THEORETICAL STUDY OF THE THERMODYNAMIC AND KINETIC FACTORS INFLUENCE ON NANOSIZED TITANIUM DIOXIDE PARTICLES GROWTH FEATURES

M.A. Grishina, *South Ural State Medical University, Chelyabinsk, Russian Federation,*
pvapva2006@yandex.ru
A.V. Potemkin, *Saint Petersburg National Research University of Information Technologies,*
Mechanics and Optics, Saint Petersburg, Russian Federation,appanpotemkin@gmail.com
O.I. Bolshakov, *South Ural State University, Chelyabinsk, Russian Federation,*
bolshakovoi@susu.ru
V.A. Potemkin, *South Ural State Medical University, Chelyabinsk, Russian Federation,*
pva@csu.ru

A theoretical study of the crystal lattice of titanium dioxide (anatase), its spatial and thermodynamic characteristics, face growth characteristics and ways of formation of its macromolecular structures is performed. It is shown that the growth along c axis of the crystal is more favorable thermodynamically. The variants for controlling of the growth of various faces by introducing of the acidic and basic components, as well as by temperature changes are proposed.

Keywords: titanium dioxide, anatase, nanostructure, thermodynamic calculations, kinetic features.

Introduction

Nanocrystalline titanium dioxide is widespread photocatalyst for destruction of organic pollutants [1], a semiconductor in solar cells [2], a component of ceramic, composite, catalytic [3] and sorption materials [4], because of its efficiency, low cost, non-toxicity, photo- and thermal stability. Frequently nanocrystalline titanium oxide used as the photocatalyst, because of its ability to form part of a pair of "electron – hole" under the UV and visible light radiation. The effectiveness of photocatalysts based on nanocrystalline titanium dioxide is determined by many factors, such as phase content, the morphology features, the specific surface area, the pore volume, the presence of dopant additives [5]. All of the above mentioned characteristics of the material are formed by the processes of hydrolytic or non-hydrolytic decomposition of TiO_2 precursors and templating agents used in the synthetic processes. Currently, a lot of technique allows to obtain photocatalysts with specified properties using a sol-gel or hydrothermal synthesis. However, most of the known methods for producing crystalline titanium oxides require high temperatures or pressures for crystallization of the amorphous precursor into the desired crystalline modification. Preparation of nanocrystalline titanium dioxide under mild conditions at a temperature close to room temperature is an important problem, the solution of which will significantly reduce the cost of production of functional materials. A way for the achievement this goal is the usage of biomineralizing agents in the synthesis of titanium dioxide that allow both to obtain crystalline titanium dioxide under mild conditions, and to control its crystalline structure, and particles sizes. An important advantage of biomineralization, along with the "ecology and economy", is unequivalent or "quasi-catalytic" nature of the process, i.e. the process does not require the equivalent amounts of template. In addition to the importance of the applied research of the crystalline phase of the titanium oxide formation, the problem of the general features determining the formation of metal oxide materials is fundamentally important. A lot of quantum DFT and *ab initio* calculations of the titanium dioxide, ranging from small particles of TiO_2, to large enough nanoclusters such as $Ti_{428}O_{856}$, for example, [6–8], was performed. But so far, a little is known on the specific ways of macromolecular structures (phases) of the titanium oxide formation, on the hydrolysis of oligomeric intermediates, as well as the on the mechanism of formation of oligomeric intermediates themselves [9, 10]. Determination of the mechanism, identification of intermediates of structure formation processes, definition of the dependence between the structure of the template and the parameters of nanocrystalline TiO_2 will create new ways for the effective control of the formation of titanium oxide nanostructures, which will allow to increase the characteristics of existing materials and yield in principally new functional materials. Therefore, the aim of this work is a

theoretical study of the crystal lattice of titanium dioxide (anatase), its spatial and thermodynamic characteristics, face growth characteristics and pathways of formation of its macromolecular structures.

Research Methodology

The crystal structure of anatase was used for the study. X-ray diffraction data for the anatase lattice was taken from [11] and Crystallography Open Database (http://www.crystallography.net/ ID 9015929). The crystal system of anatase is tetragonal, the space group is I41/amd, unit cell parameters are $a = b = 3.7845$ Å; $c = 9.5143$ Å; $\alpha = \beta = \gamma = 90°$. The cell volume is 136.268 Å^3, ideal crystal density is 3.894 g/cm3. The cell contains two formula units of titanium dioxide.

The investigation of the titanium dioxide was performed within MERA force field [12–22] beginning from one unit cell (cluster formula $Ti_{29}O_{58}$) to 30 unit cells, propagated along the a and c axes of the crystal (cluster formula $Ti_{870}O_{1740}$). In the framework of this approach the potential energy of interactions in the system is the sum of intra- and intermolecular Coulomb and Van der Waals interactions. Energy of intra- and intermolecular electrostatic interactions are calculated by the usual formula of Coulomb's law. The energy of intermolecular van der Waals interactions is calculated using the Lennard-Jones equation

$$E_V = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(-2U_{ij} \left(\frac{R_{ij}^e}{R_{ij}} \right)^6 + U_{ij} \left(\frac{R_{ij}^e}{R_{ij}} \right)^{12} \right).$$

R_{ij}^e is the equilibrium distance of the van der Waals contact of the i and j atoms, equal to the sum of their van der Waals radii calculated within the MERA model;

R_{ij} is the actual distance between the i and j atoms.

U_{ij} value corresponds to the minimum of potential energy of interaction between atoms i and j and can be calculated within the MERA model in accordance with the following formula

$$U_{ij} = \frac{7kR_{ij}^e}{48\alpha},$$

α – a constant equal to $6.662 \cdot 10^{-14}$ м/K;

k – the Boltzmann constant.

The energy of the intermolecular van der Waals interactions and hydrogen bonds is calculated as follows

$$E_{VI} = \sum_{i=1}^{M} \sum_{j=1}^{M} p_{ij} \left(-2U_{ij}R_{ij}^{e6} \left(\frac{1}{(R_{ij}+ka)^6} + \frac{1}{(R_{ij}+kb)^6} + \frac{1}{(R_{ij}+kc)^6} \right) + U_{ij}R_{ij}^{e12} \left(\frac{1}{(R_{ij}+ka)^{12}} + \frac{1}{(R_{ij}+kb)^{12}} + \frac{1}{(R_{ij}+kc)^{12}} \right) \right),$$

a, b, c – the unit cell parameters;

k – integers 0, 1, 2, 3, …

The calculation of the thermodynamic characteristics of the anatase crystal lattice was fulfilled using the MERA model by the scheme shown in [14, 20, 21]. The calculation of atomic charges, as well as the value of the charged surface was carried out within the framework of the full equalization of the orbital electronegativity formalism [23] in the modification of the model MERA [13]. The calculation of the electronegativity of crystals was performed the J. Gasteiger scheme within the formalism of full equalization of the orbital electronegativity [23].

Discussion

Calculation which was fulfilled for the anatase unit cell showed the following: the portion of a charged cell surface, responsible for soption of polar molecules (e.g., amino acids or oligopeptides that can be used for hydrolytic decomposition method of TiO_2 precursors), is low enough. Its value is only 2.19 % of the unit cell total surface (the square is 3.78 Å^2). About 80 % of the surface belongs to the side faces of the cell and just over 20 % belongs to base faces. Thus, each side face possesses about 20% of the charged surface, whereas each base face possesses just over 10 %.

Modelling of the crystal lattice growth along the a axis showed the following: the thermal effect of the unit translation along the a axis is quite significant, the standard enthalpy is –2743 kJ/mole, the entropy increment is 584 kJ/mole·K, lowering of the standard Gibbs free energy is 2917 kJ/mole. Electro-

negativity of the crystal increases with the crystal growth along *a* axis by 0.41 eV per cell unit. Thus the strength of sorption sites with respect to the positively charged hydrogens of carboxylic and ammonium groups of oligopeptides (which may be used in the synthesis of titanium dioxide nanosized particles). It should be noted that the electronegativity growth is nonlinear. The dependency represents a saturation curve (Fig. 1) and can be approximated by the following equation

$$\chi = 6.52 + \frac{3.025n}{1.671 + n},$$

χ – electronegativity of crystal eV;
n – the number of cells along the *a* axis.

Analyzing the equation, it is obvious, that the electronegativity can achieve the value 9.54 eV at the saturation. A 50 % degree of completion of the saturation process will be achieved when the number of cells will achieve *n* = 3. A 90 % degree of completion of the saturation process will be achieved when the number of cells will achieve *n* = 17. Since the length of the *a* axis is 3.7845 Å, the linear length of 17 unit cells equals 64.34 Å, or 6,434 nm, which will be the minimum size of the crystals at the equilibrium sorption of polar components.

Modelling of the crystal lattice growth along the *c* axis showed the following: the thermal effect when the unit translation along the *c* axis even greater than for the growth along *a* axis and – the standard enthalpy is –3482 kJ/mole, the increase of entropy is also significantly higher it equals 869 kJ/mole·K, lowering of the standard Gibbs free energy also greater and amounts to 3741 kJ/mole. Thus, the crystal growth along the *c* axis is more favorable than along the *a* or *b* axes under thermodynamic conditions. However, the number of side faces is twice greater than the base faces perpendicular to *c* axis.
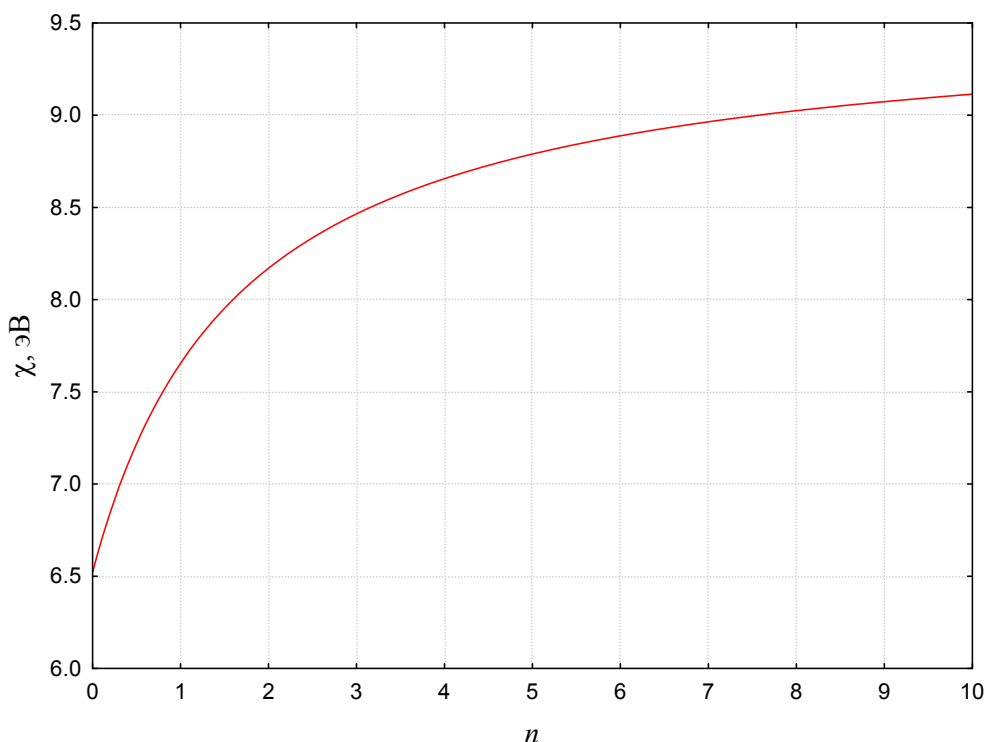

Fig. 1. The dependency of the crystal electronegativity on the number of unit cells along the *a* axis

Electronegativity of the crystal increases with growth along the *c* axis but its increment is almost twice less than for the growth along *a* axis: the increment is 0.22 eV per unit. The further electronegativity growth is nonlinear and dependency also represents a saturation curve (Fig. 2). It can be approximated using the following formula

$$\chi = 6.86 + \frac{1.6925n}{1.134 + n},$$

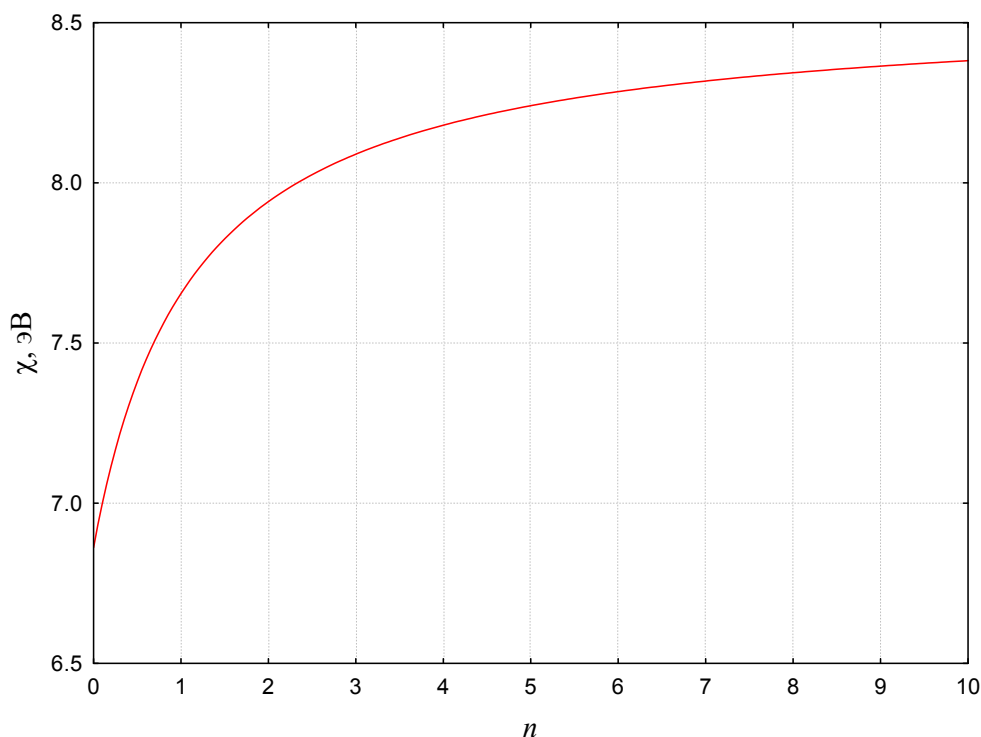*n* – the number of unit cells along the *c* axis.

Fig. 2. The dependency of the crystal electronegativity on the number of unit cells along the *c* axis

Analyzing the equation, it is obvious, that the electronegativity can achieve the value 8.55 eV, which is less than the growth along the *a* axis by almost one. A 50 % degree of completion of the saturation process will be achieved when the number of cells will achieve *n* = 4. A 90 % degree of completion of the saturation process will be achieved when the number of cells will achieve *n* = 12. Since the length of the *c* axis is 9.5143 Å, the linear length of the 12 unit cells equals 114.17 Å, or 11.417 nm, which will be the minimum size of the crystals at the equilibrium sorption of polar components.

A comparison of anatase crystal growth along the *a* and *c* axes shows that the more thermodynamically favorable is a growth along *c* axis, which must provide a crystal habit elongated along *c* axis. However, when a doubling of unit cell along *c* axis leads to a doubling of the free energy of the growth along *a* axis. So, the next step provides adding a layer of unit cells along *a* direction. Thus, the ratio of the size of the crystal during the growth under ideal thermodynamic conditions should be the ratio of the free energies of growth, i.e.

$$a : c = b : c = 2917 : 3741.$$

It is possible to make changes into this ratio in any direction under kinetic conditions. Since the electronegativity of the crystal during the growth along the *a* axis increases much stronger than during the growth along the *c* axis, the insertion components with the positively charged fragments, such as acids or conjugated acids (for example, consisting of ammonia or carboxylic group) should accelerate the growth along the *a* axis and yielding smaller particles (from 6.434 nm); the insertion of the conjugate bases or bases should accelerate growth along the *c* axis and yielding larger particles (from 11.417 nm). It is well confirmed by the data of [24], where the sorption of neutral, acidic and basic amino acids on titanium dioxide is elucidated. Since the entropy factor favors the growth along the *c*, the growth in this direction will increase with the temperature increase; a reducing of the temperature will be favorable to growth in the direction *a*. In both cases possible to obtain nanosized titanium dioxide particles.

Conclusion

Some thermodynamic and kinetic factors on the growth characteristics of nanoscale titanium dioxide particles are studied in the work. The conditions providing larger and smaller particles with higher

56

Bulletin of the South Ural State University. Ser. Chemistry.
2015, vol. 7, no. 3, pp. 53–60

and lower sorption capacity for acidic and basic peptides within hydrolytic decomposition method of titanium dioxide precursors are offered.

References

1. Macwan D.P., Dave P.N., Chaturvedi S. A Review on Nano-TiO_2 Sol–Gel Type Syntheses and its Applications. *Journal of Materials Science*, 2011, vol. 46, no. 11, pp. 3669–3686.

2. Yum J.H., Lee J.W., Kim Y., Humphry-Baker R., Park N.G., Graetzel M. Panchromatic Light Harvesting by Dye- and Quantum Dot-Sensitized Solar Cells. *Solar Energy*, 2014, vol. 109, pp. 183–188.

3. Tachikawa T., Yamashita S., Majima T. Evidence for Crystal-Face-Dependent TiO_2 Photocatalysis from Single-Molecule Imaging and Kinetic Analysis. *J. Am. Chem. Soc.*, 2011, vol. 133, pp. 7197–7204.

4. Thomas A.G., Syres K.L. Adsorption of Organic Molecules on Rutile TiO_2 and Anatase TiO_2 Single Crystal Surfaces. *Chem. Soc. Rev.*, 2012, vol. 41, pp. 4207–4217.

5. Henderson M.A., Lyubinetsky I. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO_2(110). *Chem. Rev.*, 2013, vol. 113, no. 6. pp. 4428–4455.

6. Lundqvist M.J., Nilsing M., Persson P., Lunell S. DFT Study of Bare and Dye-Sensitized TiO_2 Clusters and Nanocrystals. *Int. J. Quant. Chem.*, 2006, vol. 106, no. 15, pp. 3214–3234.

7. Vittadini A., Casarin M., Selloni A. Chemistry of and on TiO_2-Anatase Surfaces by DFT Calculations: a Partial Review. *Theor. Chem. Acc.*, 2007, vol. 117, no. 5–6, pp. 663–671.

8. Andreev A.S., Kuznetsov V.N., Chizhov Yu.V. Atomic Hydrogen Activated TiO_2 Nanocluster: DFT Calculations. *J. Phys. Chem. C*, 2012, vol. 116, no. 34, pp. 18139–18145.

9. Benedict J.B., Freindorf R., Trzop E., Cogswell J., Coppens P. Large Polyoxotitanate Clusters: Well-Defined Models for Pure-Phase TiO_2 Structures and Surfaces. *J. Am. Chem. Soc.*, 2010, vol. 132, pp. 13669–13671.

10. Seisenbaeva G.A., Daniel G., Nedelec J.M., Kessler V.G. Solution Equilibrium behind the Room-Temperature Synthesis of Nanocrystalline Titanium Dioxide. *Nanoscale*, 2013, vol. 5, pp. 3330–3336.

11. Howard C.J., Sabine T.M., Dickson, F. Structural and Thermal Parameters for Rutile and Anatase. *Acta Crystallographica. Section B*, 1991, vol. 47, pp. 462–468.

12. Potemkin V.A., Bartashevich E.V., Belik A.V. [New Representation of Spatial Shape of Molecules]. *Zhurnal Obshei Khimii* [Russian Journal of General Chemistry], 1995, vol. 65, no. 2, pp. 205–208. (in Russ.)

13. Potemkin V.A., Bartashevich E.V., Belik A.V. [Calculation of Atomic Radii Adjusted for Electrostatic Interactions]. *Zhurnal Physicheskoi Khimii* [Russian Journal of Physical Chemistry], 1995, vol. 69, no. 1, pp. 106–109. (in Russ.)

14. Potemkin V.A., Bartashevich E.V., Belik A.V. [A New Approach to Predicting the Thermodynamic Parameters of Substances from Molecular Characteristics]. *Zhurnal Physicheskoi Khimii* [Russian Journal of Physical Chemistry], 1996, vol. 70, no. 3, pp. 411–416. (in Russ.)

15. Potemkin V.A., Bartashevich E.V., Belik A.V. [A Model for Calculation of Atomic Volume Characteristics in Molecular Systems]. *Russkii Zhurnal Physicheskoi Khimii* [Russian Journal of Physical Chemistry], 1998, vol. 72, no. 4, pp. 650–656. (in Russ.)

16. Bartashevich E.V., Potemkin V.A., Grishina M.A., Belik A.V. A Method for Multiconformational Modeling of the Three-Dimensional Shape of a Molecule. *J. Struct. Chem.*, vol. 43, no. 6, pp. 1033–1039.

17. Grishina M.A., Bartashevich E.V., Potemkin V.A., Belik A.V. Genetic Algorithm for Predicting Structures and Properties of Molecular Aggregates in Organic Substances. *J. Struct. Chem.*, vol. 43, no. 6, pp. 1040–1044.

18. Potemkin V.A., Sukharev Yu.I. Formation of Liotropic Features of Zirconium Oxyhydrate Gels. *Chem. Phys. Lett.*, 2003, vol. 371, pp. 626–633.

19. Potemkin V.A., Maksakov V.A., Kirin V.P. Conformational States of Triosmium Clusters with Aminoacid Ligands: A Theoretical Study. *J. Struct. Chem.*, vol. 44, no. 5, pp. 741–747.

20. Aladko E.Ya., Ancharov A.I., Goryainov S.V., et al. New Type of Phase Transformation in Gas Hydrate Forming System at High Pressures. Some Experimental and Computational Investigations of Clathrate Hydrates Formed in the SF_6-H_2O. *J. Phys. Chem. B*, 2006, vol. 110, no. 42, pp. 21371–21376.

21. Potemkin V.A., Ivshina N.N., Maksakov V.A. Theoretical study of the conformational features of triosmium clusters. *J. Struct. Chem.*, vol. 50, no. 1, pp. 143–151.

22. Manakov A.Yu., Likhacheva A.Yu., Potemkin V.A. et al Compressibility of Gas Hydrates// *Chem. Phys. Chem*, 2011, vol. 12, no. 13, pp. 2476–2484.

23. Mortier W.J., Van Genechten K., Gasteiger J. Electronegativity Equalization: Application and Parametrization. *J. Am. Chem. Soc.*, 1985, vol. 107, pp. 829–835.

24. Okazaki S., Aoki T., Tani K. The Adsorption of Basic Alpha-Amino-Acids in an Aqueous-Solution by Titanium (IV) Oxide. *Bull. Chem. Soc. Jpn.*, 1981, vol. 54, pp. 1595–1599.

_____

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ВЛИЯНИЯ РЯДА ТЕРМОДИНАМИЧЕСКИХ И КИНЕТИЧЕСКИХ ФАКТОРОВ НА ОСОБЕННОСТИ РОСТА НАНОРАЗМЕРНЫХ ЧАСТИЦ ДВУОКИСИ ТИТАНА

М.А. Гришина[1], А.В. Потемкин[2], О.И. Большаков[3], В.А. Потемкин[1]
[1] *Южно-Уральский государственный медицинский университет, г. Челябинск,*
[2] *Санкт-Петербургский национальный исследовательский университет информационных технологий, механики и оптики, г. Санкт-Петербург,*
[3] *Южно-Уральский государственный университет, г. Челябинск*

Проведено теоретическое исследование кристаллической решетки диоксида титана (анатаза), его пространственных и термодинамических характеристик, особенностей роста граней и путей формирования его макромолекулярных структур. Показано, что термодинамически более благоприятным является рост вдоль направления с кристалла. Предложены варианты управления ростом тех или иных граней путем введения кислотных и основных компонентов, а также посредством изменения температуры.

Ключевые слова: диоксид титана, анатаз, наноструктура, термодинамические расчеты, кинетические особенности.

Литература

1. Macwan, D.P. Review on Nano-TiO_2 Sol–Gel Type Syntheses and its Applications / D.P. Macwan, P.N. Dave, S. Chaturvedi // Journal of Materials Science. – 2011. – Vol. 46. – No. 11. – P. 3669–3686.

2. Panchromatic Light Harvesting by Dye- and Quantum Dot-Sensitized Solar Cells / J.H. Yum, J.W. Lee, Y. Kim et al. // Solar Energy. – 2014. – Vol. 109. – P. 183–188.

3. Tachikawa, T. Evidence for Crystal-Face-Dependent TiO_2 Photocatalysis from Single-Molecule Imaging and Kinetic Analysis / T. Tachikawa, S. Yamashita, T. Majima // Journal of the American Chemical Society. – 2011. – Vol. 133. – P. 7197–7204.

4. Thomas, A.G. Adsorption of Organic Molecules on Rutile TiO_2 and Anatase TiO_2 Single Crystal Surfaces / A.G. Thomas, K.L. Syres // Chemical Society Reviews. – 2012. – Vol. 41. – P. 4207–4217.

5. Henderson, M.A. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on $TiO_2(110)$ / M.A. Henderson, I. Lyubinetsky // Chemical Reviews. – 2013. – Vol. 113. – No. 6. – P. 4428–4455.

6. DFT Study of Bare and Dye-Sensitized TiO_2 Clusters and Nanocrystals / M.J. Lundqvist, M. Nilsing, P. Persson et al. // International Journal of Quantum Chemistry. – 2013. – Vol. 106. – No. 15. – P. 3214–3234.

7. Vittadini, A. Chemistry of and on TiO_2-Anatase Surfaces by DFT Calculations: a Partial Review / A. Vittadini, M. Casarin, A. Selloni // Theoretical Chemistry Accounts. – 2007. – Vol. 117. – No. 5–6. – P. 663–671.

8. Andreev, A.S. Atomic Hydrogen Activated TiO_2Nanocluster: DFT Calculations /A.S. Andreev, V.N. Kuznetsov, Yu.V. Chizhov // The Journal of Physical Chemistry C. – 2012. – Vol. 116. – No. 34. – P. 18139–18145.

9. Large Polyoxotitanate Clusters: Well-Defined Models for Pure-Phase TiO_2 Structures and Surfaces / J.B. Benedict, R. Freindorf, E. Trzop et al. // Journal of the American Chemical Society. – 2010. – Vol. 132. – P. 13669–13671.

10. Seisenbaeva, G.A. Solution Equilibrium behind the Room-Temperature Synthesis of Nanocrystalline Titanium Dioxide / G.A. Seisenbaeva, G. Daniel, J.M. Nedelecet et al. // Nanoscale. – 2013. – Vol. 5. – P. 3330–3336.

11. Howard, C.J. Structural and Thermal Parameters for Rutile and Anatase/ C.J. Howard, T.M. Sabine, F. Dickson // Acta Crystallographica. Section B. – 1991. – Vol. 47. – P. 462–468.

12. Потемкин, В.А. Новые представления об объемной форме молекул / В.А. Потемкин, Е.В. Барташевич, А.В. Белик // Журн. общ. химии. – 1995. – Т. 65. – № 2. – С. 205–208.

13. Потемкин, В.А. Расчет атомных радиусов с поправкой на электростатические взаимодействия / В.А. Потемкин, Е.В. Барташевич, А.В. Белик // Журн. физ. химии. – 1995. – Т. 69. – № 1. – С. 106–109.

14. Потемкин, В.А., Новые подходы к прогнозу термодинамических параметров веществ по молекулярным данным / В.А. Потемкин, Е.В. Барташевич, А.В. Белик // Журн. физ. химии. – 1996. – Т. 70. – № 3. – С. 448–452.

15. Потемкин, В.А. Модель расчета атомных объемных характеристик в молекулярных системах./ В.А. Потемкин, Е.В. Барташевич, А.В. Белик // Журн. физ. химии. – 1998. – Т. 72. – № 4. – С. 650–656.

16. A Method for Multiconformational Modeling of the Three-Dimensional Shape of a Molecule / E.V. Bartashevich, V.A. Potemkin, M.A. Grishinaet et al. // Journal of Structural Chemistry. – 2002. – Vol. 43. – No. 6. – P. 1033–1039.

17. Genetic Algorithm for Predicting Structures and Properties of Molecular Aggregates in Organic Substances / M.A. Grishina, E.V. Bartashevich, V.A. Potemkin et al. // Journal of Structural Chemistry. – 2002. – Vol. 43. – No. 6. – P. 1040–1044.

18. Potemkin, V.A. Formation of Liotropic Features of Zirconium Oxyhydrate Gels / V.A. Potemkin, Yu.I. Sukharev // Chemical Physics Letters. – 2003. – Vol. 371. – P. 626–633.

19. Potemkin, V.A. Conformational States of Triosmium Clusters with Aminoacid Ligands: A Theoretical Study / V.A. Potemkin, V.A. Maksakov, V.P. Kirin // Journal of Structural Chemistry. – 2003. – Vol. 44. – No. 5. – P. 741–747.

20. New Type of Phase Transformation in Gas Hydrate Forming System at High Pressures. Some Experimental and Computational Investigations of Clathrate Hydrates Formed in the SF_6-H_2O / E.Ya. Aladko, A.I. Ancharov, S.V. Goryainov et al. // The Journal of Physical Chemistry B. – 2006. – Vol. 110. – No. 42. – P. 21371–21376.

21. Potemkin, V.A. Theoretical study of the conformational features of triosmium clusters / V.A. Potemkin, N.N. Ivshina, V.A. Maksakov // Journal of Structural Chemistry. – Vol. 50. – No. 1. – P. 143–151.

22. Compressibility of Gas Hydrates / A.Yu. Manakov, A.Yu. Likhacheva, V.A. Potemkin et al. // ChemPhysChem. – 2011. – Vol. 12. – No. 13. – P. 2476–2484.

23. Mortier, W.J. Electronegativity Equalization: Application and Parametrization / W.J. Mortier, K.Van Genechten, J. Gasteiger // Journal of the American Chemical Society. – 1985. – Vol. 107. – P. 829–835.

24. Okazaki, S. The Adsorption of Basic Alpha-Amino-Acids in an Aqueous-Solution by Titanium (IV) Oxide / S. Okazaki, T. Aoki, K. Tani // Bulletin of the Chemical Society of Japan. – 1981. – Vol. 54. – P. 1595–1599.

Гришина Мария Александровна – доктор химических наук, доцент, Южно-Уральский государственный медицинский университет, г. Челябинск. E-mail: pvapva2006@yandex.ru

Потемкин Андрей Владимирович – студент, Санкт-Петербургский национальный исследовательский университет информационных технологий, механики и оптики, г. Санкт-Петербург. E-mail: appanpotemkin@gmail.com

Большаков Олег Игоревич – докторант, кандидат химических наук, Южно-Уральский государственный университет, г. Челябинск. E-mail: bolshakovoi@susu.ru

Потемкин Владимир Александрович – доцент, кандидат химических наук, Южно-Уральский государственный медицинский университет, г. Челябинск. E-mail: pva@csu.ru.

60

**Bulletin of the South Ural State University. Ser. Chemistry.
2015, vol. 7, no. 3, pp. 53–60**