PHOTOELECTRIC CHARACTERIZATION OF P3HT POLYMER/PbS NANOCRYSTAL COMPOSITS

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Photoelectric properties of new type conjugated polymer-semiconductor nanocrystals hybrid solar cells were investigated. Dependencies of charge carrier generation, mobility and recombination on composition of samples and the way how the samples were prepared were evaluated by using ultrafast time-resolved fluorescence, transient photocurrent and delayed collection field techniques. The combination of several investigation techniques enabled to distinguish and investigate three processes determining solar cell efficiency: charge carrier generation, carrier recombination and extraction. Charge carrier generation was found to be limited by relatively slow electron transfer from photoexcited polymer to PbS nanoparticles, but this process was determined being independent of the electric field strength. Carrier recombination and extraction rates strongly depend on the PbS nanoparticle concentration and determine the extraction efficiency. Efficient carrier extraction at short circuit conditions is possible only in chemically and thermally treated samples with high PbS nanoparticle concentration.

Introduction

Hybrid blend nanocomposites promise to merge advantages of organic and inorganic components for fabrication of efficient, stable and cost-effective solar cells. Lead sulfide is among the most promising materials for formation of solution processable blends for solar cells because its nanocrystals have absorption in the neat IR region, thus may extend the light harvesting to the long wavelength region. However, only recently quite promising 3% efficiency of solar cells based on specifically chemically and thermally treated P3HT/PbS nanocrystal blends has been demonstrated [1]. Still better understanding of processes limiting their efficiency is necessary in order for their further improvement.

In this research poly(3-hexylthiophene) (P3HT) polymer/PbS nanocrystal composits were investigated. In this work we investigated photoelectric properties of these composits for the reason to get more information about what processes determine the efficiency of hybrid solar cells prepared by blends of conjugated polymers and colloidal inorganic semiconductor nanocrystals. Therefore, the aim of this research was to investigate properties of charge carrier generation, mobility and recombination in these new type solar cells, and to evaluate how these properties depend on composition of samples and the way how samples were made.

Experimental

During this research films (roughly 100 nm thick) of P3HT polymer doped with PbS nanocrystals were investigated by recording integrated photocurrent kinetics using "Integrated transient photocurrent", "Photo-CELIV" and "Time-delayed collection field" methods. Seven samples with different weight ratio of components and with different fabrication techniques (thermally and chemically treated or not) were investigated. Between these samples there were also pure films of nanocrystals and polymer.

Results and Discussion

Influence of the electric field on charge carrier photogeneration and extraction was investigated by using "Integrated transient photocurrent" method. Figure 1 shows dependence of the charge carrier extraction on applied voltage.

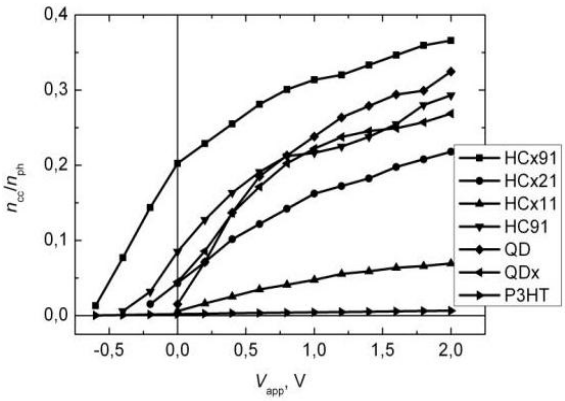

Fig. 1. Number of extracted charge carriers from different investigated samples normalised to the number of absorbed photons. HC denotes hybrid composite, x denotes that sample was thermally and chemically treated during fabrication and numbers 91, 21 and 11 denote nanoparticle to polymer weight ratio of 9/1, 2/1 and 1/1 respectively.

Charge carrier extraction efficiency at high extraction voltage weakly depends on the sample, except of P3HT and samples with low nanocrystal (QD) concentration. In case of low QD concentration, majority of photons are absorbed in P3HT and excitations do not reach interfaces with QDs. Fluorescence decay kinetics support this assumption (see Figure 2). Low efficiency in pure P3HT film is caused by very inefficient carrier generation.

The fast fluorescence decay component corresponds to the fluorescence quenching. Majority of excitations are quenched in HC91 and HCx91 samples, while less than half of excitons are quenched in samples with low QD concentration. Remaining fraction of excitons decay intrinsically and do not contribute to photocurrent.

At zero applied voltage (short circuit conditions) extracted charge strongly depends on the sample. Extracted charge reaches about 50% of that extracted at 2V only in HCx91 sample, for other samples it is much lower. Thus the main question is what processes limit extraction at short circuit, thus limit the solar cell operation efficiency.

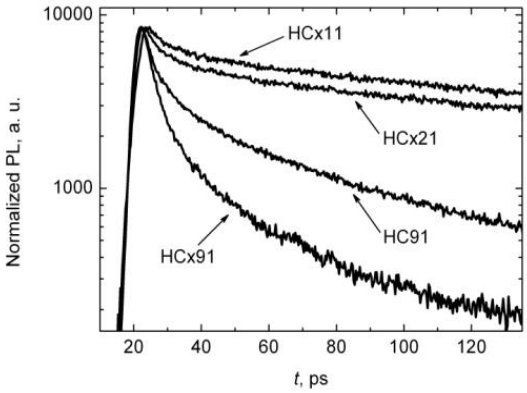

Fig. 2. Fluorescence decay kinetics for different samples.

In order to get information which of the processes, carrier generation or extraction limit the extracted charge we applied a "Time-delayed collection field" technique. By using this method, the variable voltage was applied during the optical excitation pulse (generation voltage) and after 0,5 μs extraction voltage was applied, which was independently variable. We have got dependencies of charge carrier generation and extraction efficiencies on applied electric field. All samples show very weak dependencies of the extracted charge on the generation voltage. Some weak dependence is probably caused by non ideal measurements: the extraction voltage was applied not instantaneously but with some delay, which depends on the generation voltage. During this time a fraction of charge carriers may recombine and apparently cause the observed dependence on the generation voltage. We conclude that charge carrier generation needs no electric field assistance. It means that electrons and holes are weakly bound both when they are created in QDs and when electron is transferred from photoexcited P3HT. The dependencies of the extracted charge on applied extraction voltage correlate with the results shown in Figure 1 and thus show that the carrier extraction rather than their generation limits the extracted charge. Efficient carrier extraction requires rather strong electric field and this is the major factor limiting the solar cell efficiency. The extraction efficiency strongly depends on the polymer/PbS weight ratio and the sample treating. High PbS nanocrystal concentration and the sample treating enables to separate electrons and holes in different materials and, thus, to reduce the carrier recombination rate, while keeping their high mobility.

In our research we also targeted to evaluate the mobility of charge carriers in all samples and its dependence on the composit preparation and weight ratio. This was done by using "Integrated transient photocurrent" method. We registered integrated photocurrent kinetics at few different time scales which were combined to get better resolution. Figure 3 shows the charge carrier extraction dynamics and its dependence on applied voltage. By plotting the extraction kinetics on a logarithmic time scale from the kink times charge carrier extraction time values may be evaluated. "Photo-CELIV" measurements were additionally used to evaluate the mobility values, and both types of measurements showed quite similar results. The mobilities were of the order of 10-4 cm2/Vs and were higher in samples with higher nanocrystal concentration. Charge carrier mobility was found to closely follow the $\mu \sim \exp(\sqrt{E})$ dependence, which indicated that it is governed by the carrier hopping in energetically disordered material.

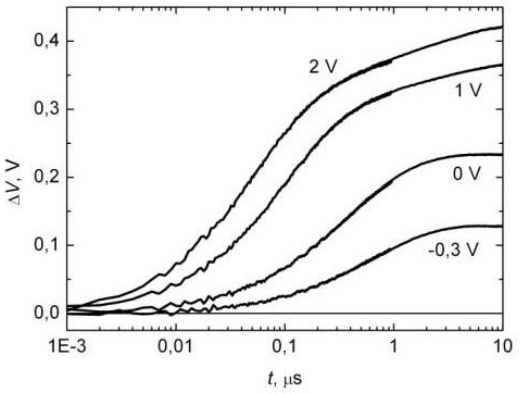

Fig. 3. Integrated photocurrent kinetics of HCx91 sample at logarithmic time scale.

Conclusions

We used several photoelectrical measurement techniques to get information about the photoelectrical properties of P3HT polymer/PbS nanocrystal compositional films. Photoelectric response revealed that the efficiency of photogenerated and extracted charge carriers depends on applied electric field. Also it depends on concentration of PbS nanocrystals and the way samples were made. Less efficiency at high applied voltages in samples with low concentration of nanocrystals is determined by quenching of spontaneous P3HT excitation not reaching interfaces with nanocrystals. Efficiency of the charge carrier extraction is determined by the ratio of charge carrier extraction and recombination. These properties have different dependencies on concentration of nanocrystals and the way samples were made. High efficiency of the best solar cells with the highest concentration of nanocrystals is determined by fast extraction of both holes and electrons and by the slowest recombination rate.

References

1. *Giansante C., Mastria R., Lerario G. et al.*, Molecular-level switching of polymer // Nanocrystal non-covalent interactions and application in hybrid solar cells. 2014. P. 1–9.