

Gabriela Lewińska (glewinska@pk.edu.pl)

Jerzy Sanetra

Institute of Physics, Faculty of Physics, Mathematics and Computer Science, Cracow
University of Technology

CuO/TiO₂ AND Cu₂O/TiO₂ NANOPARTICLES INFLUENCE ON PARAMETERS OF BULK HETEROJUNCTION ORGANIC SOLAR CELLS

WPLYW NANOCZĄSTEK CuO/TiO₂ I Cu₂O/TiO₂ NA PARAMETRY
ZŁĄCZ OBJĘTOŚCIOWYCH W ORGANICZNYCH OGNIWACH SŁONECZNYCH

Abstract

This publication presents a study conducted for related pyrazoloquinoline doped nanoparticles CuO/TiO₂ and Cu₂O/TiO₂. The mixtures were used as the active material for the construction of photovoltaic cells.

Keywords: photovoltaic cells, pyrazoloquinoline, efficiency, light absorbing materials

Streszczenie

W publikacji prezentujemy badania dotyczące pirazolochinolin domieszkowanych nanocząstkami CuO/TiO₂ oraz Cu₂O/TiO₂. Mieszaniny zostały zastosowane do konstrukcji ogniw fotowoltaicznych.

Słowa kluczowe: ogniwo fotowoltaiczne, pirazolochinoliny, wydajność, materiały absorbujące promieniowanie

1. Introduction

Due to rising costs and energy requirements, development of newer and newer technologies is essential. Technologies associated with silicon as well as subsequent generations and types of photovoltaic cells are constantly being developed. However, third generation cells are also developed, including organic cells, whose example we are presenting.

The organic heterojunctions have been the subject of interest of researchers since the 1950s [1]. Especially, they are environmentally friendly, cheap to operate and solar energy resources are infinite. On the other hand, the efficiency received, although still increasing, needs to be ameliorated [2]. The research we present was motivated by the objective of improving the efficiency of bulk-heterojunction solar cells.

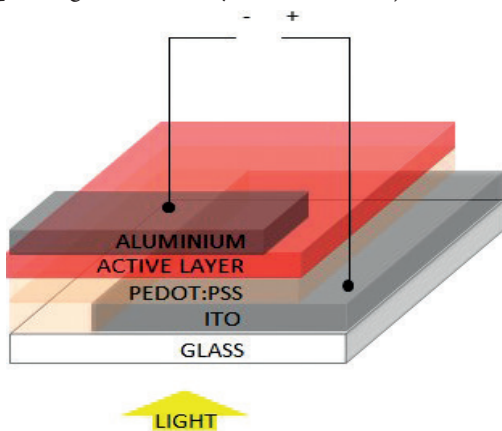


Fig. 1. The heterojunction ITO/PEDOT:PSS/active layer/Al architecture

The electrocell mechanism is customarily divided into several stages. The first step is to absorb photons with energies greater than the band gap of the material, and the exciton creation. Excitons diffuse until they achieved dissociation position, where charge separation occurs. Electric charges are transported through polymeric material to the electrodes. However, during this way may also exhibit recombination. In heterojunctions blends of two kinds of materials are used as the active layer – with a different electron affinity and ionization

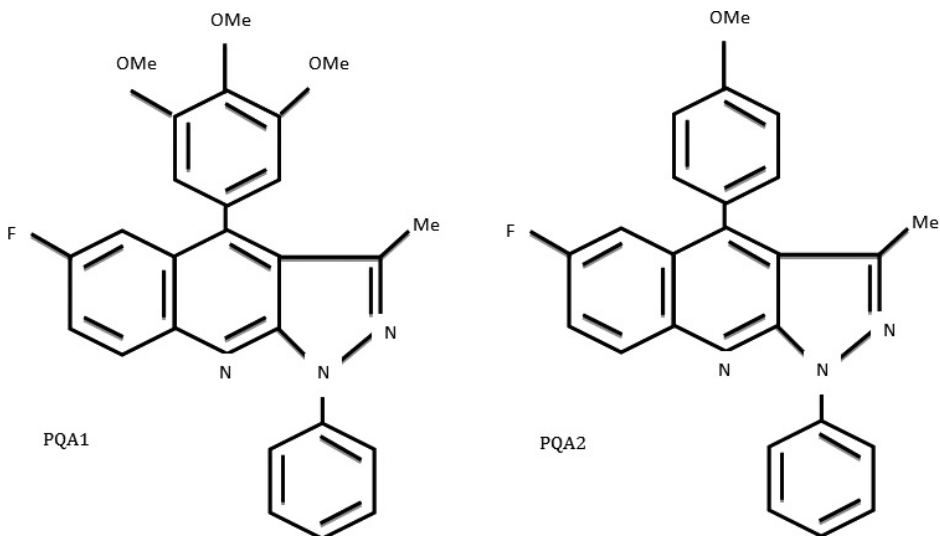


Fig. 2. Acceptor chemical formulas

potential. As a rule the electrons are attracted to the material having a greater affinity; however, a hole is attracted to the material with lower ionization potential. This type of mixture causes that the ratio of electrons in the external circuit to the number of photons entering, compared with the structure of a typical active layer, increases. Existing research indicates an increase in the absorption of the active layer doped nanoparticles [3–5], which was the motivation for research.

2. Experiment

As the active layer components pyrazoloquinolines derivatives [6–9] were used as the acceptors, (Fig. 2), poly(3-hexylthiophene-2,5-diyl), provided by Sigma Aldrich, was used as a donor. The first tests were carried out absorption measurements for compounds and mixtures. Nanoparticles were obtained by precipitation method. The composite suspension (250 cm^3) was prepared by mixing P25 powder (1 g) with $\text{Cu}(\text{NO}_3)_2$ (2.51 cm^3 for CuO/TiO_2 and 4.19 cm^3 for $\text{Cu}_2\text{O}/\text{TiO}_2$) aqueous solution (0.5 M) and deionized water. Then the suspension was sonicated for 10 minutes, finally agitated ($\sim 300\text{ rpm}$). For the CuO/TiO_2 $2.5 \cdot 10^{-5}\text{ cm}^3$ (25%) ammonia solution was diluted in 50 cm^3 of deionized was instilled. The resulting $\text{Cu}(\text{OH})_2/\text{TiO}_2$ nanocomposite was recovered after 24 h by filtration, rinsed with deionized water several times and finally dried for 12 h at 40°C in the dark.

The absorbance (Fig. 3, Fig. 4) and photoluminescence spectra (as reference was used chloroform solution) of P3HT and pyrazoloquinolines and mixtures doped with nanoparticles follow (Fig 5). The absorption maximum is observed for wavelengths, respectively: P3HT – 449 nm , PQA1 – 403 nm , PQA2 – 481 nm , for the mixture P3HT and PQA1 – 410 nm and 458 nm , for the mixture P3HT and PQA2 – 408 nm and 451 nm . Photoluminescence intensity maximum band occurs for P3HT – 401 nm , PQA1 – 489 nm , PQA2 – 446 nm , for the mixture P3HT and PQA1 – 462 nm and 570 nm , for the mixture P3HT and PQA2 – 412 nm and 455 nm . As shown, the addition of nanoparticles increases the intensity of absorption, the position of the bands is, however, unchanged.

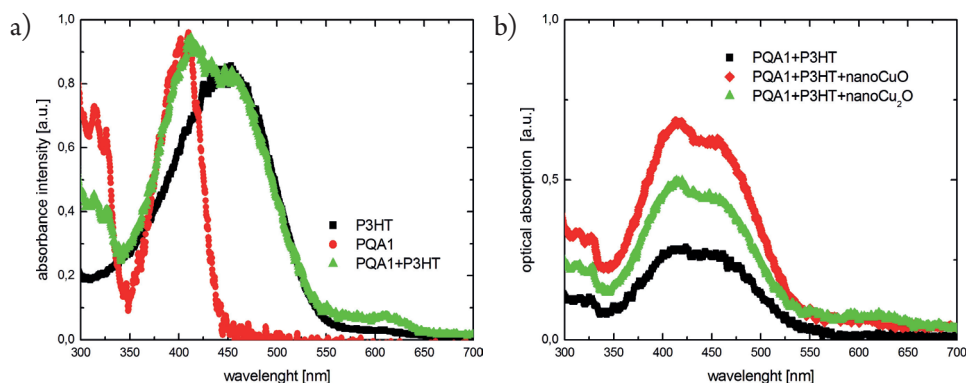


Fig. 3. Optical absorption measured in solution versus wavelength for studied systems active layers based on PQA1: a) P3HT, PQA1, mixture; b) mixture, mixture with nanoparticles CuO, mixture with nanoparticles Cu_2O

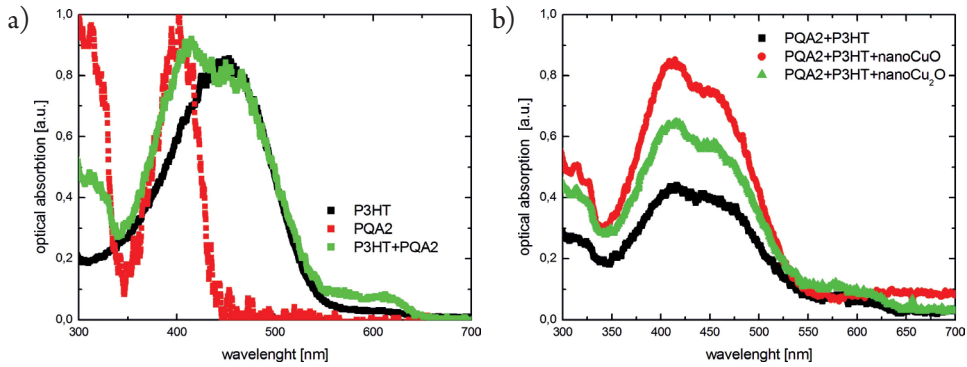


Fig. 4. Optical absorption measured in solution versus wavelength for studied systems active layers based on PQA2: a) P3HT, PQA2, mixture; b) mixture, mixture with nanoparticles CuO, mixture with nanoparticles Cu₂O

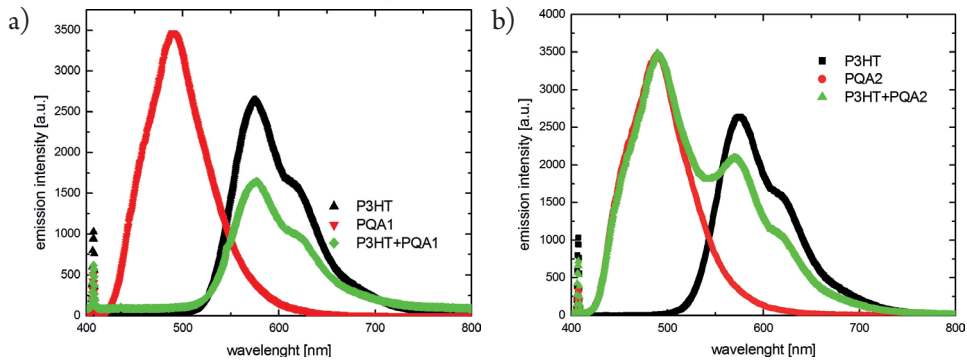


Fig. 5. Emission photoluminescence measured in solution versus wavelength: a) P3HT, PQA1 and mixture PQA1+P3HT; b) P3HT, PQA2 and mixture PQA2+P3HT. The peak in photoluminescence spectra at 405 nm corresponds to the laser

A photovoltaic cell is composed of several layers – the substrate is indium tin oxide (ITO) coated glass provided by Aldrich Chem Co. The ITO layer, forming the first electrode, is 100 nm thick, and its resistance rate is 50 Ω/sq . The second electrode is made of aluminium and has been received during process of deposition in a high vacuum. The PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-polystyrene-para-sulfonic acid) supports the transfer of holes and it is an anode buffer layer. The PEDOT:PSS and active layers were formed by spin-coating method, then followed annealing the layers in a vacuum heater.

The photocurrent density-voltage characteristics for prepared photovoltaic cells were measured with a Keithley 2400 source due to picoamperemeter. To illuminate the cells was used lamp (lamp power is approximately 1.3 mW/cm^2).

Based on experimental data, polynomial curves were fitted and the critical parameters of photovoltaic cells determined (Table 1). Parameters describing the photovoltaic cells are short current density (I_{sc}), open circuit voltage (U_{oc}), fill factor (FF) defined as

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \quad (1)$$

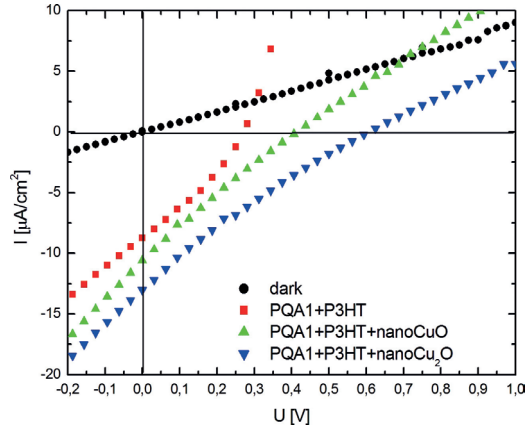


Fig. 6. Current-voltage characteristics obtained for PQA1 and P3HT mixture doped nanoparticles

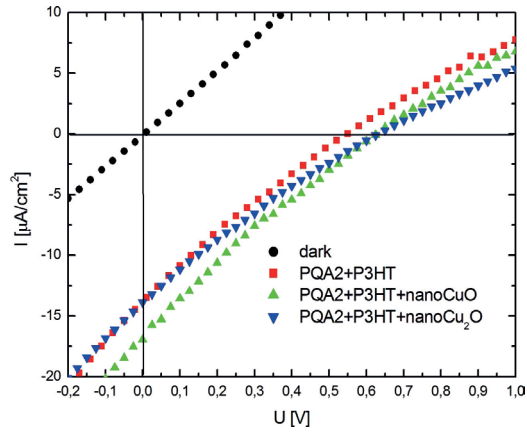


Fig. 7. Current-voltage characteristics obtained for PQA2 and P3HT mixture doped with nanoparticles and conversion efficiency (η)

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{light}} \quad (2)$$

The U_m and I_m are voltage and current of maximum power, and P_{light} is input optical power.

Table 1. Parameters describing the photovoltaic devices

	$I_{sc} [\mu A/cm^2]$	$U_{oc} [V]$	FF	$\eta [\%]$	$R_s [10^4 \Omega]$	$R_p [10^4 \Omega]$
PQA1+P3HT	20.2	0.48	0.41	0.30	1.69	1.03
PQA1+P3HT+nanoCu ₂ O	4.2	0.77	0.22	0.05	0.11	11.7
PQA1+P3HT+nanoCuO	8.9	0.77	0.22	0.13	6.78	1.76
PQA2+P3HT	17.6	0.38	0.21	0.14	2.09	40.2
PQA2+P3HT+nano Cu ₂ O	16.7	0.76	0.21	0.20	3.13	5.67
PQA2+P3HT+nanoCuO	21.5	0.88	0.19	0.29	2.62	7.34

3. Summary

For all constructed cells the fill factor were comparable. Because of the similar shape of spectrum absorption studied systems (mixtures of nanoparticles have higher absorption) depends on the quantum efficiency of the exciton diffusion path or the conductivity of electric charge. The exciton diffusion path is supported by ballistic transport (observed for nanoparticles, caused by the size reduction to a size smaller than the exciton mean free path). Cells with pyrazoloquinolines have the greatest short-circuit current (ITO/PEDOT:PSS/PQA2+P3HT/Al: $I_{sc} = 20,2; \mu A/cm^2$ ITO/PEDOT:PSS/PQA2+P3HT/Al: $I_{sc} = 17,6 \mu A/cm^2$), while a lower open-circuit voltage. Doping nanoparticles increases the voltage (for undoped cells is twice lower). The reason for changes in efficiency in the systems must be different nanoparticles charge affinity. The relatively low fill factor is caused by the fact that the resistance R_s and R_{sh} in the same order. For PQA2 both nanoparticles improved power conversion efficiency factor. The only mixture in which no cell parameter improvements were observed is the mixture PQA1. This may be due incompatible HOMO levels of nanoparticles and pyrazoloquinolines. However, the results obtained are similar to those previously obtained [10–12] with specified base chemical compounds.

The authors thank Ph.D. Eng. Robert Socha and Ph.D. Dawid Wodka (Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Cracow) for providing the nanoparticles that were used in the work.

References

- [1] Bernanose A., *Progress with Light-Emitting Polymers*, J. Chem. Phys., 1953, 50, 64.
- [2] Norris D.J., Aydil E.S., *Getting Moore from Solar Cells*, Science, 2012, 625–626.
- [3] Baoquan S., Eike M., Greenham N.C., Letters N., *Photovoltaic Devices Using Blends of Branched CdSe Nanoparticles and Conjugated Polymers*, 2003, 3 (7), 961–963.
- [4] Woo-Jun Yoon, Kyung-Young Jung, Jiwen Liu, Thirumalai Duraisamy, Rao Revur , Teixeira F.L. , Suvankar Sengupta, Berger P.R., *Plasmon-enhanced optical absorption and photocurrent in organic bulk heterojunction photovoltaic devices using self-assembled layer of silver nanoparticle*, Solar Energy Materials and Solar Cells, Vol. 94, Issue 2, February 2010, 128–132.
- [5] Kakavelakis G., Stratakis E., Kymakis E., *Aluminum nanoparticles for efficient and stable organic photovoltaics*, RSC Adv., 2013, 3, 16288–16291.
- [6] Chaczatryan K., Chaczatryan G., Danel A., Tomasik P., *The synthesis of 4-aryl-1H-pyrazolo[3,4-b]quinolines by cyclization of 4-arylidene-pyrazolin-5-ones with anilines*, ARKIVOC 2001, 2, 6.
- [7] Araki K., Funaki J., Danel A., Tomasik P., *A facile synthesis of 4-aryl-1H-pyrazolo[3,4-b]quinolines*, Polish Journal Of Chemistry, 2004, 78, 843.
- [8] Danel A., Jarosz B., Karasinski P., Sahraoui B., Armatys P., *Synthesis, photophysical and electroluminescent properties of 1,3-diphenyl-1H-benzo[g]pyrazolo[3,4-b]quinoxaline* Materials Letters, 2015, 138, 9–12.

- [9] Danel A., Danel K., *Synteza niektórych azotowych układów hetero cyklicznych oraz ich zastosowanie w komórkach elektroluminescencyjnych*, Chemik, 2010, 64, 7–8, 511–522.
- [10] Pokladko-Kowar M., Gondek E., Danel A., *Ogniwa fotowoltaiczne na bazie organicznych materiałów*, Technical Transactions, Vol. 1-NP/2011, 77–83.
- [11] Nosidlak N., Socha R.P., Kulig E., Sanetra J., *Organic photovoltaic cells built on P3HT and 1,3,4- triphenyl 6-(9-karbazolyl)-1H pyrazolo[3,4-b]quinoline with nanoparticles*, Przegląd Elektrotechniczny, Vol. 90, No. 9/2014.
- [12] Gondek E., Djaoued Y., Priya S., Balaji S., Robichaud J., Karasinski P., *Organic hybrid solar cells-Influence of ZnO nanoparticles on the photovoltaic efficiency*, Materials Letters, 2014, 131, 259–261.