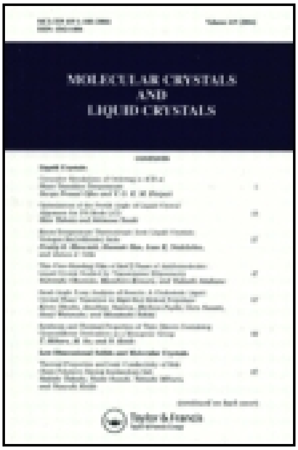

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Polyaniline – Organic Semiconductor Heterostructures

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The photovoltaic properties of electrochemically prepared polyaniline films and polyaniline/organic semiconductor heterostructures are studied. The photovoltage of the heterostructures in the range of strong absorption of an organic semiconductor is one order higher than that of a polyaniline layer. It has been shown that a built-in electric field is formed at the polyaniline/organic semiconductor interface.

Keywords: heterostructures; photovoltage; polyaniline

INTRODUCTION

Efficient absorption of solar light that results in a photogeneration of charge carriers is required for developments of solar cells [1]. At the present time, the organic solar cells arose a growing interest. The photosensitive organic films for organic devices can be fabricated using a simple technology at room temperature and under air conditions (no vacuum). Moreover, flexible solar cells can be prepared on the base of organic materials such as polymers [2–4]. However, the development of plastic solar cells, meets a lot of difficulties. One of them is a low efficiency of solar energy conversion in organic heterojunctions. A low efficient separation of charge carriers in such systems is due to a high density of uncontrollable impurities that trap excitons. Moreover, the most polymeric materials absorb solar light in a narrow spectral range that also leads to the low efficiency of photoconversion. For example,

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the heterojunctions based on conductive polymers and C_{60} derivatives absorb solar light in the range 400–700 nm [2], and the composites made of carbazol-containing polymers and polymethine dyes absorb solar light in the range 550–950 nm [3,4]. Therefore, a search for the ways to extend the photosensitivity range of organic heterostructures is the important task one must solve to produce highly efficient organic solar cells.

One of the most studied and industrially attractive conductive polymers is polyaniline [1,5]. The advantage of polyaniline is the simple synthesis, sufficiently high stability, and other suitable physical and chemical properties. The polyaniline layers have been used as active electrodes in many lightweight and flexible applications [1]. The polyaniline films can be prepared by the electrochemical method [6], as well as by the method of thermal deposition in vacuum [7]. The properties of the films depend on methods of their preparation. The advantage of electrochemically prepared polyaniline films is the efficient absorption of light in the near infra-red range [6]. Therefore, heterostructures made with the participation of these films can absorb most intensively solar light, if other component of heterostructures absorbs light in the range of transparency of polyaniline films. The disadvantage of polyaniline films is their low photosensitivity. Such a feature can be explained by the structure properties of polyamines and the high intrinsic and ion conductivity of polyaniline films. Moreover, polyaniline films can adsorb, probably, molecules of gases from air, which increases the recombination of charge carriers. But the binding energy of an adsorbed molecule to the polymer molecule is low, and the concentration of these impurities and surface states can be decreased in vacuum at heating (annealing).

The goal of this work was the search for ways to increase the photosensitivity of electrochemically prepared polyaniline films, as well as the experimental study of the photosensitivity for thin-film heterostructures made with polyaniline and organic semiconductors. We should use organic semiconductors that absorb light and photogenerate charge carriers in the range of transparency (low absorption) of polyaniline layers.

TECHNOLOGY AND EXPERIMENTAL DETAILS

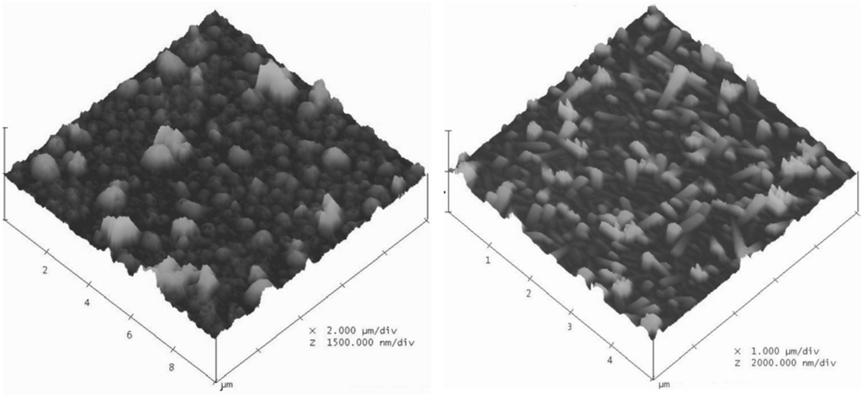
Thin films of polyaniline were prepared by electrochemical polymerization of a 0.1 M aniline solution in 0.5 M sulphate acid on the glass substrates covered with indium tin oxide (ITO) electrodes at a temperature of 293 K [6,8]. This process was carried out in a quartz cell of special construction. As the working electrode, we used a disk of 16 mm in diameter fixed with platinum brackets. The counter electrode was a platinum wire, whereas Ag/AgCl in a saturated KCl solution was used as the reference electrode. The voltage and current density for the working electrode were 0.78–0.82 V and 0.05–0.10 mA//cm^2, respectively. The cell was maintained in the working camera of a CF-46 spectrophotometer and connected to a PI-50-M1 potentiostat. The time of electrolysis was 10–15 min. The thickness of polyaniline films was controlled by their optical density at $\lambda = 750\,\mathrm{nm}$ and measured by an interference microscope MII-4.

The polyaniline/organic semiconductor heterostructures were prepared by thermal deposition of N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide {or methyl substituted perylene pigment} (MPP) [9] or pentacene (Pn) [10,11] on a polyaniline layer at 370 K. The thickness of MPP and Pn was controlled by the frequency change of a quartz resonator and after, the deposition, by the optical density spectra and with an atomic force microscope (AFM) “NanoScope IIIa”. The topology of the film surface was studied, by using AFM images. The PSI software for the AFM control allowed us to do the processing, filtration, smoothing, and statistical analysis of the surface topology. Absorption spectra were measured by a double-beam “Hitachi” and/orCA-46 spectrophotometers. Photovoltage spectra were measured by the contactless method at the modulated illumination using a laboratory-assembled set [9]. The intensity of the illumination was measured by a PPTN-02 radiometer based on a calibrated Si photodiode.

RESULTS AND DISCUSSION

I. Surface topology and photovoltaic properties of polyaniline films

The study of the surface structure of polyaniline films by AFM shows that the electrochemically prepared polyaniline films are polycrystalline (Fig. 1a). The predominant size of crystallites is about 100 nm. The small quantity of high aggregates is observed. The size of the aggregates is 0.5–1.0 μm. The parameters of the statistical analysis using a PSI software are as follows: the maximal height (Z range) is 1.1 μm, and the root-mean-square (RMS) roughness is 136 nm (Fig. 1a). After annealing of the films in vacuum during 3 h at a temperature 370 K, the size of crystallites (Z range and RMS roughness) increases only in 20%. The values of Z range and RMS roughness are close to those of thermally deposited MPP [9] and Pn [10] films. For example, the Z range is 0.865 μm, and the RMS roughness is 126 nm in MPP films deposited at 370 K (Fig. 1b).



(a) (b)

FIGURE 1 (a) AFM image of the surface for polyaniline films prepared by the electrochemical method before annealing; (b) AFM image of the surface for MPP films thermaly deposited at a substrate temperature of 370 K.

The photovoltage of the electrochemically prepared polyaniline films is two orders lower than that of thermally deposited MPP and Pn films. Therefore, the spectral dependence of photovoltage for the studied polyaniline films was failed. The photovoltage in polyaniline films was measured under illumination of the side of the free surface and the ITO contact by using the modulated illumination of light emitting diodes with various quantum energies. The photovoltage of polyaniline films under illumination through the free surface is one order lower than that under illumination through the ITO contact. This feature can be explained by a higher efficiency of charge carrier recombination at surface states that are formed on molecules of air adsorbed on the free surface.

After the annealing of the polyaniline films in vacuum during 3 h at a temperature of 370 K with the successive smooth cooling down to room temperature, the photovoltage increases by a factor of 2.5–3.0. The photovoltage increasing is higher in the range of a low absorption of light in the films (Table 1). Such a rise of the photovoltage can be caused by the desorption of various impurities and the dissociation of surface states during annealing the films.

II Photovoltaic Properties of Polyaniline/Pn and Polyaniline/MPP Heterostructures

The absorption spectra of the electrochemically prepared polyaniline films, Pn films, and double-layer polyaniline/Pn heterostructure are

TABLE 1 The Photovoltage of Thin-Film Structures Based on Polyaniline Films Prepared by Electrochemical Method on Glass Substrates Covered ITO

	Illumination energy, eV			
	1.32	1.90	2.18	2.64
Structures	Photovoltage, (a.u.)			
ITO/polyaniline before annealing	1	1	1	1
ITO/polyaniline after annealing	2.5	2.5	3	3
ITO/Pn	1	320	120	140
ITO/polyaniline/Pn	2	600	300	300
MPP	1	25	180	300
ITO/polyaniline/MPP	2	22	440	700

shown in Figure 2. We can see that the double-layer heterostructure absorbs almost all solar light in the visible and near infra-red ranges. The same feature is observed for double-layer polyaniline/MPP heterostructures. It is obvious that the deposition of a Pn film on a polyaniline layer leads to a significant rise of the light absorption (Fig. 2, curve 2) in the range of 1.9–2.7 eV or, in another words, in the range of the non-selective low absorption of a polyaniline film (Fig. 2, curve 1). The difference of these spectra (Fig. 2, curve 3) is typical of the absorption spectra of oriented polycrystalline Pn films [10].

The photovoltage of polyaniline films significantly rises after the annealing at 370 K. Therefore, Pn and MPP films were deposited on polyaniline at a substrate temperature of 370 K, since the photosensitivity of organic semiconductor layers is optimal at this temperature [9,10]. The photovoltage of the polyaniline/Pn and polyaniline/MPP heterostructures in the range of strong absorption of the organic semiconductor (Pn and MPP) is one order higher than that in the range of strong absorption for a polyaniline layer (Figs. 3 and 4). The photovoltage of the polyaniline/Pn and polyaniline/MPP heterostructures strongly depends on the illumination quantum energy (see Table 1).

The formation of polyaniline/Pn heterostructures leads to an increase of the photovoltage by several times (in comparison with the photovoltage of a Pn film deposited onto an ITO electrode) irrespective of which side of a sample is illuminated (Fig. 3). The highest increase of the photovoltage is observed in the range of low absorption of the Pn film (2.4–3.0 eV). This change of the photovoltage spectra shows the formation of a built-in electric field (potential barrier) at the interface of polyaniline/Pn with a low concentration of recombination centers for charge carriers and excitons. The charge carrier

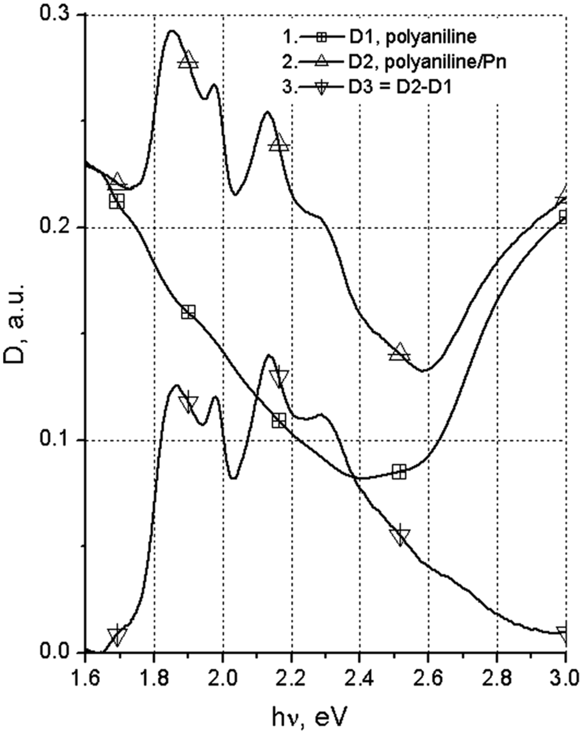


FIGURE 2 Optical density spectra of polyaniline (1) and the polyaniline/Pn heterostructure (2) and their difference (3).

recombination results in a less efficient increasing photovoltage in the range of strong absorption of the Pn layer.

The anticorrelation between the absorption and the photovoltage spectra in the range of strong absorption of the MPP film (2.4–3.1 eV) under illumination through the free surface side shows the formation of charge carrier recombination centers at a high concentration on the free surface of MPP [9]. But, for polyaniline/MPP heterostructures, the absorption and photovoltage spectra correlate in the range of 2.4–3.1 eV. The correlation of these spectra for the polyaniline/MPP heterostructures is the evidence of the formation of charge carrier recombination centers at a low concentration at the polyaniline/MPP interface. This also confirms the formation of a built-in electric field at the polyaniline/MPP interface. This field increases the efficiency of photogenerated charge carriers separation, especially charge carriers from charge transfer states (excitons) about 2.8 eV.

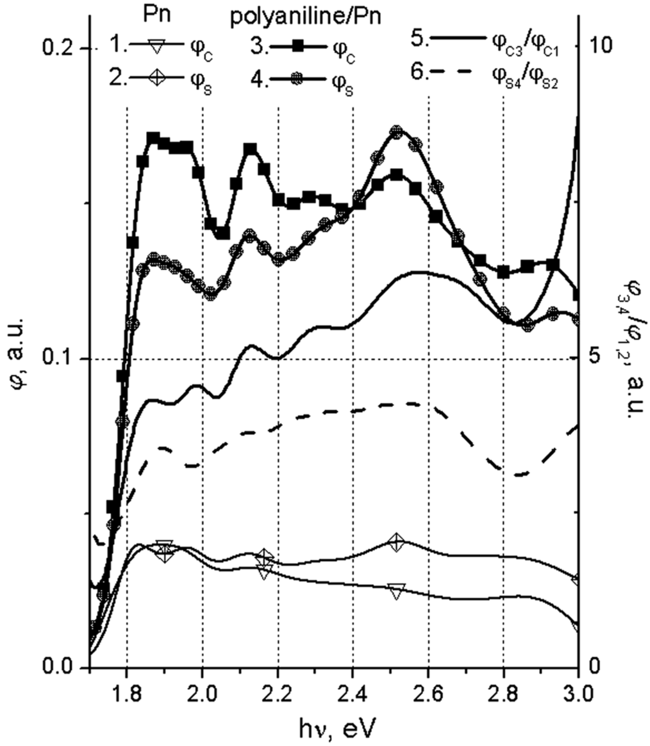


FIGURE 3 Photovoltage spectra of ITO/Pn (1,2) and heterostructures polyaniline/Pn (3,4) under illumination through ITO (1,3) and the free surface (2,4), and the spectrum of the photovoltage ratio of HS and ITO/Pn (5,6).

This feature can be explained by he difference in the photovoltaic spectra of the heterostructure and the MPP film (Fig. 4, curve 3).

The built-in field increases the efficiency of the photogenerated charge carriers separation, but it is not enough to increase the efficiency of the charge carriers photogeneration in polyaniline layers which is still very low. We hope that the optimization of the layer thickness and the preparation procedure will allow a sufficient increase in the efficiency of the photo-conversion of solar light by these structures.

CONCLUSIONS

It was observed that the photovoltage of polyaniline films electrochemically prepared onto ITO electrodes covered by a glass substrate is

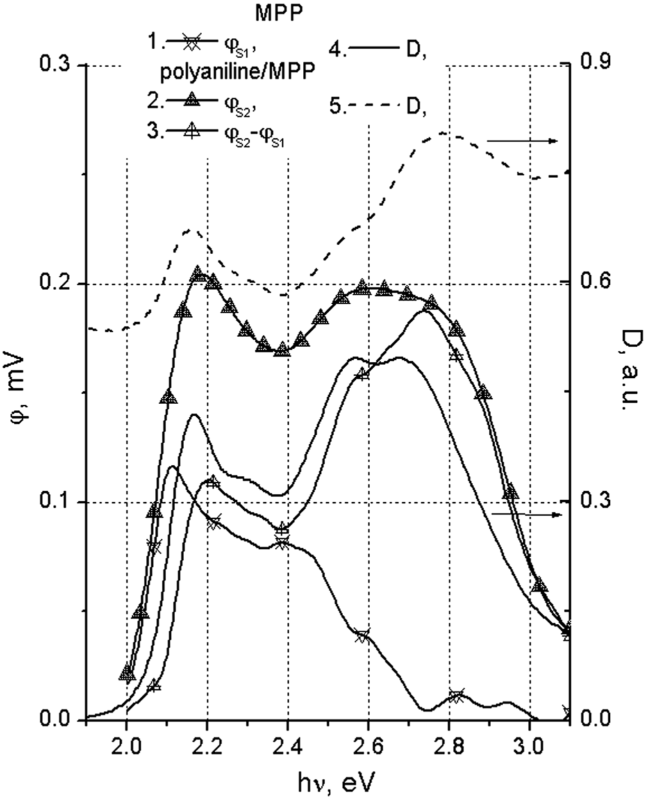


FIGURE 4 Photovoltage spectra under illumination of the free surface of ITO/MPP (1) and polyaniline/MPP (2), their difference (3), and the spectra of the optical density of ITO/MPP (4) and polyaniline/MPP (5).

2-3 orders lower than that of thermally deposited MPP and Pn films. After the annealing of the polyaniline films in vacuum during 3 h at a temperature of 370 K, the surface photovoltage in these films increases. This can testify to the formation of charge carrier recombination centers at a high concentration on the surface due to the adsorption of molecules of air. The photovoltage of the polyaniline/Pn and polyaniline/MPP heterostructures prepared at a substrate temperature of 370 K is several times higher than that of heterostructure components. The photovoltage of the heterostructures was low in the range of strong absorption of a polyaniline film, and the highest photovoltage was in the range of strong absorption of organic semiconductors. It is the evidence of the formation of a built-in electric field at the polyaniline/Pn and polyaniline/MPP interface The field increases the efficiency of the photogenerated charge carriers separation. The efficiency of the charge carriers photogeneration in a polyaniline layer is low, and the following optimization of the layer thickness and the preparation technology can sufficiently enhance the efficiency of the photo-conversion of solar light in the structures fabricated with polyaniline.

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