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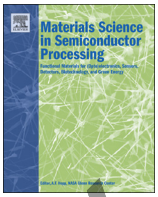

FRET-designed dye-sensitized solar cells to enhance light harvesting

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ABSTRACT

Förster resonance energy transfer between the xanthene dye (donor of energy) and a new polymethine dye (acceptor of energy) was studied on the surface of TiO_2 films in dye-sensitized solar cells. It was shown that the sensitization of semiconductor films by the donor–acceptor compound leads to a doubling of energy conversion efficiency in comparison to the cell due to only the polymethine dye. Measurements show that this is due to the widening of photosensitivity of the cell in the blue region of the spectrum. Increasing the total energy absorbed leads to increasing the number of generated charge carriers at the interface of TiO_2 and the dyes.

1. Introduction

Improving the efficiency of the conversion of solar energy to electricity is an important area of study in the field of photovoltaic solar cells. Starting from early studies, dye-sensitized solar cells have been intensively studied as inexpensive alternatives to commercially accessible silicon solar cells [1–4]. As a rule, dye-sensitized solar cells consist of dye-sensitized wide-band gap semiconductor electrodes (TiO_2 or ZnO), a liquid electrolyte that consists of redox-pairs I^-/I^{3-} [5,6], and a Pt electrode. The efficiency of such solar cells depends directly on the chemical structure of the dye and its absorption ability, the optimal location of the HOMO/LUMO orbital corresponding to the conductive band of the Ti and oxidation–reduction pair, the efficiency of the process of electron transfer from the dye to the TiO_2 surface, the pH of the medium, the size of semiconductor particles, and the morphology of the surface of films.

Usually a functional complex of Ru and Zn is used as the sensitizer dye of solar cells. Some problems are associated with the synthesis of these compounds; therefore the active search of non-metal donor–acceptor dyes has been carried out recently. The principal advantage of using such compounds is that their absorption and electrochemical properties can be changed through the method of their synthesis. Polymethine dyes were developed in the beginning of the 20th century mainly as sensitizers in silver halogenide emulsions in the photographic process. These dyes have extremely high extinction coefficients and switched absorption spectra in the entire visible and near-infrared region [7,8]. Polymethine dyes with various iconicity have been studied [9–12]. By studying the effect of an external magnetic field on the luminescence of the dye it was shown that excited singlet or triplet states can dominate the formation of electron–hole pairs.

The combination of good optical and donor–acceptor characteristics makes polymethines a promising class of

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materials for solar cells [13]. A review of research on the current–voltage characteristics of solar cells sensitized by polymethine dyes is presented in the work of Mishra et al. [14].

Recently, a long-range inductive-resonant electronic excitation energy transfer between dye molecules adsorbed on a film of TiO_2 was proposed to improve the light-harvesting characteristics of solar cells [15–20]. In solar cells, the donor (fluorescent material) absorbs high-energy photons and transmits them through the Förster resonance energy transfer (FRET) to acceptor (sensitizing dye), as shown in Fig. 1.

McGehee' group [18] developed a comprehensive model to compute the excitation transfer efficiency in a dye-sensitized solar cell for pores with cylindrical or spherical geometries and showed that the energy transfer process can be over 90% efficient in a dye-sensitized solar cell with dyes with reasonable properties. The application of FRET has the advantages of both enhancing light absorption and improving charge separation and provides a way to improve exciton harvesting by placing the exciton close to the heterojunction interface.

The energy transfer efficiency is determined by several factors, including the overlap integral of the fluorescence spectra of the donor and the acceptor absorption, the quantum yield of the energy donor, and the distance between the interacting molecules. Dye-sensitized solar cell using dyes, such as ruthenium-based and zinphthalocyanine, were explored based on the FRET idea [21,17]. Siegers et al. [20] demonstrated the use of Förster-resonant energy transfer (FRET) between covalently linked energy donor molecules to the SD attached to the titania surface. These traditional sensitizing dyes (SD) made from ruthenium-based complexes have low molar extinction coefficients (5000–20,000 $M^{-1}\ cm^{-1}$). However, organic and polymethine dyes [8] have demonstrated substantially higher molar extinction coefficients (100,000–300,000 $M^{-1}\ cm^{-1}$) and are good choices for designing dye-sensitized solar cells.

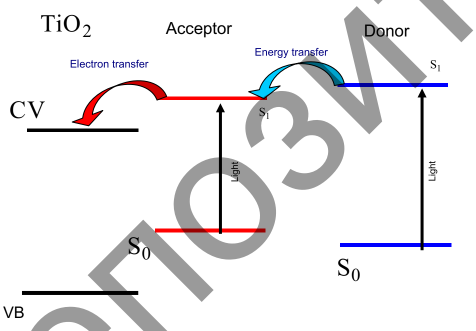

Fig. 1. Scheme of the energy transfer of solar cells sensitized by donor–acceptor compounds.

This paper demonstrates the ability to improve the electrophysical parameters of photovoltaic cells sensitized with organic dyes through the electronic excitation energy transfer between molecules of metal-free dyes directly into the solar cell. FRET between rhodamine and the new polymethine dyes adsorbed into the semiconductor TiO_2 films was studied. It was shown that the photovoltaic parameters of cells sensitized by donor–acceptor compounds improved in comparison with cells sensitized by neat acceptors.

2. Experimental part

The organic dyes, Rhodamine 6G myristinate and polymethine dye, were chosen as the donor and acceptor of energy, respectively. Rhodamine dye was synthesized in the Institute of Organic Intermediates and Dyes (NIOPIK, Russia), and squarylium dye (SQ) in the Institute of Organic Chemistry, National Academy of Sciences of Ukraine (Ukraine). Dyes were used without additional purification. The structural formulae of the compounds are shown in Fig. 2. SQ dye was chosen as the energy acceptor and the main sensitizer of the solar cell because of its optimal arrangement of HOMO–LUMO orbitals with respect to the conduction band of TiO_2.

The results of the calculation performed by the INDO method have shown that the HOMO orbital of the dye has an energy of about −6.22 eV and the LUMO orbital energy is equal to −0.80 eV. It is evident that the polymethine dye may act as an electron donor with respect to TiO_2.

The absorption and fluorescence spectra of the dye solutions and TiO_2 films were measured with a CM2203 spectrometer (Solar, Belarus). The excited-state lifetime of the donor and acceptor was measured using a pulsed spectrofluorimeter with picosecond resolution with registration in time-correlated photon counting mode (Becker & Hickl, Germany).

Solar cells were prepared and assembled according to a previously described procedure [22]. Glass substrates coated with a layer of conductive FTO were purchased from Sigma-Aldrich. Pastes “Ti-nanoxide HT” and “Ti-nanoxide D” were used for deposition of transparent and diffusing TiO_2 layers, respectively. Pastes, electrolyte “Iodolyte Z150”, Pt catalyst “Platisol” and other components were purchased from Solaronix (Switzerland). The TiO_2

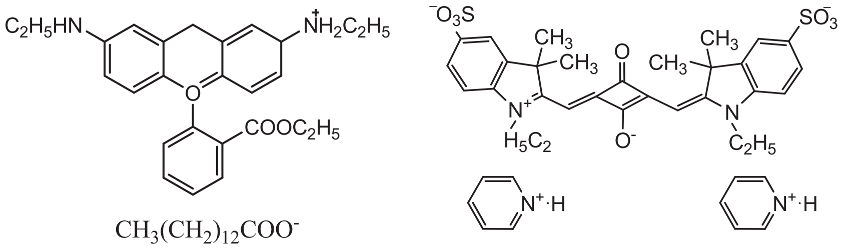

Fig. 2. Structure formulae of the donor (at the left) and acceptor of energy (at the right).

electrode was immersed into an ethanol dye solution and kept at room temperature for 24 h to assure complete sensitizer uptake.

The current–voltage characteristics of the dye-sensitized solar cells were measured at an illumination intensity of 100 mW/cm^2 with an AM1.5 solar simulator Solar Cell Tester CT50AAA (Photo Emission Tech. Inc., USA). The fill factor (*FF*) and energy conversion efficiency (η) were calculated according to the following equations:

$$FF = \frac{(I_{\max} U_{\max})}{I_{sc} U_{xx}} \tag{1}$$

$$\eta = \frac{FF\ I_{sc} V_{oc}}{P_{in}} \times 100\% = \frac{P_{cell}}{P_{in}} \tag{2}$$

where $I_{\max}$ and $U_{\max}$ are the values of maximal current and voltage, respectively; I_{sc} and V_{oc} are the values of short-circuit current and open-circuit voltage, respectively; and P_{in} is the power of the incident light.

3. Results and discussion

Co-sensitization of titania by dyes enhances light absorption and extends the spectral response of DSC through complimentary absorption spectra. In this design, each dye adsorbs intensely on the surface, transfers the charge efficiently into the TiO$_2$, has a slow recombination rate, and regenerates with the redox couple [20]. In typical DSCs, after the SD absorbs light, it transfers an electron into the titania and a hole into the electrolyte. In this new design, as shown in Fig. 1, Rhodamine 6G myristinate is utilized inside the liquid electrolyte where it absorbs high-energy photons and efficiently transfers the energy by the Förster process to the anchored SQ, increasing the absorption bandwidth of the DSC. This design mimics photosynthesis of purple bacteria [23], where light-harvesting pigments transfer their energy to the reaction center, initiating charge separation. The electron excitation energy transfer between Rhodamine 6G myristinate and SQ was studied in TiO$_2$ films sensitized with a neat donor, neat acceptor and donor–acceptor compound at various concentrations of components. For measurements of the fluorescence decay kinetics, the photoexcitation of all samples was carried out in the absorption band of donor with radiation from a laser with a wavelength (λ_{gen}) of 488 nm. Registration of donor and acceptor fluorescence was carried out at 555 and 660 nm respectively. The samples were illuminated with white light from a Xe lamp in order to create an increase in the number of excited molecules of polymethine dye by energy transfer from rhodamine dye molecules.

Fig. 3 shows the normalized absorption and fluorescence spectra of the donor and acceptor. It is shown that the fluorescence spectrum of the donor and the absorption spectrum of the acceptor overlaps, which is a prerequisite for effective electronic excitation energy transfer.

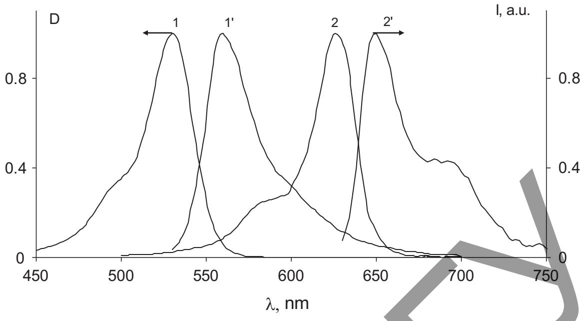

Fig. 3. Normalized absorption (1,2) and fluorescence (1′,2′) spectra of donor (1,1′) and acceptor (2,2′) at concentration $C = 10^{-5}$ mol/l.

Table 1
Calculated values of critical parameters of energy transfer.

Solution	Overlap integral, M^{-1} cm^3	R_0, Å	C_0, mol/l
Donor–acceptor	7.8×10^{-13}	29	1×10^{-2}

The Förster distance and critical concentrations were calculated in order to prepare samples with proper concentrations of donor and acceptor molecules. One of the above critical parameters indicates a distance between donor–acceptor molecules, the other is the concentration at which the probabilities of processes of electronic excitation energy transfer or its spontaneous deactivation are equal. Critical parameters were determined from the well-known Förster formula based on the spectral measurements [24–26]. Calculated values of critical parameters are presented in Table 1, where R_0 is a critical distance of energy transfer and C_0 is the critical concentration of energy transfer between donor and acceptor molecules.

The data show that the selected concentrations of the donor and acceptor are lower than the critical concentration, which means that most of the excitation energy will be transferred to acceptor molecules.

The energy transfer process from the molecules of rhodamine to the polymethine dye was registered by measurements of the donor and acceptor fluorescence decay kinetics (Fig. 4, Table 2).

The efficiency of energy transfer E_{ET} was estimated with the following Eq. (3)[24]:

$$E_{ET} = 1 - \frac{\tau_D}{\tau_{0D}} \tag{3}$$

The data presented show that the excited-state lifetime of the donor in the presence of acceptor molecules decreases with increasing concentration of the acceptor molecules. The lifetime of acceptor molecules has a value close to the lifetime of the donor which confirms the implementation of the process of energy transfer between the selected dyes.

Measurements of the fluorescence intensity of the acceptor in the presence of and without donor molecules under illumination of a xenon lamp were carried out to study the effects on the performance of the cell – co-sensitization of TiO$_2$ semiconductor film by the donor and acceptor molecules or the result of the process of energy transfer. As can be seen in Fig. 5, the addition of donor molecules leads to an increase in the luminescence intensity of the acceptor of almost 2.5 times. Maximal sensitization of acceptor occurs at donor concentration equal to 10^{-5} mol/l. Further growth of number of donor molecules

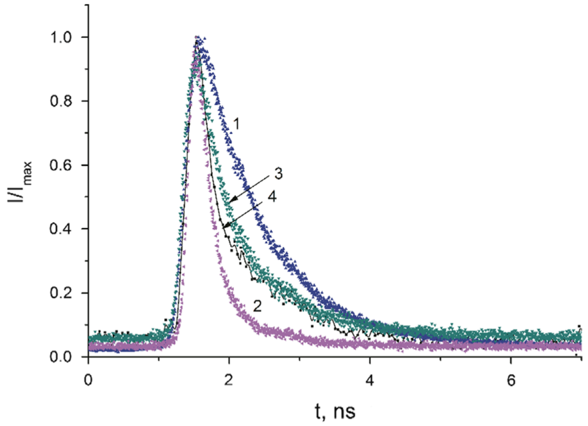

Fig. 4. Fluorescence decay kinetics of donor (1) and acceptor (2), donor in the presence of acceptor molecules (3) and sensitized fluorescence of the acceptor adsorbed onto TiO_2 films ($C_D=10^{-5}$; $C_A=10^{-5}$ mol/l), $\lambda_{ex}=$ 488 nm (4).

Table 2
Fluorescence lifetime (τ) of donor and acceptor of energy adsorbed onto TiO_2 films

Donor–acceptor concentration, mol/l	τ, ns		E_{ET}
	$\lambda_{reg}=555$ nm	$\lambda_{reg}=660$ nm	
Donor	0.9	0.9	–
Acceptor	0.5	0.5	–
10^{-4}; 10^{-6}	0.9	0.85	0
10^{-4}; 10^{-5}	0.75	0.9	0.17
10^{-4}; 10^{-4}	0.7	0.7	0.22

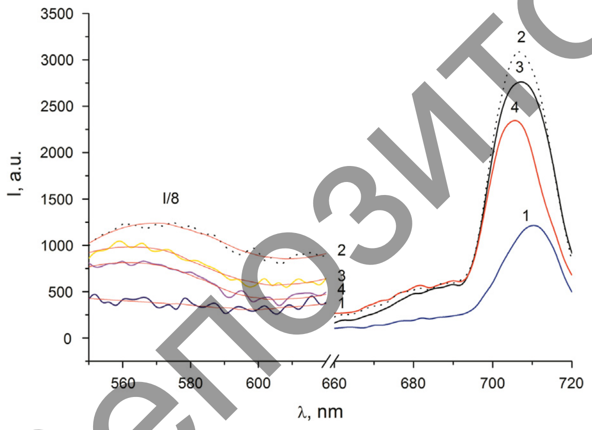

Fig. 5. Fluorescence spectra of TiO_2 films sensitized by the neat acceptor (1) and donor–acceptor compound at various concentrations of donor, mol/l: 2–10^{-5}; 3–10^{-4}; and 4–10^{-3}. Films are illuminated with white light, $C_a=10^{-4}$ mol/l.

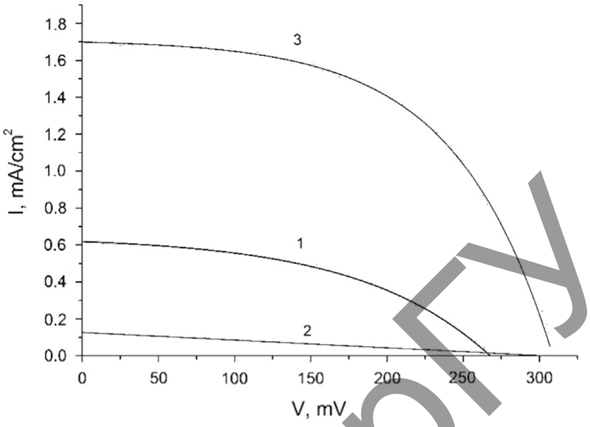

Fig. 6. The current–voltage characteristics of solar cells sensitized by the neat acceptor, neat donor and donor–acceptor compound.

Table 3
Photoelectric parameters of solar cells sensitized by acceptor molecules and donor–acceptor compounds

Donor–acceptor concentration	I_{sc}, mA/cm^2	U_{oc}, mV	*FF*	η, %	η/η_0
0; 10^{-2}	0.62	270	0.47	1.03	–
10^{-6}; 10^{-2}	0.14	180	0.47	0.2	0.2
10^{-5}; 10^{-2}	1.72	310	0.53	2.52	2.4
10^{-4}; 10^{-2}	0.8	210	0.5	0.96	0.93
10^{-3}; 10^{-2}	0.75	210	0.5	0.96	0.93
10^{-3}; 0	0.125	300	0.25	0.45	–

leads both to the quenching of fluorescence of rhodamine and polymethine dyes. Such behavior of fluorescence of donor molecules is the result of molecular aggregation of rhodamine dye [27].

The role of non-radiative energy transfer in the conversion of light energy into electrical energy with solar cells was studied next. For this aim the TiO_2 films sensitized with neat polymethine dye and TiO_2 films sensitized with the donor–acceptor compound were prepared. The concentration (C) of polymethine dye in these films was 10^{-2} mol/l and the concentration of the donor was varied from 10^{-5} to 10^{-2} mol/l.

Fig. 6 shows the current–voltage characteristics of solar cells sensitized by SQ dye molecules (curve 1), neat donor molecules (curve 2) and donor-acceptor compound (curve 3).

I_{sc} of solar cells with neat polymethine dye was equal to 0.62 mA/cm^2 and $U_{oc}=270$ mV. In the case of co-sensitization of the solar cell with donor and acceptor, the increase in the value of the current (Fig. 6, Curve 3) was recorded. The power conversion efficiency of TiO_2 solar cells containing donor–acceptor compound increased by two times over a pristine cell (Table 3). The optimum concentration of donor molecules for the co-sensitization of solar cell is 10^{-5} mol/l.

As can be seen from the table, the sum of parameters of photovoltaic cell only on the basis of a neat polymethine or rhodamine dye does not give the value recorded for the cell sensitized donor–acceptor mixture. This means that the contribution in the photocurrent gives the process of energy transfer which is higher than a phenomenon co-sensitization of semiconductor films. The decrease in the values of the photocurrent with a further increase in the concentration of the donor is a result of the process of aggregation of donor molecules. It, as a result, reduces the efficiency of energy transfer from rhodamine to polymethine dyes.

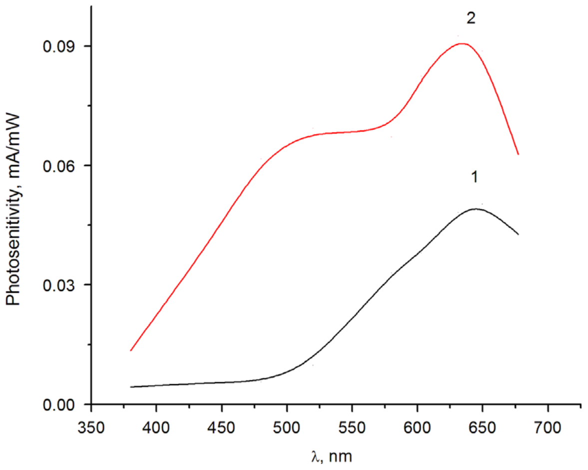

Fig. 7. Spectral photosensitivity of the solar cell based on acceptor (Curve 1, $C_a=10^{-2}$ mol/l) and donor–acceptor compound (Curve 2, $C_a=10^{-2}$ mol/l, $C_D=10^{-5}$ mol/l).

The curves of spectral photosensitivity of solar cell based on acceptor and donor–acceptor compound are shown in Fig. 7.

It is noted that the spectral photosensitivity of the cell by FRET was increased in the range of 400–500 nm, which is where the rhodamine dye absorbs the light, but the polymethine dye does not. The increase of the total energy absorbed promotes an increase of the number of generated charge carriers at the interface of TiO_2 and dyes.

4. Conclusion

In this paper we report on the investigation of FRET between molecules of rhodamine and polymethine dye in TiO_2 films.

Measuring the fluorescence decay kinetics of the energy donor showed that in the presence of acceptor molecules, there is a reduction of the lifetime of the excited state of the donor. The efficiency of energy transfer, which was evaluated according to the Förster–Dexter equation, was 22% at an acceptor molecule concentration of 10^{-4} mol/l. The intensity of sensitized fluorescence of polymethine dye upon illumination with white light almost doubles in the presence of donor molecules in the film. The photovoltaic parameters of solar cells based on the polymethine dye increased 2.5 times in the presence of rhodamine dye molecules. The main factor in the increase of the efficiency of the cell is related to the energy transfer process and is not a result of the co-sensitization of the semiconductor film with different dyes. The increase of the total energy absorbed yields an increase in the number of generated charge carriers at the interface of TiO_2 and dyes. These results can be used in assembling solar cells sensitized with organic dyes.

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