

The future of solar photovoltaics: A new challenge for chemical physics*

Oleg Shevaleevskiy

*Solar Energy Conversion Laboratory, Emanuel Institute of Biochemical Physics,
Russian Academy of Sciences, Kosygin St. 4, Moscow 119334, Russia*

Abstract: In recent times, photovoltaic (PV) technologies for solar energy conversion have gained greater recognition. World production of PV cells and modules over the last five years grew at an average of around 40 % a year. The history of modern PV science started more than half a century ago. However, the period that followed exploited the mid-20th century developments in the basics of solid-state physics and semiconductor science. With only a few exceptions, almost no major achievements were attained during a long period of time. The present paper offers an attempt of a critical retrospective look at the history and current progress of solar PV research from a personal viewpoint. It also addresses the current status of research on conventional solid-state PV devices and compares it with the alternative organic and molecular PV systems. The paper briefly describes the potential of new types of organic and mesoscopic dye-sensitized solar cells (DSCs). The paper shows that chemical physics rather than traditional solid-state physics is expected to lead to exciting challenges in the future of PV science.

Keywords: solar cells; energy conversion; photovoltaics; organic semiconductors; fullerenes; heterostructures; chemical physics.

INTRODUCTION

Starting with the energy conversion efficiency of approximately 5 % that first became available in the early 1950s [1], during the following decades the efficiency of laboratory solid-state photovoltaic (PV) cells rapidly reached extraordinary high values in Si-based systems (>20 %) and in GaAs-based heterostructural systems (>30 %). In the historical period that followed, many developed countries endeavored to improve the energy conversion characteristics of PV cells, but these efforts were not marked by a substantial progress in the area of basic sciences. Much of the research and development in PV science was focused on the applied aspects of Si-based and some other devices that were needed for technological and industrial purposes. These activities exploited the scientific achievements of the mid-20th century, but for a long time no new critical discoveries were made in the field of solid-state photovoltaics. One major exception was the development of the double heterostructure concept for AlGaAs-GaAs heterojunctions, developed in the mid-1960s (see the Nobel lecture of Zhores Alferov [2] and the refs. therein) and the application of that concept for the fabrication of a new generation of heterostructural solar cells [3]. Among other achievements, I can mention the investigations on degradation processes in amorphous silicon thin films under photoexcitation. Named the Staebler–Wronski

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effect [4], this concept is important for the processing of thin film amorphous silicon solar cells. Another interesting and promising result concerns the development of the concept for fabrication of a novel type of intermediate-band solar cells (IBSCs) that can utilize photons with the energies below the energy gap of the semiconductor [5,6]. In line with this, quantum dots (QDs) have also been proposed for engineering [7] and manufacturing [8] IBSC devices. These ideas open new possibilities for constructing PV cells based on unconventional wide band-gap materials [9,10] and to convert the energy via sub-bandgap illumination processes [11].

The critical remarks, given above, pertain only to basic studies in the PV area. I do not discuss the remarkable progress of solid-state PV technologies or the recent dramatic decrease in the cost of solar panels but prefer to draw attention to a different problem. The development of PV solar cells and PV panel production is greatly appreciated by the industrial world. However, the features of this development can hide the fact that for a long period the research efforts of a strong PV scientific community were concentrated on the limited tasks and localized applied purposes. As a result, the current situation in solar photovoltaics can be summarized as follows:

- Modern solid-state PV technology is exploiting the research achievements of the period between the 1930s and 1970s.
- The efficiencies of conventional solid-state PV devices have nearly reached their theoretical limits, and further progress in this direction is questionable.
- The next breakthrough in PV solar energy conversion can be expected to come from the area of chemistry and chemical physics rather than solid-state physics.

A notable illustration of the last point is evident in the appearance of a new branch of PV science founded by Michael Grätzel and his coworkers almost 15 years ago [12,13]. In this article, I briefly describe the possibilities that appeared in PV science with the exploration of new organic, mesoscopic, and molecular materials. At the moment, the main challenges for solar energy conversion are being addressed by chemical physics rather than traditional solid-state physics. New molecular materials, nanotechnology, and chemical physics science can bring about new unpredictable achievements that will make the utilization of solar power efficient and economical.

SOLAR PHOTOVOLTAICS: FROM IDEA TO CREATION

The PV effect was first observed by Edmond Becquerel in 1839 [14]. The first studies of the PV effect were undertaken by William Adams and Richard Day in 1876 [15] and by Sir George Minchin in the 1890s [16]. The first true solar cell was constructed around 1883 by Charles Fritts, who used junctions formed by coating selenium with a thin layer of gold [17]. By the 1930s, selenium and copper oxide cells with an efficiency of less than 1 % were being used in light-sensitive devices, such as photometers, for use in photography. Before the World War II era, photovoltaics was accomplished when in 1938 Boris Kolomiets from the Leningrad Physico-Technical Institute developed a thallium sulfide solar cell with a record efficiency of 1.1 % [18].

Today the idea of solar energy conversion on a global scale is widely accepted. However, even in the very early days of the solar photovoltaics, the world's leading scientists expected the energy of the future to come from the Sun. As early as 1931, one of the pioneers in the field of chemical physics, Nikolay Semenov (Nobel laureate in chemistry, 1956), had started emphasizing the importance and future role of solar power as a global energy resource. He wrote: "The use of solar energy is one of the most important problems in energy utilization" [19]. Later he wrote the summary of the global idea of solar energy conversion [20,21]. In the late 1930s, Abraham Ioffe, director of the Leningrad Physico-Technical Institute, submitted to the government a program for constructing, as he called them, "energy roofs", where solar batteries could be used to generate electricity. Nearly 70 years later that dream has been realized with the appearance of such national programs as "100 000 solar roofs" in Germany and "a million solar roofs" in the USA and Japan. In line with this tradition, the founder of heterostructures

and long-time director of the Ioffe Physico-Technical Institute, Zhores Alferov (Nobel laureate in physics, 2000), has been advocating the large-scale production of solar cells for decades. Recently he wrote that the “reliance on the solar-powered industry must be considered not only as a sure choice but also as the only alternative for mankind as a long-term prospect” [22]. It seems that finally we are witnessing a common understanding of solar energy, and it is not surprising to hear Eicke Weber, the director of the Fraunhofer Institute for Solar Energy Systems in Freiburg, Germany, declare that “solar power is in the long term the only kind of energy, which can solve the energy problems” [23]. A bright future is also predicted for solar PV technology by Lawrence Kazmerski, the director of the National Renewable Energy Laboratory, USA [24,25].

The modern history of solar photovoltaics came into force in 1954, when Daryl Chapin, Calvin Fuller, and Gerald Pearson from Bell Telephone Laboratories, USA, invented the first silicon-based PV device; known originally as a solar battery, the device is now called a solar cell [1]. This device exploited the main principles of the p-n junction, which were developed in the early 1950s [26]. The initial energy conversion efficiency of the cell was 6 %. However, it had reached 11 % by 1957 [27] and 14 % by 1960 [28].

As shown in Fig. 1, a review of Si-based solar cell literature, published in the field of natural science and engineering between 1957 and 2007, demonstrates a sustained increase in publications throughout an entire period. In the last two decades, there was even a logarithmic increase in publications (see the inset to Fig. 1). The PV-related publications that deal with Si were chosen because they are particularly informative and relevant: that is, investigations of Si-based PV materials and solar cells fabricated with single-crystalline, polycrystalline, and amorphous layers of Si are still dominant in the PV area. A similar situation has occurred with other types of PV cells, such as GaAs heterostructures, CdTe and CuInGaSe (CIGS) thin film p-n junction solar cells. A detailed and informative literature review of PV cell and module technologies as well as various types of PV devices up to the late 1990s was written by Lawrence Kazmerski [29].

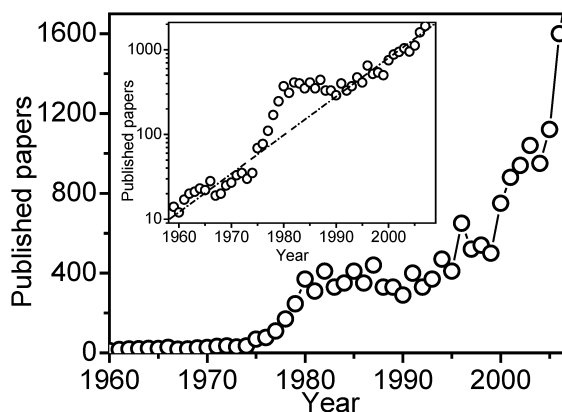


Fig. 1 The year number of articles published on Si-based solar cells in the fields of natural science and engineering over the last 50 years. The inset demonstrates a logarithmic increase of published papers over the last few decades.

Let us now critically examine the real situation with regard to the improvement of PV cell performance, from the early days of modern PV technology in the mid-1950s up to the present. First, I invite you to look at Fig. 2 and make an estimate of the results. Figure 2 shows the average values of solar energy conversion efficiencies for the widely investigated Si-based type of solar cells. The data starts from 1954, the year the modern solar cell was first introduced.

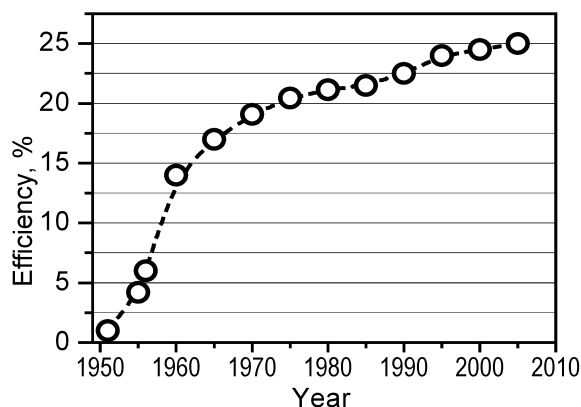


Fig. 2 The evolution of the efficiency of the best laboratory types of Si-based solar cells of the past 50 years.

Figure 2 clearly shows that the mean efficiency of Si-based solar cells has been increased from around 15 % in 1960 to around 25 % in 2007. The question then arises as how this 10 % improvement over 50 years of research should be treated. On the one hand, we see the constant increase of solar cell efficiency, i.e., the most critical parameter of the PV device. On the other hand, the graphics in Figs. 1 and 2 demonstrate a serious discrepancy between the efforts applied and the effect obtained. Note also that the data in Fig. 1 show the number of publications in the relevant scientific journals and, accordingly, reflect the activities of the scientific community. In addition, many solar cell specialists were employed in different companies where they helped improve the performance of cells without necessarily publishing academic papers. To highlight the problem, I previously published a graphic called *Decade Progress* (DP) which shows the energy conversion efficiency for a given type of PV solar cell [30]. The DP parameter represents the annual percentage growth of the energy conversion efficiency of a PV device in relation to a corresponding data of the previous decade. Figure 3 shows the appropriate data for crystalline Si solar cells. These data clearly demonstrate the real relative improvement in the energy conversion efficiency of Si-based PV devices: over the past three decades, the DP parameter (of around 5 %) was rather poor, and no critical progress is expected in the near future.

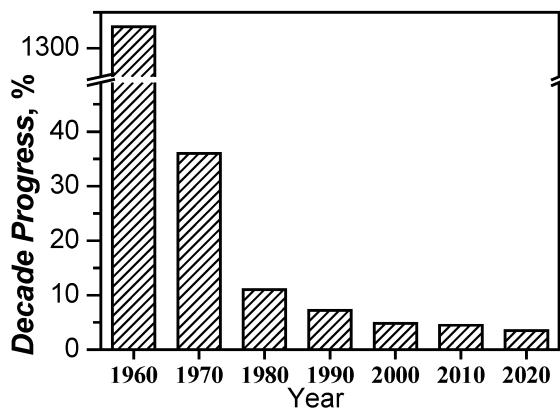


Fig. 3 The DP for Si-based PV solar cells for the period from early 1950s to 2020. The percentage growth in PV device efficiency is shown for each decade.

A similar situation has occurred in the development of other types of traditional solid-state PV solar cells. Analysis of PV devices based on thin films of amorphous Si, CdTe, and CIGS materials shows that the DP parameter has varied between 5 and 10 %, suggesting a poor prognosis for the future.

Our analysis of the progress in PV solar cells could be formally applied to GaAs-based PV solar cells. However, GaAs heterostructures represent a special case of PV devices that can operate perfectly under highly concentrated solar irradiation. Recently, these cells yielded an efficiency value of almost 40 % with around 500-suns concentrator [31,32], and this value is likely to reach around 50 % in the near future.

ORGANIC SOLAR CELLS

Condensed molecular semiconductors have been the subject of extensive research, particularly with regard to the fabrication of organic analogs of solid-state p-n junction solar cells. In 1985, Ching Tang was the first to demonstrate a fully organic solar cell with a power conversion efficiency of around 1 %: for this cell, a perylene pigment was combined with copper phthalocyanine (CuPc) [33]. During the past two decades, double-layer p-n junctions have been successfully fabricated with different types of molecular organic materials. Metal phthalocyanines, including CuPc and zinc phthalocyanine (ZnPc), are among the most widely used materials for constructing efficient organic solar cells. In the mid-1990s, Dieter Meissner and coworkers used organic semiconductor-based Schottky diodes and perylene/ZnPc to fabricate and precisely investigating the carrier production and photoconversion processes in organic solar cells [34,35]. Meissner obtained an organic solar cell with an efficiency exceeding 1 % by using a cell structure with a C₆₀-doped ZnPc layer [36].

Fullerenes C₆₀, which in condensed phase produce a narrow bandgap semiconductor material with n-type conductivity, has attracted much attention as a molecular layer with potential use in the construction of organic p-n junction solar cells. In 1994, the team at our laboratory was the first to construct and investigate the energy conversion characteristics of a fullerene/phthalocyanine double-layer organic solar cell [37]. Fabricated using a vacuum evaporation technique, this type of PV cell has the ITO/ZnPc/C₆₀/Au configuration shown in Fig. 4. Later, Yonehara and Pac reported on the fabrication of a similar type of organic p-n junction solar cell with an energy conversion efficiency of less than 1 %: that type of cell was constructed with an oxotitanium phthalocyanine (OTiPc) layer using OTiPc/C₆₀ configuration [38]. Recently, our laboratory has proposed a theoretical model for describing the behavior of the action spectra of a photocurrent in a double-layer organic PV cell. The model is based on the wavelength-dependent effects of bulk photoconductivity and results are in excellent agreement with the experimental data obtained for ZnPc/C₆₀ solar cells [39,40].

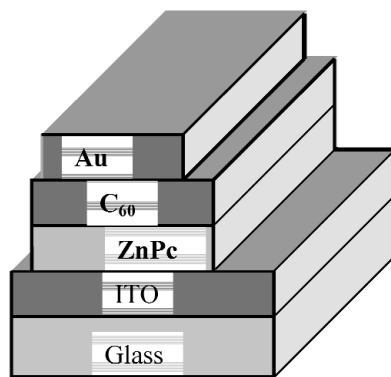


Fig. 4 A double-layer organic p-n junction PV cell with a configuration of ITO/ZnPc/C₆₀/Au [37].

In the early 1990s, Alan Heeger (Nobel laureate in chemistry, 2000), Serdar Sariciftci and coworkers at the Institute of Polymer and Organic Solids of University of California undertook basic studies on the electron transfer between fullerenes and other molecular compounds [41–44]. They investigated the photophysical properties of supramolecular composites consisting of conjugated polymers as electron donors and fullerene as an electron acceptor. They showed that fullerenes, C_{60} , can act as a strong acceptor upon photoexcitation.

Moreover, on the basis of their pioneering works they predicted that the studied processes, which were similar to the primary steps of photosynthesis, could be successfully utilized in conjugated polymer/ C_{60} -based heterojunctions for effective conversion of the solar energy into electricity. As a result, the first PV devices based on MEPPV and C_{60} were fabricated and investigated [42,45]. Subsequently, the highest energy conversion efficiency of 6.5 % was reported for an organic tandem solar cell: that cell was based on polymer-fullerene composites developed by Alan Heeger, Kwanghee Lee, and colleagues [46].

Figure 5 summarizes the evolution of energy conversion efficiencies in organic PV solar cells. The high values of DP parameter in the inset strongly exceed the appropriate values for conventional PV solar cells. Informative reviews on the current status of organic PV technology, including the design of plastic solar cells, can be found in recent publications of Serdar Sariciftci, currently the director of the Linz Institute of Organic Solar Cells at the Johannes Kepler University of Linz, Austria [47,48].

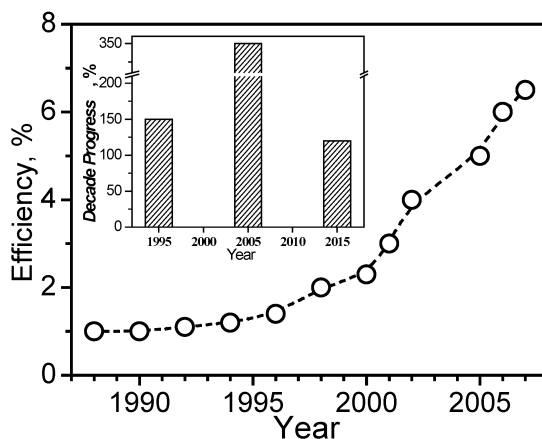


Fig. 5 The evolution of organic PV solar cell efficiencies for the period between 1986 and 2007. The inset shows the DP for this type of PV cells along with a prognosis for the next decade [39].

MOLECULAR PHOTOVOLTAICS AND MESOSCOPIC CELLS

In the 20th century, the PV field was traditionally associated with solid-state materials and solid-state physics. During this historical period, the development, fabrication, and manufacturing of PV devices depended on a limited number of conventional materials, such as crystalline and amorphous Si, as well as semiconductor compounds of the II–VI group (CdTe- and CIGS-based p-n junctions) and the III–V group (GaAs-based heterostructures). In parallel with these activities, chemical scientists, particularly those in the fields of photochemistry, electrochemistry, and chemical physics made considerable progress in developing an alternative generation of solar energy conversion PV devices. The pioneering works of Heinz Gerischer [49], Helmut Tributsch [50], Rüdiger Memming [51], Gennadiy Komissarov [52], Viktor Benderskii [53], and many others established the foundation for the new achievements that soon followed.

The early 1990s were marked by the emergence and successful development of the first competitive solar cell which exploited the principals and materials that differed from traditional physics. Michael Grätzel and coworkers from the Swiss Federal Institute of Technology, Lausanne, designed nanocrystalline dye-sensitized solar cells (DSCs), also called mesoscopic solar cells: this design was a complete departure from the principals of classic solid-state cells [13,54]. In the proposed construction, the mesoscopic morphology of an interpenetrating network of nanoscale titanium dioxide (TiO_2) particles was covered with a monolayer of sensitizing dye molecules. At the moment the efficiency of the DSCs reached a value of around 12 % [55], DSCs were competitive with the widely known amorphous Si PV devices.

Figure 6 illustrates the evolution of DSC cell performance, and the inset shows the DP for this type of PV cell over the last two decades with a prognosis for the future. As can be seen, the DP parameter of the DSCs (DP ~ 60) appears to be an order of magnitude higher than the DP parameter of conventional solid-state PV cells (compare with Fig. 3).

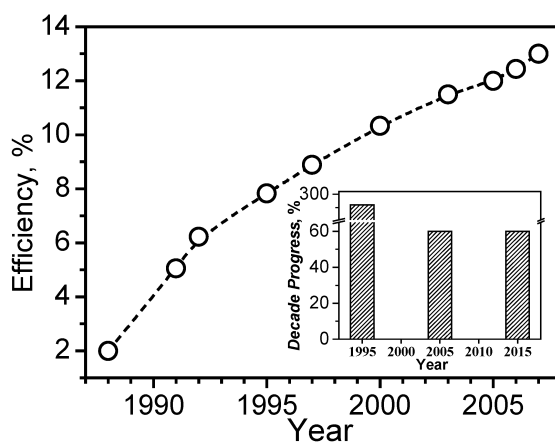


Fig. 6 The increase of DSCs efficiencies over a 20-year period. The inset shows the DP for this type of PV cells along with a prognosis for the next decade [54].

The main operating principles of DSCs are based on photoexcitation of the individual dye molecules attached to the surface of nanoporous net structure of a wide bandgap material. Excellent illustrations of the process can be found in the publication of Michael Grätzel [54,55]. The efficiency of the DSC is related to the dye's capability of injecting a photoexcited charge carrier into the conduction band of a semiconductor nanoparticle and the subsequent migration to the front electrode. DSCs with newly developed sensitizers such as N3 and Black dye [55] can generate a photocurrent with nearly unit quantum efficiency in the visible spectrum range of 400–800 nm. The further improvement of DSCs concerns such factors as technical performance, cost, and long-term stability. From a scientific point of view, the DSC efficiencies can reach 15 % and higher, enabling these types of PV devices to be highly competitive with the other types of conventional thin film PV cells described above.

The factor that limits DSC device performance is the poor optical absorption characteristic in the near-infrared region. Due to this limitation, short-circuit currents under one sun illumination fail to exceed a value of around 20 mA/cm². In the near future, dyes may be synthesized with perfect light absorption characteristics in both the visible and infrared regions. Such sensitizers, however, may not have a wide range of commercial applicability on account of their cost and possible high sensitivity to even small traces of natural humidity. Thus, considerable effort has gone into finding alternative dye materials [56]. Unfortunately, the currently available sensitizers with stable properties possess poor absorption characteristics, resulting in low conversion efficiencies.

TANDEM NANOCRYSTALLINE DYE-SENSITIZED SOLAR CELLS

The known way of improving the efficiency of the conventional solid-state PV devices is the fabrication of tandem structure. However, the construction of DSCs differs from construction of the conventional solid-state devices, and the tandem schemes used in solid-state p-n junctions and heterostructural solar cells cannot be used in DSCs.

The realization of tandem scheme for DSCs promises to increase the device efficiency. Furthermore, such a construction can be based on several different dyes with comparatively narrow absorption bands. It enables less expensive and more stable types of organic materials to be used. Recently in our laboratory we have first developed a novel type of tandem DSC (TDSC): it has two anodes sensitized with different dyes that possess overlapping optical absorption characteristics [57]. Figure 7 shows the operating principals of TDSCs. After penetrating the first thin dye-sensitized layer where it absorbs UV and visible-light photons, the TDSC can utilize the remaining near-infrared portion of solar irradiation by means of the next dye-sensitized layer, which is sensitive to the appropriate part of the solar spectrum.

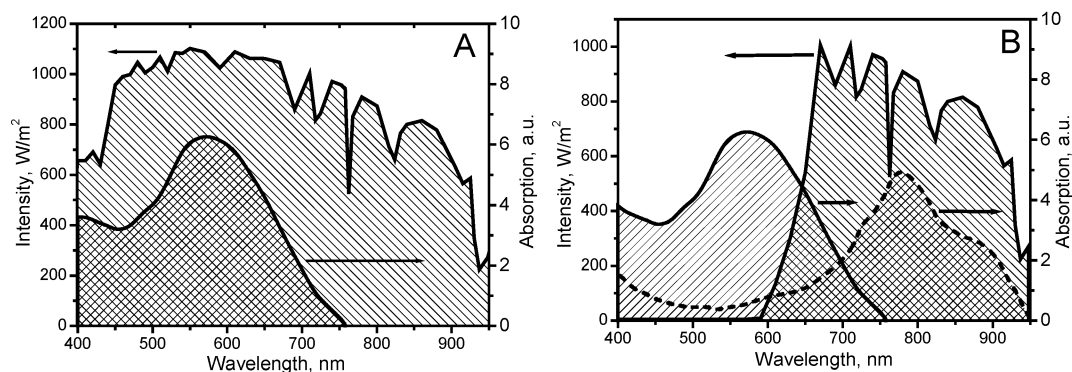


Fig. 7 An illustration of light absorption in a TDSC and the intensity of the solar spectrum under terrestrial illumination. The first electrode (A) absorbs light in a visible region and the remaining near-infrared photons can be utilized by the next dye-sensitized electrode (B) (See the schemes in Figs. 8 and 9).

Figure 8 shows the TDSC scheme that was fabricated and characterized in our laboratory. Note that in our first attempts to construct the TDSC system we applied a Pt grid as an intermediate counter electrode between the dye-sensitized TiO₂ layers [57]. The results are promising in terms of improvement in the DSC energy conversion parameters. In our experiments, we subsequently replaced the intermediate Pt grid cathode with a more transparent glass substrate covered on both sides with a thin nanosized layer; the layer of Pt was prepared with the aid of specially designed coating technology. As a result, we were able to achieve about a 1.5-fold increase in infrared solar irradiation of the bottom DSC cell.

TDSCs are very promising in terms of improving DSC energy conversion characteristics. I would also like to mention that in the first world attempt at constructing a TDSC the anode and cathode were both dye-sensitized, with p-type and n-type molecular materials. This interesting scheme, which was proposed and studied in the laboratory of Sten-Eric Lindquist at Uppsala University [58], did not utilize a metallic counter electrode and had poor energy conversion efficiency. To the best of my knowledge, no further attempts appear to have been undertaken in this direction.

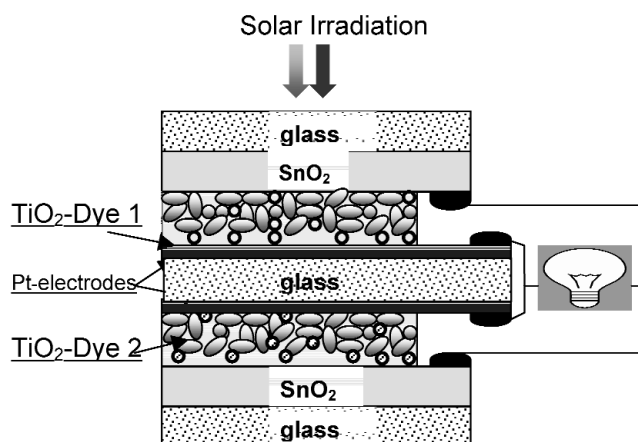


Fig. 8 The schematic construction of our proposed tandem nanocrystalline DSC with two anodes and an intermediate Pt cathode [57].

Michael Dürr and coworkers from Sony International GmbH, Stuttgart, reported very interesting results. As shown in Fig. 9, they did not use a face-to-face TDSC scheme, as was proposed in our experiments, but preferred a stacked design of two specially prepared DSCs [59]. Finally, the latest achievement in constructing nanocrystalline-based tandem solar cell with the improved parameters was recently reported by Michael Grätzel's group [60]. They demonstrated that a PV tandem cell comprising a nanocrystalline DSC as a top cell for high-energy photons and a CIGS cell for low-energy photons as a bottom cell could reach 15 % energy conversion efficiency.

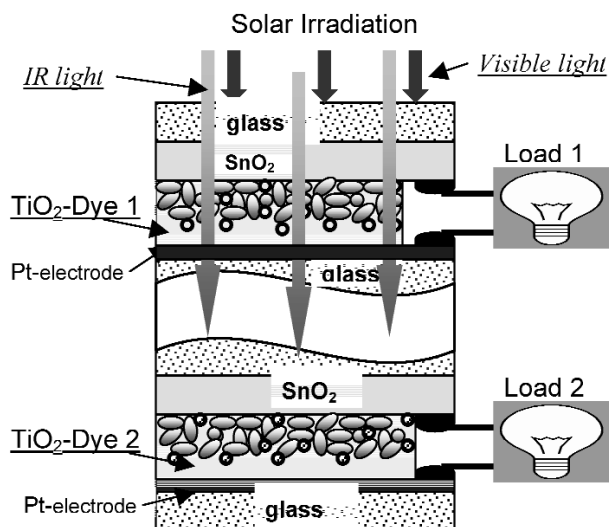


Fig. 9 Schematics of a tandem nanocrystalline DSC with the alternative configuration proposed by M. Dürr and coworkers [59].

The development in the DSC field has been exciting. Recent results have boosted the prospects for a new generation of competitive PV solar cells. I believe that this example should also demonstrate the advantages of new PV scientific directions in the chemical sciences and new achievements in nanotechnology.

CONCLUSION

A retrospective look at the history and current progress of solar PV research, given from my personal viewpoint, highlighted new fields of solar photovoltaics that require serious attention from the scientific community. To end this article, I would like to again return to the starting idea, where I mentioned that the exciting challenge for future achievements in the utilization of solar energy can be found more with chemical physics rather than with traditional PV solid-state physics. The behavior of the DP parameter, which was examined for different types of PV devices, gives a clear indication of the future directions of PV science.

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