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 \(1,100 \text{ nm}\) 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 \(\sim 25\%\) [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 wavers which are cost-intensive and also energy-intensive in their production [3]. Another disadvantage
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 Cu(In$_x$Ga$_{1-x}$)(S$_y$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

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**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*).
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.
The resulting finely interpenetrating network of polymer and fullerene domains constitutes a so-called bulk heterojunction (BHJ) \cite{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 \cite{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.

**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).
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-C$_{61}$-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
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

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**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)
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 colloidally 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

10 1 Introduction

References

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