Mesoporous C, S-doped TiO$_2$ nanostructures were obtained by solvothermal sol-gel method followed by calcination at different temperatures. It was found that with increasing calcination temperature, the crystallite size remains in the same range of 9–10 nm, while the morphology of TiO$_2$ nanoparticles significantly changes, and the anatase content increases from 42% to 95%. At the same time the nanoparticle size (from 85 to 45 nm), the specific surface area (200–130 m$^2$/g), the mesoporous area (from 170 to 70 m$^2$/g), and the carbon (0.80–0.41%) and sulfur (1.39–0.89%) contents decrease. Varying the calcination temperature allows TiO$_2$ nanostructures to be obtained with a certain balance of these structural-dimensional characteristics that provides high photocatalytic activity in the processes of ceftazidime and doxycycline photodegradation.

**Key words:** mesoporous C, S- doped TiO$_2$, thiourea, calcination, photocatalytic activity, antibiotics.

**INTRODUCTION.** Titanium dioxide (TiO$_2$) is one of the most promising materials for solving a number of modern technical and technological problems, ensuring the sustainable development of society, including harvesting of solar energy, more efficient mineral fuel consumption, environmental protection, air purification and sterilization [1, 2, 3, 4, 5]. This is caused by low cost, high availability, chemical and photocorrosion resistance of the TiO$_2$ (anatase) semiconductor, the properties of which allow separated charges (electrons and holes, $e^-/h^+$) to be generated under UV-light irradiation, which are involved in redox processes [1, 2]. Doping and co-doping of TiO$_2$ by non-metals (NM=B, C, N, F, S, etc.) for obtaining
NM-doped TiO$_2$ materials is one of the most promising ways to eliminate the inherent TiO$_2$ shortcomings, such as the wide bandgap ($E_g = 3.2$ eV for anatase), low efficiency to sunlight (~4%), fast recombination of photogenerated $e^-/h^+$ pairs, low sorption capacity, etc. [1, 2]. In addition, doping also makes it possible to increase the photocatalytic activity (PCA) of TiO$_2$. According to existing notions, nonmetal (C and/or S) doping can occur in three ways [1, 6]: substitutional doping (when dopant atoms (C [7–9] and/or S [10, 11]) substitute oxygen in the crystal lattice); interstitial doping (when the additive atom (C [7–9] and/or S [10–12]) is in the interplanar space of the crystal lattice and is associated with one or several oxygen atoms in the lattice, which leads to its distortion); and mixed (when both types of doping are realized simultaneously) [8]. At the same time, some dopant atoms may also be included in different functional groups, for example, sulfate [7, 10, 11] or carbonate [8, 9, 13], on the material surface. The implementation of these options depends on the nature of the dopant, the conditions of the doping process, the precursor of the dopant, and the conditions of post-synthetic processing [1, 2, 4, 5]. N$>$C$>$S are considered as the strongest dopants, for which all the above types of doping can be realized [1, 4, 5, 6, 12, 14, 15]. Even though the numerous calculations of the energy and electronic states of O 2p, Ti 3d and NM (N 2p, S 3p, etc.) of doped anatase (NM-doped TiO$_2$) using different models and approximations [1, 4, 5, 6, 14–16], as well as the interpretation of experimental results are rather controversial, this makes it possible to assess the state and role of dopant in NM-doped TiO$_2$ and NM-codoped TiO$_2$.

In particular, it was shown that the replacement of titanium by sulfur in the crystal lattice of anatase for S-doped and N, S-codoped TiO$_2$ is more energetically favorable [15] and leads to bandgap narrowing [16]. At the same time, from the thermodynamic stability point of view, S atoms can be localized in both O and Ti sites in S-doped anatase [17]. As a result of the mixing of O 2p, N 2p, S 3p, and Ti 3d states, the bandgap ($E_g$) decreases and the absorption band edge shifts to higher wavelength (>400 nm). In turn, the PCA (VIS) is higher for N, S-coped TiO$_2$ than for S-doped TiO$_2$ or N-doped TiO$_2$ [15]. Among C-, N-, S - doped TiO$_2$ [5], C-doped TiO$_2$ in which carbon enters the crystal lattice in the form of an anion or cation [5] is the most promising photocatalyst due to the overlap of the O 2p and C 1s states near the valence band edge and its redshift in C-doped TiO$_2$. Other authors [5] disagreed with a decrease in $E_g$ and believe that such a decrease may be very modest. At the same time, an increase for visible light response and PCA (VIS) is associated with the appearance of isolated localized states in the gap, rather than with narrowing it [1, 5, 6]. Carbon states can also overlap with the TiO$_2$ conduction band due to the rather deep location in the bandgap [15]. For N-doped TiO$_2$, both substitutional and interstitial localized occupied states are generated in the bandgap, which provides a visible light sensitivity and PCA (VIS) [6].

Simultaneous co-doping often gives more positive results compared to mono-doping due to the manifestation of synergistic effects [1, 4, 5]. From this point of view, thiourea (TU) is of particular interest as a precursor that contains simultaneously C, N, and S. TU and various titanium (IV) compounds can be used as precursors for the synthesis of (NM)-doped TiO$_2$ materials by “dry” (calcination of mechanically treated mixtures)
or “wet” (sol-gel synthesis followed by calcination) methods. It was shown that TiO₂ obtained by NM doping, where NM = (C, N, S) [7], (N, S), [7, 11, 18, 19], (N) [19], (S) [12, 20–22], (C) [8, 9], demonstrate increased PCA (VIS) in various redox processes. However, according to the calculation results and experimental data, the positive doping effect on the visible light sensitivity and PCA does not always lead to a change in the bandgap and the shift of the band edge [1, 5]. So far, intensive discussions are underway on the mechanism of doped TiO₂ photocatalytic response to visible light, and theoretical studies and experimental results are often contradictory. This can be attributed to the variety of synthesis methods for these materials and different calculation methods [5]. Because each factor affecting PCA is difficult to investigate individually, and because photocatalysis is a complex process influenced by many factors, attempts to determine a universal law of the doping effect on PCA have so far been unsuccessful [5].

Besides, doping can take place both inside the TiO₂ lattice and at the photocatalyst surface [5], which is in direct contact with the organic substrate. Therefore, the amount and nature of dopant in the surface layer may significantly affect PCA (VIS). However, the questions of the effect of the precursor concentration (in particular TU) in the sol-gel system on the number and nature of dopant atoms in (NM)-doped TiO₂, their distribution in volume and on the surface, structural and dimensional characteristics and morphology of the obtained material have hardly been addressed. With respect to available experimental results (relative to S² [10, 11, 19], S⁴⁺ [12, 19, 20], S⁶⁺ [21, 23]) the interpretation is not unambiguous. It is known [25] that the hydrothermal method allows different classes of inorganic materials in the nanocrystalline state to be obtained. The calcination temperature significantly affects the phase composition, morphology, crystallite and particle size, texture, dopant content, and their chemical state under doping of the TiO₂ nanostructures by carbon, nitrogen, and sulfur (NM) [12]. The phase content ratio in (S)-doped TiO₂ critically depends on the calcination temperature [12, 23], the sulfur precursor nature, the amount used in the reaction mixture [12, 21], and the calcination time [23].

In some cases, doped mixed phases show higher photocatalytic activity compared to the corresponding single-phase materials. The optimal anatase/rutile phase ratio for the mixed phases is 75%:25% - 85%:15% [12, 26]. Despite the fact that anatase has a higher photocatalytic activity than rutile, in some cases, doped rutile [27] is more active. Incorporation of dopants, such as sulfate, in TiO₂ stabilizes anatase before transformation into rutile [21] that begins at higher temperatures - 800°C [12, 28], 950°C [12], and does not end even at 1100°C (48% A + 52% R) [12].

High calcination temperature in air leads to the formation of sulfuric acid in the structure of TiO₂, in which S atoms are embedded interstitially [12]. There is a certain optimum sulfur content in (S)-doped TiO₂ (0.1-0.3 wt. % S), which provides a reduction of the bandgap (3.15-2.75 eV) and provides sufficient lifetime of photogenerated charge carriers [24]. The decrease of dopant content with increasing calcination temperature leads to an increase of crystallite and particle sizes (for example, the temperature increase from 200 to 600 °C induces a crystallite size growth from 9 nm to
24.9 nm [21]), resulting in deteriorating the texture characteristics, first of all, a decrease in the surface area [12, 29]. Since a larger particle size and a smaller surface area are known to reduce the number of photogenerated electrons [30, 31], such changes lead to a decrease in photocatalytic activity [1, 2, 30, 31]. Therefore, in order to obtain effective photocatalysts, it is important to choose such a composition of the reaction mixture and a calcination temperature that would provide non-metal-doped fine-crystalline (9-10 nm) anatase, characterized by an optimal balance of nanoparticles of a certain morphology, and a mesoporous structure with a developed surface, which improves the photocatalytic activity of such materials.

The rapid increase in antibiotic consumption in the last decade has led to intensive pollution of natural waters, which contributes to the development of resistance in microorganisms and, consequently, poses a threat to human health and requires high costs for the development of new antibiotics as well as materials and technologies for water purification [31, 32]. Photocatalytic processes that use the energy of sunlight [31, 32] and NM-doped TiO$_2$ materials as catalysts [1, 5, 6] are promising in this aspect.

The aim of this study was to elucidate the effect of the calcination temperature on the chemical and phase composition, texture, and morphology of TiO$_2$ nanostructures, obtained from thiourea containing sol-gel systems, and their photocatalytic activity in the doxycycline and ceftazidime antibiotics photooxidation reactions.

**EXPERIMENT AND DISCUSSION OF THE RESULTS**

Titanium tetrabutoxide (Sigma Aldrich), thiourea (ch.p) (Reachim), acetic acid (ch.p), ethanol (96%), (UKRORGSYNTEZ Ltd.), doxycycline, and ceftazidime (BCPP) were used.

Sulfur and carbon-doped TiO$_2$ nanostructures were obtained by a modified method [33] by mixing titanium tetrabutoxide with ethanol and thiourea solutions, that was prepared by dissolving 3.4 ml titanium tetrabutoxide in 30 ml anhydrous ethanol and 0.253 g of thiourea in 20 ml of absolute ethanol, followed by addition of 1 ml glacial acetic acid and 1 ml distilled water and stirring vigorously on a magnetic stirrer during 30 minutes. The resulting sol was transferred into a Teflon beaker and subjected to solvothermal treatment (STT) at 120 °C for 24 hours. The resulting precipitate was separated from the mother liquor by centrifugation and washed twice by distilled water and then dried at 100 °C for 12 hours. The obtained powder was calcined at 200, 300, 400, and 450 °C for 3 hours. The samples were labeled as (X) TiO$_2$ (T$_1$/T$_2$), where X is the molar ratio TU/Ti(OBu)$_4$, T$_1$ is the STT temperature, T$_2$ is the calcination temperature. The nitrogen and carbon content in the samples was determined using a C, H, N-analyzer “Carlo Erba 1106”. The sulfur content was determined using an X-ray fluorescence spectrometer ElvaX.

Diffractograms of the samples were recorded on a Bruker D8 Advance diffractometer using CuK$_\alpha$ radiation. Transmission (TEM) and scanning (SEM) electron micrographs were obtained on microscopes JEM 1230 and JSM-6060 LA (JEOL) at accelerating voltages of 200 kV and 30 kV, respectively. Diffuse reflection spectra were recorded on an Evolution 600 spectrophotometer (Thermo Scientific). FTIR spectra were recorded on a spectrometer Perkin Elmer Spectrum One in KBr pellets with a sample/KBr ratio of 1/100. Nitrogen adsorption/desorption isotherms were measured.
by the volumetric method at 77 K on a Sorptomatic 1990 instrument. Before measurements, the samples were degassed for 5 hours at 330 °C. The external specific surface area ($S_{\text{ext}}$) was calculated according to the method described in [34]. Thermoprogrammed desorption with mass spectrometric control (TPD-MS) was performed in a quartz tube connected to a quadrupole mass spectrometer MX7304A (Selmi) with ionization by electrons of 70 eV. The sample in the tube was heated linearly at a rate of 14 °C/min from room temperature to 800 °C. Mass spectra of the gas phase were recorded continuously during heating. X-ray photoelectron spectroscopy (XPS) spectra were recorded using an ESCALAB 250Xi spectrometer (Thermo Scientific) equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.68$ eV). The samples were pumped out in a vacuum for at least 24 hours until the base pressure in the chamber reaches $5-8 \times 10^{-10}$ mbar. High-resolution spectra were recorded at an analyzer pass energy of 20 eV, providing a spectral resolution of 0.5 eV.

The photocatalytic activity (PCA) of samples calcined at different temperature were investigated under UV and visible light irradiation (respectively PCA (UV) and PCA (VIS)) for the colorless cephalosporin (ceftazidime) and doxycycline antibiotics photodegradation processes. In the absence of a photocatalyst, solutions of ceftazidime and doxycycline remain stable for a long time. PCA (UV) and PCA (VIS) were determined by the conversion degree ($R_{60}$) for 60 minutes. A portion of the sample was suspended in aqueous solutions of doxycycline (or ceftazidime) with a concentration of $6.5 \times 10^{-5}$ M at a sample/solution ratio of 1 g/L and left overnight to establish sorption equilibrium. The suspension was irradiated with ultraviolet ($\lambda=365$ nm, UV lamp Delux 26W) and visible light (Maxus 8 W lamp, equipped with a light filter that transmits light with $\lambda > 400$ nm), with a radiation intensity near the surface of the suspension of 0.05 mW/cm² and 2.0 mW/cm² respectively. The light intensity was measured with a 91150V Reference Cell and Meter (Newport) at the distance of 40 cm that corresponds to the distance from the lamp to the surface of the suspension. An aliquot of the suspension was taken at regular intervals, centrifuged for 15 minutes, and absorption spectra were recorded on a spectrophotometer Specord 210 (Analytic Jena). The absence of doxycycline and ceftazidime in the photocatalyst after the photocatalytic experiment was controlled by UV-vis spectra (Evolution 600 (Thermo Scientific)). The content of doxycycline, ceftazidime, and its photodegradation products in the solutions after photocatalysis was monitored by HPLC (liquid chromatograph Waters Alliance E 2695 with UV detector), according to the European Pharmacopoeia (EUROPEAN PHARMACOPOEIA 10.0) and 1H-NMR.

The sol obtained from the reaction mixture containing thiourea after solvothermal treatment contains about 43% (table 1) of the anatase crystalline phase (sample (0.33) TiO$_2$ (120/0)). Thus, in the diffraction pattern of the obtained samples (fig. 1, curve 1), a set of reflexes at $2\theta = 25.2, 37.8, 48.1, 54.0, 54.9, 62.6, 68.9, 70.4, 75.2^\circ$ can be attributed to the characteristic reflexes of the anatase crystalline phase (JCPDS № 21-1272). As the calcination temperature increased (fig. 1, table 1), the anatase content calculated from the diffraction data gradually increases from 43% for (0.33) TiO$_2$ (120/0) to 90% for (0.33) TiO$_2$ (120/450) (Table 1) with a slight increase in the crystallite.
size, calculated by the Scherrer equation from 9 nm (for (0.33) TiO$_2$ (120/0)) to 10 nm (for (0.33) TiO$_2$ (120/450)). The small narrowing in the characteristic anatase reflexes with increasing calcination temperature (fig. 1) can be explained by the small increase in the anatase crystallite size.

Changes in the chemical composition and nature of the groups that occur with increasing calcination temperature were determined using elemental and thermogravimetric analysis, FTIR, XPS and UV-vis spectroscopy, and TPD MS. According to elemental analysis (table 1), with calcination temperature increase, the carbon content in the samples studied decreases from 0.80% to 0.41% and the sulfur content decreases from 1.39% to 0.89%. No nitrogen is detected in the samples.

Table 1

| Sample                | %A | d, nm | % C  | % S  | $E_g$ eV |
|-----------------------|----|-------|------|------|----------|
| (0,33) TiO$_2$ (120/0) | 43 | 9     | 85   | 0.80 | 1.39     | 3.05     |
| (0,33) TiO$_2$ (120/200) | 77 | 9     | 95   | 0.62 | 1.24     | 3.07     |
| (0,33) TiO$_2$ (120/300) | 80 | 9     | 64   | 0.53 | 1.12     | 3.07     |
| (0,33) TiO$_2$ (120/400) | 85 | 9     | 52   | 0.47 | 0.98     | 3.07     |
| (0,33) TiO$_2$ (120/450)* | 90 | 10    | 45   | 0.41 | 0.89     | 3.07     |
| (0) TiO$_2$ (120/450)* | 85 | 9     |       | 0.45 | -        | 3.09     |
| (0,17) TiO$_2$ (120/450)* | 95 | 10    |       | 0.51 | 0.48     | 3.07     |

*data from [36]

The evolution in the content of anatase in the samples (Table 1) as well as the appearance of carbon and sulfur (Table 1) with calcination temperature increase indicates the presence of an amorphous phase. The amorphous phase can be a modified amorphous titanium inorganic polymer (MATIP), similar to the one described in [35], stabilized with organic (acetate, alcohol, etc.) and inorganic (carbonate, sulfate, OH) groups.

The above-mentioned groups, which are present in MATIP, probably, prevent its destruction and anatase crystallization, as well as block the anatase crystallite growth (Table 1) and the anatase to rutile phase transformation.
This trend maintains [36] for the other calcined at 450 °C samples. For example, for (0.17) TiO$_2$ (120/450) with a crystallite size of 10 nm, the anatase content is 95%. It was previously shown [37] that anatase nanoparticles, which are formed mainly in an acidic medium, are stabilized by the surface adsorbates containing a lot of hydrogen (hydrogenated, hydrogen-rich and hydrated surfaces), which prevent the phase transformation to rutile, and the size and shape of anatase nanoparticles vary only slightly and depends on the surface chemistry (only minor changes in the particles ratio occur). However, both polymorph (anatase and rutile) nanocrystals become elongated in the case of hydrogen-depleted and oxygenated surfaces [37]. Taking into account the fact that the Ti-O-SO$_3$H groups on the TiO$_2$ surface are stable up to 600 °C [38], the results of elemental analysis (table 1), TPD MS (fig.4 a, b), and FTIR spectroscopy (fig. 2), allow to assume that the Ti-O-SO$_3$H and Ti-OH groups are also responsible for maintaining the anatase crystallites size and shape during calcination (200-450 °C).

In the FTIR spectra of (0) TiO$_2$ (120/0) (fig. 2, curve 1), the bands 1588 and 1440 cm$^{-1}$ (with $\Delta v = 144$ cm$^{-1}$) are observed, which can be attributed to the valence $\nu_2$ and $\nu$as oscillations of acetate groups bridged by CO bonds [35] (or to $\nu_1$ and $\nu_3$ of bidentate and monodentate carbonate [39]). The band at 1630 cm$^{-1}$ is characteristic for deformation oscillations of OH groups in H$_2$O [39] and/or Ti-OH [18]. The low-intensity bands at 1115, 1090, 1020 cm$^{-1}$ can be attributed to group oscillations of interstitial Ti-O-C bonds [35, 40] and/or oscillations of Ti-O-C butoxyl groups directly associated with titanium [35]. The broad band between 900 - 400 cm$^{-1}$ can be attributed to Ti-O-Ti vibrations of the frame [35, 40, 41]. The broadening of this band is assigned to the amorphous phase. In the FTIR spectra of (0.33) TiO$_2$ (120/0), (fig. 2, curve 2), these bands are preserved (with a slight shift in their position), and new low-intensity bands appear, which can be attributed to oscillations of C-O bonds $\nu_1$ (1393 cm$^{-1}$), $\nu_3$ (1598 cm$^{-1}$) for monodentate and $\nu_1$ (1463 cm$^{-1}$), $\nu_3$ (1285 cm$^{-1}$) for bidentate carbonate. The valence symmetric and asymmetric oscillations of S-O bonds $\nu_3$ (1120,1045 cm$^{-1}$), $\nu_1$ (985 cm$^{-1}$), $\nu_2$ (469 cm$^{-1}$) of bidentate sulfate, caused by a decrease in the symmetry of the sulfate ion with high-symmetric T$_d$ to low-symmetric C$_{2v}$, indicate the formation of bridge bonds with titanium ions. The band $\nu_3$ (1046 cm$^{-1}$) of monodentate sulfate [39] is identified in similar samples as Ti-O-SO$_3$H groups [38]. Since the content of the incorporated nonmetals in the obtained samples is quite low, the corresponding bands are low intense and/or manifested themselves as shoulders to the more intense bands in the FTIR spectrum. Because of this, it is difficult to quantify the changes in their intensity during calcination. Nevertheless, a number of trends in their change should be noted.

![Fig.2 FTIR spectra of the samples: 1 – (0) TiO$_2$ (120/0); 2 – (0.33) TiO$_2$ (120/0); 3 - (0.33) TiO$_2$ (120/200); 4 – (0.33) TiO$_2$ (120/300); 5 – (0.33) TiO$_2$ (120/400); 6 – (0.33) TiO$_2$ (120/450).](https://ucj.org.ua)
As can be seen from fig. 2 (curves 3–6), with calcination temperature increase, there is a tendency to a decrease in the intensity of the valence vibrations band of acetate C-O groups that are associated with a decreasing content of the amorphous phase.

Starting from 300°C, there is also a tendency of a decrease in the intensity of the bands related to monodentate and bidentate carbonate (interstitial carbon).

However, the intensity of the bands, which belong to the bridge (interstitial) sulfate, remains practically unchanged. The intensity of the bands related to the oscillations of OH groups slightly decreases but remains quite high even after calcination at 450°C (fig. 2, curve 6). This may indicate the presence of a large number of OH groups in the sample (0.33) TiO₂ (120/450). The latter fact is important for photocatalysis.

As can be seen in the thermogram (fig. 3a), for (0.33) TiO₂ (120/0) three endoeffects are observed (T_{extr} at 50, 110, 190°C). The two first extrema in the DTG and weight loss in the TG curve can be attributed to the loss of physically and chemically bound water at 50 and 110 °C, respectively. The third effect (190 °C) can be attributed to the loss of residues of organic substances (solvents) that is confirmed by the absence of this effect in the thermogram of the calcined sample (fig. 3 b). An exoeffect with T_{extr} at 370 °C is also observed in the DTA curve that corresponds to the extremum in the DTG and the mass loss in the TG curves. This effect can be associated with the combustion of acetic acid residues and other organic compounds in the modified amorphous titanium oxide inorganic polymer. The course of the DTA curve in the range of 250–650 °C with several extrema that have no correspondence in the DTG curve, may indicate the melting processes. According to the TG this process is accompanied by a slight weight loss in the temperature range 400-650 °C. The extremum in the DTA curve (about 580 °C) can be attributed to the destruction of titanyl sulfate groups on the surface. The similar peak was observed by us previously for samples of doped TiO₂, which were obtained using H₂SO₄ as a sulfur precursor (unpublished results).

In the thermogram of the calcined sample (0.33) TiO₂ (120/450) (fig. 3 b), similarly to (0.33) TiO₂ (120/0) (fig. 3 a), the two endoeffects (T_{extr} 50, 110 °C) in the DTA curve are observed. They correspond to the extrema on the DTG curve and the weight loss on the TG curve due to desorption of physically and chemically bound water. At higher temperatures, in the thermogram (Fig. 3 b) significant changes in comparison with (0.33) TiO₂ (120/0) (fig. 3 a) are observed. The mass loss in the TG curve in the range of 150–250 °C corresponds to the extremum on the DTG curve (~200 °C), and the exoeffect (T_{extr} ~215 °C) can be attributed to the combustion of residues of organic compounds that are a part of MATIP. In the temperature range 300–700 °C according to the DTG and TG curves, a barely noticeable monotonic weight loss is observed. In this case, the course of the DTA curve, which has a number of indistinct extrema, indicates the presence of several phase transitions in the temperature range of 300–700 °C. An extremum at T_{extr} about 730 °C in the DTG and the DTA corresponds to a significant mass loss on the TG curve. Similarly to the peak at 710 °C in the sample (0.33) TiO₂ (120/0) (Fig. 3 a), this effect can be associated with the destruction of the surface Ti-O-SO₃H groups [38] that are formed due to Ti-SH groups oxidation.
In TPD-MS of freshly obtained (0.33) TiO$_2$ (120/0) (fig. 4 a), maxima of TPD-MS profiles with m/z=28, m/z=34, m/z=44 can be associated with the desorption of CO$^+$, H$_2$S$^+$, and CO$_2^+$, respectively. As a result of sol-gel synthesis and STT in (0.33) TiO$_2$ (120/0), the MATIP structure is formed, in which sulfide, carbonate, and, possibly, acetate groups stabilize its structure. The close values of temperatures at which the maxima are observed in the TPD MS profiles m/z=28, m/z=34, m/z=44 in the temperature range 150–500 °C indicate that desorption and destruction processes in MATIP begins with the carbonate bridges destruction (at $T_{\text{extr}} \sim 175$ °C). The process occurs in two stages. On the first, the CO$_2^+$, H$_2$S$^+$, CO$^+$, (T$_{\text{extr}}$ 203, 216, 230°C, respectively), and at the second, H$_2$S$^+$, CO$^+$, CO$_2^+$ (T$_{\text{extr}}$ 309, 309, 317°C, respectively) are desorbed. In the temperature range of 500-800°C, extrema in TPD-MS profiles with m/z=44, m/z=34, m/z=28 (at $T_{\text{extr}}$ 639, 653, 688 °C) correspond to CO$_2^+$, H$_2$S$^+$, CO$^+$, respectively. It should be noted that in the TPD MS, the profiles with m/z=18 (H$_2$O$^+$) correspond to these three groups of extrema, at $T_{\text{extr}}$ 200, 315, and 680°C, indicating the interconnection of desorption processes of CO$^+$, H$_2$S$^+$, CO$_2^+$ and H$_2$O$^+$.
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respectively) and at T$_{\text{extr}}$ ~309, 309, 317 °C (H$_2$S$^+$, CO$^+$, CO$_2$$^+$, respectively), probably due to the gradual destruction of monodentate and bridged acetate and sulfide groups.

In TPD-MS of calcined (0.33) TiO$_2$ (120/450) (Fig. 4 b) in comparison with (0.33) (fig. 4 a), the extrema intensity on TPD MS profiles with m/z=18 (H$_2$O$^+$), m/z=28 (CO$^+$), m/z=44 (CO$_2$$^+$) is significantly lower due to the fact that in the process of calcination at 450 °C a significant part of the respective groups is removed from the sample. According to the thermogram of (0.33) TiO$_2$ (120/0) (fig. 3 a), ~90% of the mass is lost when the sample is heated to 450 °C. Of the five extrema observed on the profile with m/z=28 (CO$^+$), the first two (at T$_{\text{extr}}$ ~110, 254 °C) are probably due to the decomposition of acetate residues. The remaining three (at T$_{\text{extr}}$ ~352, 444, 615 °C), coinciding with the extrema in the TPD MS profiles with m/z=44 (CO$_2$$^+$) at a T$_{\text{extr}}$ of about 444, 617 °C, are probably due to the destruction of surface and interstitial carbonate. Next to these three extrema, the peaks in the TPD MS profile with m/z=64 at T$_{\text{extr}}$ about 435, 645 °C correspond to the desorption of SO$_2$$. Taking into account the fact that the sample (0.33) TiO$_2$ (120/450) (fig. 3 b) according to X-ray phase analysis contains 95% anatase, the desorption of CO$^+$, CO$_2$$^+$, SO$_2$$^+$ at T>300°C can be attributed as to the interstitial also to the surface adhering carbonate and sulfate groups.

Earlier, in the study of TPD of adsorbed H$_2$S and SO$_2$ on the surface of TiO$_2$ [42], it was shown that H$_2$S and elemental sulfur can be oxidized by titanium dioxide and that the desorption of SO$_2$ occurs at T$_{\text{extr}}$ ~350 °C. According to this, the presence of (0.33) TiO$_2$ (120/450) in the TPD MS profile (fig. 4 b) with m/z = 64 three extrema (at T$_{\text{extr}}$ about ~429, 461, 645 °C) corresponding to the desorption of SO$_2$$, may indicate that the main source of SO$_2$ here are sulfate groups rather than adsorbed SO$_2$$. The sulfate groups are a part of MATIP and stabilize its structure. Because of SO$_4$$^-$$^-$ groups, as well as due to the presence in the TPD MS profiles with m/z=34 (fig. 4 a) for (0.33) TiO$_2$ (120/0) extrema at T$_{\text{extr}}$ ~216°C and 309 °C, we can assume that sulfur, which is the source of H$_2$S$^+$, is not physically adsorbed but chemically bound. This fact is consistent with the XPS analysis.

The chemical composition and chemical (oxidation) states of the elements in TiO$_2$ samples are investigated by means of X-ray photoemission spectroscopy (XPS). The results on the calcined (0.33) TiO$_2$ (120/450) were reported by us previously [36]. The uncaked sample (0.33) TiO$_2$ (120/0) is discussed in detail in this work (fig. 5).

As determined from the fragment of the survey XPS spectrum, the surface of the (0.33) TiO$_2$ (120/0) is composed of titanium and oxygen atoms (30.0 at.% Ti and 52.2 at.% O) and also contains C (17.1 at.%), S (0.36 at.%), and N (0.31 at.%). The atomic Ti/O ratio calculated for the TiO$_2$ lattice oxygen (the O1s peak at 530.2 eV, fig. 5) is 1:1.74 (± 0.05). Such an oxygen deficiency is mostly caused by the coordination of Ti$^{4+}$ to other functional groups detected in the surface layer, SO$_4$$^-$$^-$, CO$_3$$^-$$^-$, OH, etc. Fig. 5 shows the high-resolution spectra fitted with Voigt profiles. The peaks at (459.1 ± 0.1) eV and (464.8 ± 0.1) eV correspond to the Ti2P$_{3/2}$ and Ti2P$_{1/2}$ components of the spin-orbit doublet. The separated doublet of lower intensity at (472.3 ± 0.1) and (478.4 ± 0.1) eV stems from plasmon satellites. Thus, the sample contains titanium in a single chemical state, which due to the synthesis conditions, can be unambiguously attributed to Ti$^{4+}$. It should be noted that the lower oxidation states Ti$^{3+}$, Ti$^{2+}$...
that usually manifest themselves at lower binding energies to the main Ti$^{4+}$ peak, are not observed in our samples.

In the high-resolution O1s XPS spectrum (fig. 5), the intense peak at (530.2 ± 0.1) eV stems from the lattice oxygen of TiO$_2$ (530.2 eV [9]). The second broader peak at (531.7 ± 0.1) eV can be referred to carbonate (533.0 eV [8]) and sulfate oxygen (531.6 [12]), as well as to oxygen in surface OH (532.0 eV [9], 532.1 eV [21]) and C-O (532.1 eV [8, 21]) groups. Despite the fact that according to the elemental analysis (Table 1), the (0.33) TiO$_2$ (120/0) does not contain nitrogen (within the sensitivity of the gas chromatography detection), a low intense N1s core-level XPS peak at 400.3 eV is observed. Since XPS is a surface-sensitive method with an information depth less than 10 nm, one can assume that the nitrogen originates from the adsorption of gaseous N$_2$, NH$_3$ from the atmosphere by the near-surface layer of the nanostructured sample [7]. Moreover, the surface sensitivity causes the abnormal inflation of the carbon atoms content compared to the CHN analysis data. In the C1s high-resolution XPS spectrum, the most intense peak at (284.8 ± 0.1) eV is mainly formed by the so-called adventitious carbon (typical range 284.5 - 285.0 eV). The latter comes from volatile organic compounds adsorbed on the surface from the atmosphere [8, 9]. Since the total (bulk) carbon content, determined by the elemental CHN analysis for this sample (Table 1), is 0.80%, one can assume that the main share of carbon (fig. 5) is adventitious and does not belong to the volume of the analyzed sample. Two other peaks of approximately the same intensity at (286.3 ± 0.1) eV and (288.8 ± 0.1) eV may correspond to the interstitially incorporated or surface adsorbed carbonate species [8, 9].

It should be noted that the binding energies of Ti2p, O1s, C1s, and N1s peaks detected for (0.33) TiO$_2$ (120/0) with an accuracy of 0.1 eV coincide with the XPS results on (0.33) TiO$_2$ (120/450) [36], indicating the proximity of the chemical states of these elements in the samples.

The peaks at (169.0 ± 0.2) eV and (170.4 ± 0.2) eV, revealed in the S2p XPS spectrum (fig. 5), correspond to the S2p$_{3/2}$ and S2p$_{1/2}$ spin-orbit components, respectively. According to the chemical shift, the XPS analysis confirms the S$^{6+}$ oxidation state of sulfur [21].

According to the authors [12], who observed similar results, this indicates the formation of sulfuric acid residues in the structure.
of TiO$_2$ during calcination and the incorporation of S$^{6+}$ sulfur in the structure of TiO$_2$ (interstitially and on the surface). This is consistent with the FTIR spectroscopy results for the samples (0.33) TiO$_2$ (120/T$_2$) (fig. 2), according to which the intensity of the bands attributed to S=O modes decreases with increasing calcination temperature. This is also confirmed by the results of TPD MS (fig. 4 a, b), where profiles with m/z 64 (SO$_2$) are observed not only for (0.33) TiO$_2$ (120/450) but also for (0.33) TiO$_2$ (120/0). In addition, for (0.33) TiO$_2$ (120/450) (fig. 4 b) in the profile with m/z 64 (SO$_2$), two peaks ($T_{\text{extr}}$ ~429 and 652$^\circ$C) of approximately the same intensity are detected and can be attributed to surface and interstitial sulfate, respectively. The S2p spectrum of the sample after calcination is very close to the uncalcined one. However, the S2p$_{1/2}$ component (170.4 eV) for the (0.33) TiO$_2$ (120/0) becomes more distinct and exhibits a small shift towards higher binding energies (for comparison, the S2p$_{1/2}$ for the calcined (0.33) TiO$_2$ (120/450) is at (169.9 ± 0.2) eV [36]). In our opinion, this may be caused by Ti-O-SO$_3$H groups in the uncalcined sample, revealed by the results of the TGA analysis (fig. 3 a). A low-intense signal about 160.9 eV corresponds to S$^2$- [10, 11, 19] that is consistent with the results of TPD MS (fig. 4a). The intensity of the peak is extremely low, probably, due to the oxidation of the S$^2$- at the surface. Thus, in addition to the CHN analysis, XPS gives reason to believe that the sample (0.33) TiO$_2$ (120/450) is supplemented with carbon and sulfur.

According to the results of elemental and thermogravimetric analysis, IR, XPS, and TPD MS investigations, the final structure of the calcined samples, in particular (0.33) TiO$_2$ (120/450), is formed due to the MATIP structure destruction during calcination, which is formed at STT and stabilized by groups (water molecules, carbonate, acetate, sulfate and, possibly, alcohol, which also contains sulfide). According to the XPS and the results of elemental analysis and TPD MS a small number of the permeable nonmetals (C, S), which are part of the interstitial and surface carbonate and sulfate groups, remains in the calcined sample. The MATIP calcination is accompanied by a gradual loss of modifying groups, including sulfate (bridge and surface), which are formed due to sulfide oxidation under calcination that creates the preconditions for the anatase crystallization.

According to the SEM image (fig. 6a) the sample (0.33) TiO$_2$ (120/0) is in the form of nanoparticles with an average size of 85 nm, consisting of an amorphous phase (58%, table 1) and anatase crystalline sheets (42%, table 1). According to the TEM study (fig. 6 b), the average size of the sheets, is of about 8x7 nm. These sheets also form rectangular units (fig. 6 b, inset) with an average size of 30x8 nm. As the result of calcination at 200 $^\circ$C, according to the SEM image (fig. 6 c), the average particle size in the sample (0.33) TiO$_2$ (120/200) increases (up to 95 nm) and their compaction occurs. The size of the anatase crystalline sheets (fig. 6 d) increases from 8x7 nm to 10x8 nm. The anatase sheets aggregate in the rectangular rods with an average size of 200x50 nm (fig. 6 d, inset). After calcination at 300 $^\circ$C in (0.33) TiO$_2$ (120/300) the average particle size decreases (up to 64 nm) and their further compaction occur. At the same time, the anatase sheet size decreases from 10x8 nm to 9x8 nm (fig. 6 e), forming aggregates in a shape of rectangular rods (fig. 6 e, inset) with an average size of 20x10 nm. In the SEM image of
Fig. 6 SEM and TEM images of the samples: a, b – (0.33) TiO₂ (120/0); c, d – (0.33) TiO₂ (120/200); e, f – (0.33) TiO₂ (120/300); g, h – (0.33) TiO₂ (120/400); i, j – (0.33) TiO₂ (120/450).

The sizes of crystallites (table 1), calculated from diffractograms (fig. 1) and TEM images (fig. 6), are slightly different. According to the calculations from the diffraction patterns (fig. 1), the average particle size in the uncalcined sample (0.33) TiO₂ (120/0) is 8 nm and increases to 9–10 nm in the calcined ones (table 1). According to the TEM images (fig. 6), the size of anatase crystallites of the rectangular sheet shape changes from 8x7nm to 10x8, 9x8, 10x9, and 10x9 nm, depending on the calcination temperature (table 1). The elevating of the crystals results in the formation of the particles of an elliptical shape, probably due to melting of their edges. The differences between the calculation results of X-ray diffraction data and TEM (table 1) may be related to the sheet formation, since the Debye-Scherrer equation is better fitted for the spherical particles. Lamellar morphology is characteristic for facet structures formed in the presence of a dopant such as fluorine [43], which binds to high-energy {001} faces and blocks the anatase crystal growth along the {001} axis. The formation of lamellar anatase crystals in the case of (0.33) TiO₂ (120/T₂) samples can be explained due to the presence of carbonate and sulfate groups on the anatase crystals surface, which, like fluorine, promote the formation of plates (110x170 nm) and hexagonal (65x65 nm) shape, are observed. Calcination at 450 °C ensures a particle size decrease in the SEM image (fig. 6 i) of (0.33) TiO₂ (120/450) to 45 nm and compaction of the material. In the TEM image (fig. 6 j), these anatase crystals are represented by rectangular particles with fused edges of medium size of 10x9 nm, as well as the anatase crystal sheet aggregates in the form of rectangular rods with an average size of 20x14 nm.

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with open faces {001}. Due to the simultaneous presence of the amorphous phase and the anatase crystalline phase in the samples studied (table 1), which according to TEM images is of the sheet shape (fig. 6), we can assume that the nanoparticles, observed in the SEM image (fig. 6) are anatase sheets or sheet agglomerates, covered by amorphous MATIP, i.e., particles of the type “core-shell”.

Isotherms of samples (0.33) TiO$_2$ (120/0) (fig. 7 a, curve 1) and (0.33) TiO$_2$ (120/450) (fig. 7 a, curve 2) can be attributed to type IV, which is characteristic for micro-mesoporous materials. The specific surface area ($S_{BET}$) for the sample (0.33) TiO$_2$ (120/0) is 190 m$^2$/g with a mesopore diameter of 5.4 nm, $S_{meso}$ of 170 m$^2$/g and a total adsorption volume of 0.25 cm$^3$/g. Nanoparticles form a mesoporous structure, which is formed already at the stage of STT [36]. After calcination at 450°C, the $S_{BET}$ decreases to 130 m$^2$/g, the total pore volume to 0.22 cm$^3$/g, the $S_{meso}$ to 70 m$^2$/g, and the mesopore diameter increases to 6.4 nm. For (0.33) TiO$_2$ (120/0) on the mesopore distribution curve (fig. 7 b, curve 1) two extrema with maxima at 5.5 and 6.4 nm are observed, and the mesopore average size is 5.4 nm, that indicate the presence of two types of mesopores.

Probably, mesopores of smaller diameter are cavities between spheroidal nanoparticles, which consist of anatase sheets (45%), covered with an amorphous phase, and mesopores of larger diameter are cavities between sheet aggregates (fig. 6 b, inset), in particular, in the form of rods. For the calcined sample (0.33) TiO$_2$ (120/450), only one extremum (6.4 nm) is observed (fig. 7 b, curve 2) and the average size of mesopores is 6.4 nm. It is possible that the mesopores here are cavities between spheroidal nanoparticles, which consist mainly of anatase crystal sheets (90%) with fused edges (fig. 6, inset), which are tightly adjacent to each other. As a result of calcination, according to TEM images (Fig. 6 d, f, h, j), the 2D anatase crystallite sizes increase, and rectangular (fig. 6 d, f) and hexagonal (fig. 6 h) sheet aggregates, as a result of calcination at 450°C, are compacted and transformed into spheroidal particles.
specific surface area for (0.33)TiO₂ (120/450) is reduced to 130 m²/g compared to 190 m²/g for (0.33)TiO₂ (120/0), which is probably due to a slight increase in the size of the crystallites and the compaction of particles in the volume of the material due to the destruction of the amorphous phase and sintering. A significant increase in the size of the crystallites (table 1) and drastic changes in the texture prevent carbon and sulfur-containing groups. Thus, the calcination temperature is a factor controlling the anatase content, the crystallite and nanoparticle sizes, as well as the textural characteristics of the obtained materials.

For non-calcined sample (0.33) TiO₂ (120/0) (table 1), the bandgap (E_g) value, calculated from the UV-Vis spectra (fig. 8 a, curve 1), is slightly smaller (3.05 eV) compared to E_g (3.2 eV) for bulk anatase. In the UV-vis spectra of samples (0.33) TiO₂ (120/T₂) (fig. 8 b, curves 1-5), the increasing calcination temperature (T₂) induces the bathochromic shift of the absorption band resulting to the slight absorption in the visible region.

In particular, for sample (0.33) TiO₂ (120/450) in the UV-vis spectrum (fig. 8 a, curve 2) the absorption maximum at 320 nm is shifted in comparison with the sample (0.33) TiO₂ (120/0) (fig. 8 a, curve 1). The latter may be due caused by an increase of the amount of titanium ions in an octahedral surrounding, which is characteristic for the anatase crystalline phase [44]. This is consistent with an increase in the anatase content in these samples with calcination temperature increase (table 1).

Besides, for uncalcined sample the absorbance at λ ≥ 400 nm is greater than for the calcined sample (table 1), that is probably due to the presence of more interstitial Ti-O-C groups in (0.33) TiO₂ (120/0), consistent with the elemental analysis results (table 1). According to the latter, the total carbon and sulfur contents decrease with calcination temperature increase.

As can be seen from the evolution of the UV-vis reflectance spectra (fig. 8 b), for the samples (0.33) TiO₂ (120/T₂), an additional absorption in the visible region at λ ≥ 400 nm
Influence of calcination temperature on structural-dimensiona
characteristics of C,S-doped TiO$_2$ nanostructures and their pho
tocatalytic activity in the ceftazidime and doxycycline pho
todegradation processes

is observed after calcination at 200°C (fig. 8 b, curve 2). This may be caused by the intersti
tial carbonate groups formed in (0.33) TiO$_2$ (120/200). The intensity of absorption decreas
es (fig. 8 b, curves 3–5) with calcination tem
perature increase. At the same time, the nature
of the bands changes, which may be associated
with the formation of interstitial sulfate groups
under these conditions. This is consistent with
the results of TPD MS (fig. 4), XPS (fig. 5),
FTIR (fig. 2), and TG (fig. 3).

Thus, based on the obtained results (FTIR,
XPS, TPD MS, XRD, SEM, TEM, nitrogen ad
sorption/desorption, elemental analysis), it
can be concluded that in the samples (0.33)
TiO$_2$ (120/T$_2$) the calcination temperature in
crease (200-450°C) induces an anatase content
crease, while amorphous phase content de
crease. At that time, the crystallite (of lamellar
morphology) size (8–10 nm) slightly increa
es. The average size of nanoparticles formed
by such crystallites together with the amor
phous phase decreases (95–45 nm), so as the
S$_{\text{BET}}$, S$_{\text{meso}}$, the total adsorption volume, and the
interstitial and surface carbonate and sulfate
groups content decrease. The bandgap insig
ificantly narrowed, reaching 3.05–3.07 eV. All
these changes lead to a significant effect on the
photocatalytic activity of (0.33) TiO$_2$ (120/T$_2$)
samples.

The effect of calcination temperature on
PCA (UV/VIS) of the samples was investigat
ed in the photodegradation reactions of cef
tazidime (fig. 9 a) and doxycycline (fig. 9 b).
The results are presented in Table 2. As can be
seen in fig. 9 a, b, the calcination temperature
significantly affects the photocatalytic activi
ty of the obtained samples in the ceftazidime
and doxycycline photodegradation processes.
The dependence of PCA (VIS) changes on the
increase in calcination temperature, in con
trast to the dependence for PCA (UV), shows
a dome-shape behaviour (fig. 9 a, b). The
conversion of ceftazidime, as well as doxycy
cline, in the presence of (0.33) TiO$_2$ (120/T$_2$)
photocatalysts under UV light irradiation in
crease with calcination temperature increase
and reaches a maximum on the sample (0.33)
TiO$_2$ (120/450) (fig. 9 a, b). The last sample
contains the largest amount of anatase (about

Fig. 9 Conversion degree of: a – ceftazidime; b – doxycycline on the obtained sample under UV (black)
and visible (grey) light irradiation
90%) among the studied samples. At the same time, when exposed to visible light, the maximum ceftazidime and doxycycline conversion (fig. 9 a, b) is observed on the sample (0.33) TiO$_2$ (120/300) with a lower content of anatase (80%) than 90% for (0.33) TiO$_2$ (120/450). Possibly, the higher photocatalytic activity of the first sample is due to the optimal nanoparticles size (64 nm) and larger number of interstitial Ti-O-C groups, the amount of which increases with an increase in the calcination temperature from 200 to 450°C. It should be noted that a similar trend in PCA (UV/VIS) changes is observed for both stained (doxycycline) and colorless (ceftazidime) antibiotics. Based on this, we can assume that the key positive effect on PCA (UV) is an increasing anatase content in the samples. This effect is also present in the case of PCA (VIS) but taking into account the non-substantial bandgap narrowing (to 3.05–3.07 eV, table 1). This effect is also present in the case of FCA (VIS). However, considering the slight narrowing of the bandgap (table 1) to 3.05–3.07 eV, it is difficult to explain this effect only by the bathochromic shift. Taking into account that the positive doping effect on the visible light sensitivity and PCA does not always lead to a change in the bandgap and shift of the band edge [1, 5] but is a result of interstitial doping and localized states formed in the mid-gap [1, 5, 6], it can be considered that the interstitial carbonate and sulfate groups may play a key role. The ratio between the latter groups changes (increases in favor of the latter) with increasing calcination temperature. Higher PCA (VIS) compared to PCA (UV) of the samples for doxycycline (fig. 9 b) in contrast to ceftazidime (fig. 9 a) photodegradation processes is probably associated with a higher adsorption capacity of these samples relative to doxycycline comparable to ceftazidime (table, 2), as well as the doxycycline photosensitizing effect.

Table 2

| Sample               | Q$_{\text{ceftazidime}}$, $10^{-5}$ mol/g | Q$_{\text{doxycycline}}$, $10^{-5}$ mol/g |
|----------------------|----------------------------------------|----------------------------------------|
| (0.33) TiO$_2$ (120/0) | 2.12                                   | 4.05                                   |
| (0.33) TiO$_2$ (120/200) | 1.93                                   | 3.64                                   |
| (0.33) TiO$_2$ (120/300) | 2.46                                   | 4.57                                   |
| (0.33) TiO$_2$ (120/400) | 1.95                                   | 3.57                                   |
| (0.33) TiO$_2$ (120/450)* | 1.97                                   | 3.78                                   |
| P-25 Evonik          | 0.13                                   | 0.46                                   |

Regardless of the samples calcination temperature, PCA (UV) in the ceftazidime photodegradation process on such samples is more than 3 times higher than the conversion value for Evonik P-25. Probably, this is due to the fact that the content of anatase in these samples is higher than in Evonik P-25 (table 1). In addition, these samples are characterized by a more developed surface and a higher adsorption capacity relative to ceftazidime compared with P-25 (table 2). When irradiated with visible light, the conversion on calcined samples (0.33) TiO$_2$ (120/T$_2$) (T$_2$ = 0, 200, 300°C) is 1.5-2 times higher than the value for Evonik P-25 and is maximum for the sample (0, 33) TiO$_2$ (120/300). This may be due to the slightly higher adsorption capacity relative to ceftazidime compared to the rest of the samples (Table 2), as well as with the optimal size (~50 nm) of nanoparticles. In addition, the interstitial carbon content in this sample is also higher, which may provide its increased PCA (VIS).
However, it is noteworthy that the PCA (UV/VIS) of (0.33) TiO$_2$ (120/$T_2$) samples in the doxycycline photodegradation processes is generally higher (1.5-1.7 times) compared with ceftazidime, which is probably due to the approximately 2 times higher adsorption capacity ($Q$, mol/g) of the corresponding samples relative to doxycycline compared to ceftazidime (Table 2). For example, PCA (UV) for (0.33) TiO$_2$ (120/450) is 43.09 and 29.29, respectively, and the average adsorption capacity for doxycycline and ceftazidime is 1.97×10$^{-5}$ mol/g and 4.02×10$^{-5}$ mol/g, respectively. The approximately two times greater adsorption capacity may be the reason for this difference between PCA (UV) relative to doxycycline and ceftazidime.

In contrast to PCA (UV), the PCA (VIS) (conversion, $R_{60}$) ratio values for the doxycycline and ceftazidime photodegradation processes ($R_{60}$ (dox)/$R_{60}$ (cef)) increases from 2.7 to 6.7 as the calcination temperature of the samples (0.33) TiO$_2$ (120/$T_2$). This may be associated not only with the greater adsorption capacity of these samples relative to doxycycline (table 2) but also with changes in the interstitial carbonate and sulfate groups amount and their ratios in (0.33) TiO$_2$ (120/$T_2$) and the photosensitization effect of the substrate (doxycycline). These assumptions are confirmed by the results of PCA (UV/VIS) comparison with Evonik P-25 in the doxycycline and ceftazidime photodegradation processes (table 2). In particular, the adsorption capacity for Evonik P-25 to doxycycline ($Q=0.49$ 10$^{-5}$ mol/g) is 3 times higher than to ceftazidime ($Q=0.13$ 10$^{-5}$ mol/g). Noteworthy that PCA (UV) for Evonik P-25 in the doxycycline ($R_{60}=21.56$%) photodegradation process is approximately also about 3 times higher than in the ceftazidime ($R_{60}=7.53$%) photodegradation process (table 2). At the same time, the PCA (VIS) is approximately 4.3 times higher. For doxycycline and ceftazidime, $R_{60}$ are 33.12 and 7.66%, respectively. Based on these comparisons, it can be assumed that the PCA (VIS) is affected by another additional factor, namely, the photosensitization effect of the substrate (antibiotic). Therefore, it can be expected that for photodegradation processes of stained antibiotics, like doxycycline, in which the absorption band edge in the UV region enters the visible region, the studied (0.33) TiO$_2$ (120/$T_2$) nanostructures will be even better photocatalysts.

From the comparison of the PCA (UV/Vis) values for the samples (0.33) TiO$_2$ (120/$T_2$) (table 2), it is seen that PCA (UV) and, especially PCA (VIS), of these photocatalysts are significantly higher in the doxycycline photodegradation processes compared to ceftazidime. The reason for that can be the lower adsorption capacity of these materials and Evonik P-25 to ceftazidime (table 2). This may be due to the ceftazidime’s greater hydrophobicity and its molecule larger size, compared to doxycycline, as a result, this substrate is less efficiently adsorbed on the photocatalyst surface. The possible influence of different donor atoms in these antibiotic molecules on the efficiency of their interaction with the surface of the photocatalyst is also not excluded.

An additional factor for the superior photocatalytic activity can be the photosensitization effect of the surface-adsorbed doxycycline, which absorbs in the UV region and contains two intense bands with maxima $\lambda_{max} = 270$ nm and $\lambda_{max} = 347$ nm, the edge of which enters the visible region. Ceftazidime, in contrast to doxycycline, absorbs light mainly in the UV region of < 300 nm.
It was previously shown [22], that the main reason for the three times higher photocatalytic activity in the methylene blue and phenol photodegradation reactions of N, S-doped TiO$_2$ samples obtained from titanyl sulfate and thiourea, compared to Degussa P25, is the small anatase crystallite size (5–6 nm). According to the authors [22], this may be due to the synergism of the interaction of sulfate and nitrogen with the TiO$_2$ lattice. In N, S-doped TiO$_2$, N-Ti-O and O-Ti-N-O are responsible for the redshift, and the sulfate group acts as a cocatalyst to increase surface acidity and to maintain a high stability of the redox cycles [22]. In the case of TiO$_2$ samples doped with C, S, obtained by us, the average crystallite size is small (9–10 nm) and both interstitial and surface sulfate groups are present. Therefore, the surface sulfate probably also acts as a cocatalyst and the photocatalysis process. According to the mechanism proposed by the authors [22], it provides for the participation of surface sulfate in the redox transformations (S$^{6+}$ $\leftrightarrow$ S$^{4+}$). The visible light absorption by (0.33) TiO$_2$ (120/T$_2$) nanostructures with a small decrease (~0.15 eV) in the bandgap width (table 1) in comparison with pure anatase is provided, mainly, by the interstitial C-O-Ti and S-O-Ti. According to [1, 5, 6], these groups can form localized states between VB and CB, helping to increase the sensitivity to visible light without significantly narrowing the bandgap. The presence of sulfate ions in the (0.33) TiO$_2$ (120/T$_2$) sample surface structure that are formed during calcinating may promote the migration of photogenerated electrons, thereby improving the photogenerated charge carriers separation, and inhibition of recombination processes, which improves the photocatalytic activity, as it was observed for N, S-doped [22] and S-doped [21] TiO$_2$ nanostructures.

As can be seen from the comparison of the PCA (UV/VIS) for (0.33) TiO$_2$ (120/T$_2$) samples and (X) TiO$_2$ (120/450) [36], the optimal calcination temperature is one of the key controlling factors for the structural and dimensional characteristics of doped TiO$_2$ nanostructures and their photocatalytic activity in the doxycycline and ceftazidime photodegradation processes. Thus, PCA (UV/VIS) for (X) TiO$_2$ (120/T$_2$) samples, in which the anatase content increases with increasing calcinating temperature, gradually increases but is smaller compared to samples with a high content of anatase (X) TiO$_2$ (120/450) (X=0; 0.17; 0.33). At the same time, the PCA (VIS) of the (0.33) TiO$_2$ (120/300) sample, which is calcined at 300°C, is higher in comparison with all other samples (Table 2), including the best sample (0.17) TiO$_2$ (120/450), which was obtained at the optimal X=TU/TBT=0.17 ratio in the reaction mixture [36]. Taking into account the above results and assumptions, we can assume that one of the reasons for this is changes in the interstitial dopants content and their ratio, that are achieved at a calcination temperature of 300 °C. This is also consistent with the results of elemental analysis (table 1) and XPS (fig.5).

It should be noted that our (0.33) TiO$_2$ (120/T$_2$) samples, containing interstitial and surface carbonate and sulfate groups, show a higher PCA (VIS), compared to those obtained by titinate nanotube with TU calcinating in vacuum at 500 °C encoded by N/S co-doped TiO$_2$ nanotubes, where N and S replace oxygen in the lattice [11], and which were tested in the methylene blue photodegradation process under close conditions. The PCA (VIS) of the (0.33) TiO$_2$ (120/T$_2$) samples is comparable
to the activity in the same process [45] of F,S-doped TiO$_2$ lamellar nanostructures with a nanoparticle size of 10–15 nm, obtained by solvothermal method (precursors F and S, respectively NH$_4$F and T U), followed by calcinating at 450 °C and in which F and S are incorporated in the lattice in the oxygen position and show a synergistic effect, that increases the concentration of superoxide and, accordingly, the growth of PCA (VIS) in the methylene blue photodegradation process. Thus, among the (0.33) TiO$_2$ (120/T$_2$) samples, the best photocatalytic activity under visible light irradiation in the doxycycline and ceftazidime photodegradation processes is demonstrated by the sample (0.33) TiO$_2$ (120/300), which is characterized by an anatase content (80%), crystallite size of 9 nm, and spherical nanoparticles (64 nm) and contains interstitial dopants (C, S), and PCA (UV/VIS), that significantly outperforms Evonik P-25.

As can be seen (fig. 9 a, b), the conversion of ceftazidime, as well as doxycycline, under UV light irradiation increases with increasing calcination temperature and reaches a maximum for the sample (0.33) TiO$_2$ (120/450) (fig. 9 b). Regardless of the calcination temperature of the samples, the PCA (UV) in the photodegradation of ceftazidime is more than 3 times higher than the conversion value for Evonik P-25. At the same time, under visible light irradiation, the maximum doxycycline conversion is observed on the sample (0.33) TiO$_2$ (120/300) and 1.5-2 times higher than the value for Evonik P-25. It is noteworthy that the PCA (UV/VIS) on the corresponding samples (0.33) C, S doped TiO$_2$ (120/T$_2$) in the doxycycline photodegradation is generally higher (1.5 - 1.7 times ) in comparison with ceftazidime (Fig. 6 a, b). However, for samples (0.33) TiO$_2$ (120/T$_2$) the ratio of PCA (VIS) (conversion after 60 min, R$_{60}$) for the doxycycline and ceftazidime photodegradation processes (R$_{60}$ (dox)/R$_{60}$ (cef)) increases from 2.7 to 6.7 as the calcination temperature increases (T$_2$ = 200-450 °C). In contrast, the PCA (UV) for these samples is remained at the same level.

**CONCLUSIONS**

Interstitially carbon and sulfur-doped TiO$_2$ nanostructures with high photocatalytic activity in the ceftazidime and doxycycline photodegradation processes were synthesized by sol-gel synthesis followed by solvothermal treatment (120 °C) and calcinating (200–450 °C). With increasing calcination temperature, the anatase content and mesopore diameter (from 5.4 to 6.4 nm) increase, while the amorphous phase content decrease in the obtained samples. The anatase crystallites of lamellar morphology slightly increase in sizes (from 8x7 nm to 10x9 nm). The anatase crystallites, together with the amorphous phase, are arranged in rectangular and hexagonal stacks that form nanoparticles. The average size of the nanoparticles decreases (95-45 nm) along with the decrease in the S$_B$ (190-130 m$^2$/g), the S$_m$ (170–70 m$^2$/g), the total adsorption volume (0.25–0.22 cm$^3$/g), and the carbon and sulfur content, which are a part of the interstitial and surface carbonate and sulfate groups.

Varying the calcination temperature allows TiO$_2$ nanostructures to be obtained with a certain balance of these characteristics that provides a high photocatalytic activity for these structures not only under ultraviolet irradiation but also under visible light. The key positive effect on the PCA (UV) of the studied samples in doxycycline and ceftazidime photodegradation processes is exerted by the high anatase
content, the large mesopore surface area, and the small crystallite and nanoparticle size. This effect is also present in the case of PCA (VIS), but here the key role is played by the interstitial carbonate and sulfate groups. The content and ratio of these groups decrease with increasing calcination temperature. The higher PCA (VIS) compared to the PCA (UV) of the (0.33) TiO$_2$ (120/T$_2$) samples to doxycycline, in contrast to the ceftazidime photodegradation process, is associated with the higher adsorption capacity of these samples, and probably with the photosensitizing effect of doxycycline.

The visible light absorption by (0.33) TiO$_2$ (120/T$_2$) samples is ensured, mainly, by the presence of interstitial C-O-Ti and S-O-Ti with a small decrease (~0.15 eV) in the width of the bandgap compared to pure anatase. The sulfate ions formed during calcination, which are present in the surface structure of C, S-doped TiO$_2$, promote the photogenerated electron migration, thereby improving the separation of photogenerated charge carriers and inhibition of recombination processes that improves photocatalytic activity.

Thus, the calcination temperature is a factor of controlling the anatase content, crystallite and nanoparticle size, morphology, textural characteristics, and the content of interstitial and surface sulfate and carbonate groups. The balance of these factors ensures their PCA (UV/VIS) in the ceftazidime and doxycycline photodegradation processes. The photocatalytic activity (PCA UV/VIS) of the samples containing carbon and sulfur only in the interstitial and surface groups and not containing (C, S) dopants incorporated directly into the lattice significantly outperform Evonik P-25 and can be used for the antibiotic photodegradation processes under sunlight irradiation.

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PHISICAL CHEMISTRY

INFLUENCE OF CALCINATION TEMPERATURE ON STRUCTURAL-DIMENSIONAL CHARACTERISTICS OF C,S-DOPED TiO₂ NANO-STRUCTURES AND THEIR PHOTOCATALYTIC ACTIVITY IN THE CEFTAZIDIME AND DOXYCYCLINE PHOTODEGRADATION PROCESSES

кардинальні зміни морфології наноструктур TiO₂. Показано, що варіювання температур кальцінування дозволяє одержати наноструктури TiO₂ з певним балансом цих характеристик, який забезпечує їхню високу фотокаталітичну активність у процесіх фотодеградації цефтазидиму та доксиксикліна, при опроміненні не лише ультрафіолетовим, а й видимим світлом.

Ключові слова: мезопористий C, S-допований TiO₂, тіосечовина, кальцінування, фотокаталітична активність, антибіотики.

Mesoroporous C, S-doped TiO₂ nanostuctures were prepared by solvotherm al-zole-gel method with subsequent calcination at different temperatures. It was established that with a small change in the size of crystallites (9–10 nm) the content of anthranil (from 42% to 95%), the size of nanoparticles (from 85 to 45 nm), specific surface area (200–130 m²/g) and mesopore area (from 170 to 70 m²/g), the content of carbon (0.80–0.41%) and sulfur (1.39–0.89%) decreases, and there are significant changes in the morphology of TiO₂ nanostructures. It is shown that the variation of the calcination temperature allows to obtain TiO₂ nanostructures with a certain balance of these characteristics, which ensures their high photocatalytic activity in the processes of photodegradation of ceftazidime and doxycycline under not only ultraviolet but also visible light.

Key words: mesoporous C, S-doped TiO₂, thiourea, calcination, photocatalytic activity, antibiotics.
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