

UDC 699.871

PHOTOCATALYTIC PROPERTIES OF TiO₂/Ag NANOSTRUCTURES

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In this paper the size and shape of the core-shell nanoparticles were determined with the help of electron microscopic studies. The process of photodegradation of the dye of methyl blue was studied. Dependence from the time of UV irradiation with films of titanium dioxide nanoparticles and without their presence was studied, as well as with the "core-shell" structure of Ag / TiO₂ composition, where the core is silver nanoparticles and shell is the titanium dioxide nanoparticles. In the result of the research the action of the photocatalyst on the basis of core-shell Ag / TiO₂ significantly accelerates the oxidation of the methylene blue dye.

Keywords: photocatalysis, core-shell, plasmonics, nanoparticle, titanium dioxide, methylene blue dye.

Introduction

One of the most advanced and environmentally friendly methods of hydrogen generation is the method of photocatalytic decomposition of water by means of semiconducting materials [1, 2]. A promising material for these purposes is titanium dioxide. Compared with other photoactive materials for hydrogen production titanium dioxide attracts increasing attention of researchers because of its relative cheapness, availability, stability and functionality as well as the possibility to obtain various nanostructures, such as nanoparticles, nanotubes, nanorods and nanowires. Physico-chemical properties of films based on nanostructures depend on the method of their production and are determined by the size and shape of the particles, imperfection, phase composition, structure and size of the film far [3].

In 1987 Anpo co-authored [4] published a paper on the effect of TiO₂ colloidal particles sizes on their photocatalytic activity. In the paper the nanoparticles of titanium dioxide of anatase and rutile modification with different particle diameters were obtained. It was shown that with decreasing size of the titanium dioxide nanoparticles photocatalytic activity increases for both anatase and rutile. It should be noted that the reactivity of the anatase modification is higher than with the rutile. The investigation of the influence of geometric characteristics on the photocatalytic properties was discussed extensively and was proved in many studies.

One of the main drawbacks of nanostructures based on titanium dioxide is a wide band gap. As it is known, the proportion of ultraviolet radiation in the solar spectrum is about 10% [5]. This fact limits the use of titanium dioxide in various applications. To solve this problem ones resort to various modifications of TiO₂ structures. Doping of titanium dioxide nanostructures by ions of Mo, Ru, Cu, Fe and N which leads to an increase in their photocatalytic activity [6]. It is believed that doping by anions, in contrast to the doping by metal cations creates less recombination centers and, therefore, is more effective for increasing the photocatalytic properties of titanium dioxide.

There are other methods of increasing the spectral sensitivity of nanostructures based on titanium dioxide, the creation of composite systems with the addition of CuO, CdS, ZnS Fe₂O₃ [7]. The proposed modification techniques have several drawbacks, foremost of which is that doping takes place during the synthesis or by thermal annealing. Upon doping during synthesis, doping elements are incorporated in the crystal structure of titanium dioxide. Tampering into the crystal lattice will change the entire structure, as a result electrical and photovoltaic properties of titanium dioxide will change too.

A promising direction of increasing the photocatalytic activity of titanium dioxide nanostructures is the use of surface plasmon resonance, which nanoparticles of a number of noble metals have (Au, Ag, Pt, Pd). Basically it is suggested to use NP of silver which have maximum plasmon effect in the visible spectral region [8]. However, the problem of oxidation of the silver nanoparticles is still unsolved. One solution to this is to use the "core-shell" structures, the core of which serves NP of metal and the shell is a semiconductor oxide metal (TiO₂). It is expected that the use of such geometrical design will protect the NP of metal from oxidation by electrolyte and significantly will increase the photocatalytic activity.

This paper presents the results of studies of the effect of silver nanoparticles on the photocatalytic properties of TiO₂ films on the basis of the "core-shell" structures.

1. Experiment. Obtaining of TiO₂ nanoparticles films.

For obtaining films of titanium dioxide nanoparticles a solution containing powder of colloidal TiO₂ (Sigma Aldrich) was prepared. The solution was prepared as follows: colloidal TiO₂ powder was ground in a porcelain mortar with a small amount of deionized water and acetone taken in a volume ratio of 10:1. Acetone was added to prevent clumping of the particles. After the formation of a homogeneous viscous paste solution of titanium dioxide nanoparticles was deposited on the FTO surface (glass coated with tin oxide doped with fluorine) by doctor-bleeding method. The resulting film was subjected to heat treatment at a temperature of 500 °C during 2 hours.

Synthesis of the "core-shell" structures.

Sodium borohydride weighing 0,001 g was dissolved in 25 ml of ethanol. Silver nitrate solution in a ratio of 0.0045 g was dissolved in 10 ml of ethanol. The resulting AgNO₃ solution with constant stirring was added to a cooled to -2°C solution of sodium borohydride in several steps with 50 microliters. For obtaining the "core-shell" structures ethanol solution of silver nanoparticles and titanium tetraisopropoxide TIPT (Ti(OCH(CH₃)₂)₄) was used. 1 ml of TIPT solution was added into 10 ml of silver nanoparticles solution.

For the synthesis of TiO₂ shell ethanol solutions TIPT and silver NP were mixed with vigorous stirring. The resulting mixture was stirred during 12 hours on a multi-functional rotator PTR-35 at a room temperature in the dark. From these structures the films were made.

For comparison of the photocatalytic activity of nanostructured TiO₂ films the reaction of photocatalytic decomposition of methylene blue dye (MB) was used by irradiation of UV light of a mercury lamp PRK-2. Sorption of dye molecules of MB into the films was carried out by keeping TiO₂ films in ethanol solution of luminophore with an initial concentration of C⁰=10⁻⁵ mol/l during 5 hours, followed by drying the film in an oven during 1 hour.

The photocatalytic efficiency of TiO₂ nanostructured films in the model reaction of photodegradation of the methylene blue dye was determined by the equation:

$$\eta = \frac{A_0 - A}{A_0} * 100\% \quad (1)$$

where A₀ - optical density of the dye without photocatalyst, A - optical density of the dye with the photocatalyst.

The absorption spectra of the films by methylene blue dye were prepared by a double-beam spectrophotometer Cary 300 UV-Vis.

The morphology of the obtained samples was investigated by using scanning electron microscopy (SEM) on a microscope MIRA 3LMU (Tescan, Czech Republic). The voltage on the accelerating electrode was from 20 to 30 kV.

2. Results and discussion

The morphology of the film surface of the nanoparticles and the "core-shell" structures are shown in Figure 1. From Figure 1, a it is evident that the film of titanium dioxide nanoparticles has a distinct granular structure. The particle size is about 25-30 nm. The thickness of the semiconductor layer is 8.3 microns.

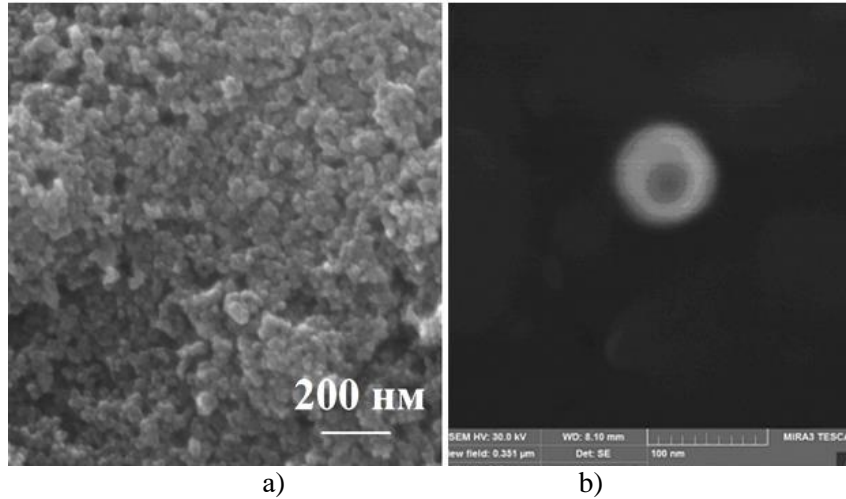


Fig. 1. SEM image of the film surface of titanium dioxide (a) and the "core-shell" structure (b).

Addition of silver nanoparticles of titanium tetraisopropoxide (TIPT) into solution the "core-shell" structure of a spherical shape is formed, which is shown in Figure 1, b. From the figure it is evident that in the center of the structure there is silver nanoparticle and the shell is formed by titanium dioxide.

Effect of silver nanoparticles on the photocatalytic activity of nanostructured TiO₂ films was investigated by the degradation of methylene blue dye molecules by the action of light.

The process of degradation of methylene blue dye can be described as follows. Irradiation with UV light leads to the generation of electron-hole (e⁻ - h⁺) pairs in TiO₂ nanostructure due to the absorption of the photon (process 2). Photogenerated electrons in the conduction band of TiO₂ react with oxygen molecules adsorbed on the TiO₂, as a result superoxide radicals (O₂⁻) are formed (process 3). In this case the holes in the valence TiO₂ zone react with water molecules and contribute to the formation of hydroxyl radicals (OH[•]) (process 4). Highly reactive hydroxyl radicals (OH[•]) and superoxide radicals (O₂⁻) react with a dye molecule adsorbed on the TiO₂ nanostructures and cause its degradation. During this reaction, there is discoloration of the dye solution (processes 5 and 6).

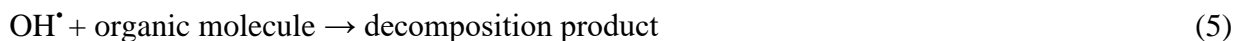


Figure 2 shows the absorption spectra of the methylene blue dye in aqueous solution.

As it is evident from the figure the absorption band of MB dye has a maximum $\lambda_1^{\text{max}} = 664 \text{ nm}$ at a wavelength and a half width $\Delta\lambda_{1/2}^{\text{absorp}} = 71 \text{ nm}$. UV irradiation of MB solution decreases the optical density of the dye molecules in ~1.1 times (Figure 2, a). When measuring the absorption

spectra of the MB dye at the presence of TiO_2 films the decrease of optical density at a wavelength of 664 nm in $\sim 1,7$ times is observed (Figure 2, b). The criterion for complete destruction of MB in the photocatalytic oxidation process is the lack of optical activity of MB solution in the range of 200 - 900 nm, which indicates the destruction of the MB molecule and its destruction products to the mineral compounds.

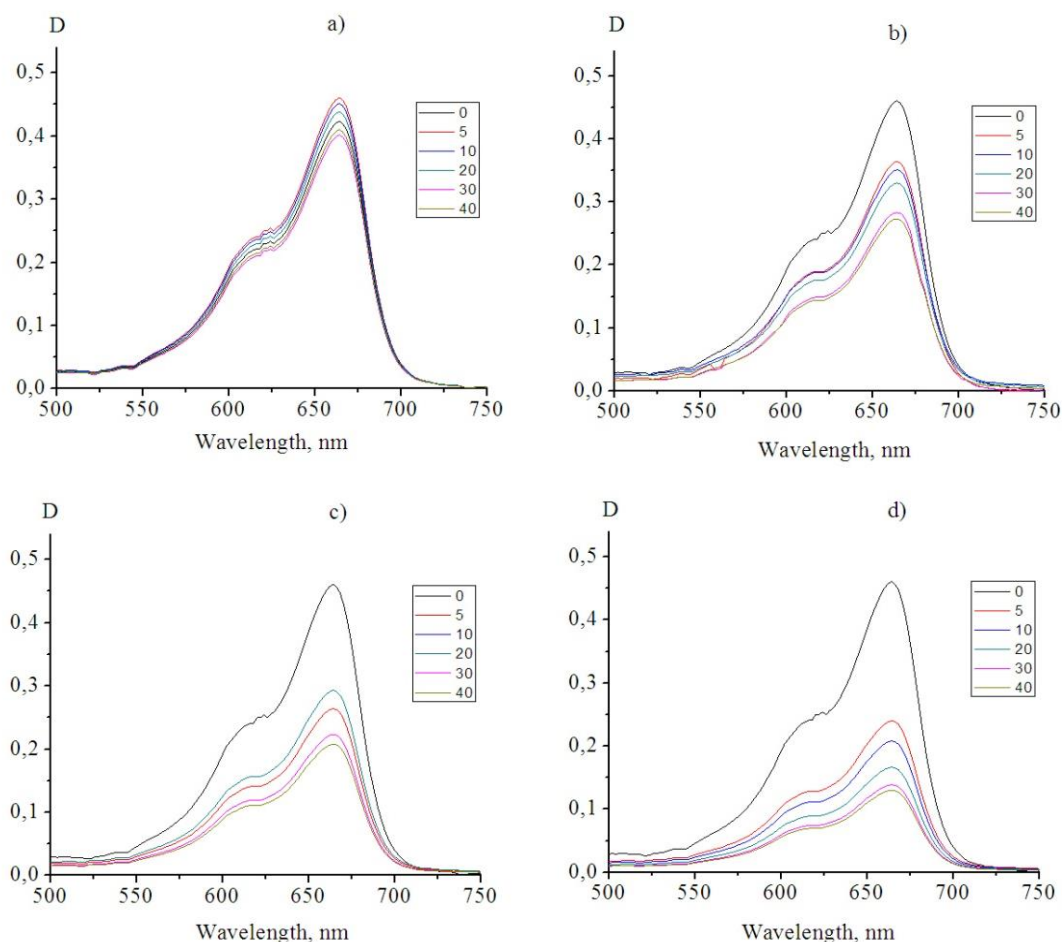


Fig. 2. The absorption spectra of the methylene blue dye in aqueous solution

When silver nanoparticles are added to the TiO_2 films the value of optical density in the MB absorption band is reduced in 2, 3 times (Figure 2, c). The presence in the solution of film dye of titanium dioxide with the "core-shell" structure leads to a decrease in the optical density in the absorption band of the dye in $\sim 3,8$ times (Figure 2, d). Wherein the position of the maximum of the absorption band and its half-width does not change.

The photocatalytic activity of the nanostructures was determined from the measurement of the optical density of the methylene blue dye on the spectrophotometer Agilent Cary 300. The dependence of the optical density D of the solution of methylene blue on oxidation time is shown in Figure 3. A comparative analysis of the impact of silver nanoparticles and the "core-shell" structure on the photocatalytic activity showed that doping of the "core-shell" structure affects more than the introduction to the system of silver nanoparticles. The calculations showed that at the dye photodecomposition without catalyst the oxidation state is $\eta=6.25\%$. When using TiO_2 films on the basis of the spherical nanoparticles oxidation degree was 35.4%, and for the "core-shell" structure was 76.6%.

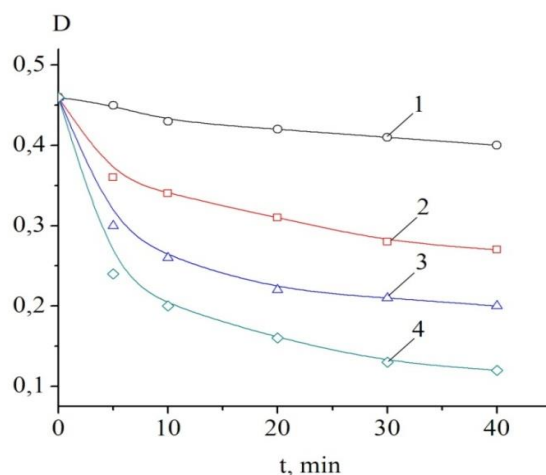


Fig.3. The dependence of the optical density of methylene blue on the irradiation time:
 1 - an aqueous solution of methylene blue; 2 - a solution with TiO₂ film;
 3 - solution with a film based on the "core-shell" structures of Ag/TiO₂ structure.

Conclusion

Thus, in the paper the photocatalytic activity of nanostructured films of titanium dioxide from nanoparticles and the "core-shell" structure was investigated. As a result of sensibilization of nanostructured films by the dye molecules of methylene blue and their UV radiation a decrease of its optical density associated with the photodegradation of the dye is observed with the lapse of time. The calculations showed that at the dye photodecomposition without catalyst the efficiency was 6,25%. The efficiency of the dye photodecomposition using films based on spherical , that the film based on the "core-shell" structure has the best photocatalytic properties.

Acknowledgments

This study was financially supported by the Committee of Science of the Ministry of Education of the Republic of Kazakhstan (General information BR05236691).

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