

Holger Borchert

Solar Cells Based on Colloidal Nanocrystals



Springer

Springer Series in Materials Science

Volume 196

Series editors

Robert Hull, Charlottesville, VA, USA

Chennupati Jagadish, Canberra, ACT, Australia

Richard M. Osgood, New York, USA

Jürgen Parisi, Oldenburg, Germany

Shin-ichi Uchida, Tokyo, Japan

Zhiming M. Wang, Chengdu, People's Republic of China

For further volumes:

<http://www.springer.com/series/856>

The Springer Series in Materials Science covers the complete spectrum of materials physics, including fundamental principles, physical properties, materials theory and design. Recognizing the increasing importance of materials science in future device technologies, the book titles in this series reflect the state-of-the-art in understanding and controlling the structure and properties of all important classes of materials.

Holger Borchert

Solar Cells Based on Colloidal Nanocrystals



Springer

Holger Borchert
Department of Physics
Carl-von-Ossietzky University
of Oldenburg
Oldenburg
Germany

ISSN 0933-033X ISSN 2196-2812 (electronic)
ISBN 978-3-319-04387-6 ISBN 978-3-319-04388-3 (eBook)
DOI 10.1007/978-3-319-04388-3
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014932969

© Springer International Publishing Switzerland 2014

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law. The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Solar cells involving colloidal nanocrystals are a rapidly developing field of research. Many physical and chemical properties of crystalline solids can significantly change when the spatial dimensions of the crystallites are reduced to the nanometer size regime. This opens possibilities to tune material properties in view of specific applications. With respect to thin film photovoltaics, semiconductor nanocrystals have the potential to be used as tunable materials for efficient absorption of sunlight, either in combination with conductive polymer or also in inorganic absorber layers. Thereby, chemical approaches to synthesize the nanoparticles in liquid media give rise to the possibility of producing absorber layers by deposition of the materials from solution. Therefore, similar as in the field of organic photovoltaics, relatively simple and cost-efficient processes like printing technologies may be used for the realization of corresponding thin films.

In the case of organic photovoltaics which itself is a comparably young and still developing field, several books have appeared in recent years, giving good overviews and deep insight into that technology. Approaches to combine conductive polymer with inorganic semiconductor nanocrystals in hybrid systems are sometimes treated as a side-aspect in books on organic photovoltaics or organic electronics, but the literature specialized particularly on solar cells with inorganic nanocrystals is still rare. On the other hand, nanoparticle-based solar cells have made an impressive development in recent years, have their own particularities, and should merit more attention in terms of books focusing particularly on them. This was the main source for my motivation to write the present book.

Research on solar cells with colloidal nanoparticles is strongly interdisciplinary and covers many aspects of physics, chemistry, and materials science. The book aims at bridging gaps between the involved scientific disciplines and collects into one work important fundamentals from different fields. The book reflects the current state of research on relevant materials and different types of nanoparticle-based solar cells. It addresses researchers, Ph.D. students, engineers, and others interested in the application of colloidal nanoparticles in photovoltaics. Moreover, the book may also serve as an advanced textbook to accompany specialized lectures in physics, chemistry, materials science, and related areas.

The book is organized into three parts, the first of them addressing specific properties of colloidal nanocrystals as well as conductive polymer in general. The second part focuses on a selection of characterization methods relevant for the field.

Thereby, short introductions to the different methods are given, and their application potential for exploring the properties of materials and solar cells is discussed. The third part of the book describes different concepts for using colloidal nanocrystals in solar cells and reviews the state of the art and recent developments and tendencies in this research area.

As the author, I would like to express my gratitude to all who supported the writing of the book, either by reading parts of the manuscript or helping me in the planning of the book. Namely, I would like to mention here my wife, Dr. Yulia Borchert, as well as my present, respectively, former colleagues Dr. Martin Knipper, Dr. Marta Kruszynska, Dr. Florian Witt, and Prof. Dr. Elizabeth von Hauff. I am also particularly grateful to Prof. Dr. Jürgen Parisi for his advice in the planning and in whose working group I got the opportunity to perform active research in the scientific field which the present book is focused on. I hope to provide with this book a useful and appealing work and hope the readers will enjoy it.

Oldenburg, February 2014

Holger Borchert

Contents

1	Introduction	1
	References	9

Part I Materials

2	Physics and Chemistry of Colloidal Semiconductor Nanocrystals .	15
2.1	Basic Concepts of Colloidal Synthesis	15
2.2	Short Overview on Materials	19
2.3	Material Properties Depending on Particle Size	20
2.4	Material Properties Related to the Surface of Colloidal Nanocrystals	29
	References	35
3	Physics and Chemistry of Conductive Polymers	39
3.1	Electrical Conductivity in Organic Materials	39
3.1.1	Hybridization	39
3.1.2	Conjugated Double Bonds	42
3.1.3	The Structure and Conductivity of Trans-Polyacetylene	45
3.2	Different Types of Conductive Polymer	51
3.3	Physical and Chemical Properties of Conductive Polymer	54
3.3.1	Structural Properties: Chain Length and Regioregularity	54
3.3.2	Absorption Properties	57
	References	59

Part II Characterization of Colloidal Nanocrystals and Thin Polymer Films

4	Electron Microscopy	63
4.1	Basics of Electron Microscopy	63
4.2	High-Resolution Transmission Electron Microscopy (HRTEM)	67
4.3	Fourier Analysis and Image Filtering	69
4.4	Particle Size Determination	71
4.5	Sample Preparation and Stability	73
4.6	Scanning Electron Microscopy (SEM).	74
4.7	Electron Tomography	74
	References	77
5	X-ray Diffraction	79
5.1	Basics of X-ray Diffraction	79
5.2	Particle Size Determination	86
5.3	Rietveld Analysis	88
5.4	Small Angle X-ray Scattering (SAXS)	91
5.5	X-ray Diffraction of Soft Matter.	92
	References	94
6	Photoelectron Spectroscopy	95
6.1	Fundamentals of X-ray Photoelectron Spectroscopy	95
6.2	Surface Sensitivity	98
6.3	High-Resolution Photoelectron Spectroscopy of Semiconductor Nanocrystals	100
6.4	Quantitative Photoelectron Spectroscopy: Depth Profiles of the Chemical Composition.	104
	References	108
7	Cyclic Voltammetry	111
7.1	Fundamentals of Cyclic Voltammetry	111
7.2	Examples for the Study of Energy Levels in Organic Semiconductors	115
7.3	Analysis of Defect States in Colloidal Semiconductor Nanocrystals	116
	References	116
8	Absorption and Photoluminescence Spectroscopy	119
8.1	Fundamentals of Absorption Spectroscopy.	119
8.2	Fundamentals of Photoluminescence Spectroscopy	121
8.3	Photoinduced Absorption Spectroscopy	123
8.4	Time-Resolved Optical Spectroscopy	125
	References	127

9	Electron Spin Resonance	129
9.1	Fundamentals of Electron Spin Resonance Spectroscopy	129
9.2	Light-Induced Electron Spin Resonance (L-ESR) Spectroscopy as a Probe for Charge Transfer Processes in Donor/Acceptor Systems	132
	References	137
10	Electrical Characterization of Solar Cells	139
10.1	Current–Voltage Measurements	139
10.1.1	Fundamentals	139
10.1.2	Measurement Conditions	142
10.2	Quantum Efficiency Measurements	146
	References	147
11	Charge Carrier Mobility Measurements	149
11.1	General Aspects of Charge Transport	149
11.2	Organic Field Effect Transistors	151
11.3	Single Carrier Diodes	153
	References	154

Part III Solar Cells with Colloidal Nanocrystals

12	Hybrid Polymer/Nanocrystal Solar Cells	159
12.1	Potential Advantages of Using Inorganic Nanocrystals as Alternative Electron Acceptors	159
12.2	Material Combinations for Hybrid Solar Cells	162
12.2.1	Solar Cells Based on Cadmium Chalcogenides	162
12.2.2	Solar Cells Based on Lead Chalcogenides	169
12.2.3	Solar Cells Based on Ternary I–III–VI Compounds	172
12.2.4	Solar Cells Based on III–V Semiconductors	176
12.2.5	Solar Cells Based on Transition Metal Oxides	176
12.2.6	Solar Cells Based on Silicon Nanocrystals	179
12.3	Elementary Processes in Hybrid Solar Cells and Strategies for Improvement	180
12.3.1	Charge Separation at the Organic–Inorganic Donor–Acceptor Interface	180
12.3.2	Charge Transport in Organic–Inorganic Hybrid Systems	183
12.3.3	Defects and Charge Carrier Trapping in Hybrid Solar Cells	185
12.3.4	Alternatives to Ligand Exchange as Requirement for Hybrid BHJ Solar Cells	195
	References	197

13 Solar Cells with Inorganic Absorber Layers Made of Nanocrystals.	203
13.1 Concepts for Solar Cells with Solution-Produced Absorber Layers Consisting of Colloidal Semiconductor Nanocrystals Without Conductive Polymer	203
13.2 Solar Cells with Inorganic Absorber Layers of Cadmium Chalcogenide Nanocrystals	206
13.3 Solar Cells with Inorganic Absorber Layers of Lead Chalcogenide Nanocrystals	207
13.4 Solar Cells with Inorganic Absorber Layers of Other Semiconductor Nanocrystals	212
References	214
14 Other Types of Solar Cells Containing Colloidally Prepared Nanocrystals.	217
14.1 Bulk Heterojunction Solar Cells with Ternary Blends of Conductive Polymer, Fullerenes and Semiconductor Nanocrystals	217
14.2 Wide Band Gap Semiconductor Nanocrystals for Interlayers in Organic Solar Cells	222
14.3 Quantum Dot-Sensitized Solar Cells	224
14.4 Metal Nanoparticles for Enhanced Light Absorption in Organic Solar Cells.	227
References	230
Index	233

Abbreviations

APCE	Absorbed photon-to-current efficiency
BHJ	Bulk heterojunction
CIS	Copper indium disulfide
CTC	Charge transfer complex
CT state	Charge transfer state
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DSSC	Dye-sensitized solar cell
EDX	Energy dispersive X-ray analysis
EPR	Electron paramagnetic resonance
EQE	External quantum efficiency
ESR	Electron spin resonance
FEG	Field emission gun
FF	Fill factor
FIB	Focused ion beam
FRET	Förster resonance energy transfer
HAADF	High angle annular dark-field
HDA	Hexadecylamine
HOMO	Highest occupied molecular orbital
HRTEM	High-resolution transmission electron microscopy
ICBA	Indene-C ₆₀ bisadduct
ICMA	Indene-C ₆₀ monoadduct
IPCE	Incident photon-to-current efficiency
IQE	Internal quantum efficiency
ITO	Indium tin oxide
LCAO	Linear combination of atomic orbitals
L-ESR	Light-induced electron spin resonance
LSPR	Localized surface plasmon resonance
LUMO	Lowest unoccupied molecular orbital
MDMO-PPV	Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]
MEG	Multiple exciton generation
MEH-PPV	Poly[2-methoxy-5-(2'-ethylhexyloxy)- <i>para</i> -phenylene vinylene]

MO	Molecular orbital
MPP	Maximum power point
OFET	Organic field effect transistor
OPV	Organic photovoltaics
P3EBT	Poly(3-(ethyl-4-butoate)thiophene)
P3HT	Poly(3-hexylthiophene)
P3OT	Poly(3-octylthiophene)
PANI	Polyaniline
PCBM	Phenyl-C ₆₁ -butyric acid methyl ester
PCE	Power conversion efficiency
PCPDTBT	Poly[2,6-(4,4-bis-(2-ethylhexyl)-4 <i>H</i> -cyclopenta[2,1- <i>b</i> ;3,4- <i>b'</i>]dithiophene)- <i>alt</i> -4,7-(2,1,3-benzothiadiazole)]
PDI	Polydispersity index
PDTPBT	Poly(2,6-(<i>N</i> -(1-octylnonyl)dithieno[3,2- <i>b</i> :20,30- <i>d</i>]pyrrole)- <i>alt</i> -4,7-(2,1,3-benzothiadiazole))
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PESA	Photoelectron spectroscopy in air
photo-CELIV	Photocharge extraction by linearly increasing voltage
PIA	Photoinduced absorption
PL	Photoluminescence
PPP	Poly(para-phenylene)
PPV	Poly(para-phenylene vinylene)
PV	Photovoltaics
PVD	Physical vapor deposition
PVP	Polyvinylpyrrolidone
Q-DLTS	Charge-based deep level transient spectroscopy
SAXS	Small-angle X-ray scattering
SCLC	Space charge limited current
SEM	Scanning electron microscopy
SILAR	Successive ionic layer adsorption and reaction
STEM	Scanning transmission electron microscopy
TBP	Tributylphosphine
TCO	Transparent conducting oxide
TDPA	Tetradecylphosphonic acid
TEM	Transmission electron microscopy
TOP	Trioctylphosphine
TOPO	Trioctylphosphine oxide
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction

Abstract Photovoltaic devices absorb sun-light and enable the conversion of solar radiation into useable electrical energy. In view of the world-wide growing energy demand, limited resources of fossil fuels and the need for more eco-friendly ways of energy production, photovoltaics is gaining more and more importance. Till date, the most common solar cell technology is based on crystalline silicon as the photoactive material. However, alternative concepts for solar cells have emerged as well. A relatively new and innovative branch of photovoltaics are organic solar cells, where the photoactive layer consists of organic materials which are able to conduct charge carriers. Organic solar cells are considered to have a high potential to become producible at low cost and have also other attractive properties. For example, they can be realized on flexible substrates, which enable their implementation in curved or flexible surfaces. On the other hand, organic solar cells still suffer from limited device efficiency and lifetime. An alternative to purely organic solar cells are hybrid devices combining organic materials with inorganic colloidal nanocrystals. Colloidal nanocrystals have interesting and partly even controllable physical and chemical properties from where arises a high potential to bring innovation to the photovoltaic technology. The present book gives an overview over the relevant fundamentals and the state-of-the-art of photovoltaic devices containing colloidal nanocrystals, and the present chapter introduces to the topic.

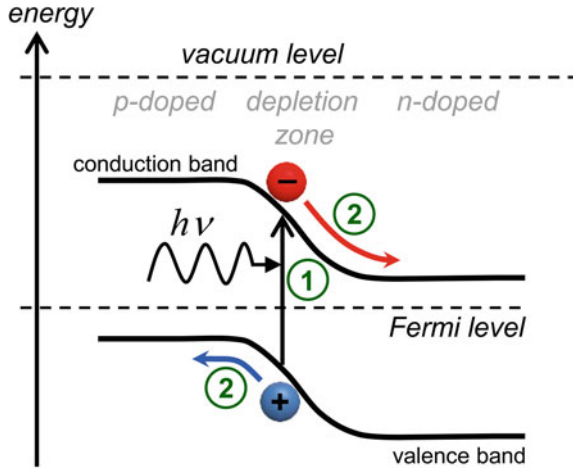
Currently, in 2014, approximately 7.2 billion people are living on the world, and the population keeps on growing by about 80 million people per year. From the growth of the world population, the ongoing growth of industry and the natural desire of human beings to improve their living conditions results a world-wide growing demand of energy [1]. Today, the by far largest part of the annually consumed energy is taken from fossil energy sources: oil, coal and gas [1, 2]. Regarding the resources of fossil fuels that are known today, there will probably be enough reserves for the next decades. However, thinking more provident, the resources of fossil fuels are finite and their exploitation may become more difficult in future, because not all of the reserves are equally easy accessible. Moreover, the combustion of fossil fuels is accompanied by the release of carbon dioxide which is believed today to have a significant impact on climate change [2]. From these

basic facts arises the need to supply the world with energy from another source than fossil fuels. A certain alternative is nuclear power, but this technology has the serious disadvantage of high safety risks and many problems related to the treatment of nuclear waste. Furthermore, also the world-wide uranium reserves are limited, at least as long as extracting uranium from sea water remains difficult. Fortunately, there is a very powerful source of carbon-free and renewable energy available on earth: the radiation coming from the sun. However, the author would not need to write this book, if the sunlight were an easy solution to the world's energy problem. Unfortunately, it remains a difficult task to convert the sunlight in efficient manner and at affordable costs into other forms.

Photovoltaics (PV) is the technology concerned with converting sunlight into electricity. Very basically, in any type of solar cell, the conversion process can be broken down into several important elementary steps. In the first step, light coming from the sun needs to be absorbed. The energy provided by the absorbed photons is used to promote electrons in the absorber material into higher energy levels. Each electron excited to a higher energy level leaves behind in its original level a *hole*, a positively charged quasiparticle which is nothing else than a missing electron. In this sense, light absorption generates charge carriers in the absorber material: electrons excited to higher energy levels and corresponding holes left behind. To make these charge carriers usable in an outer electrical circuit, the positive and negative charges need to be spatially separated and transported to two different electrodes where they can be extracted from the solar cell. Thus, the energy conversion process can be broken down into charge generation by light absorption, charge separation, charge transport and charge extraction. Various types of solar cells have been developed to put these processes into practice.

The most wide-spread PV technology till date dominating the market is based on pn-junctions with p- and n-doped crystalline silicon (Si) as absorber material [3]. Figure 1.1 reminds the energy scheme of a pn-junction in equilibrium and illustrates the basic working principle of charge separation in a corresponding solar cell. Si is an indirect semiconductor with a band gap of approximately 1.1 eV, meaning that photons with a wavelength below $\sim 1,100$ nm can be absorbed by the material and can promote electrons from the valence into the conduction band [4]. The driving force to spatially separate the electrons elevated into the conduction band and the holes remaining behind in the valence band is provided by the energetic structure of the pn-junction [3]. Silicon solar cells can reach power conversion efficiencies of up to ~ 25 % [5, 6] and exhibit also a reasonable lifetime of approximately 20 years or longer [7] which makes them suitable for installations in solar energy parks, on roof-tops of various types of buildings, and so on. Despite the relatively high efficiency and good long-term stability, Si solar cells still have difficulties to compete with electricity gained from fossil fuels or nuclear power, because the fabrication costs of these photovoltaic cells and also other costs related to the technology, e.g., the costs for the installation of photovoltaic modules, are relatively high. At least partly, this is due to the fact that crystalline Si solar cells require silicon in the form of wafers which are cost-intensive and also energy-intensive in their production [3]. Another disadvantage

Fig. 1.1 Energy scheme of a pn-junction in equilibrium. The Fermi levels of the p- and n-doped regions align in equilibrium, and a depletion zone is formed at the interface. If a photon with energy $h\nu$ larger than the band gap is absorbed, an electron-hole pair is generated (step 1). The band bending in the depletion zone provides a driving force for charge separation (step 2)

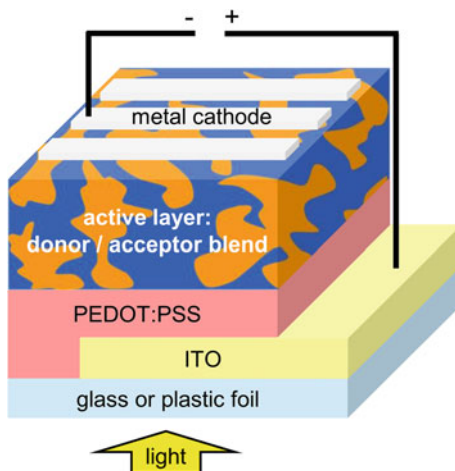


of classical crystalline Si solar cells is that the corresponding PV modules are rigid and have a relatively high weight which in turn prevents their usage on part of the surfaces that would in principle be available for PV installations.

The mentioned deficiencies of crystalline silicon solar cells gave rise to the development of alternative PV technologies. Another type are for example thin film solar cells based on $\text{Cu}(\text{In}_x\text{Ga}_{1-x})(\text{S}_y\text{Se}_{1-y})_2$ compounds which can be produced by sputtering or evaporation processes [8–11]. These compound semiconductors, often abbreviated as CIS (for pure CuInS_2), CIGS (for Ga-containing material), CISE (for Se-containing material) or CIGSe (for Ga and Se-containing material) have usually chalcopyrite structure, and the band gap can be tuned in the range from 1.04 to 2.4 eV by adjusting the elemental composition [12, 13]. Thin film solar cells of this type are commercially produced, and power conversion efficiencies approach now 20 % at the level of individual cells and about 19 % for solar cell minimodules [5]. Their production avoids the need for wafer technology, but still requires a relatively high technical effort due to the deposition of the absorber material by sputtering or evaporation technology. Another issue critically discussed is the dependence on indium which became a comparably expensive element due to its limited occurrence on earth and usage at large scale in displays and other technologies.

Other alternatives to wafer-based silicon are CdTe solar cells [9], solar cells based on amorphous or microcrystalline silicon [8], and organic photovoltaics (OPV) [14–17]. The probably best established type of photovoltaic devices with organic materials is dye-sensitized solar cells (DSSCs) [18]. In a classical dye-sensitized solar cell, an organic dye attached to porous titania is used to harvest the sunlight, and a liquid electrolyte is necessary for regeneration of the dye after electron transfer from the dye to the titania network [18]. Classical dye-sensitized solar cells reach currently up to ~ 12 % power conversion efficiency [5]. Difficulties of this technology relate for example to the long-term stability of the organic dye molecules and to the fact that the presence of a liquid electrolyte

Fig. 1.2 Schematic illustration of the device architecture of a typical organic solar cell using a bulk heterojunction of conductive polymer and an acceptor material as active layer



complicates certain aspects of handling of the corresponding devices. Remarkable progress was made in the last couple of years by introducing perovskites with a high conductivity for electrons as sensitizer. Perovskite-based solar cells were reported in peer-reviewed scientific journals to reach power conversion efficiencies up to 12.3 % [19, 20], and up to about 15 % efficiency were reported in 2013 on scientific conferences in the field.

Another type of organic-based solar cells is devices involving conductive polymer. This branch of photovoltaics falls more into the scope of this book, so that the working principle of a typical polymer-based solar cell shall be outlined in detail in this place. Figure 1.2 shows the device architecture of a typical polymer/fullerene solar cell.

Typically, the preparation starts with a piece of glass or plastic foil coated with a structured layer of indium tin oxide (ITO). ITO is a degenerate semiconductor exhibiting good conductivity and at the same time high transparency in a wide spectral range [21]. Therefore, ITO is suitable as electrode material for solar cells which still enables the penetration of light into the cell. On top of the ITO follows a thin layer of a hole conducting polymer, typically poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) which can be deposited from solution, e.g., by spin-coating or other deposition technologies. The purpose of the PEDOT:PSS layer is on the one hand simply to smoothen the surface, because commercial ITO substrates have usually a certain roughness. Furthermore, PEDOT:PSS is considered to selectively transport holes, whereas electrons cannot easily pass the layer. Next follows the active layer, which can in the case of soluble organic materials be processed from solution as well. The active layer can be considered as the heart of the organic solar cell and is in the case of the present example a binary mixture of two materials: a conductive polymer and a fullerene derivative. The two components do not form a completely homogeneous mixture. Instead, phase separation occurs, but on a length scale in the nanometer size regime.

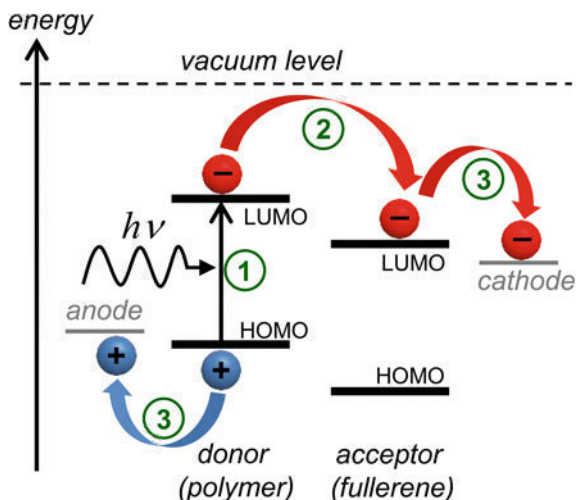


Fig. 1.3 Energy scheme of a donor/acceptor system (under open-circuit conditions). In a type II heterojunction, the electron donor material has HOMO and LUMO levels which are both higher-lying than the corresponding orbitals of the acceptor material. If a photon is absorbed in the donor, an electron is raised into the LUMO level, and a hole remains in the HOMO level (*step 1*). Due to the lower LUMO level of the acceptor, the excited electron can be transferred from the donor to the acceptor (*step 2*). After charge separation, the electrons and holes need to be transported to the cathode and anode, respectively (*step 3*)

The resulting finely interpenetrating network of polymer and fullerene domains constitutes a so-called *bulk heterojunction* (BHJ) [15–17, 22, 23]. Finally, the solar cell is finished by a metal cathode which is usually deposited on top of the active layer by thermal evaporation. It should be emphasized that the device architecture depicted here is just a typical example given to describe the working principle of BHJ solar cells. Many modifications of this specific device structure, also with more sophisticated layer sequences, can be found in practice.

In polymer/fullerene BHJ solar cells, absorption of sunlight occurs predominantly by the conductive polymer. Energetically, the polymer/fullerene blend forms a so-called *donor/acceptor system* [15–17, 24]. This means that the frontier orbitals, i.e., the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two materials have an offset as illustrated in Fig. 1.3. Both, the HOMO and the LUMO level of the acceptor are lower in energy than the respective energy levels of the donor material. This situation for the relative energetic positions of the energy levels is called a *type II heterojunction*. If light is absorbed by the polymer and an electron is raised from the HOMO into the LUMO level, it is energetically favorable, if the electron will be transferred from the LUMO level of the polymer into the lower-lying LUMO level of the fullerene acceptor. This charge transfer step leads to the spatial separation of the transferred electron and the hole which remains in the HOMO level of the donor polymer.

Note, however, that this picture is a bit simplified, because it neglects the role of Coulomb attraction between the electron and the hole. More precisely, the gain in energy due to the transfer of the electron to the lower-lying LUMO level of the acceptor must at least compensate the loss of Coulomb binding energy accompanying the charge transfer process [25]. The charge transfer across the donor/acceptor interface is an important step towards separated positive and negative charges. After charge separation, the holes need then to be transported through a network of the conductive polymer to the ITO/PEDOT:PSS anode, whereas the electrons need to be transported through the fullerene network to the metal cathode. During operation, electrons are finally extracted at the cathode, can be used in the outer electrical circuit, and are injected back into the solar cell at the anode which corresponds to hole extraction at this electrode.

Regarding the mentioned processes of charge transfer at the donor/acceptor interface and charge transport towards the electrodes, the detailed structure of the bulk heterojunction, usually referred to as the *morphology* of the active layer, plays an important role [15–17, 22, 26]. Light absorption in the polymer leads to the creation of Coulomb bound electron–hole pairs, so-called *excitons*. Compared to inorganic semiconductors, the binding energy of the excitons is relatively high in organic semiconductors [27]. Therefore, splitting of the excitons into free charge carriers requires the charge transfer process across the donor/acceptor interface as discussed above. This means, however, that an exciton created by light absorption has first of all to diffuse to the material interface. There, another property of organic semiconductors comes into play: Typically used conductive polymers have relatively short exciton diffusion lengths of the order of about 10 nm only [28], meaning that the photo-generated electron hole-pairs will simply recombine radiatively, if the donor/acceptor interface is too far away. The bulk heterojunction concept was developed to realize an active layer which is on the one hand thick enough to absorb a large fraction of the sun-light, and which at the same time brings the two material components into close vicinity. On the other hand, the rather arbitrary nature of the interpenetrating network of the two phases means that the pathways for charge transport towards the electrodes will not be ideal in general. Therefore, controlling and optimizing the morphology of the active layer in bulk heterojunction solar cells is a crucial issue in the field of organic photovoltaics [15–17, 22, 26].

Polymer/fullerene BHJ solar cells are a promising PV technology. Many of the involved organic semiconductor materials are not yet produced at large scale and low cost. On the other hand, the materials are based on carbon chemistry and do not contain rare elements. Thus, from this point of view, organic semiconductors can be considered as materials where large scale production is at least not prevented by limited occurrence of the elements on earth. An important feature of BHJ solar cells is that the organic materials are usually soluble in selected solvents. Therefore, the material layers can in principle be produced by relatively simple deposition techniques such as printing technologies or spray coating [29, 30]. This promises to save costs when compared to the wafer-based Si technology or other thin film PV technologies that are dependent on high-temperature or

vacuum processes. Furthermore, many types of OPV devices are in principle suitable for production on flexible substrates such as transparent plastic foils coated with suitable materials that can serve as conducting electrodes. This offers opportunities to use efficient roll-to-roll processes in the fabrication of OPV modules [29], and, probably even more important, opens perspectives to use organic solar cells on curved or flexible surfaces where most other established types of PV devices would not be applicable. A prominent example is the integration of PV modules in bags or other textiles. Thus, OPV devices can address a market where most other types of solar cells can simply not be used. On the other hand, it should be stated that the mass market for photovoltaics is in general not seen in the field of consumer electronics, but in large area applications like solar parks or building-integrated photovoltaics. Making the technology competitive for such large-scale applications is a real challenge for scientists and engineers working in the field of OPV.

Although, organic semiconductors comprise a large manifold of different compounds, research on their application in solar cells has focused on a relatively narrow selection of materials for a long time. In the case of conductive polymers, mainly poly(alkylthiophenes) such as poly(3-hexylthiophene) (P3HT) or derivatives of poly(para-phenylene vinylene) (PPV) have been used. Concerning the fullerene, the derivative the most widely used in OPV is certainly phenyl-C₆₁-butyric acid methyl ester (PCBM). With these materials, organic BHJ solar cells have reached up to 5 % power conversion efficiency [31]. In the last years, more attention was paid to the search for new and more suitable organic semiconductors. Progress was made by using other polymers and also fullerene derivatives, exhibiting in particular more suitable absorption properties [32–34]. The highest efficiency reported so far in peer-reviewed scientific journals for organic solar cells with a single BHJ layer is 7.4 % [34].

In so-called *tandem solar cells*, two absorber layers containing materials covering different spectral ranges are used to harvest the sunlight more efficiently [35]. With polymer-based tandem solar cells, up to 8.9 % power conversion efficiency were reported in the last years [36, 37]. With triple junction cells, containing three distinct polymer/fullerene absorber layers, 9.6 % power conversion efficiency was reached in 2013 [37]. From companies aiming at commercializing organic solar cells, even efficiencies around ~10–12 % were meanwhile reported at cell level [5, 38], with the exact information on the materials and device structures used remaining secret. For organic PV minimodules, up to ~8 % efficiency was achieved [5].

One strategy for improvement of organic BHJ solar cells is to replace the fullerene acceptor by inorganic, colloidal semiconductor nanocrystals [39–43]. The basic device structure can stay the same as depicted in Fig. 1.2, simply the electron acceptor material in the active layer is exchanged to inorganic nanoparticles. Due to the organic–inorganic nature of the binary absorber layer, such solar cells are then called *hybrid solar cells*.

Inorganic crystalline solids possess a variety of material properties which are characteristic for a given compound, examples being the melting temperature, the

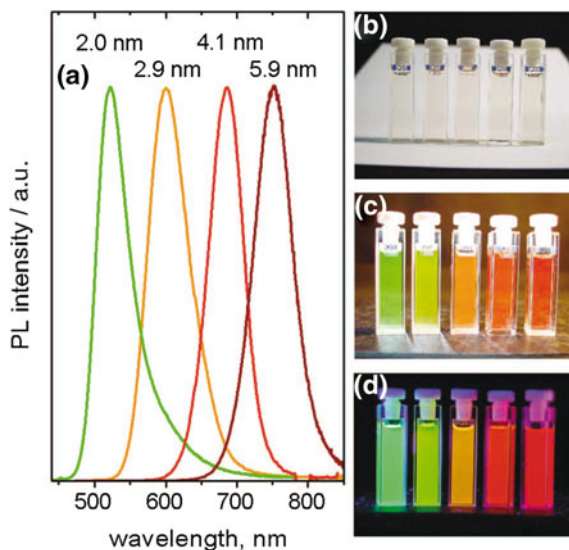


Fig. 1.4 **a** Normalized photoluminescence (PL) spectra of HF-photoetched InP nanocrystals of different particle diameter. **b** Photograph of colloidal solutions containing InP nanocrystals of different size. **c, d** Photographs of the same solutions under illumination with white flash light (**c**) and 366 nm UV light (**d**). The smallest nanoparticles (~ 2 nm diameter) emit *green* fluorescence light, whereas larger InP nanocrystals (~ 4 nm diameter) emit *red* light (Reprinted with permission from [51]. Copyright 2005, American Institute of Physics)

band gap of a semiconductor or the conductivity of a pure crystalline substance. As an interesting phenomenon it was discovered, however, that many physical and chemical material properties can change when the particle size is reduced to a few nanometers [44–49]. An impressive example is the so-called *quantum size effect*: Due to quantum mechanical effects, the band gap of semiconductors increases, if the particle size is reduced to a few nanometers [44, 45, 50]. By consequence, optical properties such as light absorption and the emission of fluorescence light become tunable by controlling the size of semiconductor nanocrystals. Figure 1.4 illustrates this phenomenon on the example of colloidal InP nanocrystals.

This example demonstrates that controlling the particle size opens possibilities to govern material properties which are of interest for applications. In the specific case of InP, potential applications relate for example to light-emitting diodes with controllable color [52]. In view of solar cells, tuning the band gap of semiconductors offers the possibility to control the absorption range of the material. This degree of control is an attractive advantage of colloidal semiconductor nanocrystals in comparison to the fullerene derivatives widely used in OPV. Beyond tunable absorption properties, there are even more features making colloidal nanocrystals interesting for usage in solar cells. For example, again related to the quantum size effect, it is also possible to tune the relative energetic position of the band edges with respect to the energy levels of a given conductive polymer. This

in turn opens perspectives to improve the voltage delivered by a corresponding BHJ solar cell [53].

Thus, inorganic semiconductor nanocrystals offer potentially some advantages over fullerenes in polymer-based BHJ solar cells. Nevertheless, hybrid solar cells using blends of conductive polymer and colloidal nanocrystals as absorber layer still lack behind in their performance when compared to polymer/fullerene devices [39–43]. Till date, up to 5.5 % efficiency has been reported for hybrid solar cells [54–56]. Thus, it was not possible yet to really benefit from the potential advantages related to inorganic nanocrystals instead of fullerene acceptors. For the further development of the field, it is an important task of current research to further deepen the understanding of the device physics of polymer-based solar cells, to elucidate the limiting factors in such PV systems, and in particular also to explore specific differences between organic polymer/fullerene and hybrid polymer/nanoparticle systems.

The present book provides insights into relevant fundamentals of the involved materials and types of solar cells, reflects the state-of-the-art of research on solar cells with colloidal semiconductor nanocrystals, and points out demands for future research in the field. The book is divided into three parts. Part I focuses on the development and important properties of relevant materials, namely colloidal nanocrystals and conductive polymer. Part II introduces to a selection of relevant characterization techniques and highlights recent findings obtained by the respective methods. Finally, Part III provides an up-to-date review of bulk heterojunction solar cells containing colloidal semiconductor nanocrystals. Another chapter in this part of the book addresses a second class of solar cells with inorganic nanocrystals: so-called *Schottky solar cells* and *depleted heterojunction solar cells*. Both of them are innovative concepts to realize PV devices with absorber layers which can be processed from solution, but as opposed to hybrid BHJ devices, the active layer consists of inorganic nanoparticles only in this case. Such type of solar cells shows currently even better performance than hybrid solar cells and is therefore an important alternative concept [57, 58]. The last chapter addresses further concepts to use colloiddally prepared nanocrystals in solar cells, among them BHJ solar cells with ternary blends of conductive polymer, fullerenes and semiconductor nanocrystals, and also quantum dot-sensitized solar cells. The latter are similar to dye-sensitized solar cells, but use semiconductor nanocrystals instead of organic dyes as sensitizer [59].

References

1. S.A. Holditch, R.R. Chianelli, MRS Bull. **33**, 317 (2008)
2. M.I. Hoffert, K. Caldeira, A.K. Jain, E.F. Haites, L.D.D. Harvey, S.D. Potter, M.E. Schlesinger, S.H. Schneider, R.G. Watts, T.M.L. Wigley, D.J. Wuebbles, Nature **395**, 881 (1998)
3. M. Tao, Electrochem. Soc. Interface **17**(4), 30 (2008)
4. C. Kittel, *Introduction to Solid State Physics*, 8th edn. (Wiley, New York, 2005)

5. M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, *Prog. Photovoltaics Res. Appl.* **22**, 1 (2014)
6. S.W. Glunz, High-efficiency crystalline silicon solar cells. *Adv. OptoElectron.* (2007). doi:[10.1155/2007/97370](https://doi.org/10.1155/2007/97370)
7. D. Heinemann, W. Jürgens, R. Knecht, J. Parisi, 30 years at the service of renewable energies. *Einblicke* (Research Journal of the University of Oldenburg, Germany) **54**, 6 (2011)
8. M.A. Green, *J. Mater. Sci.: Mater. Electron.* **18**, S15 (2007)
9. M. Powalla, D. Bonnet, Thin-film solar cells based on the polycrystalline compound semiconductors CIS and CdTe. *Adv. OptoElectron.* (2007). doi:[10.1155/2007/97545](https://doi.org/10.1155/2007/97545)
10. R. Knecht, M.S. Hammer, J. Parisi, I. Riedel, *Phys. Status Solidi A* **210**, 1392 (2013)
11. J. Keller, R. Schlesiger, I. Riedel, J. Parisi, G. Schmitz, A. Avellan, T. Dalibor, *Sol. Energy Mater. Sol. Cells* **117**, 592 (2013)
12. T. Tinoco, C. Rincon, M. Quintero, G. Sanchez Perez, *Phys. Status Solidi A* **124**, 427 (1991)
13. V.S. Saji, S.-M. Lee, C.W. Lee, *J. Korean Electrochem. Soc.* **14**, 61 (2011)
14. S.E. Shaheen, D.S. Ginley, G.E. Jabbour, *MRS Bull.* **30**, 10 (2005)
15. B.C. Thompson, J.M.J. Frechet, *Angew. Chem. Int. Ed.* **47**, 58 (2008)
16. C. Deibel, V. Dyakonov, *Rep. Prog. Phys.* **73**, 096401 (2010)
17. C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S. Jia, S.P. Williams, *Adv. Mater.* **22**, 3839 (2010)
18. M. Grätzel, *J. Photochem. Photobiol., C* **4**, 145 (2003)
19. M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, *Science* **338**, 643 (2012)
20. J.M. Ball, M.M. Lee, A. Hey, H.J. Snaith, *Energy Environ. Sci.* **6**, 1739 (2013)
21. S.K. Hau, H.-L. Yip, J. Zou, A.K.-Y. Jen, *Org. Electron.* **10**, 1401 (2009)
22. H. Hoppe, N.S. Sariciftci, *J. Mater. Chem.* **16**, 45 (2006)
23. J.E. Slot, X. He, W.T.S. Huck, *Nano Today* **5**, 231 (2010)
24. P.W.M. Blom, V.D. Mihailetchi, L.J.A. Koster, D.E. Markov, *Adv. Mater.* **19**, 1551 (2007)
25. C. Deibel, T. Strobel, V. Dyakonov, *Adv. Mater.* **22**, 4097 (2010)
26. L.-M. Chen, Z. Hong, G. Li, Y. Yang, *Adv. Mater.* **21**, 1434 (2009)
27. M. Knapfer, *Appl. Phys. A* **77**, 623 (2003)
28. P.E. Shaw, A. Ruseckas, I.D.W. Samuel, *Adv. Mater.* **20**, 3516 (2008)
29. A.C. Hübler, H. Kempa, in *Organic Photovoltaics*, ed. by C. Brabec, V. Dyakonov, U. Scherf (Wiley-VCH, Weinheim, 2008)
30. C. Girotto, B.P. Rand, J. Genoe, P. Heremans, *Sol. Energy Mater. Sol. Cells* **93**, 454 (2009)
31. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005)
32. S.H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, *Nat. Photonics* **3**, 297 (2009)
33. H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, *Nat. Photonics* **3**, 649 (2009)
34. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **22**, E135 (2010)
35. T. Ameri, G. Dennler, C. Lungenschmied, C.J. Brabec, *Energy Environ. Sci.* **2**, 347 (2009)
36. L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li, Y. Yang, *Nat. Photonics* **6**, 180 (2012)
37. W. Li, A. Furlan, K.H. Hendriks, M.M. Wienk, R.A.J. Janssen, *J. Am. Chem. Soc.* **135**, 5529 (2013)
38. R.F. Service, *Science* **332**, 293 (2011)
39. W.E.J. Beek, R.A.J. Janssen, in *Hybrid Nanocomposites for Nanotechnology*, ed. by L. Merhari (Springer Science+Business Media, New York, 2009)
40. Y. Zhou, M. Eck, M. Krüger, *Energy Environ. Sci.* **3**, 1851 (2010)
41. H. Borchert, *Energy Environ. Sci.* **3**, 1682 (2010)
42. T. Xu, Q. Qiao, *Energy Environ. Sci.* **4**, 2700 (2011)
43. M. Wright, A. Uddin, *Sol. Energy Mater. Sol. Cells* **107**, 87 (2012)
44. H. Weller, *Angew. Chem. Int. Ed.* **32**, 41 (1993)
45. H. Weller, *Adv. Mater.* **5**, 88 (1993)
46. A.P. Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996)

47. A. Eychmüller, J. Phys. Chem. B **104**, 6514 (2000)
48. R. Schlögl, S.B. Abd Hamid, Angew. Chem. Int. Ed. **43**, 1628 (2004)
49. C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, Chem. Rev. **105**, 1025 (2005)
50. D.V. Talapin, N. Gaponik, H. Borchert, A.L. Rogach, M. Haase, H. Weller, J. Phys. Chem. B **106**, 12659 (2002)
51. S. Adam, D.V. Talapin, H. Borchert, A. Lobo, C. McGinley, A.R.B. de Castro, M. Haase, H. Weller, T. Möller, J. Chem. Phys. **123**, 084706 (2005)
52. F. Hatami, W.T. Masselink, J.S. Harris, Nanotechnology **17**, 3703 (2006)
53. J.E. Brandenburg, X. Jin, M. Kruszynska, J. Ohland, J. Kolny-Olesiak, I. Riedel, H. Borchert, J. Parisi, J. Appl. Phys. **110**, 064509 (2011)
54. S. Ren, L.-Y. Chang, S.-K. Lim, J. Zhao, M. Smith, N. Zhao, V. Bulovic, M. Bawendi, S. Gradecak, Nano Lett. **11**, 3998 (2011)
55. R. Zhou, R. Stalder, D. Xie, W. Cao, Y. Zheng, Y. Yang, M. Plaisant, P.H. Holloway, K.S. Schanze, J.R. Reynolds, J. Xue, ACS Nano **7**, 4846 (2013)
56. Z. Liu, Y. Sun, J. Yuan, H. Wei, X. Huang, L. Han, W. Wang, H. Wang, W. Ma, Adv. Mater. **25**, 5772 (2013)
57. F. Hetsch, X. Xu, H. Wang, S.V. Kershaw, A.L. Rogach, J. Phys. Chem. Lett. **2**, 1879 (2011)
58. E.H. Sargent, Nat. Photonics **6**, 133 (2012)
59. P.V. Kamat, J. Phys. Chem. C **111**, 2834 (2007)