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Ways to Improve the Efficiency of TiO_2-based Photocatalysts (Review)

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Water and air pollutants pose a significant environmental problem worldwide and photocatalysis is one way to address this global issue. Photocatalytic degradation of toxic substances under the influence of visible electromagnetic radiation is widely used for wastewater treatment. The most promising method of pollutant removal is the use of photocatalysts based on titanium (IV) oxide, which are recognized as one of the most effective due to chemical resistance, non-toxicity and low cost. However, their practical application is limited by the rapid recombination of photogenerated charge carriers and selective absorption of light in the UV region due to the large width of band gap. To solve this scientific and practical problem, it is necessary to modify the TiO_2 surface, for example, through metallic or nonmetallic doping, in order to increase its photocatalytic activity due to additional absorption in the visible range of the spectrum. This review presents an analysis of current research on ways to increase the efficiency of TiO_2-based photocatalysts.

Keywords: titanium dioxide, photocatalysis, degradation, photocatalytic activity, doping.

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Content

Introduction

Environmental pollution, caused by both natural and anthropogenic factors, requires the search for new approaches to the disposal of harmful substances concentrated in particular in water bodies and in the air. Photocatalysis is one of the solutions to improve the environment [1].

There are many typical photocatalytic processes, such as water splitting, pollutant degradation, selective organic conversion, and CO_2 restoration for fuel production [2]. Considerable attention in the study of catalytic processes is paid to the use of nanostructured semiconductors to remove both organic and inorganic contaminants from aqueous or gas-phase systems [3]. Photocatalytic processes are widely used in industry for photocatalytic purification of water and air, conversion of solar energy to chemical and electrical ones, in the processes of organic synthesis, etc. Various combinations of homogeneous and heterogeneous photocatalysis are effectively used in wastewater and air treatment from organic pollutants. The processes are based on the formation of a strong oxidant-hydroxyl radical $OH^{\bullet}$, which is able to quickly and non-selectively oxidize a huge amount of organic matter until their complete mineralization [4, 5].

Photocatalytic degradation of toxic organic substances under the influence of visible electromagnetic radiation has become widely used for wastewater treatment. Purification systems mainly use heterogeneous semiconductor photocatalysts based on titanium (IV) oxide. Since Fujishima and Honda [6] reported the photocatalytic activity of TiO_2 under UV light in water

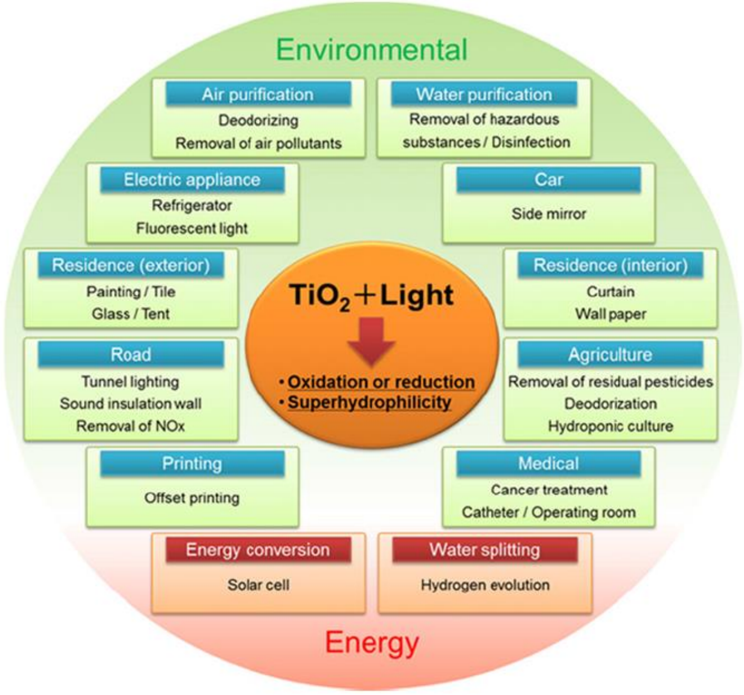

Fig. 1. Application of photocatalysts based on TiO_2 [7].

fission reactions in 1972, TiO_2 has become one of the most effective and widely used materials in the field of photocatalysis (Fig. 1 [7]). This is due to its significant photocatalytic activity, high chemical stability and redox capacity, low cost and no toxicity [3-5, 8, 9]. However, photocatalysis using TiO_2 has many significant disadvantages. In particular, the band gap of TiO_2 (energy range in electronic band structure determining light absorbtion and photocatalytic properties) is 3.0 - 3.2 eV. The absorption band lies in the ultraviolet range, so the photocatalytic efficiency under visible light is rtestricted [3]. UV radiation accounts for only about 4 % of the total solar spectrum, which significantly limits the use of TiO_2 as photocatalyst. Therefore, the aim of numerous studies on TiO_2 is to improve absorption of visible and infrared radiation [8, 10]. Quantum yield of photo-transformation on TiO_2 surface is rather low, which is associated with a high degree of recombination of charge carriers, low specific surface area and low adsorption capacity [4, 5, 9].

The very important scientific and practical task is creation of TiO_2-based catalysts with narrower band gap, which would work in the visible range of radiation. To solve this task, it is proposed to modify TiO_2 structure or create nanocomposites with titania [4]. One of the methods of increasing the photocatalytic activity of TiO_2-based catalysts is the application of TiO_2 to a suitable carrier, which makes it possible to increase the specific surface area of the catalysts and to facilitate access of the reactants to the active TiO_2 centers. Another method is the doping of TiO_2 with nonmetal atoms or nanoparticles of metals. This guarantees additional absorption in the visible range of the spectrum and at the same time increases the efficiency of the charge separation process [5]. Therefore, the purpose of this review was to study the basic principles of photocatalysis and ways to increase the photocatalytic activity of TiO_2, in particular the method of doping the surface of TiO_2 with metals and nonmetals.

I. Basic principles of photocatalysis

The shortest definition of the term "photocatalysis" is the one proposed by IUPAC: photocatalysis is a catalytic reaction involving the absorption of light by a catalyst or substrate. Based on this formulation, a more expanded and concretized interpretation of this concept was proposed [11]: photocatalysis is the phenomenon of induction or acceleration of chemical transformations under the action of light on systems containing chemical compounds – reaction substrates and substances called catalysts or photocatalysts that participate in intermediate transformations, but are not included stoichiometrically in the total process.

The main features of photocatalytic reactions [11] are the following:

1) the reactions take place under the action of light from a longer wavelength part of the spectrum than the light absorbed by the reactants – the catalyst performs the function of a sensitizer;

2) the primary process is the phototransfer of an electron inside the catalyst molecules or its complexes with the oxidant;

3) primary products of the photocatalytic reaction are free radicals or ion radicals;

4) the catalyst, undergoing continuous redox transformation under the action of oxygen and other substances, is constantly updated.

It follows that the catalyst, which has these features, can rightly be called a photocatalyst.

When considering photocatalytic systems, three features are important: which of the components is activated by light, the phase composition of the system and the belonging of the photocatalyst to the class of semiconductors or the class of transition metal complexes [11].

The photocatalytic reaction is initiated when the photocatalyst (PC) absorbs a quantum of light and goes into an excited state [5]:

$$PC + h\nu \rightarrow PC^{**} \qquad (1)$$

The electronically excited state does not last long and the photocatalyst quickly goes into the ground state or in another lower energy state. This process is accompanied by the release of heat or light energy. Similar processes in photocatalysis on semiconductors (SC) correspond to the formation of an electron-hole pair (e^- and h+), which are quite mobile and extremely reactive. Some of them recombine during motion in the semiconductor particle, and the rest come to the surface and are kept there [5].

The excited photocatalyst has a high redox potential of approximately –0.1 and +3 V relative to the normal hydrogen electrode for the electron and hole, respectively. Therefore, the presence of an electron-hole pair (e^- and h+) generates such chain reactions [3, 5]:

photoinduction: $SC + h\nu \rightarrow e^- + h^+$; (2)

oxygen adsorption: $(O_2)_{ads} + e^- \rightarrow O_2\bullet^-$; (3)

ionization of water: $H_2O \rightarrow OH^- + H^+$; (4)

protonation: $O_2\bullet^- + H^+ \rightarrow HOO\bullet$. (5)

The mechanism of photocatalytic processes, including chemical reactions, is shown in Fig. 2 [1]. Photocatalytic processes are quite complex and depend on many factors, namely the intensity of light, the nature and concentration of the substrate and photocatalyst, the pH of the medium and the reaction temperature [5].

1.1. Photocatalytic activity of TiO_2

Natural TiO_2 has three polymorphs: anatase, rutile and brookite (Fig. 3) [12]. Rutile and anatase are the modifications mainly used in photocatalysis. Anatase and rutile have crystalline tetragonal structures consisting of TiO_6 octahedra. In anatase, TiO_6 octahedra have common edges lying in the plane (001) and (100). Each octahedron has four common edges with neighbors that form zigzag chains. In rutile, TiO_2 octahedra are connected by ribs in the (001) plane with two adjacent octahedra and form long ribbons in the crystal lattice [13, 14]. The difference in the structural lattices of anatase and rutile determines their different density and electronic band structure. Therefore, the absorption of light by anatase and rutile is at a wavelength of 388 and 413 nm, respectively [4, 15].

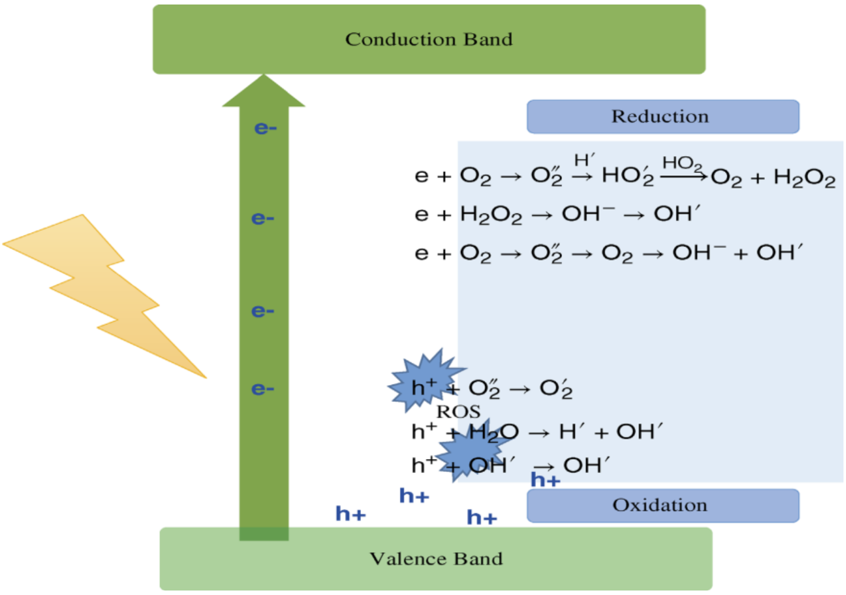

Fig. 2. The mechanism of photocatalysis [1].

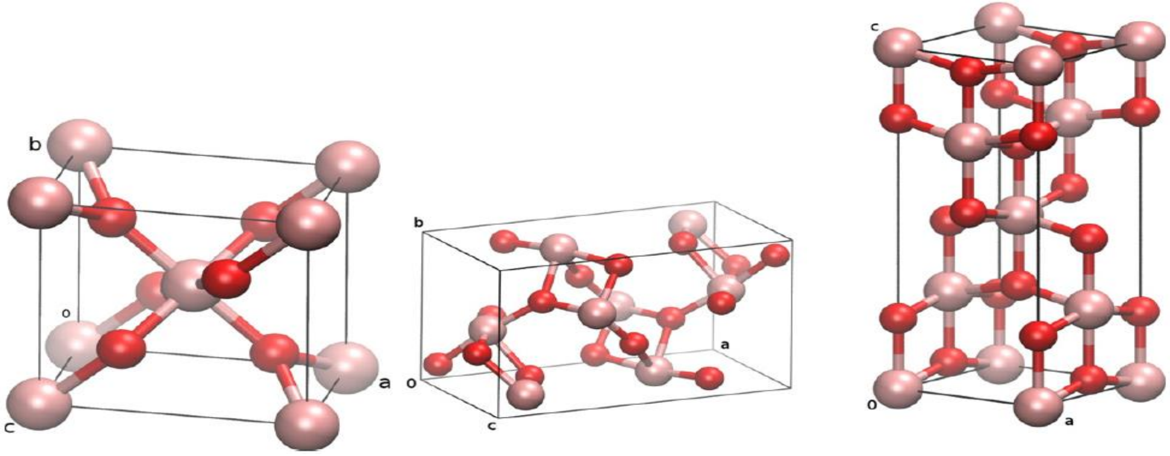

Fig. 3. Polymorphic modifications of TiO_2: a) rutile; b) brookite; c) anatase [12].

Rutile has a higher photocatalytic activity than anatase, which is probably due to its smaller width of the band gap. The width of the band gap is a very important parameter for photocatalysis because it controls the rate of electron transfer and hence the rate of charge recombination [16].

Formation of the photoactive surface TiO_2 includes the appearance of holes in the valence zone (h^+) and electrons in the conduction zone (e^-) due to the absorption of photon energy. The last must be greater than or equal to the width of the band gap of TiO_2 (for rutile – 3.0 eV, for anatase – 3.2 eV [8]). The holes contribute to the formation of hydroxyl radicals and oxidation of organic compounds, and electrons contribute formation of peroxide radicals and decomposition/ oxidation reactions [4].

Hydroxide and peroxide radicals are formed according to the following reactions [17]:

$$TiO_2 + h \rightarrow TiO_2\,(e^-\,CB + h^+VB); \qquad (6)$$

$$TiO_2\,(h^+VB + e^-\,CB) \rightarrow TiO_2\ (\text{recombination}); \qquad (7)$$

$$TiO_2\,(h^+VB) + OH^- \rightarrow TiO_2 + OH^{\bullet}; \qquad (8)$$

$$TiO_2\,(e^-\,CB) + O_2 \rightarrow TiO_2 + O_2^{\bullet}, \qquad (9)$$

where CB is the conduction band and VB is the valence band.

The photocatalytic activity of TiO_2 comprehensively depends on various parameters, in particular, on the properties of TiO_2 (crystallinity, surface area, particle size, defect position, surface charge), as well as on the substrate-surface interaction. In particular, for the effective conduct of the photocatalytic process TiO_2 should have a high specific surface area and small particle sizes. Therefore, the study of photocatalytic activity requires a comprehensive analysis of many parameters [16].

1.2. Influence of chemical state of TiO_2 surface on its photocatalytic activity

The chemical state of TiO_2 surface has a significant effect on photocatalytic activity. The complex of surface physicochemical properties of TiO_2 photocatalysts is shown in Fig. 4 [2]. Surface charge plays an important role in determining the photocatalytic activity, especially for the kinetics of photooxidation of organic dyes. The properties of the surface charge TiO_2 in water at different pH values depend on the point of zero charge pH_{zpc}. Acid-base equilibrium reactions for titanol groups TiO_2 can be written as follows [2, 17]:

$$>Ti\text{–}OH_2^+ \leftrightarrow\ >Ti\text{–}OH + H^+\ (pK_{a1}); \qquad (10)$$

$$>Ti\text{–}OH \leftrightarrow\ >Ti\text{–}O^- + H^+\ (pK_{a2}). \qquad (11)$$

The average value of pK $(pK_{a1}+pK_{a2}) / 2$ corresponds to the pH of the zero charge point. The point of zero charge, pH_{zpc}, is obtained experimentally by measuring the electrokinetic potential (zeta potential) of the suspended particles at different pH values. For example, the pH_{zpc} of titanium dioxide P25 from Degussa is ~ 6.2 (pK_{a1} =4,5 and pK_{a2} = 8) [18]. At $pH < 6.2$ the surface of TiO_2 particles is positively charged, and at $pH > 6.2$ it has a negative charge [2, 17]. More efficient generation of hydroxyl radicals TiO_2 is achieved by a weak alkaline medium due to the optimal concentration of OH^-, which contributes to the photocatalytic degradation of organic compounds in aqueous solution [2].

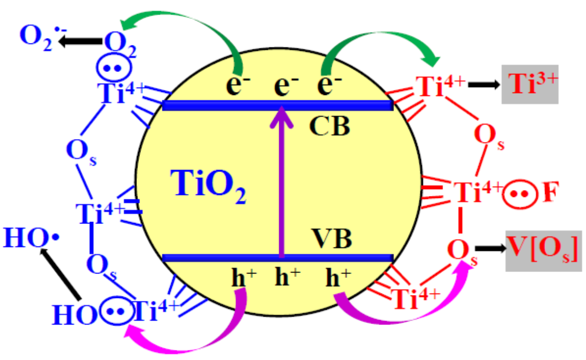

Fig. 4. Chemical state of the surface of modified photocatalysts based on TiO_2 [2].

The pH of the solution also changes the energy levels of TiO_2 according to Nernst (–59 mV/pH) due to the pH dependence of the surface charge [17]:

$$E_{CB}(V\ vs\ NHE) = -0.1 - 0.059pH. \qquad (12)$$

II. Effect of chemical modification of TiO_2 on its photocatalytic activity

Impurity-free (chemically pure) TiO_2 usually has unfavorable dynamics of charge transfer and the width of the band gap. Therefore, it is necessary to change the chemical state of the TiO_2 surface to improve photocatalytic activity. Based on the mechanism of photocatalysis, the following basic surface modification strategies can be identified for the development of highly active photocatalysts based on TiO_2 [2]:

1) reducing the width of the band gap by doping;
2) layering visible light photosensitizers on TiO_2 to increase the available part of the solar spectrum;
3) creation of surface heterojunctions to improve the dynamics of the charge carrier;
4) loading of nanosized cocatalysts to inhibit surface charge recombination processes;
5) increasing the available surface areas to improve photocatalytic activity;
6) introduction of surface F-effects in TiO_2 to increase the concentration of free radicals OH●, thereby increasing the efficiency of photodegradation;
7) irradiation of highly reactive faces to increase the surface-active areas and redox capacity.

Many studies have been conducted to develop a TiO_2-based photocatalyst that would absorb a photon in the visible light region and have a low electron-hole recombination coefficient [10, 19].

2.1. Modification of TiO_2 by metals

Modification of TiO_2 with cationic dopants, in particular precious (Au, Ag, Ru, Rh, Pd, Os, Ir, Pt) [20–28], transitional (Cu, Co, Ni, Cr, Mn, Mo, Nb, V, W, Zn, Fe, Sn etc.) [29–43] and rare earth (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd, Yb, etc.) [44-48] metals is widely studied. Deposition of metal on semiconductor nanoparticles is an important factor in achieving maximum efficiency of the photocatalytic reaction [14]. Dopants change the chemical nature and electronic structure of the doped oxide. TiO_2 performance is improved by narrowing the energy band gap, which leads to increased photoactivity in the visible region of the spectrum [13, 49].

The authors [21] investigate the photocatalytic reduction of methyl orange (MO) on Au/TiO_2 semiconductors. In the presence of gold, there is a shift of the band gap from 3.2 eV (Degussa P25) to 2.9-2.8 eV (Au/TiO_2). For Au/TiO_2 semiconductors, high catalytic activity for MO reduction was obtained, and the reduction rate constant improved 3.2 times compared to undoped TiO_2. The results of the study indicate the important role of Au in the photoreduction reactions of organic compounds. In another study [22], a 9-fold increase in the photocatalytic decomposition of methyl orange under visible light was observed by integrating plasmonic Au nanoparticles with TiO_2. Irradiation of Au nanoparticles at their resonant frequency creates intense electric fields that can be used to increase the rate of electron-hole pair generation in semiconductors. In a study [23], the authors synthesized plasmonic Au/TiO_2 nanohybrids by chemical attachment of Au nanoparticles to TiO_2 nanostructures. Au/TiO_2 nanohybrids degraded methylene blue (MB), methyl orange (MO), mixture of MB and MO and 4-nitrophenol in water under sunlight. It was found that the degradation efficiency is 94 % with MB, 85 % with MO and 87% with MB + MO in just 20 minutes when irradiated with sunlight. The photocatalytic activity of Au/TiO_2 was 3.3 times greater than that of unmodified TiO_2.

Spherical nanoparticles noble metal / titanium (IV) oxide in work [24] were synthesized by laser pyrolysis (CW CO_2, 10.6 μm; ethylene as a sensitizer) followed by impregnation with three aqueous solutions of precursors of precious metals ($AgNO_3$ (Chemical Company, purity 99.5 %), $KAuCl_4$ (Fisher, purity 98 %), $H_2PtCl_6 \cdot 6H_2O$ (Merk, purity 99.95 %)) and reduction involving $NaBH_4$ (Aldrich, purity 98 %). TiO_2-based nanocomposites loaded with precious metals (0.01 - 0.28%) show a decrease in the width of the band gap (up to 2.77 eV) due to two factors: atmospheric pressure in the method of laser pyrolysis and the addition of metal to the surface of TiO_2 nanoparticles through surface plasmon resonance. Photocatalytic parameters of the nanocomposites in the visible and UV range indicate that Ag/TiO_2 is a highly effective catalyst in the photodegradation of aqueous MO (the rate constant for the UV range is $28.74x10^{-3}min^{-1}$ and for the visible range is $16.78x10^{-3}min^{-1}$). Therefore, doping of TiO_2 with precious metals increases the efficiency of photodegradation of pollutants and contributes to the development of environmentally friendly methods for water purification [24]. In a study [26], modification of TiO_2 nanotubes by Ag nanoparticles increased the efficiency of photoconversion (11.68 %) and the rate of hydrogen evolution (10.69 mmol / h) under UV radiation. The modification reduced electron-hole recombination and improved photocatalytic activity. The authors [28] synthesized monometallic Au-TiO_2 and Pt-TiO_2 and bimetallic Pt/Au-TiO_2 nanocomposites by the sol-gel method. Photocatalytic activity in visible light ($\lambda > 420$ nm and $\lambda > 455$ nm) was evaluated by the degradation of phenol in aqueous medium. The best photocatalytic activity was observed for the samples (0.5)Pt-TiO_2 and (0.5Pt/(0.5)Au-TiO_2.

The authors [31] synthesized V-containing TiO_2 and investigated its photocatalytic activity in the degradation of water-soluble PCP-Na during solar irradiation. XPS analysis showed that vanadium exists in the forms V^{4+} and V^{5+} on the surface of TiO_2, and V^{5+} is the dominant component, the content of which is 3.5 times higher than V^{4+}. The width of the band gap decreases from 2.91 eV to 2.71 and 2.57 eV with vanadium doping of 0.5 and 1 atomic %, respectively. Nanoaggregates of V/TiO_2 with the addition 0.5 atomic % of V showed optimal photocatalytic degradation activity.

In study [33], porous TiO_2 doped with Mo/V/W transition metals ions was synthesized on commercial pure titanium (Cp-Ti) by electrolytic plasma oxidation for photocatalytic applications in wastewater treatment. The effect of doping of transition metal ions on the phase composition of TiO_2 coating, surface morphology, corrosion, wettability, width of the band gap, charge separation and electron-hole recombination rate was investigated (Fig. 5). Doped TiO_2 samples showed high surface porosity and active surface area, thereby enhancing photocatalytic activity. W/TiO_2 samples showed good charge separation with 95 % degradation and 71% mineralization of the methylene blue dye when irradiated with visible light for 180 min.

The authors [35] investigated the photocatalytic oxidation of gaseous benzene, toluene and xylene under UV and visible irradiation over Mn-doped TiO_2 nanoparticles. The efficiency of photocatalytic decomposition and oxidation products were determined. The main products of the final oxidation by UV photocatalysis were CO_2, CO and H_2O. The decomposition of benzene, toluene and xylene over Mn-TiO_2 under UV irradiation and in the presence of oxygen is quite high, which leads to the release of CO_2 and CO with a yield of 92.6 %, 82.9 % and 75 %, respectively. The percentage of conversion of benzene, toluene and xylene to CO_2 was 63.6 %, 56.4 %, 51.8 % and to CO 29 %, 26.5 %, 23.2 %, respectively.

In [37], the authors investigated iron-doped TiO_2 nanoparticles. The reflectance spectra showed enhanced light absorption in the visible region (wavelength greater than 400 nm) for Fe-doped TiO_2. The photocatalytic activity of the samples was investigated by the method of degradation of the dye reactive orange 16 under UV irradiation. The results indicate that the photocatalytic activity of Fe/TiO_2 is greater than that of unmodified TiO_2, due to the smaller crystal size, larger surface area, and greater ability to absorb light. In study [38], the photocatalytic activity of Fe-doped TiO_2 powders was evaluated using methylene blue (MB). Degradation experiments were performed when irradiated with simulated sunlight. It is shown that TiO_2 doped with 0.1 wt.% Fe has the highest activity in the photocatalytic degradation of MB. In work [39] photocatalysts Fe/TiO_2 (0.05 - 1 mol% Fe) were synthesized to study the degradation of organic pollutants (MO and 4-CP) during irradiation with light with a wavelength ≥ 320 nm. The results showed that TiO_2 doped with 0.1 mol% Fe showed the highest photocatalytic activity for degradation reactions. It is proved that the increased

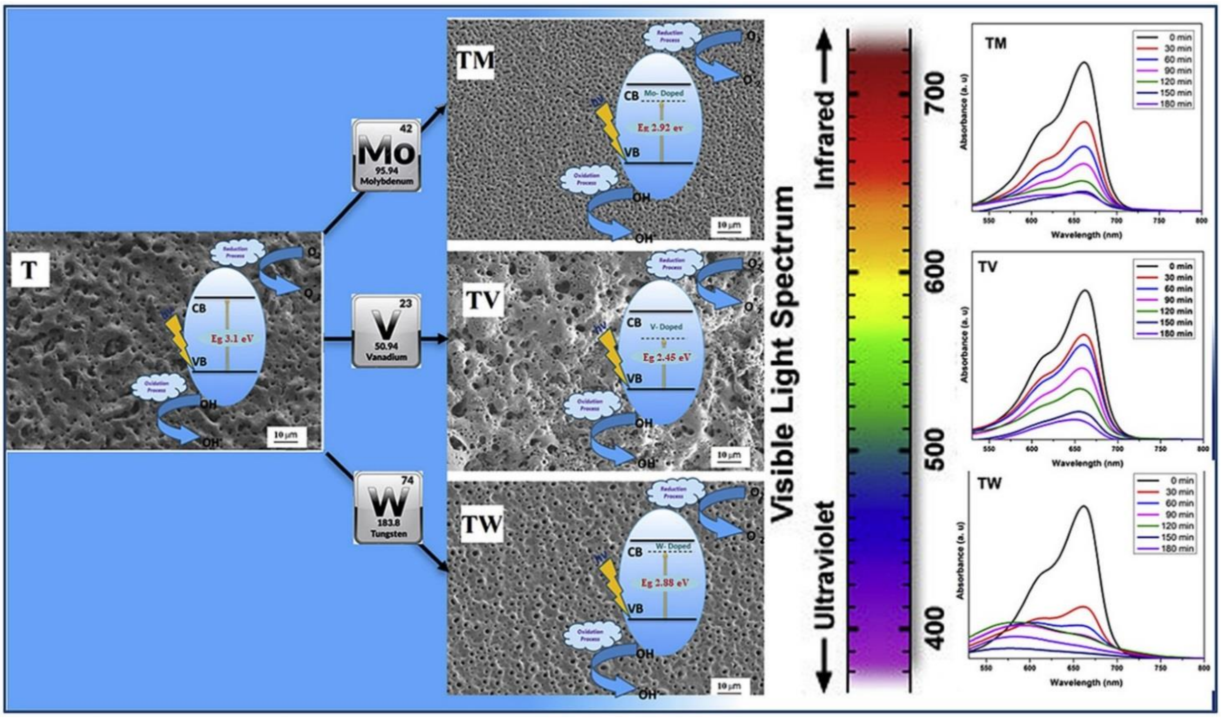

Fig. 5. Photocatalytic properties of Mo/V/W-doped TiO_2 samples [33].

surface area, small particle size and enhanced absorption of visible light are the reasons for improving the photocatalytic activity of doped materials. The authors of [40] studied the photocatalytic activity of nanocrystalline Fe/TiO_2 films. Analysis of nanofilms shows a decrease in the size of the crystallites with increasing concentration of Fe^{3+} (14 nm for 1 % Fe and 8 nm for 7 % Fe) and a high specific surface area. The width of the TiO_2 band gap decreases from 3.32 to 2.57 eV. Photocatalytic activity was determined by the decomposition of methylene blue when irradiated with visible light. The results showed that Fe/TiO_2 nanofilms show a high level of photocatalytic activity due to iron doping.

In work [42], using sol-gel method, TiO_2 nanomaterials doped with Ni, Cu and Fe were synthesized and their photocatalytic activity during degradation of 4-chlorophenol (4-CP) and naproxen (NPX) sodium as water pollutants was evaluated under the influence of UV radiation. It was found that T-Cu 1.0 was the best material during the degradation of 4-CP, with a degradation efficiency of 90 % ($0.1827\ L\cdot g^{-1}\cdot min^{-1}$) after 6 hours of reaction, and T-Fe 1.0 – during the degradation of NPX, with a degradation efficiency of 97 % ($0.1111\ L\cdot g^{-1}\cdot min^{-1}$) also after 6 hours of reaction. The authors [43] synthesized nanopowders of titanium (IV) oxide doped with Co and Ni. The photocatalytic activity of the samples was evaluated using a test for photodegradation of 10 mg / L solution of methylene blue under UV irradiation. The efficiency of photocatalysis was increased by the presence of Co and Ni as dopants in TiO_2 crystal lattice, compared with unmodified TiO_2 (97.7 %, 98.9 % and 88.0 % for 0.05 mol of Co-doped, Ni-doped and underdosed TiO_2, respectively).

In [45], doped TiO_2 nanoparticles with lanthanide ions La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Yb^{3+} were synthesized by the sol-gel method. Their photocatalytic activity was evaluated using the dye Direct Blue (DB53). The results showed that Gd^{3+}/TiO_2 has the smallest particle size, as well as the largest surface area and pore volume. Lanthanides ions can to some extent enhance the photocatalytic activity of TiO_2 compared to unmodified TiO_2, and it was found that Gd^{3+}/TiO_2 is the most effective photocatalyst. Photocatalytic studies show that under optimal conditions (lighting time 40 minutes, $pH \approx 4$, photocatalyst loading 0.3 g/L and 100 ppm DB53) the efficiency of dye removal was 100 %. Rare earth metals (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd) were also used for the modification of TiO_2 [47]. The photocatalytic activity of the prepared samples was evaluated by photocatalytic decomposition of Orange II dye in aqueous suspension under irradiation with wavelengths of 254, 365 and 400 nm. Samples doped with Nd^{3+} ions ($k = 0.0272\ min^{-1}$ for UV radiation and $0.0143\ min^{-1}$ for visible light) have the best photocatalytic properties in visible light.

2.2. Modification of TiO_2 by nonmetals

Non-metallic doping of TiO_2 is more effective than metal doping due to the reduction of recombination centers [19]. Various nonmetals (N [50–56], B [57-60], C [61-65], P [66-69], S [70-72], F [73-78], Br [79, 80]) are used to improve the photocatalytic activity of TiO_2 in the field of visible light [10, 19, 81].

In the study [50] N-doped TiO_2 was first successfully synthesized by a new single-stage flame method. This method of synthesis directs nitrogen atoms mainly to the internodal positions of the TiO_2 lattice, which reduces the width of the band gap (from 3.12 to ~ 2.51 eV) in the synthesized N/TiO_2. The presence of a large amount of intermediate N can change the structure and reduce the recombination efficiency of photogenerated electron-hole pairs, which will increase the photocatalytic activity of TiO_2 in visible or sunlight. To evaluate the photocatalytic properties, degradation of phenol under visible light was performed, which proved the high photocatalytic activity of N-doped TiO_2. In work [51], N-doped TiO_2 nanoparticles with a high specific surface area and photocatalytic activity in visible light were obtained using the sol-gel method with urea. The method of UV-diffuse reflectance revealed decrease in the width of the band gap from 3.24 to 2.79 eV due nitrogen doping. The maximum photocatalytic activity in the degradation of the methylene blue dye was achieved for N/TiO_2 powders with the lowest molar ratio of urea: TiO_2 (1.5).

In a study [55], a photocatalyst C, N/TiO_2 of mesoporous structure was synthesized. The material has improved photocatalytic activity during degradation of 4-nitrophenol under simulated solar irradiation. The photocatalytic efficiency of C, N/TiO_2 was significantly higher than A-TiO_2 (anatase). Using zebrafish embryos, it has been shown that products of photocatalytic degradation of 4-nitrophenol have higher toxicity than the parent compound. The results demonstrated the importance of evaluating the effectiveness of photocatalytic degradation in combination with the evaluation of the toxicity of degradation compounds. In another study [56] using C, N-doped TiO_2 was investigated in photocatalytic degradation in visible light of phenol and 2-chlorophenol, which was 92 % and 90 %, respectively. The photocatalytic reaction rate constants for phenol and 2-chlorophenol in the porous spheres of doped TiO_2 were approximately 4 and 2 times higher, respectively, than in the P25 photocatalyst from Degussa. This is due to the fact that C, N-doped porous TiO_2 not only prolongs the photo response to the visible light range (because C, N doping narrows the width of the band gap to 2.7 eV), but also opens a large number of surface-active areas that prefer reactions in visible radiation. In addition, the porous structure of the doped photocatalyst contributes to the multiple reflection of photons, while increasing the light absorption.

In [57], mesoporous crystals of B, N-doped TiO_2 were obtained by the sol-gel method followed by the nitrate melt process to change the morphology of the sample. Boron ions were included in the TiO_2 lattice through the O – Ti – N and Ti – B – O bonds, as a result of which B, N-doped TiO_2 shifted the maximum of light absorption to the long-wavelength (red) range. The photocatalytic activity of various catalysts was evaluated by the method of degradation of the dye methylene blue (MB) under irradiation with visible light. B-N-TiO_2 showed the best performance with the removal of 97 % of MS after 150 minutes, B-TiO_2 - 78 % and only 23 % of MB was degraded in the presence of pure TiO_2. The rate constant with B-N-TiO_2 is ~ 4 times higher than that with B-TiO_2 and more than 10 times higher than pure TiO_2. This indicates that the synthesis of photocatalysts by a new method of nitrate melt can be effective for increasing the photocatalytic activity of TiO_2 in visible light. In another study [58], the authors using microarc oxidation synthesized a photocatalyst TiO_2, doped with N and B, to increase the photocatalytic activity in the visible light. During the microarc oxidation process, which is known as an energy-saving and environmentally friendly method, B and N ions in the electrolyte were included in the intermediate positions of TiO_2 and partially N was chemically adsorbed on the surface of TiO_2. To evaluate the photocatalytic activity, decomposition reactions of the aniline blue dye were performed. The mechanism of photocatalysis for B, N/TiO_2 is shown in Fig. 6 [58]. It was found that the rate constants for dye degradation were as follows: $5.69 \cdot 10^{-4} min^{-1}$ for pure TiO_2; $9.81 \cdot 10^{-4} min^{-1}$ for B-doped TiO_2; $13.92 \cdot 10^{-4} min^{-1}$ for N-doped TiO_2; $16.25 \cdot 10^{-4} min^{-1}$ for B,N-doped TiO_2. B,N-doped TiO_2 showed a significantly higher efficiency of dye degradation and rate constant compared to other photocatalysts, due to the existence of the Ti-O-B-N structure, which is formed by intermediate B, and an increase in chemisorbed NO_x species. The authors [60] synthesized undoped and B-doped one-dimensional TiO_2 nanotubes by a two-stage hydrothermal method. The photocatalytic activity of the obtained nanotubes was evaluated by the degradation of methylene blue. Addition of boron (up to 0.5 %) to TiO_2 nanotubes increased the efficiency of photocatalytic destruction of MB. The highest degradation efficiency was 81 % and it was found that higher (> 5 %) boron doping leads to a decrease in degradation efficiency.

In a study [61], C/TiO_2 coatings were obtained by reactive magnetron sputtering of Ti and C in an Ar/O_2 atmosphere. After deposition, all coatings were annealed in air at 873 K for 30 minutes to obtain the desired crystalline structure, and then analyzed. The content of C in the coatings varied from about 5 to 9 atomic %, while the atomic percentage of C atoms incorporated in place of the Ti atoms varied from about 0.5 to 1.8 atomic %. Decomposition of methylene blue and stearic acid and photoinduced hydrophilicity measurement were used to evaluate the photocatalytic properties of C-doped TiO_2 and unmodified TiO_2 under the action of UV and visible radiation. The results of all three tests showed that the photocatalytic activity of C/TiO_2 significantly exceeds the undoped TiO_2. However, excessive doping of C led to the blocking of active positions and loss of photocatalytic properties. In another study by the same researchers [62], C/TiO_2 coatings were also obtained by reactive magnetron sputtering, but using mixtures of CO_2 and O_2 as reactive gas. The content of C in the coatings was approximately 4 - 6.5 wt.%. The width of the TiO_2 band gap narrowed to 2.02 eV as a result of carbon doping, compared to pure TiO_2 (3.2 eV). Photocatalytic properties of thin films were evaluated by irradiation with UV and visible light using tests for the decomposition of methylene blue and stearic acid. Photocatalytic activity under UV irradiation of unmodified TiO_2 for both pollutants was higher than C-doped TiO_2. It was found that the photoactivity of C-doped samples in visible light was better in the case of degradation of MB, while the results of decomposition of stearic acid under visible light were low for all studied films.

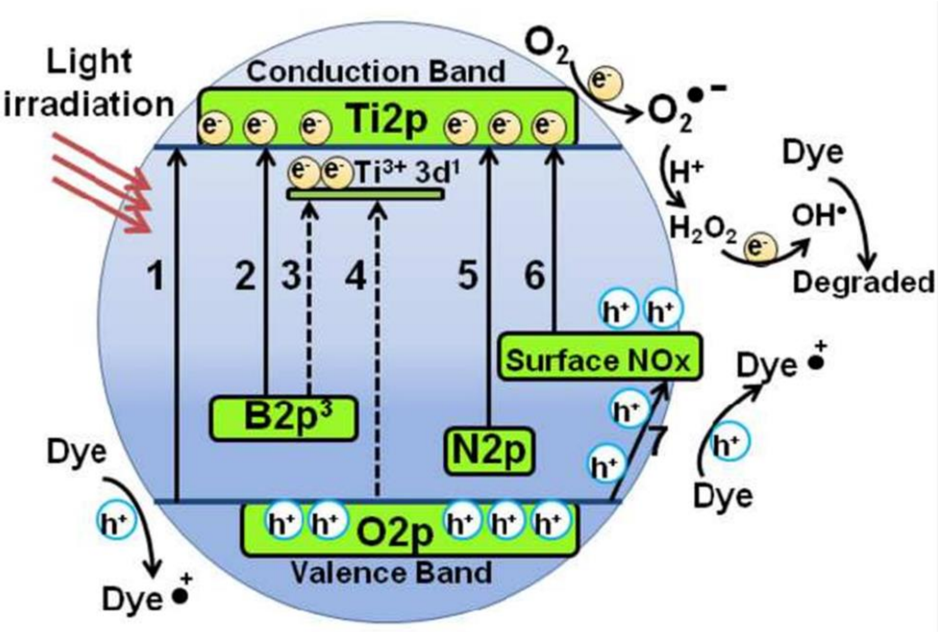

Fig. 6. The mechanism of photocatalysis for B, N-doped TiO_2 [58].

In paper [67], P-doped TiO_2 with surface oxygen vacancies were obtained, which showed effective photocatalytic activity for the degradation of antibacterial fluoroquinolone (ciprofloxacin) when irradiated with visible light. The doped sample showed a rate constant of 0.065 min^{-1} for the degradation of ciprofloxacin and was approximately 16.2 times greater than in undoped TiO_2 (0.004 min^{-1}). It was found that the synergistic effect between P-doping and surface oxygen vacancies on TiO_2 significantly improved the efficiency of transfer and separation of photogenerated charges, thereby increasing the photocatalytic activity of TiO_2 in visible light. In work [68] P-doped TiO_2 was prepared by hydrothermal method using tetrabutyl titanate as a precursor of titanium and H_3PO_4 as a source of phosphorus. Titanium nanotubes (TNT) were used as raw material for reprocessing of the sample by two methods – hydrothermal and calcinations. In the first method, 0.1 g of TNT was introduced into a 0.01 mol/L solution of HNO_3, maintained at a constant temperature at 150 ^{0}C for 12 hours and cooled to room temperature. Then the solid was washed with deionized water and dried at 70 ℃ for 6 hours (this sample was called ETNT). In the second method, 0.2 g of TNT was kept in a muffle furnace for 4 hours at a temperature of 400 ^{0}C (this sample was called DTNT). P-doped ETNT and DTNT nanotubes had an anatase structure. DTNT was a multiwall nanotube with an inner diameter of about 4 nm and an outer diameter of about 10 nm. UV-vis diffuse reflectance spectroscopy showed that the width of the band gap of DTNT has the lowest value (only 2.09 eV). The BET surface area for DTNT ranged from 335 cm^2/g to 134 cm^2/g after the second calcinations. Experiments have shown that DTNT is the best photocatalyst, which can lead to more than 75 % of phenol degradation after lighting for 120 minutes. It is proved that during the photocatalytic oxidation reaction the rate of formation of the hydroxyl radical (•OH) is 1.505 min^{-1} [68].

In a study [70] a new method of flame pyrolysis was developed for the synthesis of S-doped TiO_2 photocatalysts in visible light for water purification. As a result, the width of the band gap was reduced to 2.78 eV and visible light absorption was improved. The addition of S to TiO_2 contributed to the conversion of anatase to rutile in the prepared samples. Among all the synthesized compounds, the catalyst with 2M sulfuric acid as a precursor demonstrated striking performance for photocatalysis caused by visible light ($S^{6+}/S^{4+} = 5.61$). The presence of S^{6+} plays an important role in increasing the photocatalytic activity, which was evaluated by the degradation of acetaldehyde when exposed to visible light.

The authors [72] using the sol-gel method on aluminum substrates synthesized thin films of titanium dioxide, which are doped with C/S/N. Sample C/S/N/ TiO_2 showed greater photocatalytic activity in the degradation of benzene in visible light, compared with undoped TiO_2 (Fig. 7). According to the results of the analysis of absorption spectra, doped TiO_2 showed higher absorption of visible light compared to unmodified TiO_2.

In paper [73], F-doped nanoparticles of anatase TiO_2 were synthesized by the sol-gel method. Photocatalytic activity was evaluated by decomposition of methylene blue in atmospheric air in visible light. The photocatalytic efficiency was 84 % for TiO_2 nanoparticles with a content of 5 wt.% F. The authors [74] obtained two types of TiO_2 nanoparticles (with fluorine F-TiO_2 and without fluorine H-TiO_2) by sol-gel synthesis and conducted a comparative study of their photocatalytic properties. F-TiO_2 nanoparticles showed increased photocatalytic activity compared to H-TiO_2, which is due to the presence of chemisorbed F on the surface. In the study [75] sol-gel method prepared F-doped photoelectrodes TiO_2 with honeycomb morphology and studied the photoelectrocatalysis by degradation of methylene blue under irradiation with

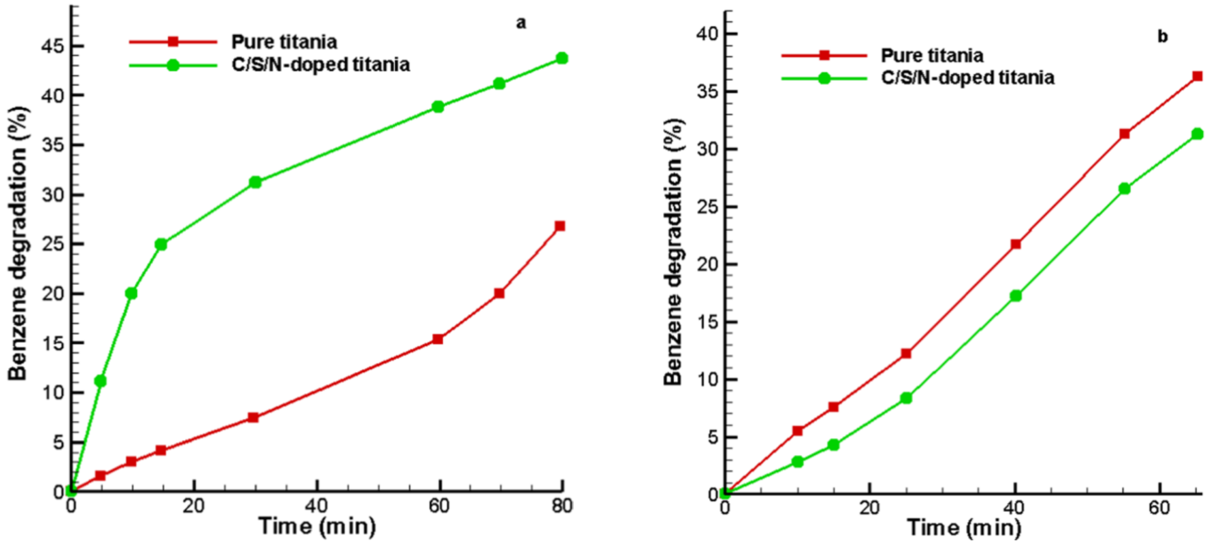

Fig. 7. Photodegradation of benzene in the presence of basic TiO_2 and C / S / N-doped TiO_2 at visible (a) and UV radiation (b) [72].

visible light. The maximum percentage of discoloration (97.8 %) was reached at pH 9.94 after 4 hours of exposure to visible light. The high rates of photoelectrocatalysis for F-TiO_2 are explained by the efficient separation of electron-hole pairs and the creation of active hydroxyl radicals.

In paper [79], Br-doped TiO_2 photocatalysts were prepared by the hydrothermal method. As the Br content increased, the width of the TiO_2 band gap decreased from 2.85 to 1.75 eV, and the maximum light absorption in the long-wavelength (red) region shifted from 395 to 517 nm, which further enhances the photocatalytic activity of Br/TiO_2. Photodegradation of RhB, MO and MB is more than 98 % (0.5 Br-TiO_2) with a dye concentration of 10 mg/L after 40, 30 and 30 min, respectively.

Conclusions

Modern technologies for cleaning the environment from chemical organic and inorganic pollutants include use of photocatalysts that are able to remove pollutants from water and air due to formation of free hydroxyl radicals. The functionality of photocatalysts is largely due to their spectral sensitivity. When creating them, alloying additives are introduced into the composition, which ensure the formation of chemical compounds that shift the spectral sensitivity to the visible region of solar radiation.

Photocatalysts based on titanium (IV) oxide are considered to be among the most effective due to their high chemical resistance, non-toxicity and low cost. The use of photocatalysts based on TiO_2 includes three main stages: light absorption and formation of photogenerated electron-hole pairs; separation and transfer of photogenerated electron-hole pairs; redox reactions on the surface of TiO_2. These sequential actions together determine the photocatalytic efficiency of photocatalysts based on TiO_2. The quantum efficiency of the photocatalytic process is determined by the competition of two processes involving charge carriers (photogenerated electrons and holes): redox reactions and recombination processes. Many studies have focused on methods to reduce recombination, such as the creation of "semiconductor-metal" or "semiconductor-nonmetal" composites. The formation of such heterogeneous systems leads to a significant change in the physicochemical properties of the surface and electronic structure of titanium (IV) oxide.

The analysis of modern scientific research indicates that the chemical modification of the TiO_2 surface has a great influence on its photocatalytic activity during the degradation of chemical pollutants during irradiation with visible light. Doping of photocatalysts based on TiO_2 with metallic and non-metallic nanoparticles changes the chemical nature and electronic structure of the doped compound, thereby increasing the efficiency of photodegradation of pollutants. TiO_2 performance is improved by reducing the width of the energy band gap, which leads to increased photocatalytic activity when exposed to visible light. All this contributes to the creation of promising and environmentally friendly methods for water purification using photoactive catalysts based on TiO_2.

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[1] T. Tatarchuk, A. Peter, B. Al-Najar, J. Vijaya, M. Bououdina, Nanotechnol. Environ. Sci. 1-2, 209 (2018) (doi:10.1002/9783527808854.ch8).

[2] J. Wen, X. Li, W. Liu, Y. Fang, J. Xie, Y. Xu, Cuihua Xuebao/Chinese J. Catal. 36(12), 2049 (2015) (doi:10.1016/S1872-2067(15)60999-8).

[3] R.M. Mohamed, D.L. McKinney, W.M. Sigmund, Mater. Sci. Eng. R Reports 73(1), 1 (2012) (doi:10.1016/j.mser.2011.09.001).

[4] T.A. Doncova, I.N. Ivanenko, I.M. Astrelin, Himiya, fizyka ta tekhnologiya poverhni 6(1), 85 (2015).

[5] S.V. Ryabov, S.I. Sinel'nikov, O.A. Opanasenko, Polimernyi Zhurnal 35(2), 126 (2013).

[6] A. Fujishima, K. Honda, Nature 238, 37 (1972) (doi:10.1038/238037a0).

[7] K. Nakata, A. Fujishima, J. Photochem. Photobiol. C Photochem. Rev. 13(3), 169 (2012) (doi:10.1016/j.jphotochemrev.2012.06.001).

[8] S. Feng, M. Wang, Y. Zhou, P. Li, W. Tu, Z. Zou, APL Mater. 3(10), 104416 (2015) (doi:10.1063/1.4930043).

[9] Y.H. Chung, K. Han, C.Y. Lin, D. O'Neill, G. Mul, B. Mei, C.M. Yang, Catal. Today, (2019) (doi:10.1016/j.cattod.2019.07.042).

[10] H. Abdullah, M.M.R. Khan, H.R. Ong, Z. Yaakob, J. CO_2 Util., 22, 15 (2017) (doi:10.1016/j.jcou.2017.08.004).

[11] A.I. Kriukov, A.L. Stroiuk, S.Ya. Kuchmiy, V.D. Pokhodenko, Nanofotokataliz (Akademperi, Kiev, 2013).

[12] J. Moellmann, S. Ehrlich, R. Tonner, S. Grimme, J. Phys. Condens. Matter, 24(42), 424206 (2012) (doi:10.1088/0953-8984/24/42/424206).

[13] N. Rahimi, R.A. Pax, E.M.A. Gray, Prog. Solid State Chem. 44(3), 86 (2016) (doi:10.1016/j.progsolidstchem.2016.07.002).

[14] A. Bumajdad, M. Madkour, Physical Chemistry Chemical Physics 16(16), 7146 (2014) (doi:10.1039/c3cp54411g).

[15] I. Ali, M. Suhail, Z.A. Alothman, A. Alwarthan, RSC Adv. 8(53), 30125 (2018) (doi:10.1039/c8ra06517a).

[16] H. Park, Y. Park, W. Kim, W. Choi, J. Photochem. Photobiol. C Photochem. Rev. 15, 1 (2013) (doi:10.1016/j.jphotochemrev.2012.10.001).

[17] J.Y. Park, C. Lee, K.W. Jung, D. Jung, Bull. Korean Chem. Soc. 30(2), 402 (2009) (doi:10.5012/bkcs.2009.30.2.402).

[18] C. Yogi, K. Kojima, T. Takai, N. Wada, J. Mater. Sci. 44(3), 821 (2009) (doi:10.1007/s10853-008-3151-7).

[19] H. Agbe, E. Nyankson, N. Raza, D. Dodoo-Arhin, A. Chauhan, G. Osei, V. Kumar, K.H. Kim, J. Ind. Eng. Chem. 72, 31 (2019) (doi:10.1016/j.jiec.2019.01.004).

[20] A. Ayati, A. Ahmadpour, F.F. Bamoharram, B. Tanhaei, M. Mänttäri, M. Sillanpää, Chemosphere 107, 163 (2014) (doi:10.1016/j.chemosphere.2014.01.040).

[21] S. Oros-Ruiz, R. Gómez, R. López, A. Hernández-Gordillo, J.A. Pedraza-Avella, E. Moctezuma, E. Pérez, Catal. Commun. 21, 72 (2012) (doi:10.1016/J.CATCOM.2012.01.028).

[22] W. Hou, Z. Liu, P. Pavaskar, W.H. Hung, S.B. Cronin, J. Catal. 277(2), 149 (2011) (doi:10.1016/J.JCAT.2010.11.001).

[23] J. Singh, K. Sahu, B. Satpati, J. Shah, R.K. Kotnala, S. Mohapatra, J. Phys. Chem. Solids 135, 109100 (2019) (doi:10.1016/j.jpcs.2019.109100).

[24] M. Scarisoreanu, A.G. Ilie, E. Goncearenco, A.M. Banici, I.P. Morjan, E. Dutu, E. Tanasa, I. Fort, M. Stan, C.N. Mihailescu, C. Fleaca, Appl. Surf. Sci. 509, 145217 (2020) (doi:10.1016/J.APSUSC.2019.145217).

[25] M.M. Khan, S. Kalathil, J. Lee, M.H. Cho, Bull. Korean Chem. Soc. 33(5), 1753 (2012) (doi:10.5012/bkcs.2012.33.5.1753).

[26] T.C. Pan, S.H. Wang, Y.S. Lai, J.M. Jehng, S.J. Huang, Appl. Surf. Sci. 296, 189 (2014) (doi:10.1016/j.apsusc.2014.01.077).

[27] K. Nanaji, R.K. Siri Kiran Janardhana, T.N. Rao, S. Anandan, J. Alloys Compd. 794, 662 (2019) (doi:10.1016/J.JALLCOM.2019.04.283).

[28] A. Gołąbiewska, W. Lisowski, M. Jarek, G. Nowaczyk, M. Michalska, S. Jurga, A. Zaleska-Medynska, Mol. Catal. 442, 154 (2017) (doi:10.1016/J.MCAT.2017.09.004).

[29] A.K.P.D. Savio, J. Fletcher, F.C. Robles Hernández, Ceram. Int. 39(3), 2753 (2013) (doi:10.1016/j.ceramint.2012.09.042).

[30] C.-C. Wang, P.-H. Chou, Y.-H. Yu, C.-C. Kei, Electrochim. Acta 284, 211 (2018) (doi:10.1016/J.ELECTACTA.2018.07.164).

[31] R. Han, J. Liu, N. Chen, G. Wang, Y. Guo, H. Wang, RSC Adv. 9, 34862 (2019) (doi:10.1039/c9ra05480d).

[32] Z. Zafar, I. Ali, S. Park, J.-O. Kim, Ceram. Int. 46(3), 3353 (2020) (doi:10.1016/J.CERAMINT.2019.10.045).

[33] P. Manojkumar, E. Lokeshkumar, A. Saikiran, B. Govardhanan, M. Ashok, N. Rameshbabu, J. Alloys Compd. 825, 154092 (2020) (doi:10.1016/J.JALLCOM.2020.154092).

[34] P.D. Bhange, S.V. Awate, R.S. Gholap, G.S. Gokavi, D.S. Bhange, Mater. Res. Bull. 76, 264 (2016) (doi:10.1016/J.MATERRESBULL.2015.12.041).

[35] V. Binas, V. Stefanopoulos, G. Kiriakidis, P. Papagiannakopoulos, J. Mater. 5(1), 56 (2019) (doi:10.1016/j.jmat.2018.12.003).

[36] F. Han, V.S.R. Kambala, R. Dharmarajan, Y. Liu, R. Naidu, Environ. Technol. Innov. 12, 27 (2018) (doi:10.1016/J.ETI.2018.07.004).

[37] M. Safari, R. Talebi, M.H. Rostami, M. Nikazar, M. Dadvar, J. Environ. Heal. Sci. Eng. 12(1), 1 (2014) (doi:10.1186/2052-336X-12-19).

[38] I. Ganesh, A.K. Gupta, P.P. Kumar, P.S. Chandra Sekhar, K. Radha, G. Padmanabham, G. Sundararajan, Processing and Application of Ceramics 6(1), 21 (2012).

[39] M. Ismael, J. Environ. Chem. Eng. 8(2), 103676 (2020) (doi:10.1016/J.JECE.2020.103676).

[40] D. Komaraiah, E. Radha, J. Sivakumar, M.V. Ramana Reddy, R. Sayanna, Surfaces and Interfaces 17, 100368 (2019) (doi:10.1016/J.SURFIN.2019.100368).

[41] M.J. Valero-Romero, J.G. Santaclara, L. Oar-Arteta, L. van Koppen, D.Y. Osadchii, J. Gascon, F. Kapteijn, Chem. Eng. J. 360, 75 (2019) (doi:10.1016/J.CEJ.2018.11.132).

[42] M. Hinojosa – Reyes, R. Camposeco – Solis, F. Ruiz, V. Rodríguez – González, E. Moctezuma, Mater. Sci. Semicond. Process. 100, 130 (2019) (doi:10.1016/J.MSSP.2019.04.050).

[43] M.S. Mohseni-Salehi, E. Taheri-Nassaj, M. Hosseini-Zori, J. Photochem. Photobiol. A Chem. 356, 57 (2018) (doi:10.1016/J.JPHOTOCHEM.2017.12.027).

[44] S.J. Armaković, M. Grujić-Brojčin, M. Šćepanović, S. Armaković, A. Golubović, B. Babić, B.F. Abramović, Arab. J. Chem. 12, 5355 (2019) (doi:10.1016/J.ARABJC.2017.01.001).

[45] [45Z.M. El-Bahy, A.A. Ismail, R.M. Mohamed, J. Hazard. Mater., 166 (1), 138 (2009) (doi:10.101/j.jhazmat.2008.11.022).

[46] N. us Saqib, R. Adnan, I. Shah, Environ. Sci. Pollut. Res. 23, 15941 (2016) (doi:10.1007/s11356-016-6984-7).

[47] V. Štengl, S. Bakardjieva, N. Murafa, Mater. Chem. Phys. 114(1), 217 (2009) (doi:10.1016/j.matchemphys.2008.09.025).

[48] R.R. Nair, J. Arulraj, K.R. Sunaja Devi, Mater. Today Proc. 3(6), 1643 (2016) (doi:10.1016/J.MATPR.2016.04.054).

[49] V. Kumaravel, S. Mathew, J. Bartlett, S.C. Pillai, Appl. Catal. B Environ. 244, 1021 (2019) (doi:10.1016/j.apcatb.2018.11.080).

[50] P.G. Smirniotis, T. Boningari, D. Damma, S.N.R. Inturi, Catal. Commun. 113, 1 (2018) (doi:10.1016/J.CATCOM.2018.04.019).

[51] J. Marques, T.D. Gomes, M.A. Forte, R.F. Silva, C.J. Tavares, Catal. Today 326, 36 (2019) (doi:10.1016/J.CATTOD.2018.09.002).

[52] E. Acayanka, J.-B. Tarkwa, K.N. Nchimi, S.A.Y. Voufouo, A. Tiya-Djowe, G.Y. Kamgang, S. Laminsi, Surfaces and Interfaces 17, 100361 (2019) (doi:10.1016/J.SURFIN.2019.100361).

[53] R. Quesada-Cabrera, C. Sotelo-Vázquez, M. Quesada-González, E.P. Melián, N. Chadwick, I.P. Parkin, J. Photochem. Photobiol. A Chem. 333, 49 (2017) (doi:10.1016/J.JPHOTOCHEM.2016.10.013).

[54] M. Zalas, Catal. Today, 230, 91 (2014) (doi:10.1016/J.CATTOD.2013.12.032).

[55] O.A. Osin, T. Yu, X. Cai, Y. Jiang, G. Peng, X. Cheng, R. Li, Y. Qin, S. Lin, Front. Chem., 6, 192 (2018) (doi:10.3389/fchem.2018.00192).

[56] J. Zhang, Z. Xing, J. Cui, Z. Li, S. Tan, J. Yin, J. Zou, Q. Zhu, W. Zhou, Dalt. Trans. 47 (14), 4877 (2018) (doi:10.1039/c8dt00262b).

[57] H. Shindume L, Z. Zhao, N. Wang, H. Liu, A. Umar, J. Zhang, T. Wu, Z. Guo, J. Nanosci. Nanotechnol. 19(2), 839 (2018) (doi:10.1166/jnn.2019.15745).

[58] J.-H. Lee, J.-I. Youn, Y.-J. Kim, I.-K. Kim, K.-W. Jang, H.-J. Oh, Ceram. Int. 41(9), 11899 (2015) (doi:10.1016/J.CERAMINT.2015.05.157).

[59] W.H.M. Abdelraheem, M.K. Patil, M.N. Nadagouda, D.D. Dionysiou, Appl. Catal. B Environ. 241, 598 (2019) (doi:10.1016/J.APCATB.2018.09.039).

[60] H.L. Hoşgün, M.T.A. Aydın, J. Mol. Struct. 1180, 676 (2019) (doi:10.1016/J.MOLSTRUC.2018.12.056).

[61] M. Ratova, R. Klaysri, P. Praserthdam, P.J. Kelly, Vacuum 149, 214 (2018) (doi:10.1016/J.VACUUM.2018.01.003).

[62] R. Klaysri, M. Ratova, P. Praserthdam, P.J. Kelly, Nanomaterials 7, 113 (2017) (doi:10.3390/nano7050113).

[63] J. He, G. Zi, Z. Yan, Y. Li, J. Xie, D. Duan, Y. Chen, J. Wang, J. Environ. Sci. 26(5), 1195 (2014) (doi:10.1016/S1001-0742(13)60475-1).

[64] E. Ovodok, H. Maltanava, S. Poznyak, M. Ivanovskaya, A. Kudlash, N. Scharnagl, J. Tedim, Mater. Today Proc., 5 (9), 17422 (2018) (doi:10.1016/J.MATPR.2018.06.044).

[65] R. Purbia, R. Borah, S. Paria, Inorg. Chem. 56(16), 10107 (2017) (doi:10.1021/acs.inorgchem.7b01864).

[66] S. Guo, S. Han, M. Haifeng, C. Zeng, Y. Sun, B. Chi, J. Pu, J. Li, Mater. Res. Bull. 48(9), 3032 (2013) (doi:10.1016/J.MATERRESBULL.2013.04.056).

[67] X. Feng, P. Wang, J. Hou, J. Qian, Y. Ao, C. Wang, J. Hazard. Mater. 351, 196 (2018) (doi:10.1016/J.JHAZMAT.2018.03.013).

[68] J. Niu, P. Dai, G. Qi, Q. Zhang, B. Yao, X. Yu, C. Liu, Integr. Ferroelectr. 176, 150 (2016) (doi:10.1080/10584587.2016.1250601).

[69] S.R. Gul, M. Khan, B. Wu, Z. Yi, Mater. Res. Express 4(6), 065502 (2017) (doi:10.1088/2053-1591/aa75e8).

[70] T. Boningari, S.N.R. Inturi, M. Suidan, P.G. Smirniotis, Chem. Eng. J. 339, 249 (2018) (doi:10.1016/J.CEJ.2018.01.063).

[71] L.G. Devi, R. Kavitha, Mater. Chem. Phys. 143(3), 1300 (2014) (doi:10.1016/J.MATCHEMPHYS.2013.11.038).

[72] S. Modanlu, A. Shafiekhani, Sci. Rep. 9(1), 1 (2019) (doi:10.1038/s41598-019-53189-z).
[73] G.D. Gena, T.H. Freeda, K.M. Prabu, Int. J. Sci. Res. Phys. Appl. Sci. 6(2), 1 (2018) (doi:10.26438/ijsrpas/v6i2.14).
[74] D.-H. Lee, B. Swain, D. Shin, N.-K. Ahn, J.-R. Park, K.-S. Park, Mater. Res. Bull. 109, 227 (2019) (doi:10.1016/J.MATERRESBULL.2018.09.027).
[75] D. Liu, R. Tian, J. Wang, E. Nie, X. Piao, X. Li, Z. Sun, Chemosphere 185, 574 (2017) (doi:10.1016/J.CHEMOSPHERE.2017.07.071).
[76] Q. Gao, F. Si, S. Zhang, Y. Fang, X. Chen, S. Yang, Int. J. Hydrogen Energy 44(16), 8011 (2019) (doi:10.1016/J.IJHYDENE.2019.01.233).
[77] X. Zhao, J., Li, W., Li, X., & Zhang, RSC Adv. 7(35), 21547 (2017) (doi:10.1039/c7ra00850c).
[78] C. Li, Z. Sun, R. Ma, Y. Xue, S. Zheng, Microporous Mesoporous Mater. 243, 281 (2017) (doi:10.1016/J.MICROMESO.2017.02.053).
[79] Q. Wang, S. Zhu, Y. et al. Liang, J Nanopart Res. 19, 72 (2017) (doi:10.1007/s11051-017-3765-2).
[80] Q. Wang, S. Zhu, Y. Liang, Z. Cui, X. Yang, C. Liang, A. Inoue, Mater. Res. Bull. 86, 248 (2017) (doi:10.1016/J.MATERRESBULL.2016.10.026).
[81] L.G. Devi, R. Kavitha, Appl. Catal. B Environ. 140-141, 559 (2013) (doi:10.1016/j.apcatb.2013.04.035).

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Способи підвищення ефективності фотокаталізаторів на основі TiO_2 (огляд)

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Забруднювачі води та повітря створюють значну екологічну проблему навколишнього середовища по всьому світу і фотокаталіз є одним з методів вирішення цього глобального питання. Фотокаталітична деградація токсичних речовин під впливом видимого електромагнітного випромінювання широко застосовується для очищення стічних вод. Найперспективнішим методом видалення полютантів є використання фотокаталізаторів на основі титан(IV) оксиду, які визнані одними з найефективніших завдяки хімічній стійкості, нетоксичності та низькій вартості. Проте їх практичне застосування обмежене швидкою рекомбінацією фотогенерованих носіїв заряду і вибірковим поглинанням світла в УФ-області через велику ширину забороненої зони. Щоб вирішити це науково-практичне завдання потрібно модифікувати поверхню TiO_2, наприклад, через металеве або неметалеве допування, з метою підвищення його фотокаталітичної активності за рахунок додаткового поглинання у видимому діапазоні спектру. У даному огляді приведений аналіз сучасних наукових досліджень щодо способів підвищення ефективності фотокаталізаторів на основі TiO_2.

Ключові слова: титан діоксид, фотокаталіз, деградація, фотокаталітична активність, допування.