PHOTOCATALYTIC REDUCTION OF METHYLENE BLUE ON THE HETEROSTRUCTURAL MATERIALS BASED ON TITANIUM DIOXIDE WITH BISQINOCYANINE PIGMENT

*Igor KOBASA[1], Nataliya HUSYAK[1] , Sonia GUTT[2]

[1] Yuriy Fedkovych National University of Chernivtsi, Kotsiybynsky St., 2, Chernivtsi 58012, Ukraine.
E-mail: imk-11@hotmail.com
[2] Stefan cel Mare University of Suceava, University Street nr. 13, 720 229 Suceava, Romania
*Corresponding author

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Abstract. *New light sensitive heterostructures working through all visible light range and containing a semiconducting material (TiO_2), a bisquinocyanine pigment-sensitizer, and a polyepoxypropylcarbazole polymer, which protects the material from dissolution have been developed. Our results prove that such heterostructures can be used as active photocatalysts. Dependence of their photoactivity on the quantitative composition has been established and energy characteristics of the electronic processes occurring at the light absorption have been analyzed. We have also proposed mechanism explaining photocatalytic activity of these complex materials.*

Key words: *titanium dioxide, bisquinocyanine pigment, heterostructures, photocatalytic activity, reaction mechanism*

Introduction

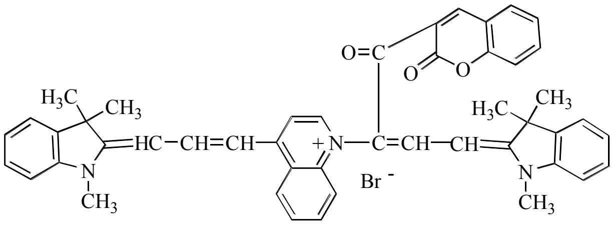
Selective sensitizing of photo catalytic systems promotes its activity within some wavelength range and this is one of important fields in the photo catalytic systems design and development. Some photocatalytic systems can be suitable for use in the visible and infrared solar energy transformation and accumulation equipment, which is very promising direction [1-7]. Previous investigations proved that systems combining photoactive oxide (TiO_2) with pigment-sensitizer or other long wave sensitizing compound can be effectively used as photo catalysts [8-14]. Some systems can be applied in the wastewater and water decontamination technologies.

Here we describe a method of design the solid and structurally oriented photosensitive hetero structures (the blocks). Needful amount of the pigment should be applied on the semiconductor surface and then protected from dissolution by the polymer film, which does not prevent any component to take part in the electron transferring processes occurring on the interfacial bound. Heterostructures of this class have been synthesized in [1, 8] and showed good efficiency in the photo catalytic water decomposition process. Obviously, we should determine if this method can be used as a universal tool for synthesis of other photo catalytic materials for other redox processes. It is also interesting to investigate if other classes of pigments and semiconductors can be used as source materials for the photocatalytic blocks.

We have synthesized a series of new heterostructures based on titanium dioxide and a bisquinocyanine class pigment. Then activity of the heterostructures has been measured in the test photocatalytic reaction of methylene blue (MB) reduction.

Experimental

We used pyrogenic titanium dioxide to obtain a photosensitive heterostructure F/P/TiO_2. Titanium dioxide was produced through the high temperature hydrolysis of $TiCl_4$ vapour in the air-hydrogen flame and the specific surface area of the material was S_{sp} = 50 m^2/g. Bromide N-[α-(3-coumarinylecarbo) - 1,3,3 - trimethyl-2-indolinyliden) propenile] (4-quinolile)(1,3,3-trimethyl–2–indolinyliden) trimethyncyanine was used as a pigment (P) and the polymer film was formed using polyepoxypropylcarbazole (F).



The heterostructures were formed from the pigment and semiconductor (P/TiO_2) using following operations. TiO_2 suspension was mixed with the alcohol solution of the pigment at the room temperature. Then this mixture was remained until the solvent evaporated completely. Then we applied a benzene solution of the pigment, which formed protective film.

Spectrophotometer SF-46 was used to record absorption spectra of the solutions while the diffusion reflection spectra of the heterostructures of P/TiO_2 and F/P/TiO_2 were recorded at spectrophotometer Perkin Elmer Lambda Bio 40 with integrating sphere. Then the Kubelka-Munk method [15] was engaged to transform the latter spectra into the absorption spectra using parameter $(1 – R^2)/2R$, where R means % of the diffusion reflection at the given wavelength.

Photocatalytic activity of the heterostructures was determined through MB discolouring rate. Photocatalytic reaction of MB discolouring also involves formaldehyde and ethanol as reducing agents [12]. Activity of the heterostructures was calculated by the formula: $PA = (C_0 \cdot 1000)/(\tau_{1/2} \cdot S \cdot m)$, where PA means specific photocatalytic activity (mg/ml·min·m^2), C_0 – initial concentration of the pigment (mg/ml), $\tau_{1/2}$ – time of semi-discolouring (min), S – specific surface area (m^2/g), and m – weight of the sample.

Results and discussion

Absorption spectra of P/TiO_2 and F/P/TiO_2 heterostructures (calculated by Kubelka-Munk method from diffusion reflection spectra) are shown in Fig. 1 together with the absorption spectra of an alcohol solution of the pure pigment. Comparison of the spectra shows that association processes become more intense as a result of applying the pigment on the solid substrate (similar result was reported in [16]). This process results in a change of intensity of the narrow bands with λ_{max} = 446 nm (lg ε = 4,52) and λ_{max} = 632 nm (lg ε = 5,02), which widen and almost join into the single band extending over a significant part of the visible light region. Polymer component of the heterostructure gives no influence on the pigment association ratio and pattern of the band. This component slightly changes the band intensity only.

We found that the homogeneous alcohol solution of the pigment undergoes photo discolouring under the visible light irradiation. This phenomenon is caused by reduction of the pigment in the electron-donoring media and this is a typical process for many pigments [12-14]. Investigation of oxidation and reduction of some bisquinocyanine pigments resulted in the following redox potentials for our pigment: $E_{P/P^{\cdot +}} = + 0,38$ V and $E_{P/P^{\cdot -}} = - 0, 24$ V (all the potentials are given here and below regarding the normal hydrogen electrode potential). We used these values as references to compare the redox properties of the pigment in its basic state. Redox potentials of the excited pigment molecules were calculated from the basic state values.

Therefore, we calculated the redox potentials for the singlet excited state after absorption of light (λ_{max} = 632 nm, E* = 1,96 V). Using equations $E_{P^*/P^{\cdot+}} = E_{P/P^{\cdot+}} - E^*$ and $E_{P^*/P^{\cdot-}} = E_{P/P^{\cdot-}} + E^*$ [17] we obtain the following values: $E_{P^*/P^{\cdot+}}$ = - 1,58 V and $E_{P^*/P^{\cdot-}}$ = + 1,72 V. Comparing these values to electrochemical potential of ethanol (E = - 0,15 V [18]), free radical $CH_3\dot{C}HOH$ (E = - 1,25 V [19]), $E_{P/P^{\cdot+}}$, and $E_{P/P^{\cdot-}}$ we can conclude that the following reactions are thermodynamically allowed and can take place in the solution at the visible light irradiation: $P^* + P \rightarrow P^{\cdot-} + P^{\cdot+}$, $P^{\cdot-} + P \rightarrow P^{2-} + P^{\cdot+}$, $P^{\cdot+} + C_2H_5OH \rightarrow P + CH_3\dot{C}HOH + H^+$, $P + CH_3\dot{C}HOH \rightarrow P^{\cdot-} + CH_3CHO + H^+$, $P^{\cdot-} + CH_3\dot{C}HOH \rightarrow P^{2-} + CH_3CHO + H^+$. Some other reactions can also take place. Each of these reactions contributes to the process of the pigment discolouring. Adding of TiO_2 or F/P/TiO_2 suspension and active stirring of the solution accelerates the process in several times. Settling of the suspended particles stops after the stirring discontinued and the reaction rate returns to its initial value. This proves that visible light-inactive titanium dioxide can catalyze the photoreduction only if there are pigment molecules adsorbed on TiO_2 surface.

A character of the heterostructures influence on photoreduction of MB depends on wavelength of the irradiation light. The visible light can be absorbed by both pigment-sensitizer of the heterostructure and dissolved MB.

Table 1

Dependence of the heterostructures photocatalytic activity on the pigment concentration at various wavelength light irradiation

Pigment content (mg/g)	Photocatalytic activity, (mg/mL·min·m^2)	
	310 < λ < 400 (nm)	λ > 400 (nm)
0	$1{,}6\cdot10^{-1}$	0
0,019	$8{,}5\cdot10^{-2}$	$1{,}7\cdot10^{-2}$
0,094	$2{,}7\cdot10^{-2}$	$1{,}4\cdot10^{-1}$
0,188	$1{,}0\cdot10^{-2}$	$2{,}6\cdot10^{-1}$
0,94	$6{,}4\cdot10^{-3}$	$1{,}1\cdot10^{-1}$
1,88	$4{,}1\cdot10^{-3}$	$4{,}6\cdot10^{-3}$

Therefore, photoreduction of MB runs under the visible light irradiation through the photocatalytic action of the heterostructures. Our results proved that the photoreduction is almost completely inactive if a system does not contain F/P/TiO_2 or contains only TiO_2. Photocatalytic activity of a system containing heterostructures initially rises as concentration of the pigment increases. Then it reaches the maximum value and further portions of the pigment cause decrease in the photocatalytic activity (see Table 1).

UV-light irradiation is being absorbed mainly by TiO_2 particles and results in a different kind of relation where non-modified source material shows the highest activity level (see Table 1, experiment 1), which smoothly decreases as concentration of the pigment rises (see Table 1, experiments 2-6).

The investigation proved that thickness of the polymer film deposited on the heterostructure does not provide significant influence on its photocatalytic activity until this thickness remains within some range.

A content of 0,2 mg/g of the pigment in the F/P/TiO_2 material is the optimal and does not influence any electron transferring processes on the solid/solution interface.

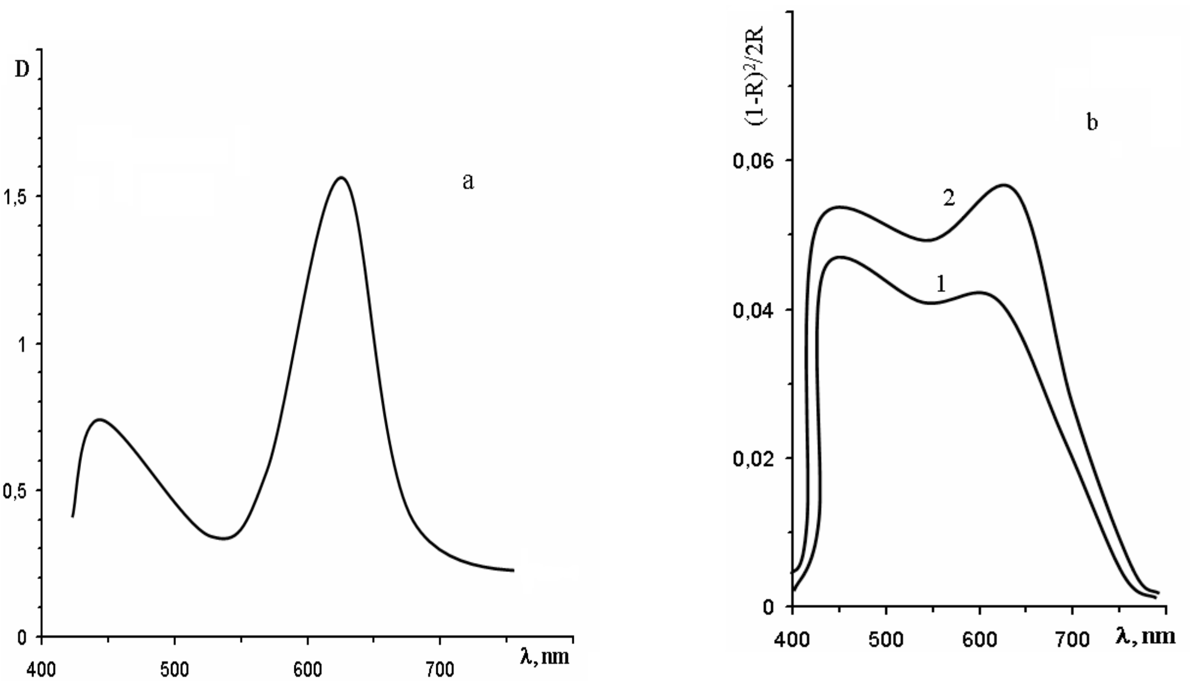


Figure 1. Absorption spectra: a – alcohol solution of the pigment; b – alcohol solution of the heterostructures P/TiO$_2$ (1) and F/P/TiO$_2$ (2)

On other hand, such a content of the polymer prevents dissolution of the pigment. Raise in the polymer concentration to 1,8 mg/g causes decrease of 20 % in the photocatalytic activity.

We have built energy transformation diagrams for the photocatalytic systems based on F/P/TiO$_2$ heterostructures and schemes of various light-generated electron transferring processes. Information related to location of TiO$_2$ conductivity and valence bands (E_{CB} = - 0,54 V, E_{VB} = + 2,66 V at pH = 7 [20]) and redox potentials of normal and excited molecules of the pigment (E_{MB/MB^-} =+0,011 V [20]) and polyepoxypropylcarbazole (E_{F/F^+} =+1,28 V [1]) has been used to build the diagrams and schemes.

As seen from Fig. 2, the process of an electron injection to the conductivity band of TiO$_2$ followed by its transferring to MB molecule can occur at photoexcitation of the pigment by the light radiation with λ = 632 nm. Both processes should be rather fast because of quite a significant potentials differences $\Delta E_1 = | E_{P^*/P^+} - E_{CB} |$ = 1,04 V and $\Delta E_2 = | E_{CB} - E_{MB/MB^-} |$ = 0,55 V. A molecule of the pigment-sensitizer P is oxidized to the cation-radical P$^+$ and redox potential of this process is E_{P/P^+} = 0,38 V. This cation-radical should easily react with a strong electron donoring agents such as formaldehyde (E = - 1,08 V at pH = 14 and E = - 0,06 V at pH = 1,0 [21]) or ethanol (E = - 0,15 V). These processes are thermodynamically advantageous since their energy gaps are rather wide and they should run fast ensuring reduction of the source form of the pigment-sensitizer. In fact, we did not observe any colour change at irradiation of F/P/TiO$_2$ heterostructures while MB-related light absorption decreased. Therefore, we can conclude that sensitizing of the semiconducting photocatalyst to the visible light and photocatalytic reduction of MB are caused by the electron transferring processes described above.

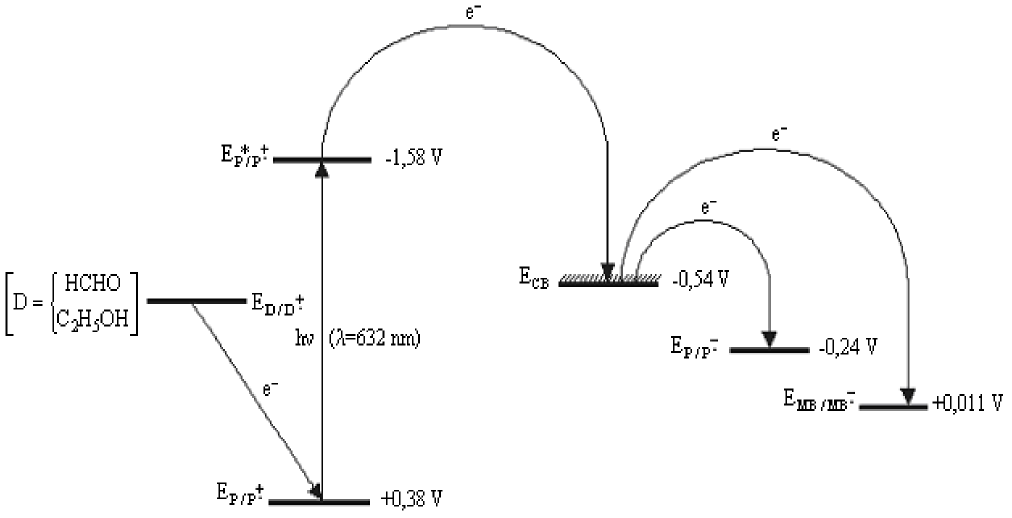


Figure 2. Energy transformation diagram of a photocatalytic system based on the heterostructure containing of TiO_2 and bromide N-[α - (3-coumarinylecarbo)-1,3,3- trimethyl-2-indolinyliden) propenile] (4- quinolile) (1,3,3-trimethyl – 2 – indolinyliden) trimethyncyanine and scheme of the electron transferring processes at the visible light irradiation

As supposed from this description, photocatalytic activity of a sample should rise at increase of concentration of the pigment-sensitizer ensuring more effective absorption of the light. One can see (Table 1) that experimental results prove this assumption. On other hand, lower activity of the samples with higher concentration of the pigment can be caused by lower photosensitivity of the associates, which form at such concentration.

Analysis of the energetic diagrams shows that transferring of excited electrons on the pigment and electron-hole recombination involving the pigment molecules are the key processes in the photoexcitation of the heterostructures with TiO_2-absorbable light (λ<400 nm).

The higher is the pigment concentration, the lower is probability of the direct transferring of an electron from the conductivity band to MB molecule. Then probability of the recombination will rise causing decrease of the heterostructures photocatalytic activity. Experimental data (see Table 1) completely confirm this assumption.

Conclusion

New heterostructures consisting of a semiconductor, pigment-sensitizer, and polymer material have been designed. Analysis of our results proves that combination of such three parts can be used as a general method to develop various light sensitive materials using various source materials, which can be applied in various fields including solar energy conservation and transformation, water and wastewater decontamination, etc.

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