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SYNTHESIS, OPTICAL AND PHOTOCATALYTIC PROPERTIES OF MESOPOROUS IRON DOPED TITANIA FILMS

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Semiconductive films based on iron doped titania are investigated to clarify the role of the doping agent content on their optical features, adsorption capability and photocatalytic properties. The titania films doped with iron ions (1–50 mol %) with highly developed mesoporous surface are synthesized by sol-gel method. The band edge shift towards visible part of the absorption spectrum becomes more pronounced with the increase in iron content pointing on the narrowing of the band gap of the semiconductor. Inhomogeneous distribution of iron atoms in the titania matrix between surface and bulk takes place as shown by EDS analysis. The formation of nanosized particles in the range of 25–50 nm is revealed by SEM images. The adsorption degree of the tetracycline hydrochloride molecules onto the film surface is strongly dependent on the film composition. Twice and thrice enhancement in the photocatalytic destruction of tetracycline hydrochloride under visible irradiation is fixed for the films containing 25 and 50 % iron ions, respectively, comparing with the pristine titania. It is proven that the photocatalytic degradation of tetracycline hydrochloride follows onto the surface of the photocatalyst.

Keywords: iron-doped titania, sol-gel synthesis, optical properties, photocatalytic activity

INTRODUCTION

The worldwide contamination of water sources, soil and air by dangerous toxic substances requires the design of new functional materials sensitive to the visible light. Nowadays, titania is recognized as the most used photocatalyst due to its chemical stability, non-toxicity and high photocatalytic activity in the UV region of solar spectrum [1]. The use of titania in photocatalytic purification of the surrounding from organic compounds and heavy metal ions is comparably in expensive and ecologically pure technology [2]. However, titania absorbs only 4 % solar light limiting its usage in ecological photocatalysis. The perspective approach to wide its spectral range under light with lower energy is the structure modification by metal ions doping [3, 4]. Incorporation of metal ions in the semiconductive matrix leads to the alteration of optical, structural and photocatalytic properties. Iron is well-known among the metals as an effective doping agent for photocatalytic destruction of dyes [5, 6] and other organic compounds [7, 8]. Photocatalytic dinitrogen

fixation, that is one of the most important processes of artificial photosynthesis, was performed and experimentally found in the presence of iron titanate films [9]. An effective way to remove As(III) ions from groundwater was reported to be the visible light irradiation over Fe/TiO_2 powders where the photocatalysts exhibited the high chemical stability and photocatalytic activity [10]. The increased photocatalytic activity in the Rhodamine B destruction under both UV and visible light and the stability after multiple use in water purification process were reported in the presence of 5 % content of Fe^{3+} ions in TiO_2 films covered in the optical fibers [11]. The investigation of electronic properties of iron doped titania catalysts showed that the modification of semiconductor by iron ions effected the electronic structure, iron valence and chemical state of the obtained materials [12, 13]. Iron ions incorporation in the titania mesoporous thin films stimulated the trapping of the photogenerated charges leading to the recombination rate decrease [14]. It is confirmed that Fe^{3+} ions are situated onto the titania surface at the low content of the doping agent and are

capable to form the sites for electron-hole transition that are beneficial for enhancement in photocatalytic activity of the materials. When the iron content is increased, its ions are embedded into titania bulk acting as recombination centers [15]. However, the presence of iron ions in titania led to the narrowing of band gap of the semiconductor forcing to the possibility to absorb quantum of visible light as indicated herein [16]. The band gap energy values of Fe-TiO$_2$ films varied from 3.3 to 2.8 eV with iron content increase from 0 to 25 %, respectively [17]. Influence of iron doping on the electronic and structural properties of TiO$_2$ by density functional theory (DFT) showed that the increase in Fe^{3+}/TiO$_2$ photoactivity occurred due to the formation of additional electronic levels in the band gap of titania [18]. It must be noted that the radius of Fe(III) ions is 0.64 Å that is similar to Ti(IV) (0.68 Å) and the substitution of titanium ions by iron ones can follow quite easy.

In spite of a number of publications intended to the systems based on iron doped titania synthesized by different methods, the use of such photocatalysts is limited by their low efficiency under visible light or low chemical stability. The high photocatalytic activity under visible light as well under UV was rarely reported [9, 15]. It is known [5–18] that the physico-chemical properties of iron-doped titania nanostructures are strongly dependent on the synthesis route and its conditions as well as on the doping agent content. Therefore, the properties of materials obtained by different method significantly vary, such as the valence of the elements, electronic structure, morphology of the surface, iron ions distribution, structural properties (the formation of iron titanate or separated oxide phases) and, in turn, photocatalytic activity. It must be noted that the fabrication of the photocatalysts in the form of thin nanosized films with high surface area is under interest due to the more convenient application for environmental purification.

Sol-gel method is known as the most frequently used one to obtain the iron containing photocatalysts due to its simple route that can be carried out at low temperature, where the control of microstructure, porosity, particle size and component distribution over the films can be achieved [19]. As known [9], the formation of iron titanate phase was responsible for high photoactivity under UV light. Therefore, the synthesis of iron doped titania films in the wide range of iron content (1–50 mol %) with highly developed surface and study on their optical and structural properties as well as on the influence of iron content on the sensitivity to visible light are the scope of this work.

EXPERIMENTAL

The mesoporous titania and iron doped titania films with different Fe^{3+} ions content (1, 5, 10, 25 and 50 mol %) were synthesized by sol-gel method. Titanium tetraisopropoxide, unhydrous iron chloride, a three-block copolymer of polyethyleneoxide and polypropyleneoxide (PEO)$_{20}$(PPO)$_{70}$(PEO)$_{20}$ (Pluronic P123) as a template in alcoholic medium and acetylacetone as a stabilizing agent were used. Concentrated perchloric acid was added to reach acidic pH (1–2) and prevent the precipitation of the oxides. The diagram of the synthesis steps is presented in Scheme 1. The six-layered films were deposited by dip-coating procedure at a withdrawal rate 1.5 mm/s allowing the uniform covering of the film onto the glass substrate with a certain thickness. Every layer was dried at 100 °C for 30 min. The films were treated in air at 450 °C for 1 h with the heating rate of 3 °C/min.
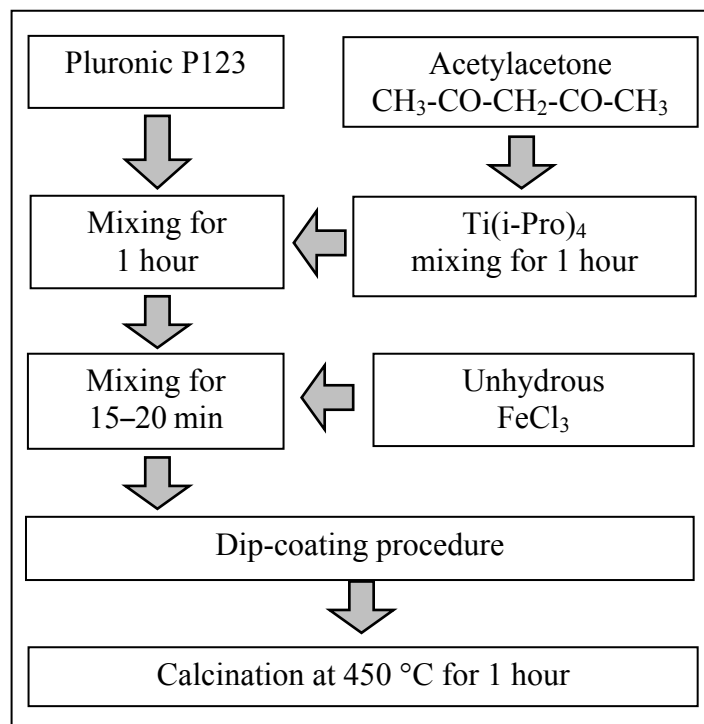
The absorption spectra of the films were recorded by a Lambda 35 UV-vis spectrophotometer (PerkinElmer) in the wavelength range from 200 to 700 nm.

Photocatalytic activity of the films was assessed via tetracycline hydrochloride (TC) degradation (the structural formula is given in Fig. 1) under both UV and visible light. The film was immersed in 40 ml of 2×10^{-5} mol/L TC aqueous solution until complete adsorption in the dark occurred and then irradiated by a 1000 W middle-pressure mercury lamp for 90 min. The reaction temperature was kept constant (20 °C) during the experimental procedure. The change of TC concentration was monitored with a Lambda 35 UV-vis spectrophotometer (PerkinElmer) every 20 min at $\lambda = 357$ nm. The distance lamp-reactor was set at 90 cm. A blank experiment was carried out where a bare glass was used instead of the film. No significant change in the absorption spectra of the liquid was observed for the blank. For testing the visible light sensitivity, a filter transmitting light with $\lambda > 380$ nm was introduced into the photocatalytic setup.

The study of TC adsorption-desorption onto/from the film surface in the dark was performed by the film immersion in the 40 ml of 2×10^{-5} mol/L TC aqueous solution for certain time (from 20 min to 24 h) and then, the desorption of the adsorbed TC molecules from the film surface to distilled water was carried out for certain time.

SEM images were registered on a SEM LEO-1530 apparatus. EDS spectra were obtained using a Brucker AXS X-ray detector.

Scheme 1. The synthesis steps of iron doped titania films
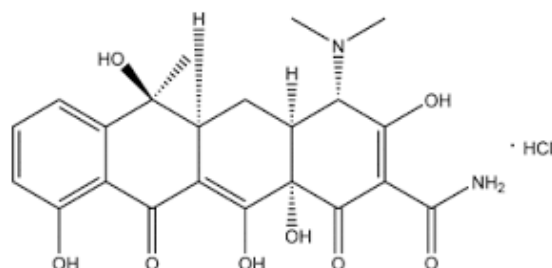

Fig. 1. Tetracycline hydrochloride

RESULTS AND DISCUSSION

To investigate the influence of iron ions and their content on the optical properties of the films, the absorption spectra and the calculated values of band gap energy were obtained. The synthesized films treated after 450 °C possessed the excellent optical quality that is confirmed by the absorption spectra presented in Fig. 2.

It is clear that the presence of iron ions in the titania structure leads to the change in its optical property. It is obvious that the band edge is shifted to the longer wavelength part of the spectrum compared to the undoped one. It must

be noted: the more iron content, the stronger shift is observed. The observed band edge shift can be caused by the excitation of 3d-electrons of Fe^{3+} and the charge transfer to the conduction band of TiO_2 resulting in the color change of the synthesized samples [18]. It is reported [20] that Fe^{3+} ions are capable of acting with the surface hydroxyl group of titania where upon the formed $(OH)Fe^{3+}$ complexes provide the charge transfer centers. The intensive absorption in the visible part of the spectrum with the appearance of some maxima situated at different wavelengths for the films containing various amounts of iron ions is

attributed to the interference phenomenon. The position of interference maxima is determined by the refractive index and the film thickness. Since the thickness of all films is similar, the above-mentioned peaks are caused by the different refractive indices due to the change in iron content. It is also confirmed by the optical spectra of the films obtained under the same conditions and having the different thickness (not shown here) where the interference peaks are spread over the visible part of the absorption spectrum.
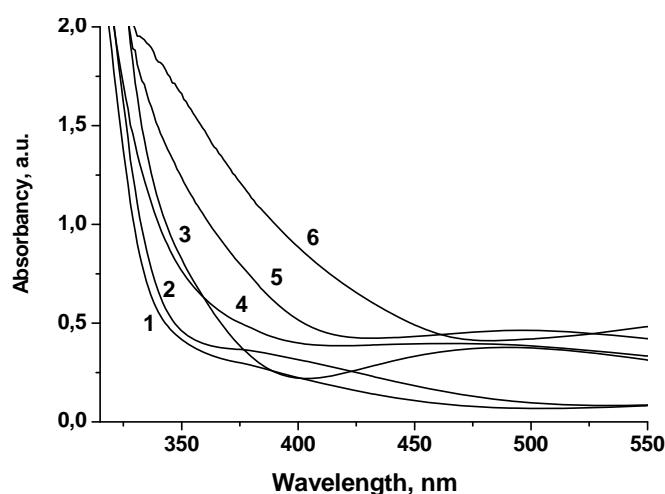

Fig. 2. Absorption spectra of titania film (*1*) and Fe^{3+}/TiO_2 films with different iron content (1 % – curve 2, 5 % – curve 3, 10 % – curve 4, 25 % – curve 5, and 50 % – curve 6)

To estimate the band gap values (E_g), the dependence of the absorption coefficient obtained from $\alpha = 4\pi k/\lambda$ *vs* energy of the incident light was obtained. It is known that the absorption coefficient α is proportional to $(h\nu\text{-}E_g)^2$ for direct-gap materials while to $(h\nu\text{-}E_g)^{1/2}$ for indirect-gap materials. The band gap energy of titania is 3.2 eV and an indirect electronic transition is assumed. In the case of the direct electronic transition, the extrapolation of the linear parts of the $(\alpha h\nu)^2 \sim f(h\nu)$ was performed to find out the E_g^{dr} values, while the E_g^{indr} values are determined as $E_g^{indr} = 0.5 \times (E_1\text{-}E_2)$

as shown in Fig. 3 where E_1 and E_2 are the intersection points of the extrapolated lines with abscissa [21, 22].

The dependence of the absorption coefficient $\alpha^{1/2}$ for the indirect electronic transition on E (eV) for TiO_2 and 50 % Fe^{3+}/TiO_2 films is presented in Fig. 3.

The band gap energy values of the films for the direct electronic transition E_g^{dr} and indirect electronic transition E_g^{indr} are considered and presented in the Table.

Table. The band gap energy values of the films for both electronic transitions

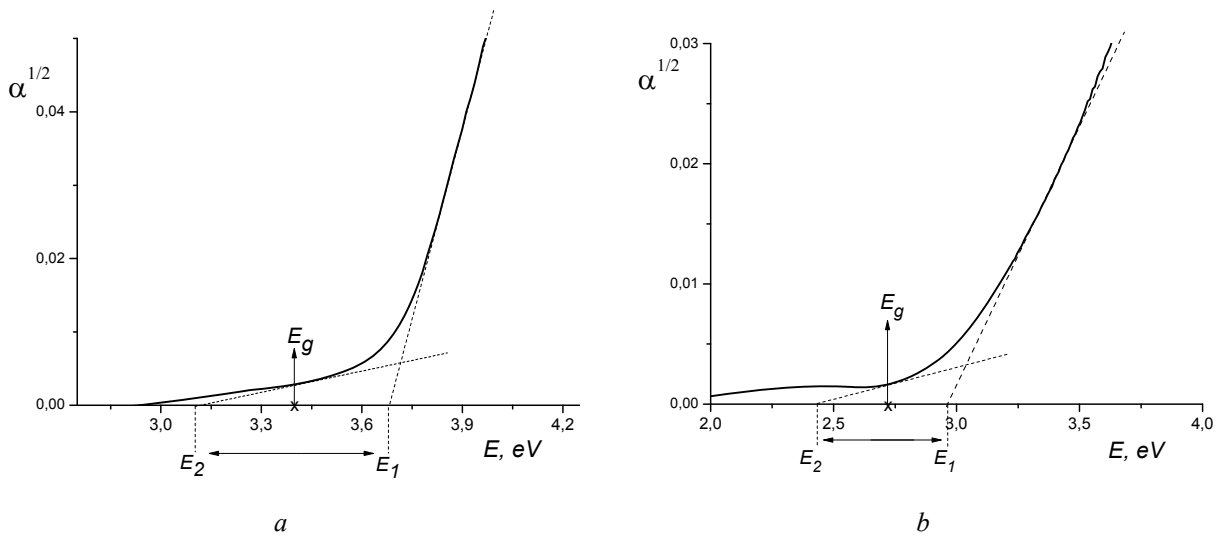| Iron content in the sample, %	0	1	5	10	25	50
E_g^{dr}, eV	3.8	3.8	3.7	3.8	3.8	3.5
E_g^{indr}, eV	3.4	3.3	3.2	3.1	2.9	2.7

Fig. 3. Dependence of $(\alpha)^{1/2}$ on E (eV) for $TiO_2 - a$ and 50 % $Fe^{3+}/TiO_2 - b$ films

The best fitting of the linear parts of the dependence $(\alpha h\nu)^{1/2} \sim f(h\nu)$ is observed for all the samples assuming the predominance of the indirect electronic transition over the direct one. Additionally, the sharp decrease in the band gap energy values with the increase in iron content is noted for the indirect electronic transition. The band gap narrowing is a result of the incorporation of metal ions into the titania structure and/or the formation of the new phase, namely iron titanate one as reported herein [23].

The ratio of Ti to Fe on the surface of the 50 %Fe/TiO₂ film obtained by EDX method (Fig. 4) is calculated as 1 to 0.6 even though the molar ratio of the components in the sol is 1 to 1. It means that the inhomogeneous distribution of iron atoms in the titania matrix between surface and bulk takes place when the films are synthesized by the above-mentioned procedure. The nanosized particles (in the range of 25–50 nm) of the 50 % Fe^{3+}/TiO_2 can be formed using the method presented in this work as clearly seen from SEM image (Fig. 5).
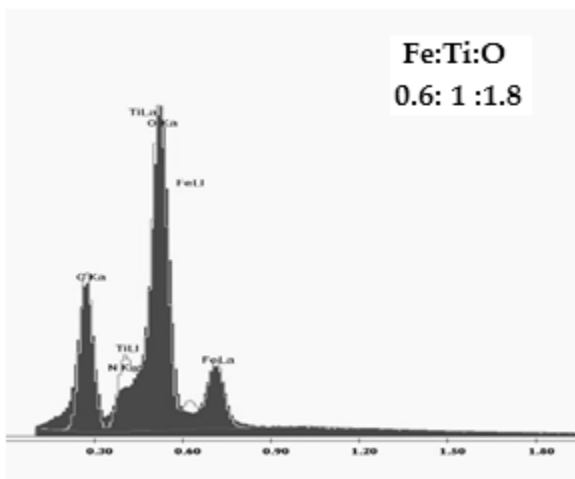

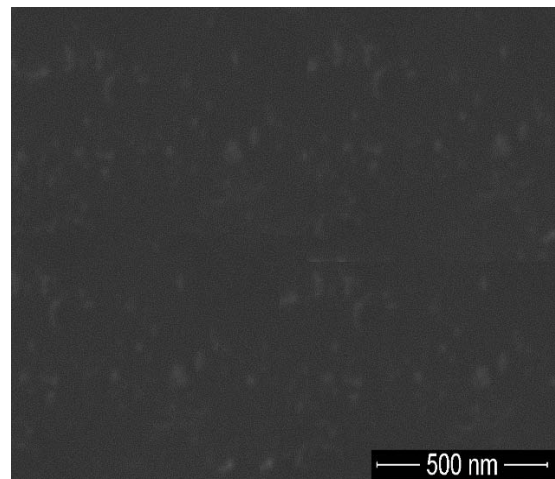**Fig. 4.** EDX spectrum of 50 % Fe^{3+}/TiO_2 mesoporous film

Fig. 5. SEM images of 50 % Fe^{3+}/TiO_2 mesoporous film

The adsorption capability of TC onto the surface of the films with various amounts of iron ions carried out in the dark was also studied (Fig. 6). It is shown that the formation of new adsorption sites takes place and the percentage of the adsorbed TC molecules is strongly dependent on the film content. It is obvious that the higher iron ions, the higher adsorption of TC onto the film surface. Hence, the relatively low compared to early published results [9, 23] treatment temperature of the films and the use of the templating agent allowed to keep the developed surface area caused to the high adsorption of the pollutant molecules (Fig. 6).
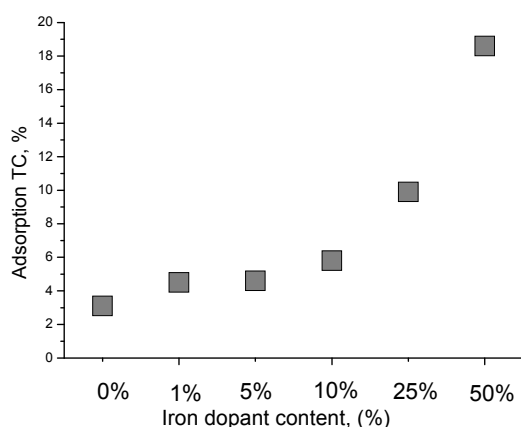
The kinetic dependence of TC adsorption onto the film in the dark was studied. The film was immersed in the aqueous solution of TC for certain time (from 20 min to 24 h) and then, desorption of TC from the film to distillated water took place. The increase in TC concentration with desorption time was noted (Fig. 7, column 1–3). However, the low concentration of desorbed TC was registered after the film irradiation during 90 min taking into account that the adsorption was carried out for 24 h (Fig. 7, column 4). This clearly shows that the adsorbed TC molecules are firstly involved into the photocatalytic reaction rather than the molecules from liquid-solid interface.
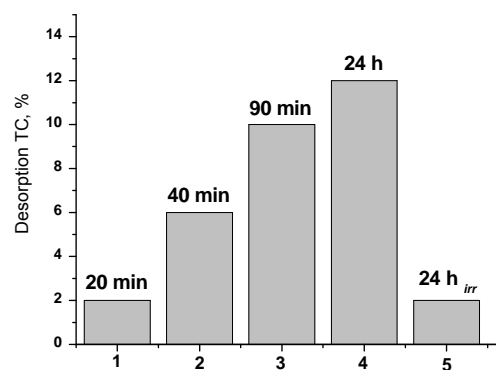

Fig. 6. Percentage of adsorbed TC molecules onto the film surface *vs* the film composition

Fig. 7. Amount of desorbed TC from the 50 %Fe/TiO$_2$ film surface after 20 min (*1*), 40 min (*2*), 90 min (*3*), 24 hours (*4*) of TC adsorption and after 24 hours adsorption followed by 90 min irradiation (*5*)

The photocatalytic activity of the films was tested in the process of TC destruction under both UV and visible light. The light action on the aqueous TC solution without film did not lead to the significant changes in TC absorption spectra, i.e. the TC concentration was decreased for 6 and 2 % after 90 min irradiation under UV and visible light, respectively.

As seen from Fig. 8, the increase in TC conversion degree compared with that for undoped TiO$_2$ film is only observed for 25 and 50 % Fe^{3+}/TiO$_2$ films under UV light. It can be caused by the decrease in the recombination rate of photoformed charges. It must be noted that the lower iron content exhibited the opposite effect (Fig. 8 *a*). However, these films exhibited the

enhanced in several times photoactivity under visible irradiation. The different mechanism of photocatalytic processes take place under visible light compared to the action of light with higher energy. Independently on the origin of visible light absorption in dopants discrete energy states, the low photocatalytic efficiency is mainly attributed to the limited photo-excitation of electrons in such narrow states, the very low mobility of the corresponding photo-generated holes [24], and the concomitant increase in the recombination rate due to the creation of oxygen vacancies by doping [25]. Photosensibilization and the formation of iron titanate phase characterized by much lower band gap values (Table) can be responsible for the effective

photocatalytic process under visible light. It is clear that the doping agent amount plays a key

role in the increased photoactivity of the films under visible light [26].
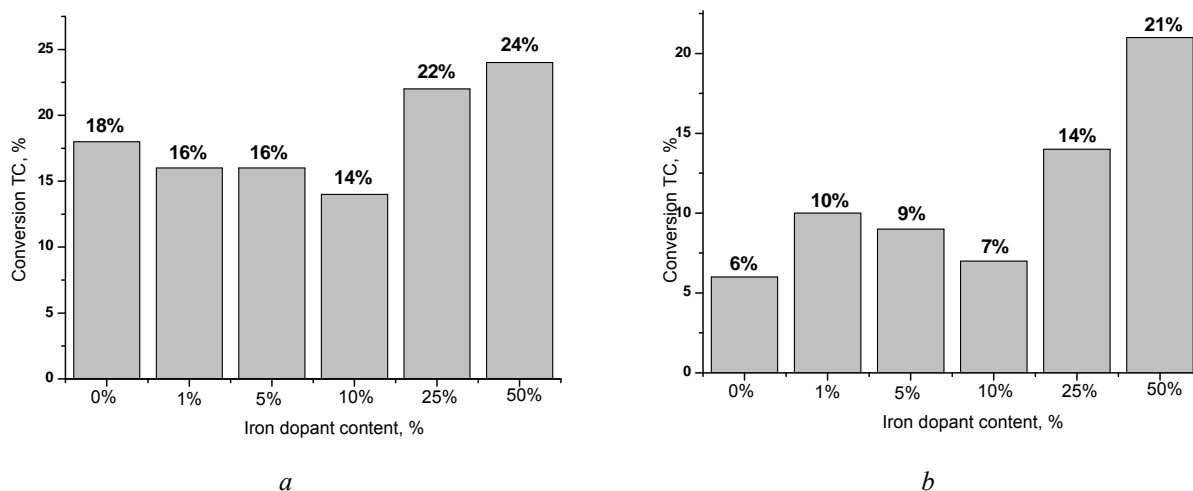

Fig. 8. The conversion degree (%) of TC during photocatalytic destruction under UV (*a*) and visible (*b*) light for titania and iron doped titania films

CONCLUSIONS

Mesoporous iron doped titania films are synthesized by low-temperature sol-gel method. The influence of the iron ions content in titania matrix on the optical and photocatalytic properties is shown. The broad absorption in visible part of the spectrum and the narrowing of band gap energy values are observed with the increase of iron ions content in the film composition. Adsorption capability of the films is increased with the increase in iron content that is connected with the number of active adsorption sites that, in turn, effects on the photocatalytic activity. It is proven that the photocatalytic degradation of TC molecules follows on the surface of the photocatalyst rather than in liquid-solid interface. The high photocatalytic activity under visible light was observed for the films with the higher iron content.

ACKNOWLEDGEMENTS

Синтез, оптичні та фотокаталітичні властивості мезопористих залізовмісних плівок діоксиду титану

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Мезопористі плівки модифікованого діоксиду титану з різним вмістом (1–50 %) йонів заліза синтезовано золь-гель методом. Збільшення вмісту йонів заліза в плівках TiO_2 призводить до звуження ширини забороненої зони, розрахованої з оптичних спектрів. Встановлено, що під дією видимого світла активність синтезованих зразків в реакції деструкції тетрацикліну гідрохлориду зростала для плівок з 25 та 50 % вмістом допанта більш ніж в два та три рази, відповідно, у порівнянні з недопованим TiO_2. Спостерігається підвищення адсорбційної здатності плівок зі збільшенням вмісту заліза в структурі TiO_2.

Ключові слова: *діоксид титану, золь-гель метод, оптичні властивості, фотокаталітична активність*

Синтез, оптические и фотокаталитические свойства мезопористых железосодержащих плёнок диоксида титана

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Мезопористые плёнки модифицированного диоксида титана с различным содержанием (1–50 %) ионов железа синтезированы золь-гель методом. Увеличение количества ионов железа в плёнках TiO_2 приводит к сужению ширины запрещенной зоны, величину которой рассчитывали с оптических спектров. Установлено, что под действием видимого света активность синтезированных образцов в реакции деструкции тетрациклина гидрохлорида увеличивалась для пленок с 25 и 50 % содержанием допанта более чем в два и три раза, соответственно, по сравнению с недопированным TiO_2. Наблюдается повышение адсорбционной способности плёнок с увеличением содержания железа в структуре TiO_2.

Ключевые слова: *диоксид титана, золь-гель метод, оптические свойства, фотокаталитическая активность*

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