membrane / V. Balakrishnan, Ch. Ko, and Sh. Ramanathana // J. Mater. Res. – 2012. – Vol. 27. – P. 1476–1481.

7. Osmolovskaya O. M. Sintez, magnetic and electric properties of nanostructure of vanadium dioxide on a surface of SiO$_2$ and Si : PhD Thesis / O. M. Osmolovskaya. – St.-Petersburg, 2008. – 150 p.

8. The Radiation Enhanced "Slow" Phase Transitionon the Surface of Vanadium Dioxide / V. N. Kaurkovskaya, A. P. Shakhov, V. V. Lobanov, I. R. Entinzon // High Energy Chemistry. – 2010. – Vol. 44, № 2. – P. 101–104.

9. General atomic and molecular electronic structure system / M. W. Schmidt, K. K. Baldridge, J. A. Boatz [et al.] // J. Comput. Chem. – 1993. – Vol. 14, № 11. – P. 1347–1363.

Каурковська В. М., Гребенюк А. Г., Лобанов В. В.

ВПЛИВ АДСОРБЦІЇ ПРОСТИХ МОЛЕКУЛ НА ФАЗОВИЙ ПЕРЕХІД У ДІОКСИДІ ВАНАДІЮ

Вплив адсорбції простих молекул на температуру фазового переходу (T = 338–339 К) досліджено з використанням моделей поверхні діоксиду ванадію, співвимірних із цими молекулами. Температурні залежності вільної енергії фаз до та після переходу перетинаються за температур 200–216 К, що відомо для наноструктур діоксиду ванадію. Показано, що використання методу теорії функціоналу густини з гібридним функціоналом B3LYP дає результати, майже ідентичні отриманим ab initio.

Ключові слова: діоксид ванадію, параметри фазового переходу, квантова хімія, кластерне наближення.

O. Smirnova, A. Grebenyuk, O. Linnik, N. Chorna, V. Lobanov

EFFECT OF NITROGEN DOPING ON THE SPATIAL AND ELECTRONIC STRUCTURE OF TIO$_2$ THIN FILMS AND ON THE EFFICIENCY OF WATER MOLECULES ADSORPTION ONTO THEIR SURFACES

Nitrogen incorporation into the lattice structure of titania films was proved by XPS measurements. Quantum chemical calculations were performed to find out the difference in the adsorption of water molecules onto the pure titania and nitrogen doped titania films. The effect of nitrogen doping on the values of adsorption energy of water molecules on titania species has been found, as well as a decrease in adsorption energy, which can be responsible for promotion of their photocatalytic activity The total energy values of the optimized geometrical structures of different size TiO$_2$ and TiO$_2$(N) cluster models (including 3 to 9 titanium atoms) was calculated by using the density functional theory method (DFT) and the hybrid B3LYP potential with basis set 6-31G(d, p) by means of the software package PC GAMESS (version FireFly 8.1.0 by A. Granovsky).

Keywords: nitrogen doped titania, electronic structure, XPS spectra, water adsorption, quantum chemical calculations, density functional theory method.

Introduction

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. Titanium dioxide thin films with highly developed surface are perspective materials for removing of toxic compounds from liquid and gaseous media. High adsorption capability, corrosive as well as photocorrosive stability, and non-toxicity are the key properties of its application in ecological photocatalysis, production of antibacterial covering and self-cleaning coatings.

Porous and non-porous nitrogen doped titania thin films using ethanolamines as doping agent synthesized by sol-gel method was reported [1]. It has been shown that the synthesis route influences on the titania particle sizes and, consequently, on the band gap energy values. Contrary to the doping-free TiO_2 films, the well-pronounced randomly distributed larger size crystallites developed on the film surface using ethanolamines are noted. As shown, the nonporous TiO_2 films synthesized with diethanolamine are perspective in photocatalytic reduction of dichromate ions under visible light. The influence of the synthesis conditions and structure of ethanolamines on the photocatalytic activity under visible light are pointed in [1].

The mutual influence both metal (Zn^{2+} or Zr^{4+}) and non-metal (nitrogen) doping agents on the electronic, optical and photocatalytic properties of TiO_2 films were studied. Absorption intensity in the visible region and the band gap values vary depending on the metal nature and the amount of added urea. Anatase formation in the films with double doping agents is proven by Raman measurements. XPS clarified the chemical state of the elements, their surface ratios and the incorporation of nitrogen into the film matrixes. The substitutional nitrogen incorporation is only registered for zirconium containing films. However, the enhancement in the photocatalytic activity by factor three is noted for nitrogen doped titania [2].

Pulse Laser deposition (PLD) method was applied to obtain the non-metal doped thin TiO_2/ZrO_2 films. The influence of synthesis conditions on the efficiency of nitrogen incorporation in the atmosphere of dinitrogen and methane is described in [3]. The film synthesized at minimum methane content in N_2/CH_4 mixture and minimum pressure exhibits the maximum reaction rate constant of photoreaction as well as the highest possible distribution of Ti2p and N1s states attributed to O-Ti-N bonds. An appearance of oxygen vacancies leading to O-Ti-N formation could be caused by direct interaction of carbon atoms and oxygen radicals formed under laser pulse. The next detailed investigation has shown that the PLD synthesis conditions dictate the type and level of nitrogen doping. The best ratio of gases as well as the pressure during synthesis procedure was identified for the optimum photocatalytic activity of semiconductive materials. The correlation between the zirconia content and the efficiency of substitutional N incorporation was noticed. The distortion of TiO_2 lattice occurred due to the larger radius of zirconium ions. The relative high stability of Ti^{3+} states was assigned to the presence of Zr^{4+} ions. The highest conversion percent of photoreduced dichromate ions under UV and visible irradiation was fixed for 10 % ZrO_2 in TiO_2 obtained in N_2/CH_4 (5:1) atmosphere and 1 mbar pressure. It is suggested that level of the interstitial N atoms in TiO_2 matrix is essential for photocatalytic capability of the semiconductor under both UV and visible light [4].

The available experimental data can be verified by means of theoretical methods, in particular quantum chemical calculations. This article describes the results of a combined (both experimental and theoretical) study on the spatial and electronic structure of pure and nitrogen doped titania nanoparticles as well as on their capabilities to adsorb water molecules.

Experimental

PLD depositions of the films were performed using a KrF* laser source model COMPexPro 205 (Lambda Physics-Coherent) that operated at a repetition rate of 20 Hz. The laser fluence was of 4.5 J/cm² whereas the laser spot area was set to 10 mm². In order to avoid the drilling, during multipulse laser irradiation, the target was rotated at the rate of 0.4 Hz. The films were grown at the substrate temperature of 450 °C while the target-substrate separation distance was of 5 cm. The samples were deposited at 0.03 mixed N_2:CH_4 atmospheres with 5:1 ratio. XPS spectra were explored with an electron spectrometer EC-2402 equipped with a PHOIBOS-100_SPECS energy analyzer. Nonmono-chromatic X-rays (MgK_α 1253.6 eV) were employed at a power of P = 200 W [4].

Quantum chemical calculations were carried out within the frameworks of so-call cluster approximation [5]. Computations on the total energy values of the optimized geometrical structures of different size TiO_2 – $TiO_2(N)$ cluster models (including 3 to 9 titanium atoms) were performed using density functional theory method (DFT) [6] and the hybrid B3LYP [7] potential with basis set 6-31G(d, p). Calculations were carried out by means

of the software package PC GAMESS [8] (version FireFly 8.1.0, http://classic.chem.msu.su/gran/firefly/index.html by A. Granovsky).

Results and discussion

Titanium oxide clusters have been considered both theoretically and experimentally. Aside from the many works devoted to the TiO_2 molecule [9], and from the experimental study of the TiO_2 trimer [10], positively charged titanium–oxygen clusters Ti_nO_{2n-d} ($n = 1–7$, $d = 0–4$) have been investigated with mass spectrometry and collision induced dissociation [11]. The energy different from the HOMO–LUMO gap usually defined as the difference between the

ionization potential and the electron affinity A. Here we analyze the atomic and electronic properties of the series of Ti_nO_{2n} ($n = 3, 6, 9$), the structure of nitrogen doped TiO_2 and the effect of nitrogen incorporation on the adsorption of water molecules.

Using an ab initio approach based on Density Functional Theory (DFT), we simulate low energy Ti_nO_{2n} isomers, both pure and doped with nitrogen. We discuss the size dependence of the electron affinity and the excitation gap. Through a careful comparison with the experimental results, we show that the electronic properties can be used to help in the identification of the most stable complexes. In order to find out the ground state configurations, we start from structures $Ti_3O_{11}H_{10}$.

Table 1. **Theoretically calculated and experimental binding energy values of the clusters**

Cluster (Fig. 3)	Theoretical values							Experimental values (Fig. 2)
	1	1A	1B	2	2A	3	3A	
Ti2p	453.72	452.59	452.51	454.52	454.30	457.56	454.33	457.5
O1s	521.27	521.43	521.22	521.56	521.91	521.53	521.39	528.90
N1s	–	390.55	391.04	–	390.37	–	389.66	395.80

$Ti_3O_{11}H_{10}$	$Ti_3O_9N_2H_{10}$	$Ti_3O_9N_2H_{10}$
-3382.51	-3341.25	-3341.27
1	*1a*	*1b*

$Ti_6O_{19}H_{14}$	$Ti_6O_{17}N_2H_{14}$
-6535.76	-6494.65
2	*2a*

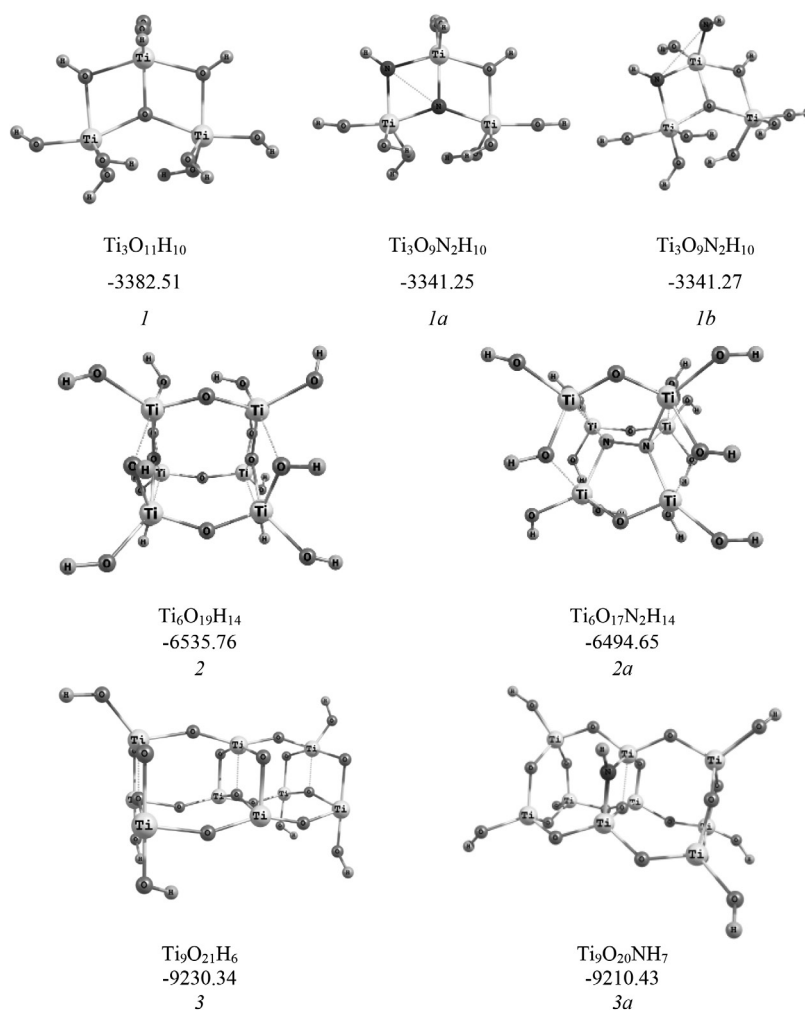|	
$Ti_9O_{21}H_6$	$Ti_9O_{20}NH_7$
-9230.34	-9210.43
3	*3a*

Fig. 1. Total energy values and optimized geometrical structures of different titania (*1–3*) and nitrogen doped titania clusters *(1a–3a)* (DFT B3LYP/6-31(d, p))
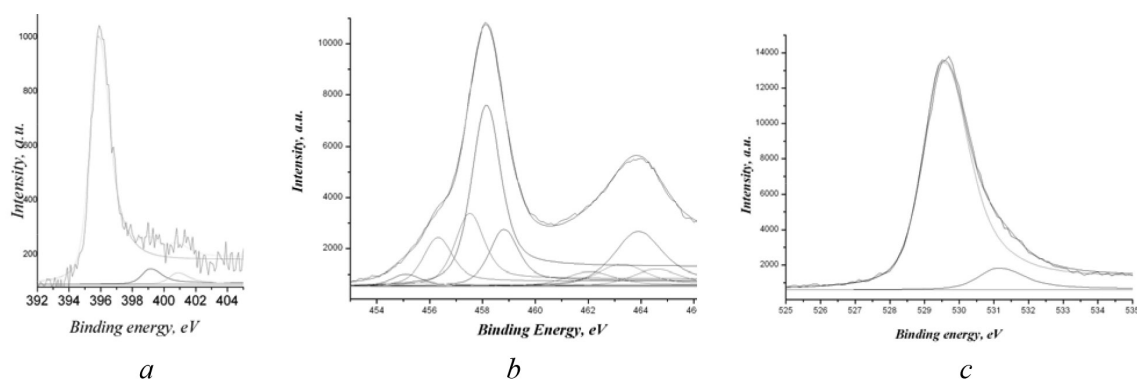
Fig. 2. XPS spectra of N1s *(a)*, Ti2p *(b)* and O1s *(c)* binding energy for nitrogen doped titania [4]

To optimize the geometry and electronic parameters of bare titania and its nitrogen doped clusters, the following structures $Ti_3O_{11}H_{10}$, $Ti_3O_9N_2H_{10}$, $Ti_6O_{19}H_{14}$, $Ti_6O_{17}N_2H_{14}$ and $Ti_9O_{21}H_6$ were used in DFT calculation (Fig. 1).

The theoretically calculated binding energy values are well correlated with the experimental data for all investigated titania and nitrogen doped clusters (Table 1 and Fig. 2). These results provide a starting point for investigating larger, more complex models.

Ti atom has four valence electrons and is six-coordinated in TiO_2. There are two types of Ti-O bonds in the bulk crystals: short (1.934 Å in anatase, 1.947 Å in rutile) and long (1.98 Å in both anatase and rutile). We consider the Ti bonding as a combination of four covalent and two dative bonds.

Basic settings of optimized titania geometries with various compositions are given in Table 2.

Since the calculated values of geometric parameters of the clusters coincide with the experimental data [12–15], these clusters can be considered as acceptable models for further studies of real structures.

The geometrical parameters of the clusters contained one nitrogen atom bonded with hydrogen atom (Ti-N-H) and two nitrogen atoms without

hydrogen bond (N-Ti-N) were calculated. It is found that the bond lengths of the cluster with two nitrogen atoms in the crystal lattice are decreased comparing with those in pure titania. Increasing the number of nitrogen atoms in the cluster leads to further reduction in bond lengths.

We examine several aspects of water binding on the anatase clusters. We discuss the theoretical methods used in this study and the cluster models employed to represent the adsorption sites. The results for the structures and energies of the molecular adsorption and dissociative adsorption of water are shown in Fig. 4.

Calculated parameters for the models of water adsorption on TiO_2 surface of different composition have shown that if the titania cluster is doped by single nitrogen atom, the energy of water adsorption increases ($E_{a, 0 K}$ = -60.07 kJ/mol for cluster $Ti_3O_{11}H_{10} + H_2O$ to -48.50 kJ/mol for cluster $Ti_3O_9N_2H_{10}+H_2O$). These calculations correlate with the literature data (E_a = 36.96 kJ/mol [16]).

Calculated parameters for the models of water adsorption on TiO_2 surface of different composition have shown that if the titania cluster is doped by single nitrogen atom, the energy of water adsorption increases ($E_{a, 0 K}$ = -60.07 kJ/mol for cluster $Ti_3O_{11}H_{10} + H_2O$ to -48.50 kJ/mol for cluster

Table 2. **Calculated bond lenght (R, Å) and angle of Ti-O-Ti bond (DFT B3LYP/6-31(d, p))**

Parameters	Theoretical values			Experimental values
	$Ti_3O_{11}H_{10}$ **1**	$Ti_6O_{19}H_{14}$ **2**	$Ti_9O_{21}H_6$ **3**	
R_{Ti-O}	1.98706 2.02832	1.80515 1.80747	1.83634 1.86918	1.934 [12] 1.979 [12] 1.91 [13] 1.95 [14]
R_{Ti-Ti}	3.18833 3.68209	3.27460 3.74884	3.30344 3.73439	3.04 [13] 3.79 [14]
R_{O-O}	2.34950 2.34817 2.75686	2.94945 2.92602 2.36874	2.87 2.88 3.20	2.45 [13] 2.80 [14] 3.04 [15]
<Ti-O-Ti	111.190	149.707	130.476	156.18 [12]

$Ti_3O_9N_2H_{10} + H_2O$). These calculations correlate with the literature data (Ea = 36.96 kJ/mol [16]).

The results of calculations at T = 278 K for the same clusters of TiO_2 show a positive adsorption Gibbs energy (Ea, $_{278 K}$ = 1.46 kJ/mol for cluster $Ti_9H_6O_{21} + H_2O$ to 13.63 kJ/mol for cluster $Ti_9NH_7O_{20} + H_2O$).

Thus, the nitrogen doping TiO_2 results in hydrophobicity of titania surface. Adsorption energy decreases if the temperature increase, and at room temperature no adsorption of water takes place on titania (the energy absorption value is positive). The transition from hydrophobic to hydrophilic state of pure titania occurs at 223 K,

while doped titania becomes hydrophobic at the temperature of 217 K.

Thus, by varying the temperature of adsorption and by embedding nitrogen atoms into the crystal lattice of TiO_2, we can control the hydrophobic properties of the system.

Overall, the hydrophobization of the titania surface due to the substitution nitrogen incorporation could be one of the crucial properties of the materials in photocatalytic application. Competition between the adsorption of water molecule and pollutant molecule can stimulate the enhanced photocatalytic performance where the separated charge electron-hole couple directly interacts with a pollutant species.
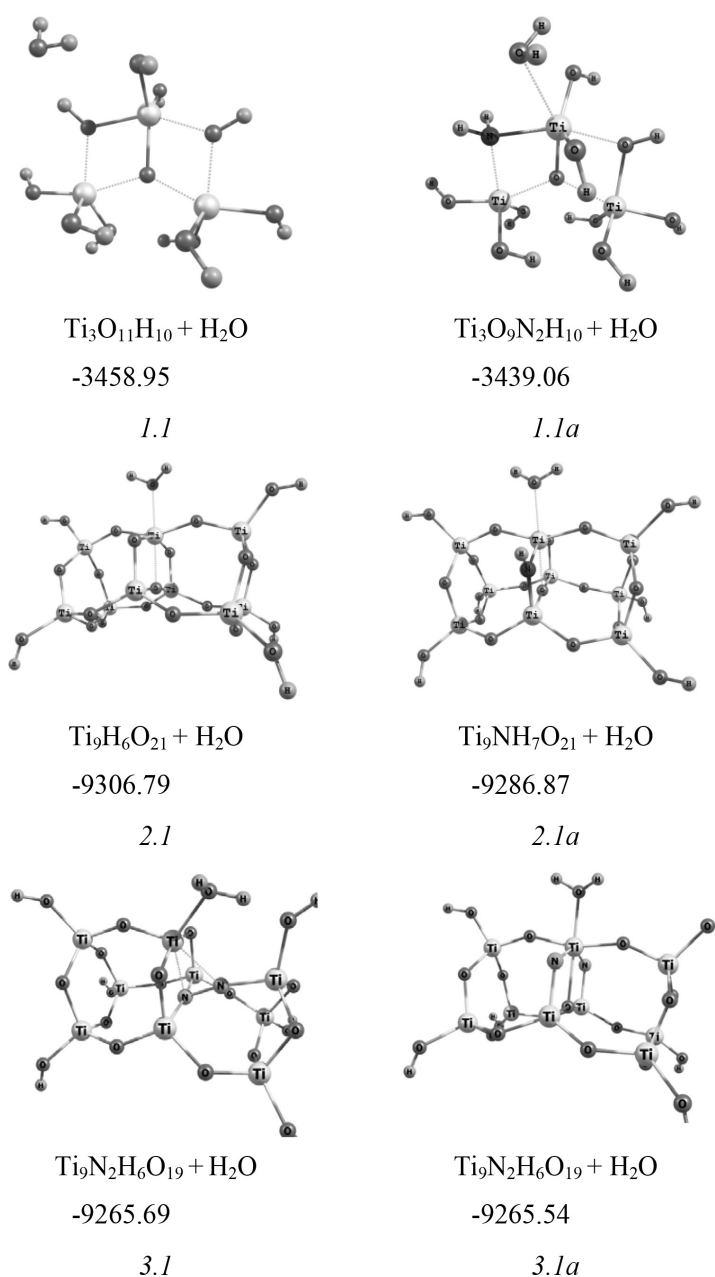

$Ti_3O_{11}H_{10} + H_2O$

-3458.95

1.1

$Ti_3O_9N_2H_{10} + H_2O$

-3439.06

1.1a

$Ti_9H_6O_{21} + H_2O$

-9306.79

2.1

$Ti_9NH_7O_{21} + H_2O$

-9286.87

2.1a

$Ti_9N_2H_6O_{19} + H_2O$

-9265.69

3.1

$Ti_9N_2H_6O_{19} + H_2O$

-9265.54

3.1a

Fig. 3. Optimized geometrical structure, E_{total}, a.u. of different titania *(1–3)* and nitrogen doped titania clusters with adsorbed water molecule referred to *1.1–3.1a*

Conclusions

Optimization of the geometry and electronic parameters of bare titania and related nitrogen doped clusters ($Ti_3O_{11}H_{10}$, $Ti_3O_9N_2H_{10}$, $Ti_6O_{19}H_{14}$, $Ti_6O_{17}N_2H_{14}$ and $Ti_9O_{21}H_6$) was performed.

The theoretically calculated binding energy values and the geometric parameters are well correlated with the experimental data for all investigated titania and nitrogen doped clusters.

Nitrogen doping leads to the hydrophobization of the titania surface where the adsorption of a pollutant molecule onto the surface can be more preferential than a water molecule. This effect can bring to the improvement in the photocatalytic efficiency of the material.

References

1. Sol-gel synthesis, optical properties, morphology and photocatalytic activity of titania films modified with ethanolamines as nitrogen source / O. P. Linnik, N. O. Shestopal, N. P. Smirnova [et al.] // Surface. – 2012. – Vol. 4 (19). – P. 105–110.

2. Shestopal N. Influence of metal and non-metal ions doping on the structural and photocatalytic properties of titania films / N. Shestopal, O. Linnik, N. Smirnova // Chemistry, Physics and Technology of Surface. – 2015. – Vol. 6, № 2. – P. 203–210.

3. TiO_2/ZrO_2 thin films synthesized by PLD in low pressure N-, C- and/or O-containing gases: structural, optical and photocatalytic properties / O. Linnik, I. Petrik, N. Smirnova [et al.] // Digest Journal of Nanomaterials and Biostructures. – 2012. – Vol. 7, № 3. – P. 1343–1352.

4. Correlation between electronic structure and photocatalytic properties of non-metal doped TiO_2 films obtained by pulsed laser deposition method / O. Linnik, N. Shestopal, N. Smirnova [et al.] // Vacuum. – 2015. – Vol. 114. – P. 166–171.

5. Sauer J. Molecular Models in ab Initio Studies of Solids and Surfaces: From Ionic Crystals and Semiconductors to Catalysts / J. Sauer // Chem. Rev. – 1989. – Vol. 89, № 1. – P. 199–255.

6. Becke A. Density-functional thermochemistry. III. The role of exact exchange / A. Becke // J. Chem. Phys. – 1993. – Vol. 98, № 7. – P. 5647–5652.

7. Cohen A. J. Challenges for density functional theory / A. J. Cohen, P. Mori-Sanchez, W. Yang // Chem. Rev. – 2012. – Vol. 112. – P. 289–320.

8. General Atomic and Molecular Electronic Structure System / M. Schmidt, K. Baldridge, J. Boatz [et al.] // J. Comput. Chem. – 1993. – Vol. 14. – P. 1347–1359.

9. Barnes M. Optical–Optical Double Resonance Spectroscopy of Jet-Cooled TiO: New 3 F and 3 P States near 4 eV / M. Barnes, A. J. Merer, G. F. Metha // J. Mol. Spectrosc. – 1997. – Vol. 181, № 1. – P. 180–193.

10. McIntyre N. S. Spectroscopy of Titanium Oxide and Titanium Dioxide Molecules in Inert Matrices at 4°K / N. S. McIntyre, K. R. Thompson, W. Weltner // J. Phys. Chem. – 1971. – Vol. 75. – P. 3243–3249.

11. Yu W. Formation and Fragmentation of Gas-Phase Titanium/Oxygen Cluster Positive Ions / W. Yu, R. B. Freas, J. Am // Chem. Soc. – 1990. – Vol. 112. – P. 7126–7133.

12. Photoluminescence in TiO_2 anatase single crystals / H. Tang, H. Berger, P. E. Schmid [et al.] // Solid State Communications. – 1993. – Vol. 87, № 9. – P. 847–850.

13. Gritzel M. The Artificial Leaf, Molecular Photovoltaics Achieve Efficient Generation of Electricity from Sunlight / M. Gritzel // Comments Inorg. Chem. – 1991. – Vol. 12. – P. 93–111.

14. Berger H. Growth and Raman spectroscopic characterization of TiO_2 anatase single crystals / H. Berger, H. Tang, F. Levy // J. Cryst. Growth. – 1993. – Vol. 130. – P. 108–112.

15. High-mobility n-type charge-carriers in large single-crystals of anatase (TiO_2) / L. Forro, O. Chauvet, D. Emin [et al.] // Journal of Applied Physics. – 1994. – Vol. 75, № 1. – P. 633–635.

16. Computational Studies of Catechol and Water Interactions with Titanium Oxide Nanoparticles / P. C. Redfern, P. Zapol, L. A. Curtiss [et al.] // J. Phys. Chem. B. – 2003. – Vol. 107. – P. 11419–11427.

Смірнова О. В., Гребенюк А. Г., Ліннік О. П., Чорна Н. О., Лобанов В. В.

ВПЛИВ ДОПУВАННЯ АЗОТОМ НА ПРОСТОРОВУ ТА ЕЛЕКТРОННУ СТРУКТУРУ ТОНКИХ ПЛІВОК ТІО₂ ТА НА ЕФЕКТИВНІСТЬ АДСОРБЦІЇ МОЛЕКУЛ ВОДИ НА ЇХНІХ ПОВЕРХНЯХ

Структуру легованих азотом плівок TiO_2 і їхню здатність до адсорбції молекул води було визначено за допомогою вимірів XPS і квантово-хімічних розрахунків. Квантово-хімічні розрахунки повної енергії оптимізованих геометричних структур різного розміру моделей кластера $TiO_2 – TiO_2(N)$ (від 3 до 9 атомів титану) проводили з використанням методу теорії функціоналу густини (DFT) і гібридного потенціалу B3LYP з базисним набором 6-31G(d, p) за допомогою програмного пакета PC GAMESS (версія 8.1.0 FireFly A. Granovsky).

Було виявлено ефект впливу легування азотом на величину енергії адсорбції молекул води на оксиді титану, а також зменшення енергії адсорбції, що може бути причиною зростання їхньої фотокаталітичної активності.

Ключові слова: азот-легований оксид титану, електронна структура, спектри XPS, адсорбція води, квантово-хімічні розрахунки, метод теорії функціоналу густини.