

DOI 10.31489/2022No1/26-33

UDC 538.9;535.215; 539.23; 535.3

INFLUENCE OF PHTHALOCYANINE NANOSTRUCTURES ON OPTICAL AND PHOTOVOLTAIC CHARACTERISTICS OF A POLYMER SOLAR CELL

Aimukhanov A.K.*, Zeinidenov A.K., Rozhkova X.S., Akhatova Zh.Zh.

E.A. Buketov Karaganda University, Scientific Center for Nanotechnology and Functional Nanomaterials, Karaganda, Kazakhstan, a_k_aitbek@mail.ru

Nanocomposite polymer solar cells were obtained. Nanostructures of phthalocyanines were added to a mixture of photoactive layer at a concentration of 0.5%. The photoactive layer was applied by centrifugation at a rotation speed of 1500 rpm. Atomic force microscope images of the surface of the films were measured. Absorption spectra of composite films were measured. It was found that the introduction of phthalocyanine nanostructures into the photoactive layer leads to a broadening of the spectrum and an increase in the optical density at the absorption maximum by 2.1 times for nanorods and 1.9 times for nanoparticles. The current-voltage characteristics of composite organic solar cells were measured. To do this, an aluminum electrode with a thickness of 100 nm was sprayed onto the surface of the photoactive layer at 10^{-5} Torr. It is shown that when the photoactive layer was doped with nanorods and phthalocyanine nanoparticles, the short-circuit current density of the current-voltage characteristics increased by 8% and 5%, respectively, and the efficiency value increased to 4.58% and 4.51%, respectively. The impedance spectra of composite organic solar cells were measured. Analysis of hodographs of nanocomposite films showed that doping of the photoactive layer with nanorods and phthalocyanine nanoparticles leads to an increase in the diffusion length by 2.2 times and 1.8 times, respectively, and an increase in the mobility of charge carriers by 1.4 times and 1.2 times.

Keywords: semiconductor polymers, metallophthalocyanines, generation and transport of charge carriers, photovoltaics.

Introduction

The study of the generation and transport of charge carriers in organic semiconductors is relevant today. This is due to the fact that they have a low cost and inexpensive manufacturing technology compared to traditional inorganic semiconductors. Organic semiconductors have found wide application in quantum electronics, biology, medicine, as well as in the development of sensors, sensors and converters [1-3]. These include various temperature and gas sensors, pressure sensors and electromagnetic radiation. The development of polymer nanocomposite solar cells is one of the ways to increase the efficiency of converting solar energy into electrical energy. In such films, doping of the polymer matrix with nanoscale organic materials makes it possible to create a hybrid layer in which the conductivity of the polymer material will be combined with high optical and electrical properties of organic nanostructures. It should be noted that the advantage of these composite materials is a simplified process of manufacturing a solar cell [4, 5]. However, the study of the influence of structural features of molecular clusters on the efficiency of generation, separation of charges and their transport remains relevant in the development of organic semiconductor devices. The charge transfer and semiconductor properties of polymers are very sensitive to the morphology of polymer chains and local structural ordering within the film. Thus, structural and energy disorder in conjugated polymer systems are important for describing charge transfer involving various mechanisms and electronic processes [6].

Despite the obvious progress made in the creation of polymer solar cells, there are various limitations that prevent further improvement of the efficiency of solar energy conversion. For

example, a big problem is increasing the absorption of light in the photoactive layer and reducing the recombination of charge carriers [7, 8]. Currently, various approaches are used to increase light absorption without increasing the thickness of the photoactive layer. To solve this problem, the use of nanocomposites is proposed. To create such systems, nanostructures introduced by doping into a photoactive polymer material can be used. This makes it possible to create hybrid layers in which the conductivity of polymer materials increases.

Despite a fairly large number of works devoted to composite polymer solar cells, their optical and photo-electrophysical parameters are poorly studied. The study of the mechanisms of generation and transport of charge carriers in nanocomposite structures that affect the efficiency of solar energy conversion is the subject of discussion.

1. Methods and materials

To create solar cells as a donor was used poly [4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt -(4-(2-ethylhexyl)-3-fluorotieno [3,4-b]thiophene-)-2-carboxylate -2-6-diil] (PTB7-Th), as an acceptor – 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)indanon))-5,5,11,11-tetrakis(4-hexylphenyl)dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b'] dithiophene (ITIC). The preparation of the substrates was carried out according to the method [6]. Methods of physical gradient-temperature vapor deposition (TG-PVD) and laser ablation in liquid were used for the synthesis of phthalocyanine nanostructures [7, 8]. The photoactive PTB7-Th:ITIC layer was applied by centrifugation at a rotation speed of 1500 r/pm. After that, the samples were annealed in an air atmosphere at a temperature of 110°C for 10 minutes. Then, at the CY-1700x-spc-2 spraying plant (Zhengzhou CY Scientific Instruments Co., Ltd), an aluminum electrode with a thickness of 100 nm was sprayed onto the surface of the photoactive layer at a vacuum of 10^{-5} Torr. The structure of the polymer solar cell is shown in Fig.1.

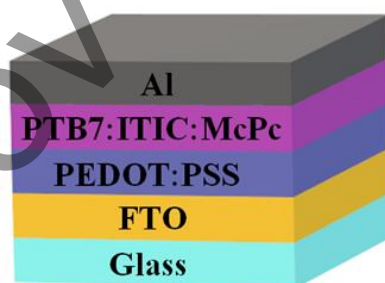


Fig.1. Solar cell structure.

Polymer and nanocomposite solar cells were obtained according to the method [9]. To create nanocomposite samples of solar cells, nanostructures of phthalocyanines were added to the prepared solution of the polymer PTB7-Th:ITIC at a concentration of 0.5% by weight of the polymer. The morphology of the surface of the obtained samples was studied using the atomic force microscope JSPM-5400 (JEOL Ltd, Japan). The optical characteristics of the films were studied using the Avantes AvaSpec-ULS2048CL-EVO spectrometer. A combined deuterium-halogen AvaLight-DHc light source with an operating range of 200-2500nm was used as a radiation source. The impedance spectra were measured using a measuring system P45X in the impedance mode. The current-voltage characteristics of photosensitive cells was determined by the Sol 3A Class AAA Solar Simulators (Newport) with PVIV-1 A I-V Test Station.

2. Results and discussion

AFM images of phthalocyanine nanostructures are shown in Figure 2. Nanoscale rods of phthalocyanines have an average width of 70 nm and a length of 500 nm. Phthalocyanine nanoparticles are mostly rounded in shape with an average size of about 50 nm. The same Figure 2 shows the AFM image of the PTB7-TH:ITIC film. It can be seen from the figure that the PTB7-TH:ITIC film has a homogeneous structure.

Figure 3 shows the absorption spectra of PTB7-Th:ITIC composite films doped with nanorods (a) and nanoparticles (b) of phthalocyanine and its metal complexes. The figure shows that the absorption spectrum of the PTB7-Th:ITIC film is located in the range of 450-780 nm with peaks at 642 nm and 694 nm and a half-width of 160 nm. Doping of the photoactive PTB7-Th:ITIC layer with nanorods and phthalocyanine nanoparticles leads to an increase in the optical density of the absorption spectrum. Thus, when the bulk heterojunction is doped with nanorods and ZnPc nanoparticles, the maximum increase in the optical density value in the absorption spectrum is observed (by 2.1 and 1.9 times, respectively). The half-width of the absorption spectrum increased slightly.

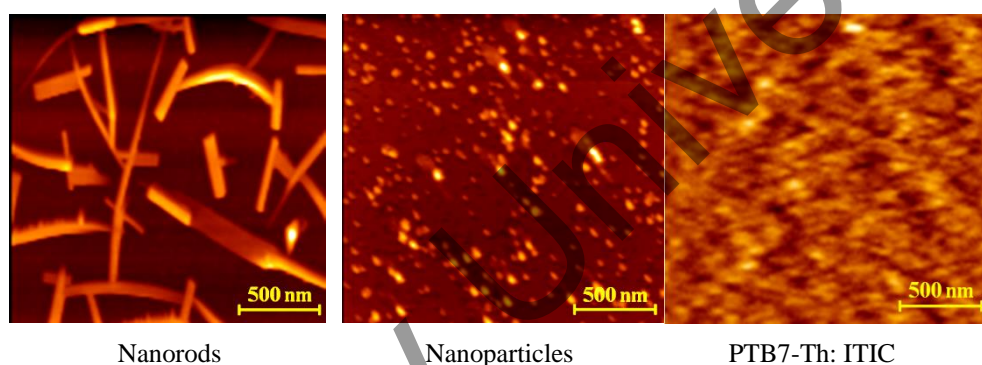


Fig.2. AFM images of phthalocyanine nanostructures and photoactive layer.

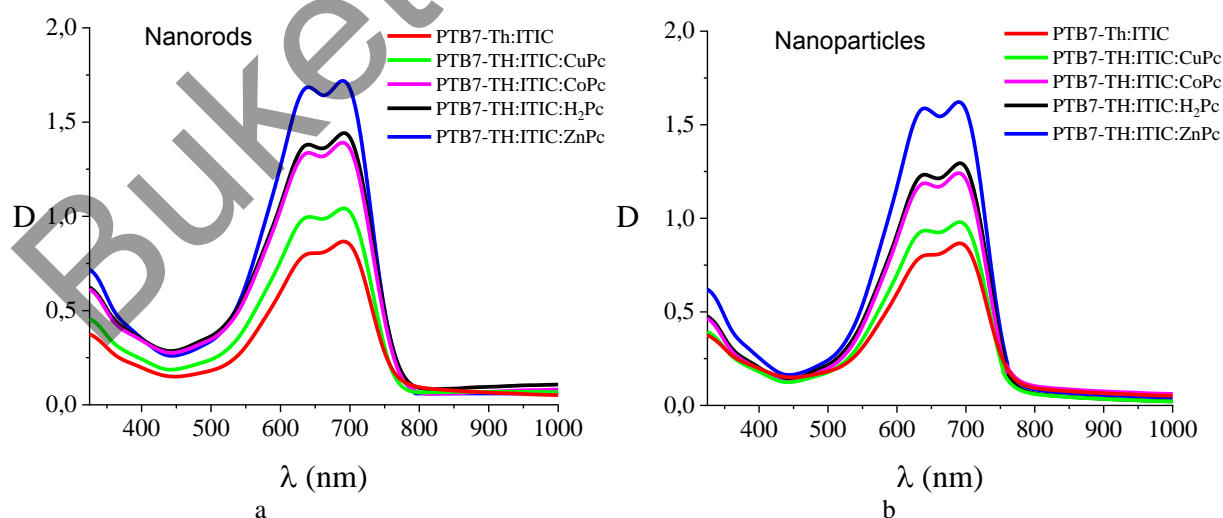


Fig.3. Absorption spectrum of pure polymer PTB7-TH:ITIC and absorption spectra of PTB7- TH:ITIC nanocomposites doped with nanorods (a) and nanoparticles (b) of phthalocyanines.

When doped with CuPc nanorods and nanoparticles, the optical density increased by a smaller amount (by 1.2 times). When doping with H₂Pc and CoPc nanostructures, an increase in the optical density value is also observed. Table 1 shows the main optical characteristics of the obtained samples.

Thus, the introduction of nanorods and nanoparticles due to additional absorption contributes to an increase in the absorption of the photoactive layer of the polymer solar cell. One of the most important indicators of any photovoltaic devices is the efficiency of energy conversion (further EFF). The efficiency is determined by the following formula:

$$\eta = \frac{U_{OC} \cdot J_{SC} \cdot FF}{P_{IN}}, \quad (1)$$

where U_{OC} is the no-load voltage; J_{SC} is the short-circuit current density; FF is the fill factor; P_{IN} is the input power of the incident radiation.

The filling factor (FF) determines the efficiency of the charge carrier generation process in the SC. The fill factor is determined by the ratio of the maximum power of the solar cell to the product of the no-load voltage and the short-circuit current density:

$$FF = \frac{J_{MP} \cdot U_{MP}}{J_{SC} \cdot U_{OC}}, \quad (2)$$

where J_{MP} and U_{MP} are the current density and voltage at the point of maximum power of the solar cell.

Table 1. Optical characteristics of PTB7-Th:ITIC thin films.

Sample	Maximum absorption		D ₁	D ₂	Half-width, nm
	λ_1 , nm	λ_2 , nm			
PTB7-Th:ITIC	642	694	0.81	0.88	160
Nanorods					
PTB7-TH:ITIC:CuPc	640	692	0.99	1.06	165
PTB7-TH:ITIC:CoPc	639	694	1.34	1.41	169
PTB7-TH:ITIC:H ₂ Pc	641	693	1.38	1.45	168
PTB7-TH:ITIC:ZnPc	639	691	1.69	1.76	167
Nanoparticles					
PTB7-TH:ITIC:CuPc	639	691	0.94	0.99	164
PTB7-TH:ITIC:CoPc	640	693	1.19	1.24	168
PTB7-TH:ITIC:H ₂ Pc	639	694	1.25	1.30	167
PTB7-TH:ITIC:ZnPc	640	692	1.59	1.64	166

Figure 4 shows the voltage characteristics of composite organic solar cells. The figure shows that the doping of the photoactive PTB7-Th:ITIC layer with nanorods (a) and nanoparticles (b) of phthalocyanines affects the parameters of the current-voltage characteristics cells. For example, the filling factor of a composite cell with nanorods and PTB7-Th:ITIC:CuPc nanoparticles was FF = 0.55 and 0.54 respectively, and the value of the short-circuit current density is equal to $J_{sc} = 10.62 \text{ mA/cm}^2$ and 10.53 mA/cm^2 . The same changes are observed for composite cells doped with H₂Pc and CoPc nanostructures.

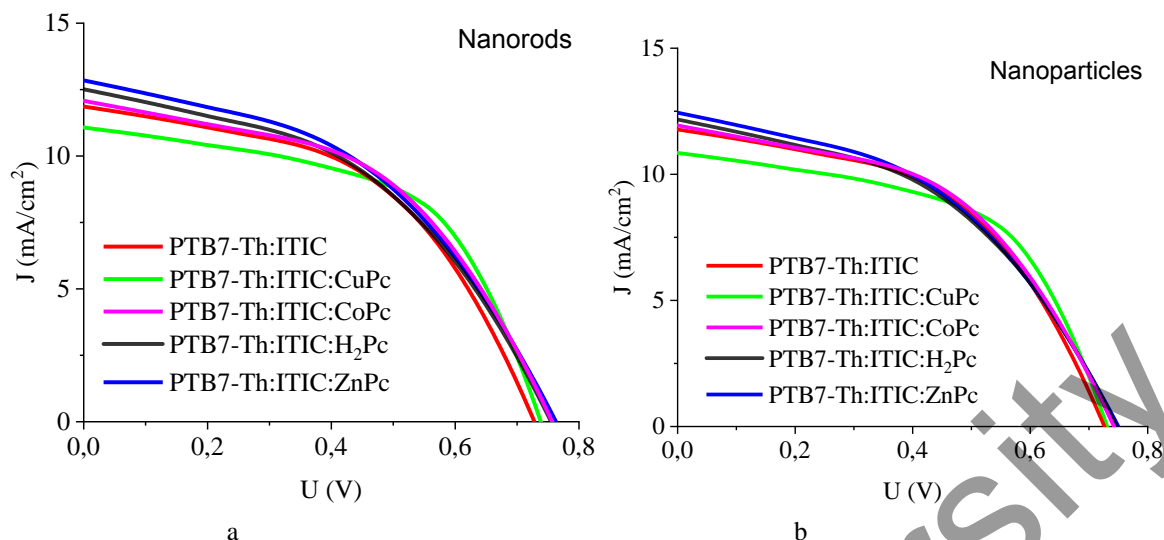


Fig.4. Voltage characteristics of nanocomposite solar cells based on PTB7-Th:ITIC doped with nanorods (a) and nanoparticles (b).

The maximum value of the increase in the CVC parameters is observed for a composite cell with PTB7-Th:ITIC:ZnPc nanostructures, so the short-circuit current density when doped with nanoparticles increased by 5%, the efficiency value was 4.51%, when doped with nanorods, the short-circuit current density increased by 8%, the efficiency was 4.58%. The parameters of the CVC cells are given in Table 2.

Figure 5a shows a charge carrier transfer scheme in a composite photoactive layer. The photo voltage generated in the heterojunction is determined by the difference between the quasi-fermi level of electrons in the acceptor and the quasifermi level of holes in the donor under illumination [10, 11]. It is obvious that the nanostructures of phthalocyanines in the photoactive layer will influence the position of the quasi-level of holes in PTB7-Th. As can be seen from the energy diagram (Figure 5b), the position of the bottom of the phthalocyanine conduction band is above the bottom of the ITIC conduction band.

Table2. Photovoltaic characteristics of organic solar cells.

Sample	J_{sc} , (mA/cm ²)	J_{max} , (mA/cm ²)	U_{oc} , (V)	U_{max} , (V)	FF	Efficiency, %
PTB7-TH:ITIC	11.93	8.32	0.73	0.51	0.46	4.24
Nanorods						
PTB7-TH:ITIC:CuPc	10.62	7.54	0.74	0.57	0.55	4.29
PTB7-TH:ITIC:CoPc	11.94	8.34	0.75	0.53	0.49	4.42
PTB7-TH:ITIC:H ₂ Pc	12.43	8.77	0.75	0.51	0.48	4.47
PTB7-TH:ITIC:ZnPc	12.84	8.97	0.76	0.51	0.47	4.58
Nanoparticles						
PTB7-TH:ITIC:CuPc	10.53	7.59	0.74	0.56	0.54	4.25
PTB7-TH:ITIC:CoPc	11.94	8.28	0.74	0.52	0.49	4.31
PTB7-TH:ITIC:H ₂ Pc	12.38	8.64	0.75	0.51	0.48	4.41
PTB7-TH:ITIC:ZnPc	12.54	8.85	0.75	0.51	0.47	4.51

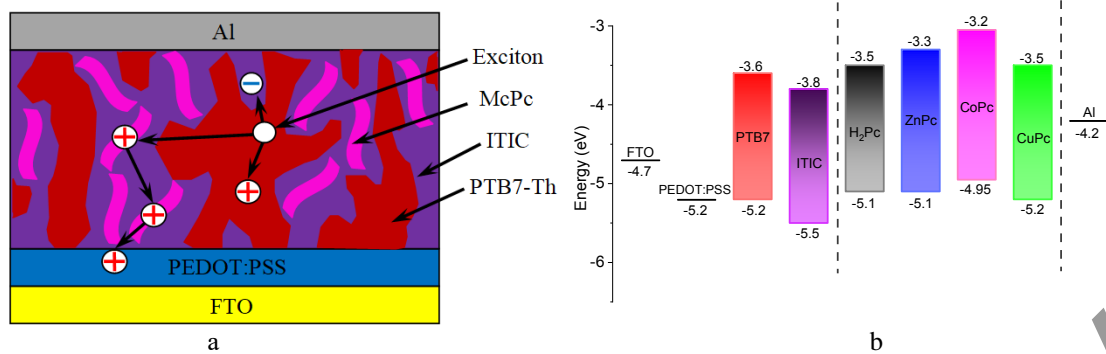


Fig.5. The carrier transfer scheme in the cell (a) and the energy diagram of the composite photo converter (b).

This contributes to the formation of a potential barrier for the injection of electrons from the ITIC conduction band into the conduction band of phthalocyanine nanostructures. In turn, as can be seen from the energy diagram, the upper level of the PTB7-Th valence band is slightly lower than the upper level of the phthalocyanine valence band. As a result, a built-in electric field is formed at the PTB7-Th/phthalocyanine interface, which transfers holes from the valence band of PTB7-Th to the valence band of phthalocyanine nanostructures. Also, due to the formation of nanorods and phthalocyanine nanoparticles, holes are more efficiently transported to PEDOT:PSS, which leads to an increase in photocurrent.

An increase in the value of the short-circuit current of the CVC and the efficiency of the cells can be associated with a number of reasons: a decrease in the recombination of charge carriers in the active layer, an increase in the transport of charge carriers due to an increase in the interface area [12, 13]. In order to determine the effect of phthalocyanine nanostructures on the transport and recombination of charge carriers, measurements of the impedance spectra of composite cells were carried out. To interpret the impedance spectra of solar cells, an equivalent electrical circuit was used, where R_1 (R_w) is the equivalent resistance of a multilayer film (the resistance of a photoactive layer), R_2 (R_{rec}) is the resistance of the PTB7-Th/ITIC interface, characterizing the recombination of electrons with holes (Figure 6a). The charge transport scheme in the cell is shown in Figure 6b.



Fig.6. Equivalent electrical circuit (a) and charge transport circuit in the cell (b).

The fitting of the spectrum parameters was carried out using the EIS-analyzer software package. The analysis of the impedance measurement results was carried out according to the diffusion-recombination model [14,15]. As a result of the analysis of the impedance spectra, the following electric transport parameters were determined: τ_{eff} – the effective lifetime of charge carriers; k_{eff} – the effective rate of extraction of charge carriers, D_{eff} – the effective diffusion coefficient of charge carriers and μ – the mobility of charge carriers. Analysis of hodographs (Figure 7) of nanocomposite films showed that doping of the photoactive layer with nanorods (a) and nanoparticles (b) of phthalocyanines leads to an increase in the diffusion length (D_{eff}) and an increase in the mobility of charge carriers (μ) (Table 3).

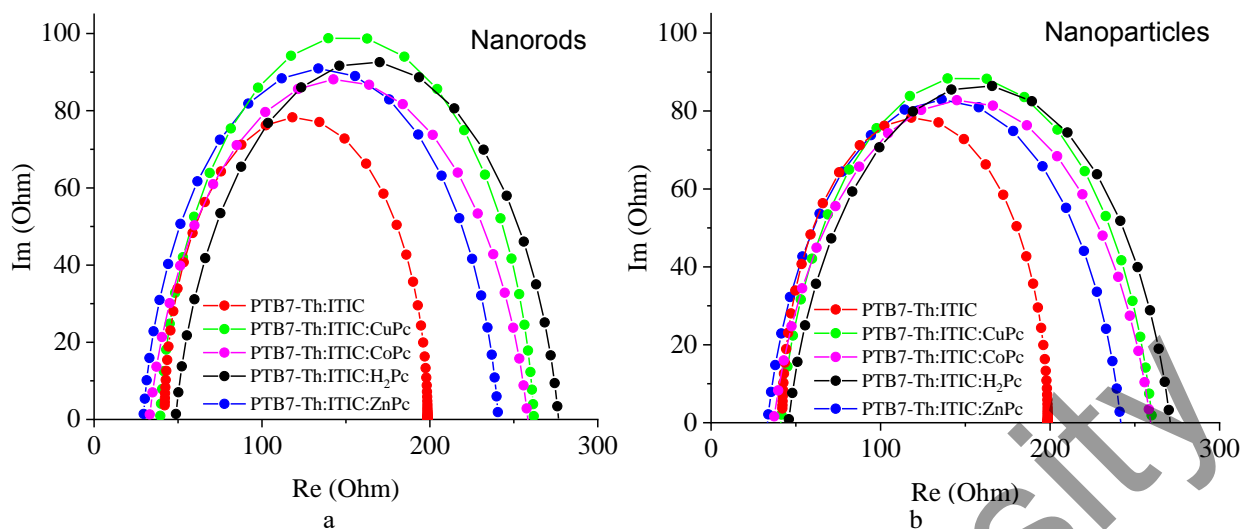


Fig.7. Hodographs of the impedance of solar cells based on the photoactive PTB7-TH:ITIC layer and nanocomposites doped with nanorods (a) and nanoparticles (b).

Doping of the photoactive PTB7-Th:ITIC layer with ZnPc nanorods and nanoparticles leads to a maximum 2.2 fold (for nanorods) and 1.8 fold (for nanoparticles) increase in the D_{eff} value and a decrease in the R_w value by 1.5 fold (for nanorods) and 1.3 fold (for nanoparticles).

Table 3. Electric transport properties of the obtained samples of nanocomposite SC with different structures.

Sample	D_{eff} , ($\text{cm}^2 \cdot \text{s}^{-1}$)	k_{eff} , (s^{-1})	τ_{eff} , (ms)	R_{rec} (Ohm)	R_w , (Ohm)	μ , (cm^2/Vs)
PTB7-TH:ITIC	$2.09 \cdot 10^{-5}$	45846	0.021	198.3	43.3	$2.82 \cdot 10^{-4}$
Nanorods						
PTB7-TH:ITIC:CuPc	$3.32 \cdot 10^{-5}$	49924	0.020	261.4	39.3	$3.12 \cdot 10^{-4}$
PTB7-TH:ITIC:CoPc	$3.87 \cdot 10^{-5}$	48835	0.020	258.4	32.6	$3.25 \cdot 10^{-4}$
PTB7-TH:ITIC:H ₂ Pc	$2.71 \cdot 10^{-5}$	47589	0.021	276.1	48.4	$2.97 \cdot 10^{-4}$
PTB7-TH:ITIC:ZnPc	$4.54 \cdot 10^{-5}$	53486	0.019	240.2	28.3	$3.86 \cdot 10^{-4}$
Nanoparticles						
PTB7-TH:ITIC:CuPc	$3.01 \cdot 10^{-5}$	48466	0.020	258.6	41.7	$3.01 \cdot 10^{-4}$
PTB7-TH:ITIC:CoPc	$3.38 \cdot 10^{-5}$	47377	0.021	258.4	36.2	$3.14 \cdot 10^{-4}$
PTB7-TH:ITIC:H ₂ Pc	$2.69 \cdot 10^{-5}$	46024	0.021	268.1	45.8	$2.87 \cdot 10^{-4}$
PTB7-TH:ITIC:ZnPc	$3.86 \cdot 10^{-5}$	52028	0.019	241.9	32.6	$3.49 \cdot 10^{-4}$

Conclusion

Nanocomposite polymer solar cells containing nanostructures of phthalocyanines have been obtained. According to AFM images of the surface, using the Win SPMII Data-Processing Software package, an analysis of the surface of nanostructures and a photoactive layer was carried out. The measurement of the absorption spectra of nanocomposite cells showed that nanostructures in the photoactive PTB7-Th:ITIC layer lead to an increase in the optical density values in the maxima on average from 0.81 to 1.69 and the half-width of the absorption spectrum from 160 to 167 nm. This means that in a composite cell, when light is absorbed by a photoactive layer, the density of charge

carriers increases. Measurements of the CVC of composite cells have shown that nanostructures, minimizing the probability of charge recombination, more efficiently transport holes into PEDOT:PSS, and thus increase the short-circuit current to 12.84 mA/cm² and efficiency to 4.58%. Experiments were conducted on the effect of nanostructures on the transport and recombination of charge carriers in composite cells. It is shown that nanostructures contribute to an increase in recombination resistance at the PTB7-Th/ITIC boundary by 1.2 times and a decrease in the resistance of a multilayer film by 1.5 times. Thus, the results obtained showed the possibility of using nanostructures as promising composite materials for photovoltaic organic solar cells. The development of composite solar cells has the prospect of creating lightweight, technologically advanced and cheap in mass production autonomous power sources for a wide range of electronic devices.

Acknowledgments

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08856176)

REFERENCES

- 1 Brau A., Farges J.P. Organic Semiconductors. *Org. Conduct. Fundam. Appl. Marcel Dekker*, 1994, pp.311–357.
- 2 Hohnholz D., Steinbrecher S., Hanack M. Applications of phthalocyanines in organic light emitting devices. *Journal of Molecular Structure*, 2000, Vol. 521, pp. 231-237. doi: 10.1016/S0022-2860(99)00438-X.
- 3 Itoh E., Ohmori Y., Miyairi K. Photovoltaic Properties of Organic p-n Junction Devices Consisting of Phthalocyanine and n-Type Porphyrin Deposited on an n-Type TiO₂ Layer. *Japanese J. Appl. Physics. Part 1 Regul. Pap. Short Notes Rev. Pap.* 2004, Vol. 43, Is.2., pp 817-821. doi: 10.1143/JJAP.43.817.
- 4 Wagenpfahl A., Deibel C., Dyakonov V. Organic solar cell efficiencies under the aspect of reduced surface recombination velocities. *IEEE J. Sel. Top. Quantum Electron.* 2010, Vol.16, Is.6, pp. 1759-1763.
- 5 Bi X., WuZ., ZhangT., AnC., XuY., MaK., et al. Reduced Nonradiative Recombination Energy Loss Enabled Efficient Polymer Solar Cells via Tuning Alkyl Chain Positions on Pendant Benzene Units of Polymers. *ACS Appl. Mater. Interfaces.* 2020, Vol.12, pp. 24184-24191. doi: 10.1021/acsami.0c04397.
- 6 Kim K., Ihm K., Kim B. Surface Property of Indium Tin Oxide (ITO) After Various Methods of Cleaning. *Acta Physica Polonica.* 2014, Vol. 127, No. 4, pp. 1176-1179. doi: 10.12693/APhysPolA.127.1176.
- 7 Hashizume M., Kunitake T. Preparation and functionalization of self-supporting (polymer/metal oxide) composite ultrathin films. *RIKEN Rev.* 2001, Vol. 38, pp. 36–39.
- 8 Pakhomov G.L., Gaponova D.M., Lukyanov A.Yu., Leonov E. S. Luminescence in phthalocyanine thin films. *Solid state physics.* 2005, Vol.47, No.1, pp.164-167.
- 9 Zeinidenov A.K., Aimukhanov A.K., Kambar D.S., Ilyassov B.R., Zavgorodniy A.V. Effects of phthalocyanine nanostructure on photovoltaic performance of its polymer composite thin films. *Materials Chemistry and Physics.* 2021, Vol. 267, p.124680. doi: 10.1016/j.matchemphys.2021.124680.
- 10 Gregg B.A., Hanna M.C. Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation. *Journal of Applied Physics.* 2003, Vol.93, Is.6, pp. 3605 - 3614. doi: 10.1063/1.1544413.
- 11 Ellison D.J., Kim J.Y., Stevens D.M., Frisbie C.D. Determination of quasi-fermi levels across illuminated organic donor/acceptor heterojunctions by kelvin probe force microscopy. *J. Am. Chem. Soc.* 2011, Vol.133, Is.35, pp.13802-13805. doi: 10.1021/ja2034574.
- 12 Yang H., Song Q., Lu Z., Guo C., et al. Electrochemically polymerized nanostructured poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) buffer layer for a high performance polymer solar cell. *Energy and Environ. Science.* 2010, Vol. 3, pp.1580-1586. doi: 10.1039/C0EE00117A.
- 13 Yuan X., Song C., Wang H., Zhang J. *EIS Equivalent Circuits In Electrochemical Impedance Spectroscopy in PEM Fuel Cells.* California: Springer, 2010, doi:10.1007/978-1-84882-846-9.
- 14 Zavgorodniy A.V., Aimukhanov A.K., Zeinidenov A.K., et al. The influence of the magnetic field on the current-voltage characteristics of cupc nanostructures. *Eurasian phys. tech. j.* 2019, Vol.16, No.1(31), P.54-61.
- 15 Aimukhanov A.K., Zeinidenov A.K., Ilyassov B.R., Zavgorodniy A.V. The research of photo-electrophysical properties of cobalt phthalocyanine film. *Eurasian phys. tech. j.* 2019, Vol.16, No.2(32), P.16-20.