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New light-sensitive materials with photocatalytic activity in the visible and near infrared ranges, based on titanium dioxide and a polymethine dye

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Some spectral, electrochemical and energy transformation parameters have been investigated for the polymethine dye 2,4,5,7-tetranitro-9-(3-(2,4,5,7-tetranitro-9H-fluoren-9-ylidene)prop-1-en-1-yl)-9H-fluoren-9-ide triethylammonium (D), which exhibits three absorbance bands. The nature of the electrode processes was elucidated and the reduction and oxidation potentials of the dye were determined using cyclic voltammogram data recorded for the ground state of the dye. Then they were recalculated into the corresponding photoexcited reduction and oxidation potentials. The heterostructure (HS) titanium dioxide/dye/polyepoxypropylcarbazole (P/D/TiO_2) has been synthesized and the diffuse reflectance spectra were recorded. Then they were transformed into the absorbance spectra for a series of HS with different compositions. Afterwards, the main parameters of HS spectra were found: the short-wavelength and long-wavelength polymethine absorbance maximum positions, their widths and intensity ratio. A comparison between the spectra of D as a component of HS and D as a solute has also been done. Photocatalytic activity (PA) of HS was determined for the model reaction of methylene blue reduction running under irradiation with light of different spectral ranges. The HS spectral parameters and corresponding PA values were analyzed for the samples with different dye content. The results are analyzed in terms of the energy transformation related to the electron exchange processes running in HS.

Keywords: anionic polymethine dye, sensitization, heterostructure, titanium dioxide.

Нові світлочутливі матеріали з фотокаталітичною активністю у видимому та ближньому інфрачервоному діапазонах на основі титан(IV) оксиду і поліметинового барвника. *І.М.Кобаса, І.В.Кондрачук, І.В.Курдюкова, О.О.Іщенко, А.Я.Велика*

Проведено дослідження спектральних, електрохімічних і енергетичних характеристик поліметинового барвника триетиламонію 2,4,5,7-тетранітро-9-(3-(2,4,5,7-тетранітро-9H-флуорен-9-іліден)проп-1-ен-1-іл)-9H-флуорен-9-іду (Б) з трьома смугами поглинання. Визначено природу електродних процесів, методом циклічної вольтамперометрії (ЦВА) одержано величини потенціалів окиснення та відновлення для основного стану барвника і розраховано їх значення у збудженому стані. Одержано гетероструктури (ГС) "титан(IV) оксид — барвник — поліепоксипропілкарбазол (П)" (П/Б/TiO_2). Записано спектри дифузного відбивання, які трансформовані у спектри поглинання ГС різного кількісного складу. Визначено основні параметри спектрів ГС: розташування максимумів, що відповідають короткохвильовій (к.х.) та довгохвильовій (д.х.) смугам поглинання у молекулі поліметину, їх ширину та співвідношення інтенсивностей. Проведено зіставлення параметрів спектрів Б, що знаходяться у складі ГС, із параметрами їх спектрів у розчині. Досліджено фотокаталітичну активність (ФА) ГС у модельній реакції відновлення метиленового блакитного при дії світла різних спектральних ділянок. Проведено зіставлення даних про зміну спектральних параметрів ГС залежно від вмісту в них барвника із даними про ФА цих матеріалів. На основі розгляду енергетики електронних процесів запропоновано й обгрунтовано трактування одержаних результатів.

Исследованы спектральные, электрохимические и энергетические характеристики полиметинового красителя триэтиламмония 2,4,5,7-тетранитро-9-(3-(2,4,5,7-тетранитро-9Н-флуорен-9-илиден)проп-1-ен-1-ил)-9Н-флуорен-9-ида (К) с тремя полосами поглощения. Определена природа электродных процессов, методом циклической вольтамперометрии получены величины потенциалов окисления и восстановления для основного состояния красителя и рассчитаны их значения в возбужденном состоянии. Получены гетероструктуры (ГС) "диоксид титана — краситель — полиэпоксипропилкарбазол (П)" (П/Б/TiO_2). Записаны спектры диффузного отражения, которые трансформированы в спектры поглощения ГС различного количественного состава. Определены основные параметры спектров ГС: положение максимумов, отвечающих коротковолновой и длинноволновой полосам поглощения в молекуле полиметина, их ширина и соотношение интенсивностей. Проведено сопоставление параметров спектров К, находящихся в составе ГС, с параметрами их спектров в растворе. Определена фотокаталитическая активность (ФА) ГС в модельной реакции восстановления метиленового голубого при действии света различного спектрального диапазона. Проведено сопоставление данных об изменении спектральных параметров ГС от содержания в них красителя с результатами ФА этих материалов. На основании рассмотрения енергетики электронных процессов предложено и обосновано трактовку полученных результатов.

1. Introduction

The photocatalytic systems based on some inorganic oxides (in particular, TiO_2) exhibiting light-sensitivity in the visible and near-IR ranges are promising materials for solar light energy conversion and accumulation [1–8], decontamination of some industrial wastes [9], development of novel, non-traditional synthesis technologies [10] etc. All these challenges require an improved light efficiency and higher quantum yields of the photocatalytic processes. This raises the question of the development of new advanced photocatalysts and photocatalytic systems. The heterostructure (HS) consisting of a semiconductor, the dye-sensitizer and, optionally, some other components (photocatalytic blocks) are known as a way-forward solution for the development of advanced wide-range photosensitive materials.

The photocatalytic blocks built of the HS Dye/TiO_2, containing cationic [11], anionic [12], merocyanine [13], squaraine [14] dye-sensitizer with one chromophore and cyanine dye with two chromophores [15–17] are known as active compounds in the photocatalytic processes of methylene blue (MB) reduction, iodide ions oxidation and production of hydrogen gas from the water-alcohol mixtures [18]. However, the range of their photoactivity is restricted by the visible part of spectrum [14–17] and it does not cover a practically important adjacent near-IR part.

Tetranitrofluorene is a strong electron acceptor that can be used as a sensitizer for the photocatalytic blocks [19]. The dyes with such moiety exhibit quite intense absorbance bands located in different spectral ranges. They appear due to the electron transfer processes involving the electron levels of the nitrogroups participating in the common π-conjugated system [20]. These absorption bands cover almost entire visible and the near IR spectral ranges, which means that a wider array of light quanta can potentially take part in the photoprocesses.

This work deals with an investigation of the sensitizing activity of such a polymethine dye that has not been checked before.

2. Experimental

The P25 titania by Degussa, polyepoxypropylcarbazole (P) and the polymethine dye (D) [20] (see the formula below) were used to build a light sensitive HS P/D/TiO_2.

The HS were obtained by the treatment of the TiO_2 suspension with the dimethylformamide solution of D at room temperature, followed by slow evaporation of the solvent [21]. Then the HS were covered with the protective polymer film deposited from the benzene solution. As reported in [18], if the content of P in the HS is ranged within

0.02–0.20 mg/g, the film can efficiently protect D from the wash-off, while no obstacles arise for the photocatalytic processes running between the solvent, TiO_2 and the dye adsorbed on its surface.

An Ocean USB 2000+XR spectrophotometer was used to record the absorption spectra of the solutions of D and MB. The HS diffuse reflectance spectra were obtained using a spectrophotometer Perkin Elmer Lambda Bio-40 equipped with an integrating sphere. Then the latter spectra were transformed into the absorption spectra by the Kubelka-Munk method. Oxidation $E_{D/D^{+\bullet}}$ and reduction $E_{D/D^{-\bullet}}$ potentials of the dye were determined according to the method given in [22]; CVA were obtained with a BAS 100B/W Electrochemical Workstation potentiometer equipped with a standard three-electrode cell in argon atmosphere. The potential scan rate was kept 100 $mV \cdot s^{-1}$ throughout the entire experimental series. The HS PA was evaluated in the process of MB discoloration caused by reduction of the dye [23]. A 500 W incandescent lamp and a mercury lamp DRT-230 were used to irradiate the samples while all required spectral ranges were cut off using the appropriate light filter sets (UFS-6, λ = 310–400 nm and KS-19, $\lambda > 700$ nm).

3. Results and discussion

There are two absorbance bands of the polymethine dye: one is in the visible part of the spectrum at 595 nm and the other is in the near-IR part at 872 nm (Fig. 1a). The absorbance bandwidths have been determined at 2/3 of their height (Fig. 1a) and these values were 32 nm for the short-wavelength "sw" and 133 nm the long-wavelength "lw" bands.

The comparison between the spectrum of $P/D/TiO_2$ HS and the spectrum of a solution of the dye shows that in the former case, the both bands are wider (Fig. 1b). Moreover, this difference increases with a raise in the D content (see Table 1). For instance, for the sample 5, the "sw" bandwidth was 72 nm, while its "lw" bandwidth was 224 nm (Table 1), i.e. they are 2.25 and 1.68 times wider than the corresponding bands in the solution. It should be noted that neither pattern of the solution bands nor a ratio between their intensities change with concentration of D and the Bouguer-Lambert-Beer law remains observed. Some broadening of the absorption bands and a dependence of their intensities on the surface content of D in stronger association of D with TiO_2 [24, 25]. As a result, the intensities of the absorption band change, the bands become wider and cover almost entire visible and near-IR spectral ranges.

As it can be seen in Fig. 1b, a bathochromic shift was registered for the "lw" band after deposition of D on TiO_2. The maxima of the HS "lw" band for the samples 5, 4, 3, 2 and 1 correspond, respectively, to 921, 918, 921, 920 and 912 nm and are shifted by 40–49 nm relative to the same maxima for the bands of the dissolved dye (Fig. 1a, b). A further increase of the dye content in the HS results in a deeper association between its molecules.

Table 1. Some spectral and electrochemical characteristics of HS $P/D/TiO_2$

Sample No.	Dye content, mg/g	λ_{1max}, nm (δ, nm)	λ_{2max}, nm (δ, nm)	$I_{sw.}/I_{lw}$	$E_{D/D^{+\bullet}}$ (lw), eV	$E_{D/D^{-\bullet}}$ (lw), eV
1	0.02	–	912	–	–0.84	+0.80
		–	–			
2	0.10	590	920	0.63	–0.83	+0.79
		(33)	(186)			
3	0.20	592	921	0.53	–0.83	+0.79
		(52)	(200)			
4	1.00	591	918	0.74	–0.83	+0.79
		(61)	(213)			
5	2.00	592	921	0.53	–0.83	+0.79
		(72)	(224)			
Solution	$1.25 \cdot 10^{-4}$ mol/dm^3	595	872	1.33	–0.90	+0.87
		(32)	(133)			

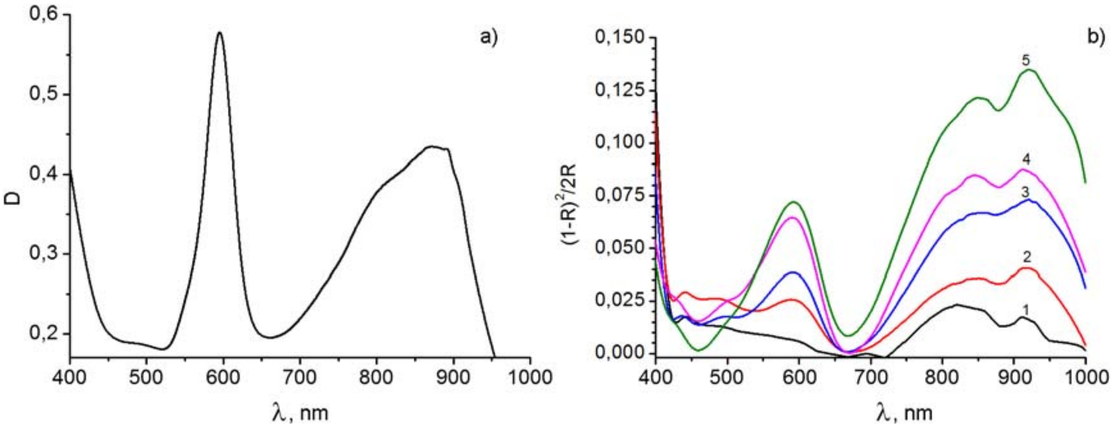

Fig. 1. Absorbance spectra of the dimethylformamide solution of D at $C = 1.25{\cdot}10^{-5}$ M, $l = 1$ cm (a) and HS P/D/TiO$_2$ (b). The dye contents in the HS (mg/g) were: *1* — 0.02, *2* — 0.10, *3* — 0.20, 4 — 1.00, 5 — 2.00.

Besides, the hypsochromic shifts have also been registered. Some new absorbance bands appeared (Fig. 1b) and their maxima corresponded to the shorter wavelengths comparing to those for the monomer dye. These new maxima can be seen at 851, 844, 850, 851 and 832 nm for the samples 5, 4, 3, 2 and 1, respectively. Based on these experimental data, one can summarize that both "sandwich" and "head-tail" type associates can be formed for this dye [26].

Another self-consistent and non-contradictory explanation for the spectral changes may be based on the effect of a semiconductor on the mutual arrangement of the adsorbed D molecules on TiO_2. A spatial configuration of bound choromophore molecules can be calculated from the ratio of the intensities of the absorbance bands [27]. The intensity of the "sw" band is greater than that of the "lw" band ($I_{sw}/I_{lw} > 1$) if the angle between the chromophores is sharp; while this ratio is opposite ($I_{sw}/I_{lw} < 1$) when the angle is obtuse.

A similar calculation for the case of HS gives the ratios 0.53, 0.74, 0.53 and 0.63 for the samples 5, 4, 3 and 2, respectively (Table 1). Thus, the obtuse spatial configuration seems more stable for the deposited D.

The dye-sensitizer oxidation $E_{D/D}{}^{+\bullet}$ and reduction $E_{D/D}{}^{-\bullet}$ potentials were +0.52 V and −0.56 V, respectively (hereafter all potentials are given vs the standard hydrogen electrode). Then the excited state oxidation $E^*{}_{D/D}{}^{+\bullet}$ and reduction $E^*{}_{D/D}{}^{-\bullet}$ potentials were calculated for the dye molecules using the equations $E^*{}_{D/D}{}^{+\bullet} = E_{D/D}{}^{+\bullet} - E^*$ and $E^*{}_{D/D}{}^{-\bullet} = E_{D/D}{}^{-\bullet} + E^*$ and the energy values for the absorption band maxima (E^*). These potentials are shown in Table 1 for the "lw" absorption band.

The diagrams of energy transformation and the schemes of light-induced electron transfer were built for the HS using the edge potentials of the conductivity $E_{CB} = -0.54$ V and the valence $E_{VB} = 2.66$ V bands of TiO_2 at pH = 7 [28], the reduction potential of MB $E_{MB/MB}{}^{-\bullet} = +0.011$ V [29] and the oxidation potentials of formaldehyde $E_{F/F}{}^{+\bullet} = -0.50$ V [30] and P $E_{P/P}{}^{+\bullet} = +1.28$ V [31]. These diagrams are shown in Fig. 2 for the HS sample containing 0.20 mg/g of the polymethine dye.

Photocatalytic activity of various HS samples under irradiation by the light from different spectral ranges is given in Table 2.

It is important to develop highly ordered photocatalytic systems [32] to obtain highly efficient photocatalysts, and the following requirements must be met: a high level of the functional organization (correct selection of the photocatalytic and sensitizing compounds); the energy exchange organization (the correct choice of the components with the correct energy parameters — oxidation and reduction potentials) and, finally, the structural organization (elimination of the kinetic obstacles associated with the short lifetime of the photo-generated charge carriers — proper construction of the heterostructure blocks).

As it is seen from the energy transformation diagram (Fig. 2), the P/D/TiO$_2$ HS meets all the requirements for the block components — functional, energy exchange and structural organization. These compliances are observed both at absorption of light by the dye (Fig. 2a) and at photoexcita-

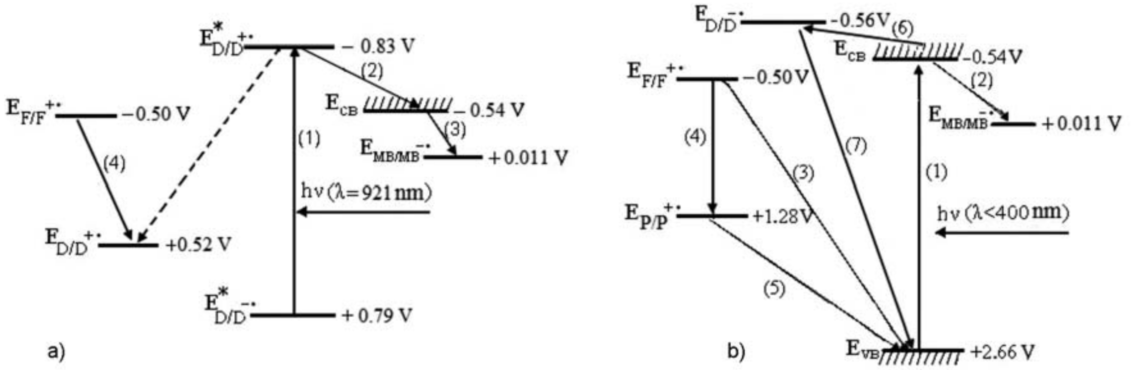

Fig. 2. Energy transformation diagrams for P/D/TiO_2 based photocatalytic systems and schemes of the electron transfer processes induced by the light absorption by polymethine (a) and semiconductor (b).

tion of the semiconductor component of the HS (Fig. 2b). A transfer of the excited electrons from dye molecules towards the conductivity zone of TiO_2 is a key stage governing the processes, if light is absorbed by D. An ability of the sensitizer to donate its electrons depends on the energy gap between the excited oxidation potential $E^*_{D/D}{}^{+\bullet}$ and the edge potential E_{CB} of the semiconductor conductivity band [32]. As it can be seen from the diagram in Fig. 2a (see process 2), this gap is wide enough to maintain the electrons transfer as a thermodynamically allowed transformation. Moreover, there is no thermodynamic obstacles (ΔE = 0.53 V) for the further transfer of electrons to MB (process 3). Since formaldehyde is a strong reduction agent, the regeneration of the dye-sensitizer molecules from the cation-radicals D/$D^{+\bullet}$ (formed as a result of the electrons transfer to TiO_2; this process is shown by the dotted lines in Fig. 2a) should also run smoothly.

If light is absorbed by TiO_2 (Fig. 2b), a transfer of electrons from the conductivity band to the molecules of MB (process 2) becomes possible after generation of the electron-hole pair (process 1). This results in reduction of the MB molecules. The photocatalytic loop closes when a hole in the valence band of TiO_2 will be filled with an electron coming from the reduction agent. This process may run either directly (process 3) or involving the polymer (processes 4 and 5, see Fig. 2b). It is important to note that a competition between the two processes is possible in the photocatalytic system. This competition is supported by the proximity of the gaps values $\Delta E = E_{CB} - E_{MB/MB}{}^{-\bullet}$ and $\Delta E = E_{CB} - E_{D/D}{}^{-\bullet}$. These values are related to the motive forces of the reaction 2 and the processes 6 and 7 resulting in deactivation of the excited HS. In our opinion, these processes are responsible for the gradual decrease in the HS photoactivity with an increase in the dye content.

An analysis of the energy transformation diagrams built for the HS P/D/TiO_2 proves that there are no complications for the electron transfer processes required both for the direct or sensitized photocatalytic reduction of MB. Therefore, this reduction meets no thermodynamic barriers and should run with high efficiency.

Comparing an influence of the heterosystems on photoreduction of MB and D (Table 2), one can note that they may act in a different way depending on the wavelength of the photoexcitation light. The visible light can be absorbed by both D as a component of HS

Table 2. Photocatalytic activity (PA) of the HS P/D/TiO_2 at various dye contents and under irradiation by the light of different spectral ranges

No.	Dye content in the HS, mg/g	PA, mg/ml·min·m^2	
		λ = 310–400 nm	λ > 700 nm
1	0	$1.4\cdot10^{-1}$	0
2	0.02	$9.8\cdot10^{-2}$	$4.5\cdot10^{-2}$
3	0.10	$4.7\cdot10^{-2}$	$2.1\cdot10^{-1}$
4	0.20	$2.3\cdot10^{-2}$	$5.4\cdot10^{-1}$
5	1.00	$7.2\cdot10^{-3}$	$2.8\cdot10^{-1}$
6	2.00	$5.7\cdot10^{-3}$	$7.7\cdot10^{-3}$

* HS P/D/TiO_2 were stable during at least 18 h after the UV irradiation with the 230 W lamp. The loss of activity was less than 5 %.

and dissolved MB. In this case, the photoreduction of MB is caused by the photocatalytic action of HS. This conclusion is proved by the fact that the MB photoreduction efficiency is practically zero in systems that do not contain HS or contain only pure TiO_2 and are irradiated with visible light. When a content of D in the HS is increasing, the PA is also growing, reaches some maximum and then turns to a decrease. The situation is different when the light is absorbed by TiO_2. In this case, the PA is gradually decreases with an increase in the sensitizer content (see Table 2). As it can be seen in Fig. 2b, the dye competes with MB for the electrons coming from the conductivity band, and this indirect electron-hole recombination results in a partial deactivation of the photoexcited semiconductor. The rate of this process increases with growth of the D content in TiO_2 causing further deceleration of the MB reduction. Besides, the spectral data prove that D exhibits absorption near 400 nm. This effect can cause some lowering in the PA of the HS when it is irradiated by UV light. This assumption is in good agreement with the experimental data (Table 2).

It should be emphasized that D exhibits a rather high photoactivity in the near-IR range. Usually, the dye photoactivity can be extended to this range through increasing the length of its polymethine chain [33]. However, the LUMO energy level would adversely decrease at this process [34] and it can drop below the TiO_2 conductivity zone edge. As a result, the dye photoactivity would either decrease significantly or even disappear completely.

In this context, it should be mentioned that the reported dye exhibits some absorbance in the near-IR range, while its polymethine chain length remains comparatively short. It consists of only three methine groups, while other dyes require at least seven groups to absorb the light from that spectral range [35]. A deep coloring of D is due to the well-developed π-system of the fluorene nucleus [20].

Therefore, it is expected that this group of polymethine dyes will be used as various highly effective sensitizers of the hybrid organic-inorganic heterostructures exhibiting activity in the near-IR range and usable in the field of photocatalysis and the others related to conversion of the solar energy. They can be used for development of the Gratzel cells [36], which require various dyes that absorb light in the visible range [4, 36, 37]. Higher photo- and thermostability of the short-chain polymethine dyes bring extra perspectives for this class of the dyes [26, 33].

A general scheme of the thermodynamically adjusted mechanism of the photocatalytic process can be outlined on the basis of an analysis the absorption spectra pattern and changes in the PA occurring under irradiation with the light absorbed by D. When irradiated with IR light, it was found that the PA rose at first and then decreased with the dye content increase. There are two possible reasons for such a pattern of the dependence of the PA on the HS composition. First, a greater number of the photoexcited D molecules are generated if their concentration is growing. This process leads to a slight increase in light absorption, promotes a better level of sensitization and supports PA growth. On the other hand, application of each new D molecular layer gradually increases the distance between the layer and the substrate; this leads to a weakening of the interaction between them. This process attenuates the transfer of electrons from the molecules of the photoexcited sensitizer and promotes more active electron-hole recombination.

4. Conclusion

Some new heterostructures (HS) containing TiO_2, anionic polymethine dye-sensitizer with three chromophores and a polymer protective cover have been synthesized. They are photosensitive over the visible and near-IR spectral ranges and can be used as highly effective redox-catalysts for reduction of methylene blue (MB). The dependence of the HS activity on its composition has been established, energy transfer processes occurring upon absorption of light have been outlined and the mechanism of the photocatalytic action (PA) has been discussed.

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