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SYNTHESIS AND CHARACTERIZATION OF NITROGEN AND ZIRCONIUM IONS DOPED TiO₂ FILMS FOR PHOTOCATALYTIC APPLICATION

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Codoped by nitrogen and zirconium ions titania thin films have been obtained by sol-gel and pulse laser deposition (PLD) methods to investigate the influence of zirconium ions as well as the synthesis procedure on the efficiency of nitrogen incorporation into semiconductive lattice that, in turns, effected on the film activity under ultraviolet and visible light. The composition of the films and the synthesis methods changed the optical properties of the materials as namely almost no effect of both doping agents on the band gap energy value was noted for the films obtained by pulse laser deposition technique, while its sharp narrowing was observed for nitrogen doped titania sol-gel sample. Additionally, the high absorption in the visible part of the spectra with the different maxima were registered for sol-gel films. Substitutional and interstitial nitrogen incorporation occurred in the case of sol-gel titania doped by both doping agents and only nitrogen, respectively. However, both types of nitrogen atoms were detected by X-ray photoelectron spectroscopy measurements for the laser deposited films and the relative intensity of its state was dependent whether single or double doping agents was used. Incorporation of each doping agent in titania matrix positively influenced on the photocatalytic activity of the sol-gel films under both ultraviolet and visible light. In the case of pulse laser deposited films, the presence of double doping agent stimulated the activity under UV light and the doping only by nitrogen led to the increase of photoactivity in visible light.

Keywords: nitrogen doped titania, zirconium ions, sol-gel method, PLD, photocatalysis

INTRODUCTION

Titania application is encircled as a photocatalyst in heterogeneous catalysis, for the production of hydrogen and electric energy in solar cells, as white pigments for cosmetic and paint industries, as a gas sensor, as an anticorrosive coating, as an optical coating, in electrical devices, in ceramics and others. The thin TiO₂ films are extremely used as antireflective coatings, dielectric mirrors for lasers, metal mirrors with enhanced reflection, and filters. Despite high band gap energy of titania (about 3 eV), it is the most preferred photocatalyst and photoelectrode due to its high photo-corrosion resistance in aqueous media, chemical stability, low cost and non-toxicity. Given its indirect band gap transition, the anatase in comparison to rutile and brookite phases of TiO₂ is the most preferred phase for photoassisted applications. Titania is a semiconductive material with band edges suitable for water oxidation reaction [1]. Several efforts are made to reduce titania band gap energy leading to its absorption of a larger portion of sunlight that reaches the surface of the earth. Non-metal doping agents (nitrogen, carbon, fluor, sulfur i.e.)

embedded in a semiconductor structure are responsible for visible light absorption by nanomaterials based on TiO₂. Another approach to change the physical, optical, structural and photocatalytic properties of titania includes an employment of *d*-block metal ions (zinc, zirconium, iron, chromium, nickel, vanadium or copper). Modifications of TiO₂ with such metals have extended the spectral response of TiO₂ into the UV and visible region also improving photocatalytic activity [2, 3]. However, the presence of transition metal ions in the semiconductive structure may also act as the recombination sites for photoformed an electron and a hole leading to the decrease in the quantum efficiency.

A number of key questions are still opened to summarize the properties and behavior of N-TiO₂: i) the chemical nature of nitrogen atom (substitutional N_s or interstitial N_i); ii) the electronic structure of the doped material and its influence on the change of the optical gap (band gap narrowing, impurity energy levels, oxygen vacancy); iii) the role of the nitrogen species in photocatalytic process.

There are three different main opinions regarding modification mechanism of TiO₂ doped with nonmetals. The first one is band gap narrowing: Asashi *et al.* [4] found that N2*p* state hybrids with O2*p* states in doped anatase. It caused their energies to be very close, and thus the band gap of N-TiO₂ was narrowed and capable to absorb visible light (Fig. 1 *a*). The second one is the formation of impurity energy levels proposed by Irie *et al.* [5]. It is considered that oxygen sites in titania matrix substituted by nitrogen atoms form the isolated impurity energy levels above the

valence band of semiconductor where irradiation with UV light excites electrons from both the VB and the impurity energy levels. However, the illumination with visible light only excites electrons from the impurity energy level (Fig. 1 *b*). The third approach is the formation of oxygen vacancies proposed by Serpone *et al.* [6] where the commonality in the doped titania rests with formation of oxygen vacancies and the advent of color centers (e.g. F, F⁺, F⁺⁺, and Ti³⁺) that absorb the visible light radiation (Fig. 1 *c*).

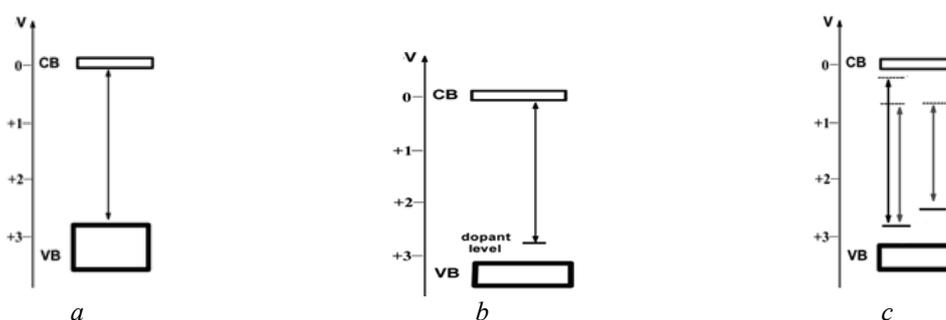


Fig. 1. Schematic representation of different electronic structure of doped titania



Fig. 2. Models for incorporated nitrogen: *a* – substitutional nitrogen (N_s) and *b* – interstitial nitrogen (N_i)

Table 1. Nitrogen bond types and their binding energy values taken from literature [7–14]

Bond type	Binding energy, eV
N1 <i>s</i>	
N _s	~396
N _i	396–397
NO, NO ₂	398–400
NH _x , N-C	400–403
Ti2 <i>p</i> _{3/2}	
Ti-N	456, 457
Ti-O	458–459

The nature of the nitrogen species responsible for the visible-light activity of nitrogen-modified titania is still under debate. The binding energy values for nitrogen and titanium species in the semiconductive matrix are summarized in Table 1. Most conclusions are based on the results of the XPS measurement of N1*s* binding energy values. Values of near 396 eV and higher to 397 eV are assigned to the formation of the bond corresponded to N-Ti-N bonds [7, 8] and O-Ti-N [9, 10], respectively. Higher energies of 400–401, 402–403, and even 407–408 eV were proposed to correspond

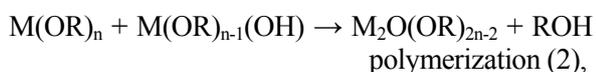
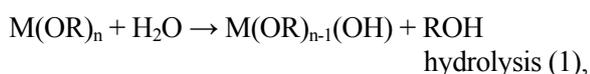
to N-N, N-O, or N-C groups [9, 11], chemisorbed N₂ [12] or NO_x (x < 2) and NO₂ groups [13], respectively.

In overall, there is no definite opinion in the literature about the crucial points connected with the electronic structure of the doped semiconductor, the synthesis of high photocatalytic active materials under visible light, the chemical state of incorporated nitrogen in the metal oxide structure. The aim of this paper is to clarify the role of the presence of single and double doping agent in titania structure in the optical, electronic and photocatalytic characteristics of the materials; to estimate the efficiency of nitrogen incorporation in the pure and Zr ions doped TiO₂ films obtained by sol-gel and PLD methods and the influence of synthesis conditions on the nature of incorporated nitrogen species; as well as to compare their photocatalytic properties.

SOL-GEL AND PULSE LASER DEPOSITION SYNTHESIS OF MODIFIED TITANIA FILMS

Nitrogen-doped titania can be obtained by the following methods: i) sputtering and implantation techniques, ii) calcination of undoped material under N-containing atmosphere generated by nitrogen compounds like ammonia, amines, or urea, and iii) by sol-gel methods [14–16].

In a typical sol-gel process, inorganic metal salts or metal organic compounds (metal alkoxides) are used in the hydrolysis and polymerization reactions followed by sol formation. Complete polymerization and loss of solvent lead to the transition from the liquid sol into a solid gel phase (reactions 1–3).



where *M* – Ti and Zr, *R* – organic species.

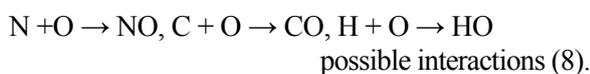
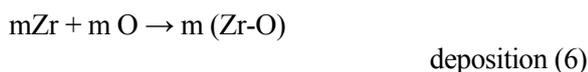
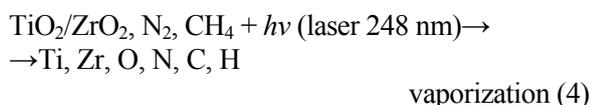
Thin films can be produced on a substrate by spin-coating or dip-coating. A wet gel will be formed with the following transformation to a dense ceramic. In the template method, organic templates are used for organizing network forming metal oxide species in nonaqueous solutions. The most commonly used organic templates are

amphiphilic poly(alkylene oxide) block copolymers, such as Pluronic P-123 HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H.

Mesoporous pure and doped TiO₂ thin films synthesized with the sol-gel technique using titanium tetraisopropoxide (TTIP) as the titania source and a three-block copolymer of polyethylene oxide and polypropylene oxide (PEO)₂₀(PPO)₇₀(PEO)₂₀ (PluronicP123 or P123) in alcoholic medium are reported in this paper. Concentrated HClO₄ and acetylacetone (AcAc) were added to the precursor as stabilizers. The molar ratio of the components in the sol for films deposition was as following: TTIP : P123 : AcAc : H₂O : C₂H₅OH: HClO₄ = 1 : 0.05 : 0.5 : 1 : 40 : 1. A solution of urea in ethanol and/or zirconium propoxide (Zr(OCH₂CH₂CH₃)₄) were added under vigorous stirring to obtain the sol contained 5 mol. % both doping agents. The one-layered films were deposited by dip-coating procedure at a withdrawal rate 1.5 mm/s. The films were left for 1 hour for hydrolysis and heated in air at 450 °C for 1 hour with the heating rate of 3 °C/min [16]. The key point during the N doped material synthesis is the temperature and rate of calcination. The heating has to be performed at lower temperature than 500 °C and at certain rate to prevent not only nitrogen release from the gel but also crystallization of anatase to rutile [17].

The pulsed laser deposition method of the film synthesis allows an easy doping or multilayer structures formation, a high purity compound formation, a fine control of thickness, the use of different types of the substrates, the various types of thin films (complex oxides, high-temperature superconducting, protective or ultrahard coatings, polymer or organic thin films) [18]. PLD is a physical vapour deposition process based on the vaporization of condensed matter by means of photons [19, 20]. A high power pulsed laser beam is focused to strike a target of the desired composition. Material is then vaporized and deposited as a thin film on a substrate facing the target. This process can occur in ultrahigh vacuum or in the presence of a background gas. If the laser fluence exceeds a specific threshold, each tiny quantity of ablated material by a laser pulse is directed forward the deposition substrate, where the growing film is formed by recondensation [20]. In the most common set-up geometry, the collector is placed parallel to the target, at a certain distance and the laser pulses hit the target under 45 °. The target is normally rotated in order to get uniform

ablation of its surface, avoiding cracking, and thus obtaining a homogenous film. The obtained film may also be heated if a high degree of crystallinity:



PLD experiments were performed using a KrF* laser source (COMPexPro 205 Coherent, $\tau\text{FWHM} \leq 25 \text{ ns}$). Pure TiO_2 or 5 wt. % $\text{ZrO}_2/\text{TiO}_2$ targets were laser ablated to grow coatings on glass plates. The films were synthesized at substrate temperatures of 450°C . The samples were deposited at 100 Pa pressure in the atmosphere of N_2 and CH_4 with 5:1 ratio. The composition of the gas atmosphere was chosen to approach the synthesis conditions for both types of the films. It is known that the carbon species are still present in the structure of sol-gel films [21] after heating at 450°C , the presence of methane in dinitrogen in the ratio 1 to 5 was proposed.

OPTICAL PROPERTIES OF THE FILMS

The optical properties of the films were checked by means of the absorption spectra and calculated band gap energy values. It is clear that the optical properties of the films obtained by both methods are different. The PLD films exhibited the continues absorbance in the visible part of the spectrum. It must be noted that the blue shift of band edge of the curve for N/Zr/TiO_2 film has occurred compared to N/TiO_2 one (Fig. 3). Among sol-gel titania films doped with different amount of urea, the film contained 5 % of its showed the highest absorption intensity in the visible region and significant shift of absorption band edge to the longer wavelengths as well as the photocatalytic activity, this composition was chosen for the further investigation [16]. The UV-visible absorption measurements (Fig. 3) indicates that the

sol-gel films noticeably absorb the visible light and have high absorbance, whereas the absorbance of PLD samples is much lower in this part of spectrum. The peaks with maximum at about 400 and 450 nm are observed for the sol-gel N/Zr/TiO_2 and N/TiO_2 films (Fig. 3, curve 1 and 2), respectively. The difference in the position of these peaks could be attributed to the formation of the different nitrogen-containing species in the structure of the films. Thus, the presence of zirconium ions leads to the sharp change in optical properties of the photocatalysts.

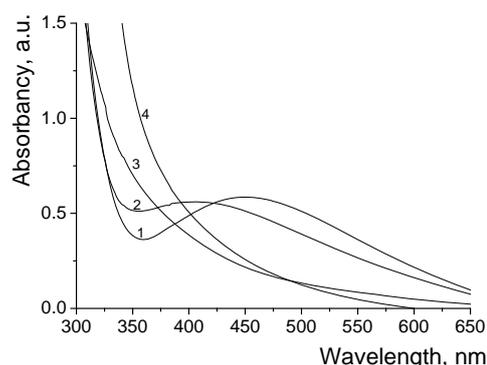


Fig. 3. Absorption spectra of sol-gel N/TiO_2 (1), N/Zr/TiO_2 (2) and PLD N/Zr/TiO_2 (3), N/TiO_2 (4) methods

The values of band gap energy (E_{bg}) calculated by extrapolating the linear parts of the $(\alpha h\nu)^{1/2}$ vs $f(h\nu)$ curves assuming an indirect electronic transition are presented in Fig. 4 and Table 2. The slight E_{bg} increase of Zr/TiO_2 compared to TiO_2 samples is explained by the presence of zirconium ions as a result of mutual Ti-O-Zr bond formation [22] or the decrease of the crystalline particle size, i.e. the quantum-size effect [23].

Table 2. The band gap energy values of TiO_2 doped films synthesized by both methods

TiO_2 doped film	E_{bg} , eV	
	PLD [21]	Sol-gel [16]
TiO_2	3.3	3.6
Zr/TiO_2	3.4	3.7
N/TiO_2	3.3	3.3
N/Zr/TiO_2	3.3	3.7

When titania is doped by nitrogen, no significant change in E_{bg} is observed for PLD films while its decrease to 3.3 eV is noted for sol-gel sample. However, the increase in E_{bg} value of sol-gel N/Zr/TiO_2 pointed on the effect of zirconium ions. Hence, the electronic structure of

the photocatalyst affects the optical characteristics of the films which, in turns, depend on the

composition and the synthesis ways of the materials.

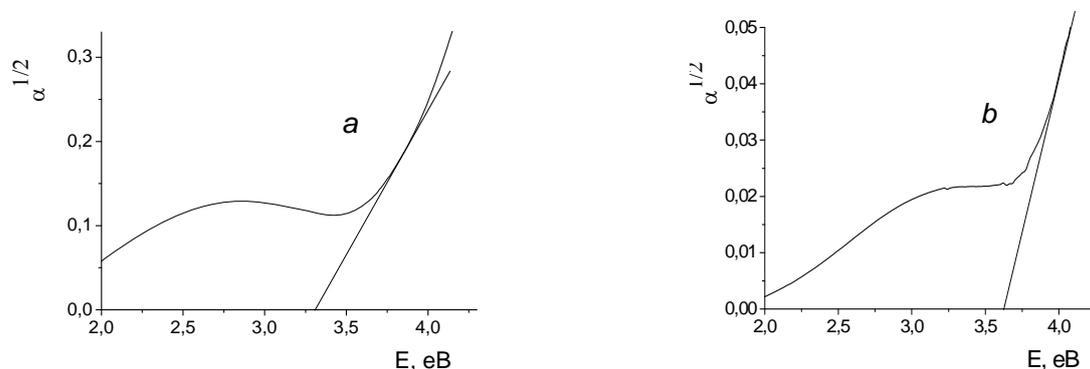


Fig. 4. The variation of $\alpha^{1/2}$ with excitation energy for sol-gel N/TiO₂ (a) and N/Zr/TiO₂ (b) films

Considering the dependence of one second absorption coefficients vs excitation energy, the absorption thresholds at low excitation energy could be taken into account with the E_{bg} values equal to 1.5 and 2.0 eV for N/TiO₂ and N/Zr/TiO₂, respectively. Similar results are reported herein [24] where the three absorption thresholds in the $\alpha^{1/2}$ vs $h\nu$ curves were as signed to three possible compositions of modified titania films. The doping of nitrogen and carbon responsible for the band gap energies lower than 2 eV was deduced. Analyzing the XPS N1s binding energy (see below) and the different positions of the absorption maximum for sol-gel N/TiO₂ and N/Zr/TiO₂ films, it could be concluded that the optical properties of the materials are dependent on the type of incorporated nitrogen.

ELECTRONIC STRUCTURES

XPS is widely used to clarify the chemical state of elements and their surface ratio. There is no definite opinion about the XPS measurements of N1s binding energy where the values of 396–397 eV are assigned to the N-Ti-N [8] or O-Ti-N bonds [9]. The formation of N-N or N-C or N-O groups or chemisorbed dinitrogen is suggested at higher energies of 400–403 eV [9, 11, 25]. Nitrogen 1s binding energies of 399.2 and 400.5 eV are measured for a mixture of solid urea and TiO₂ powder calcined at 400 °C corresponded to carbon nitrides (399–400 eV, C=N-C) and similar graphite-like phases (400.6 eV, N-C_{sp2}), and of polycyanogen (399.0, 400.5 eV (-C=N-x)) [26].

Ti2p_{3/2} line of all sol-gel samples contains a single peak in the range of 459.2–459.4 eV confirming the presence of Ti^(IV)O₂ [27]. The XPS

O1s peak in the range of 530–531 eV corresponds to O²⁻ ions of crystalline oxide matrix. The presence of C-C (elemental carbon) bonds in the sol-gel structure is confirmed by E_{BE} at 283.9 eV [38]. Zr3d_{5/2} line with E_{BE} at 182.3 eV is attributed to the Zr⁴⁺ ions surrounded by O²⁻ ions [28]. The N1s peak with the maximum at 396.0 eV (Table 3) indicated the formation of substitutional nitrogen as namely Ti-N bonds in N/Zr/TiO₂ while the N1s peak of N/TiO₂ films at 400.6 eV could be related to the N-N or N-C, N-O or even chemisorbed dinitrogen species formation in TiO₂ matrix [11, 25]. Note that N1s binding energies of 399.1 and 400.5 eV measured for modified by urea commercially available TiO₂ powder were assigned to carbon nitrides (399–400 eV, C=N-C), graphite-like phases (400.6 eV, N-C_{sp2}) and to polycyanogen (399.0, 400.5 eV (-C=N-x)) [29]. It can be concluded that zirconium ions have an influence on the formation of rather substitutional nitrogen incorporated in the oxide matrix.

Table 3. XPS binding energy values and their relative intensities of sol-gel films [16]

Element	N/TiO ₂		N/Zr/TiO ₂	
	E _{BE} , eV	I, %	E _{BE} , eV	I, %
Ti2p _{3/2}	459.4	4.7	459.2	3.5
N1s	400.6	0.6	396.0	0.4
O1s	530.9	20.5	530.7	23.8
C1s	283.9	73.1	283.7	71.8
Zr3d _{5/2}	–	–	182.7	0.5

In the case of PLD films, the N1s line was deconvoluted into the four lines with the certain binding energy values. The intensity belonging to

the substitutional N_s lines at 395.8 eV is increased for N/Zr/TiO₂ in comparison with N/TiO₂ as clearly seen in Table 4. In an opposite way, the intensity of binding energy at 397.8 eV related to interstitial N_i is higher for N/TiO₂. It is supposed that the peak at 399.2 eV could be related to the N-C formation and/or N₂ adsorption onto the surface. The higher energy peak at 400.8 eV is assigned to the formation of N₂ or NO species (Fig. 5).

Significant peak intensity at 457.5 eV assigned to the Ti-N bonds is observed for N/TiO₂ while the intensity of this peak for N/Zr/TiO₂ is only 5 %. It is also attributed to the presence of Ti³⁺ states where such titanium species have oxidation states between +3 and +4 [30]. The peaks of Ti2p_{3/2} at 458.1 and 458.8 eV belong to Ti⁴⁺ ions surrounded by oxygen ions. Similar to sol-gel films, the Zr3d_{5/2} line ($E_{BE} = 182.3$ eV) was recorded indicating the

formation of Zr⁴⁺ ions surrounded by O²⁻ ions [31]. No signal pointing on the formation of Ti-O-Zr bonds is observed.

Table 4. N1s and Ti2p_{3/2} binding energy values and their relative intensities of PLD films [21]

BE, eV	N/TiO ₂	N/Zr/TiO ₂
	I, %	
N1s		
395.8	9.7	13.4
397.8	27.4	18.1
399.1	39.6	47.0
400.8	23.3	21.5
Ti2p_{3/2}		
457.5	24.4	5.1
458.1	60.6	63.5
458.8	15.0	31.4

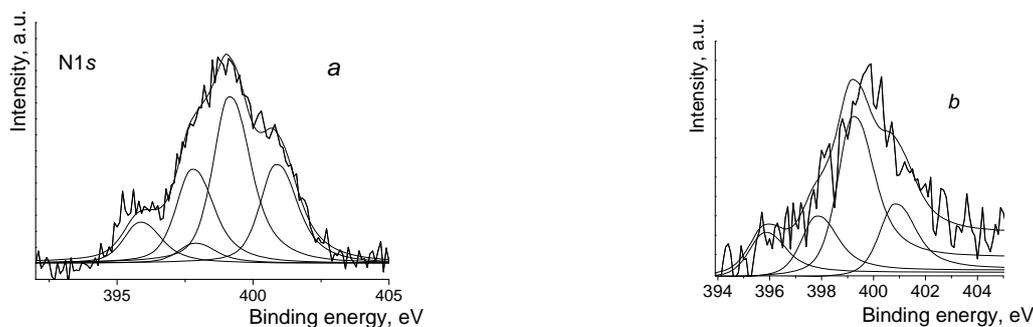


Fig. 5. XPS spectra of N1s region of N/TiO₂ (a) and N/Zr/TiO₂ (b) synthesized by PLD method

PHOTOCATALYTIC ACTIVITY

Photocatalytic activity of the sol-gel films was assessed via tetracycline hydrochloride (TC) degradation. The film was immersed in 40 ml of an aqueous solution of 2×10^{-5} mol/L TC. 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 film was immersed in the solution until complete adsorption in the dark occurred and then irradiated by 1000 W middle-pressure mercury lamp for 90 min. The distance lamp-reactor was set at 90 cm. A blank experiment was carried out where a bare glass was used instead of film. No significant changes in the absorption spectra of the liquid were observed for the blank. For testing the visible light sensitivity, a filter transmitting light with $\lambda > 380$ nm was introduced in the photocatalytic setup [16].

Reduction of toxic dichromate ions was monitored via the photocatalytic activity of the PLD films. The detailed description of photocatalytic setup is given elsewhere [28]. The change of Cr(VI) ions concentration was monitored with a Lambda 35 UV-Vis spectrophotometer (Lambda 35, PerkinElmer) every 20 min at $\lambda = 350$ nm. The reaction conversion means the percentage of photoreduced amount of Cr(VI) ions. The film was immersed in the solution until complete adsorption in the dark occurred, and then irradiated by 1000 W middle-pressure mercury lamp for 120 min. The distance from lamp to reactor was set at 90 cm. No significant changes in the absorption spectra of the liquid phase were observed for two blanks: dark condition and irradiation without film. A filter transmitting light with $\lambda > 380$ nm was introduced in the photocatalytic setup under visible light irradiation.

In the case of sol-gel films, the photocatalytic activity of N/TiO₂ films is increased in comparison

with that of pure TiO₂ film under both UV and visible light (Table 5). The highest activity under visible light is observed for the N/TiO₂ film (in three times higher than TiO₂). The threefold increase in photocatalytic activity under UV light for Zr/TiO₂ films is noted as a result of the higher surface acidity leading to the better adsorption of TC molecules onto the surface compared to TiO₂ film and the changed positions of the conduction and valence bands of the semiconductor [23, 6]. Under visible light, no absorption by a semiconductor takes place and the photocatalytic process can only follow through i) an excitation of an electron from the additional N-sublevels formed in the valence band of TiO₂; ii) the excitation of TC molecule. As a result, TC can be degraded through a photoexcitation of TC molecule (indirect photocatalysis) and an excitation of the electron from the N-sublevels to CB. The decrease in the photocatalytic activity is noted for N/Zr/TiO₂ under visible light comparing with N/TiO₂ films suggesting the formation of the structure defects by double doping that makes easier the recombination process.

Table 5. The conversion level of TC destruction and dichromate reduction over the films under UV and visible light

Film	Sol-gel [16]		PLD [21]	
	UV,%	Vis.,%	UV,%	Vis.,%
TiO ₂	11	5	24	3
N/TiO ₂	30	16	25	9
Zr/TiO ₂	29	11	20	2
N/Zr/TiO ₂	26	10	30	6

Concerning PLD films, the Zr/TiO₂ film exhibits a lower activity under both UV and visible light compared with those of titania films (Table 5). The photocatalytic performance of the N/Zr/TiO₂ film is the highest under UV and is lower under visible light than that of N/TiO₂. Thus, the highest conversion yield is obtained for N/Zr/TiO₂ film under UV light suggesting the crucial role of zirconium ions as effective trapping sites for the photogenerated charges. However, these ions suppress the photoactivity when visible light is applied. It follows that the substitutional nitrogen (Ti-N) is basically responsible for the observed photoactivity under UV light as the higher

percentage of it is noted for N/Zr/TiO₂ film (Table 3), contrary to N/TiO₂, where the more interstitial nitrogen ions are formed suggesting their significant role in the photocatalysis under visible light. In particular, the interstitial N impurities give rise to the higher energy states in the gap, and might behave as stronger hole trapping sites, reducing the direct oxidation activity of the sample in the photocatalytic process [32].

CONCLUSIONS

Optical, electronic and photocatalytic properties of nitrogen doped semiconductive films based on titania synthesized by both sol-gel and PLD methods are opposed to clarify the key points responsible for photocatalytic activity under visible irradiation. It is certainly revealed that the nature of incorporated nitrogen in titania is strongly dependent on the nitrogen source and the synthetic procedure, even though the calcination temperature was 450 °C for both methods and determines the optical properties of the material, as namely no significant change in band gap energy values is noted for PLD nitrogen doped titania films while the sharp narrowing of E_{bg} value is observed for the sol-gel samples. The difference in the position of N1s peaks is attributed to the formation of the different nitrogen containing species in the structure of the films. As shown by XPS results, no incorporation of Zr⁴⁺ ions in TiO₂ lattice takes place for both methods, however, the presence of metal ions has an effect on the chemical state of nitrogen atoms (sol-gel method) and the efficiency of nitrogen incorporation (PLD method). Comparing the photocatalytic activity of the modified titania films synthesized by both methods, the increase in photoresponse under visible light is only noted for nitrogen-containing TiO₂. Modification of sol-gel TiO₂ by double doping agent leads to the fall in the photocatalytic activity indicating the enhancement of recombination rate caused by the presence of Zr⁴⁺ ions, while the presence of nitrogen and zirconium ions stimulates the activity under UV light in the case of pulse laser deposited films.

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Синтез та характеристики TiO_2 , допованого йонами нітрогену та цирконію, для застосування у фотокаталізі

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Тонкі плівки діоксиду титану, допованого йонами нітрогену та цирконію, були одержані золь-гель методом та методом лазерного переосадження. Показано, що оптичні властивості залежать від складу плівки та типу інкорпорованого нітрогену. Хімічний стан неметалу в структурі напівпровідника залежить від наявності йонів цирконію, як показано рентгено-фотоелектронною спектроскопією. Введення йонів нітрогену або цирконію в структуру діоксиду титану позитивно впливає на фотокаталітичну активність під УФ та видимим світлом у випадку золь-гель плівок. Однак, наявність йонів як нітрогену, так і цирконію сприяє підвищенню активності під УФ світлом, а модифікування тільки нітрогеном призводить до покращення фотокаталітичних властивостей під видимим світлом плівок, синтезованих методом лазерного переосадження.

Ключові слова: *нітрогенвмісний діоксид титану, йони цирконію, золь-гель метод, метод лазерного переосадження*

Синтез и свойства TiO_2 , допированного ионами азота и циркония для применения в фотокатализе

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Тонкие пленки диоксида титана, допированного ионами азота и циркония, были получены золь-гель методом и методом лазерного переосаждения. Показано, что оптические свойства зависят от состава пленки и типа инкорпорированного азота. Химическое состояние неметалла в структуре полупроводника зависит от присутствия ионов циркония, как показывает рентгено-фотоэлектронная спектроскопия. Введение ионов азота или циркония в структуру диоксида титана положительно влияет на фотокаталитическую активность под УФ и видимым светом в случае золь-гель пленок. Однако, наличие ионов как азота, так и циркония способствует повышению активности под УФ светом, а модифицирование только азотом приводит к улучшению фотокаталитических свойств под видимым светом пленок, синтезированных методом лазерного переосаждения.

Ключевые слова: *азотсодержащий диоксид титана, ионы циркония, золь-гель метод, метод лазерного переосаждения*

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