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STRUCTURE, PROPERTIES, PRODUCTION AND PHOTOCATALYTIC PROCESSES OF TITANIUM (IV) OXIDE

Byts O.V., Ivanenko I.M., Fedenko Yu.M.
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
Peremogy Ave., 37, 03056, Kyiv
byc.olena@gmail.com, irinaivanenko@hotmail.com, fedenkoyura@ukr.net

Titanium (IV) oxide is an important commercial product today. The titanium (IV) oxide market continues to grow rapidly. This is primarily characterized by the possibility of wide consumption of this compound in various industries. Titanium (IV) oxide is a useful semiconductor material and combines unique characteristics such as low cost, simplicity of use, non-toxicity, and resistance to photochemical and chemical degradation. These advantages allow it to be used widely in industry.

TiO_2 combines interesting properties such as transparency in visible light, UV absorption, and an exceptionally high refractive index. This combination of properties makes TiO_2 a substance suitable for protecting composite, and polymeric materials from the harmful effects of natural ultraviolet radiation.

Titanium (IV) oxide can exist in various polymorphic forms. The best-known natural modifications of TiO_2 are anatase, rutile, and brookite. Only the first two crystalline forms are used in industry.

For photocatalytic purposes, the anatase modification is mainly used. Studies have shown that rutile and brookite can also be highly efficient photocatalysts, but they have not yet gained as much importance as anatase.

The photocatalysis of titanium (IV) oxide is based on its semiconducting properties. The first stage of semiconductor photocatalysis involves the absorption of photons and the associated excitation of electrons from the upper filled edge of the valence band (VB) to the lower free edge of the conduction band (CB) with a higher energy level. A prerequisite for this process is the absorption of irradiation energy that should be greater than or equal to the width of the band gap.

An important application area of titanium (IV) oxide and other semiconductors as photocatalysts is in the field of environmental protection. In the next few decades, the role of water bodies protection, drinking water treatment, and wastewater purification will grow in importance. Another important application area of photoactive semiconductors is the decomposition of pollutants in the air.

Key words: titanium (IV) oxide, anatase, photocatalysis, semiconductor, conduction band, valence band.

Структура, властивості, отримання та фотокаталітичні процеси титан (IV) оксиду. Биць О.В., Іваненко І.М., Феденко Ю.М.

Титан (IV) оксид на сьогоднішній день виступає важливим комерційним продуктом. Ринок титан (IV) оксиду продовжує стрімко розвиватися. В першу чергу це характеризується можливістю широкого споживання даної сполуки в різних областях промисловості. Титан (IV) оксид є корисним напівпровідниковим матеріалом і поєднує в собі унікальні характеристики, такі як низька вартість, легкість експлуатації, нетоксичність і стійкість до фотохімічного та хімічного руйнування. Ці переваги дозволяють широко використовувати його в промисловості.

TiO_2 поєднує в собі цікаві властивості, такі як прозорість у видимій частині світла, поглинання УФ-випромінювання та винятково високий коефіцієнт заломлення. Дана комбінація властивостей робить TiO_2 речовиною, придатною для захисту композитних і полімерних матеріалів від шкідливого впливу природнього ультрафіолетового випромінювання.

Титан (IV) оксид може перебувати в різних поліморфних формах. Найвідомішими природними модифікаціями TiO_2 є анатаз, рутил і брукіт. В промисловості використовують лише перші дві кристалічні форми.

Для фотокаталітичних цілей використовується переважно модифікація анатазу. Дослідження показали, що рутил та брукіт також можуть бути високоефективними фотокаталізаторами, однак вони досі не набули такого великого значення, як анатаз.

Фотокаталіз титан (IV) оксиду ґрунтується на його напівпровідникових властивостях. На першому етапі напівпровідникового фотокаталізу відбувається поглинання фотонів та, пов'язане з цим, збудження електронів від верхнього заповненого краю валентної зони (VB) до нижнього вільного краю зони провідності (CB) з вищим енергетичним рівнем. Передумовою цього процесу є поглинання енергії випромінювання, яка є більшою або дорівнює ширині забороненої зони.

Важливою областю застосування титан (IV) оксиду та інших напівпровідників як фотокаталізаторів є охорона навколишнього середовища. У найближчі кілька десятиліть роль захисту водних об'єктів та очищення питних і стічних вод зростатиме. Ще однією важливою областю застосування для фотоактивних напівпровідників є розкладання полютантів, що містяться в повітрі.

Ключові слова: титан (IV) оксид, анатаз, фотокаталіз, напівпровідник, зона провідності, валентна зона.

Introduction. Titanium (IV) oxide is an inorganic white compound that has been used by industry for over 100 years. Today it is an important commercial product. Global production of TiO_2 amounted to 5080 thousand tons in 2004. The titanium (IV) oxide market continues to develop rapidly. First of all, it is characterized by the possibility of wide consumption of this compound in various industries [1–2].

Table 1

Properties of TiO_2 modifications [14–16]

Characteristics	Rutile	Anatase	Brookite
Band gap, eV	3,0	3,2	3,1
Crystal lattice	Tetragonal	Tetragonal	Orthorhombic
Crystal lattice parameters			
a, nm	0.459	0.379	0.918
b, nm	0.459	0.379	0.545
c, nm	0.296	0.951	0.525
Density, g/cm^3	4.21	4.06	4.13
Refractive index (at 550 nm)	2.7	2.5	2.6

Titanium (IV) oxide is a useful semiconductor material that combines unique characteristics such as low cost, simplicity of use, non-toxicity, and resistance to photochemical and chemical degradation [3]. These advantages allow it to be widely used in industry. TiO_2 is mainly used as a pigment in the production of paints, cosmetics, paper, and even as a food additive [4–5]. In addition, it is used as a nanomaterial in many technical fields, such as photocatalysis, electricity generation and storage, and sensor technology [6–7]. Its use is based on the material's properties or on its interaction with other materials or light. For example, the strong opacity of titanium (IV) oxide is due to its high refractive index (>2.5) [5], so it can be used in sunscreen products due to the absorption and scattering of ultraviolet light.

TiO_2 combines interesting properties such as transparency in the visible light, UV absorption, and an exceptionally high refractive index. These material characteristics depend on the respective crystal form, which is described in more detail below. In addition, titanium (IV) oxide is extremely resistant to chemicals and is only soluble in fluoride or hot sulfuric acid [8]. This combination of properties makes TiO_2 a substance suitable for protecting composite and polymeric materials from the harmful effects of natural ultraviolet radiation [10–11].

Modifications of titanium (IV) oxide crystals

Titanium (IV) oxide can exist in various polymorphic forms. The best-known natural modifications of TiO_2 are anatase, rutile, and brookite. Only the first two crystalline forms are used in industry [11].

Among the three modifications, rutile is the most thermodynamically stable form. It is formed from anatase and brookite when heated to a temperature of 600–800°C depending on the atmosphere [5]. Anatase and rutile belong to tetrahedral crystal systems, while brookite belongs to orthorhombic crystal systems. In all three modifications, oxygen atoms are arranged around titanium atoms in the form of curved octahedra. In rutile, the oxygen atoms have a hexagonal tight packing, while in anatase and brookite, they have a cubic tight packing. Half of the octahedral spaces in rutile and tetrahedral spaces in anatase are occupied by titanium cations [12–13].

Table 1 shows some of the properties of TiO_2 modifications. The characteristics of the phases strongly depend on the production conditions. In addition, crystalline TiO_2 is a metal oxide with anisotropic optical and electrical properties. The strength of the anisotropy depends on the crystal structure. For example, rutile exhibits stronger anisotropy than anatase.

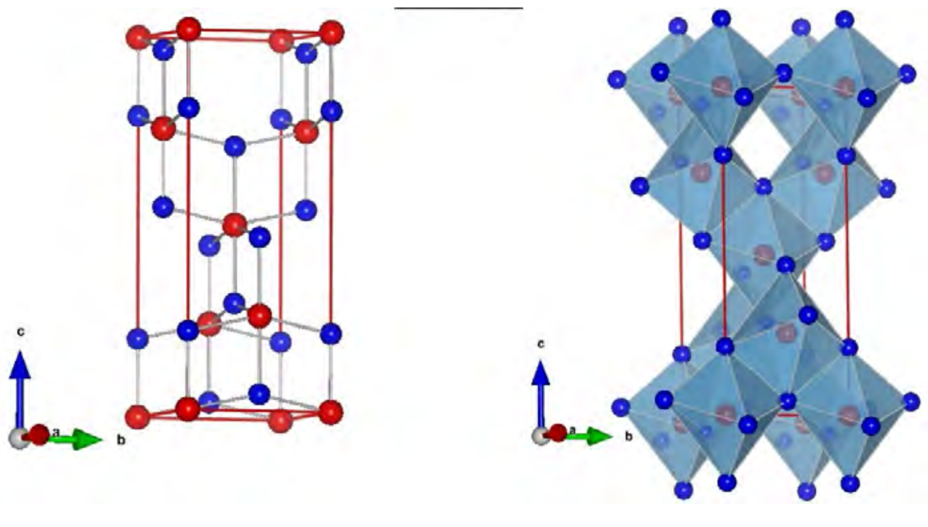

Fig. 1. Schematic representation of a unit cell (left) and a fragment of the crystal structure (right) of anatase. Oxygen atoms are represented by blue spheres, titanium atoms by red ones [16]

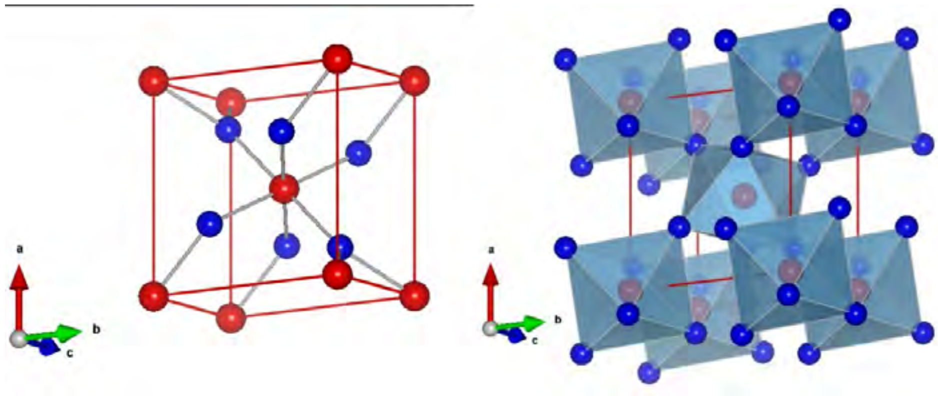

Fig. 2. Schematic representation of a unit cell (left) and a fragment of the crystal structure (right) of rutile. Oxygen atoms are represented by blue spheres, titanium atoms by red ones [16]

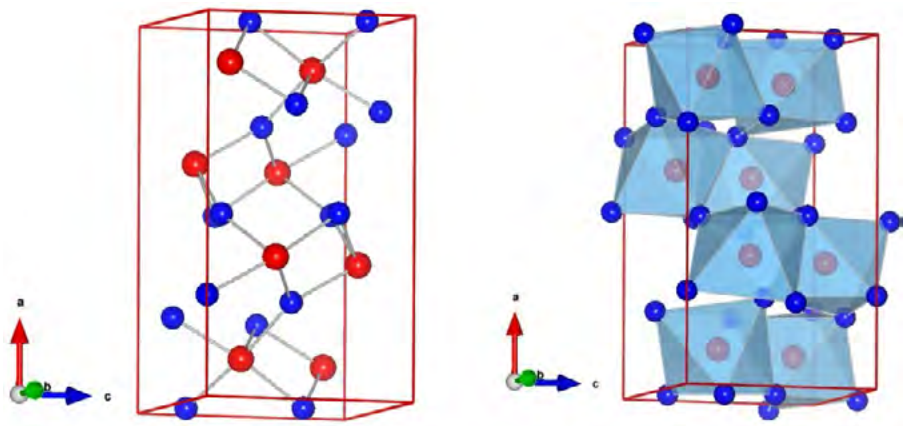

Fig. 3. Schematic representation of a unit cell (left) and a fragment of the crystal structure (right) of brookite. Oxygen atoms are represented by blue spheres, titanium atoms by red ones [16]

Figs. 1–3 schematically depict the unit cells and crystal structure sections of the three TiO_2 modifications. For photocatalytic purposes, the modification of anatase is mainly used. Studies have shown that rutile and brookite can also be highly efficient photocatalysts, but they have not yet gained as much importance as anatase [17–18].

Photocatalytic activity depends on many factors. One of them is the width of the band gap. Titanium (IV) oxide is a semiconductor material and, therefore, has a band gap. For example, the energy gap between the conduction band and the valence band of anatase is 3.2 eV, and that of rutile is 3.0 eV [19–20]. However, energy values were found that differ from those determined earlier. For example, for brookite, the width of the band gap was found to be both smaller and larger than the value of the anatase band gap. Since the exact width of the band gap is unknown, the position of the valence band and conduction band cannot be determined precisely [21]. The upper edge of the valence band determines the oxidation potential, and the lower edge of the conduction band determines the reduction potential (Fig. 4).

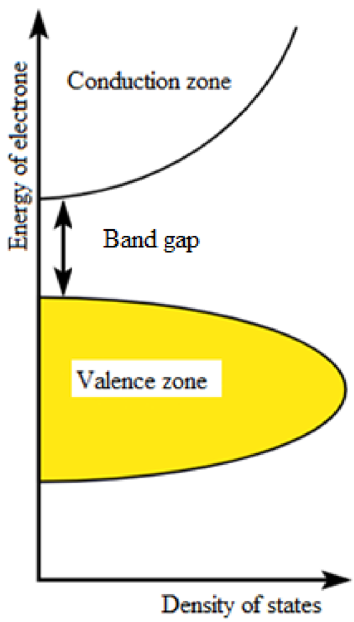

Fig. 4. Band structure of semiconductors [22]

In the case of anatase, it is assumed that the energy levels correspond to the redox potential of the adsorbed molecules. This facilitates the transfer of electrons from titanium (IV) oxide to the adsorbed molecule. Other effects, such as surface and crystal properties, also play a role. The experiments described in [23] showed that a decrease in the recombination rate due to a high degree of crystallinity and an improvement in adsorption capacity due to surface properties may mean that brookite can also be a promising photocatalyst.

Mechanism of photocatalytic processes

The heterogeneous photocatalytic process can be carried out in various media, such as a gas phase, a pure liquid organic phase, and aqueous solutions. Classical heterogeneous photocatalysis can be divided into the following sub-steps [24]:

1) transportation of reagents to the photocatalyst surface;
2) adsorption of reagents on the surface;
3) the chemical reaction itself;
4) desorption of products to the surface;
5) removal of products from the photocatalyst surface.

Photocatalysis of titanium (IV) oxide is based on its semiconductor properties. At the first stage of semiconductor photocatalysis, photon absorption and the associated excitation of electrons from the upper filled edge of the valence band (VB) to the lower free edge of the conduction band (CB) with a higher energy level occur. A prerequisite for this process is the absorption of radiation energy that is greater than or equal to the width of the band gap. In the case of TiO_2 in the anatase modification, the energy difference between the conduction band and the valence band corresponds to near-infrared radiation (315–400 nm). The absorption of radiation leads to an increase in the energy of the electron in the conduction band (e_{CB}^-). At the same time, a defect appears in the valence zone with a positive charge (h_{VB}^+). Negative and positive charges form electron-hole pairs (excitons) due to the Coulomb attraction forces. If the recombination of opposite charges has not yet occurred inside or on the surface of the semiconductor, they are available on the surface to react with adsorbed organic and inorganic compounds [25]. Fig. 5 shows a simplified model of the photocatalytic process using titanium (IV) oxide as an example.

The main reason for the excellent photocatalytic properties of titanium (IV) oxide is the high oxidizing activity of photogenerated h^+ charges in a semiconductor whose redox potential at pH 7 is about +2.53 V relative to a standard hydrogen electrode [25]. The redox potential of the corresponding electrons is only -0.52 V relative to a standard hydrogen electrode, but this is sufficient for the formation of superoxide radicals ($O_2^{\bullet-}$) and hydrogen peroxide (H_2O_2). Positive charges h^+ either react directly with the adsorbed organic compounds or initially with water, whereby hydroxyl ions are oxidized to hydroxyl radicals ($OH^{\bullet}$). These, in turn, can combine to form reactive hydrogen peroxide. The formation of singlet molecular oxygen is also possible $^1O_2$. All reactive radicals formed are capable of decomposing pollutants [25]. The radicals either react directly on the TiO_2 surface with adsorbed compounds (heterogeneous photocatalytic process) or transfer to the gas phase and initiate the decomposition of gaseous reagents there (homogeneous catalytic process).

Application of the photocatalytic processes onto TiO_2

An important area of application for titanium (IV) oxide and other semiconductors as photocatalysts is environmental protection. In the next few decades, the role of water bodies protection, drinking water treatment, and wastewater purification will grow in importance. Another important application area of photoactive semiconductors is the decomposition of pollutants in the air. In the case of titanium (IV) oxide, many applications have been described. Test facilities already exist to investigate the industrial use of the photocatalytic process. Titanium (IV) oxide is also used in the construction sector. Photoactive facades, glass, roof tiles and similar products can, in addition to preserving the aesthetics of a building, help reduce the level of air pollutants. Some examples of the use of photocatalytic processes on TiO_2 are presented below.

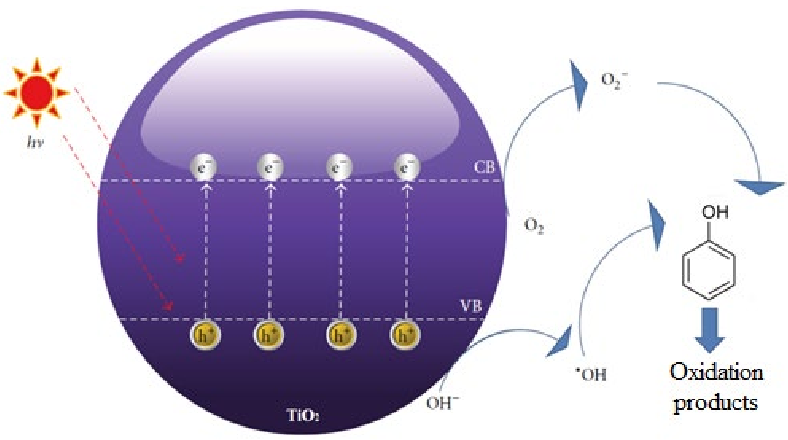

Fig. 5. Scheme of the photocatalytic process on the example of TiO_2 [26]

Nitrogen oxides NO_x represent an important group of air pollutants that accumulate in cities with heavy traffic. By using titanium (IV) oxide as a photocatalyst, these gases can be oxidized and converted into harmless compounds. Building facades can be used as catalyst application surfaces. In the case of NO_x oxidation, it is adsorbed on the TiO_2 surface and oxidized to nitrate by superoxide and hydroxyl radicals, which are also adsorbed. Nitrate is then desorbed from the surface in the form of nitric acid or bound to the main components of building materials [23]. A diagram of this process is shown in Fig. 6.

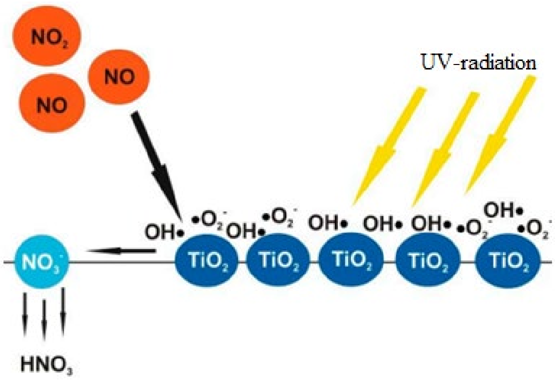

Fig. 6. Schematic representation of NO_x oxidation by titanium (IV) oxide under sunlight [28]

Similar to the oxidation of NO_x, another hazardous air pollutant, formaldehyde, is also decomposed. The photocatalytic decomposition of formaldehyde is similar to the process described above [25]. It is also adsorbed on the surface of the semiconductor, where it is decomposed by radicals, forming the final products – carbon dioxide and water. In [25], results were presented in which a building material containing titanium dioxide acts as a photocatalyst in the decomposition of hydrocarbons in the gas phase. Titanium (IV) oxide can also be successfully used to remove fluorinated hydrocarbons from the air, which are present in large quantities in the atmosphere [26].

The treatment of drinking and process water is another area of application for photocatalysis on TiO_2. For example, [25] shows that various pollutants in wastewater can be broken down using titanium (IV) oxide. TiO_2 can also be successfully used as a photocatalyst in the treatment of drinking water [26]. Not only the decomposition of organic pollutants, but also the decomposition of microorganisms using titanium (IV) oxide has been studied. In addition to the decomposition of pollutants in aqueous solutions and in the gas phase, the self-cleaning properties of TiO_2 are also used in various products. These self-cleaning surfaces are based on the superhydrophilicity of TiO_2, for example, mirrors on which moisture does not condense.

For the purposes presented, particles consisting of a core and a shell can also be used. Since photocatalysis is a surface phenomenon, TiO_2 can be coated on the surface of the core, and thus the particle will have the same properties as pure titanium (IV) oxide. If the core is made of an inexpensive, readily available inert material (an industrial by-product, such as silica dust), the price of the photocatalyst will decrease without reducing its functionality [24]. Another advantage of using a core is the ability to introduce new properties into the system. For example, it is possible to make the core from a material that has magnetic properties, which will help to separate the photocatalyst more easily from the process solution to be purified. Several promising approaches are presented in [25–26].

Treatment of waste, drinking and process water is one of the most important applications for titanium (IV) oxide photocatalysis. In addition, building materials containing TiO_2 can contribute to environmental protection as they can decompose air pollutants such as NO_x.

Water purification from organic pollutants by TiO_2

Water pollution has become a serious environmental problem around the world today [24]. Wastewater treatment is based on various mechanical, biological, physical and chemical processes. Once the particles are removed in suspension, biological treatment remains the ideal process for wastewater treatment, especially at low pollutant concentrations. However, some organic pollutants are not biodegradable. Despite their low concentration, these pollutants cause serious health problems due to their high ability to disrupt the endocrine system and genotoxicity [25]. Therefore, the effective removal of these pollutants is of great interest.

One of the most promising methods of wastewater treatment is heterogeneous catalysis due to mild operating conditions, a wide range of pollutants capable of decomposition, and its high efficiency until the complete mineralization of organic matter to carbon dioxide and water [26]. Titanium (IV) oxide is the most widely used photocatalyst. It shows high efficiency in the complete mineralization of various biologically persistent organic substances, such as organochlorine compounds, organic acids, pesticides, herbicides, and dyes [23].

In [24], the photocatalytic decomposition of tetracycline, a widely used antibiotic in the world, was analyzed. Photocatalysis removes more than 95% of tetracycline within 40 minutes under UV radiation. The concentration of tetracycline was 40 mg/dm^3 and the concentration of TiO_2 was 1000 mg/dm^3. The efficiency of antibiotic decomposition improved in the presence of dissolved oxygen. Within 60 minutes, 60% of total organic carbon was also removed. The degradation of tetracycline includes electron transfer, hydroxylation, open ring reactions, and cleavage of the central carbon. One of the end products of degradation is NH_4^+.

The effect of the pollutant concentration was studied in [25–26] using the methylene blue dye as an example. The photocatalytic decomposition of the pollutant decreased with an increase in the initial concentration of the dye from 5 to 20 mg/dm^3. This is because ultraviolet light passes through the titanium (IV) oxide irradiation solution more easily when the initial dye concentration is lower. At high concentrations, a large amount of the pollutant is adsorbed to the TiO_2 particles, which prevents the dye molecule from reacting with free radicals and electron holes. With an initial concentration of methylene blue of 5 mg/dm^3, its residual concentration after 5 hours is zero.

Phenolic compounds are major environmental pollutants due to their widespread use in various industries. They are highly toxic with carcinogenic and mutagenic properties at low concentrations. Photocatalysis is a promising method for the destruction of phenols in wastewater [24]. With an increase in the concentration of phenol, its degree of decomposition decreases: with a pollutant content of 100 mg/dm^3 in wastewater, the degree of decomposition is 18%, with a content of 10 mg/dm^3 – 88% [26].

References

1. Ola O., Maroto-Valer M. Review of material design and reactor engineering on TiO_2 photocatalysis for CO_2 reduction. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2015. № 24. P. 16–42.
2. Strini A., Cassese S., Schiavi L. Measurement of benzene, toluene, ethylbenzene and o-xylene gas phase photodegradation by titanium dioxide dispersed in cementitious materials using a mixed flow reactor. *Applied Catalysis*. 2005. № 61. P. 90–97.
3. Sharmila Devi R., Venckatesh Dr. R., Rajeshwari S. Dr. Synthesis of Titanium Dioxide Nanoparticles by Sol-Gel Technique. *International Journal of Innovative Research in Science, Engineering and Technology.* 2014. Vol. 3, № 8, P. 15206–15211.
4. Chen X., Mao S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical Reviews.* 2007. № 7. P. 2891–2959.
5. Hanaor D., Sorrell C. Review of the anatase to rutile phase transformation. *Journal of Materials science*. 2011. № 46. P. 855–874.
6. Chen X., Liu L., Yu P. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science*. 2011. № 331. P. 746–750.
7. Controlling Adsorption Structure of Eosin Y Dye on Nanocrystalline TiO_2 Films for Improved Photovoltaic Performances / F. Zhang et. al. *The Journal of Physical Chemistry*. 2013. № 117. P. 14659–14666.
8. Exploring potential Environmental applications of TiO_2 Nanoparticles / A. J. Haider et. al. *Energy Procedia*. 2017. № 119. P. 332–345.
9. Brookite versus anatase TiO_2 photocatalysts: phase transformations and photocatalytic activities / T. A. Kandiel et. al. *Photochemical and Photobiological Sciences*. 2013. Vol. 12, № 4. P. 602–609.
10. Electrochemical and optical properties of TiO_2 nanoparticles/polytyramine composite film / A. Ehsani et. al. *Journal of Electroanalytical Chemistry*. 2014. № 713. P. 91–97.
11. Solvothermal Synthesis of TiO_2 Nanocrystal Colloids from Peroxotitanate Complex Solution and Their Photocatalytic Activities / J. Liao et. al. *Journal of Physical Chemistry*. 2009. № 113. P. 18778–18783.
12. Controllable synthesis of spherical hydroxyapatite nanoparticles using inverse microemulsion method / X. Ma et. al. *Materials Chemistry and Physics*. 2016. № 183. P. 220–229.
13. Synthesis of TiO_2 particles by reverse microemulsion method using nonionic surfactants with different hydrophilic and hydrophobic group and their photocatalytic activity / M. S. Lee at. Al. *Catalysis Today*. 2005. № 101. P. 283–290.
14. An overview of titanium deposits in Norway / A. Korneliussen at. al. *Norges geologiske undersøkelse Bulletin*. 2000. № 436. P. 27–38.
15. Hydrothermal Synthesis, Characterization and Photocatalytic Activity of Nanosized TiO_2 Based Catalysts for Rhodamine B Degradation / F. Sayilkan et. al. *Turkish Journal of Chemistry*. 2007. № 31. P. 211–221.
16. Progress in the synthesis and applications of hierarchical flower-like TiO_2 nanostructures / Z. Wu et. al. *Particuology*. 2013. № 15. P. 61–70.
17. Monodisperse rutile microspheres with ultrasmall nanorods on surfaces: Synthesis, characterization, luminescence, and photocatalysis / Y. Tian et. al. *Journal of Colloid and Interface Science*. 2012. № 385. P. 1–7.
18. Solvothermal synthesis of nanocrystalline TiO_2 in toluene with surfactant / C.-S. Kim et. al. *Journal of Crystal Growth*. 2003. № 257. P. 309–315.
19. Landmann M., Rauls E., Schmidt W. The electronic structure and optical response of rutile, anatase and brookite TiO_2. *Journal of Physics: Condensed Matter*. 2012. № 24. P. 1–6.
20. Hashimoto K., Irie H., Fujishima A. TiO_2 Photocatalysis: A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics*. 2005. № 44. P. 8269–8285.
21. Paola A., Bellardita M., Palmisano L. Brookite, the Least Known TiO_2 Photocatalyst. *Catalysis*. 2013. № 3. P. 36–73.
22. Solvothermal Synthesis of TiO_2 Nanocrystal Colloids from Peroxotitanate Complex Solution and Their Photocatalytic Activities / J. Liao et. al. *Journal of Physical Chemistry*. 2009. № 113. P. 18778–18783.
23. Highly photocatalytic activity of brookite/rutile TiO_2 nanocrystals with semi-embedded structure / Y. Cao et. al. *Applied Catalysis B: Environmental*. 2015. № 180. P. 551–558.
24. Ahmed S., Haider W. Heterogeneous photocatalysis and its potential applications in water and wastewater treatment: a review. *Nanotechnology*. 2018. Vol. 29, № 34. P. 1361–1369.
25. Kaneko M., Okura I. Photocatalysis: Science and Technology. *Springer*. 2002. Vol. 3., № 160. P. 225–239.
26. Haider A. J., Jameel Z. N., Al-Hussaini H. M. Review on: Titanium Dioxide Applications. *Energy Procedia*. 2019. № 157. P. 17–29.