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**HUMAN HEALTH:
REALITIES AND PROSPECTS**

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Volume 4**

**HEALTH
and
BIOSENSORS**

**Edited by Nadiya Skotna, Svitlana Voloshanska,
Taras Kavetsky, Oleh Smutok, Mykhailo Gonchar**

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This research work belongs to a group of authors, contains an in-depth study of the health preservation problem and the use of biosensors for this purpose, fixes the scientific priority, provides society with the primary scientific information on health promotion, the formation of environmental responsibility.

The monograph is intended primarily for scientists and meets by its content and form of publication, but will be interesting for a wide range of public. The clarity of the wording and presentation of the material, the logic of coverage for the basic ideas and concepts in it are of particular importance. Requirements to the essence of the presentation of the material in the sections of the monograph, similar to the requirements of other scientific publications with certain features of their purpose. Moreover, the issues raised in this monograph are still the subject of lively discussion among contemporary domestic and foreign scholars.

We will be glad if the monograph will not leave you indifferent and you will want to share your impressions of it.

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Chapter 11. CREATION OF EFFECTIVE PHOTOCATALYTIC SYSTEMS WITH EXPANDED LIGHT SENSITIVITY RANGE

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Abstract. The search for effective photocatalytic systems is in the phase of intensive research which mostly focuses on such urgent human problems as photocatalytic transformation and the storage of solar energy. Solar power belongs to one of the most promising areas of the rapidly developing eco-power industry. In particular, the studies in this area also provide an environmental aspect, which is to preserve the stocks of traditional energy sources, fossil fuels, the consumption of which will lead to the inevitable exhaustion accompanied by pollution of the environment.

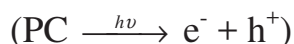
Despite the large number of studies carried out in the field of photocatalysis, the problem of creating highly efficient, cost-effective and energy-efficient photocatalytic systems is still unresolved. The most important prerequisite for the success in these areas is to create such photocatalytic systems that would ensure the flow of appropriate chemical reactions with high quantum yields. This gives grounds to regard topical the research aimed at increasing the activity of photo catalysts and expanding the range of their photosensitivity, on the development of such materials and on the application of their peculiarities in the course of various chemical transformations.

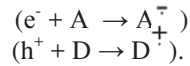
Keywords: Photocatalyst; Heterostructure; Sensitizer; Polymethinedye.

Introduction

The construction of photocatalytic systems is based on the principles of classical photocatalysis; however, a more actual is nanocatalysis aimed at the creation of an energy-balanced photocatalytic system for both nano- and micro-sized catalysts; is very effective for semiconductor and metal-complex materials and nanosystems.

The simplest redox photocatalytic system should contain a semiconductor photocatalyst (PC) and two reagents, one of which is an electron acceptor (A) and the other – electron donor (D). A closed photocatalytic cycle is realized in the case when after photogeneration of the pair electron-hole acceptor takes an electron from the conduction band while the hole is transferred to the donor. Subsequent reactions of intermediate products $A^{\cdot-}$ and $D^{\cdot+}$ can take place without the participation of the photocatalyst and the action of light [20, 21].





A necessary condition for the functioning of the photocatalytic system is the balance of the thermodynamic and energy characteristics of the components of the system, which leads to the formation of products that in turn would lead to the oxidation of D and the restoration of A. Thus formed ion-radicals enter into further dark interactions leading to obtaining finite stable products (P):



or after the inter-combination conversion to the triplet state of T_1 . The energy diagram of the simplest photocatalytic systems and the electronic processes occurring in them are presented in Fig. 1. [19].

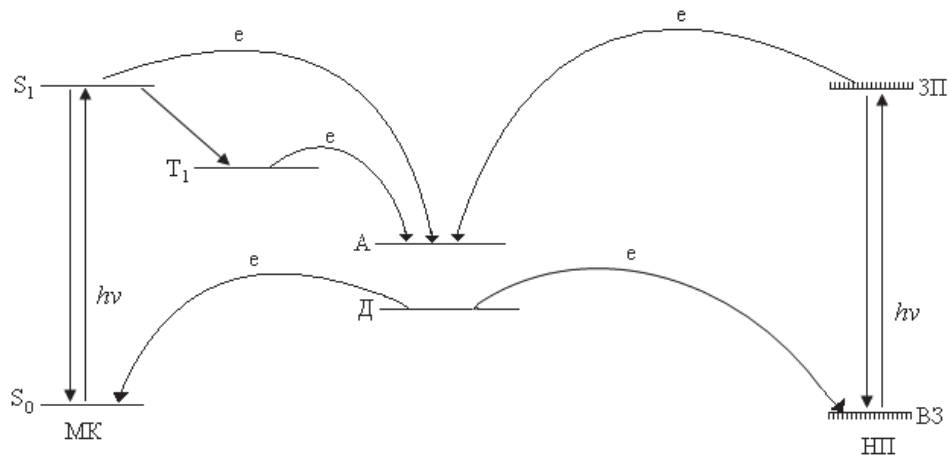


Fig. 1. Mutual arrangement of energy levels of photocatalyst zones and two reagents (acceptor A and donor D) and directions of electronic processes that arise in the simplest photocatalytic system [19]

A closed cycle in a semiconductor photocatalytic system can be realized providing that the potential of the conduction band (E_{CB}) is more negative than the recovery potential of the acceptor (E_A^{red}), and the valence band potential (E_{VB}) is more positive than the potential of the oxidation of the donor (E_D^{ox}), that is:

$$E_{CB} < E_A^{red}, E_{VB} > E_D^{ox}.$$

The effectiveness of oxidation-reduction reactions according to [20] should increase with increasing energy clefts that characterize the moving force of reactions, which is confirmed by the results of studies [16, 9, 6].

$$\Delta E_{red} = E_A^{red} - E_{CB};$$

$$\Delta E_{ox} = E_{VB} - E_{D}^{ox}.$$

This approach to construction is confirmed by numerical studies of photocatalytic activity in the redox reactions of a number of colorants with the participation of TiO₂ [2,17].

From the above-discussed regularities it is clear that a photocatalyst plays the key role in redox processes and the increased efficiency of its activity is crucial for the wide introduction of photocatalysis into practice. With this in mind, it is advisable to consider the requirements for semiconductors as photocatalysts and the main factors that determine their activity. When choosing a semiconductor photocatalyst for this or that reaction, the following requirements must be taken into account: [19]

- ability of photocatalysts to absorb the light of a corresponding spectral range with the transition to excitatory states, to be reactive with respect to the donor and the electron acceptor;
- coherence of the energy levels of the photocatalyst and the energy correspondence of the oxidation-reducing characteristics of the excited photocatalyst and the components of the reaction mixture corresponding to the oxidation and recovery potentials of both photocatalytic system reagents (the bottom of the conduction band and the valence band ceiling, as well as the relative positioning of the energy levels of the zones of the two donor D reagents and acceptor A);
- relative stability of the system, which excludes the most obvious possibilities of irreversible ones, including destructive changes of the photocatalyst when it interacts with the main or excited states with the reaction participants, primary, intermediate and end products.

In particular, factors that determine the activity of photocatalyst should be taken into account since the rate and quantum yields of the oxidation-reduction reaction can be low. To ensure the necessary conditions, according to [19-21], it is necessary:

1. That during its lifetime, the excited state photocatalyst should collide with at least one of the components of the reaction mixture so that the electron transfer could take place. Such transitions can be $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ in the molecular photocatalyst and electron-hole recombination in a semiconductor photocatalyst. Consequently, one of the factors determining the speed of the total process of obtaining end products is the frequency and effectiveness of the collisions mentioned above.
2. The influence of thermodynamic and kinetic characteristics of reactions that are not related to the closed photocatalytic cycle, that is, the transformations of the primary products D and A, which result in the formation of end products.
3. The factor associated with the properties of the photocatalyst itself, namely: the type of electronic transitions under the action of a quantum of light, the orbital nature of excited states, and the time of their life.
4. A factor that adversely affects the efficiency of the photocatalytic process is the possibility of reactions of the radical ions $D^{\cdot\pm}$ and $A^{\cdot\pm}$ with ionic radicals of the molecular photocatalyst $M^{\cdot\pm}$ and M^{\pm} or an electron or hole of the photo-excited semiconductor, which in many cases proceed much faster than the reactions leading to the formation of end products.
5. Give a photocatalyst the appropriate form and look, where it will exhibit the highest photocatalytic activity, which also depends on the size of the semiconductor particles, their surface condition, the presence of impurities, the use of carriers of different nature, etc.

Consideration of such principles is also relevant for further search, studies and development as they have not yet been sufficiently clarified and require a more detailed study.

Thus, the above principles of the organization of photocatalytic systems allow us to "construct" an optimal photocatalyst with the highest photocatalytic activity and increase the efficiency of its photocatalytic action.

According to [8; 12; 19-21; 22] semiconductor photocatalytic materials should absorb light in the near UV – or in the visible area and the position of their conduction zones (CZ) and valence (VZ) zones in the potential scale should be such that there would be thermodynamically winning processes of photogeneration of electrons and holes with a large number of substances, both organic and inorganic.

The location of the valence band of the semiconductor determines the oxidizing capacity of the photogenerated holes, and the arrangement of the conduction band is the restorer power of electrons excited to this zone.

For the effective conversion of solar energy, the materials are required with width of the band gap $E_g = 1.3 \pm 0.3$ eV, corresponding to the absorption of light with a wavelength of 1000 ± 250 nm. If E_g is small, semiconductor stability is unsatisfactory. In addition, taking into account the values of the overvoltage, value $E_g \geq 2$ eV is required to carry out electron transport reactions.

Fig. 2 shows the location of different semiconductor zones in a solution at pH = 1 in comparison with the standard potentials of some redox pairs [19].

The location of the valence band of the semiconductor determines the oxidizing capacity of the photo-generated holes whereas the arrangement of the conduction band is the restoring property of the electrons photo-excited to this band. The analysis of the diagrams (*Figure 2*) shows that the semiconductor compounds SnO_2 ($E_g = 3.6$ eV), TiO_2 ($E_g = 3.2$ eV), ZnO ($E_g = 3.2$ eV), WO_3 ($E_g = 2.8$ eV), CdS ($E_g = 2.5$ eV) and others are wide-band and may be suitable for use as photocatalyst in contrast to narrow-band, such as GaAs ($E_g = 1.4$ eV), CdSe ($E_g = 1.7$ eV).

They cannot be used as photocatalytically active substances, since the electrons of the conduction band of narrow-band semiconductors are weak restorers, and valence holes are weak oxidizers, and as a result, the photocatalytic cycle cannot be completed.

Therefore, the most active broadband semiconductors proved to be metal oxides (SnO_2 , TiO_2 , ZnO) [8; 12; 22].

However, most studies are devoted to TiO_2 , therefore, let us dwell in detail on a number of publications related to the study of its characteristics.

Titanium (IV) oxide exhibits the properties of a broadband semiconductor. The width of the bandgap of direct transitions in the bulk material is 3.1-3.2 eV for the anatase, for the rutile 2.96-3.03 eV, for the brookite about 3.04 eV. Of the three major structural modifications of TiO_2 (rutile, anatase and brookite), the crystalline structures of which are depicted in *Fig. 3*, the most used are anatase and rutile, but the highest photocatalytic activity is the crystalline modification of anatase [31; 32].

Transitions in anatase at a band gap of 3.2 eV are indirect. In accordance with the modern view, electrons can be in two states: free and bound. In the first state electrons move along a crystal lattice formed by cations Ti^{4+} and oxygen anions O^{2-} .

In the second state – basically the electrons are bound with some ion of the crystal lattice and take part in the formation of the chemical bond.

For the transition of an electron from a bound state to a free energy, it is necessary to use energy greater than 3.2 eV (the width of the anatase band gap). This energy can be delivered by quanta of light with a wavelength $\lambda \leq 390$ nm.

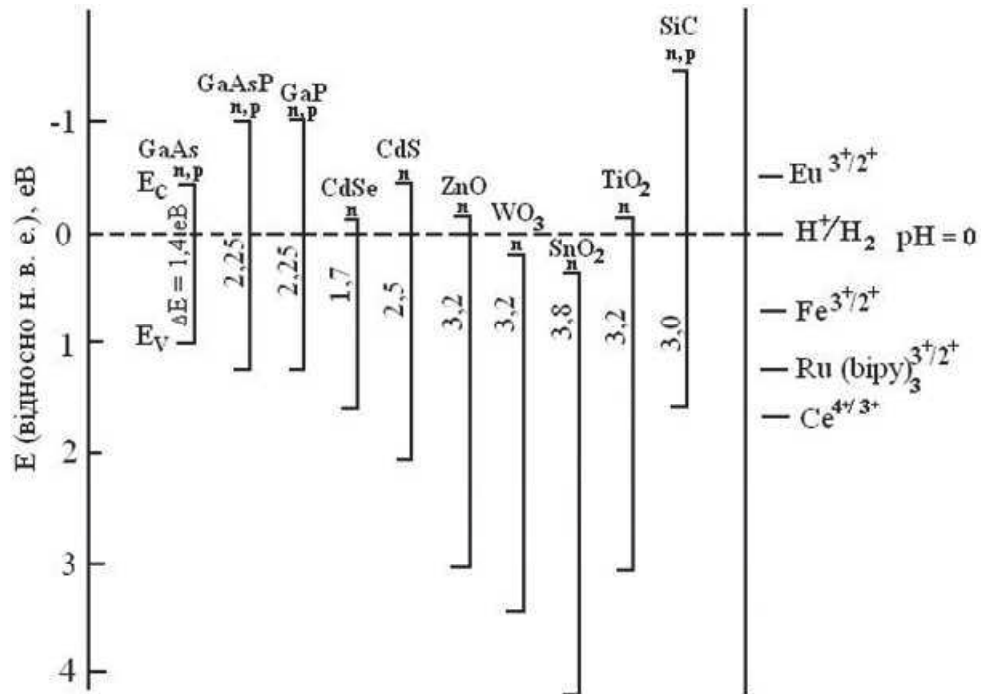


Fig. 2. The positions of energy levels (valence band and conduction band) for a number of semiconductors along with redox potentials [19]

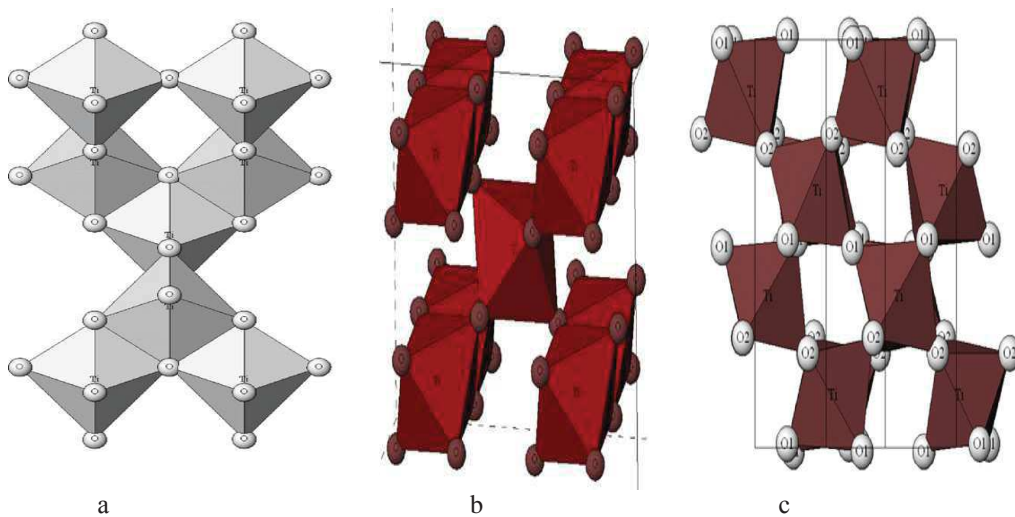


Fig. 3. Projection of the crystalline structure of anatase (a), rutile (b) and brookite (c)

Accordingly, only a small part of the sunlight can be used to carry out photocatalytic processes involving anatase. Nevertheless, among a wide range of semiconductor materials TiO_2 is most often used as a photocatalyst due to its stability in aqueous solutions, cheapness, harmlessness for living organisms [25], and also due to the large oxidizing capacity of photo-generated holes ($E = 2.9 \text{ V}$ at $\text{pH} = 0$) [24].

The possibility of using semiconductor materials as photocatalyst is also determined by structural parameters that influence photocatalytic activity, namely: phase composition, morphological properties, pH-medium, composition of surface groups, and the presence of defects in both surface and volume of crystals. It was determined [4; 18; 27] that photocatalytic activity of TiO_2 is rather sensitive to its particle size, degree of crystallinity and phase composition.

The physicochemical properties of a semiconductor according to [5; 29] are influenced by a collective factor (the position of the chemical potential of electrons and holes), which is the driving force of charge transfer to a semiconductor, as well as a local factor – the nature and concentration of defects taking part in the formation of active centers. The interaction of the two factors affects the electronic system of the conductor changing the adsorption and catalytic properties. Unfortunately, there are no reliable correlations that connect the activity with the property of the surface of the semiconductor to this day. The efficiency of the catalyst can be increased by the method of sensitization of the photocatalyst in the long-wave area with the initial separation of the photogenerated particles and the catalysis of the dark stages of the photocatalytic process.

There are two known ways to implement the process:

- creation of compositions (addition of a reagent to a photocatalyst);
- creation of the HS.

In the first case, kinetic problems are created for the implementation of electronic processes that involve the need for convergence and connection of components over a short period of time of the excited state of a photocatalyst or sensitizer for the possibility of their interaction. The photocatalyst only partially reacts with the addition to absorption of a quantum of light, which promotes rapid recombination of the electron and hole and reduces the catalytic process in general.

The second, more effective method of constructing systems is based on the creation of composite materials (hetero-structures), which in their composition contain additional components – photocatalytic blocks [16], which prevent or reduce the negative effect of the recombination process. In particular, for such systems, the convergence of components is not required, since the direct deposition of the component (colorant) takes place directly on the surface of the semiconductor particles and the component in the conditions of photo-excitation easily enters the electron interaction with the photocatalyst. The use of photo blocks makes possible to exclude the process of light-filtering due to the presence of a component (colorant) in an optimal amount. Some components of the hetero-structures are primary mediators that can capture the hole and pass on the reagent contained in the solution volume.

Non-metals, metals and metal oxides, electrically-conductive polymers, colorants that are capable to enter the oxidation-reduction reaction are used as additional components that play the role of photocatalytic units.

Doping with dyes. This method is used to improve photocatalytic properties and relates to nanocatalytic systems. Among the photosensitive semiconductor materials, a special place is occupied by systems consisting of a semiconductor and a dye-sensitizer retained on its surface due to chemisorption or physical adsorption, which occurs due to weak Van der Waals forces between the dye molecule and the TiO_2 surface. The quantum-dimensional effect is manifested in increasing the width of the band gap with the corresponding shift of the

absorption band into the short-wave region.

Sensibilizers, which are used in sensitized dyes in photosensitive systems, can be conveniently divided into two groups: organic and inorganic [3]. The latter include polypyridine complexes of ruthenium and osmium, porphyrins, phthalocyanines. Organic sensibilizers include natural and synthetic anthocyanins, chlorophylls, which are less thermally and chemically stable than inorganic ones.

The general structure of a typical organic sensitizer: "donor – π -bond – acceptor" is that its absorption region is shifted to the IR region of the spectrum, which causes increased absorption of light. Other advantages of using organic dye as sensitizer are: high absorption coefficient due to intermolecular π - π^* -transitions, low cost and lack of expensive components. This direction is rapidly evolving and is effective in converting energy into solar cells using organic dyes. The effectiveness of such cells is already equivalent to those constructed using polypyridyl ruthenium sensibilizers, most often Ru (II), Ru (III)), which central ion is surrounded by neutral and (or) anionic ligands [28]. The advantage of ruthenium complexes is the wide absorption band in the visible area of the spectrum, due to photo-induced electronic transitions of metal ions/ligands, which leads to the formation of excited states of dye molecules with their lifetime being tens of picoseconds.

The authors [1] developed sensitizers based on coumarin derivatives and achieved the efficiency factor of 7.6%. A group of researchers [10] reached the efficiency of energy conversion at the level of about 9.0% using complex indolinium dyes.

In the paper [13], the implementation of chlorophyll is proposed, which use allowed to obtain the value of the solar energy conversion efficiency of 2.6%. In [11] natural anthocyanin cyanine dye was used as an organic dye-sensibilizer, the absorption properties of which can be altered by the formation of complexes with polyphenols, pectins, and ions Al^{3+} , Fe^{3+} , Cr^{3+} , Ti^{4+} , Sn^{4+} shifting the absorption spectrum to the long-wave side.

Polymethine dyes have proved to be active transducers of solar radiation energy, which is of great importance when used in highly-effective solar cell sensitized dyes [15]. The first dye in this series was synthesized in 1856, which was named "cyanine", the chemical structure of which was established in 1906 but found its practical application as a dye-sensibilizer only in the 20th century. The studies in this field were initiated by Academician A.I. Kiprianov and later were continued by his students: V.M. Zubarovskiy, G.T. Pilyugin, G.G. Dyadyusha, A.I. Tolmachov, O.O. Ishchenko and others [15] who sought to find dyes with given spectral and chemical properties.

It is polymethines with the widest assortment in the whole visible and near infrared range of the spectrum of photophysical and photochemical properties of organic dyes that are promising for the creation of photosensitive materials by introducing into their chromophore bridge formations [33], which has solved a number of practical issues linked with the transformation of solar energy.

An important study in the transformation of solar energy is the simultaneous adsorption of several different dyes with different absorption maxima on TiO_2 electrode, which increases the efficiency of absorption of solar radiation. It was found in [7] that the efficiency of TiO_2 -electrode is increased, which is stipulated by the use of a mixture of two dyes, $Ru(dcbpy)_2(NCS)_2$ and scarred cyanine dye (in a molecular ratio (100:1) that the photocurrent and efficiency drastically decreased when the ratio of the two dyes is 1:1. However, this approach has a limit. Using a mixture of three different dyes, yellow, red and blue to attract the entire spectrum, the quantum yield of products was very low (10%) in the entire long-wave region [34]. The combined sensitizing effect of using several dyes is very interesting but not at all simple. It is established that the efficiency of the photocurrent is high if there is a strong interaction between different dyes as the electron and energy transfer is ensured much better.

Thus, the analysis of the above facts indicates the relevance of the study aimed at increasing the activity of photocatalysts and expanding the range of their photosensitivity, the development of such materials and the search for ways of their practical application.

The purpose of the study:

- determine photocatalytic activity;
- establish connections of photocatalytic activity depending on the composition and nature of the interaction of components; to find out the features of their participation in photo-catalytic processes and the possibilities of their practical use;
- design and obtain new photosensitive materials on the basis of titanium (IV) oxide and dye-sensibilizer with the extended range of photosensitivity.

Material and methods

The research material is the physico-chemical organization of effective redox systems with an extended range of photosensitivity, which provides them with the intended necessary set of properties; redox photocatalytic processes involving these systems.

Methods of research – spectrophotometry, spectroscopy of diffuse reflection.

Results and discussion

To study the sensitizing effect of the dye (B) on the semiconductor, heterostructures were constructed using titanium (IV) oxide type P25 (Degussa), polymer polyepoxypropylcarbazole (PEPC) and various dyes. The structure of these hetero-structures is shown in *Fig. 4*

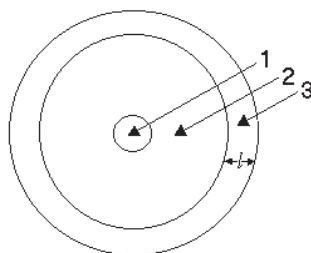
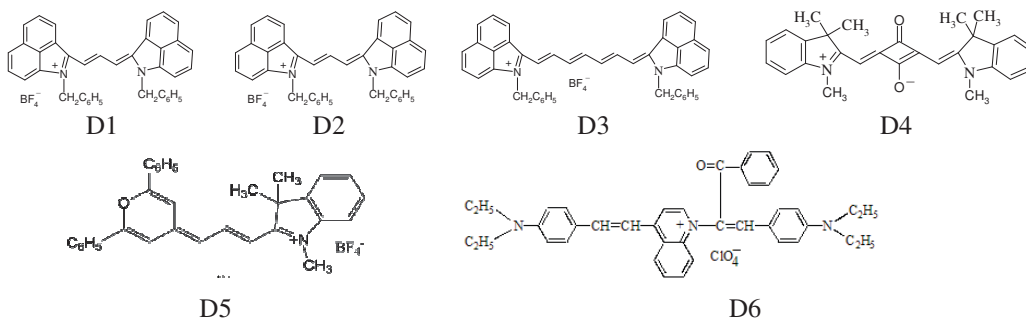


Fig. 4. *The structure of the HS TiO₂/B/P: 1 – the particle of the TiO₂ semiconductor, 2 – dye-sensibilizer; 3 – polymer film (l – thickness of the polymer layer)*

The method [26] was used, which consisted in processing their dispersions with alcoholic solutions of a certain concentration followed by complete evaporation, which lead to the precipitation of the dye on semiconductor particles. After drying the resulting heterostructures at 40°C, to remove the solvent completely a similar procedure was carried out using a solution of PEPC in benzene in which the dye does not dissolve. As a result, the heterostructure was covered with a thin film of the polymer, which protected them from dissolution and, at the same time, did not interfere with electronic interactions with the components of the solution. During the experiment it was found that the optimum content of PEPC in HS is 0.02 – 0.2 mg/g. Due to protection from the action of the solvent, we obtained hetero-structures with a very wide content of applied biscyanin containing the amounts at which poly-molecular layers are formed. The studied dyes were synthesized in the Color and Organic Compounds Department at the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine under the direction of Prof. Ishchenko O.O. and provided for research of their photocatalytic properties to the Department of Chemical Analysis, Expertise and Food Safety at Yuriy Fedkovych Chernivtsi National University.

Synthesis and optical characteristics of the studied polymethine dyes given below are described in [14; 23].



Spectral analysis of cationic symmetrical colorants D1-D3 was carried out. Among them are: cationic symmetric D1-D3 and cation-anionic (flower-ionic) D4 containing one conjugate chromophore and cationic asymmetric D5-D6 with two conjugate chromophores. The structure of the squaraine type D4 dye contains a quaternary cycle with a substituted cyclobutenone oxygen atom in the middle of the polymethine chain, which should enhance the conjugation of the system. However, a smaller number of methane groups in the D4 molecule can simultaneously reduce conjugation [31].

It was studied that the structure of the dye and the location of the functional groups substantially affects its sensiblizing ability, and, accordingly, the photocatalytic activity of the hetero-structures on its basis. The analysis of absorption spectra of cationic symmetrical dyes D1-D3 shows that they contain an intensive absorption band in the long-wavelength region of the spectrum corresponding to the transition $S_0 \rightarrow S_1$ with a characteristic shoulder of oscillatory nature. Such linear conjugate systems that contain the same finite groups but differ in the number of vinylene groups in the conjugation chain form the so-called vinylogous series, in which, when the polymethine chain extends, the maximum absorption moves to the long-wave region. Symmetrical PBs have the greatest value of the vinylene shift when lengthening the conjugation circuit. It was established that the extension of the polymethine chain in the studied cationic symmetrical dyes D1-D3 to one vinylene group leads to a regular linear bathochromic displacement of the maximum absorption band for 110 and 117 nm, respectively (*Fig. 5*).

To establish the nature of photoreactions that run on the surface of semiconductors sensitized with dyes, it is necessary to know the spectral sensitivity of these photo-processes. However, due to the light scattering process, optical measurements of surface absorption spectra are difficult and the obtained results are inaccurate. In order to obtain the correct values, Halman and his colleagues used the method of diffuse reflection spectroscopy to determine the band gap width and spectral sensitivity of semiconductor dispersions. For all the investigated HS diffuse reflection spectra were obtained, which are listed by the Kubelka-Munk method in the absorption spectra for comparative analysis.

Figs. 6-7 show absorption spectra of dye D1 in DMF ($C = 1.0 \times 10^{-5}$ mol/l) (a) and HS $\text{TiO}_2/\text{D1/P}$ (b). Dye-sensitizer content in HS: 1 – 0.02; 2 – 0.1; 3 – 0.2; 4 – 1.0; 5 – 2.0 mg/g. The absorption spectrum of the dye solution D1 with a maximum $\lambda_{\text{max}} = 766$ nm is expanded in the absorption spectrum of the hetero-structure with the coverage of the ultraviolet, visible and part of the near infrared region. The same pattern is observed for HS with the use of dyes D2 and D3 which have similar narrow spectra with intense peaks at a maximum $\lambda_{\text{max}} = 876$ and $\lambda_{\text{max}} = 993$ nm respectively.

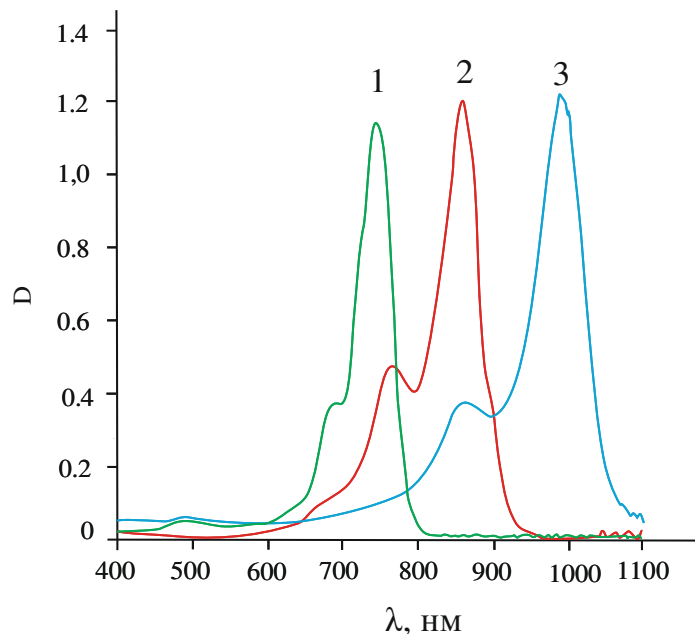


Fig. 5. Absorption spectra of dichloromethane solutions of symmetric cationic dyes D1-D3. The concentration of the dye solution is $2.5 \cdot 10^{-5}$ mol/dm³

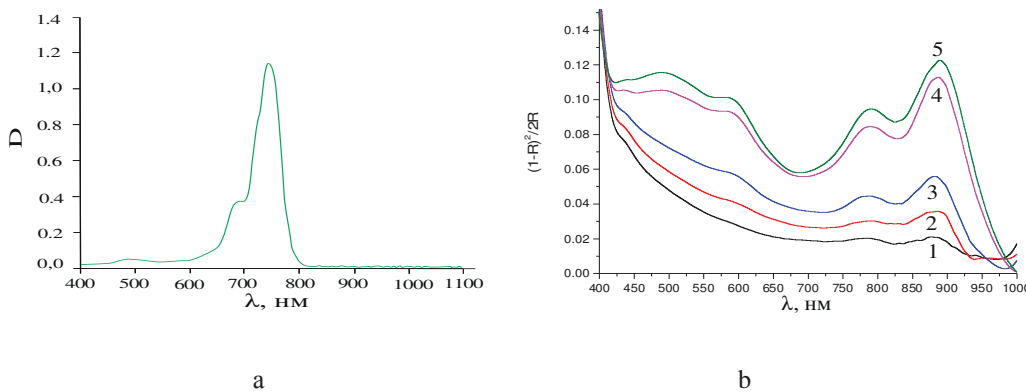


Fig. 6. Absorption spectra of dye D1 in DMF ($C = 1.0 \times 10^{-5}$ mol/l) (a) and HS P/D1/TiO₂ (b). Dye content in HS: 1 – 0.02; 2 – 0.1; 3 – 0.2; 4 – 1.0; 5 – 2.0 mg/g

As can be seen from the comparison of the spectra (Figs. 7 and 8), depending on where the dye is (in solution or as a part of the hetero-structure), there is a different spectral arrangement of the absorption bands of the dye. In the spectrum of dimethylformamide solution of dye D2 (Fig. 7), the maximum absorption band is at $\lambda = 876$ nm and in the absorption spectrum of the HS with a content equal to 1 - 0.02; 2 - 0.1; 3 - 0.2; 4 - 1.0; 5 - 2.0 mg/g, shifts in the gap $\lambda = 880$ -895 nm respectively. The largest shift of the absorption band is observed in the case of a dye concentration equal to 0.2 mg/g.

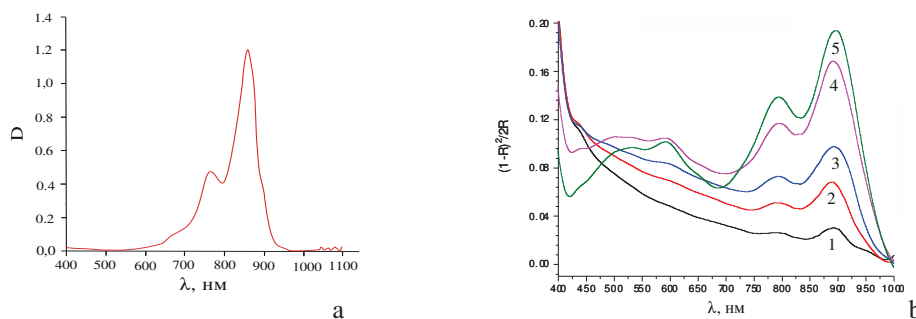


Fig. 7. Absorption spectra of dye D2 in DMF ($C = 1.0 \times 10^{-5}$ mol/l) (a) and HS P/D2TiO₂ (b). Dye content in the HS: 1 – 0.02; 2 – 0.1; 3 – 0.2; 4 – 1.0; 5 – 2.0 mg/g

For dye D3 (Fig. 8), the maximum absorption band is located at $\lambda_{\max} = 993$ nm, which allows it to attract light from the near infrared region.

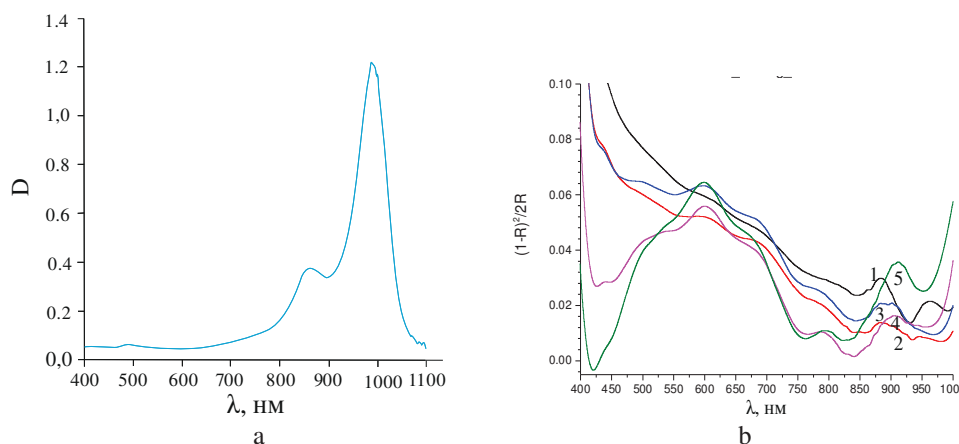


Fig. 8. Absorption spectra of D3 dyes in DMF ($C = 1.0 \times 10^{-5}$ mol/l) (a) and HS II/D3/TiO₂ (b). Dye content in HS: 1 – 0.02; 2 – 0.1; 3 – 0.2; 4 – 1.0; 5 – 2.0 mg/g

When applied to the surface of titanium (IV) oxide, the absorption band expands and covers almost the entire band of the visible and near-infrared absorption spectrum (from 450 to 950 nm). This creates a potential for use in the photocatalytic process of light quanta of a wide energy band. The results of the analysis of absorption spectra of the HS testify to the significant influence of the semiconductor on the electronic system of dye molecules. This clearly illustrates the use as a sensitizer biscyanine dye D4.

Absorption spectra of dichloromethane dye solution of D4 squaraine type with a dye solution concentration of $2.5 \cdot 10^{-5}$ mol/dm³ is shown in Fig. 9. The maximum of its spectrum $\lambda_{\max} = 632$ nm, which is an order of magnitude greater than the TiO₂ absorption region, indicates that this dye works in the visible region and therefore can attract light of a wider range. In particular, the dye structure of D4, which contains a quaternary cycle with a substituted cyclobutene oxygen atom in the middle of the polymethine chain, which should ensure its sensitizing ability, and, accordingly, also the photocatalytic activity of the hetero-structures on its basis.

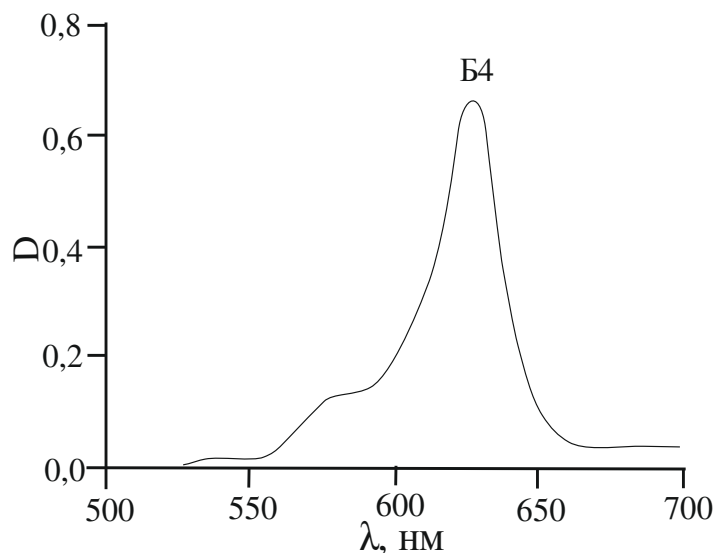


Fig. 9. Absorption spectrum of dichloromethane solution of dye D4. Dye solution concentration is $2.5 \cdot 10^{-5} \text{ mol/dm}^3$

Comparison of absorption spectra of D4 dye contained in the solution (Fig. 9) and included in the HS (Fig. 10) shows that applying it to a solid substrate leads to an increase in the association processes. On the TiO_2 surface, presumably, associates are formed, namely excimers (J- and H-states), which is quite characteristic for this type of dyes. The above is confirmed by the fact that in the case of the formation of associates, new additional bands are usually formed in a region with smaller wavelengths than the dye-monomer. At the same time, the intensity of the narrow band $\lambda_{\text{max}} = 632 \text{ nm}$ ($\epsilon = 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) changes, it expands strongly and covers most of the visible band. This creates the potential for use in the photocatalytic process of light quanta of a wide energy range.

Fig. 10 shows the spectrum of absorption of acetonitrile solution of biscyanine dye D4 ($C = 1.25 \cdot 10^{-4} \text{ mol/l}$, $l = 1 \text{ cm}$) and HS P/D4/ TiO_2 with different dye content: 2 – 0.02; 3 – 0.1; 4 – 0.2; 5 – 1.0; 6 – 2.0 mg/g.

Similar dependences are observed for samples of HS containing other studied dyes, in particular, biscyanine dyes D5 and D6, their spectra are shown in Fig. 11.

The analysis of the results shows that the application of dye to the TiO_2 surface leads to an increase in the association processes, which results in a change in the intensity ratio of the narrow bands with absorption maxima of the dye solution $\lambda_{\text{max}} = 587 \text{ nm}$ i $\lambda_{\text{max}} = 626 \text{ nm}$. In the absorption spectrum of the hetero-structure, they expand and almost merge into a single band that covers most of the visible region (Fig. 11). On the surface of the titanium (IV) oxide, it is likely that aggregates (associates) are formed. They cannot be called polymers because they are not chemically bonded. These associates can be called J- and H-aggregates. Their formation is characteristic of this type of dyes, and they are described in the literature. The width of the absorption band was determined (at 2/3 of the height of the maximum) for the short-wave (sw) and long-wave (lw) band and the values were obtained – 45 and 38 nm respectively. Ratio of intensities $I_{\text{sw}}/I_{\text{lw}} = 0.93$. In the spectra of the HS P/D5/ TiO_2 lw the band is wider than the one observed in the absorption spectra of the solution (Fig. 11).

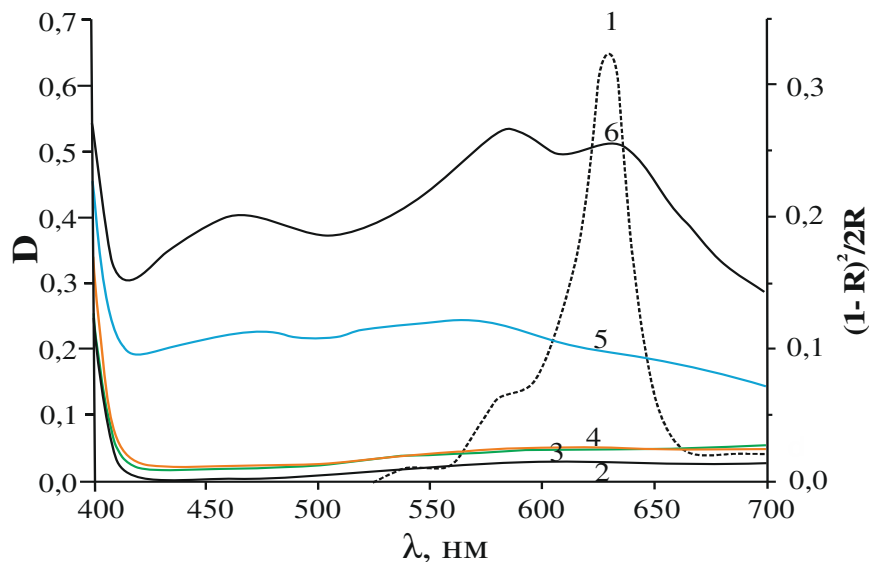


Fig. 10. Absorption spectra: 1 – D4 in acetonitrile ($C = 1.25 \cdot 10^{-4}$ mol / l, $l = 1$ cm) and HS P/D4/ TiO_2 with different dye content: 2 – 0.02; 3 – 0.1; 4 – 0.2, 5 – 1.0; 6 – 2.0 mg/g

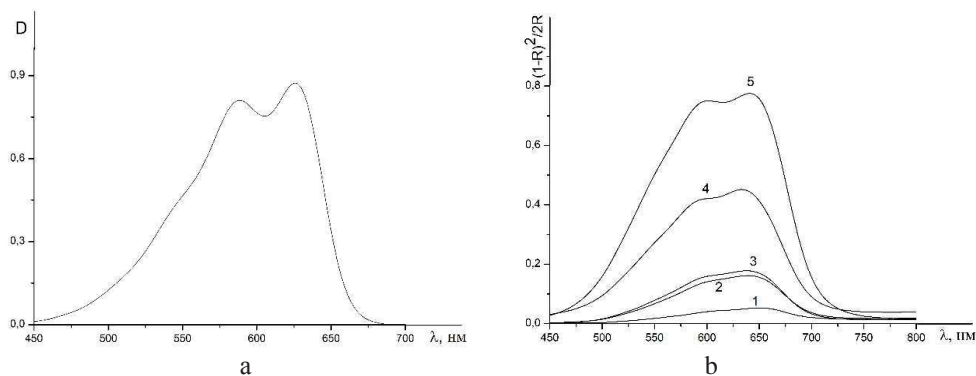


Fig. 11. Absorption spectra of dye D5 in alcohol solution (a) and hetero-structures P/D5/ TiO_2 (b). Dye content in the HS (mg/g): 1 – 0.02, 2 – 0.1, 3 – 0.2, 4 – 1.0, 5 – 2.0

The absorption spectra of the HS can trace changes in the most important parameters that occur when the dye is deposited on the titanium (IV) oxide particles and when its content is increased in these materials. The analysis of spectral data showed, firstly, that the position of the two bands depends on how much dye is in the HS. It is shown that λ_{max} of the sw band in samples 5, 4, 3 containing a sensitizer in the amount of 2.0, 1.0, and 0.2 mg/g are placed, respectively, at 599, 602, and 606 nm and the position of the lw band for the same samples are located, respectively, at 641, 633, and 637 nm. We failed to determine the position of λ_{max} of sw and lw bands for samples 1 and 2 containing a sensitizer in the amounts of 0.1 and 0.02 mg/g due to their large blurring.

The second important change that occurs when switching from solution to HS is a significant increase in the absorption bandwidth, which increases their overlap. Thus, in the sample 5, the width of the sw band is 1.5 times larger than in the spectrum of the solution and similarly, the lw band is characterized by no less smaller value.

A characteristic feature of biscyanines is the presence of the two absorption bands that arise as a result of the interaction of chromophore and the resulting splitting due to this singlet level S at a level with greater and lesser energy. It is shown (*Fig. 12*) that the precipitation of D6 on the surface of TiO₂ leads to a bathochromic displacement of both absorption bands, the magnitude of which is in the antibiotic dependence on its content in the HS. In the case of the HS of the dye D6 from TiO₂ (*Fig. 12*), the short-wave band ($\lambda_{\max} = 432$ nm) undergoes a shift of 19 and 24 nm, while the long-wave ($\lambda_{\max} = 603$ nm) is 27 and 21 nm with a dye content of 2.0 and 1.0 mg/g respectively. It was also established that during the application of the dye on the surface of TiO₂ the ratio of the intensity of the short-wave (I_{sw}) and the long-wave (I_{lw}) absorption bands changes, which, according to the theory of biscyanine spectra, indicates a change in the angle between the directions of chromophore from the obtuse ($I_{sw}/I_{lw} < 1$) to acute ($I_{sw}/I_{lw} > 1$) (*Table 1*).

Besides, we found the inverse relation of the degree of change of the parameters of the spectrum λ_{\max} and I_{sw}/I_{lw} on the quantity of dye molecules in the HS, which is explained as a result of the decrease of the influence of TiO₂ on their electronic system, that is, weakening of the interaction of the components resulting in deterioration of the conditions for the electron transport photoconductive processes and, consequently, decrease in photocatalytic activity. In all cases as has been established the initial increase in photocatalytic activity is caused by an increase in the number of dye molecules that absorb visible light. With the increase of dye content in the HS the displacement decreases. This is due to the gradual filling of the surface of the semiconductor particles and the transition from the monomolecular layer to the polymolecular coatings.

We also note that even with a hundredfold increase in the amount of dye, the small margin of location of the maximum bands remains, and the mutual influence of the HS components is not completely eliminated. Comparison of the intensity of the bands in the spectrum of absorption of the alcoholic solution of the test bisquinocyanine (*Table 1*) gave the value of $I_{sw}/I_{lw} = 0.76$, indicating that the chromophore are arranged at a obtuse angle relative to one another. The analysis of the spectra of the hetero-structures (*Fig. 12*) showed for samples 5, 4, and 3 the values of I_{sw}/I_{lw} , which equal, respectively, 1.02, 1.38, and 1.8, which shows that for a precipitated dye, conformations with acute angles between the directions of chromophore are more advantageous. Changes in the parameter I_{sw}/I_{lw} as well as the displacement of the maximum bands, are in the inverse relation on the number of its molecules in the HS, and this is satisfactorily explained by the weakening of the influence of the electronic system of titanium (IV) oxide on them.

Therefore, proceeding from the above-discussed regularities one can see that deep-colored dyes significantly affect the photosensitivity and increase the efficiency of the photocatalyst and play a decisive role for the wide introduction of this type of photocatalysis into practice.

Conclusions

We have studied the spectral characteristics of different polymethine dyes: cationic symmetric D1-D3 and cation-anionic (flower-ionic) D4 containing one conjugate chromophore and cationic asymmetric D5-D6 with two conjugate chromophores. And we have also established the regularities that connect the spectral properties of polymethine dyes with the length of the polymethine chain and various end heterocyclic groups.

The possibility of predicting photocatalytic activity of semiconductor – dye-sensitizer – polymer film heterostructures is shown on the basis of the spectral characteristics of titanium (IV) oxide and polymethine dye.

It has been found that during the application of polymethine dye on the surface of titanium (IV) oxide, the ratio of the intensity of the short-wave and long-wave absorption bands changes, which is accompanied by the expansion of the light sensitivity range.

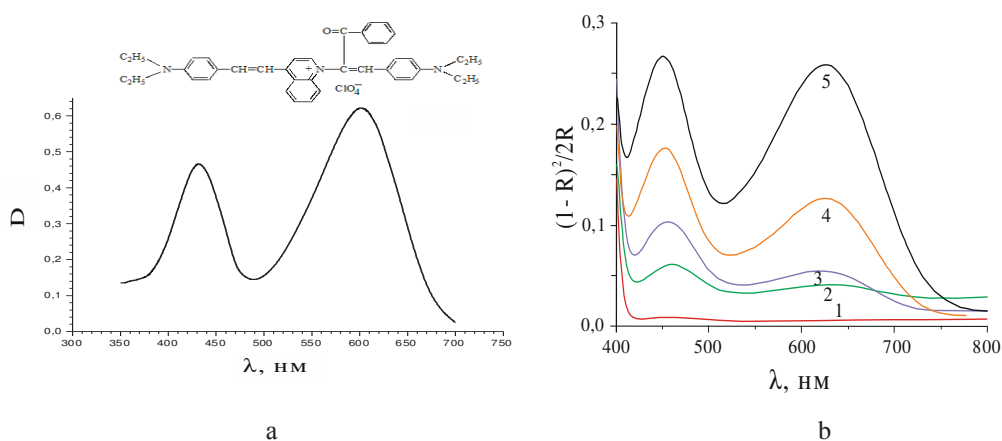


Fig. 12. Absorption spectra of dye solution (a) and HS P/D6/TiO₂ with different dye content: 1 – 0.02; 2 – 0.1; 3 – 0.2; 4 – 1.0; 5 – 2.0 mg/g

Table 1

Spectral parameters of D6 dye in solution and samples of HS P/D6/TiO₂: maximum of short-wave (sw) and long-wave (lw) absorption bands and their intensity ratios.

Sample	Dye content, mg/g	$\lambda_{1\max}$, nm	$\lambda_{2\max}$, nm	I_{sw}/I_{lw}
3	0.2	456	630	1.87
4	1.0	452	626	1.38
5	2.0	451	624	1.02
Solution	$C = 1.0 \times 10^{-5}$ mol/l	432	603	0.76

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