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Nitrogen-iron co-doped titania films as solar light sensitive photocatalysts

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Iron and nitrogen-iron co-doped titania films (non-porous and mesoporous) on glass substrates were obtained using a sol-gel method via different synthesis routes. The photocatalytic degradation of anthropogenic pollutant tetracycline hydrochloride over synthesized films was studied. It is shown that the photocatalytic response of the films is sharply depended on the synthesis procedure and calcination temperature. The non-porous three layered iron-doped and nitrogen-iron co-doped titania treated at 450°C exhibited the highest photocatalytic activity under UV and simulated solar light, respectively. The crystallization of iron titanates accompanied by the formation of new active sites led the high adsorbability of TC molecules onto the surface that, in turns, stimulate the high conversion of tetracycline hydrohloride.

Keywords: photocatalysis, iron-doped titania, nitrogen-iron co-doped titania films, tetracycline hydrochloride degradation.

Плівки діоксиду титану, модифіковані азотом та залізом, як фотокаталізатори, активні під сонячним опроміненням. *О.Лінник, Н.Смірнова, І.Лагута, А.Єременко*

Плівки діоксиду титану, модифіковані залізом або азотом та залізом (непористі та мезопористі) на скляних підкладках, одержано золь-гель методом за різних умов синтезу. Досліджено фотокаталітичну деструкцію антропогенного забруднювача тетрацикліну гідрохлориду за участі синтезованих плівок. Показано, що фотокаталітична активність плівок суттєво залежить від процедури синтезу та температури прожарення. Найактивнішими фотокаталізаторами під дією УФ та видимого світла є непористі тришарові, модифіковані залізом та співмодифіковані залізом та азотом плівки діоксиду титану, прожарені при 450°C. Насичення поверхні йонами заліза та утворення нових активних центрів може бути причиною високого ступеню адсорбції молекул тетрацикліну на поверхні плівок та, відповідно, високої ефективності розкладу молекул тетрацикліну.

Пленки диоксида титана (непористые и мезопористые), модифицированные железом или ко-допированные азотом и железом, на стеклянных подложках получены золь-гель методом, различными способами синтеза. Изучена фотокаталитическая деструкция антропогенного загрязнителя тетрациклина гидрохлорида на синтезированных пленках. Показано, что фотокаталитическая активность пленок зависит от способа синтеза и температуры прокаливания. Наиболее активными фотокатализаторами под действием УФ и видимого света являются непористые трехслойные пленки диоксида титана, модифицированные железом или железом и азотом, после термообработки при 450°C. Насыщение поверхности ионами железа и образование новых активных центров может быть причиной высокой степени адсорбции тетрациклина, и, соответственно, высокой эффективности фотодеструкции молекул тетрациклина.

1. Introduction

Design and synthesis of nanocomposites based on titania presents important points in the creation of active materials as photocatalysts, catalysts, sensors and adsorbents. Titania doping leads to the change of its electronic structure, formation of new semiconductive structures and creation of new active adsorption sites. The chemical nature and content of doping agent as well as the synthesis procedure influence on the properties of materials [1–5]. The investigation of co-doped titania by metal and nonmetal ions for photocatalytic application is intensively developed for the last decade [6–9]. Among the frequently used co-doped metals' ions incorporated in titania, the most promising dopant is iron (III) ions [9–14] due to the photocatalytic response of formed materials under both UV and visible light . To avoid high energy costs for the filtration of the powder catalyst from the aqueous media, the photocatalysts in the form of thin films are the most promise and convenient materials to be applied.

Photocatalytic purification of aqueous media from anthropogenic pollutants is perspective course in the field of Ecological chemistry. Nowadays, the modern medical technology development leads to the wide usage of antibiotics for various fields of application. In 2012, the estimated usage of tetracyclines (in particular, its overuse in veterinary, animal feeding and aquaculture) was of 5954.36 and 113.2 tons in the United States and the European Commonwealth, respectively, and has tendency to rise [15]. Global antibiotic consumption in livestock was conservatively estimated as nearly two-thirds of the worldwide antibiotic production [16]. The great interest to develop effective techniques for rapid degradation of tetracyclines is still actual. Among the strategies for the improvement of degradation efficiency are intensively discussed heteroatoms or ion doping for light response improvement.

In our previous work [17, 18], the investigation of tetracycline hydrochloride (TC) degradation efficiency over titania based films synthesized by sol-gel method was reported. The most active photocatalysts are shown to be co-doped titania films. It was found that TC degradation took place on the surface of film and adsorption-desorption equilibrium of TC molecules and its intermediates on surface plays a crucial role for TC mineralization.

The aim of this work is to synthesized the iron and nitrogen co-doped titania films obtained at different synthesis conditions and to investigate their morphology, optical properties and photocatalytic activity in the degradation process of anthropogenic pollutant tetracycline hydrochloride, on their structure, optical and photocatalytic properties.

2. Experimental

The different synthesis procedures were applied to obtain the single (only iron ions) and co-doped (nitrogen and iron ions) titania films:

i) mesoporous films; ii) non-porous films; and iii) the mesoporous titania films covered by non-porous doped titania layer. For all synthesis procedure, the calculated amount of solid urea (5 mol.%) was added and the molar ratio of elements was N:Fe:Ti = 0.05:1:1.

ii) The mesoporous iron doped titania films (Fe/Ti-*mp*) and nitrogen doped iron contained titania films (N/Fe/Ti-*mp*) were obtained from the sol contained appropriate amounts of titanium tetraisopropoxide (TTIP), unhydrous $FeCl_3$, concentrated perchloric acid a three-block copolymer of polyethyleneoxide and polypropyleneoxide $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ (Pluronic P123) and acetylacetone in alcoholic medium. The three 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.

ii) Non-porous iron titanate (Fe/Ti-*np*) and nitrogen doped iron titanate films (N/Fe/Ti-*np*) films were synthesized according to procedure describe herein [10]. An alcoholic solution of urea (if needed), $FeCl_3$ and TTIP was heated at 40°C with the continuous stirring. The cleaned hot substrates were immediately used for dip-coating with the withdrawal speed of 1.5 mm/s. The obtained films coated on a glass substrate by one or three times (calcining two layers at 300°C for 20 min) were left for 24 h in humid air for hydrolysis before the calcination. An annealing of the films was performed at 450, 500 or 600°C for 20 min with heating rate at 7°C/min.

iii) The photocatalyst consists of three layers of mesoporous TiO_2 obtained according to the procedure described for the first case and calcined at 450°C with the following covering by iron ($Fe/Ti/TiO_2$) or nitrogen/iron ($N/Fe/Ti/TiO_2$) contained titanium sol. Afterwards, the sample was left for 24 h in humid air for hydrolysis and heated at 450, 500 or 600°C.

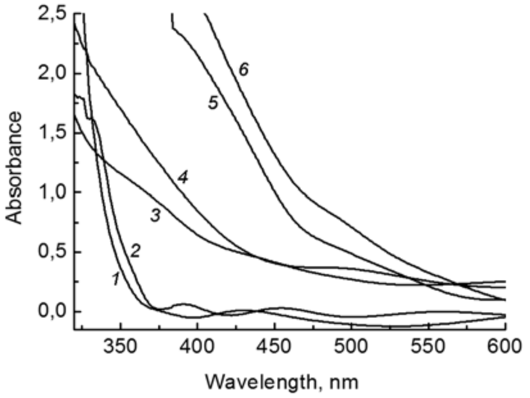


Fig. 1. Absorption spectra of the films calcined at 450°C : *1* — TiO_2, *2* — N/TiO_2, *3* — Fe/Ti-*mp*, *4* — N/Fe/Ti-*mp*, *5* — N/Fe/Ti-*np*, *6* — Fe/Ti-*np*.

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.

Energy dispersive X-rays analysis (EDS) were performed using an instrument endowed with a liquid nitrogen-cooled SiLi detector from EDAX Co. mounted inside a FEI Quanta Inspect S Scanning Electron Microscope working under up to 30 kV acceleration voltage. For general estimations the EDS errors are at 1 % for heavy elements and 2–3 % for light elements (Be–F).

The photocatalytic performance of the films under UV and simulated solar light was estimated as reported in [10]. The change in TC concentration was monitored with a Lambda 35 UV-vis spectrophotometer (PerkinElmer) every 20 min; the conversion percentage was calculated from the change in absorption intensity at λ = 357 nm.

3. Results and discussion

To investigate the effect of nitrogen and iron co-doping as well as an influence of synthesis condition (number of deposited layers, porous structure and calcinations temperature) on 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 by excellent optical quality that is confirmed by the absorption spectra presented in Fig. 1.

No shift of the absorption band edge toward the long-wavelength region is noted for N/TiO_2 film. The iron doped and iron-nitrogen co-doped samples exhibit an intense absorption in the visible part of the spectrum. It is obvious that iron ions in the titania lattice are responsible for such optical behavior due to the excitation of 3*d*-electrons of Fe(III) ions and charge transfer from Fe3*d*-orbitals to the conduction band of TiO_2 causing the orange-wine color of the samples [19]. Some iron doped films exhibited the shoulder at a wavelength of around 460–580 nm that can be attributed to the formation of the second phase as proposed in [10].

As seen from Fig. 2, the optical properties of the one-layered films is sharply differed on three layered obtained at the same conditions. It is clear that the number of applied layers and the calcination temperature affect the optical properties of the films. As reported by us [10, 20], the sequential layer to layer coating with the two layers calcination at 300°C and third layer at 450°C leads to the crystallization of iron titanates phases, as namely pseudobrookite and landauite. The existence of these phases brings to the extensive visible light absorption and allows to obtain two band gap energy (EBG)

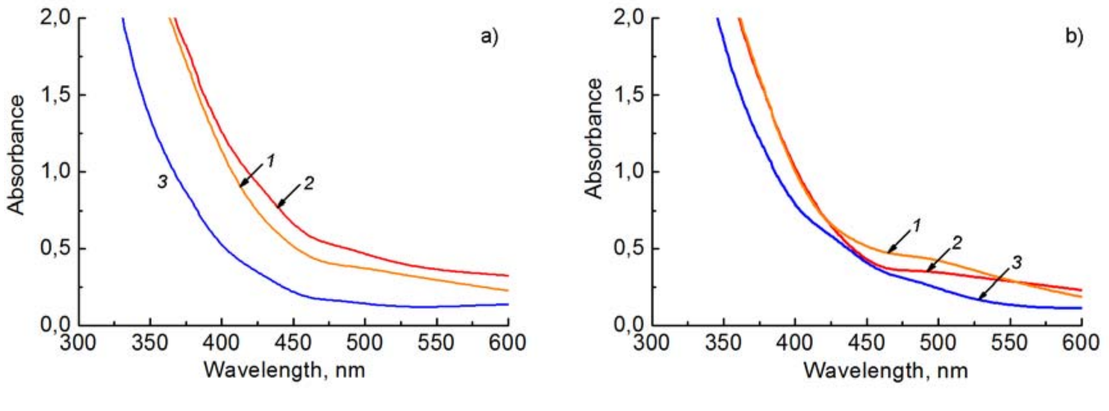


Fig. 2. Absorption spectra of one layered films: Fe/Ti-*np* (a), and N/Fe/Ti-*np* (b) obtained at 450° — *1*, 500° — *2* and 600°C — *3*.

Table 1. The band gap energy values of indirect transition for the modified TiO_2 films obtained at different conditions

The film	Number of layers	E_{BG}, eV		
		450°C	500°C	600°C
Fe/Ti-*np*	3	2.2; 2.8	2.3; 2.7	2.5; 3.0
N/Fe/Ti-*np*	3	2.1; 2.7	2.3; 2.7	2.2; 2.7
Fe/Ti-*np*	1	2.8	2.7	3.0
N/Fe/Ti-*np*	1	2.9	2.8	2.8
$Fe/Ti/TiO_2$	3+1	2.8	2.7	2.2; 3.1
$N/Fe/Ti/TiO_2$	3+1	2.7	2.9	2.6; 3.2
Fe/Ti-*mp*	3	2.6; 3.8		
N/Fe/Ti-*mp*	3	2.7		

[*] 3 + 1 layers = 3 layers of TiO_2 + 1 layer Fe/Ti or N/Fe/Ti.

values (Table 1), whereas the only one EBG is determined for all one layered films.

It must be noted the films synthesised by different procedures and heat treatment at 600°C (excepting one- and three layered N/Fe/Ti-*np* films) are characterized by the shift of absorption band (Fig. 2) to the blue part of the spectrum that can be caused by the crystallization of anatase or rutile [10] with corresponding EBG values (Table 1).

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 indirect electron transition. The band gap narrowing is a result of the incorporation of metal ions into the titania structure and/or the formation of the iron titanate phase as reported herein [10, 21, 22]. The calculated two band gap energy values for some iron contained films are an additional evident of two phase formation. As previously reported [10], non-porous iron and nitrogen-iron doped titania (Fe/Ti-np and N/Fe/Ti-*np*) films treated at 450 and 500°C were crystallized forming pseudobrookite and landauite as proven by XRD. No separate titania phase, anatase or rutile, is formed after calcination at 450 and 500°C whereas rutile is detected only for Fe/Ti-*np* after 600°C pointing on the iron titanate transformation during heating at higher temperatures. The presence of urea in the synthesis procedure not only promoted the crystallization rate of iron titanate but also stabilize them at higher temperature treatment. XRD pattern of mesoporous (Fe/Ti-*mp* and N/Fe/Ti-*mp*) films (450°C) pointed on amorphous structure with low intensive XRD peaks belong to anatase.

Photocatalytic TC degradation over the iron and nitrogen-iron co-doped films obtained at different ways and treated at various temperatures was performed (Fig. 3). The photocatalytic response is enhanced for the non-porous three layered Fe/Ti films under both UV and simulated solar light. The pronounced increase in almost three times was observed for these films treated at 450°C that can be caused by the effective charge separation after light absorption by two formed iron titanate phases [10], [20]. No significant difference in photoactivity is noted for the one layered films treated at different temperatures. In the case of $Fe/Ti/TiO_2$ treated at 450 and 500°C, the TC conversion is raised in 1.8 and 2–3 times compared to one layered film under UV and simulated solar light, respectively. The films calcined at 600°C possessed the lower activity among the tested films.

The use of urea in films' synthesis lead to the change in the photocatalytic properties of the films, as namely the activity of nitrogen-iron doped titania compared to the iron doped one is decreased under UV light while the tendency regarding to the TC degradation efficiency is remained. However, the conversion of TC molecules is increased over three layered N/Fe/Ti-*np* film (450°C) under simulated solar light (compare Fig. 3b and 3d). No increase in activity was noted for other nitrogen-iron contained films.

Quite surprisingly, no effect of iron as well as iron-nitrogen doping on the photocatalytic efficiency was observed for three layered mesoporous films under both UV and simulated solar light that can be caused by low crystallinity degree. However, both Fe/Ti-*mp* (17 and 5) and N/Fe/Ti-*mp* (26 and 16) films exhibited higher activity than

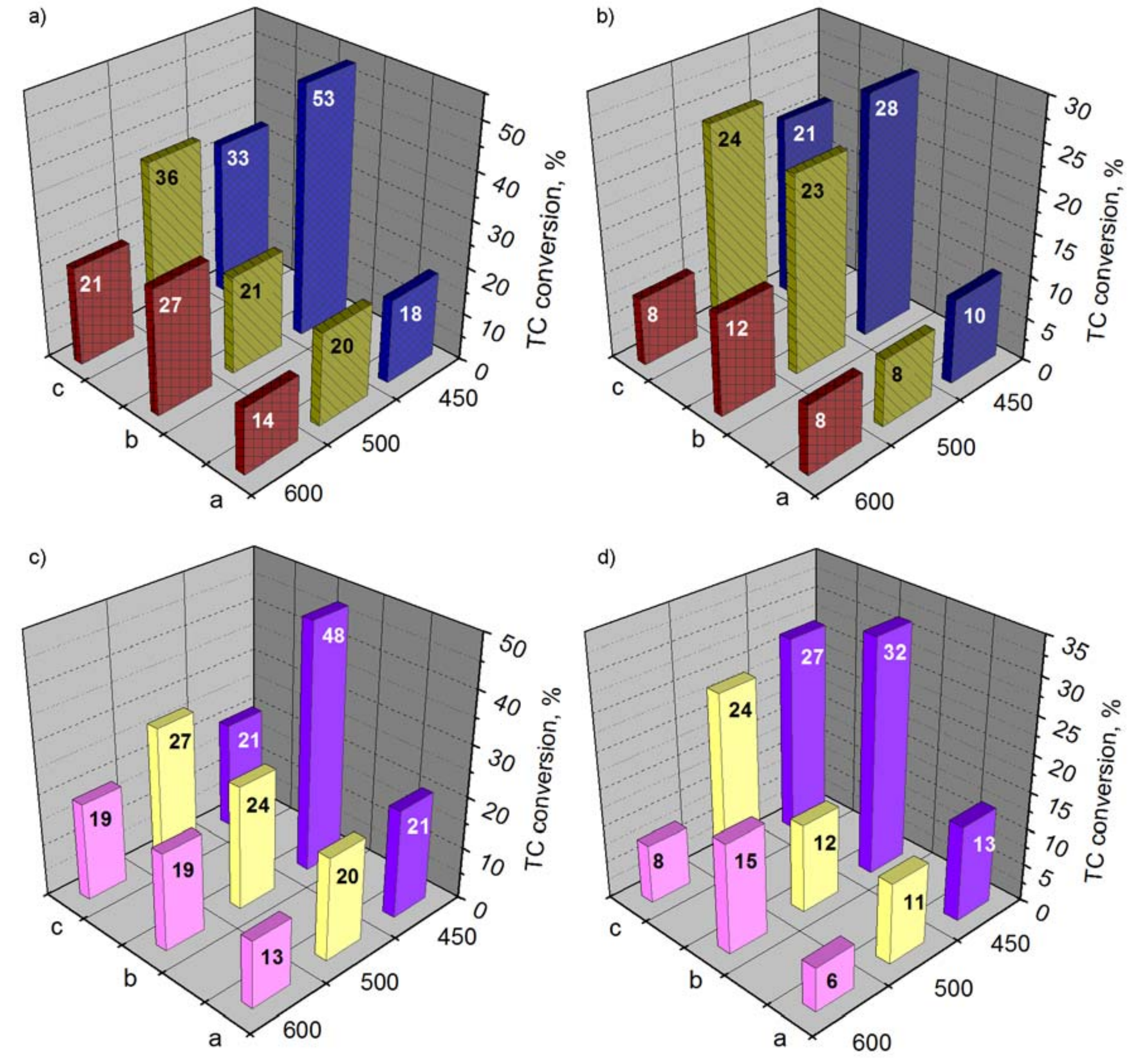


Fig. 3. Photocatalytic activity of the iron doped (a, b) and iron and nitrogen co-doped (c, d) films treated at different temperatures under both UV light (a, c) and simulated solar light (b, d): a — $(N)/Fe/Ti_{np}$ one layered; b — $(N)/Fe/Ti_{np}$ three layered; c — $(N)/Fe/Ti//TiO_2$.

pure TiO_2 (11 and 5 % of TC conversion) but less than nitrogen doped titania (30 and 16 %) under UV and simulated solar light, respectively.

Comparing the TC adsorption degree (the average value of four experimental measurements) of the films (Fig. 4), it is concluded that the adsorption capability is strongly depended on i) the treatment temperature pointing the higher the temperature, the lower the adsorption; ii) the number of Fe/Ti layers where the more the layers, the higher the adsorption; iii) co-doping by urea leads to higher adsorption. It must be noted that Fe/Ti-*mp* and N/Fe/Ti-*mp* films were able to adsorb only 5 and 7 % of TC, respectively even though the template used during synthesis expected the formation of mesoporous structure. Hence, the synthesis procedure as well as the treatment temperature influenced on the formation of the surface active sites for TC adsorption on the surface which correlated with the photocatalytic activity.

SEM images of synthesized films shown in Fig. 5 demonstrate that the morphology of non-porous and mesoporous films is different. Developed irregular structure with some cracks on the surface registered for mesoporous films synthesized via templated sol-gel procedure.

The EDS area scanning technique was used to detect the ratio of the elements in the bulk of the composites (Table 2). Almost

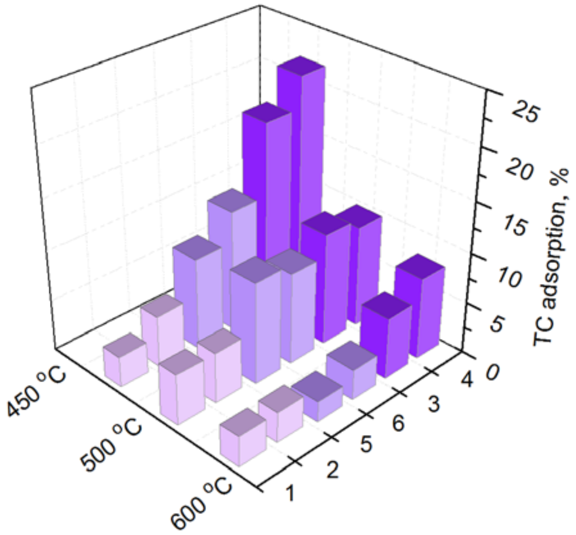


Fig. 4. TC adsorption degree onto: one layered Fe/Ti_{np} (*1*) and $N/Fe/Ti_{np}$ (*2*); three layered Fe/Ti_{np} (*3*) and $N/Fe/Ti_{np}$ (*4*); $Fe/Ti/TiO_2$ (*5*) and $N/Fe/Ti/TiO_2$ (*6*).

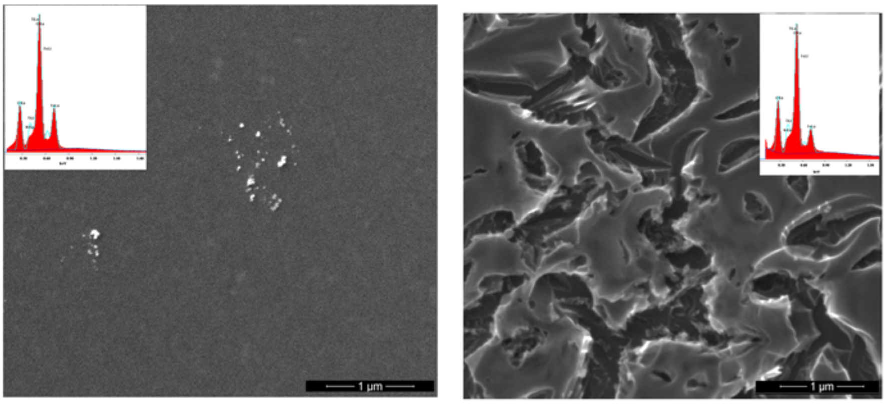
twice lower content of iron to titanium is detected for the mesoporous doped titania films. The lower ratio of oxygen to metal atoms is seemed to be connected with the unexpected low content of iron.

The ratio of metals in the bulk reaches to 1 to 1 in the case of non-porous Fe/Ti-*np* (450°C) sample. However, iron atomic percent is slightly decreased for Fe/Ti-*np* 500°C, while the enrichment of iron by 10 % is noted for nitrogen-iron doped films treated at 450 and 500°C.

As previously studied by us [10, 17], the adsorption degree of the tetracycline hydrochloride molecules onto the film surface is strongly dependent on the film composition. It was proven that the photocatalytic degradation of tetracycline hydrochloride follows onto the surface of the photocatalyst, obviously due to the presence of surface active sites. Therefore, the nonuniform distribution of iron ions in the structure of mesoporous films (possibly due to the removal of a large amount of the organic component during heat treatment) as well as low crystallinity degree are responsible for a decrease in a number of surface active sites in comparison with non-porous films.

4. Conclusions

The synthesized doped and co-doped films with the high ratio of iron to titanium were tested as the potential photocatalysts in tetracycline hydrochloride decomposition process. It is shown that the photocatalytic response of the films is sharply depended on the synthesis procedure and calcination temperature. The thrice increase in photocatalytic activity is observed for the non-porous three layered iron-doped and nitrogen-iron doped films treated at 450°C under UV and simulated solar light, respectively. It can be prompted by the formation of new adsorption sited as well as the photocatalytically active iron titanate phases. A decrease in the number of active centers of the surface of mesoporous films in comparison with non-porous led to drop of their photocatalytic activity. The presence of underlayers of mesoporous titania in the films led to 1.8 and 2–3 times increase in the TC conversion under UV and simulated solar light, respectively. The films calcined at 600°C possessed the lower activity among the tested films due to the change of the structural properties. The high adsorption of the pollutant molecules onto the surface films is one of the key points to reach the high photocatalytic degradation. The use of syn-



a) b)

Fig. 5. SEM and EDS images (insert) of three-layered N/Fe/Ti-*np* (a) and N/Fe/Ti-*mp* (b) films obtained at 450°.

Table 2. The atomic percentage and ratio of the elements of the films obtained by EDS technique

Element	Fe	Ti	O	Fe:Ti:O
Film	At. content,%			Ratio
N/$Fe_xTi_yO_z$ 450°C	20.63	19.19	38.74	1.1:1.0:2.0
$Fe_xTi_yO_z$ 450°C	18.99	19.43	39.3	1.0:1.0:2.0
N/$Fe_xTi_yO_z$ 500°C	21.61	20.95	42.23	1.0:1.0:2.0
$Fe_xTi_yO_z$ 500°C	19.64	20.91	40.86	0.9:1.0:2.0
*mp*N/$Fe_xTi_yO_z$ 450°C	18.00	29.65	52.35	0.6:1.0:1.8
mp$Fe_xTi_yO_z$ 450°C	17.85	29.08	53.07	0.6:1.0:1.8

thesis procedure for non-porous films allows to obtain the homogeneous distribution of the elements contrary to the one applied for the mesoporous structure.

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