



Session 1: Paper 3

ABSTRACT

ORGANIC PHOTOVOLTAICS: UTILIZATION OF COLORANTS
IN MOLECULAR, AMORPHOUS & CRYSTALLINE STATES

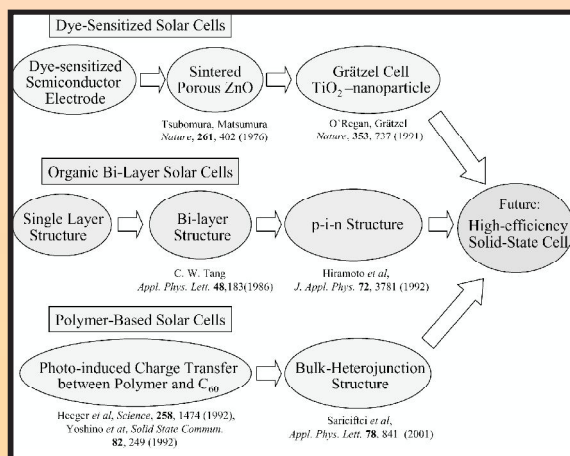
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Three types of organic photovoltaics are reviewed. They are dye-sensitized solar cells, organic solid-state solar cells, and polymer-based solar cells. Dye-sensitized solar cells have improved drastically and efficiency reached as high as 10%. The drawback of solar cells is that they include liquid electrolytes. To solve the problem, utilization of solid-state conductors or gelled electrolytes has been studied. Organic solid-state photovoltaics have a long history. However, the efficiency had been low until the invention of the organic bilayer structure: they are made of electron-donor and acceptor-materials. This structure is useful because excitons are separated into carriers at high efficiency at the interface. Polymer-based photovoltaics are improving & seem to be most promising. They are made of a mixed layer containing a conducting polymer and a fullerene derivative. The two components are separated & form interface which is widespread over the layer. This structure is very useful for generating carriers from excitons. The control of the mixed structure is the key to further improve efficiency. Finally, a new method for making an effective mixed structure developed in our group is reported. When microcrystalline & amorphous materials were stacked and annealed, the amorphous material penetrated into grain boundary of microcrystalline material and formed an ideal bulk-heterojunction structure.

Introduction

Chemical energy accumulates on Earth through the photosynthesis by green plants, in which chlorophylls are used as the photoactive materials. However, stored energy is decreasing due to consumption of fossil energies at an accelerating rate. However, as a result of invention of solar cells, human beings have acquired the method for utilizing solar light as an alternative to conventional energy sources. The first practical solar cell was invented in 1954. Through innovations and scaling-up of production, the price of solar cells has decreased dramatically. However, the cost performance of solar cells is much lower than that of conventional power generation methods such as thermal or nuclear power generation. Solar cells are mostly made of single-crystalline or multicrystalline silicon. Such cells need a complicated process in their fabrication and room for reducing the cost is limited. In addition, currently, as a result of rapid expansion of the production of solar cells, insufficient supply of silicon wafers becomes a serious problem. Hence, the development of new type solar cells based on alternative materials becomes a current topic. There are some candidate materials for low-cost solar cell: they are compound

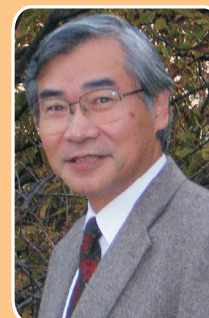
semiconductors and organic materials. The performance of the cells made inorganic compound semiconductor materials is high. However, the compound semiconductors are made of harmful elements (Cd, As) or scarce elements (In, I). On the other hand, solar cells made of organic materials are safe and environmentally benign, and organic solar cells are recognized as the state-of-the-art replica of photosynthesis of plants. However, efficiency of organic solar cells is low and many efforts are being made to improve it. There are three approaches in the study on organic solar cells: dye-sensitized solar cells, organic bi-layer solar cells and polymer-based solar cells, as shown in Fig. 1.



Dye-sensitized Solar Cells (Use of Colorants in Molecular State)

Dye-sensitized solar cells (DSSCs) are most successful among the organic solar cells. They were invented through the studies of dye-sensitization effect on photoresponses of wide bandgap semiconductors.

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The first DSSC was fabricated by Matsumura et al. in 1976. The cell was made of porous ZnO as a semiconductor electrode, Rose Bengal as a sensitizing dye, and an iodide/triiodide (I⁻/I₃⁻) redox couple as a mediator. Its energy conversion efficiency was about 1%. In 1991, O'Regan and Grätzel modified this system and improved the efficiency using porous TiO₂ as an electrode and a Ru-complex as a sensitizer. The energy conversion efficiency of their cell was about 7.5%, and its efficiency has reached 10% or more. The mechanism of photocurrent generation in DSSCs is as follows: (1) photoabsorption and excitation of dye molecules, (2) electron injection from photo-excited dye molecules into the conduction band of an inorganic semiconductor, (3) flow of an electrons through an external circuit, (4) reduction of a redox couple, such as I⁻/I₃⁻, included in the electrolyte, and (5) supply of an electron to an oxidized dye molecule, which has lost an electron by injecting an electron into the semiconductor, from a redox couple. As a result of improvements in these processes, the photocurrent density of DSSCs has reached 12 mA/cm², which is comparable to that of solar cells based on amorphous Si. A most serious drawback of DSSCs is that a liquid electrolyte is included in the cell. This sometimes causes a problem in the stability of the cell. To overcome this problem, the use of solid electrolytes has been proposed. Unfortunately, however, the energy conversion efficiency of the cells fabricated with these solid state substances is lower than that made with a liquid electrolyte, owing mainly to the low ionic conductivity of the solid-state electrolyte and poor interfacial contact at electrode/solid-state electrolyte interface.

Organic Bi-layer Solar Cells (Use of Colorants in Crystalline State). In 1986, Tang reported efficiency of 0.95% organic solar cells made of stacked solid-state organic layers. Although the efficiency was still low, the efficiency was about 100 times higher than the previous organic solid state solar cells, and opened a way to organic solid-state solar cells. The organic bilayers used by Tang were made of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PV). The reasons for the improvement in the efficiency are as follows: (1) Increased number of absorbed photons, which was achieved by the combination of two organic materials with different absorption regions, (2) improvement in a fill factor due to the adoption of organic materials with high conductivities, (3) enhanced efficiency of charge-separation from excitons. Among these factors, the last one contributed the most to the improvement of the performance. Before Tang's report, organic single-layer solar cells had long been investigated. However, their energy conversion efficiency was very low (0.1% or lower), except for a cell made of merocyanine, which showed an efficiency of 0.7%. In organic solar cells, in contrast to inorganic semiconductors, binding energy of excitons is usually strong and excitons are hardly split into charge carriers by the inner electric field developed by built-in potential of the cells. However, by combining an electron donor material and an acceptor material, the excitons are efficiently separated into charge carriers at their interface as a result charge-transfer reaction between those two molecules, and the efficiency is improved. To further improve the efficiency, the interfacial structure should be improved because the exciton diffusion lengths in organic layers are very short.

Polymer-Based Solar Cells (Use of Colorants in Amorphous State)

Solid-state organic solar cells have also been made of conductive polymers for about two decades. They originated from the discovery of efficient photo-induced charge transfer reaction between poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), which is a derivative of poly(p-phenylene vinylene) (PPV), and fullerene (C₆₀) that is blended in MEH-PPV. This phenomenon was first reported in 1992 by Heeger's group and Yoshino's group. By utilizing this phenomenon, Sariciftci et al. fabricated a bulk-heterojunction structure solar cells using poly[2-methyl-5-(3',7''-dimethyloctyloxy)-p-phenylene vinylene] (MDMO-PPV) and a soluble fullerene derivative 1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C₆₁ (PCBM). The energy conversion efficiency of bulk-heterojunction solar cells is now reaching about 5% by replacing MDMO-PPV with poly(3-hexylthiophene) (P3HT), which has a high hole mobility. The principles of charge generation in bulk-heterojunction solar cells based on polymers are same as those of organic bi-layer solar cells. In polymer bulk-hetrojunction solar cells, the polymers act as an electron donor and fullerene (or its derivatives) acts as an electron acceptor. The most attractive advantage of the bulk-heterojunction structure is that the organic/organic interface is widespread in the blended layer. As a result, excitons generated in the organic layer easily reach the interface. This allows many excitations formed in the organic layer to separate into carriers at the interface. Easy fabrication of polymer-based solar cells is another important advantage of the polymer-based solar cells because the polymer are fabricated by a printing method without using a vacuum process.

Formation of a New Bulk Heterojunction in Solid-State Organic Solar Cells (Use of Crystalline and Amorphous Materials)

Although the polymer-based solar cells seem very attractive, the control of the bulk heterojunction structure is rather difficult. The two components in the polymer layer should be separated and form respective channels for electrons and holes. The construction of such a structure has been difficulty. However, we recently developed a new method, in which a microcrystalline material and an amorphous material, which were deposited by vacuum sublimation. The microcrystalline material we used was fullerene (C₆₀) and the amorphous material was an aromatic amine (TPD). When the stacked layer was annealed at temperatures above the glass transition temperature of TPD, the TPD molecules wedged into the grain boundaries of C₆₀, which formed columnar grains normal to the electrodes. The structure formed was an ideal bulk heterojunction. However, the efficiency was 1.1%, which was determined by the poor photoabsorptivity of the materials. If we can successfully replace the materials with those having stronger photoabsorption, the efficiency will increase drastically.