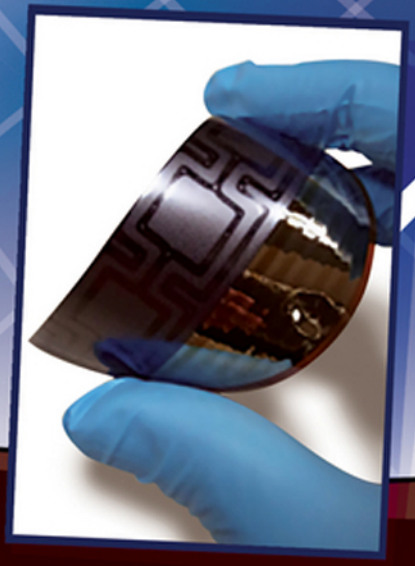
Advances in Solar Cetll Materials and Storage

Printable Solar Cells



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Printable Solar Cells

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Advances in Solar Cell Materials and Storage

Series Editors: Nurdan Demirci Sankir and Mehmet Sankir

Scope: Because the use of solar energy as a primary source of energy will exponentially increase for the foreseeable future, this new series on Advances in Solar Cell Materials and Storage will focus on new and novel solar cell materials and their application for storage. The scope of this series deals with the solution-based manufacturing methods, nanomaterials, organic solar cells, flexible solar cells, batteries and supercapacitors for solar energy storage, and solar cells for space.

Submission to the series: Please submit book proposals to Nurdan Sankir at dnurdan@yahoo.com

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Part IV Inorganic Materials and Process Technologies for Printable Solar Cells

Preface

The sun provides energy for the immense diversity of life forms found on earth. Conversion of this energy into electricity by means of photoelectric effect with an acceptable efficiency and price may provide all the energy needs for humankind. New materials and manufacturing techniques are key issues for increasing the efficiency and reducing the cost of photovoltaic devices. Hence, this book series focuses on materials and manufacturing techniques as well as the storage applications for solar cells. The first volume of the series, *Printable Solar Cells,* compiles the objectives related to the new materials from solution processing and manufacturing techniques for solar cell applications. The chapters are written by distinguished authors who have extensive experience in their fields. A broader point of view and coverage of the topic are provided due to the multidisciplinary contributor profile, including physics, chemistry, materials science, biochemical engineering, optoelectronic information, photovoltaic and renewable energy engineering, electrical engineering, mechanical and manufacturing engineering. Therefore, readers will absolutely have a chance to learn about not only the fundamentals but also the various aspects of materials science and manufacturing technologies for printable solar cells. The book contains information which could be presented in energy and materials science-related courses at both undergraduate and graduate levels.

This book is organized into four parts. Part I (Chapters 1–5) covers the organic and inorganic hybrid materials and solar cell manufacturing techniques. In this section, descriptions of the operational principles and types of hybrid solar cells, physical and chemical principles of film formation by solution processes, polymer/quantum dot hybrid solar cells, hole transporting layers and solution processing techniques are described. Part II (Chapters 6–8) is devoted to organic materials and processing technologies. Details of the spray-coating technologies and the organic materials used in these methods are given in this section. Part II also demonstrates the key features of interface engineering for printable organic solar cells. This phenomenon is very important to increase the device performance and decrease the production cost of printable solar cells. Finally, structural,

optical, electrical and electronic properties are presented as well as the fabrication parameters of thin films of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), which is one of the most commonly used organic polymers for photovoltaic applications. The main focus of Part III (Chapters 9–11) is perovskite solar cells, which is a new and promising family for photovoltaic applications. Working principle, device architectures, deposition methods and stability of the perovskite solar cells are given in this section. In addition, the optical properties and photovoltaic performance of organometal trihalide perovskite absorbers are also addressed. Finally, information on dye-sensitized solar cells, the inkjet printing process and modules based on advanced nanocomposite materials are described.

This book concludes with Part IV (Chapters 12–15), inorganic materials and process technologies for printable solar cells. Structural, optical and electrical properties of kesterites, device architecture and deposition strategies are extensively summarized in this part. As described in Part III, tremendous progress has been made in perovskite solar cells over the last few years and the efficiency of these devices has exceeded 20%. Inorganic hole transport materials for transition metal-oxide perovskite solar cells, including Cu_2O, CuSCN, $CuInS_2$ and Cu_2ZnSnS_4, are discussed in Part IV. These materials inevitably affect the device performance and stability. Electrode materials and photonic crystals for solar cell applications are the last two topics covered in this book. Top and bottom electrodes used in thin film solar cells implement the transmission of sunlight through the absorber layer and the electron collection. In other words, optical, electrical and mechanical properties of the electrode materials are important to ensure good photovoltaic performance as well as compatibility with substrate materials and printing techniques. In this respect, transparent conjugated polymers, carbon-based nanomaterials, metallic nanostructures and ultrathin metal films are summarized in Part IV. Finally, new and promising developments of photon management in solar cells based on photonic crystals are given. Fundamentals of photonic crystals, fabrication strategies and utilization of these materials in photovoltaic devices as reflector and absorber layers are summarized in the last section.

In conclusion, we would like to emphasize that the first volume of the Advances in Solar Cell Materials and Storage series provides an overall view of new and highly promising materials and their fabrication technologies for printable solar cell applications. In addition, the materials property–manufacturing method–photovoltaic performance relationship of the organic, inorganic and hybrid structures have been extensively discussed in this book. Therefore, readers from diverse fields, such as chemistry,

physics, materials science and engineering, and mechanical and chemical engineering, will definitely take advantage of this book to comprehend the impacts of the new materials and solution-based manufacturing on the inevitable rise of solar power.

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Part I

HYBRID MATERIALS AND PROCESS TECHNOLOGIES FOR PRINTABLE SOLAR CELLS

1

Organic and Inorganic Hybrid Solar Cells

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Abstract

The dream of conversion of sunlight into electricity via cheap and cost-effective routes has led researchers to develop the so-called third generation organic and hybrid solar cells in the last two decades. The hybrid solar cells combine the advantages of the organic semiconductors, such as easy tuning of the chemical and physical properties and desirable thin film-forming properties, with that of the inorganic semiconductors such as well-defined electronic structure, high charge mobilities and thermal stabilities. Many research studies have been performed to find the ideal organic/inorganic hybrid material combinations and device architectures, which has resulted in significant progress being achieved. During the last three years a new family of photovoltaic compounds called "perovskites" have been the focus of attention. Such organic/inorganic hybrid solar cells based on ionic salts of organic compounds with lead halides show efficiencies up to 22%. In this chapter, we will analyze the progress of research in hybrid solar cells, and the limitations and routes to be followed for their further improvement will be discussed.

***Keywords*:** Organic solar cells, hybrid solar cells, polymer solar cells, conjugated polymers, inorganic nanoparticles, third generation photovoltaics, bulk heterojunction solar cells, conducting polymers

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1.1 Introduction

The need for the supply of clean energy is one of the challenges of our decade since the conventional routes used until recently as a source of energy, such as coal and oil, are limited and will run out [1]. Environmentally friendly, cost-effective, efficient solutions are of great interest to solve the clean energy supply problem. Solar cells which convert sunlight into electricity are foreseen as a viable tool to produce electricity from the sun. Solar energy is clean, abundant and cost-free.

Solar cell technologies are traditionally divided into three main categories which are called generations. The first generation solar cell technology involves techniques which are cost and energy intensive [2]. They include single- and multi-crystal silicon solar cells which are produced on a wafer bearing either only one crystal or crystal grains. The recent power conversion efficiency (PCE) of a single crystal silicon solar cell is 25% whereas a multicrystal silicon solar cell exhibits a PCE of 21% [3].

Second generation solar cells consist of a-Si thin films, mc-Si, CdTe, CIS and CIGS. The PCEs of CIGS (minimodule) is 18% whereas for CdTe (cell) PCE is recorded as 21% [3]. For a-Si and mc-Si thin-film solar cells, PCEs are 10% and 11% respectively [3]. Although the second generation solar cells are less efficient than the first generation solar cells, their costs are lower; on the other hand, they are more likely applicable to the building integrations and are more compatible with flexible substrates [2].

Third generation solar cells include nanocrystal solar cells, organic/hybrid solar cells and dye-sensitized solar cells and perovskite solar cells. Third generation solar cells are novel technologies which are cost and energy effective, suitable for flexible substrates and can be easily integrated. Despite many advantages, their comparably lower efficiencies and stability issues stand as major drawbacks towards their commercialization. However, a new family of photovoltaic compounds called “perovskites” have been the focus of attention and if the stability issues of these new types of photovoltaics can be addressed and solved they will be candidates to compete with the other PV technologies which have already taken their place in the PV market.

In this chapter, among the three different generations of solar cells, we will mostly focus on the organic/inorganic hybrid solar cells which belong to the third generation group and will analyze the progress of research, their limitations and will discuss the routes to be followed for their further improvement.

1.2 Organic/Inorganic Hybrid Solar Cells

1.2.1 Introduction to Hybrid Solar Cells

Although first and second generation solar cells have received considerable attention due to their high power conversion efficiencies, the high production costs and availability problems related to the materials, such as indium (In), continue to be the main issues to be overcome to meet the recent demand [4]. The advantages such as the low cost, flexibility, easy production and scalability offered by organic solar cells put this field somewhere between applied science and engineering research [5]. There has been a tremendous increase in the power conversion efficiency of solution-processed organic solar cells from 2.5% [6] to ca. 11% [7] within only 14 years. However, stability issues due to the sensitivity of organic materials to oxygen and moisture still remain to be solved. Inorganic semiconductors have high charge carrier mobilities and also good chemical stabilities. The idea of combining the advantages of both organic and inorganic semiconductors has led to the birth of the concept of hybrid solar cells. A hybrid solar cell consists of both organic and inorganic semiconductors in which the advantages, such as high solubility, good film formation, flexibility and low cost, offered by organic semiconductors are combined with the advantages, such as high charge carrier mobility and good stability, offered by inorganic semiconductors. Many different concepts have been realized to fabricate hybrid solar cells. Their power conversion efficiencies are still lower than their inorganic counterparts. However, the parameter space to choose from is large and only a fraction of possible combinations have been realized [8]. Further research and development strategies for optimization of different types of hybrid solar cells will be discussed below.

1.2.2 Hybrid Solar Cells

1.2.2.1 Operational Principles of Bulk Heterojunction Hybrid Solar Cells

Hybrid solar cells consist of blend films of inorganic semiconductors and conjugated polymers sandwiched between two metal electrodes (see Figure 1.1). The difference in the organic solar cells is the use of inorganic semiconductors in the device configuration. Therefore, the operational principles of hybrid solar cells is very close to organic solar cells and consists of the following consequent steps [4]:

i. Absorption of photons;
ii. Generation of excitons within the active layer;

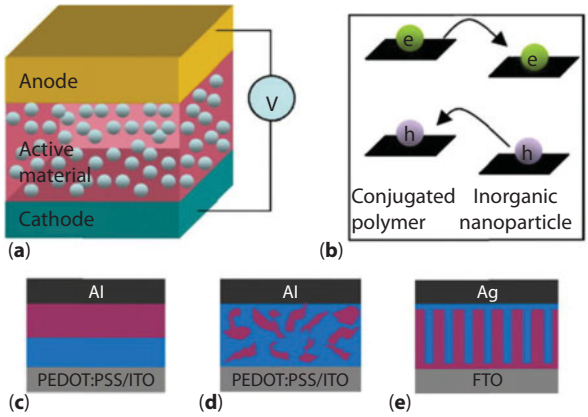

Figure 1.1 General structure of a hybrid solar cell: (a) representation for working principle of polymer/nanoparticles, (b) energy level diagram and charge transfer process, (c) bilayer, (d) bulk, and (e) ordered heterojunction. (Reprinted with permission from [4]; Copyright 2014 © Elsevier)

iii. Diffusion of excitons;
iv. Dissociation of excitons;
v. Transport of charges to the appropriate electrodes;
vi. Collection of holes and electrons at the electrodes.

The photoactive layer of the bulk heterojunction hybrid solar cells consists of inorganic semiconductor nanoparticles and conjugated polymers. Inorganic semiconductors have been widely used to transport the electrons (as acceptors) whereas conjugated polymers have been used to transport the holes (as donors). Organic materials may have a donor or an acceptor character. Molecular materials that have a low ionization potential and thus can easily donate an electron are denoted as electron donors. Materials that have a high electron affinity and thus can easily take up an electron are denoted as electron acceptors. They can be efficient electron or hole transporters, which is determined by intermolecular orbital overlap in the solid state [9]. They can also be both hole and electron transporters. Recently, [6,6]-phenyl-C_{61}-butyric acid methylester (PCBM) has been demonstrated to have a similar hole mobility to its electron mobility. An ideal donor should permit efficient hole transport, that is, p type, whereas an ideal acceptor should permit efficient electron transport, that is, *n* type. In the case of organics, the *n*- and *p*-type definitions refer to the fact that *n*-type semiconductors are good electron conductors, whereas *p*-type ones are good hole conductors. Therefore, an

alternative definition for organic semiconductors is donor for the *p* type and acceptor for the *n* type. In organic and hybrid solar cell terminology, the donor gives electrons to the acceptor [9]. In the case of inorganic semiconductors, for example, *n*-type silicon is achieved by introducing donor impurities. Doping mechanisms in organic and inorganic semiconductors are totally different. Most semiconducting polymers are hole conductors as donor polymers. However, they can also be electron conductors.

For a favaroble charge transfer the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the inorganic nanoparticles and the conjugated polymers should be chosen properly. The LUMO and the HOMO of the conjugated polymers should lie above the conduction and valence band edges of the inorganic nanoparticles, respectively, for an efficient charge transfer. In this case, the electrons are transferred from the LUMO level of the conjugated polymer to the conduction band of the inorganic semiconductor whereas the holes are transferred from the valence band of the inorganic semiconductor to the HOMO level of the conjugated polymer [4]. The photoexcitations in organic materials lead to bound electron-hole pairs, which are called excitons. Excitons have to be separated into free charge carriers within their lifetime. Otherwise, they may recombine, which is not a preferential step for the solar cell operation. Exciton diffusion length for the organic materials is within the range of 5–10 nm. A p-n junction is used to separate the excitons into free charge carriers. In the bulk heterojunction concept, by blending the *p*- and *n*-type semiconductors, p-n junction is distrubuted throughout the bulk of the film so that each exciton reaching the junction can be separated into free charge carriers, which is called exciton dissociation. Distributing the p-n junction throughout the film increases the probability of exciton dissociation within the lifetime of the excitons and also within the distance of exciton diffusion length. This is one of the reasons why the short circuit current density, and thereby the power conversion efficiencies of bulk heterojunction solar cells, is higher than that of bilayer heterojunction solar cells which consist of individual bilayer films of *n*- and *p*-type semiconductors sandwiched between two metal electrodes.

As previously mentioned, blend films of inorganic semiconductors and conjugated polymers are sandwiched between two metal electrodes. As substrates, conducting electrodes (for example, glass or plastic covered with ITO) are used. As a transparent conductive electrode, ITO (indium tin oxide) allows light to pass through the cell. On the transparent conducting substrate, PEDOT:PSS, poly(3,4-ethylene-dioxythiophene) doped

with polystyrene-sulphonic acid, is commonly coated from an aqueous solution. This PEDOT:PSS layer improves the surface quality of the ITO electrode (reducing the probability of shorts) and facilitates hole injection/extraction. Furthermore, the work function of this electrode can be changed by chemical/electrochemical manipulation of the PEDOT layer [10]. A photoactive layer consisting of blends of conjugated polymer and inorganic nanoparticles is cast on top of the PEDOT:PSS coated ITO substrates from solution. The choices for the second metal electrode have been aluminum (Al), silver (Ag), gold (Au), etc. The choice of the metal should ensure that an ohmic contact is formed between the metal and the semiconductor.

1.2.2.2 Bulk Heterojunction Hybrid Solar Cells

Initial efforts to fabricate hybrid solar cells started with mimicking the bulk heterojunction concept studied in organic solar cell research. The bulk heterojunction concept in organic solar cells has been realized by blending two organic semiconductors, one of which is an electron donor and the other an electron acceptor. The same concept has been applied to hybrid solar cells by blending inorganic semiconductors as nanoparticles with conjugated polymers.

The advantages of this concept can be summarized as following:

1. Inorganic semiconductors may have high absorption coefficients and high charge carrier mobilities [11].
2. Band gap of the inorganic materials can easily be tuned via synthetic routes using the size quantization effect. Therefore, inorganic nanoparticles absorbing at different wavelengths can be available [11].
3. The availability problem of acceptor materials, as is the case in organic solar cells, may be overcome by controlling the *n*- and *p*-type doping levels of inorganic nanoparticles via synthetic routes.

In the initial studies of hybrid solar cells, inorganic nanoparticles took the place of the fullerene-based acceptors which have been widely used in organic solar cells. The synthesis of fullerenes is rather energy intensive and difficult. On the other hand, the colloidal synthesis of inorganic nanoparticles is comparably easier. Also, the absorption range of inorganic nanoparticles is wider than that of fullerenes, which in turn means that thinner devices can be fabricated.

The CdSe nanocrystals were the first nanocrystals studied in hybrid solar cells. They have absoprtion at a spectral range between 300 nm to 650 nm [12].

One of the first studies on hybrid bulk heterojunction solar cells using CdSe nanoparticles was published by Huynh *et al.* [13]. They demonstrated that hybrid solar cells could be fabricated using semiconductor nanorods together with polymers. The control of the nanorod length enabled efficient electron transport through the device and also the tunability of the nanorod radius led the authors to tune the bandgap, which in turn helped the overlapping between the absorption of the nanorods and the solar emission spectrum. They achieved a PCE of almost 2% under air mass (AM) 1.5 global solar conditions [13].

The main success behind the efficient hybrid bulk heterojunction solar cells using nanocomposites is the ability of the dispersion of the nanoparticles into the polymer matrix to create a high interfacial area between two materials for a better charge transport [14]. Organic ligands are adsorbed onto the surface of the nanoparticles which passivate the surface for stability and make them soluble. Although organic ligands are indispensible for the nanoparticles, dispersion of nanoparticles into the polymer matrix is highly affected by the existence of these ligands and effective dispersion of the nanoparticles is highly necessary. It has been demonstrated by Huynh *et al.* that the use of binary solvents is effective in helping the dispersion of nanoparticles within the polymer matrix [14]. It has also been demonstrated that the heat treatment furthers the removal of the ligand and increases the photocurrent and thereby the power conversion efficiency.

Later studies revealed that the choice of the morphology of the CdSe, whether being either nanoparticle, nanorod or tetrapod, played a role in the overall efficiency of the hybrid solar cells. Greenham *et al.* demonstrated that hybrid bulk heterojunction solar cells using blends of branched CdSe nanoparticles and polymers gave a better photovoltaic performance as compared to the hybrid solar cells fabricated from nanorod/polymer blends. They achieved a PCE of almost 2% under AM 1.5 illumination [15]. They have shown that the electron extraction in the devices employing 3D CdSe tetrapods is more efficient as compared to the devices employing 1D nanorods and added that the control of the nanoparticle shape in 3D CdSe tetrapods helps to control the morphology and the efficiency of the devices comprising nanoparticle/polymer blends.

Besides the morphology of the CdSe nanoparticles the choice of the polymer is also important for the overall performance of hybrid solar cells. The use of a low band gap polymer (PCPDTBT) and CdSe tetrapod blend in the hybrid bulk heterojunction devices led to a PCE over 3%. The

PCPDTBT, which is a low band gap polymer offering a broad absorption spectrum, was helpful for efficient photon harvesting. Therefore, the idea of making use of the better overlap of the polymer absorption and the solar emission spectrum led to a better performance [16].

Another choice of inorganic semiconductor used in hybrid solar cells has been CdS nanorods. Devices comprising multiarmed CdS nanorods and MEH-PPV polymer exhibited a PCE over 1% under AM 1.5 illumination. The improved efficiency of the devices was attributed to the use of pyridine as a solvent instead of HDA. Pyridine, which was attached to the surface of CdS nanocrystals during refluxing, improved the solubility of CdS nanocrsytals and also the dispersion in MEH-PPV film. As a result of an efficient charge transfer and exciton dissociation, power conversion efficiency was improved [17].

Most of the studies in the literature have focused on either the morphology of the nanoparticles or the choice of the polymer. However, interface between the nanoparticles/nanorods and the polymer is also an important issue. It has been demonstrated that interface modification of CdS nanorod surface can improve the efficiency of hybrid bulk heterojunction devices. Chen *et al.* used aromatic acids as interface modifiers. They achieved a better efficiency upon addition of an aromatic acid. This better performance was attributed to the reduced surface trap and defects of CdS nanorods, rearragement of the surface energy level via dipole formation and prevention of the back charge transfer, and finally the improved compatibility between CdS nanorods and P3HT [18].

Although the use of CdSe and CdS nanoparticles in hybrid solar cells has attracted considerable attention, the limited power conversion efficiencies as compared to organic and inorganic solar cells have led researchers to search for other inorganic semiconductor nanoparticles to investigate in hybrid solar cells. $CuInS_2$ (CIS) and $CuInSe_2$ have been other choices of materials investigated in hybrid solar cells. CIS has a high absorption coefficient ($\alpha = 10^5\ cm^{-1}$) and photoconductivity and also its type of conductivity (n or p type) can be tuned via controlling the stoichiometry [19]. On the other hand, CISE has a low band gap and good radiation stability [20, 21]. Although these have been the first studies to focus on evaluating the synthesis and use of organic ligand-capped CIS and CISE in hybrid solar cells, the PCE of hybrid solar cells using these nanocrystals was rather limited. Morphology problems due to the limited dispersion of the inorganic nanocrystals and the conjugated polymer because of the existence of the organic ligand and the high serial resistances can be counted as the reasons for the poor device performance.

Although the hybrid solar cells consisting of blends of CdSe, CdS, $CuInS_2$, $CuInSe_2$ and conjugated polymers have been widely investigated,