Spectral characteristics of cyanidin chloride and zinc octaethyl porphyrin sorbed by protonated potassium polytitanate

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Abstract. The work is devoted to the investigation of interaction of cyanidin chloride (3,3’,4’,5,7-pentahydroxyflavilyum chloride) and 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-zinc porphyrin, which are widely used in photovoltaic cells, with particles of protonated potassium polytitanate (PPPT) applied as new semiconductor matrix material. It has been established that the values of the sorption capacity of the matrix have correlation with the data of dyes fluorescence anisotropy, but a violation of this dependence for cyanidin chloride allows suggesting penetration of dye into the interlayer spaces of the PPPT particles. The calculated values of the extinction coefficients of the dyes in the PPPT-dye system and the values of the energies of the dyes transition into the excited state indicate the prospects to use the PPPT matrix in manufacturing of photovoltaic cells.

1. Introduction

At present, titanium dioxide is widely used as a semiconductor in manufacturing of solar cells [1, 2]. However, various forms of TiO₂ only absorb solar radiation in the ultraviolet region of the spectrum. To expand the spectral range of solar cells, titanium dioxide is modified by dye molecules capable to absorb radiation in the visible spectral range (spectral sensitization), which contributes to a significant improvement in the photoelectric characteristics [2-4].

In order to increase the efficiency of light conversion, we propose new kind of sensitized semiconductors, which are represented with new semiconductor matrix material suitable to adsorb molecules of photo-stable organic dyes [5, 6].

The purpose of this work was to study the spectral characteristics of some popular organic dyes, i.e. cyanidin chloride and zinc octaethyl porphyrin (2,3,7,8,12,13,17,18 octaethyl -21H, 23H – porphine zinc (II), ZnOEP), adsorbed onto the protonated form of potassium polytitanate (PPPT) to determine the prospects of these systems application in the producing photosensitive semiconductor layers of photovoltaic cells using non-aqueous solutions of organic dyes. Both above mentioned dyes are insoluble in water and soluble in organic solvents, therefore, this way of sensitization could prevent dissolution of adsorbed dyes in the aqueous solutions used as electrolytes at manufacturing of photovoltaic cells [3].

For our studies we used protonated potassium polytitanate (PPPT) as the matrix-semiconductor of the photosensitive layer. This substance has a higher specific surface area in comparison with nanoscale TiO₂ (215 and 45 m²/g, respectively). The platy PPPT particles (figure 1a) have a layered...
structure characterized with a large interlayer distance (up to 1 nm), which provides adsorption of different organic dyes onto the internal surface and promotes a great sorption capacity of this powder for the organic dyes [7-9]. Furthermore, a bandgap value of the SiO$_2$ doped PPPT is lower than this one for TiO$_2$ (2.9 and 3.0-3.2 eV, respectively [10,11]) and supports increased absorption of solar radiation by this semiconductor substrate even without sensitization. Finally, the PPPT has a lower price (9-12 USD per 1 kg in comparison with 25-30 USD per 1 kg for nanoscale TiO$_2$ powder of Degussa P25 trademark).

Cyanidin chloride (anthocyanin’s group of dyes) has carbonyl and hydroxyl groups in its structure (figure 1b), which allows it to be adsorbed onto the hydroxidated surface of different oxide materials [3]. This compound belongs to the group of cationic dyes and can participate in the electrostatic binding with the surface of potassium polytitanate particles whose layers are formed by polyanions [9]. Finally, the anthocyanins, to which cyanidin chloride belongs, have an intensive absorption in the visible region of the spectrum, which broadens the spectral range of solar energy conversion when used as a sensitizing additive of semiconductor materials.

Zinc octaethyl porphyrin (ZnOEP, figure 1c) is chosen due to the fact that it has a high photochemical stability [12] and intense absorption bands in the visible spectral range, which is important for solar energy converters. The porphyrins are currently considered to be one of the best sensitizers of electron transfer in photovoltaic cells [13, 14]. There are various methods to modify the structure of porphyrin molecules (such as attachment of anchor groups, electron donor groups), as well as the addition of structural groups that enhance absorption in the 500-600 nm region [14].

2. Materials and methods

The PPPT sample was obtained by treatment of the parent potassium polytitanate powder (PTK-4 trademark, Nanocomposite Ltd., Russia, having a molar ratio of TiO$_2$:K$_2$O = 4.1) in the 30 % aqueous solution of H$_2$SO$_4$ with a stirring at room temperature until the pH value of the suspension reached 6.5 points (the point of zero charge of the PPPT particles surface). As a result, a monodisperse powder was obtained after the washing with distilled water, according to the electron transmission microscopy data (TEM, Microscope TESLA 5M, Czechia). This powder consisted of PPPT particles characterized by spectrophotometric methods with a molar ratio of TiO$_2$:K$_2$O = 11.5 and having platy shape with an average effective diameter of 230 nm and a thickness of 10-20 nm.

The PPPT particles size distribution was determined in water with laser analyzer Analysette 22 MicroTec Plus (Fritsch, Germany). The dose of PPPT in all used suspensions was of 1 mg / ml.

For fluorescent and absorption experimental studies we used cyanidin chloride solutions (purity ≥ 95%, HPLC, SIGMA-ALDRICH) in ethanol (purity ≥ 98%) ZnOEP in toluene (purity ≥ 99%, SIGMA-ALDRICH).

The absorption spectra of dyes and PPPT in ethanol and toluene suspensions were obtained with a spectrophotometer Evolution 300 (Thermo Scientific, USA). Fluorescence and excitation spectra were studied by means of a fluorescent spectrometer LS55 (Perkin Elmer, USA), at which polarization measurements were also performed.

The concentration of dyes and the experimental conditions were chosen in such a way that the law of light absorption by Bouguer-Lambert-Beer was fulfilled. The anisotropy of the dyes fluorescence was determined by the formula:

\[ r = \frac{I_\parallel}{I_\perp} / \frac{I_\parallel + 2I_\perp}{2} \]

where $I_\parallel$ is fluorescence intensity, recorded under the condition when the polarizer is oriented parallel to the plane of polarization of the exciting light; $I_\perp$ is the fluorescence intensity, when the polarizer is perpendicular to the plane of polarization of the exciting light.
The adsorption processes of selected dyes onto the PPPT particles were studied by means of spectral methods as well as absorption, fluorescence, and polarization spectroscopy. In the initial stage of the experiments, a sorption capacity of protonated potassium polytitanate to cyanidin chloride and ZnOEP was performed by the classical adsorption model of Langmuir using the following equation

\[
C_e = \frac{1}{q_e} + \frac{1}{q_0 K_L} C_e
\]

where \(C_e\) (mg/l) is an equilibrium concentration of the dye estimated from the adsorption spectra for different initial concentrations of dye in the organic solution; \(q_e\) (mg/g) is the amount of the adsorbed dye per weight unit of the adsorbent; \(q_0\) is sorption capacity.

The dependence of cyanidin chloride optical density on its concentration (Fig 4, c) was plotted using cyanidin chloride absorption spectra in the PPPT suspension and used to determine the extinction coefficient of cyanidin chloride in the suspension of PPPT.

3. Results and discussion
The experimental adsorption isotherms obtained for cyanidin chloride in ethanol and ZnOEP in toluene are reported in figure 2. The obtained isotherms have non-linear character in the range of high concentration of dyes, indicating a complex character of the adsorption mechanism. However, the obtained Langmuir isotherms allow estimating a sorption capacity of cyanidin chloride on PPPT in ethanol and ZnOEP on PPPT in toluene by extrapolation of linear parts of the isotherms onto the axis 1/C_e (figure 2). The obtained extrapolations correspond to the PPPT sorption capacity \(q_0\) equal to 1.73 mg/g for cyanidin chloride in ethanol and 0.53 mg/g for ZnOEP in toluene.
Figure 2. The organic dyes adsorption isotherms (PPPT) obtained using the Langmuir model for cyanidin chloride in ethanol (1) and ZnOEP in toluene (2).

Figure 3 represents the absorption and fluorescence spectra of ZnOEP in the toluene PPPT suspension at various concentrations of ZnOEP. From the obtained absorption spectra, the optical density at the absorption maximum was plotted against the concentration of ZnOEP (figure 3, inset).

Figure 3. Absorption (a) and fluorescence (b) spectra of ZnOEP in the toluene suspension of PPPT (doze of 1 g/dm$^3$) at [ZnOEP] = 6.74 (1), 20.2 (2) and 67.4 (3) μM/dm$^3$ and influence of the dye concentration on optical density of ZnOEP/PPPT toluene suspension.

It follows from figure 3 that ZnOEP has two absorption and fluorescence bands. The data presented in figure 3 were used to determine the optical density values as well as extinction coefficients of
ZnOEP in pure toluene and in the presence of dispersed PPPT particles in this solution. The values of extinction coefficients for ZnOEP in toluene+PPPT was 27000 ± 3000 M⁻¹·cm⁻¹. The value of excitation energy for ZnOEP in toluene+PPPT is 2.083 eV which is in agreement with literature data [11].

The ZnOEP have a platy structure which favors penetration of the ZnOEP molecules into the interlayer space of the PPPT particles and their intensive adsorption, especially at high concentrations (figure 2). A presence and location of the high-lying occupied molecular orbitals (HOMO) and a low-lying vacant molecular orbitals (LUMO) makes it possible for ZnOEP to attach from one to four π-electrons or lose one or two π-electrons. The spectral data confirm intensive interaction of ZnOEP with PPPT particles.

The data obtained for different dyes indicate that an increase of the PPPT adsorption capacity is accompanied with increased dye fluorescence anisotropy. This phenomenon could be explained taking into account steric factor; the adsorbed chromophore groups of the organic dye are oriented along the PPPT layers promoting increased fluorescence anisotropy.

The fluorescence spectra of cyanidin chloride in the ethanol suspension of PPPT at various concentrations of cyanidin chloride are shown in figure 4. The introduction of nanoparticles of PPPT in the ethanol solution leads to a significant increase in the fluorescence intensity of cyanidin chloride, apparently due to its adsorption on the surface of the PPPT particles and, as a result, the loss of chromophore ions mobility.

![Figure 4. Absorption (a) and fluorescence (b) spectra of cyanidin chloride (CyCl) in the ethanol suspension of PPPT (dose of 1 g/dm³) at [CyCl] = 6.74 (1), 20.0 (2) and 40 (3) μM/dm³ and Influence of the cyanidin chloride concentration on its optical density (c).](image)

Studies of the polarization of fluorescence dyes have revealed an increase in the anisotropy of the fluorescence of ZnOEP from 0.02 (pure toluene) to 0.08 (suspension of PPPT in toluene); in the case of cyanidin chloride this parameters changed from 0.08 (pure ethanol) to 0.12 (PPPT suspension in ethanol). This fact can be explained by decrease of mobility in the dye molecules due to a sorption onto the PPPT particles surface. Also extinction of cyanidin chloride in the ethanol suspension of PPPT was determined as 46000 ± 1000 M⁻¹·cm⁻¹.

The excitation energy (energy of the transition of dyes from the ground state to the excited state) obtained from the absorption and fluorescence spectrum of dyes was also obtained. The value for
cyanidin chloride in the ethanol suspension of PPPT was 2.035 (585 nm). Upon the transition from ethanol to PPPT ethanol suspension, a brief wavelength shift of the maximum in the cyanidin chloride fluorescence spectrum is observed. This one indicates a change in the microenvironment of the cyanidin cation upon transition from ethanol to a PPPT as a result of its adsorption.

A value of the ZnOEP and cyanidin chloride extinction coefficients (27000 and 46000 M⁻¹ cm⁻¹, respectively) indicates a possibility of the efficient absorption of light energy by thin layers of PPPT particles modified by selected dyes in a wide range of wavelengths from 400 nm to 620 nm.

The energy gap corresponding to the transfer of the dyes into the exciting state (Eg) was calculated on the basis of the first maximum in the absorption spectrum using the formula: 

\[ E_g = \frac{hc}{\lambda_{cr}} \]

where \( \lambda_{cr} \) corresponds to the edge of the absorption spectrum of the dyes (nm). In the case of cyanidine chloride dissolved in the ethanol suspension of PPPT, \( \lambda_{cr} = 600 \) nm and \( E_g = 2.07 \) eV, while, in accordance with [8] (figure 5), \( E_{\text{HOMO}} = -6.28 \) eV; \( E_{\text{LUMO}} = -3.48 \) eV and \( E_g = 2.81 \) eV.

\[ \text{Figure 5. The energy diagram of the investigated systems based on literature data (PPPT [7], cyanidine chloride [8], and Zn porphyrin [9]).} \]

The spectrum of ZnOEP dissolved in the toluene suspension of PPPT (\( \lambda_{cr} = 580 \) nm) allows to determine the absorption energy gap for this dye as \( E_g = 2.12 \) eV. The absorption spectra of 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphyrin (OEP) and ZnOEP are given in [12] and indicate that a value of \( E_g \) for the long-wave part of these absorption spectrum at a wavelength of 580 nm coincided with our experimental data. Taking into account an absence of the data on \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) for the ZnOEP molecules, we estimated their location using a value mentioned in [9] for the zinc tetra phenyl porphyrin (ZnTPP) (\( E_{\text{HOMO}} = -4.98 \) eV), indicating \( E_{\text{LUMO}} = E_g - E_{\text{HOMO}} = -2.86 \) eV, which is noted in figure 5.

To proper operation of the photocell, the photoexcited electron have to be transferred from the higher filled molecular orbital (HOMO) of the dye to its lower free molecular orbital (LUMO) and then to the conduction band of the PPPT (\( E_g = 2.9 \) eV [7]). The last transition is only possible if a LUMO level is located above a lower edge of the conductivity zone of a semiconductor. According to the energy scheme reported in figure 5, these conditions are satisfied in the investigated systems.

Taking into account the structure of cyanidin chloride molecules (figure 1), it is possible to assume that cyanidin ions adsorb onto the protonated PPT particles forming hydrogen chemical bonds similar to the case of this dye adsorption by TiO₂ [13, 14]. The ZnOEP molecules don not contain active
functional groups and the mechanism of these molecules binding with PPPT particles is not evident but has to be similar to the case of adsorption of other porphyrins onto the hydrated surface of titanium dioxide [15].

The obtained results indicate increased adsorption of the organic dyes onto the surface of protonated potassium polytitanate characterized with high specific surface area which promotes increased extinction coefficients of these sensitizers in comparison with nanoscale TiO$_2$ traditionally applied as semiconductor material in manufacturing of photovoltaic cells. The data on photoelectrical properties of the photovoltaic cells based on the investigated systems have confirmed this statement and presented some additional interesting effects which will be reported later.

4. Conclusion
The investigation of the processes taking place in the system of protonated potassium polytitanate (PPPT) – organic solvent – organic dye leads to the following conclusions. Energy band gap values obtained by us from absorption spectra allow to conclude that transfer of electron from the highest filled molecular orbital (HOMO) of a dye to its lower free molecular orbital (LUMO), and then to the conduction band of potassium polytitanate is possible.

It has been found that the cyanidin ions adsorbed onto the surface of PPPT are characterized with much higher extinction coefficient in comparison with the same disposed in the ethanol, presumably due to the formation of multiple hydrogen bonds with the substrate, which affects the electronic structure of the adsorbed ions.

On the base of obtained results we may conclude that the mechanism of the adsorption process of cyanidin chloride from ethanol and ZnOEP from toluene has complicated character and cannot be described in frame of the simple adsorption models of Langmuir due to diffusion of the dyes adsorbed onto the external surface into the interlayer space of the PPPT particles. This phenomenon is confirmed by increased fluorescence anisotropy accompanying increased sorption capacity.

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