

Photovoltaic properties of cadmium selenide-titanyl phthalocyanine planar heterojunction devices

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Abstract Photovoltaic phenomenon taking place in cadmium selenide (CdSe)/titanyl phthalocyanine (TiOPc) planar heterojunction devices is described. Mechanisms of free charge carrier generation and their recombination in the dark and under illumination are analyzed, chosen photovoltaic parameters are presented.

Keywords hybrid organic-inorganic solar cells; cadmium selenide; titanyl phthalocyanine

1 Introduction Need for inexpensive solar cells resulted in intensive research in the field of organic [1-3] and hybrid [4-6] systems. Such hybrid organic – inorganic systems attract considerable attention since they combine advantages of both types of semiconductors. If materials are chosen properly efficient charge carrier generation is observed not only in the vicinity of heterojunction of these semiconductors but also within the bulk of the inorganic semiconductor. We focus our research on systems based on phthalocyanine/II-IV semiconductor materials, since phthalocyanines (Pc) show very high absorption coefficients in a wide range of wavelengths up to 900 nm and, what is especially important, thin phthalocyanine layers of good quality can be produced, while efficient direct band to band transitions and relatively high mobility of free charge carriers are characteristic for such II-IV semiconductors. Utilization of strong absorption of both materials and good transport properties of inorganic semiconductors should result in high efficiency solar cells. This work presents photovoltaic properties of cadmium selenide (CdSe)/titanyl phthalocyanine (TiOPc) planar heterojunction. CdSe/TiOPc is a novel heterojunction, though these materials have already been studied in the field of photovoltaics in devices based on TiOPc/perylene [7], TiOPc/C₆₀ [8-11] and CdSe/CuPc [12], for example. The main purpose of our work is identification of generation and recombination mechanisms in the investigated system.

2 Materials and methods In the course of this study planar bilayer ITO/CdSe/TiOPc/MoO₃/Ag cells and ITO/TiOPc/MoO₃/Ag devices for the reference were fabricated. Chemical structure of titanyl phthalocyanine and a schematic structure of fabricated cells along with a schematic energy band diagram for all materials used in this study are shown in Fig.1. Energy levels, i.e. ITO and Ag work functions, conduction and valence band levels of CdSe and MoO₃ as well as HOMO and LUMO positions of TiOPc were taken from literature [9,13-15] and their uncertainty is about 0.2 ÷ 0.5 eV. MoO₃/Ag bilayer, commonly used as an anode in organic solar cells [1,2,10,13,14], serves the role of a high work function electrode in the considered system, while charge carrier transport through the MoO₃ layer is realized via states localized in the energy band gap of this material. It is worth noticing that different values of energy levels for this material can also be found [16]. All samples were prepared on glass substrates partially covered by ITO (sheet resistance of 40 Ω/square, purchased from PGO), cleaned in an ultrasonic bath (in acetone and isopropanol) and dried in a hot air flow. Thin layers of CdSe (140 nm), TiOPc (80 nm), MoO₃ (10 nm) and Ag (40 nm) were deposited by means of PVD (Physical Vapour Deposition) under high vacuum (Auto 306 Turbo, Edwards, p=3·10⁻⁴ Pa). All the aforementioned layers were deposited successively in the same cycle without breaking the vacuum. As a result devices with active area of 0.05 cm² were fabricated.

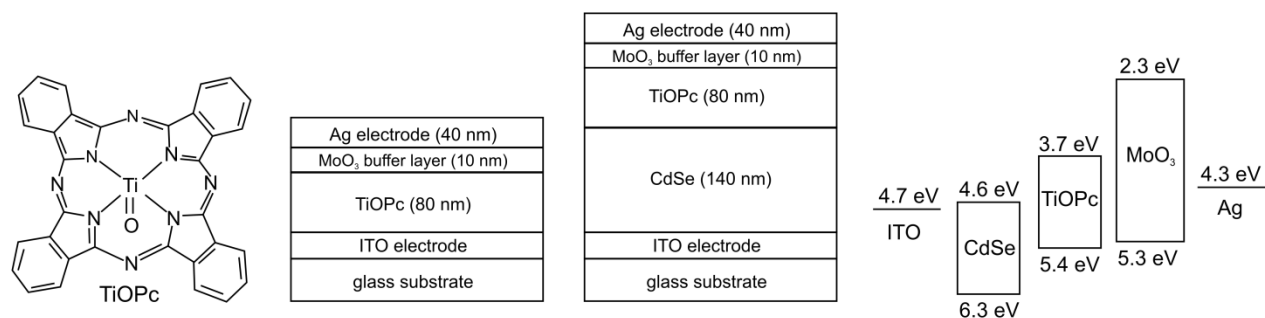


Figure 1 Chemical structure of TiOPc, schematic structure of prepared devices and energy band diagram for used materials.

All measurements were performed in ambient air, at room temperature, without encapsulation at least few hours after fabrication of samples and exposure to air. Signs of sample degradation were observed after few days of measurements run under electric bias and illumination. Quite good reproducibility of results was obtained since variations in the values of measured photovoltaic parameters for the whole set of fabricated devices were not greater than 10%. Absorption spectra were measured with Shimadzu 1240 UV-VIS spectrometer. Short-circuit current density (j_{sc}) and open-circuit voltage (U_{oc}) action spectra were collected using CM110 monochromator under constant photon flux of 10^{15} or 10^{14} photons/(cm²s). The same equipment was applied to measure j_{sc} and U_{oc} as a function of incident light intensity (I_0). Current-voltage curves were obtained in the dark as well as under monochromatic illumination of intensity $I_0=10^{15}$ photons/(cm²s) using Keithley 6517 electrometer with computer controlled voltage source.

3 Results Short-circuit current action spectra collected for the ITO/CdSe/TiOPc/MoO₃/Ag cell illuminated either through the ITO electrode ($I_0=10^{15}$ photons/(cm²s)) or through the Ag electrode ($I_0=10^{14}$ photons/(cm²s)) are shown in Fig.2A. For the reference also j_{sc} action spectrum for the ITO/ TiOPc/MoO₃/Ag cell obtained at light intensity of 10^{15} photons/(cm²s) and illumination through the ITO electrode, as well as, absorption spectra of CdSe and TiOPc films were plotted at the same graph. Note, that all the aforementioned action spectra are presented in a semi-log scale. As one can see, j_{sc} action spectrum recorded for the ITO/TiOPc/MoO₃/Ag cell is symbatic, i.e. it follows the absorption spectrum of TiOPc, within the whole investigated range of wavelengths. Situation changes when CdSe is introduced into the cell structure. In this case, under illumination through the front contact value of j_{sc} is one order of magnitude higher than in case of single layer ITO/TiOPc/MoO₃/Ag cells and its action spectrum remains symbatic to absorption spectra of both semiconductors as long as absorption of CdSe is not too pronounced. At shorter wavelengths, where CdSe shows strong absorption, filtering effect is observed and j_{sc} action spectrum becomes antibatic to absorption spectrum of CdSe. When the sample is illuminated through the back Ag electrode short-circuit current action spectrum is antibatic to absorption spectrum of TiOPc. Action spectra of the open-circuit voltage measured at light intensity of 10^{15} photons/(cm²s) and illumination through front electrode for both investigated systems (Fig.2B) were the same as their j_{sc} counterparts. Moreover, a major improvement of U_{oc} in the whole spectral range was observed as a result of introduction of CdSe. Thus, we may conclude that in case of the ITO/TiOPc/MoO₃/Ag cell there is only one mechanism of free charge carrier generation, i.e. dissociation of excitons generated in the phthalocyanine layer taking place in the vicinity of the front ITO contact, whereas two different mechanisms can be distinguished for the ITO/CdSe/TiOPc/MoO₃/Ag system: 1-generation of excitons in the phthalocyanine layer and their subsequent dissociation at the CdSe/TiOPc interface, where electrons are injected into the CdSe layer while holes remain in the TiOPc layer; 2- band to band electron transfer in the CdSe layer. The observed filtering effect lets us infer that the latter process of free charge carrier generation occurs in the whole volume of CdSe layer but probably only charges created near the active CdSe/TiOPc interface contribute to the current flow which may be attributed to the short diffusion length for holes in this material. Furthermore, for sure the CdSe/TiOPc heterojunction is more effective in free charge carrier generation than ITO/TiOPc interface and obtaining higher values of current density in case of such ITO/CdSe/TiOPc/MoO₃/Ag system should be the matter of proper layer thickness optimization.

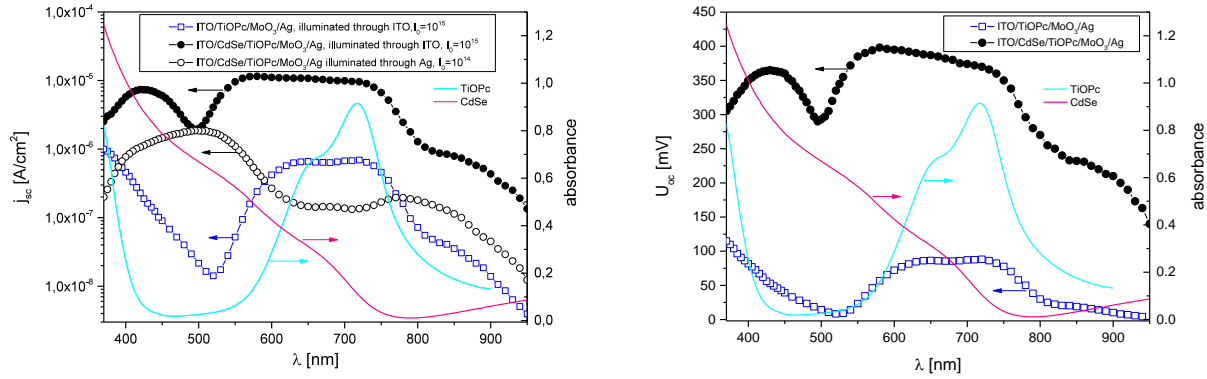


Figure 2 Short-circuit current density (A) and open-circuit voltage (B) as a function of wavelength for ITO/TiOPc/MoO₃/Ag and ITO/CdSe/TiOPc/MoO₃/Ag cells measured at a constant light intensity of 10¹⁵ photons/(cm²s) when illuminated through the ITO electrode and 10¹⁴ photons/(cm²s) when illuminated through Ag electrode. Absorbance of CdSe and TiOPc were plotted on both graphs for the reference. Note the semi-log scale for j_{sc} .

Dominating type of recombination of free charge carriers in both investigated systems can be inferred from the log-log plots of illumination intensity dependence of j_{sc} and U_{oc} presented in Fig.3. These data were collected under illumination through the front electrode with monochromatic light of wavelength $\lambda=580$ nm and $\lambda=720$ nm referring to the j_{sc} peak for the bilayer CdSe/TiOPc cell and the single layer TiOPc cell, respectively. For both types of cells a well-known relation between short-circuit current and illumination intensity I_0 for light intensities up to 10¹⁶ photons/(cm²s) was found:

$$j_{sc} \sim I_0^b, \quad (1)$$

where value of b determines the type of recombination. Values close to 1 are characteristic for monomolecular recombination of free charge carriers [17,18], which is the case of both investigated systems ($b=0.96$ for ITO/CdSe/TiOPc/MoO₃/Ag and $b=0.99$ for ITO/TiOPc/MoO₃/Ag). Very often the following formula describes the dependence of U_{oc} on I_0 for organic and mixed organic/inorganic photovoltaic cells [8,9,13,14,18]:

$$U_{oc} = m \frac{kT}{e} \ln(j_{ph}/j_0 + 1) \approx m \frac{kT}{e} \ln(\beta I_0), \quad (2)$$

where j_{ph} is the density of the current photogenerated at the junction of two semiconductors, j_0 stands for the saturation current density of the junction resulting from thermal generation of free charge carriers at this junction, β is a constant, e is the elementary charge, k is Boltzmann's constant, T denotes absolute temperature, while m is the diode ideality factor under illumination and the latter is dependent on recombination mechanisms. Value of $m=1.77$ was obtained for a bilayer cell, which indicates that under open-circuit conditions trap-assisted recombination in the vicinity of the CdSe/TiOPc junction is the predominant type of recombination. If we take eqs. 1 and 2 and note that j_{ph} is usually much greater than j_0 and short-circuit current density is directly proportional to j_{ph} , we will understand why the shapes of U_{oc} action spectra obtained for both systems are identical as the shapes of j_{sc} plotted for these samples in a semi-log scale ($U_{oc} \sim \ln(cj_{sc})$, where c is a constant).

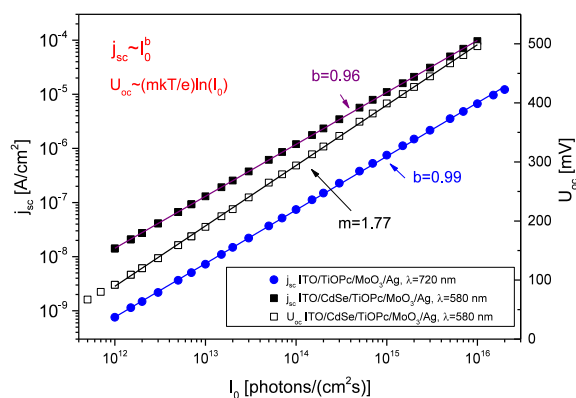


Figure 3 Log-log plots of open-circuit voltage dependence on light intensity for the ITO/CdSe/TiOPc/MoO₃/Ag cell at $\lambda=580$ nm and short-circuit current density as a function of light intensity measured for the ITO/TiOPc/MoO₃/Ag cell at $\lambda=720$ nm and for the ITO/CdSe/TiOPc/MoO₃/Ag cell at $\lambda=580$ nm.

The value of the diode-ideality factor in the dark and under different illumination conditions, as well as other parameters describing performance of a cell may be deduced from the current-voltage graphs. Semi-log current density versus voltage plots in the dark and under monochromatic illumination of wavelength $\lambda=580$ nm and intensity $I_0=10^{15}$ photons/(cm²s) are shown in Fig.4 (the inset of the graph shows the linear plot of the j-V curve obtained under illumination), where negative bias refers to negative polarization of Ag electrode with respect to ITO. In a limited range of bias (up to about 0.2 V) dark current density j_d for the ITO/CdSe/TiOPc/MoO₃/Ag cell can be expressed by Shockley equation:

$$j_d = j_0[\exp(eU/mkT) - 1], \quad (3)$$

On this basis, the diode ideality factor $m=2.13$ and dark saturation current $j_0=1.65$ nA/cm² were found. Such value of m suggests that in the dark trap-assisted recombination of free charge carriers at the CdSe/TiOPc heterojunction takes place and the current flowing through the cell is a recombination current. The open-circuit voltage obtained under aforementioned monochromatic illumination was 0.41 V and the fill factor was 0.4, which is relatively high as for a cell stored and measured in the ambient air. Knowing the dark saturation current density and diode ideality factor under illumination at the open-circuit we may calculate the photogeneration current density j_{ph} , which, according to eq.2, is equal to 14 μ A/cm² under investigated illumination conditions. Saturation of U_{oc} was observed when the cell was illuminated with Xe lamp at the intensity greater than 150 mW/cm² and the maximum value of this parameter was 0.55 V, which is 0.25 V lower than the predicted maximum value of this parameter resulting from the HOMO of TiOPc - conduction band of CdSe offset. Such relation between the experimental and theoretical maximum value of U_{oc} is quite common for organic solar cells [5,8,9].



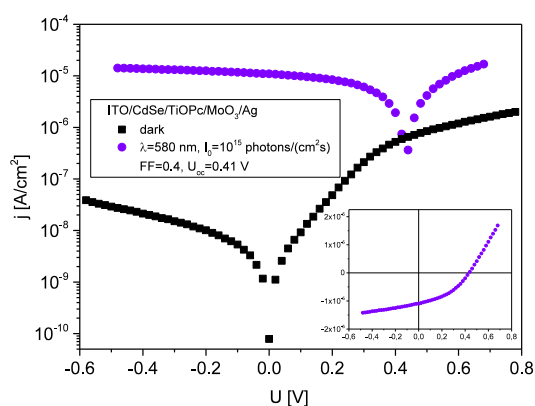


Figure 4 Semi-log current – voltage curves obtained in the dark and under monochromatic illumination of wavelength $\lambda=580$ nm and intensity $I_0=10^{15}$ photons/(cm^2s); inset shows the linear plot of the j - V curve obtained under illumination.

Since under forward bias the photogenerated current and the dark current flow in opposite directions, the total current density j , i.e. density of the current flowing through the cell under external bias U under illumination, in good photovoltaic cells follows the relation

$$j = j_d - j_{ph}. \quad (4)$$

Therefore, under high forward bias, for which the injected current is much greater than the photogenerated one, photocurrent j flowing through such cell is practically the same as the current j_d flowing through it in the dark, hence these two curves overlap each other. One may notice that this is not the case of the investigated bilayer cells for which voltage dependence of photocurrent j and dark current j_d is shown in Fig.4. We think that it mainly follows from photoconductivity of the CdSe layer originating from band to band transitions, as well as, from the presence of light-induced charge carrier detrapping in the TiOPc layer.

4 Conclusions Investigated ITO/CdSe/TiOPc/MoO₃/Ag system has proved its ability of free charge carrier generation practically in the whole visible range of electromagnetic radiation. Two mechanisms of free charge carrier photogeneration can be distinguished: 1- photoexcitation of the phthalocyanine layer followed by exciton dissociation at the CdSe/TiOPc interface and 2 - band to band electron transfer in the CdSe layer. At short circuit, open circuit and under bias in the dark free charge carriers undergo monomolecular trap-assisted Shockley-Read-Hall recombination. We think that low values of current density obtained in this study follow from large thickness of layers of both used semiconductors. Maximum measured value of U_{oc} was 0.55 V, while relatively high fill factor of 0.4 was obtained under monochromatic illumination though investigated cells were stored and measured in the ambient air without encapsulation. Results of theoretical study present values of electron and hole transport level offset proper for inorganic-organic hybrid solar cells [19] and such offset characterizes the CdSe/TiOPc heterojunction. Therefore, we believe that the ITO/CdSe/TiOPc/MoO₃/Ag structure may show good performance if proper layer thickness optimisation taking into account short diffusion length of holes in CdSe and short exciton diffusion length in TiOPc is made.

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