

UDC 544.526+54.057

**SOL-GEL SYNTHESIS, OPTICAL PROPERTIES,  
MORPHOLOGY AND PHOTOCATALYTIC ACTIVITY OF  
TITANIA FILMS MODIFIED WITH ETHANOLAMINES AS  
NITROGEN SOURCE**

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*In this work the titania films modified with ethanolamines are synthesized by sol-gel method using two different routes. Introduction of template during sol ripening leading to the formation of porous structure and a single stage synthesis resulting in non-porous surface are proposed. The optical properties and calculated band-gap values of the films are presented. The titania particle size of the modified films is increased in comparison with the bare one as results of Root mean square (RMS) and Roughness average (Ra) values. The influence of the synthesis conditions and structure of ethanolamines on the photocatalytic activity under visible light are reported.*

### **Introduction**

Photocatalysts which are sensitive to visible light have been paid much attention for their potential use of solar energy [1]. Nitrogen doped titania was first prepared by Sato [2] calcinating titanium hydroxide with ammonium ions, after that the sensitization of TiO<sub>2</sub> powders due to NO<sub>x</sub> impurities has been occurred. In particular, nitrogen-doped TiO<sub>2</sub> is known to be a promising photocatalyst sensitive to visible light [3]. Therefore, a number of studies on the synthesis and characterization of various types of N-doped TiO<sub>2</sub>, including thin films [3-5], single crystals [6] and powders [1, 7] has been reported. Based on theoretically calculation of band energies, Asahi et al. [1] concluded that the substitution of nitrogen in the TiO<sub>2</sub> lattice by mixing the N 2p and O 2p state on the top of valence band could narrow the band gap energy. The mechanism of band gap reduction is not clear due to the problem in locating the exact position of N in the TiO<sub>2</sub> lattice. However, XPS analysis claimed the state of doped nitrogen to be N-anion [8], atomic β-nitrogen [9], and oxidation of TiN [10].

Mesoporous materials are getting considerable attention because of their potential applications in the field of catalysis, bio-medical engineering, energy storage and conversion, separation technology. Mesoporous titania is of particular interest due to photocatalytic and photovoltaic applications [11, 12]. The preparation of mesoporous titania mainly relies on soft template (supra molecular assemblies of surfactants or block copolymers) and hard template (porous alumina, porous silica, porous carbon, polystyrene spheres) [13]. Template - free approach based on different mechanisms was also developed to synthesize titania particles with great activity [14].

We have attempted to prepare nitrogen doped titania from mono-, di-, and triethanolamine by sol-gel method. The present paper deals with the synthesis of the nonporous films by a soft chemical route that is template - free or a three-block copolymer of polyethyleneoxide and polypropyleneoxide (PEO)<sub>20</sub>(PPO)<sub>70</sub>(PEO)<sub>20</sub> (Pluronic P123) as a

template for the porous samples preparation. Since incorporated nitrogen release from titania matrix as well as the acceleration of titania crystallization took place at above 500 °C [15], the films were treated at 450 °C with heating rate 3 °C/min. The photocatalytic activity of the UV and visible light active photocatalyst was evaluated towards the reduction of toxic Cr(VI) ions as a model reaction.

## Experimental

Titanium dioxide films were synthesized by sol-gel method and in detail described herein [16]. The nitrogen containing films were synthesized by two procedures named as sol-gel I and sol-gel II. All synthesis stages of sol-gel I were carried out analogous to bare titania films with the final addition of doping agents (10 or 20 mol. %), namely, mono- (MEA), di- (DEA) or triethanolamine (TEA). The entity of the sol-gel II was to add titanium isopropoxide (10 mol. %) to the previously heated (65 °C, water bath) doping agent with the following stirring of the resulting mixture for 20 min. The one-layered films were deposited by dipping at the withdrawal rate of 1.5 mm/s onto previously cleaned glasses. Thermal treatment was carried at 450 °C with heating rate of 3 °C/min.

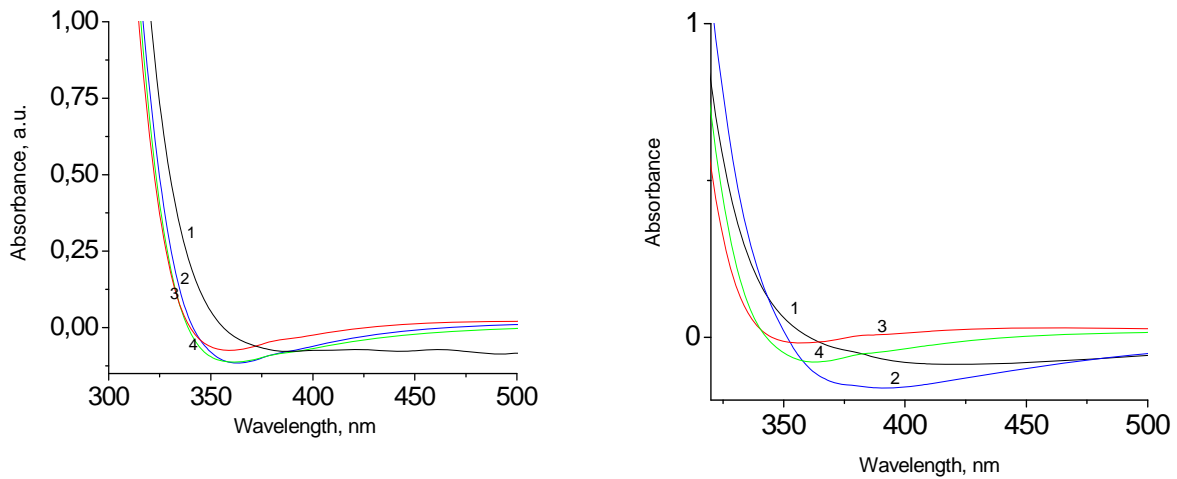
Photocatalytic activity of the films was assessed via Cr(VI) ions reduction reaction. The film was immersed in 40 ml of an aqueous solution of potassium bichromate (in all experiments, the initial concentration of bichromate ions was  $2 \times 10^{-4}$  M) and the reducing agent (disodium salt of ethylenediaminetetraacetic acid (Na<sub>2</sub>EDTA)) in the molar ratio 2:1 adjusted to 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 Lambda 35 UV-vis spectrophotometer (PerkinElmer) every 20 min at  $\lambda=350$  nm. The distance between the lamp and the reactor was set at 50 cm. For testing the visible light sensitivity, a filter transmitting light with  $\lambda > 350$  nm was introduced in the photocatalytic setup.

An irradiation source of UV light was 1000 W middle - pressure mercury lamp. The absorption spectra of the films were recorded by a Lambda 35 UV-Vis spectrophotometer (PerkinElmer) in the range of 200-1000 nm. AFM images were recorded using the microscope is Nanonics Multiview 4000 with phase feedback, intermittent mode. Scanning area: 40 $\mu$ m $\times$ 40 $\mu$ m; scan resolution: 256 lines; scanning speed: 6.12 lines/s; resonance frequency: 40 kHz; aperture diameter: 20 nm; active quality factor: 1600. The Nanonics Multiview 4000 is working in tapped mode (intermittent contact) with a tuning fork probe with Cr/Au coating.

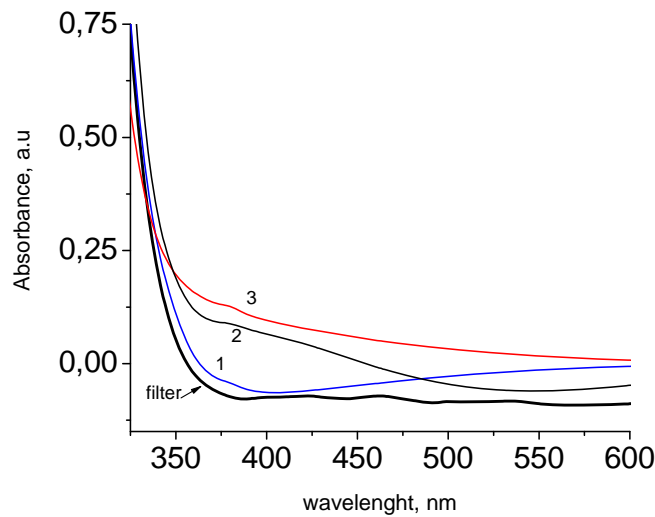
## Results and discussion

To investigate the influence of nitrogen source and its amount on the optical properties of the samples, 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 absorbance data.

As clearly seen the introduction of nitrogen containing compounds in concentration of 10 and 20 mol % to titania sol (sol-gel I) leads to the shift of absorption onset to the short wavelengths (Fig. 1). It can be explained by the increase of band-gap ( $E_g$ ) width due to anatase particle size decrease [17] or the Burstein-Moss effect [18]. Such effect occurs in semiconductors at the rising of dopant content and defines as the separation in energy between the top of the valence band and the unoccupied energy states in the conduction band. The shift arises because the Fermi energy ( $E_F$ ) lies in the conduction band for n-type doping (or in the valence band for p-type doping). The filled states therefore block thermal or optical excitation. Consequently the measured band gap determined from the onset of interband absorption moves to higher energy.



**Fig. 1.** Absorption spectra of the films (sol-gel I) with 10% (a) and 20% (b) doping agent: 1 -  $\text{TiO}_2$ , 2- $\text{TiO}_2/\text{DEA}$ , 3- $\text{TiO}_2/\text{MEA}$ , 4- $\text{TiO}_2/\text{TEA}$ ).



**Fig. 2.** Absorption spectra of N/ $\text{TiO}_2$  films sol-gel II: 1 -  $\text{TiO}_2/\text{MEA}$ , 2 -  $\text{TiO}_2/\text{TEA}$  and 3 -  $\text{TiO}_2/\text{DEA}$ .

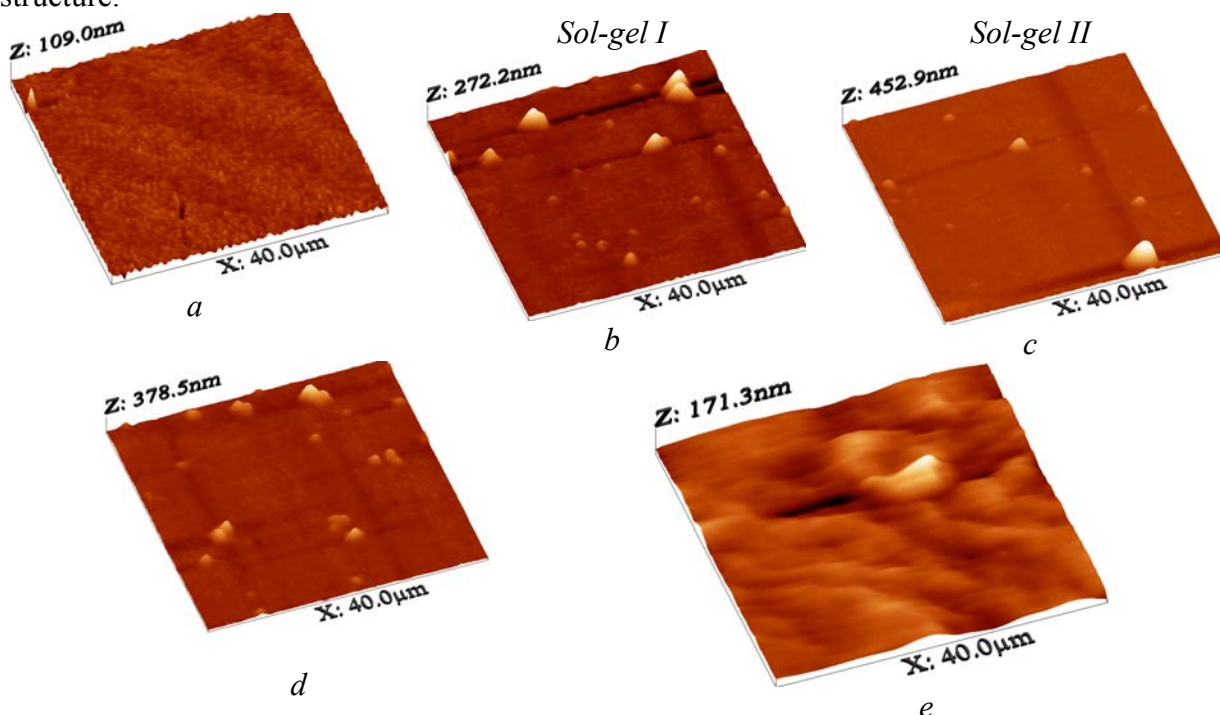
In opposite, the shift of absorption onset to the red region is observed for the films synthesized by sol-gel II (Fig. 2). The narrowing of the band gap energy without any shift of the conduction and valence bands position is considered an effect of N - generated mid-gap level [19].

As follows, the optical absorption coefficient calculating from  $\alpha = 4\pi k/\lambda$  can be used to estimate the band gap values of the samples. Indirect and direct transitions in a semiconductor can be distinguished by the energy dependence of the optical absorption coefficient near the absorption edge. The values of  $E_g$  for the samples with indirect and direct characteristics were obtained by extrapolation of the plots of  $(ah\nu)^{1/2}$  and  $(ah\nu)^2$  versus  $h\nu$ , respectively. It has been found from well distribution of experimental points that indirect electronic transition is permitted for  $\text{TiO}_2$  as well as doped  $\text{TiO}_2$  films synthesized by us. The band gap values of indirect electronic transition are in the range from 3.36 to 3.49 eV for doped samples and 3.42 eV for pure titania film (Tab. 1).

**Table 1.** The band-gap values of the films for indirect electronic transitions

Sample	E <sub>g</sub> , eV sol-gel I		E <sub>g</sub> , eV sol-gel II
	10%	20%	
TiO <sub>2</sub> /MEA	3.47	3.54	3.36
TiO <sub>2</sub> /DEA	3.44	3.36	3.49
TiO <sub>2</sub> /TEA	3.45	3.42	3.36
TiO <sub>2</sub>	3.42		

The lowering in band-gap values is noted for the TiO<sub>2</sub> films doped with 20 % BEA (sol-gel I), MEA and TEA (sol-gel II). Such narrowing can be explained by the presence of additional level above valence band as a result of nitrogen substitution for oxygen in the titania structure.



**Fig. 3.** AFM images of the films synthesized by sol-gel I (left) and sol-gel II (right): TiO<sub>2</sub> (a), TiO<sub>2</sub>/DEA (b and c), TiO<sub>2</sub>/TEA (d and e).

For undoped TiO<sub>2</sub> films we have evidenced a homogeneous, small-grain structure. By the modification with ethanolamines the homogeneity of the film is affected. Well-pronounced randomly distributed larger size crystallites developed on the film surface. The rough surface texture is confirmed by the relatively higher values of the RMS. For the film containing DEA the difference between the morphology of the films prepared by sol-gel I and sol-gel II is not significant. For the films containing TEA the difference between the morphology of the films prepared by sol-gel I and sol-gel II is important. For the modified titania, the biggest crystallite size was obtained by the TEA modification using sol-gel II method.

The synthesized films were tested in photocatalytic reduction of bichromate ions in the presence of sodium salt of EDTA at pH  $\geq$  2. Two blank experiments were carried out as the catalytic reduction of dichromate ions (dark condition) and photoreduction reaction (a glass substrate was used instead of a film). No significant changes in the absorption spectra of the CrVI solution were observed for both blanks.

**Table 3.** RMS and Ra values of the films

Sample	Root mean square (RMS) (nm)	Roughness average (Ra) (nm)
TiO <sub>2</sub>	5.28	3.99
TiO <sub>2</sub> /DEA (sol-gel II)	21.22	7.72
TiO <sub>2</sub> /TEA (sol-gel II)	13.44	9.76
TiO <sub>2</sub> /10%DEA (sol-gel I)	15.97	7.51
TiO <sub>2</sub> /10%TEA(sol-gel I)	19.22	9.83

The kinetics of the photocatalytic reduction under UV light showed that bare TiO<sub>2</sub> film exhibited higher activity in comparison with doped films where the first order reaction was shown with reaction rate constant  $11.9 \times 10^{-5} \text{ s}^{-1}$ . In the case of doped samples, the zero order of the reaction is observed and the calculated reaction rate constants are given in table 4. The highest reaction rate under UV light is obtained for 10% MEA/TiO<sub>2</sub> film (sol-gel I) while other tested films possessed the activity comparable to the blank. It can be explained by the electronic structure modification due to the nitrogen incorporation. As follows, the recombination of photogenerated electrons and holes are assisted by nitrogen doping leading to the deceleration of bichromate ions reduction. A similar result is reported herein [20] where the reaction rate of stearic acid photooxidation is lowered with the increasing of nitrogen content in titania.

**Table 4.** The reaction rate constants of photocatalytic reduction of bichromate ions

Sample	$k \times 10^5$ $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$	$k \times 10^6$ $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
<i>Exposed light</i>	<i>UV</i>	<i>Vis</i>
Blank (glass)	2.4	4.0
TiO <sub>2</sub>		8.0
TiO <sub>2</sub> /10 % MEA (sol-gel I)	5.1	4.2
TiO <sub>2</sub> /10 % DEA (sol-gel I)	2.5	5.1
TiO <sub>2</sub> /10 % TEA (sol-gel I)	2.0	5.7
TiO <sub>2</sub> /20 % MEA (sol-gel I)	1.6	6.3
TiO <sub>2</sub> /20 % DEA (sol-gel I)	2.5	4.8
TiO <sub>2</sub> /20 % TEA (sol-gel I)	1.6	7.1
TiO <sub>2</sub> /MEA (sol-gel II)	2.5	8.0
TiO <sub>2</sub> /DEA (sol-gel II)	3.6	10.0
TiO <sub>2</sub> /TEA (sol-gel II)	2.7	8.8

When comparing the reaction rate constants under visible light, the films synthesized by sol-gel I are found to be less active than TiO<sub>2</sub>. In opposite, the insignificant increase of reaction rates is

observed for doped TiO<sub>2</sub> films synthesized by sol-gel II. Among them, the film with DEA possessed the highest activity. It must be noted that the concurrent intensity decrease at 350 nm and increase at 550 nm characterizing the formation as a product of non-toxic Cr(III) ions are observed in the presence of such doped titania films. The significant absorption in visible region is demonstrated by the TiO<sub>2</sub>/DEA and TiO<sub>2</sub>/TEA films (Fig. 2) although the band gap value of TiO<sub>2</sub>/DEA is too high to absorb the light with energy less than 3.5 eV. We expect that exactly this evidence is responsible for improved photocatalytic activity of TiO<sub>2</sub>/DEA film.

## Conclusions

The optically transparent nitrogen doped titania thin films have been synthesized by sol-gel approach using various amount of MEA, DEA and TEA as doping agent. It was also applied the technologically more simple route (sol-gel II) of film synthesis. Titania and doped titania films showed the indirect electronic transition found from optical dependencies. The surface morphology of doped films is differed from bare titania. The growth of anatase crystallite sizes in the presence of ethanolamines has been observed. As shown TiO<sub>2</sub>/DEA (sol-gel II) films are perspective in photocatalytic reduction of bichromate ions under visible light.

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**ЗОЛЬ-ГЕЛЬ СИНТЕЗ, ОПТИЧНІ ВЛАСТИВОСТІ, МОРФОЛОГІЯ ТА  
ФОТОКАТАЛІТИЧНА АКТИВНІСТЬ ДІОКСИД ТИТАНОВИХ ПЛІВОК,  
МОДИФІКОВАНИХ ЕТАНОЛАМИНАМИ ЯК ДЖЕРЕЛО АЗОТУ**

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*Синтезовано плівки діоксиду титану, модифіковані етаноламінами. Описано золь-гель метод з використанням різних підходів. Введення темплату під час дозрівання золю призводить до утворення пористої структури, а запропонований одностадійний синтез формує непористу поверхню. Досліджено оптичні властивості плівок та розраховано їхні величини ширини забороненої зони. Розмір частинок модифікованих плівок діоксиду титану зростає в порівнянні з немодифікованим, як показано представленими значеннями RMS і Ra. Вивчено вплив умов синтезу і структури етаноламінів на фотокаталітичну активність під видимим світлом.*

**ЗОЛЬ-ГЕЛЬ СИНТЕЗ, ОПТИЧЕСКИЕ СВОЙСТВА, МОРФОЛОГИЯ И  
ФОТОКАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ ДИОКСИД ТИТАНОВЫХ ПЛЕНОК,  
МОДИФИЦИРОВАННЫХ ЭТАНОЛАМИНАМИ КАК ИСТОЧНИК АЗОТА**

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*В данной работе синтезированы пленки диоксида титана, модифицированные этаноламинами. Описан золь-гель метод с использованием различных. Введение темплат во время созревания золя приводит к образованию пористой структуры, а предложенный одностадийный синтез формирует непористую поверхность. Исследованы оптические свойства пленок и рассчитаны их величины ширины запрещенной зоны. Размер частиц модифицированных пленок диоксида титана возрастает по сравнению с немодифицированным, как показано представленными значениями RMS и Ra. Изучено влияние условий синтеза и структуры этаноламинов на фотокаталитическую активность под видимым светом.*