

INORGANIC MATERIALS FOR PHOTOCATALYTIC PROCESSES

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The inorganic materials for using in the process of water photolysis were investigated. The mechanism of photoactive surface formation non-doped and doped TiO₂ was described. It is allows identify ways of increasing the photocatalytic properties of catalysts. The materials based on TiO₂, and other catalysts are considered. Key parameters affecting photoactivity of catalysts were found.

Keywords: photocatalyst, water photolysis, photoactivity, TiO₂, doping.

Introduction. A catalytic material plays the main role in processes such as photocatalytic hydrogen producing and photocatalytic wastewater and air treatment. Among the many inorganic photocatalytic materials the most popular there is titanium (IV) oxide (TiO₂). For the first time photocatalytic activity of TiO₂ was found by Fujishima and Honda in 1972 in photoelectrochemical process, whose effectiveness did not exceed 10% [1]. Since then, many researchers have tried to increase the photocatalytic activity of TiO₂. In addition, in photocatalytic hydrogen production studied other inorganic materials also (Fig. 1): binary metal oxides, oxides consisting of three or even four metals, metal sulfides, nitrides and oxynitrides, oxysulfides, nanocomposites and heterostructures based on semiconductors and other materials [2-5]. In these studies it was found that nanostructured photocatalysts have higher photocatalytic efficiency than photocatalysts with large particles [5, 6].

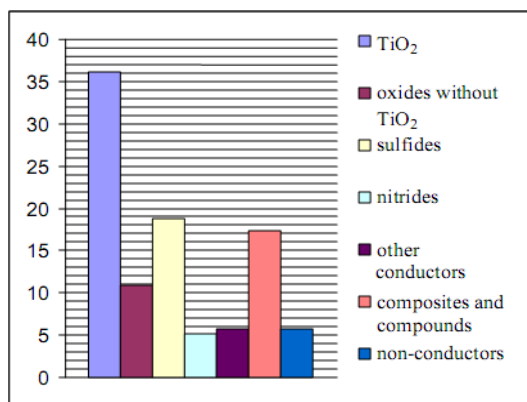


Fig. 1. The statistical distribution of publications devoted to inorganic materials for photocatalytic hydrogen production (according to [5])

It is difficult today to determine which material is ideal for photocatalytic processes or better than other because there isn't any photocatalysts, which would meet all requirements. In addition, all candidates have their own specific disadvantages. The requirements for the photocatalysts include the following. It must be chemically stable, corrosion resistant, photocatalytic active and working in the visible light [2-7].

To improve the photocatalytic process as a whole photocatalysts should be nanostructured (to reduce transport distance charge carriers to the surface); also they must have a large surface area (for better absorption of light). In addition, special attention should be given to the size of particles, chemical composition (including impurities), microstructure, crystalline phase, morphology, gap width and position of the Fermi level, which can be changed by adding

different elements [8]. So, the properties of semiconductor photocatalysts are highly dependent on the structural and electronic characteristics. The last is very important when choosing material for creating based on it photocatalysts, that is caused by its chemical composition, doping agents and additives.

The objective of this paper is consideration the mechanism of photocatalytic activity the catalysts and ways to increase it; identify the most perspective materials for use in photocatalytic processes.

The mechanism of photoactive surface formation on non-doped and doped TiO₂. Photocatalysts based on metal oxides are known as promising materials. However, most of metal oxides show low photocatalytic efficiency in the visible range of light, but they are cheap materials, resistant to corrosion and therefore show stable operation for a long time [5].

According to the literature [2-8], TiO₂ is and will be one of the most important photocatalysts for hydrogen production due to its availability, low cost, no toxicity, stability, rather high (compared to other metal oxides) photoactivity.

Photoactivity of TiO₂ is due to its absorption of photons with energy equal to or greater than band-gap of the photocatalysts. In this time, on the surface TiO₂ is formed the electron-hole pair. Electron is in the conduction area, while the positive hole - in the valence band. Then excited electrons and holes recombine, transforming energy into heat, or react with adsorbed molecules and charged particles located on the semiconductor surface. As a result, electrons and holes form hydroxyl radicals (Fig. 2, hv_1), which have very high oxidation potential [7].

Generalized photocatalysis mechanism (with primary and secondary photocatalytic reactions) on the TiO₂ surface is shown in [9].

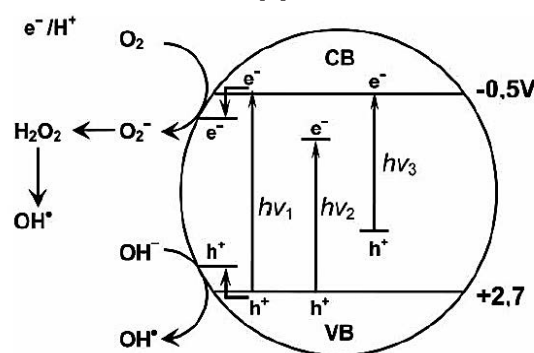


Fig. 2. The mechanism of hydroxyl radical's formation on TiO₂ surface (according to [7])

The significant drawback using of TiO₂ as photocatalyst is its low activity in the visible light. To increase the TiO₂ activity under visible light irradiation

it is necessary to change its electronic structure. This is possible by doping metals or non-metals on surface of TiO_2 and modification with semiconductors, which have smaller bandgap than TiO_2 .

Photoactivity of catalysts, doped with metals, is explained by emergence of new energy level in the bandgap by dispersing nanoparticles of metal in the catalyst matrix. The electron is excited from lattice defect into conductor zone (Fig. 2, $h\nu_2$). An additional advantage of doped photocatalysts is prevent the recombination during illumination due to stronger retention of electrons [7, 10].

Photoactivity of catalysts, doped with non-metals, is explained by three mechanisms. In the first mechanism, decreases the Fermi level of the photocatalysts. In [11] it is associated with the fact that nitrogen orbitals form hybrids with oxygen. Because their energy is proximity, it becomes possible absorption of visible light.

Another mechanism of increasing the catalyst photoactivity is the presence of an additional energy level (Fig. 2, $h\nu_3$), which is that nitrogen replaces the oxygen in TiO_2 and thus form an additional energy level over the valence band [12]. UV light excites valence band and an additional level, while visible light is absorbed only on the additional level. In the third mechanism in doping with non-metals appears deficit of the oxygen, when nitrogen takes places, depleted by oxygen [13, 14].

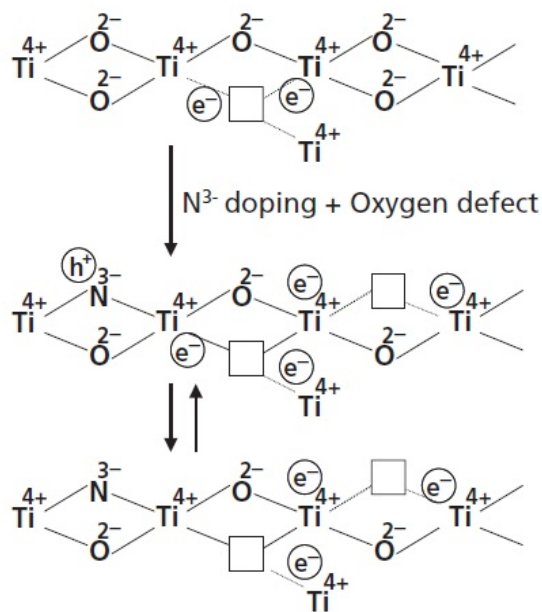


Fig. 3. The mechanism of substitution oxygen by nitrogen (according to [17])

Materials based on titanium (IV) oxide for water photolysis. TiO_2 is considered the most promising photocatalysts for water photolysis due to its stability in aqueous electrolyte solutions [5], prevalence, a small bandgap (3,0-3,2 eV) and the limit of the bandgap is wider than the potential of oxygen and hydrogen release from water.

TiO_2 can exist in three crystalline forms: rutile, anatase and brookite. They are in the form of octahedra, which are combined in two (rutile), three (brookite) or four (anatase), and as a result, these forms have different values of bandgap from 3 eV (rutile) to 3.2 eV (anatase). In [7, 15] revealed that the maximum photoelectrochemical efficiency is achieved by using mixture of about 20% rutile and 80% anatase.

Pure TiO_2 shows not enough photoactivity during the water photolysis, especially in pure water. This

is explained by fast recombination of photoexcited electron in the conduction band and holes in the valence band. For more efficient process are necessary donors of electron. As electron donors can be used various organic compounds that can be oxidized by holes from the valence band of TiO_2 : EDTA, methanol, ethanol, lactic acid, formaldehyde, etc. [6].

Additional doping TiO_2 by noble metals further increases the efficiency of water photolysis. Since the Fermi level of the noble metals are lower than TiO_2 , the photoexcited electrons are moving to the conduction band of metals, while photogenerated holes are on TiO_2 . This greatly increases the possibility of electron-hole pair's formation, which ultimately increases the catalyst photoactivity and the efficiency of water photolysis in general. Among all noble metals the most effective is Pt [16]. Thus, in addition Pt as co-catalyst to TiO_2 , were achieved producing H_2 and O_2 from acetic acid solution. At the same time, clean TiO_2 (without addition Pt) didn't produce H_2 [17].

Also addition of relatively inexpensive metals such as copper, nickel, silver increases the activity of TiO_2 [6, 18]. Today were investigated the effect of 21 metals as dopant on photoactivity of TiO_2 and found that doping allows do its photoactive in visible light, while non-doped TiO_2 is active only in the UV spectrum.

From the investigated 21 metals positive effect on the photoactivity of TiO_2 have given copper, manganese, iron, molybdenum, ruthenium, osmium, rhenium, vanadium, rhodium, etc. [6,15,18]. It was found that copper, manganese, iron is more effective than chromium, cobalt, nickel, because they capture both types of charge carriers, i.e. electrons and holes [6].

Also, doping method has influence on the photocatalytic activity of catalyst. When dopant is included into the crystal lattice of catalyst, it shows less activity than if dopant is located on the surface. Thus, according to research presented in [6, 15, 17, 18], have following conclusions: photocatalyst activity depends on the proximity of placing metal particles to the surface of catalyst, as well as amount of metal ions (there is an optimal amount of dopant), temperature and pH during doping affect on the activity of the catalyst.

When TiO_2 is combined with oxides of other metals, are formed titanates, having an intermediate value of bandgap (between the titanium oxide and other metal oxide). The first in the process of water photolysis was investigated strontium titanate with a bandgap of 3.2 eV, which produced only hydrogen [18]. When in [19] added other metal oxides to strontium titanate, water decomposes during photolysis on stoichiometric amounts of oxygen and hydrogen under UV light. Additional doping strontium titanate with metals allows for process of water photolysis in visible light (wavelength 420 nm) [17]. That is, strontium titanate observed almost the same regularities as that have TiO_2 . And as proof, SrTiO_3 as TiO_2 , is able to change the angle of wettability depending on the absorbed UV light. The irradiation may reduce wettability angle of 70° to 20° , i.e., the surface becomes more hydrophilic [16].

Other photocatalysts. Some of metals oxides with layer and tunnel structure are photoactive also [17]. To them carry tantalates, niobates, and vanadates. Tantalates have quite high bandgap, but they are active even in pure form. Adding dopants increases the photocatalytic activity.

Niobates, which are in the same group as the tantalates also exhibit photocatalytic properties. The main difference in photocatalytic properties niobates

and tantalates is the bandgap value. The lower limit of bandgap in $\text{Sr}_2\text{Ta}_2\text{O}_7$ stands at -1.6 eV, and in $\text{Sr}_2\text{Nb}_2\text{O}_7$ – at -0.9 eV [17]. This indicates that the photogenerated electrons tantalates can release hydrogen from water much easier than niobates.

Very promising are niobate AgNbO_3 (with perovskite structure, bandgap 2.86 eV) and vanadate BiVO_4 with monoclinic structure, bandgap 2.4 eV). They exhibit photocatalytic activity and produce oxygen from water in visible light with a wavelength of 420 nm. Also there is a tendency that the catalysts prepared from solutions, exhibit greater activity than catalysts prepared by solid-phase synthesis. This is explained by presence or absence of defects in the lattice, different morphology and structural characteristics [17].

Conclusions. Considered inorganic materials are promising for use them in photocatalytic processes, particularly in water photolysis. However, the most appropriate materials are based on titanium (IV) oxide because of its low cost, availability and possibility of modifying its photocatalytic properties. The mechanism of photoactive surface formation on doped and non-doped TiO_2 shows that for increasing the photocatalytic properties of catalysts is required them doping with localization dopant on surface. This will not only increase the activity of the catalyst but shift the process of water photolysis in the visible light area. Also, the key parameters affecting the catalysts photoactivity is the presence of dopant (defect) in lattices and on its surface, its small dimension, high porosity and specific surface area.

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НЕОРГАНІЧНІ МАТЕРІАЛИ ДЛЯ ФОТОКАТАЛІТИЧНИХ ПРОЦЕСІВ

Анотація

Розглянуто неорганічні матеріали, що досліджуються для використання їх в процесах фотолізу води. Описано механізм утворення фотоактивної поверхні недопованого і допованого TiO_2 . Останнє дозволяє виявити шляхи збільшення фотокаталітичних властивостей каталізаторів. Розглянуті каталізатори на основі TiO_2 і інші матеріали. Встановлені ключові параметри, що впливають на фотоактивність каталізаторів.

Ключові слова: фотокаталізатор, фотоліз води, фотоактивність, TiO_2 , допування.

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НЕОРГАНИЧЕСКИЕ МАТЕРИАЛЫ ДЛЯ ФОТОКАТАЛИТИЧЕСКИХ ПРОЦЕССОВ

Аннотация

Рассмотрены неорганические материалы, которые исследуются для использования в процессах фотолиза воды. Описан механизм образования фотоактивной поверхности недопированного и допированного TiO_2 . Последнее позволяет выявить пути увеличения фотокаталитических свойств катализаторов. Рассмотрены катализаторы на основе TiO_2 и другие материалы. Установлены ключевые параметры, влияющие на фотоактивность катализаторов.

Ключевые слова: фотокатализатор, фотолиз воды, фотоактивность, TiO_2 , допирование.