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Organic photovoltaic cells built on P3HT and 1,3,4- triphenyl 6-(9-karbazolyl)-1H pyrazolo[3,4-b]quinoline with nanoparticles

Abstract. This paper presents the application of nanoparticles in photovoltaic (PV) cells. The nanoparticles used in this work were dispersed in the active layer of the cell. This modification raised power conversion efficiency and open circuit voltage of PV cells. Organic single layered PV device has been developed using ITO/PEDOT:PSS (poly(3,4-ethylene dioxythiophene)-poly-(styrene sulphonate)/active layer with nano-sized particles/Al architecture.

Streszczenie. W artykule przedstawione zostały organiczne ogniwa fotowoltaiczne z dodatkiem nanocząstek. Zastosowane nanocząstki zostały wprowadzone do całej objętości warstwy aktywnej ogniwa, dzięki czemu zaobserwowano wzrost wydajności konwersji mocy oraz napięcia obwodu otwartego ogniwa. Struktura ogniwa była wykonana w sposób warstwowy ITO/PEDOT:PSS/warstwa aktywna z nanocząstkami/Al. (Organiczne ogniwa fotowoltaiczne zbudowane na bazie P3HT i 1,3,4- trifenylo 6-(9-karbazolo)-1H pirazolo[3,4-b]chinoliny z dodatkiem nanocząstek).

Keywords: organic photovoltaic cells, absorption, photoluminescence, nanoparticles.
Słowa kluczowe: organiczne ogniwa fotowoltaiczne, absorpcja, fotoluminescencja, nanocząstki.

Introduction

The last twenty years brought enormous development of electronic devices based on organic materials. Single layer systems with PV activity based on semiconducting polymers are easy to built using deposition techniques such as spin coating or vacuum evaporating. In comparison with inorganic PV devices the contemporary organic ones have an advantage of the lower weight, flexible shape, versatile technological process and the low cost in large-scale industrial production [1]. The organic PVs are designed by an interchange between exciton diffusion and optical absorption, a solution not possible with inorganic semiconducting materials.

Generally the process of PV response involves several actions: starting with photoabsorption by active chromophore absorbers, then formation of excitons and their propagation through conduction polymer chains depending on exciton diffusion length, later exciton dissociation on the donor-acceptor borders, and finally carrier separation and gathering of the appropriate carriers to ITO anode and metallic cathode [2].

Parameters describing fulfilled solar cells:
V_{OC} – open circuit voltage,
I_{SC} – short circuit current,
I_m, V_m – current and voltage at the maximum power point,
FF – fill factor determined by

(1)
$$FF = \frac{J_m V_m}{J_{SC} V_{OC}}$$

η – energy conversion efficiency determined by equation

(2)
$$\eta = \frac{J_{SC} V_{OC} FF}{P_{light}}$$

where P_{light} – power irradiated at cell surface unit [3].

Experimental

For the purpose of this article the regioregular P3HT (poly 3-heksylthiophene) (Fig. 1a) with HOMO level of about – 4.8 eV and LUMO level about – 2.7 eV, as polymer matrice were choosen [4,5]. The active layer of solar cells contain P3HT, 111Ek (1,3,4- triphenyl 6-(9-karbazolyl)-1H pyrazolo[3,4-b]quinoline) [6] (Fig. 1b) and various nano-size particles as listed in Table 1. 111Ek was synthesized in Department of Chemistry, Agricultural University of Krakow and it is not commercially available. HOMO and LUMO levels of 111Ek were calculated using HyperChem 8.0. and they are respectively - 8.3 eV and – 1.4 eV. The application

of nano-size particles allows to increase open circuit voltage (V_{OC}) larger than 1V, furthermore the increase of R_{sh} value and the decrease of R_s value. Consequently positive charges to ITO electrode are allowed [7]. The applied nanoparticles decreased the losses during the charge transport.
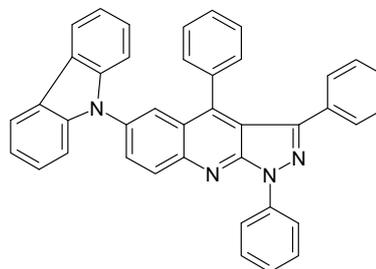
a)
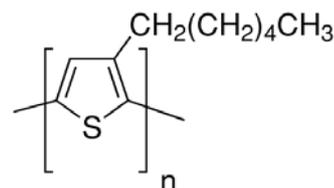
b)

Fig.1. (a) The principal molecular chemical formula for poly(3-heksylthiophene). (b) Investigated chromophore molecule of (1,3,4- triphenyl 6-(9-karbazolyl)-1H pyrazolo[3,4-b]quinoline)

Table 1. Contents of nanoparticles in the whole solution

Sample	Nanoparticles	wt. % of nanoparticles	Nanoparticles band gap (eV)
PV0	-	-	-
PV1	TiO$_2$ reduced in H$_2$ in 700°C	47	3.00
PV2	Cu(OH)$_2$/TiO$_2$	33	2.90
PV3	TiO$_2$ as received	37	3.00
PV4	Fe@Au	41	-

Preparation of the reduced TiO$_2$
The samples were obtained by reduction of the TiO$_2$ powder in hydrogen (5.0 purity, 33.34 mol.% in He(5.0), Air Liquide) at the temperatures either 100 or 700°C. The reduction process was performed for 1 hour in the hydrogen flow of 30 cm^3/min.

Preparation of Cu(OH)$_2$/TiO$_2$
The CuO/TiO$_2$ nanocomposites were obtained by precipitation method. The composite suspension (250 ml)

was prepared by mixing P25 powder (1 g) with 2.51 ml of $Cu(NO)_3$ aqueous solution (0.5 M) and deionized water. Then suspension was sonicated for 10 minutes, finally agitated (~300 rpm) and 250µl (25%) amonium solution diluted in 50ml of deionized was instilled. The resulting $Cu(OH)_2/TiO_2$ nanocomposite was recovered after 24h by filtration, rinsed with deionized water several times and finally dried for 12 h at 40°C in the dark.

Preparation of Fe@Au

The Fe@Au core/shell nanoparticles were prepared according to a reverse micelle procedure [8]. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was used as surfactant, methanol as the polar phase and isooctane as the oil phase. All steps of the procedure were conducted by mixing the reverse emulsion containing metal ions with the reverse emulsion containing the reducing agent ($NaBH_4$).

Absorption and photoluminescent features

Fig. 2 presents the absorption spectra for the investigated molecules in the chloroform solution.
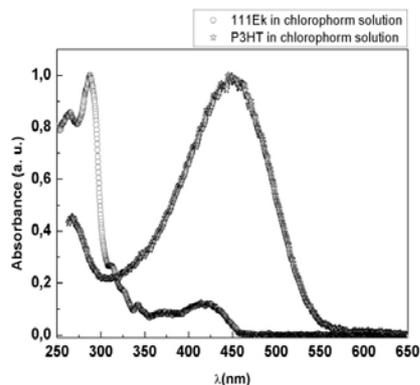

Fig. 2. Experimental absorption spectra of 111Ek and P3HT dissolved in chloroform
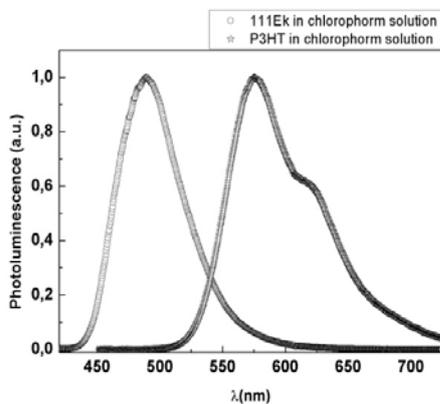

Fig.3. Experimental PL spectra of 111Ek and P3HT dissolved in chloroform

Fig. 2 presents the absorption spectra for the investigated molecules in the chloroform solution. It can be seen, that 111Ek posses three absorption bands at wavelength about 250–300 nm, 300-390 nm and 400-460 nm. P3HT posses only one wide absorption band at wavelengths about 500 nm. The photoluminescent (PL) maximum for 111Ek is about 489 nm, whereas P3HT posses two PL maxima in 575 nm and 619 nm. There are PL spectra obtained for the 111Ek and P3HT presented in Fig. 3, as well.

Photovoltaic cell preparation

Photovoltaic cells were fabricated on ITO (Indium Tin Oxide) covered glass slides (15 mm×15 mm) which were cleaned in an ultrasonic bath using organic solvents. Next the ITO was covered with PEDOT:PSS thin film by spin-coating and left for 30 minutes in a vacuum heater at 70°C. After 30 minutes the active layer (P3HT, 111Ek) with nanoparticles was spinned over. At the end photovoltaic cells were defined by aluminum electrodes thermally evaporated in vacuum. The device has the following architecture: ITO/PEDOT:PSS (poly(3,4-ethylene dioxythiophene)-poly-(styrene sulphonate)/active layer with nano-sized particles/Al. The aluminum electrode acts as cathode (collecting electrons) while ITO is applied as the anode for the purposes of collecting holes. The active layer thickness is about 150 nm. The overall architecture of the device is presented in Fig. 4.
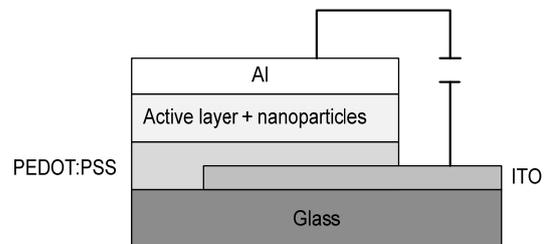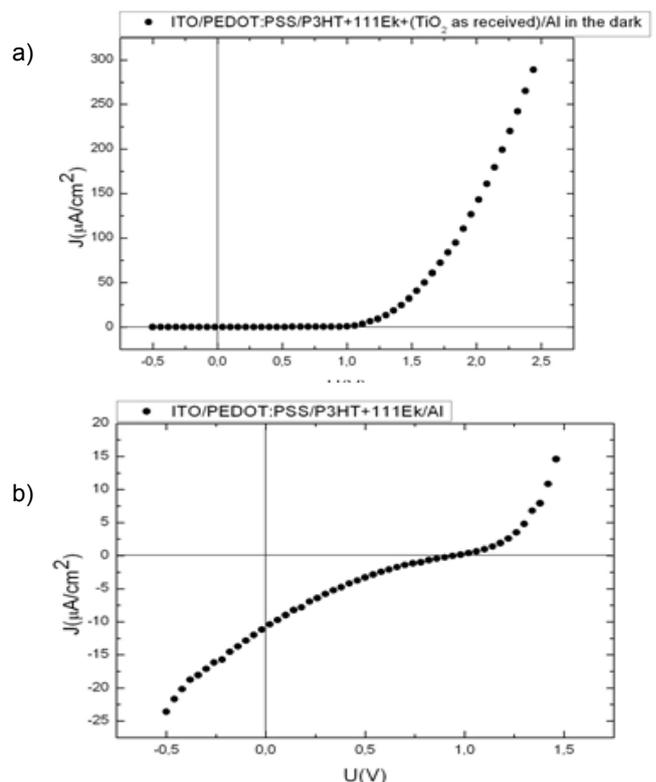

Fig.4. Typical architecture of the organic photovoltaic device

Results and discussion

The current-voltage (I-V) characteristics of the device were measured using the Keithley 2400 source-meter. The device was illuminated with the maximum intensity of 1.3 mW/cm^2. I-V characteristics after illumination and in the dark are given in the Fig. 5. They show good efficiency of this devices.

Following the data presented in Table 2 one can conclude that the applied nanoparticles increase the V_{OC} values to more than 1 V for all samples except PV4, while the Rs values decrease, except for the PV4 sample. The energy conversion efficiency is also much smaller for PV1 and PV4 than for the other samples which means that TiO_2 reduced in H_2 and Fe@Au nanoparticles do not improve parameters of PV1 and PV4.

c) ITO/PEDOT:PSS/P3HT+111Ek+(TiO₂ reduced in H₂ in 700°C)/Al

e) ITO/PEDOT:PSS/P3HT+111Ek+(TiO₂ as received)/Al

d) ITO/PEDOT:PSS/P3HT+111Ek+(Cu(OH)₂/TiO₂)/Al

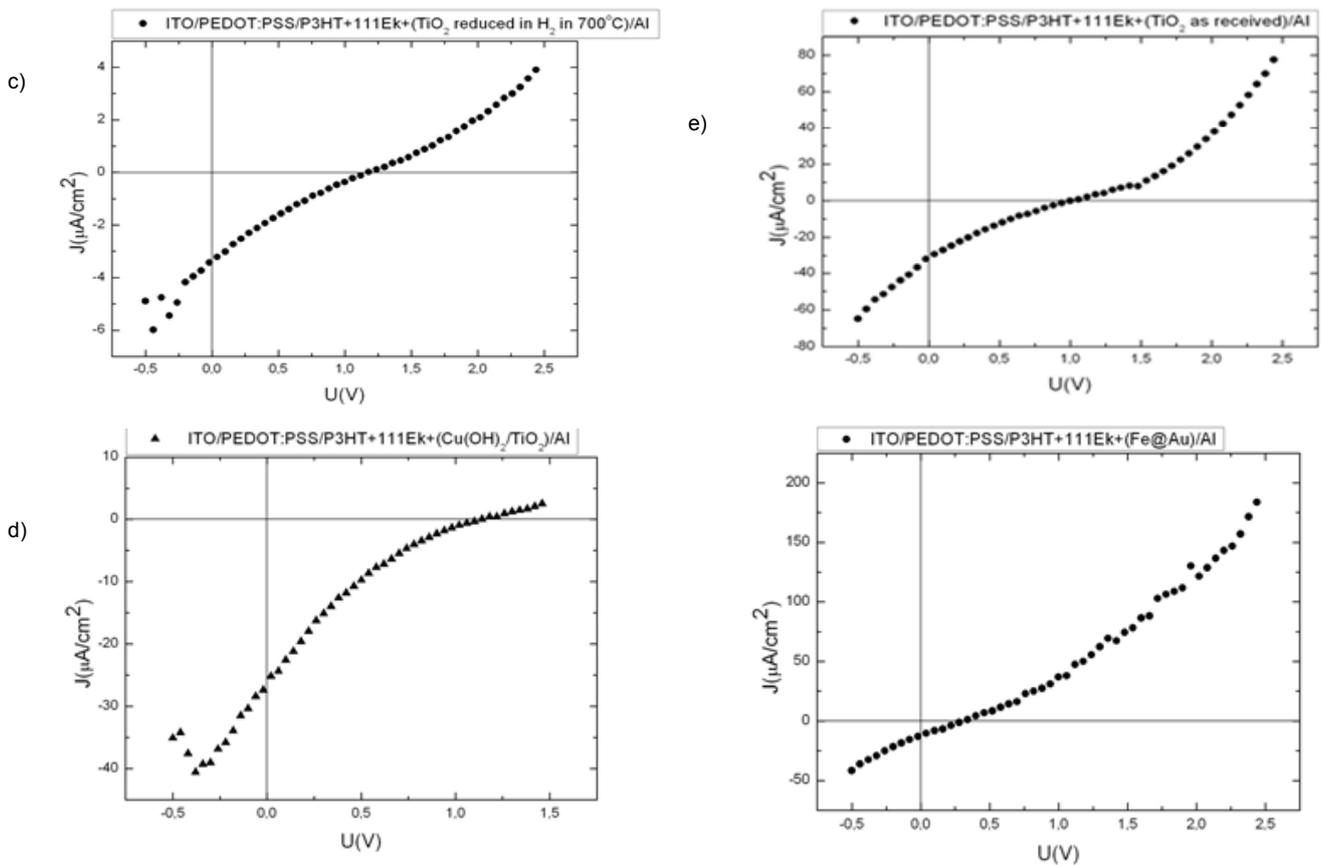ITO/PEDOT:PSS/P3HT+111Ek+(Fe@Au)/Al

Fig.5. I-V characteristics of (a) Sample in the dark, (b) PV0, (c) PV1, (d) PV2, (e) PV3, (f) PV4

Table 2. Data extracted from I-V characteristics in the Fig. 5.

Sample	V_{OC} [V]	J_{SC} [μA/cm²]	FF	η [%]	R_{Sh} [Ω]	R_S [Ω]
PV0	0.95	10.96	0.172	0.14	$0.091*10^6$	$0.011*10^6$
PV1	1.18	3.35	0.212	0.06	$0.245*10^6$	$0.302*10^6$
PV2	1.14	26.19	0.164	0.37	$0.022*10^6$	$0.133*10^6$
PV3	1.03	30.51	0.199	0.47	$0.019*10^6$	$0.015*10^6$
PV4	0.26	20.61	0.219	0.09	$0.014*10^6$	$0.008*10^6$

Charge transport efficiency is limited by recombination especially when the applied material used as transporting medium is the same for electrons and holes. The purpose of applying nanoparticles was to decrease the losses during the charge transport. Application of nanoparticles provides more light penetrating the active layer.

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