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EFFECT OF COPPER PHTHALOCYANIN NANOSTRUCTURES ON THE PHOTOVOLTAIC CHARACTERISTICS OF A POLYMER SOLAR CELL

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The results of studying the influence of copper phthalocyanine (CuPc) *nanostructures on the generation and transfer of charge carriers in the semiconductor polymer poly-(3hexylthiophene) (P3HT) are presented. It is shown that the observed broadening and shift of maxima in the absorption spectra of P3HT upon the addition of nanostructures to the polymer are associated with an increase in the film crystallization degree. The observed increase in the short-circuit current and negative magnetic effect upon the addition of* CuPc *nanostructures is associated with the size effects.*

Keywords: P3HT, copper phthalocyanine, nanoparticles, nanowires, current-voltage characteristic, magnetic effect, spin state.

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 of inorganic compounds. High mechanical properties of the polymers, their processing ability, and high absorption coefficient in the optical range allow their use in the form of ultrathin (several hundred nanometers) films deposited from solutions under normal pressure on flexible substrates of unlimited area, which makes it possible to produce polymer SCs using mass cheap production methods, such as inkjet printing and stamping [2].

Derivatives of phenylenevinylene, thiophene, etc., synthesized in recent years, are most successfully used as polymer matrices in polymer SCs. The conjugated polymer poly-(3-hexylthiophene) (P3HT) is one of the most well-studied polymers used as active layers of SCs, since it is characterized by high values of hole mobility [1, 3]. High conductivity of the P3HT polymer is due to the crystal structure and packing of the thiophene links in the chain. It is important to note that P3HT molecules, when deposited on substrates, also have the ability to self-ordering at the nanoscale. Despite the fact that the most effective SCs have been created on the basis of P3HT, they nevertheless have such disadvantages as a narrow optical absorption range, low carrier mobility, and high degree of degradation in the air [4].

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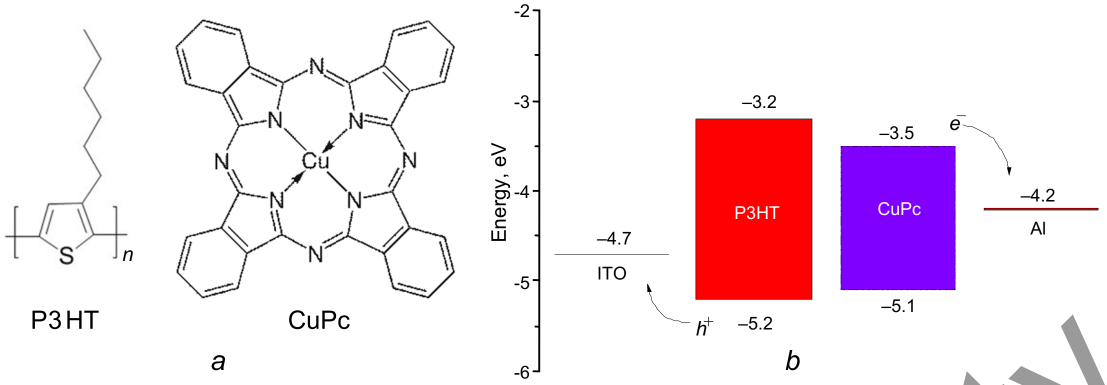

Fig. 1. Structural formulas of P3HT and CuPc (*a*), energy level diagram (*b*).

Recently, 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, possess photoconductivity and high catalytic activity. High mobility of charge carriers and the efficiency of light energy conversion make it possible to consider metallophthalocyanines as promising materials for photoelectric converters [5, 6]. It should also be noted that the photoelectric and magnetic properties of metallophthalocyanines strongly depend on the dimensionality of the system.

One of the approaches to increase 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, the energy conversion efficiency can be improved. The introduction of organic materials into polymer films allows the creation of hybrid layers in which the conductivity of polymer materials is combined with the excellent optical and electrical properties of organic nanostructures. However, mechanisms of charge carrier generation in such composite structures that affect the efficiency of solar cells are still the subject of discussion.

To elucidate the mechanism of charge carrier formation involving excited singlet and triplet states in organic semiconductors, along with traditional optical and electrical methods, new ones based on the influence of an external magnetic field on the photoelectrical processes began to be widely used. The specificity of the influence of the magnetic field allows us to judge the role of spin states in the processes of generation and transfer of charge carriers.

The paper presents the results of studying the generation and transfer of charge carriers in a polymer based on thiophene P3HT using copper phthalocyanine (CuPc) nanostructures as a sensitizer. The effect of a magnetic field on the photo-induced processes in a polymer with the addition of CuPc nanostructures in the form of nanowires and nanoparticles was studied.

EXPERIMENTAL TECHNIQUE

The structural formulas of the compounds are shown in Fig. 1*a*. Preparation of substrates for photosensitive cells based on ITO was carried out according to the procedure [7]. The CuPc nanowires (NWs) were grown by the method of temperature gradient physical vapor deposition (TG-PVD) [8]. The temperature control in the evaporation zone was carried out using a PID controller. Heating was carried out to a temperature of 465°C; the argon flow rate through the reaction zone was 150 cm^3/min. The nanowire growth time was 5 hours. The CuPc nanoparticles (NPs) were obtained by laser ablation of a CuPc sample in ethanol by second-harmonic radiation of a Solar LQ 529 solid-state Nd:YAG laser (the generation wavelength 532 nm, E_{pulse} = 180 mJ, and pulse duration of 10 ns) [9]. The laser pulse repetition rate was 20 Hz, the ablation time under constant stirring of the solution was 20 min. To create a photoactive polymer layer, 20 mg of P3HT polymer (Solaris) was dissolved in 1 ml of chlorobenzene. The solution was kept at a temperature of 45°C with vigorous stirring on a magnetic stirrer with heating for at least 24 hours. After that, the

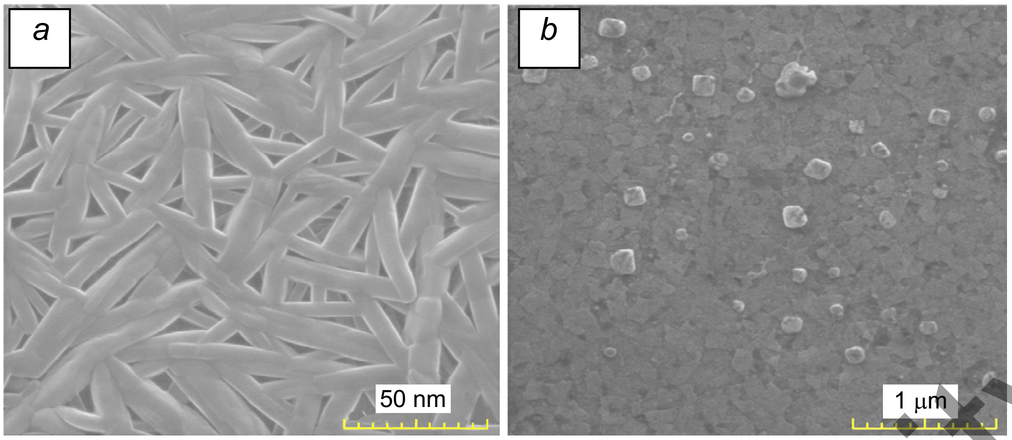

Fig. 2. SEM images of the obtained samples: CuPc(NWs) (*a*) and CuPc(NPs) (*b*).

solution was filtered through a 0.45 μm filter. Then, CuPc nanoparticles with the concentration of 0.5% of the weight of polymer were added to the P3HT polymer solution. Films were obtained by spin-coating. For this, at a spin-coating rotation speed of 2000 rpm, solutions containing a P3HT polymer, a P3HT/CuPc (NPs) mixture, and a P3HT/CuPc (NWs) mixture were deposited on the ITO surface and held at this speed 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 P3HT and the quality of the film as a whole. After that, an aluminum electrode with a thickness of 150 nm was deposited on the sample surface by thermal vacuum deposition method in a vacuum of 10^{-5} Torr at a speed of 1 nm/s using a Carl Zeiss Jena HBA 120/2 setup. The choice of aluminum and ITO as contact layers to the heterostructure is due to the fact that in this case, acceptable ohmic contacts to the organic layer are formed (Fig. 1*b*).

The absorption spectra of the studied samples were recorded with a SM2203 (Solar) spectrophotometer.

The influence of the magnetic field on the current-voltage (I-V) characteristic of an organic photosensitive cell was measured using a P20X potentiostat-galvanostat in a linear sweep mode on the setup described in detail in [10]. The sample was placed between the poles of a permanent electromagnet and the cell surface was illuminated with a 100 mW/cm^2 xenon lamp.

The effect of the magnetic field (MFE) was determined by changing the value of the short-circuit current of the solar cell when changing the magnitude of the magnetic field induction B from 0 to 0.6 T. The MFE was calculated according to the following formula [11]:

$$\mathrm{MFE} = \frac{I_B - I_0}{I_0} 100\,\% , \quad (1)$$

where I_B is the short-circuit current in a magnetic field, I_0 is the short-circuit current without the influence of a magnetic field.

A study of the surface morphology and determination of the average sizes of the obtained nanostructures were carried out using a MIRA 3 LMU scanning electron microscope (Tescan).

RESULTS AND DISCUSSION

It was found that the average length of the grown nanowires consisting of the densely packed copper phthalocyanine molecules, was 137 nm (Fig. 2*a*). The average diameter of a single nanowire was 4.5 nm. The average size of CuPc nanoparticles obtained by laser ablation varied in the range 70–110 nm (Fig. 2*b*).

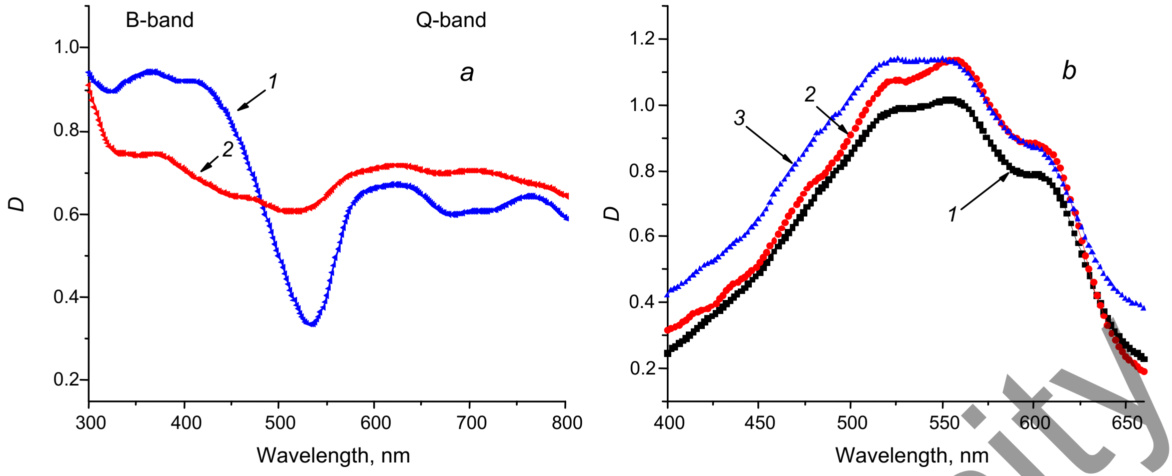

Fig. 3. Absorption spectra of: CuPc(NWs) (*1*) and CuPc(NPs) (*2*) (*a*) and of P3HT with addition of CuPc nanostructures (*b*): P3HT (*1*), P3HT/CuPc(NPs) (*2*), and P3HT/CuPc(NWs) (*3*).

Figure 3*a* shows the absorption spectra of films of copper phthalocyanine nanostructures. In the absorption spectra, there are two intense bands in the range of 300–400 nm (the Soret band or the B-band), which correspond to the mixed $\pi-\pi^*$ and n–π transitions $a_{2u}\rightarrow{}^2e_g$ and $b_{2u}\rightarrow{}^2e_g$, and the absorption band in the range of 650 –700 nm (Q-range), which corresponds to the $\pi-\pi^*$ transition $a_{1u}\rightarrow{}^2e_g$ [12]. The characteristic splitting of the nanostructures' absorption in the Q-range into two peaks is associated with the Davydov splitting [13]. In the spectrum of CuPc (NPs) (Fig. 3*a*, curve *2*), the absorption band broadens in the Soret range. The absorption band in the Q-range is also broadened. In addition, the absorption spectrum of CuPc (NWs) exhibits a rather strong broadening of the absorption bands in the B- and Q-ranges and a bathochromic shift of the absorption maxima. This is due to the fact that copper phthalocyanine, depending on the angle between the planes of molecules in the studied structure, can form one of three possible crystalline phases: η-CuPc, α-CuPc, and β-CuPc [14]. In case of nanoparticles, the molecules are in the β phase, and in the nanowires, the molecules form the η phase.

Figure 3*b* shows the absorption spectra of P3HT films without and with the addition of CuPc nanostructures. The absorption spectrum of the P3HT polymer (curve *1*) is characterized by peaks in the spectral regions of 528 and 546 nm and a shoulder in the range of 580–620 nm, which are caused by $\pi-\pi^*$ transitions in the polymer conjugation chain. After thermal annealing, a shoulder with a maximum at 610 nm appears in the absorption spectrum of P3HT. The authors of [15] attribute the appearance of this shoulder to the presence of crystalline regions in the film structure formed after thermal annealing of the polymer. It should be noted that in the P3HT absorption spectrum without preliminary annealing, this shoulder has a weak intensity. Thus, the intensity of this shoulder gives a qualitative indicator of the polymer crystallization degree. Upon the addition of CuPc nanoparticles (Fig. 3*b*, curve *2*), the absorption spectrum of the film broadens by 6 nm. At the same time, the absorption spectrum of a polymer film with CuPc nanowires is broadened by 26 nm compared to that of the P3HT polymer film.

For P3HT samples with the addition of CuPc nanostructures, the charge carrier mobility was determined using the DI-SCLC (Dark Injection Space-Charge-Limited Current) method [16]. It was found that the P3HT sample has a charge carrier mobility of $1.50\cdot10^{-5}$ cm^2/(V·s), while the addition of the CuPc nanostructures increases the mobility to $1.56\cdot10^{-5}$ and $1.60\cdot10^{-5}$ cm^2/(V·s) for P3HT/CuPc (NPs) and P3HT/CuPc (NWs), respectively. Obviously, when CuPc nanostructures are added to the semiconductor polymer, the CuPc (with the mobility of 10^{-3} cm^2/(V·s)) makes the main contribution to the quantitative value of the nanocomposite mobility, since the quantitative value of the P3HT mobility is lower (10^{-5} cm^2/(V·s)) than for CuPc [17].

Figure 4*a* shows the I–V characteristics of cells based on the semiconductor polymer P3HT and nanocomposites P3HT/CuPc (NPs) and P3HT/CuPc (NWs). The values of the open circuit voltage U_{oc}, short-circuit

TABLE 1. Photoelectrical Characteristics of Photovoltaic Cells

Sample	U_{oc}, V	J_{sc}, μA/cm^2	U_{max}, V	J_{max}, μA/cm^2	*FF*
P3HT	1.21	6.57	0.65	3.70	0.26
P3HT/CuPc(NPs)	1.20	9.22	0.65	5.00	0.33
P3HT/CuPc(NWs)	1.20	12.00	0.67	6.51	0.3

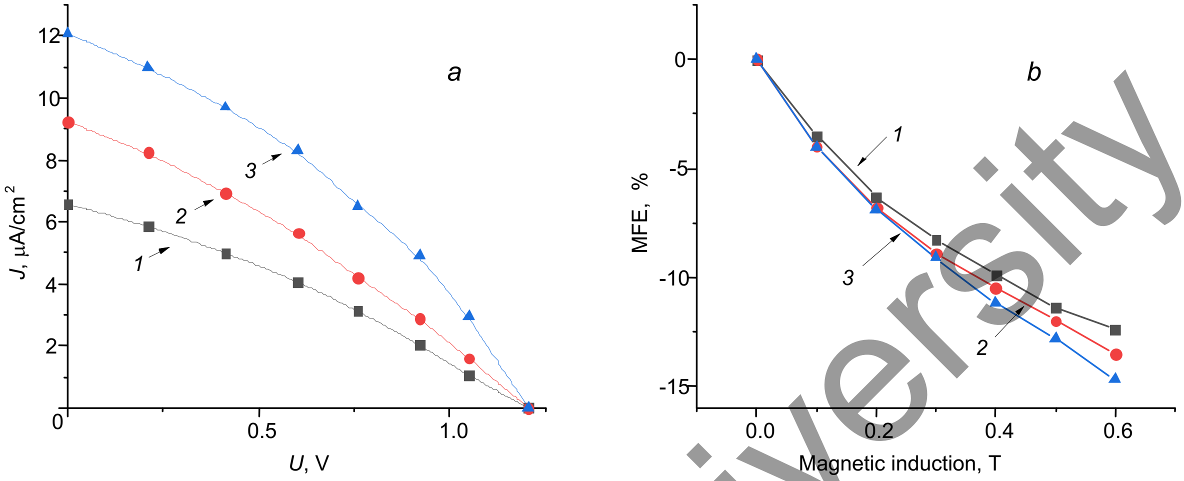

Fig. 4. Comparison of characteristics: I–V characteristic (*a*) and MFE (*b*) for pure polymer P3HT (*1*), P3HT/CuPc (NPs) (*2*), and P3HT/CuPc (NWs) (*3*).

current density J_{sc}, as well as the values U_{max} and J_{max} determined according to the procedure [18], based on which the fill factor *FF* was calculated, are given in Table 1.

When CuPc nanostructures are introduced into P3HT, the fraction of the incident light absorption increases due to the spectral sensitization of the polymer by CuPc molecules (Fig. 3). As a result, the number of charge carriers in the polymer conduction band increases, thereby increasing the short-circuit current in the composite cell.

In turn, in the P3HT thiophene polymer film, due to the narrow band and low optical density in the absorption spectrum compared to nanocomposites, the efficiency of charge carrier generation is low, as indicated by the low value of the short-circuit current of the P3HT I–V characteristic (Fig. 4*a*, curve *1*).

To elucidate the mechanism of formation of charge carriers involving spin states, methods based on the influence of an external magnetic field on the current-voltage characteristics are used. Figure 4*b* shows the dependences of the current-voltage characteristics of the cells for the induction of an external magnetic field equal to 0.2, 0.4, and 0.6 T, respectively. Table 2 shows the values of short-circuit currents of the obtained samples.

According to the data given in Table 2, the addition of CuPc nanostructures to the P3HT polymer leads to the fact that upon applying an external magnetic field of 0.6 T (Fig. 4*b*, curves *2* and *3*), a negative magnetic effect is observed: 12% for P3HT, 14% for the P3HT/CuPc (NPs) composite, and 15% for P3H/CuPc (NWs).

An external magnetic field influences the ratio of singlet and triplet states of polaron pairs in P3HT [19]. At the external magnetic field values below the internal field of the system, the rate of intersystem crossing of the polaron pair decreases. As a result, the number of polarons in the singlet state increases. Since singlet states have a high dissociation rate into free charge carriers, a large number of charge carriers will be generated in the system. In case of an external magnetic field comparable with the internal field, the rate of intersystem crossing of the polaron pair to the triplet state increases. Since triplet states have a longer lifetime compared to singlet ones, they have a low probability of dissociation into free charge carriers. As a result, the number of charge carriers in the studied system decreases. Thus, the observed change in the short-circuit current under the influence of an external magnetic field is due to the quantitative ratio of polaron pairs in singlet and triplet states of the polymer.

TABLE 2. Comparison of the Short-Circuit Current of the Obtained Samples when Modulated by an External Magnetic Field

Sample	I_{sc}, μA (at 0 T)	I_{sc}, μA (at 0.2 T)	I_{sc}, μA (at 0.4 T)	I_{sc}, μA (at 0.6 T)
P3HT	3.04	0.57	0.40	0.34
P3HT/CuPc(NPs)	4.31	0.46	0.34	0.37
P3HT/CuPc(NWs)	5.43	0.39	0.32	0.29

The observed size effects are due to the fact that charge carrier transport in copper phthalocyanine nanostructures is due to bipolaron formation, provided that the polarons have different spin components [20]. After the dissociation of the bipolaron, the polaron is able to jump to an adjacent trap. As a result of jumping to nearby traps with the formation of bipolarons, charge transfer occurs in the studied system. An external magnetic field affects the spin state of polarons [21]. When an external magnetic field is applied, the spins of two positively charged polarons are oriented in the same direction. In this case, the bipolaron formation channel is blocked. This mechanism is called “spin blocking” [22]. Since CuPc in the system under study is a donor of holes for a semiconductor polymer, the action of a magnetic field will reduce the probability of formation of the bipolaron and thereby reduce the total short-circuit current of the nanocomposite cell. A decrease in the dimensionality of the system of CuPc nanostructures leads to a high probability of re-collision of polarons on traps, therefore, the effect of “spin blocking”" will be more pronounced upon modulation by an external magnetic field.

CONCLUSIONS

Thus, the studies showed that the use of the composite nanostructures P3HT/CuPc (NPs) and P3HT/CuPc (NWs) in solar cells made it possible to increase the efficiency of light energy conversion by increasing the light absorption and short-circuit current by 1.5 times and 2 times, respectively.

The observed negative effect of the magnetic field at the short-circuit current, which manifests itself when CuPc nanostructures are added to the semiconductor P3HT polymer, is associated with the size effects. The obtained experimental results on the influence of the dimensionality of CuPc nanostructures on the effect of “spin blocking” can be used in the development of basic elements of spintronics.

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