

Sensitization of Nanocrystalline Solar Cells with Phthalocyanines

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In the last decade photovoltaic devices using organic semiconductors as an active layer have undergone a very rapid development [1]. These materials are now widely investigated for fabrication the organic heterojunctions, Shottky barrier cells and also for sensitizing widebandgap inorganic semiconductors in nanocrystalline photoelectrochemical solar cells [2,3]. Among other molecular materials metal phthalocyanines, MePc (where Me = Cu, Zn, H₂, TiO etc.) present a special interest due to its low cost and potentially high photoelectronic properties. Meantime, the devices using MePc dyes possess low conversion efficiencies that need to be improved.

We have already reported on the fabrication of solid-state solar cells based on TiO₂ monocrystals [4], photoelectronic properties of condensed layers of metal phthalocyanines [5], the studies of photoconductivity action spectra and the absorption in thin evaporated layers of different metal phthalocyanines [6]. At the same time the light absorption and photoelectronic processes in the molecular layers of organic semiconductors covering the nanocrystalline layers may originate from different or combined effects. The latter is connected with the fact that besides the monolayer of organic molecules, responsible for sensitization, the cluster agglomeration process may also take place. In this study we paid special attention to the mentioned effects in the bulk of the nanocrystalline electrode and compared them with its solid-state analogs. We report on the studies of photoelectronic and spectral characteristics in nanocrystalline TiO₂ layers sensitized with different metal phthalocyanines and present the parameters of solar cells fabricated on the base of these materials.

Sufficient information about the mechanisms of charge transfer may be extracted from the action spectra of short-circuit photocurrent of the solar cell ($I_{s.c.}$). Fig.1 presents a typical view (curve 1) obtained for nanocrystalline TiO₂/ZnPc cell illuminated from TiO₂ electrode direction. The same figure shows for comparison the earlier reported action spectra in TiO₂/ZnPc heterojunction, where ZnPc layer (120 nm thick) was sublimated on top of TiO₂ monocrystal [4] and the depletion layer was found to be about 15 nm thick. The action spectra of the photocurrent in CuPc- and TiOPc-based solar cells do not differ much from the one given in Fig.1.

We have found, that the absorption spectra of dye-sensitized electrodes follow the absorption of condensed layers but not of individual molecules in solution. At the same time their peak positions were shifted against each another. We suggest that the obtained absorption of dye sensitized layers are actually the combined values of two different contributions from the monomolecular layer and also from the organized clusters consisting of the same molecules. The mathematical evaluation shows that the volume content of nonaggregated part of dye molecules is at least three times large than the volume of aggregated organized

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clusters. This assumption coincides also with the data obtained from photocurrent action spectra of the solar cell under short-circuit conditions.

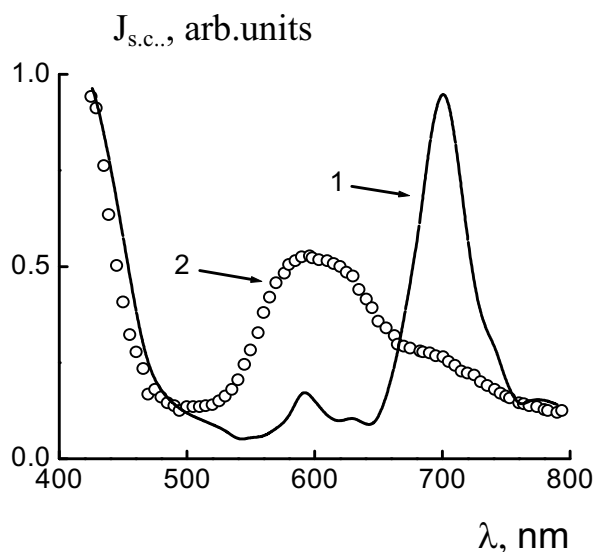


Figure 1. Action spectra of short circuit photocurrent ($J_{s.c.}$) for nanocrystalline cell of $TiO_2/ZnPc$ (1) and for the same type of solid state cell (2).

To conclude, we have fabricated and investigated the photovoltaic energy conversion devices with nanocrystalline porous TiO_2 layers sensitized with Zn Cu and TiO phthalocyanines. The current-voltage characteristics of the given solar cells show relatively high values of the open circuit voltages and fill-factors. The energy conversion efficiencies over an order of magnitude exceed that of their solid state analogs. It is also shown that the optical absorption spectra in the nanocrystalline layers after sensitization do not follow the shape of the photocurrent action spectra and the peak positions are also different. The given phenomenon is explained by the assumption that only the molecular monolayers of dye molecules absorbed on the nanocrystalline TiO_2 surfaces are responsible for the photoelectronic properties of the cells under consideration.

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