0	—	—	n	45
Poly(ethylene imine)	2.5	0.5	7.7	p	20
Diethylamine	3.6	0.4	—	p	16
Octylamine	1.7	0.1	4.2	p	6
Dodecylamine	1.7	0.2	5.5	p	1.5
PEG monooleate	2.1	—	6.5	n	22.5
No additives	3.2	—	—	n	5.5

ence in the crystal structure of strongly electronegative elements, acting as electron donors, considerably hinders the charge transfer, but assists in their efficient separation. Such materials, as a rule, are characterized by either p-type or ionic conductivity.

The assumption of a low activity of the tertiary amino group of poly(ethyloxazoline) in combination with OH—Ti≡ is confirmed by the data in Table 2. For such a film, the highest photo-emf of 45 mV is observed, which results from the formation of the least defective crystals and the n-type conductivity. Characteristics of the TiO_2 film modified with PEG monooleate are given for comparison, which also displays low coordinating activity in the complexation reactions. The data obtained show that both films possess high photoactivity and the n-type conductivity.

Primary and secondary amines characterized by high activity promote the formation of stable inorganic frameworks in the process of synthesis, in which the nitrogen is chemically bound to Ti^{4+} through the OH group. After calcination, an acceptor impurity of nitrogen remains in such materials, which forms additional energy levels. At the same time, when a polymeric molecule of poly(ethylene imine) was used as a template, films with highly developed surface and photoactivity were formed due to the presence of a large number of developed electron-withdrawing groups. In the order diethylamine—octylamine—dodecylamine, the photoactivity sharply decreases simultaneously with the decrease in the amine basicity.

In conclusion, we carried out a comparative analysis of how the type of molecular template affects the structure and photoactivity of hybrid organic-inorganic films formed by the sol—gel technology. It was shown that the use of hybrids, whose structure contains product of the reaction of titanium tetraisopropylate with primary and secondary amines, promotes formation of coatings with a high spatial organization. The use of poly(ethyloxazoline) as a molecular template in the formation of hybrid nanomaterials and films based on titanium dioxide does not lead to the formation of mesostructures because of weak activity of tertiary amino groups. It was found that the basicity and nature of amine significantly affect the value of film photoresponse. According to the values of photo-emf developed by hybrid coatings containing organic amines upon irradiation with a mercury lamp, compounds under study can be ordered as follows: poly(ethyloxazoline) (45 mV), poly(ethylene imine) (20 mV), diethylamine (16 mV), octylamine (6 mV), dodecylamine (1.5 mV).

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