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Featured Review

New Trends in Solar Photovoltaics: from Physics to Chemistry

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Abstract−The paper briefly discusses the current situation in the field of traditional and unconventional photovoltaic materials and solar cells. It emphasizes the fact that the main basic achievements in the field of solid-state solar photovoltaics were gained at least two decades ago and the further progress focused on the improvement of cell parameters and technological aspects. Finally, the article concludes that this scientific area has nearly fulfilled its historical task. Indeed, the last decade has brought many new achievements in the field of the alternative, molecular-based materials. The future of solar energy conversion seems to be mainly connected with chemistry, chemical physics and chemical engineering but not with solid-state physics as in the twentieth century. The paper gives also a short overview of some promising organic semiconductors, fullerenes and TiO_2 nanocrystalline structures used now in a new generation of molecular solar cells.

Key words: Organic Semiconductors, Solar Cells, Fullerenes, Zinc Phthalocyanine

INTRODUCTION

It is generally understood today that renewable energies, including solar energy, will play a major role in the near future. So the main scientific and engineering problem can be seen in preparing the appropriate solar energy conversion materials that will meet the requirements of cheap, non-pollution and wide range production of high efficiency photovoltaic solar cells. On one hand, one may suppose that the problem has been already solved: modern solid state photovoltaic batteries, based on Si, a-Si, GaAs and CdS(CdSe), have been widely investigated and show excellent photo conversion parameters [Goetzberger et al., 2000]. Meanwhile, speaking about global application of solar power, the possibility of wide scale production of solid-state cells for this purpose will create more questions than answers. There are at least two main problems, still not clearly recognized. The first one concerns the situation in the field of basic scientific studies of traditional solar cells. The main achievements in this field, gained two or even three decades ago, were strictly connected with the necessity to design adequate solar batteries for space flight purposes. In the beginning of 70's this task was solved and no serious basic problems remained [Green, 2000]. At the same time a great number of research groups and institution all over the world were involved in the research process, trying to achieve as high conversion efficiencies of solar cells as possible.

Fig. 1 demonstrates the historical progress in the improvement of solar energy conversion efficiencies for the main types of conversional solid-state solar cells. Initially, much attention was focused on Si-based cells that till now have been the most promising solid-state photovoltaic devices. As one can see, no big progress in past two decades was really gained. This does not denote the lack of the appropriate efforts being applied it only shows that the main tasks in this field of science had been successfully fulfilled and the parameters of these solar cells had nearly reached the possible theoretical limits.

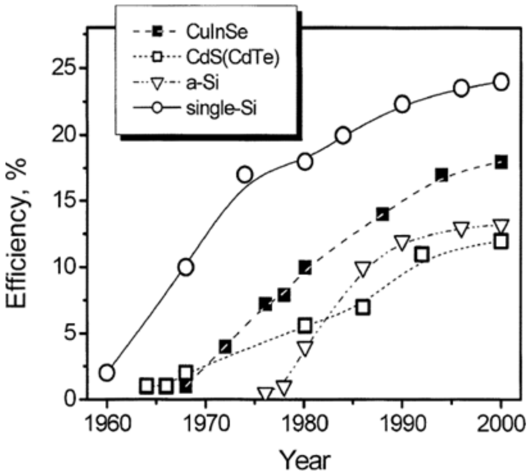

Fig. 1. Parameters of cell conversion efficiencies improvement over time.

The situation becomes even more clear if we examine the so-called "decade progress" curve, given in Fig. 2. The value of decade progress denotes the percentage ratio of maximum efficiency of the solar cell gained by the moment (year 2000), to the appropriate decade increase of the given type of solar device. This graphic confirms that the main progress took place nearly 30 years ago and no serious results are foreseen to appear in the future decade (2000-

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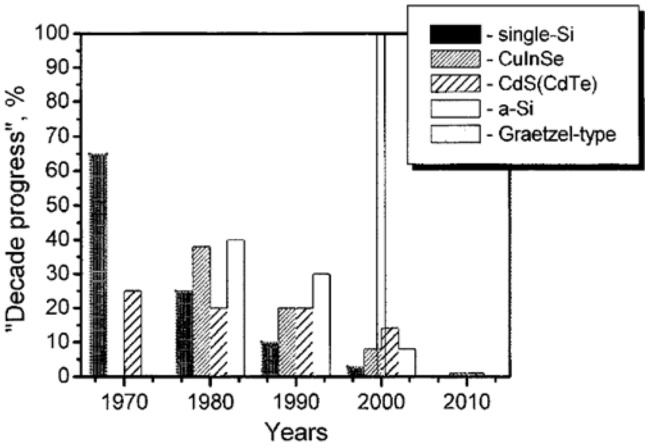

Fig. 2. Decreasing of "decade progress" in solid-state solar cells conversion efficiencies. The first decade of the new century does not promise much.

2010). However, the given example does not mean that it is already time to diminish the efforts, connected with constructing solid-state cells. It only shows that the time of basic achievements has passed and now the main problems should be focused on production technique and be carefully examined from the economical point of view. Also, there is another problem that has not yet been fully recognized. It concerns the ecological aspect that we may face in case of wide production of Si- or CuInSe based materials for solar cells [Greijer et al., 2001] In addition, high semiconductor technologies, that are necessary to apply in this case, will keep the cost of these devices rather expensive.

So the question arises, are there any other possibilities to get the electric power from solar energy, but cheaper, cleaner and without using expensive technologies? It seems that now we may answer yes, and this positive argument is based on new achievements that have appeared in last decade from chemists and chemical laboratories [ORegan et al., 1991].

NEW PROBLEMS

Along with specialists in solid-state physics the problem of solar energy conversion into electric power was investigated by chemists. Photoelectrochemical solar cells with semiconductor electrodes were extensively studied but they possessed poor conversion efficiencies and bad stability [Pleskov et al., 1986; Memming, 1994]. At the same time, the last decade has brought new ideas and promising new achievements. The most interesting is the appearance of nanocrystalline dye-sensitized photoelectrochemical cells, recognized now as Graetsel-type solar cells [Hagfeldt et al., 1994]. In less than ten years the efficiency of these cells has jumped from the value of one up to more than 10 percent [Grätzel et al., 1999]. The diagram in Fig. 2 shows the appropriate progress in comparison with traditional devices. A thin layer organic solar cell, based on molecular semiconductors, has been also developed. The most important problem is to carefully investigate and design new types of molecular materials for unconventional solar cells. In this contribution we present an example of the appropriate studies of some interesting up to date materials and solar cells.

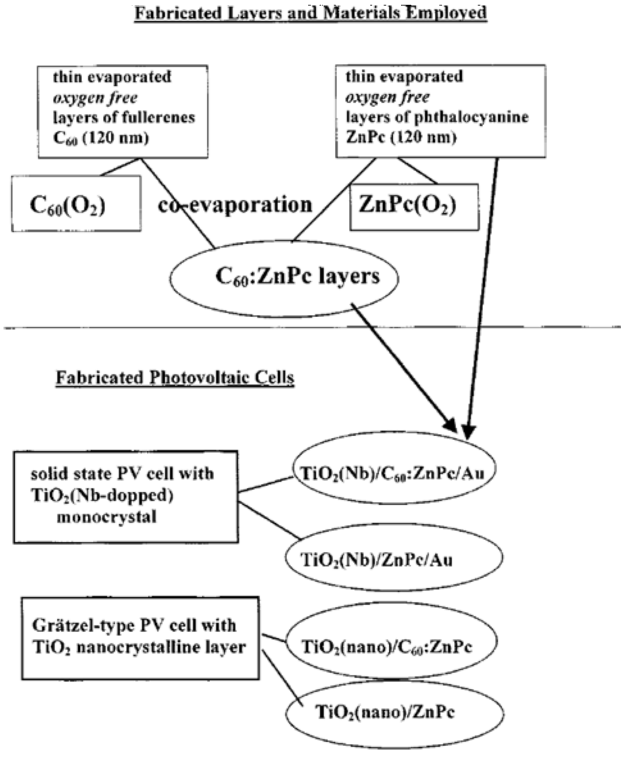

Fig. 3. Fabricated solar cells and materials employed.

GRÄTZEL TYPE CELLS AND PHTHALOCYANINES

Solar cells, developed in the research group at the Swiss Federal Institute of Technology conducted by Grätzel, use the prinicples that differentiate the processes of light absorption and charge separation [Hagfeldt et al., 1994]. In contrast to solid cells, where the absorption of light and separation of created charge carriers perform simultaneously and provide many problems, the given structure is independent of many processes diminishing the efficiency in solid devices [Grätzel, 1999]. The general operating principles of Grätzel-type cells have been presented in many publications [O'Regan et al., 1991; Grätzel, 1999]. At the same time, the main active organic layer, used as a photosensitizer, is usually based on ruthenium complexes with optical absorption, nearly following the wavelength distribution of the solar spectra. Given high efficiencies, these dyes are at the same time relatively expensive and no information is available concerning their long-term stability. So in some laboratories now they try to use other types of dyes, including well-known molecular materials like phthalocyanines. In our group we have also performed experiments with different phtholocyanines and phthalocyanine-fullerene composites for TiO_2 nanocrystalline layers sensitization. The main steps of preparation of the dye materials and the appropriate solar cells are schematically given in Fig. 3.

EXPERIMENTS AND RESULTS

In our studies we tried to use new types of fullerene-phthalocyanine composites (C_{60} : ZnPc) for sensitizing nanocrystalline layer of solar devices. To fulfill this we have also studied the photophysical properties of single layers of C_{60} : ZnPc composites including the transport parameters and photoconductivity. Using these composites as sensitizers we have fabricated two new types of TiO_2-based solar cells: (i) Grätzel-type cells and (ii) solid-state photovoltaic heterojunctions with niobium doped TiO_2 single-crystal, and examined the performance of photoconversion characteristics in these cells in comparison with those sensitized by pure ZnPc dye.

To fabricate C_{60} : ZnPc composites, commercially available powders of C_{60} (99.9% purity) from Merck Co. and zinc phthalocyanine, $(C_8H_4N_2)_4Zn$ from Eastman Kodak Co. were vacuum sublimated (10^{-6} Torr) on ITO coated glass supports (Corning 7059) using two different resistively heated quartz crucibles. Just before deposition C_{60} powder was kept under vacuum (10^{-7} Torr) during 24 hours to diminish the initial oxygen content. ZnPc powder was predominantly purified under conditions reported previously [Shevaleevski et al., 1995]. The percentage of volume content in C_{60} : ZnPc composite was controlled by Raman spectroscopy measurements. For conductivity measurements gold back co-planar contacts with a thickness of 50 nm and an area of 20 mm^2 were vacuum evaporated on top of the layers. Using the same depositing conditions single-layer samples of C_{60}, ZnPc and C_{60} : ZnPc were prepared for UV-visible absorption spectra measurements.

Solid-state cells were fabricated using single-crystal n-TiO_2 samples (rutile), doped with 10^{16} mol/cm^3 of Nb. Single-crystal was cut into 1.5 mm thick plates with (001) surface and optically polished at both sides and then supplied with back electrical contacts of indium. Solid-state cells were manufactured by evaporating of around 100 nm thick layers of ZnPc or C_{60} : ZnPc on TiO_2(Nb) single-crystal surfaces. To complete the cell construction, the 30 nm gold contacts were subsequently evaporated through a special mask. TiO_2 8 μm thick nanostructural layers on ITO coated glass substrates were prepared from 20 nm interconnecting TiO_2 particles according to standard technique, described in [Hagfeldt et al., 1995]. To fulfill the cell construction the substrates were put into chemical solution with the appropriate dye for about 12 hours and then photoelectrochemical cells were fabricated as described [O'Regan et al., 1991]. The dark and photo-conductivity in all single-layers were measured in dc mode between the ITO as front and Au layer as back electrodes under 0.5 V bias voltage applied and possessed an ohmic behavior with no photoresponse observed. During photocurrent action spectra measurements the irradiation of samples from 500 W xenon lamp through a monochromator was appropriately filtered and calibrated to obtain the constant incident photon flux of around 10^{14} cm^{-2} sec^{-1} for the wavelengths between 380 and 850 nm. Current density - voltage characteristics were measured under illumination of 10 mW/cm^2 intensity by halogen lamp in front of the substrate.

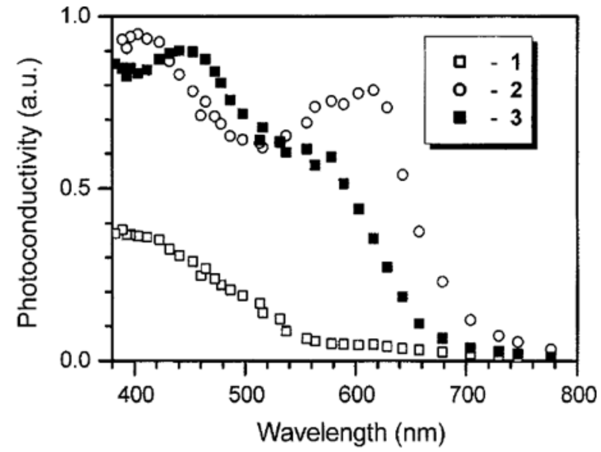

Fig. 5. Action spectra of photoconductivity for thin films of air exposed (1) and oxygen free (3) films of condensed C_{60}. Curve (2) air exposed C_{60} : ZnPc composite.

1. Single Layers of C_{60}-Based Composites

Fig. 4 shows the absorption curves for C_{60} and ZnPc vacuum evaporated layers (150 nm thick) and also for C_{60} : ZnPc films with two different partial concentrations of both components. It is seen that in case of small ZnPc concentration the resulting absorption does not present a superposition of both curves but may be treated as a modification of C_{60} absorption curve by non organized ZnPc molecules showing the Q-band of organic solution spectra (curve 3). Fig. 5 presents a comparative view of the action spectra of photocon-

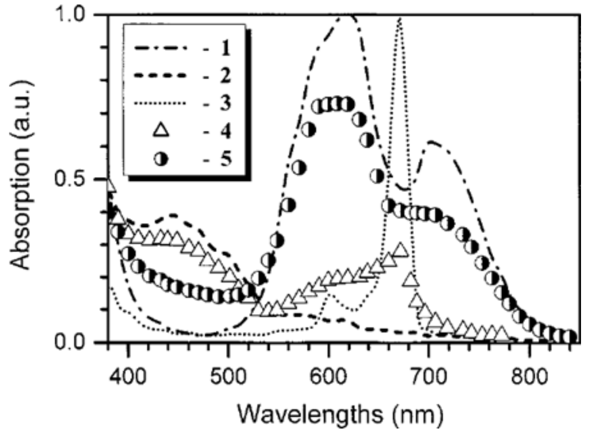

Fig. 4. Absorption curves of 150 nm thick evaporated layers of ZnPc (1), C_{60} (2) and their composites: C_{60} : ZnPc (80 : 20 vol%) - (4) and C_{60} : ZnPc (20 : 80 vol%) - (5) content. Curve 3 - the absorption of 0.06 molar ZnPc-solution in N,N dimethylformamid.

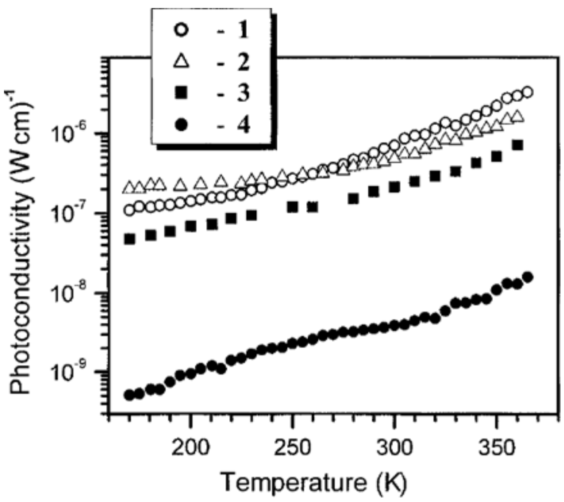

Fig. 6. Temperature dependences of bulk photoconductivity in thin films of air exposed (2) and oxygen free (1) C_{60} films. Curves (3) and (4) denote respectively to air exposed composites of C_{60} : ZnPc (80 : 20 vol%) and C_{60} : ZnPc (20 : 80 vol%).

ductivities for the same samples.

The values of specific conductivities (σ_d) for C_{60} and ZnPc single-layers in the dark were found to be appropriately σ_d=1.5×10^{-7} S/cm and σ_d=5×10^{-10} S/cm. C_{60} films were examined just after the deposition to exclude the influence of the oxygen doping, whereas ZnPc was stored in air for several hours under normal conditions to induce a process of oxygen doping. The oxygen doping significantly reduces the conductivity of C_{60} layer [Wan-Xi Chen et al., 1995]. Alternatively, a short period of air exposure initiates the rise of ZnPc conductivity. A different situation was observed for C_{60} : ZnPc composites. To investigate the photoconductivity behavior we have provided the temperature measurements in 170-350 K temperature interval that are given in Fig. 6.

From the data presented in Figs. 5 and 6 it can be concluded that even in case of small ZnPc concentration the oxygen influence on the electric properties of C_{60} : ZnPc composite is negligible, while the value of photoconductivity sufficiently increases.

2. Single-Crystal TiO_2-Based Solar Cell

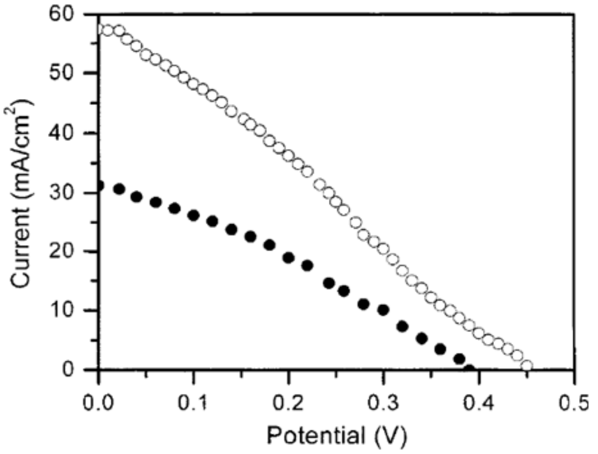

Fig. 7. Current density-voltage characteristics obtained under 10 mW/cm² halogen lamp illumination for TiO_2(Nb) solid-state cells with evaporated layers of ZnPc (black circles) and C_{60} : ZnPc composite (open circles).

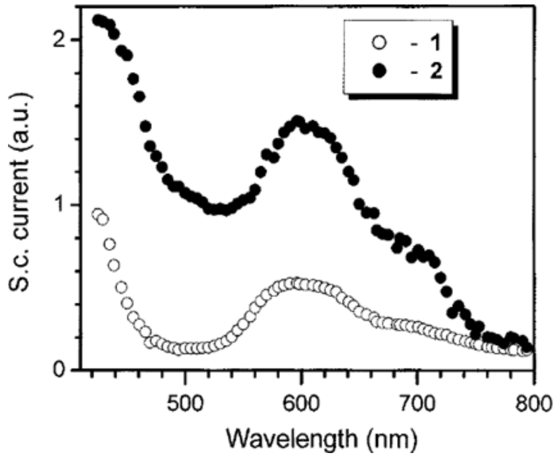

Fig. 8. Normalized spectral responses of short-circuit currents in solid-state cells of In/TiO_2(Nb)/ZnPc/Au (Curve 1) and In/TiO_2(Nb)/C_{60} : ZnPc/Au cell (Curve 2).

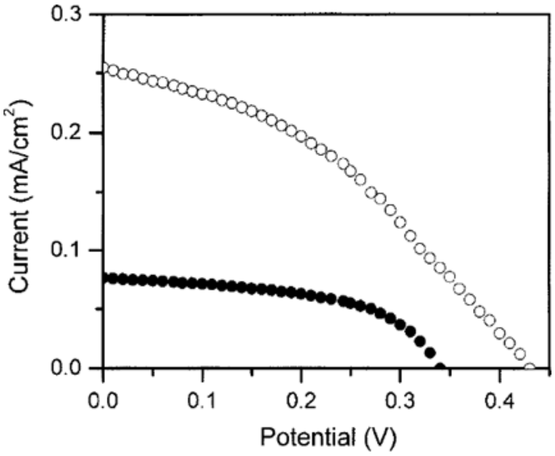

Fig. 9. Current density-voltage characteristics obtained under 10 mW/cm² halogen lamp illumination of TiO_2 nanostructured Grätzel-type cells, sensitized with ZnPc (black circles) and C_{60} : ZnPc (open circles) dyes.

Fig. 7 shows the current-voltage characteristics measured under halogen lamp full light illumination (10 mW/cm²) for TiO_2(Nb)/ZnPc and TiO_2(Nb)/ZnPc : C_{60} solid-state heterojunctions. The light comes from TiO_2 direction. Fig. 8 presents the experimental curve of short circuit photocurrent spectral response measured for the same samples. The solar cells parameters extracted from the J-V curves for the cell in which C_{60} : ZnPc composite was used as a sensitizer are the following (the values for the cell with pure ZnPc dye are given in brackets): short-circuit photocurrent, $I_{s.c.}$=0.058 mA/cm² (0.032 mA/cm²), open-circuit photovoltage, $V_{o.c.}$=0.45 V (0.39 V), a fill factor, ff=0.22 (0.23) and the energy conversion efficiency is equal to around 0.1%, while when using ZnPc the appropriate value is twice less. The shape of the J-V curves and low values of the fill factors denote to a high series resistance of organic semiconductors used in both cells.

3. TiO_2-Based Nanocrystalline Cell

Fig. 9 presents a comparative view of V-A characteristics of dye-sensitized TiO_2 nanocrystalline solar cells with C_{60} : ZnPc and ZnPc dyes. The measured parameters of TiO_2/ZnPc cell were the following: V_{OC}=0.34 V, I_{SC}=77×10^{-6} A/cm², ff=0.54 and the conversion efficiency under 10 mW illumination was equal to 0.138%. At the same time the application of C_{60} : ZnPc composite increases the value of photocurrent (I_{SC}=0.26 mA/cm²) and the conversion efficiency of the cell becomes nearly twice larger.

To summarize, we have fabricated and examined a new type of molecular semiconductor based on fullerene/zinc phthalocyanine composites. The comparative studies of photo transport parameters show the advantages of C_{60}-based composites when compared with pure phthalocyanine samples. Using these dyes we have manufactured new types of solid-state cells: In/n-TiO_2(Nb)/ZnPc/Au and In/n-TiO_2(Nb)/C_{60} : ZnPc/Au. We also applied these dyes for fabricating Grätzel-type solar cells. It was shown that the application of C_{60} : ZnPc composites in nanocrystalline solar cells show the improved photoconversion parameters. In case of solid state cell configuration we think that the advantages of C_{60} : ZnPc composites may be explained by improvement of wavelength dependence of series resistance due to the bulk photoconductivty effects.

In conclusion we want to repeat that the wide investigation of new types of organic semiconductors for molecular-based solar cells seem to be one of the most promising directions in solar photovoltaics in the coming century. Now it is enough clear, that solid-state physics, which administrated solar photovoltaics in previous decades, should now extensively cooperate with chemical physics and chemical engineering, because new achievements in the field of solar energy conversion will now appear from this direction. Some examples of the appropriate experimental investigations given above have shown the possible ways of studying and designing the new and promising types of organic photovoltaic cells.

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