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The effect of CuPc nanostructures on the photo and electrophysical characteristics of the active layer P3HT/PCBM

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The paper presents the results of a study of the influence of copper phthalocyanine (CuPc) nanostructures on the generation and transfer of charge carriers in the photoactive P3HT/PCBM layer. It was shown that the observed broadening and the shift in the maxima of the absorption spectra of P3HT/PCBM upon the addition of nanostructures to the polymer are associated with an increase in the degree of crystallization of the film. Using the method of impedance spectroscopy, it was found that CuPc nanostructures enhance the rate of recombination of charge carriers, which is probably due to the formation of surface defects. These defects are electron capture centers through which carrier recombination occurs. Despite that polymer solar cells with CuPc nanostructures have enhanced recombination rate, their photovoltaic properties were better than pure polymer solar cells due to enhanced light absorption and increased film conductivity.

Keywords: P3HT/PCBM, copper phthalocyanine, nanoparticles, nanowires, IVC, impedance spectroscopy.

Introduction

Polymer solar cells (SCs) are attracting increasing attention as components of modern flexible organic electronics due to their manufacturability and low cost of mass production [1]. Due to their flexibility, organic solar cells have an undeniably large number of advantages compared to solar cells from inorganic compounds. The favorable mechanical properties of the polymers, their recyclability, and the

high absorption coefficient in the optical range allows their use in the form of ultrathin (several hundred nanometers) films deposited from solutions under ordinary conditions on flexible substrates of unlimited area, which makes it possible to fabricate polymer SCs using cheap mass production methods, such as inkjet printing and stamping [2].

Synthetic derivatives of phenylene-vinylene, thiophene, and others synthesized in recent years are most successfully used as the photoactive component in polymer solar cells. To increase the efficiency of converting solar energy into electrical energy, composite materials are used: a mixture of materials with electronic and hole conductivity. An example of such a composite material is a mixture of a semiconductor conjugated polymer P3HT and fullerene derivatives [60] PCBM, [70] PCBM in the form of a bulk heterojunction, which is widely used as active layers of polymer SCs. However, solar cells based on a thiophene: fullerene mixture have some disadvantages, such as a narrow optical absorption range, low mobility of charge carriers, and a high degree of degradation in air [4].

In addition, there is currently an increased interest in organic semiconductors due to the comparative simplicity of production technologies and their low cost. It is very important that the use of organic molecules of various configurations opens up wide possibilities for modifying both the electrophysical and optical properties of the material. Among the variety of organic semiconductors, metallophthalocyanines, which represent an extensive class of macroheterocyclic compounds, have become very attractive. This is due to the fact that these compounds are chemically and thermally stable; most of them easily form ordered thin films and have photoconductivity as well as high catalytic activity. The high charge carrier mobility and the efficiency of light energy conversion make it possible to consider metallophthalocyanines as promising materials for photoelectric converters [5, 6].

One of the approaches to increasing the efficiency of converting solar energy into electrical energy is the development of new polymer nanocomposites. By creating new polymer and composite materials, including nanoscale structures and particles, energy conversion efficiency can be improved. In such films, the integration of organic materials allows the creation of hybrid layers in which the conductivity of polymeric materials is combined with the excellent optical and electrical properties of organic nanostructures. However, the mechanisms of generation of charge carriers in such composite structures that affect the efficiency of solar cells are still the subject of discussion. This paper presents the results of a study of the generation and transfer of charge carriers in a film based on P3HT/PCBM using CuPc nanostructures as a sensitizer.

Experimental method and results

The preparation of substrates for photosensitive cells on the basis of ITO was carried out according to the method [7]. CuPc nanowires on the surface of a substrate with a conductive ITO coating were obtained using temperature gradient physical vapor deposition (TG-PVD) [8]. CuPc nanoparticles were obtained by laser ablation in alcohol [9]. To create a polymer photoactive layer, 20 mg of a

mixture of P3HT/PCBM (Solaris, RR-95%; Sigma Aldrich) was dissolved in 1 ml of chlorobenzene (weight ratio of 1:1.08). The solution was kept at a temperature of 45 °C on a magnetic stirrer with heating for at least 24 hours. After that, the solution was filtered with a 0.45 micrometer filter. Then, CuPc nanoparticles and nanowires were added to the P3HT/PCBM polymer solution at a concentration of 0.5% by weight of the polymer. Solutions containing P3HT/PCBM polymer, P3HT/PCBM/NPs mixture and P3HT/PCBM/NWs mixture were applied onto the ITO surface to obtain films by the spin coating method. Then the films were kept at a rotation speed of a centrifuge of 2000 rpm for at least 20 s until the solvent was completely evaporated. At the last stage, the obtained samples were annealed in an atmosphere of chlorobenzene at a temperature of 120 °C for 30 min to increase the degree of crystallization of the photoactive layer and the quality of the film as a whole. An aluminum electrode was deposited on the surface of an obtained samples by thermal evaporation in a vacuum of 10⁻⁵ Torr at a rate of 1 nm/s using a Carl Zeiss Jena HBA 120/2 installation.

The absorption spectrum of copper phthalocyanine was measured on a CM2203 (Solar) spectrofluorometer. The IVC of an organic photosensitive cell were measured using a P20X potentiostat-galvanostat in linear sweep mode. The kinetics of transport and carrier recombination were studied on a Z-500 PRO impedance meter (Elins). In both cases, the cell surface was illuminated using a xenon lamp with a power of 100 mW/cm².

For photovoltaic measurements, samples of photovoltaic cells were prepared, consisting of several layers: 1 – a glass substrate; 2 – transparent conductive layer ITO (anode); 3 – photoactive layer; 4 – aluminum electrode (cathode).

The surface morphology of the obtained nanostructures (Figure 1) was measured using a TESCAN Mira3 LMU electron microscope. The average height of the grown nanowires, consisting of stacks of copper phthalocyanine molecules, was ≈ 137 nm. The average diameter of one nanowire was ≈ 4.5 nm. The average size of nanoparticles obtained by laser ablation varies in the range of ≈ 70-110 nm.

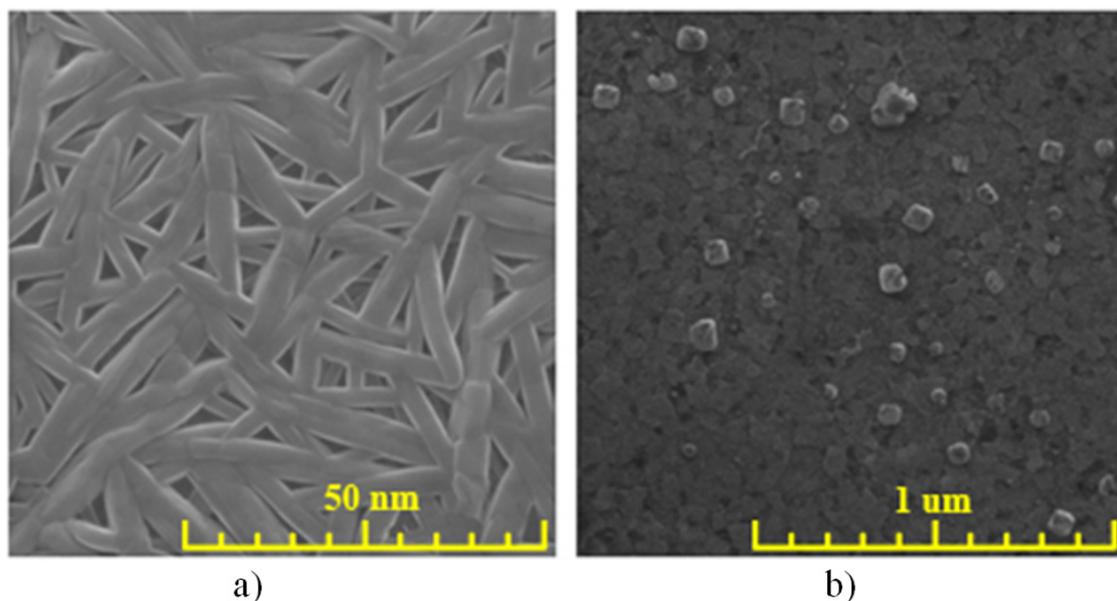


Figure 1. SEM images of the obtained samples: a) CuPc nanowires; b) CuPc nanoparticles.

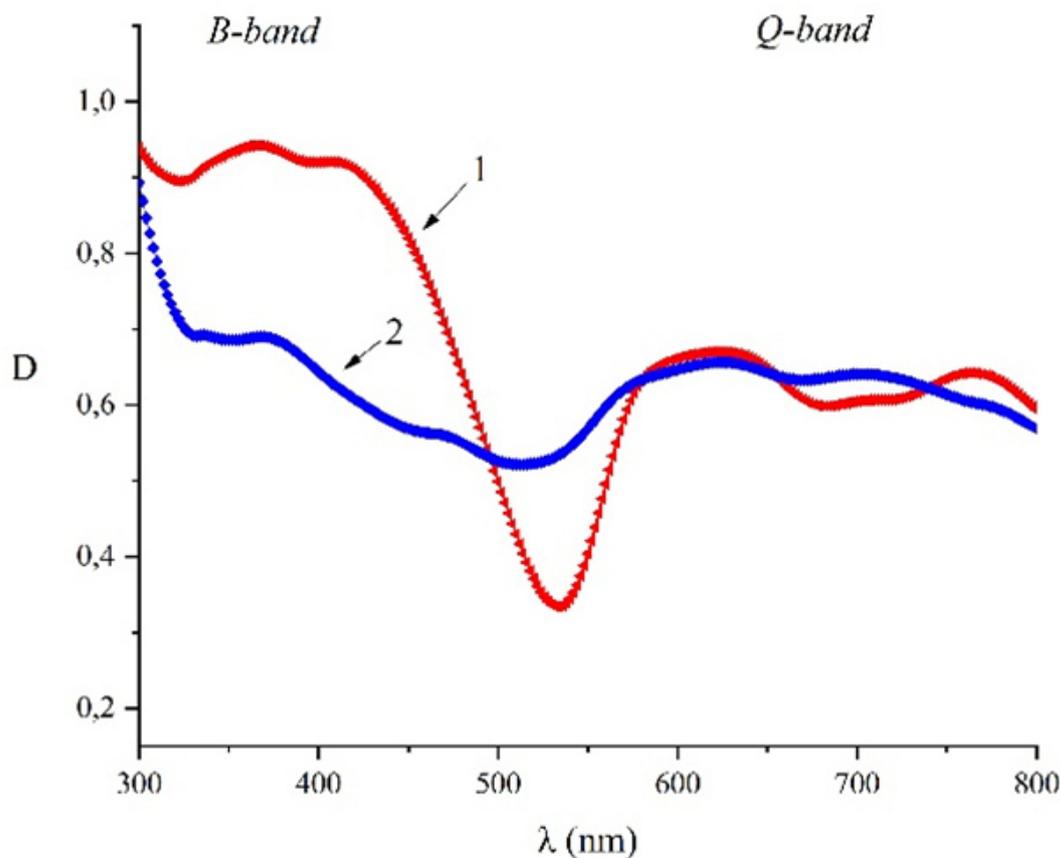


Figure 2. Absorption spectrum of CuPc: 1 – CuPc nanowires; 2 – CuPc nanoparticles.

Figure 2 shows the absorption spectra of copper phthalocyanine nanostructures. In the absorption spectra there are two very intense bands in the region of 300-400 nm (the Soret band or B-band), which corresponds to the mixed $\pi - \pi^*$ and $n - \pi$ transitions $a_{2u} \rightarrow {}^2e_g$ and $b_{2u} \rightarrow {}^2e_g$, and the absorption band in the region 650-700 nm (Q-band), which corresponds to the $\pi - \pi^*$ transition $a_{1u} \rightarrow {}^2e_g$ [11]. The characteristic splitting of the absorption of nanostructures in the Q-band into two peaks is associated with the Davydov splitting [12]. In the spectrum of CuPc nanoparticles (Figure 2, curve 2), the absorption band broadens in the Sora region. The absorption band in the Q-band is also broadened; in addition, the absorption spectrum of nanowires exhibits a rather strong broadening of the absorption bands in the B- and Q-bands and a bathochromic shift of the absorption maxima. The observed band broadening and maximum shift in the B- and Q-bands in the absorption spectra of CuPc nanostructures is due to the fact that molecules of copper phthalocinine, depending on the angle between the planes of the molecules in the structure under study, can form one of three possible crystalline phases: η -CuPc, α -CuPc, β -CuPc [13, 14]. Thus, in the case of nanoparticles, the molecules are in the β - phase; in nanowires, the molecules form the η - phase.

Figure 3 shows the absorption spectra of a P3HT/PCBM film without and with the addition of CuPc nanostructures. As can be seen from Figure 3, the absorption spectrum of the P3HT/PCBM polymer (curve 1) is characterized by the presence of peaks in the spectral region of ≈ 510 nm and a peak in the region of ≈ 600 nm, which are due to $\pi - \pi^*$ transitions in the conjugation chain of the P3HT polymer. The appearance of a peak in the region of ≈ 600 nm in the absorption spectrum was attributed to the presence of crystalline regions in the film structure that formed after thermal annealing of the polymer [15]. It should be noted that in the P3HT absorption spectrum without pre-annealing, this peak has a weak intensity. Thus, the intensity of this peak gives a qualitative indicator of the degree of crystallization of the polymer. When CuPc nanoparticles are added (Figure 3, curve 2), the absorption spectrum of the film broadens by 4 nm. At the same time, the absorption spectrum of a polymer film with CuPc nanowires is broadened by 10 nm compared to the P3HT/PCBM polymer film. Table 1 shows the spectral characteristics of the obtained samples.

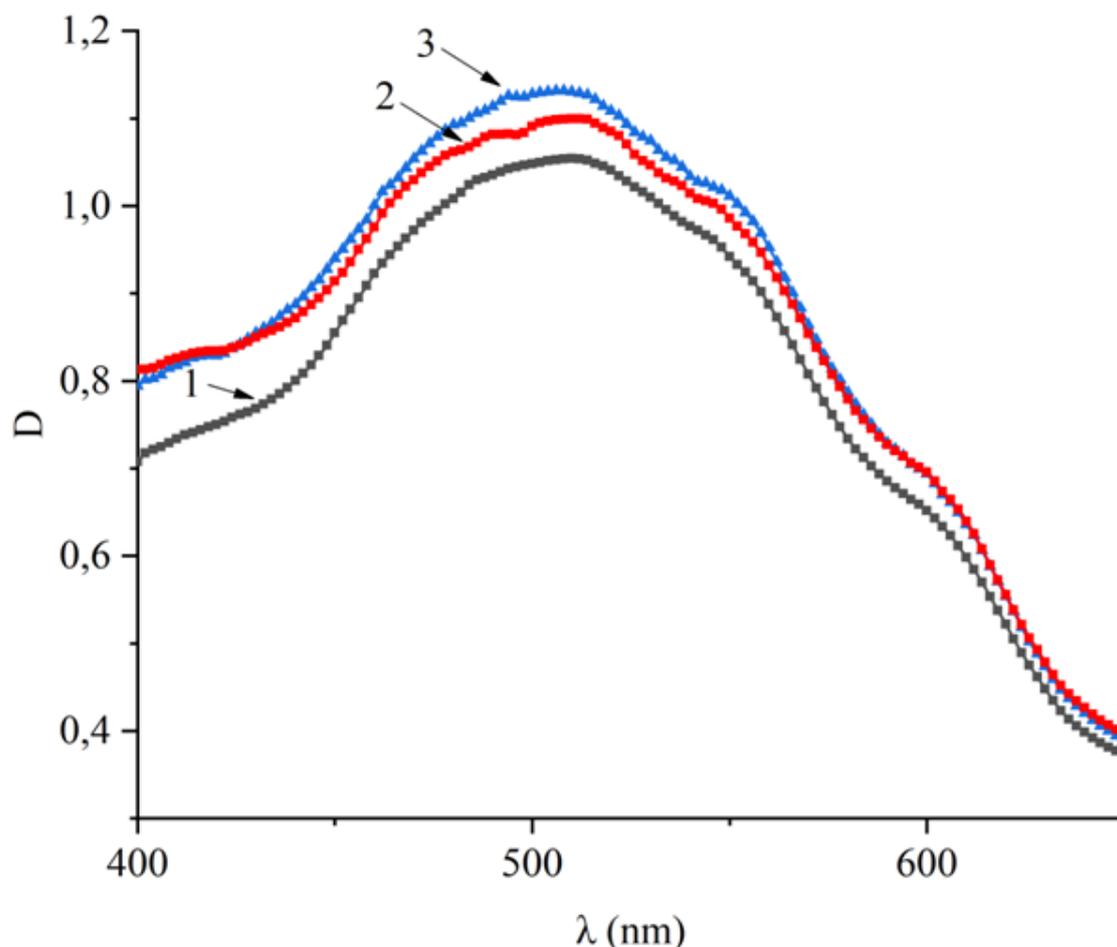


Figure 3. Absorption spectrum of P3HT/PCBM with the addition of CuPc nanostructures: 1 – P3HT/PCBM; 2 – P3HT/PCBM/NPs; 3 – P3HT/PCBM/NWs.

Table 1.

Spectral characteristics of P3HT/PCBM with the addition of copper phthalocyanine nanostructures.

Sample	Absorption maximum, nm	D	FWHM, nm
P3HT/PCBM	$\lambda=510$	1.05	100
P3HT/PCBM/NPs	$\lambda=512$	1.1	104
P3HT/PCBM/NWs	$\lambda=494, \lambda=508$	1.14	110

Figure 4 shows the I-V characteristics of the cells based on P3HT/PCBM and the P3HT/PCBM/NPs and P3HT/PCBM/NWs nanocomposites. The values of open-circuit voltage U_{oc} , short-circuit current I_{sc} , and fill factor FF were determined according to the method [16]. Table 2 shows the photoelectric characteristics of the obtained photovoltaic cells.

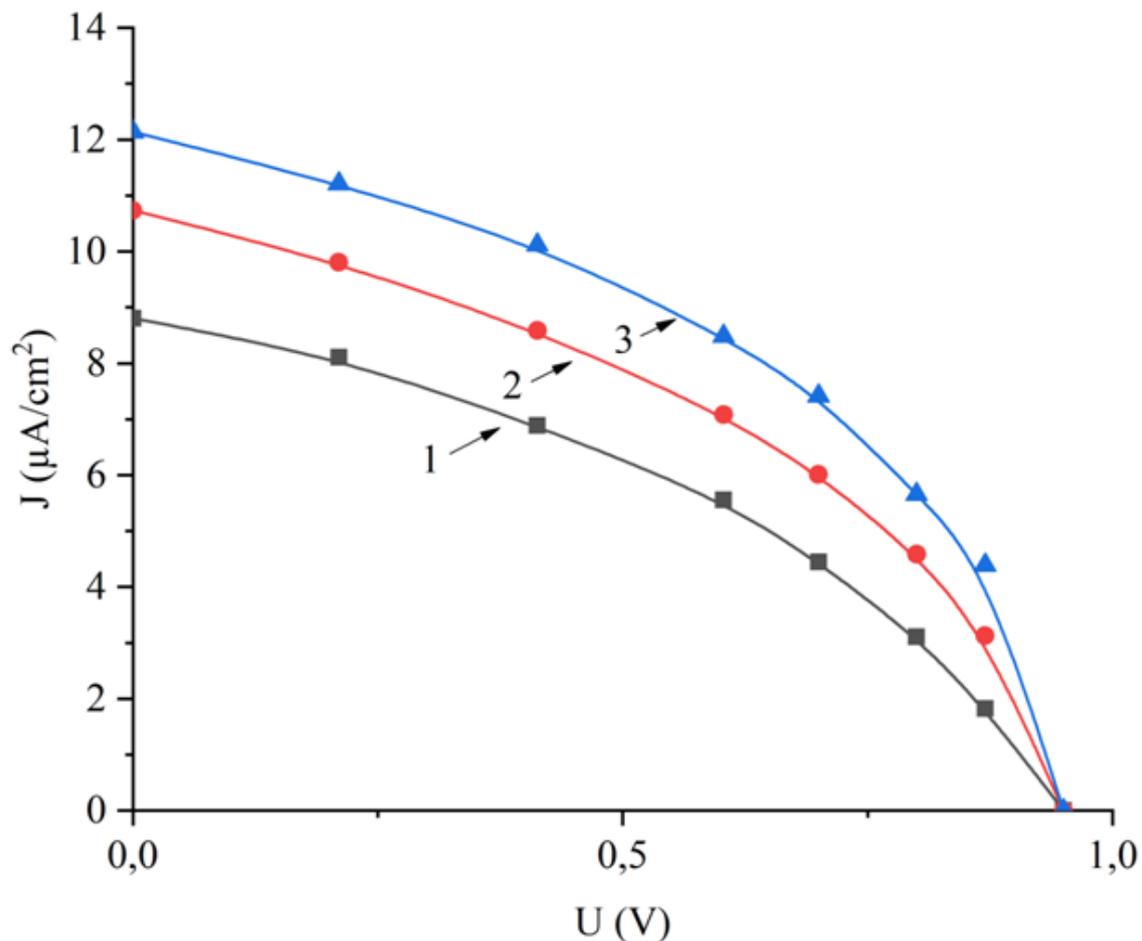


Figure 4. Comparison of current-voltage characteristics: 1 – P3HT/PCBM; 2 – P3HT/PCBM/NPs; 3 – P3HT/PCBM/NWs.

When CuPc nanostructures are introduced into the P3HT/PCBM polymer due to spectral sensitization of the polymer by CuPc molecules, the fraction of absorption of incident light increases (Figure 2), as a result of which a larger number of charge carriers are formed in the polymer conduction band. In this way, the short circuit current in the composite cell is increased.

Table 2.
Photoelectric characteristics of photovoltaic cells.

Sample	U_{oc} (V)	J_{sc} ($\mu\text{A}/\text{cm}^2$)	U_{max} (V)	J_{max} ($\mu\text{A}/\text{cm}^2$)	FF
P3HT/PCBM	0.97	8.9	0.59	5.1	0.35
P3HT/PCBM/NPs	0.94	10.7	0.67	7.3	0.48
P3HT/PCBM/NWs	0.94	12.1	0.63	8	0.44

Thereby, as indicated by the values of the short-circuit current, the efficiency of carrier generation in the P3HT/PCBM film is lower than that in the phthalocyanine nanocomposite films due the narrower absorption band and lower optical density (Figure 4, curve 1).

Studies of the mechanisms of transport and recombination of charge carriers in a nanocomposite mixture were carried out by impedance spectroscopy. To interpret the impedance spectra, we used the equivalent electrical circuit of the photovoltaic cell (Figure 5a), where $R1$ (R_s) is the equivalent resistance of the multilayer film ($R_{ITO} + R_{Al}$ + resistance of the photoactive layer), $R2$ (R_{rec}) resistance, which characterizes the recombination of localized electrons (from fullerene) with holes (in the polymer) (Figure 5b).

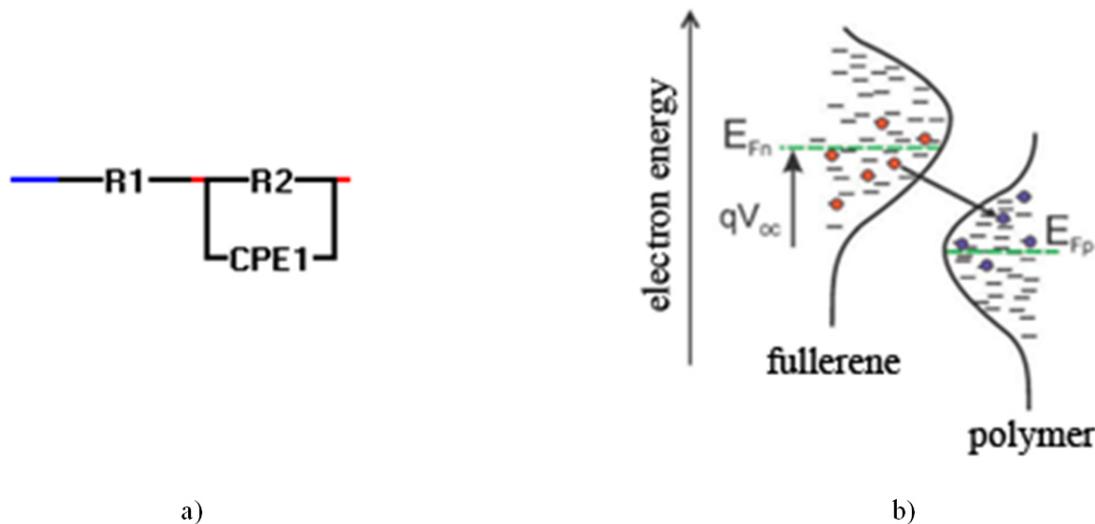


Figure 5. (a) An equivalent electrical circuit and (b) a schematic representation of the recombination of charge carriers in a polymer: fullerene mixture.

The impedance spectra in Nyquist coordinates based on P3HT/PCBM films with CuPc nanostructures are shown in Figure 6. The spectra were fitted using the EIS-analyzer software package. The main electric transport properties of polymer SCs were calculated (Table 3), where k_{eff} is the effective recombination rate of charge carriers, and τ_{eff} is the effective electron lifetime (in fullerene). The analysis of impedance measurements was carried out according to the diffusion-recombination model [17].

An analysis of the impedance spectra shows that adding CuPc nanostructures improves the conductivity of the multilayer composite film, which is determined by the value of R_s . As can be seen from Table 3, R_s has the greatest value for the cell based on P3HT/PCBM. With the addition of CuPc nanoparticles R_s decreases,

but with the introduction of CuPc nanowires R_s decreases more strongly. The observed effect is most likely associated with improved contact between the electrode and the photoactive layer. A lower value of R_s of cells with CuPc nanowires also suggests that nanowires facilitate the transfer of charge carriers to the electrode.

Despite the improvement in the transport properties of the cells, the results of impedance spectroscopy show that CuPc nanostructures increase the rate of recombination of charge carriers and decrease the effective electron lifetime (τ_{eff}) (in fullerene). A decrease in τ_{eff} by an order of magnitude is observed. This indicates that the incorporation of CuPc nanostructures forms surface defects through which recombination occurs. More detailed studies of recombination mechanisms in such complex composite materials are required to reduce recombination rate of charge carriers.

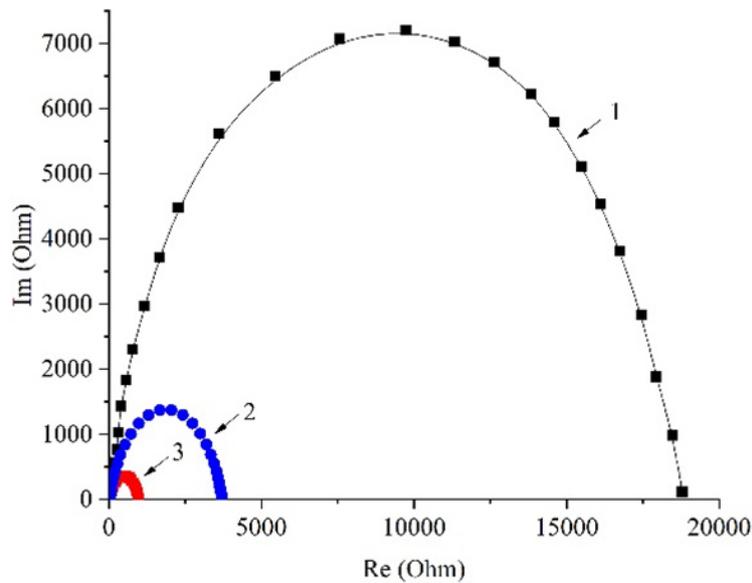


Figure 6. Impedance spectra of P3HT/PCBM composite films with CuPc nanoparticles and nanowires: 1 – P3HT/PCBM; 2 – P3HT/PCBM/NWs; 3 – P3HT/PCBM/NPs.

Table 3 shows the values of the electrophysical parameters of films with CuPc nanostructures. Using the EIS-analyzer software package, R_{rec} and R_s are calculated; k_{eff} value is determined by the maximum of the hodograph arc according to the formula $\omega_{max} = k_{eff}$. The value of the effective lifetime of charge carriers in the films is calculated by the formula $\tau_{eff} = \frac{1}{k_{eff}}$.

Table 3.

The value of the electrophysical parameters of films with CuPc nanostructures.

Sample	k_{eff} , (s^{-1})	τ_{eff} , (ms)	R_{rec} , (Ohm)	R_s , (Ohm)	Con , ($Ohm\,cm\,s^{-1}$)	L , (cm)
P3HT/PCBM	372.6	2.7	15961	38.0	71.3	$120 \cdot 10^{-7}$
P3HT/PCBM /NPs	7196.8	0.14	944.4	24.0	81.6	$120 \cdot 10^{-7}$
P3HT/PCBM NWs	1389.5	0.72	3696.3	17.5	60.6	$118 \cdot 10^{-7}$

Conclusion

Thus, the studies showed that the addition of CuPc nanostructures to the P3HT/PCBM film leads to a broadening of the band and a shift of the maxima in the absorption spectra, as well as to an increase in the optical density of the photoactive layer. The value of the short-circuit current in the composite cells P3HT/PCBM/NPs and P3HT/PCBM/NWs increased by 1.2 times and 1.5 times, respectively, due to an increase in the optical density of the photoactive layer and the conductivity of the films. However, CuPc nanostructures enhance the rate of recombination of charge carriers, which may be due to the formation of surface defects in the photoactive layer, which are recombination channels.

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