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NONPOROUS PLATINUM DOPED TITANIA FILMS: SYNTHESIS, OPTICAL AND PHOTOCATALYTIC CHARACTERISTICS

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The simple and fast route of the synthesis of platinum ions doped titania thin films is designed where platinum(II) acetylacetonate is used as a perspective doping agent due to the possibility of platinum incorporation in the form of the different valence states. Additionally, the multilayered films showing the varied properties are obtained. The increase in Pt content as well as the number of layers leads to the higher absorbance and the band edge shift to the red part of the spectrum. The indirect electronic transition is suggested and the calculated band gap values are depended on the film compositions as well as the number of layers. The significant decrease in the band gap value of titania is noted for 0.5 % Pt/TiO₂ films. Pure titania and doped titania films contain anatase phase only with the average crystallite size near 14 nm. The conversion percentage of photocatalytic dichromate ions reduction is increased in the presence of three-layered 0.5 % Pt/TiO₂ films under both UV and visible light. The activity of three-layered films is higher compare to the single layered samples. The film contained 0.1 % Pt exhibited the similar activity to titania one.

Keywords: *platinum doped titania films, dichromate ions reduction, optical properties, band-gap narrowing, photocatalysis*

INTRODUCTION

Titania is extensively studied as a photocatalyst owing to its low-cost, non-toxicity, chemical and biological inertness, and photostability. However, the low quantum yields of visible light absorption hinder its practical application. There are some main strategies to improve the photocatalytic activity under UV and visible light utilization of TiO₂: i) coupling with different semiconductors (TiO₂/Fe₂O₃, TiO₂/CdS, TiO₂/RuO₂, iron titanates), ii) combining with noble metals TiO₂/Au, TiO₂/Ag, TiO₂/Pt, and iii) doping with metal ions and/or non-metals (TiO₂/N, TiO₂/Fe³⁺/N, TiO₂/Zr⁴⁺/N etc.) [1–7].

Noble metals such as Au, Ag and Pt are frequently used to modify the TiO₂ surfaces in the form of reduced nanoparticles [5]. There are various approaches to obtain the noble metal nanoparticles, among them photo- and thermal treatment as well as the use of the reducing agents. The photocatalytic activity of the semiconductive materials is strongly dependent on the metal–support properties. Commonly, the

investigations of the noble metal doped titania active only under UV light are extensively carried out whereas the platinum ions doped semiconductors exhibit the low activity under UV irradiation but are prospective photocatalysts under visible light [8–11].

There are numerous publications reported about the high activity of the pollutants conversion by TiO₂ under UV light, but efficient recovery of fine TiO₂ powder from treated liquid phase is still a challenge. Therefore, our investigation is focused on the fabrication of semiconductive films, that are more suitable in their practical application, and leads to the cost reduction in the environment treatment process. Thus, the scope of this investigation is to synthesize the platinum ions doped titania films and to investigate their optical, structural as well as photocatalytic properties in the dichromate ions reduction under both UV and visible light. Here, we firstly proposed the simplest and fast route of the synthesis of platinum ions doped titania in the form of the thin nanocrystalline films. It is firstly reported the application of

platinum(II) acetylacetonate as a platinum source in the films synthesis owing to some reasons: i) divalent platinum can be reduced or oxidized depending on the goal of the investigation; ii) the presence of divalent platinum in the structure of the semiconductor can act as the active trapping sites for a photogenerated charge; iii) acetylacetonate as a counter ion can be easily involved in the organic network of titania sol causing the sufficient incorporation the doping agent ions into titania lattice and iv) exclude the influence of chloride ions in photocatalytic reactions [3] contrary to the chloroplatinic acid use. Additionally, the creation of multilayered films induced by the gradual crystallization of every layer at 300 °C results in the change of optical, structural and photocatalytic properties of nanomaterials [7].

EXPERIMENTAL PART

The non-porous platinum doped titania films were synthesized by sol-gel method [3, 7]. To the preliminary cold and acidified (concentrated perchloric acid) ethanol solution, Pt(II) acetylacetonate dissolved in acetone was added. After mixing for 15 min, 5 ml of titanium isopropoxide (TTIP) was drop-wisely added under continuous stirring. The sol was ready for the dip-coating procedure after 15 min stirring. The molar ratio of the component in the resulting sol ratio to TTIP:Pt(acac)₂:(CH₃)₂CO:C₂H₅OH:HClO₄ corresponded to 1:0.001:0.8:24.1:0.06 and 1:0.005:3.2:21.3:0.06 for 0.1 % Pt/TiO₂ and 0.5 % Pt/TiO₂, respectively. The one- and 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. The first two layers for the multi-layered films were dried to 300 °C for 20 min and at 300 °C for 10 min. The films after hydrolysis in air for 10–60 min 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 (Perkin Elmer) in the wavelength range from 200 to 700 nm.

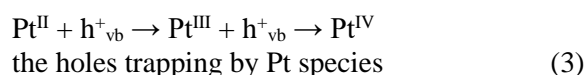
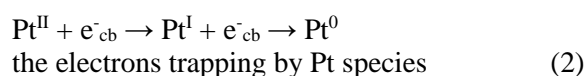
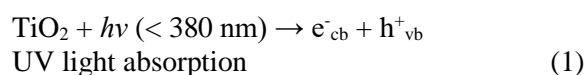
XRD patterns were performed on a DRON-4-07 using CuK_α irradiation ($\lambda = 1.5418 \text{ \AA}$). The anatase crystal size for undoped or platinum ions doped titania films is estimated from the most intensive peak at $2\theta = 25.2^\circ$ peak applying the Scherrer equation.

For XRD measurements, the film was scratched off.

Photocatalytic activity of the films was assessed via Cr(VI) ions reduction reaction. The film was immersed in 40 ml of an aqueous solution of potassium dichromate (in all experiments, the concentration of dichromate ions was $5 \times 10^{-3} \text{ M}$) and the reducing agent (disodium salt of ethylenediaminetetraacetic acid, Na₂EDTA) in the molar ratio 2:1 adjusted to $\text{pH} \geq 2$ by perchloric acid. The reaction temperature was kept constant (20 °C) during the experimental procedure. The change of Cr(VI) ions concentration was monitored with a UV-vis spectrophotometer every 20 min at $\lambda = 348 \text{ nm}$. An irradiation source of UV light was 1000 W middle-pressure mercury lamp. The distance between the lamp and the reactor was set at 124 cm. For testing the visible light sensitivity, a filter transmitting light with $\lambda > 350 \text{ nm}$ was introduced in the photocatalytic setup.

RESULTS AND DISSUSSION

The sol-gel method is the fast and low cost synthesis process and can be more potential for practical application in comparison with the traditional techniques. The non-porous platinum doped titania films were synthesized using platinum(II) acetylacetonate as the divalent platinum ions can be the trapping sites through the consecutive reduction/oxidation ways consuming considerable amounts of photogenerated electrons and holes (reaction 1–3):



It should be noted that the transformation of Pt^{IV} to Pt⁰ (and *vice versa*) is a reversible and cycled process under certain reaction conditions [12] and the oxidation state of Pt species is the most important parameter in determining the photocatalytic activity of Pt/TiO₂ samples [8]. Therefore, to avoid any other trapping species in the structure of the films (for example Cl[−] ions [3]), acetylacetonate as the counter ions was

chosen in the synthesis procedure of Pt/TiO₂ films.

To investigate the influence of platinum content and the thickness of the film on the optical properties, the absorption spectra and band-gap values were obtained. The optical absorbance of the films was determined by UV-vis spectroscopy and the band gap energies (E_g) were calculated from the dependence of $\alpha \cdot h\nu^{1/2}$ vs E for indirect and $\alpha \cdot h\nu$ vs E for direct electronic transitions. As clearly seen (Fig. 1), the introduction of platinum ions in the concentration of 0.1 and 0.5 mol. % to titania sol leads to the change in the optical properties. No

significant change in the position of the band edge is observed in the case of 0.1 % Pt/TiO₂ comparing to TiO₂ for both one- (1L) and three-layered (3L) films. On the other hand, the increase in Pt content as well as the number of layer led to the higher absorbance and the band edge shift to the red part of the spectrum. It has to be emphasized that the absorption efficiency in the long-wavelength region is raised for three-layered films for both platinum-containing films. It points on the increase of platinum ions in the film structure and the possibility to absorb the light with lower energy.

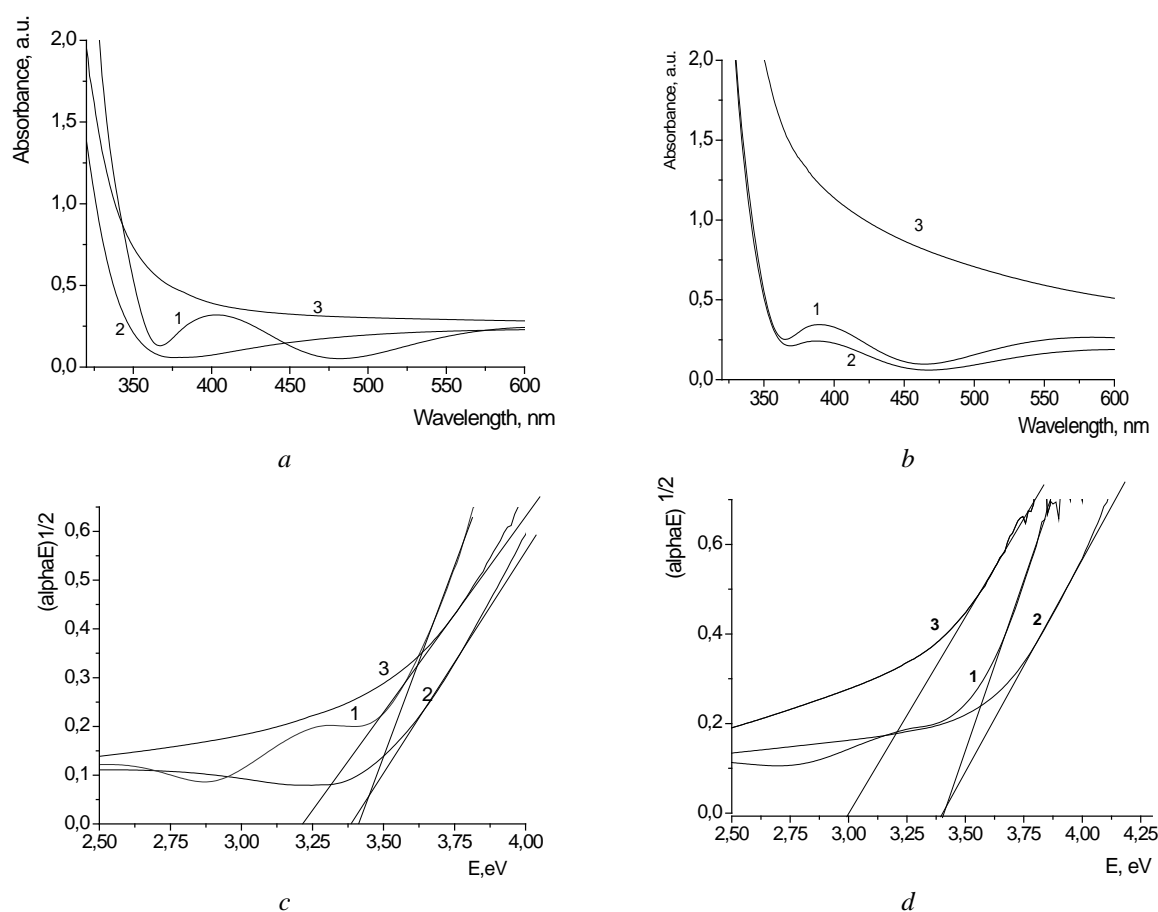


Fig. 1. Absorption spectra (a, b) and $\alpha h\nu^{1/2}$ vs E (c, d) of one- (a, c) and three- (b, d) layered films treated at 450 °C: 1 – TiO₂, 2 – 0.1 % Pt/TiO₂, 3 – 0.5 % Pt/TiO₂

The indirect electronic transition is predominant over the direct one as the best extrapolation of the straight line is noted for the dependence of $\alpha \cdot h\nu^{1/2}$ vs E (eV) and their calculated band gap values are approached to the found value for anatase 3.2 eV (Fig. 1 c, d and Table). The increased E_g values for titania films

by 0.2 eV can be explained by the anatase particle size decrease [13]. No change in the E_g values is observed for TiO₂ and 0.1 % Pt/TiO₂ films suggesting the extremely low content of platinum ions and their homogeneous distribution over titania lattice. However, the increase in Pt content to 0.5 % leads to the band

gap narrowing: E_g values are 3.2 and 3.0 eV for 1L and 3L films, respectively. It is obviously that the presence of 0.5 % platinum ions leads to the decrease in the band gap value of titania as a result of their incorporation into titania lattice and this value depends on the number of film layers due to the increase in the platinum loading.

XRD analysis is used to investigate the changes in the phase structure and crystallite size of the bare titania and Pt doped one (Fig. 2). Pure titania films contain anatase phase characterizing by the diffraction peaks at about 25.4° (101), 37.9° (004), 48.1° (200), 53.9° (105), 54.9° (211), 62.6° (204), 68.9° (213), 70.1° (220) and 75.7° (215) (JCPDS 21-1272). In the case of Pt ions

loaded titania films, all the diffraction peaks belonging to anatase are observed. An addition peak at 31.8° appeared in XRD spectrum of 0.1 % Pt/TiO₂ (it is not observed for 0.5 % Pt/TiO₂) is not matched with PtO, PtO₂ or other crystalline forms of titania. No other diffraction peaks belonging to Pt species are detected as a result of the low content of Pt loading or Pt ions incorporation into titania matrix [14]. To understand which types of platinum-containing species in titania (Pt⁰, Pt²⁺ and/or Pt⁴⁺) are formed after annealing in the samples synthesized by us, the additional investigations of the films composition are required. The average anatase crystallite size for all samples is about 14 nm.

Table. The band gap energy values (eV) of semiconducting systems for direct (α^2) and indirect ($\alpha^{1/2}$) electronic transition

x % Pt in TiO ₂	0 %	0.1 %	0.5 %	0 %	0.1 %	0.5 %
	one – layered film			three – layered film		
$\alpha^{1/2}$	3.4	3.4	3.2	3.4	3.4	3.0
α^2	3.7	3.7	3.5	3.8	3.9	3.8

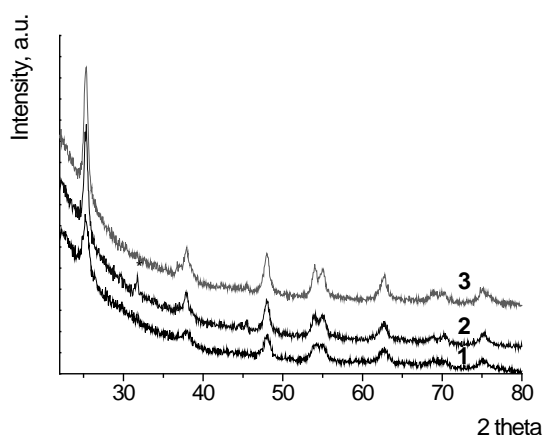


Fig. 2. XRD patterns of TiO₂ (1), 0.1 % Pt/TiO₂ (2) and 0.5 % Pt/TiO₂ (3)

To the best of our knowledge, there is no reported investigation related to the dichromate ions photocatalytic reduction over platinum ions doped titania films. The dichromate ions concentrations vs the irradiation time in the presence of platinum ions doped titania films under UV and visible light are shown in Fig. 3. Among one-layered films, the highest activity is observed for pure titania film under UV light. It can be caused by the increased recombination

rate of the photogenerated charges during UV illumination over platinum doped titania films.

Under visible irradiation, the activity of one-layered doped films is also decreased comparing to undoped one. The visible light reduction of Cr(VI) ions in the presence of undoped titania (near 10 %) can be explained by the catalytic reduction process [15].

Considering the photocatalytic activity of three-layered films, the conversion percentage of dichromate ions reduction is increased in the

presence of 0.5 % Pt/TiO₂ films. The film contained 0.1 % Pt exhibited the similar activity to titania one. It should be noted that the activity of three-layered film containing 0.1 % Pt ions is higher than that of one-layered one under UV and visible light. It reflects the analysis of optical properties mentioned above where the more intensive absorption in the visible region of the spectrum was observed for three-layered film suggesting its higher degree absorption of the light of lower energy. The highest efficiency was noted for 0.5 % Pt/TiO₂ among all tested films under visible light. It is clear that the conversion percentage of photocatalytic reduction in the

presence of doped films is still low under visible light. It can be explained by i) insufficient separation of the photogenerated charges or ii) an increased recombination rate between the photoformed electron and hole in the proposed composites.

The concurrent intensity decrease at 350 nm and its increase at 530–600 nm related to the formation of non-toxic Cr(III) ions are observed in the presence of 0.5 % Pt/TiO₂ film under UV light (Fig. 4). It is evident that the toxic dichromate ions are reduced to non-toxic Cr(III) ions over the tested films.

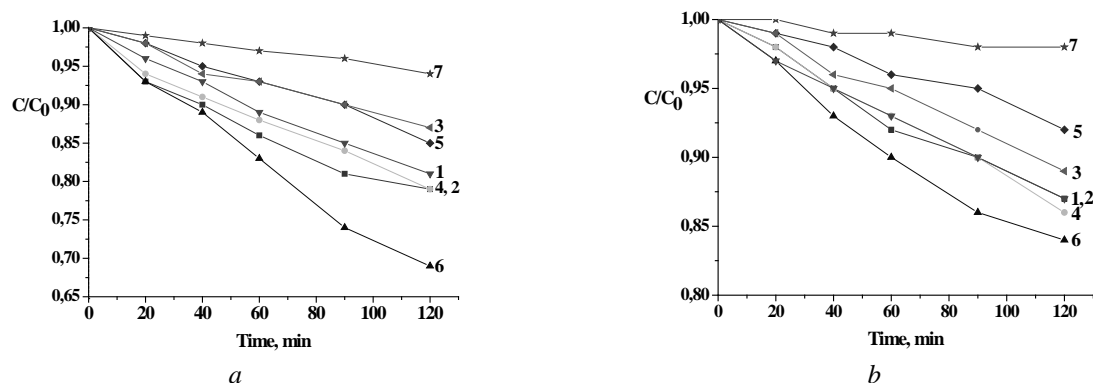


Fig. 3. The dependence of C/C_0 on the irradiation time in the presence of TiO₂ (1L – 1, 3L – 2), 0.1 % Pt/TiO₂ (1L – 3, 3L – 4), 0.5 % Pt/TiO₂ (1L – 5, 3L – 6) and blank experiment (7) under UV (a) and visible (b) irradiation

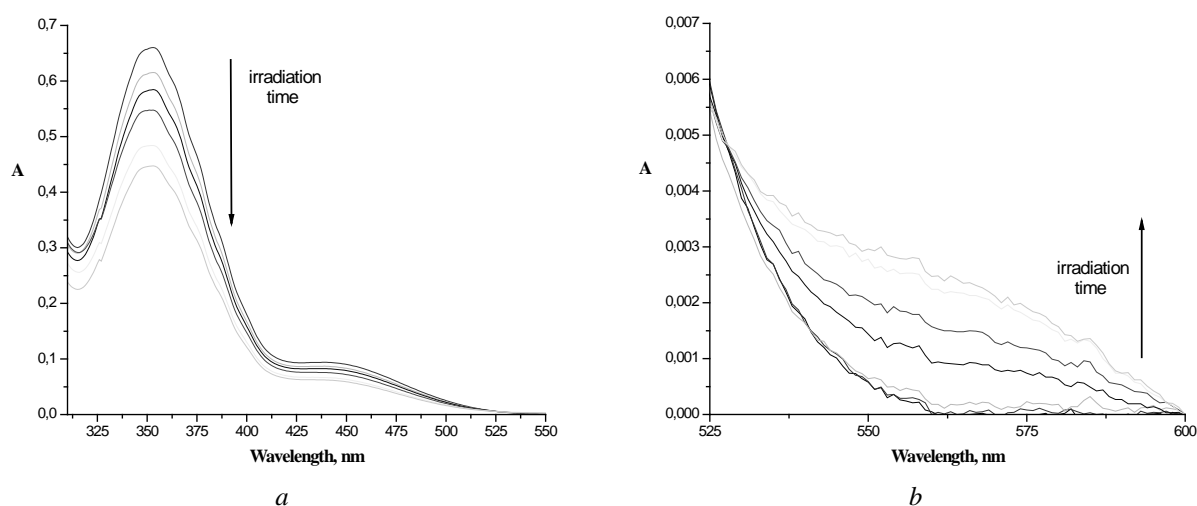


Fig. 4. Evolution of the absorption spectra of dichromate ions reduction (a) and accumulation of Cr(III) ions (b) in the presence of 0.5 % Pt/TiO₂ film during UV irradiation

Overall, the limited photo-excitation of electrons in the intragap localized states, the low

mobility of photogenerated holes [16], the high recombination rate due to the creation of oxygen

vacancies by doping [17] are the reasons of the low photocatalytic efficiency of the semiconductive composites. Thus, the photoreactivity of doped TiO_2 appeared to be a complex function of the doping agent concentration, the energy level of doping agent within the TiO_2 lattice, their d -electronic configurations, the ionic radius of doped metal, the distribution of doping agent, the electron donor concentrations and light intensity.

CONCLUSIONS

The synthesis conditions of non-porous platinum doped titania films using platinum(II) acetylacetonate are designed. The films with the

different contents of doping agent and thickness (one- and three-layered films) have been synthesized. The absorption spectra pointed on the influence of the film compositions as well as the thickness on the optical properties of the samples. The obtained band-gap values showed that the incorporation of 0.5 mol. % platinum ions in the TiO_2 structure led to its band gap narrowing. The sharp narrowing of the band gap energy to 3.0 eV is observed for the three-layered 0.5 % Pt/ TiO_2 . The efficiency of toxic dichromate ions reduction is increased with the platinum ions content growth in the semiconductive structure.

Непористі плівки діоксиду титану, модифікованого платиною: синтез, оптичні та фотокаталітичні характеристики

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Розроблено умови синтезу непористих TiO_2 плівок, допованих йонами платини, з використанням платини(II) ацетилацетонату. Синтезовано зразки з різним вмістом допанту і різною товщиною плівки. Спектри поглинання плівок вказують на вплив складу плівки та її товщини на оптичні властивості систем. Інкорпорування TiO_2 йонами платини приводить до звуження ширини забороненої зони напівпровідника, як свідчать дані, розраховані з оптичних спектрів. Найменше значення ширини забороненої зони (3.0 eV) і найвища ефективність у реакції відновлення дихромат йонів спостерігались для тришарової плівки 0.5 % Pt/ TiO_2 .

Ключові слова: плівки діоксиду титану, допованого платиною, відновлення дихромат йонів, оптичні властивості, звуження ширини забороненої зони, фотокаталіз

Непористые пленки диоксида титана, модифицированные платиной: синтез, оптические и фотокаталитические характеристики

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Разработаны условия синтеза непористых TiO_2 пленок, допированных ионами платины с использованием платины(II) ацетилацетоната. Синтезированы образцы с разным составом допанта и разной толщиной пленки. Спектры поглощения пленок указывают на влияние состава и толщины пленки на оптические свойства систем. Инкорпорирование TiO_2 ионами платины приводит к сужению ширины запрещенной зоны полупроводника, как свидетельствуют данные,

рассчитанные из оптических спектров. Наименьшее значение ширины запрещенной зоны (3.0 eV) и наивысшая эффективность наблюдались для образца 0.5 % Pt/TiO₂.

Ключевые слова: пленки диоксида титана, допированного платиной, восстановление дихромат ионов, оптические свойства, сужение ширины запрещенной зоны, фотокатализ

REFERENCES

1. Fujishima A., Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*. 1972. **238**: 37.
2. Serpone N, Lawless D, Disdier J, Herrmann J.M. Spectroscopic, photoconductivity and photocatalytic studies of TiO₂ colloids—naked and with the lattice doped with Cr³⁺, Fe³⁺, and V⁵⁺ cations. *Langmuir*. 1994. **10**(3): 643.
3. Linnik O., Kisch H. On the mechanism of nitrogen fixation at nanostructured iron titanate films. *Photochem. Photobiol. Sci.* 2006. **5**: 938.
4. Linnik O., Kisch H. Dinitrogen photofixation at ruthenium-modified titania films. *Mendeleev Communications*. 2008. **18**(1): 10.
5. Eremenko A., Smirnova N., Gnatiuk Yu, Linnik O., Vityuk N., Mukha Yu., Korduban A. *Photoelectrochemical and photocatalytic properties of mesoporous TiO₂ films modified with silver and gold nanoparticles. Silver and Gold Nanoparticles on Sol-Gel TiO₂, ZrO₂, SiO₂ Surfaces: Optical Spectra, Photocatalytic Activity, Bactericide Properties*. (Chapter in Book 3: Composite Materials, INTECH, 2011).
6. Smirnova N., Gnatiuk Yu., Vityuk N., Linnik O., Eremenko A., Vorobets V., Kolbasov G. Nanosized TiO₂-based mixed oxide films: sol-gel synthesis, structure, electrochemical characteristics and photocatalytic activity. *International Journal of Materials Engineering*. 2013. **3**(6): 124.
7. Linnik O., Chorna N., Smirnova N. Nonporous iron titanate thin films doped with nitrogen: optical, structural and photocatalytic properties. *Nanoscale Research Letters*. 2017. **12**: 249.
8. Lee J., Choi W. Photocatalytic Reactivity of Surface Platinized TiO₂: Substrate Specificity and the Effect of Pt Oxidation State. *J. Phys. Chem. B*. 2005. **109**(15): 7399.
9. Choi J., Park H., Hoffmann M. Combinatorial doping of TiO₂ with Pt, Cr, V, and Ni to achieve enhanced photocatalytic activity with visible light irradiation. *J. Mater. Res.* 2010. **25**(1): 149.
10. Zhao W., Sun Y., Castellano F.N. Visible-light induced water detoxification catalyzed by PtII dye sensitized titania. *J. Am. Chem. Soc.* 2008. **130**(38): 12566.
11. Ishibai Y., Sato J., Nishikawa T., Miyagishi S. Synthesis of visible-light active TiO₂ photocatalyst with Pt-modification: Role of TiO₂ substrate for high photocatalytic activity. *Appl. Catal. B*. 2008. **79**(2): 117.
12. Subramanian V., Wolf E.E., Kamat P.V. Influence of metal/metal ion concentration on the photocatalytic activity of TiO₂-Au composite nanoparticles. *Langmuir*. 2003. **19**(2): 469.
13. Fujishima A., Rao T.N., Tryk D.A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C*. 2000. **1**(1): 1.
14. Kim S., Hwang S.J., Choi W. Visible light active platinum-ion-doped TiO₂ photocatalyst. *J. Phys. Chem. B*. 2005. **109**(51): 24260.
15. Yang C., Meldon J.H., Lee B., Yi H. Investigation on the catalytic reduction kinetics of hexavalentchromium by viral-templated palladium nanocatalysts. *Catal. Today*. 2014. **233**:108.
16. Hashimoto K., Irie H., Fujishima A. TiO₂ Photocatalysis: A historical overview and future prospects. *Jpn. J. Appl. Phys.* 2005. **44**(12): 8269.
17. Katoh R., Furube A., Yamanaka K., Morikawa T. Charge separation and trapping in N-doped TiO₂ photocatalysts: a time-resolved microwave conductivity study. *J. Phys. Chem. Lett.* 2010. **1**(22): 3261.

Received 29.05.2017, accepted 30.10.2017