

The Physics of Solar Energy Conversion

Juan Bisquert

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Preface

The investigation of solar energy conversion materials and devices has come to the forefront of global scientific research, and it reached a state of maturity in recent decades. Nonetheless, enormous challenges lie ahead. Substantial scientific innovation will be necessary to obtain the essential contributions and steps towards a clean energy-based economy that is still only a promise.

The conversion of photons to electricity using light-absorbing semiconductors in a stable and highly efficient device that withstands operation over time is an extraordinarily complex process requiring matching physical processes in tailored materials at multiple spatial and temporal scales. The operation of solar energy conversion involves a set of concepts and tools that fluctuate among different disciplines of physics or chemistry. Examples of rather broad concepts and methods for such applications include: the synthesis of active molecules and solids that generate and transfer charge; the actuation of Fermi levels in thin films; and the detailed balance of light absorption and emission.

Following several decades of intensive investigation, a new broad landscape of candidate materials and devices were discovered and systematically studied and reported, including organic, inorganic, solid, liquid, soft matter and their combinations, and a myriad of contact materials and interfacial processes. In this evolution and expansion of the classes of materials in the past three decades, with a particular emphasis on dye-sensitized solar cells, the organic solar cells, and the metal halide perovskite solar cells, the conceptual picture of a solar cell has been extended and refined. New concepts and a powerful picture that embraces very different types of devices have been established based upon many discussions as well as conceptual clashes.

The resulting scientific consensus is the story I want to tell. The realization of this project, this volume, took one decade and came about through the consecutive publication of three original separate books, as different units of the plan were being fulfilled:

- Nanostructured Energy Devices. Equilibrium Concepts and Kinetics
- Nanostructured Energy Devices. Foundation of Carrier Transport
- Physics of Solar Cells. Perovskites, Organics, and Fundamentals of Photovoltaics

This book has been formed by merging the three previous separate volumes and in 2020 updating several chapters to reflect the latest scientific advances of the field. The preceding trilogy was already conceived as a unity at the time of the first publication. Hence the chapters of this volume, *Physics of Solar Energy Conversion*, follow in most cases the sequence of chapters of the previous books, but are now numerated sequentially. However, cross citation between chapters, which is used frequently and emphasizes the intricate web of concepts, ideas and methods, is now much easier.

In this volume the reader will obtain a firm basis for understanding solar energy conversion devices, which may be formed by a great variety of materials, at the same time obeying general principles and constraints in order to reach the final goal of forming useful energy conversion technologies. The principal spirit of this approach is to facilitate starting researchers to get an overall picture of what needs to be known, and also hopefully support experts to achieve a summarizing scheme.

Solar cell light absorber materials can be inversely operated for light emission and also in electrochemical solar fuel conversion. A broad class of devices for such types of purposes use electrochemical setups, thin films, and organic materials, normally formed by solution-processed routes for low-cost applications. Due to the existence of these strong direct material and conceptual connections, one goal of this volume is to put energy devices of solar cells in a wider perspective, including a range of energy devices that are operationally related and often based on similar materials. From the broader standpoint, the text covers the main concepts that apply to several types of devices so that the reader gains an insight into the general view of principles of operation of the energy devices. We analyze the fundamental concepts, main properties, and key applications of energy devices including perovskite solar cells, organic solar cells, electrochemical batteries, diodes, LEDs and OLEDs, transistors, and the direct conversion of solar radiation to chemical fuels. One benefit of the broader perspective is that innovations can be shared and exported across communities producing cross-fertilization. Such principles will be discussed in connection with an array of physical, electrochemical, and optoelectronic measurement techniques and theoretical simulation methods that are widely used and constitute essential tools in the field.

The book has been organized to provide an introduction to the fundamentals of operation of very different devices that nonetheless have operational or material relationships. A unified view of the device operation is emphasized based on some general concepts such as the energy diagrams and the electrochemical potentials. We aim to pull together the views and terminologies used by several communities including the solid state science, surface science, electrochemistry, and electronic devices physics. The book does not aim to exhaustively list materials and their properties but rather takes some prototypical and representative cases of materials widely used for devices and applications, with the main focus being on laying conceptual foundations rather than summarizing innovations of the past decades.

The first part of the book, Chapters 1–9, examines fundamental principles of semiconductor energetics, interfacial charge transfer, basic concepts and methods of measurement, and the properties of important classes of materials such as metal oxides and organic semiconductors. These materials and their properties are important in the operation of organic and perovskite solar cells either as the bulk absorber or as a selective contact structure. Electrolytic and solid ionic conductor properties also play relevant roles in organic and perovskite solar cells. This part is mainly focused on equilibrium properties at open circuit condition, often represented in energy diagrams, and also on the basic aspect of carrier kinetics.

The second part, Chapters 10–16, presents a catalog of the physics of carrier transport in semiconductors with a view to establishing energy device models. This part systematically explains the diffusion-drift model that is central to solar cell operation, the different responses of band bending and electrical field distribution that occur when a voltage is applied to a device with contacts, and the central issue of injection and mechanisms of contacts. The carrier transport in disordered materials is explored, as these often appear as good candidates for easily processed solar cells. There are also excursions into other important topics such as the transistor configuration and frequency domain techniques, such as Impedance Spectroscopy, that produce central experimental tools for the characterization of these devices.

The third part, Chapters 17–19, consists of the background to essential physical and material properties about electromagnetic radiation fields, optical properties

of semiconductors, and the interaction of light with the latter causing the generation of carriers that are at the heart of photovoltaic action: creating energetic electrons that go around an external circuit.

The fourth part, Chapters 20–27, addresses the main goal of the book: to provide an explanation of the operation of solar energy conversion devices, which embraces concepts from a diversity of classes of solar cells, from nanostructured and highly disordered materials to highly efficient devices such as the metal halide perovskite solar cells. The approach is to establish from the beginning a simple but very rich model of a solar cell, in order to develop and understand step-by-step the photovoltaic operation according to fundamental physical properties and constraints. The subject matter is initiated by formulating the physical basis of the recombination diode, and from the standpoint of the built-in asymmetry of the flow of electrons and holes, state the effects of the interaction of light and the semiconductors, the creation of the split of Fermi levels, and the production of output electrical power. In many textbooks, solar cell operation is related to a diode element as the starting point. Here, the physical mechanisms determining the operation of the diode in photovoltaic conversion is clarified, as this is an essential point for the understanding and design of solar cell structures. This model was developed historically from the central insights of William Shockley, Hans-Joachim Queisser and Robert T. Ross in papers published 50 years ago (see Chapter 22). It focuses on the aspects pertaining to the functioning of a solar cell and the determination of limiting efficiencies of energy conversion, by intentionally removing the many avoidable losses such as transport gradients, which are treated in the final chapters. This is then extended to the physical limitations to optimal conversion obtaining more realistic and specific effects, configurations, and shortcomings that provide a summary of the multitude of effects that may come into play at the time of experimental investigations and technological development.

Building on the knowledge that has been gathered in the book allows exploration of the physical and electrochemical properties of devices, from molecular aspects to macroscopic models, which can provide the reader with a strong foundation both for understanding solar cell operation and for exploring related materials and a broader class of possibilities for solar energy conversion devices.

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Author



Juan Bisquert is a professor of applied physics at the Universitat Jaume I de Castelló and the funding director of the Institute of Advanced Materials at UJI. He earned an MSc in physics in 1985 and a PhD from the Universitat de València in 1992. The research work is in perovskite solar cells, semiconductor optoelectronics, mixed ionic-electronic conductors, and solar fuel converters based on visible light and semiconductors for water splitting and CO₂ reduction. His most well-known work is about the mechanisms governing the operation of nanostructured

and solution-processed thin film solar cells. He has developed insights in the electronic processes in hybrid organic–inorganic solar cells, combining the novel theory of semiconductor nanostructures, photoelectrochemistry, and systematic experimental demonstration. His contributions produced a broad range of concepts and characterization methods to analyze the operation of photovoltaic and optoelectronic devices. He is a senior editor of the *Journal of Physical Chemistry Letters*. He has been distinguished several times in the list of ISI Highly Cited Researchers. Bisquert created nanoGe Conferences and is the president of the Fundació Scito. He wrote a novel of speculative fiction, *The Canamel Conjecture*.



1 Introduction to Energy Devices

A system far removed from its condition of equilibrium is the one chosen if we wish to harness its processes for the doing of useful work.

(G. N. Lewis and M. Randall,
Thermodynamics, 1923, p. 111)

Many technologies have been developed throughout history to provide for human needs: procuring heat, light, and mechanical work for homes, agricultural and industrial use, transportation, and in general to facilitate a broad set of activities of life. These technologies and systems share many features, and the concept that unifies them is *energy*.

In physics, energy is the capacity to do work, meaning that a force can displace an object along a distance. But this is later generalized to a large number of energies, such as thermal energy, related to heat; kinetic energy, in moving objects; chemical energy; electric energy; and many others. The connection of energy to the history of civilization has been well summarized by Smil (2017).

While we live in the midst of thermal energy that is readily available, the energy that we are interested in is one that we could utilize readily for our needs. We wish to easily direct such energy to power a machine or portable electronics that will perform the desired task. The energy flowing in the environment as heat is not useful for these purposes. Energy that is able to do work has to be produced from available sources. Usable energy also has to be stored for use at the time when it is needed, or transported to the required place of consumption.

This book is about using a combination of materials for a useful purpose, either related to energy production and storage or for some practical need that consumes energy. Such an arrangement is called a “device.” It is usually operated electrically; therefore, it has contacts where we plug in the external circuit, and internally it is composed of a variety of condensed phase components. Here, we will not examine the basic properties of the materials as a wide variety of books are available on that topic, either from a chemistry or solid-state physics angle. Rather, here we will discuss the methods of analysis of the properties of combinations of the materials in a device, the contacts between the phases, the conductivity, the light absorption or luminescence, the production of chemical species, and their use in providing output power. We will discuss the generation of electricity that does not involve any macroscopic moveable parts and no

other motion than the electrons around the circuit. This is achieved by using different kinds of species: photons impinging on light absorber materials and electrons and ions in the solid state and in liquid electrolytes. The final use of energy devices is to transform energy from raw sources to usable energy, to store that usable energy, and also, in some cases, to produce desired processes with substantial energy resource savings.

Industry, transportation, lighting, and communication depend on the supply and utilization of low-priced electricity and clean fuels. As a result of the rising population and increasing living standards around the world, the need for a reliable, convenient, and adaptable energy supply has become a central concern. Currently, chemical energy is the most convenient and useful form of portable energy, and this explains the dependence on fossil fuels (coal, petroleum, and natural gas). However, extensive use of fossil fuels has had a dramatic impact on the world, particularly in environmental change and effects on health. Many people believe that profound changes need to occur in the production, delivery, and utilization of energy. Another important concern is the rising demand of power storage and supply in a variety of forms for feeding portable electronics and electric cars as well as for the continuous availability of solar or wind energy. The development of new energy devices can deeply transform the ways in which energy is obtained and produced, with broad implications for the environment and for the human needs.

A formulation of the desirable system of renewable energy supply is well understood. Sunlight and water are, in effect, inexhaustible resources to provide the required diversity of energy supplies. Sunlight is the largest energy resource base currently available. Solar energy is well distributed across the most populated areas of the globe, making the resource accessible where it is most needed. Furthermore, because solar energy is carbon-neutral and environmentally benign, its conversion represents an ideal method of powering the planet.

However, the conversion of solar photons into a usable form of energy is a huge challenge. Solar energy on earth is dispersed in many ways: light arrives at low concentration (1 kW m^{-2} at midday), in an intermittent fashion, and with a wide dispersion of frequencies across the electromagnetic spectrum. Analogous to photosynthesis, storing solar energy in chemical bonds (i.e., solar fuels) would be an ideal method to provide usable energy. It is

particularly attractive to use solar energy to split water into H_2 and O_2 , and subsequently the H_2 could be used in a fuel cell or other energy conversion scheme. High-performance lightweight batteries can be used to propel electric vehicles. However, major technological advances are required to achieve systems that have the capability to produce electricity, break H_2O bonds, and store the energy either in batteries, as molecular hydrogen, or in carbonized fuel compounds. Large-scale reduction of CO_2 assisted by solar photons can alleviate the greenhouse effect and form the basis for useful chemistries. Currently, such systems pose formidable challenges in terms of the required materials, efficiency, cost, and design of practical devices.

For several billion years, bacteria and plants have been effectively converting solar energy into chemical fuel by means of photosynthesis. To compensate for the low concentration of solar energy, living systems spread wide area converters—the leaves—built with organic components that can self-heal when failure occurs during the photochemical operation. To counter the degradation of the organic components, the solar collectors in plants can ultimately be dropped and renewed. These systems are thought to provide a main source of inspiration for the formation of artificial systems for large-scale supply of clean energy. However, we must note that photosynthesis, on average, has a conversion efficiency of only about 1%.

The operation of energy devices is rooted in fundamental physical principles. One key concept that should be kept in mind is the unidirectional flow of all systems toward the final state of equilibrium. The flows of the carriers in the device will be regulated by the entropy as a quantity that is always increasing in all natural phenomena. This approach focuses attention on this irreversible process (Tolman and Fine, 1948). Lewis and Randall developed a conclusion in 1923: a system far removed from its condition of equilibrium is the one chosen if we wish to harness its processes for the doing of useful work. While a battery at open circuit is usually regarded as an equilibrated system (from an electrical point of view), we should look at this system as either far from equilibrium or useless. In energy systems for sunlight energy conversion, as in batteries used for energy storage, we must arrange electrons and ions in materials in a far-from-equilibrium, highly reactive state, which in order to be productive should react only in a very specific way. Thus, in a solar cell, the primary excitation created by a photon is an energetic electron-hole pair. The pair would naturally react (or recombine) at the site of creation, but instead the energy is harnessed by provoking the recombination in an external circuit. This requires

a directional arrangement that funnels the potentially reacting carriers toward separate pathways.

Since solar energy is diffuse and intermittent, the power conversion efficiency of viable devices must be high. Light absorption and forward process must be optimized and backward reaction cannot be afforded. In general, the cornerstone of energy devices is to find an effective way to channel processes in a given direction and avoid reciprocal processes that constitute a waste. Another stratagem that is widely used is to deploy specific layers covering the contact that will realize the selection of one specific carrier from a homogeneous film. Such layers are termed selective contacts (Bisquert et al., 2004). In a charged lithium battery, the two electrodes contain electrons that withstand an energy distance of 3–4 eV (Goodenough and Kim, 2010). The high-energy (strongly reducing) electrons in the negative electrode tend to fall to the low-energy state in the positive electrode (the cathode), and such flow is contained by an electrolyte that conducts ions and not electrons. However, the electrons cascade if the electrolyte is reduced or oxidized. The electrochemical stability of the electrolyte limits the voltage that can be gained by modifying the lithium intercalation materials to high positive values in the electrochemical scale. In contrast to the solar cell and any thermal engine, a crucial feature of the battery is the noncyclic character of its operation. Once the useful energy has been degraded by using the battery, the initial (charged) state has to be restored from the outside via a flux of negative entropy toward the battery, which cannot be spontaneous.

The need for a large area for effective scale energy production leads us to search for materials combinations and systems that can combine low fabrication cost with medium-to-high conversion efficiencies. The general term nanotechnology refers to the technology of design, manufacture, and application of nanostructures and nanomaterials, while nanoscience is the study of the fundamental relationships between physical and chemical phenomena in materials dimensions on a nanometric scale. Nanoscale materials and devices for energy harvesting, storage, delivery, and for improving the energy efficiency of certain needs have been successfully developed. Nanosized materials and their combinations provided several opportunities for innovation and improvement of certain functions required in energy devices. Beneficial features are an increased surface area, better tolerance to volume changes, increased functionality at the interface between the different phases of the device, and the formation of transport pathways toward the active interfaces or the charge-accumulation phases. The small dimension of semiconductor nanostructures

also permits the tailoring of physicochemical properties, such as the light absorption or thermodynamics of carriers, basically controlling the size of nanoparticles, nanowires, or nanotubes.

Nanostructured materials, based on combinations of inorganic and organic materials, emerged to efficiently convert solar energy into electricity or fuels. Large-area devices can be obtained by low-temperature solution-processed techniques. An archetypical energy device is a nanostructured electrode in which a porous layer with the required properties is deposited on a conducting substrate that allows electrical manipulation of the internal structure. Examples of metal oxide mesoporous electrodes are shown in Figure 1.1. Figure 1.2 shows an example of TiO_2 made of octahedron-like single crystal anatase particles, deposited on transparent conducting oxide (TCO) over glass. The structure of individual single crystals of anatase phase is shown in the inset of Figure 1.2, and Figure 1.3 shows the atomic structure of the nanocrystallite, which is about 10 unit cells wide. The fundamental electronic operation of this type of electrode (Wang et al., 2014) can be seen in Figure 1.4: specific electronic processes occurring in the semiconductor matrix allow the exchange of electrons with the substrate, via the transport in the nanostructured film, and such electrons enter the outer circuit where they serve to do electric work. Figure 1.4 also suggests a density of electronic states (DOS) in the TiO_2 nanoparticles, which is associated to disorder in this kind of material, although a broad DOS can be found even in the case of crystallites, due to grain boundaries, small size effects, interaction with the medium in the pores, and other effects. The main structural unit of electrical operation, however, requires two contacts so that electrons can go around the circuit. Separation between the active electrode and the second contact is also required in order to avoid a short circuit that disables the device. One way to achieve the operational architecture is by utilizing a redox electrolyte to contact the active electrode and counterelectrode, as shown in Figure 1.5. The liquid medium forms a barrier to electrons in the nanostructure, so that electrons are channeled to the substrate. However, the generation and extraction of electron requires their replenishment for a continuous process to be maintained. This can be achieved by the transport of ionic species that take or give electrons by electrochemical reaction at the interfaces. Thus, the electrochemical reaction provides a fundamental switch between electronic and ion conduction with numerous implications for energy devices such as batteries and photoelectrochemical solar cells.

The actual energy conversion process relies on a set of sequential steps, as outlined in Figure 1.6. Photon

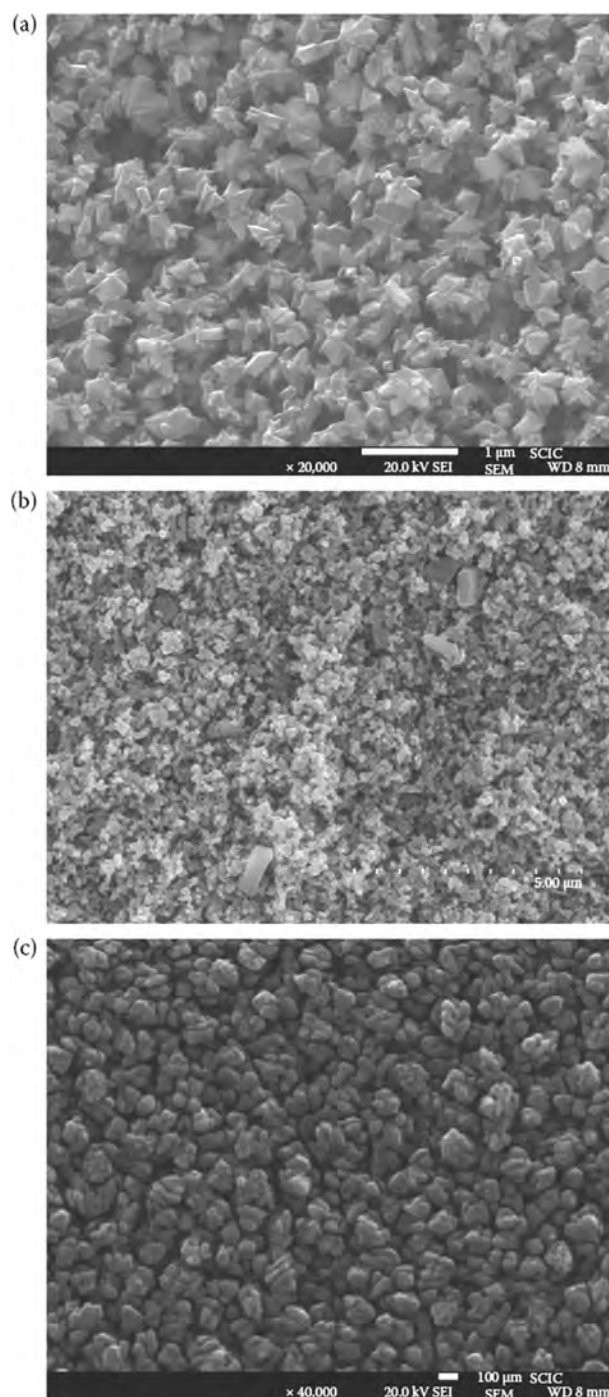


FIGURE 1.1 Top view micrographs of mesoporous films composed by different nanostructured metal oxides deposited on transparent conducting substrates: (a) TiO_2 nanoparticles, 250 nm particle size, (b) WO_3 nanoparticles processed by hydrothermal synthesis, (c) Fe_2O_3 deposited by spray pyrolysis. (Courtesy of Sixto Giménez.)

absorption creates electronic excitation of the absorbing component with concomitant electronic charge creation. The excitation can be an electron-hole pair in a semiconductor or an electronic excitation of a

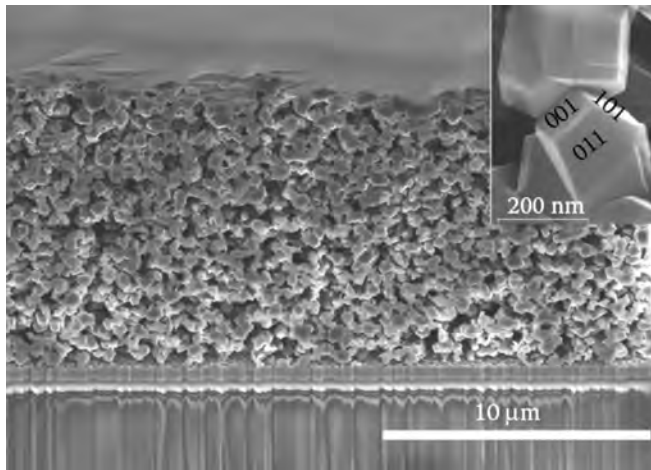


FIGURE 1.2 SEM image of the cross section of a porous electrode formed by sintered TiO₂ anatase crystals (inset), deposited on a transparent substrate that consists of a glass support and thin TCO layer. (Courtesy of Ronen Gottesman and Arie Zaban.)

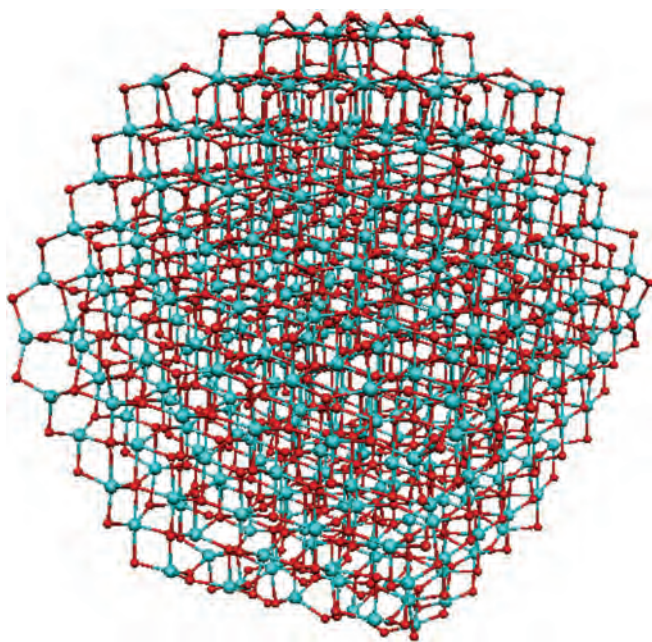


FIGURE 1.3 Atomic structure of anatase TiO₂ nanocrystal. (Adapted from Nunzi, F. et al., *Energy and Environmental Science* 2013, 6, 1221–1229. With permission.)

molecule or polymer, usually in the form of excitons. Separation of the electronic charges before they return to the ground state (recombination) allows investing the energy of the carriers in the required energy production functionality. Basically, the carriers are transported to contacts or reactive sites, using the cell structure described earlier, so that either a photocurrent emerges as the output or a desired chemical reaction is performed. The energy converter has to satisfy a series

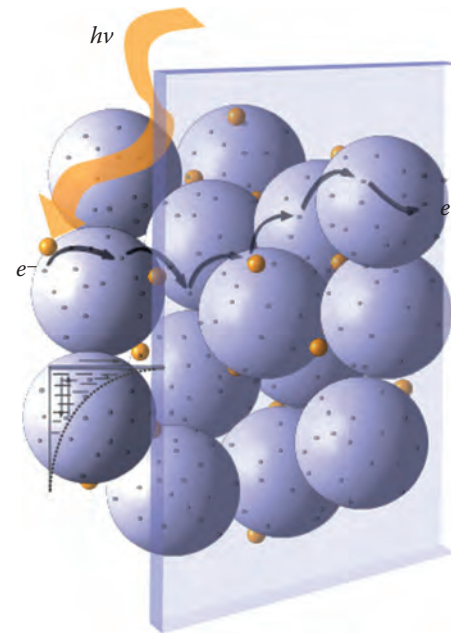


FIGURE 1.4 Scheme of electron transport in a metal oxide nanostructure, showing a photogeneration event, and the density of states in the semiconductor bandgap. (Courtesy of Juan A. Anta and José P. González.)

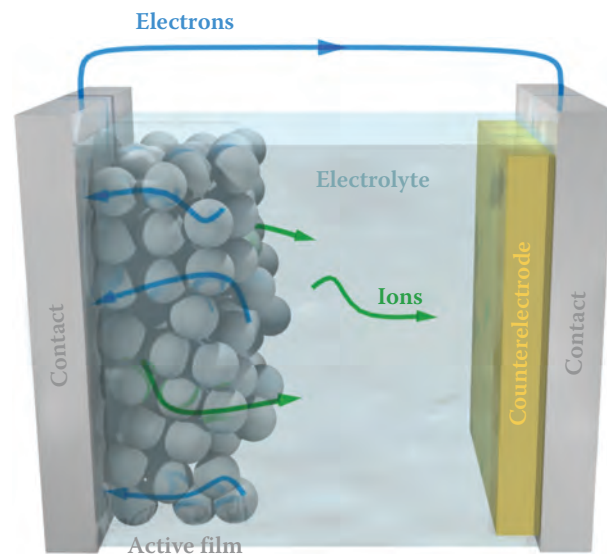


FIGURE 1.5 Scheme of an electrochemical cell consisting of a nanostructured semiconductor electrode that realizes efficient electron transport to the substrate contact, an electrolyte filling the pores, and transport of ions in the electrolyte. (Courtesy of Emilio J. Juárez-Pérez.)

of stringent requirements, including a narrow forbidden energy gap for photon absorption; a large light absorption coefficient; a high photon-to-charge conversion yield; good charge separation properties and long diffusion lengths (electrons and holes directed toward

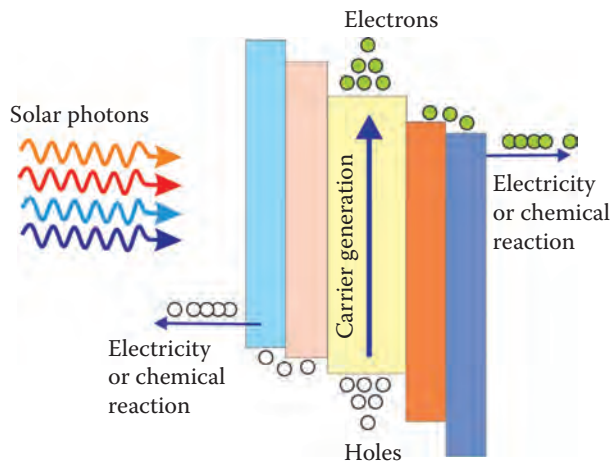


FIGURE 1.6 Scheme of solar energy conversion scheme using nanoheterostructures.

the useful function); a strong rate of product formation (electricity/chemical fuel) by good contact selectivity; and fast charge transfer kinetics of the forward reactions. The final requirements include robustness, duration, and low materials process costs.

In the second half of the twentieth century, a great deal of research effort was invested in the search for specific inorganic semiconductors that would perform *all* of the required functions in the conversion of solar photons into electricity or fuel. Success was obtained in the case of photovoltaic cells, with the development of defect-free, high-purity crystalline silicon solar cells. The quest for a semiconductor able to perform photoelectrochemical water splitting without degradation by corrosion was not successful and was abandoned in the mid-1980s. In 1990s, photovoltaic devices, pioneered by M. Grätzel, A. J. Heeger, and many others, were suggested, that operate on the basis of a combination of materials that takes advantage of the properties and phenomena occurring in nanoscale units and at interfaces (O'Regan and Grätzel, 1991; Scharber et al., 2006). Various specific photovoltaic nanostructured devices as well as some of their main physical properties are summarized in Figure 1.7. Nanoporosity was demonstrated to be a very efficient feature for effective charge separation and transport in different phases. Thus, dye-sensitized solar cells (DSC), inorganic quantum-dot sensitized cells, and organic

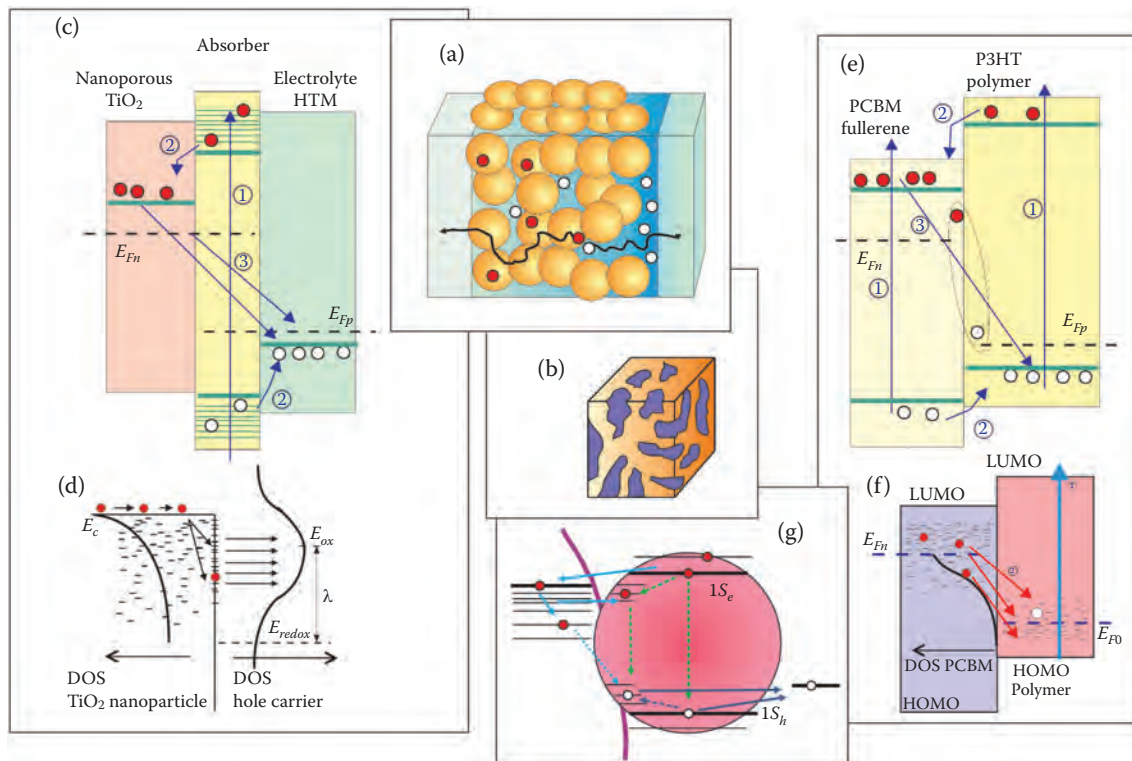


FIGURE 1.7 (a) Scheme of nanostructure that carries electrons and holes in different phases, (b) the structure of bulk heterojunction solar cells, with two organic phases closely mixed and separately interconnected, (c) energetic scheme of a dye-sensitized solar cell, showing the absorber dye molecule between electron transport material, and hole transport material, (d) the energetic disorder in recombination process, (e) energetic scheme of a bulk heterojunction solar cell, with carrier generation in both fullerene PCBM and polymer P3HT, (f) the energetic disorder in recombination process, (g) generation and charge transfer in a quantum-dot sensitizer.

solar cells (especially bulk heterojunction solar cells) became topics of major interest in research, both for their fundamental properties as well as reachable technological realizations. Semiconductor quantum dots also emerged as a very important sensitizer for photovoltaics, due to several attractive features such as the tunability of absorption by size and high extinction coefficients.

The schemes for solar energy conversion using low-cost, large-area nanostructures involve directed transfer of photogenerated carriers from the generation site to the final energy production step. These carriers use several physical phenomena that occur in nanomaterials and at their interfaces, including carrier accumulation, transport, and transfer across the interface. Insights into the physical rules that govern such phenomena in relation to specific materials and interface properties is a key element in the future design of energy conversion devices based on nanostructured, low-cost organic and inorganic materials. This will be an important topic of this book.

Research on solution-processed materials for solar cells produced significant outcomes in materials that can also

operate as thin films. Semiconductor materials based on metal halide perovskite have now been extensively investigated because of their exceptional opto-electronic properties, which allow for applications in areas such as solar cells, light emitting diodes (LED), X-ray detectors, and so on; see Figure 1.8. Research in this area initially branched off from the field of dye solar cell research. In the quest for an efficient inorganic quantum-dot sensitized liquid cell, this topic rapidly formed a huge field of its own.

The perovskite crystal structure shown in Figure 1.8a has been adopted by a large class of materials formed by a combination of three elements or molecules placed on the corners of the lattice and inner regular octahedral configuration. The chemical formula of the perovskite can be described as ABX_3 , where A = monovalent cations such as methylammonium (MA), formamidinium (FA), cesium (Cs), B = divalent cations such as lead (Pb), tin (Sn) and X = halide anions including chloride (Cl), bromide (Br), iodide (I). $MAPbX_3$ was first synthesized by Weber in 1978; see the crystals shown in Figure 1.9. The first attempt to apply methylammonium lead halide

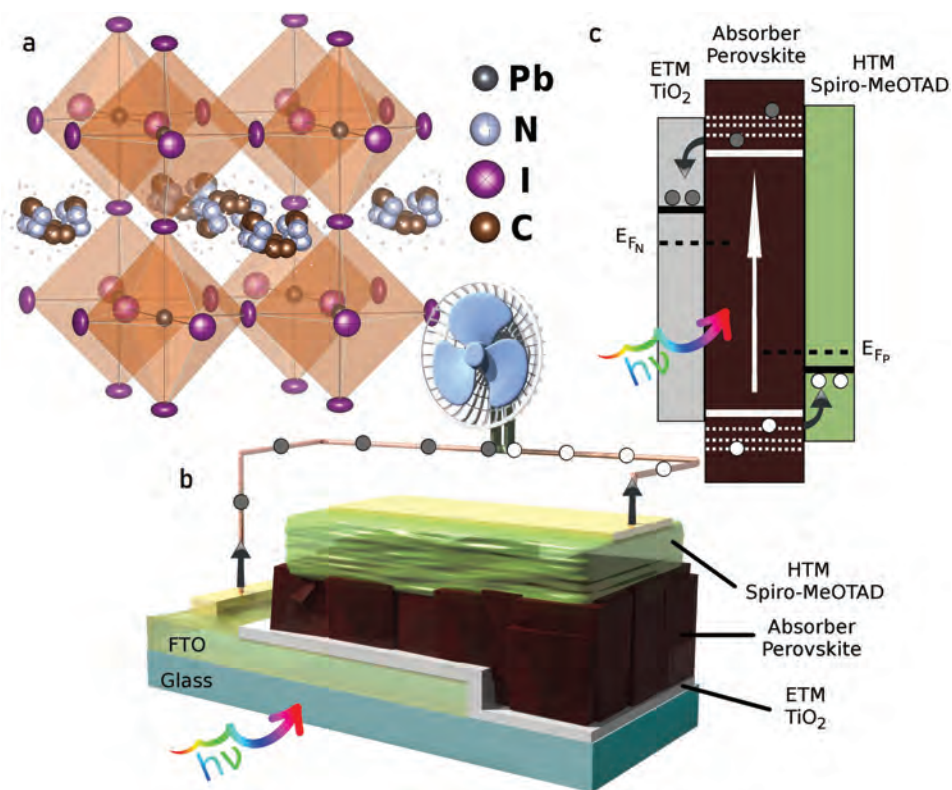


FIGURE 1.8 (a) Tetragonal crystal structure of $CH_3NH_3PbI_3$ perovskite as determined from XRD measurements in single crystal (ref no. 238610, Inorganic Crystal Structure Database), (b) perovskite solar cell conventional stack section using glass, FTO, TiO_2 compact layer, perovskite absorber, and Spiro-MeOTAD layer, holes are extracted from the Spiro-MeOTAD side and electrons from TiO_2 compact layer side; both meet again on the load in this case represented by a fan closing the electric circuit, (c) simplified energy band scheme for perovskite solar cell stack showing hybrid perovskite absorber material sandwiched between electron transport material (ETM, TiO_2) and hole transport material (HTM, Spiro-MeOTAD). (Courtesy of Emilio J. Juárez-Pérez.)

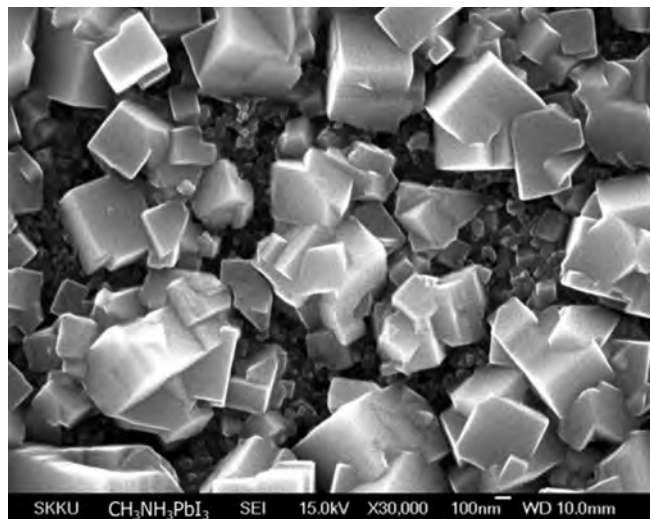


FIGURE 1.9 SEM picture of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals.

(bromide, iodide) (MAPbBr_3 , MAPbI_3) in solar cells was reported by T. Miyasaka and coworkers in 2009. They introduced perovskite nanocrystals as a light absorber into a conventional sensitized solar cell using iodide/triiodide liquid electrolyte. In 2011, higher concentrated precursor solutions almost doubled the power conversion efficiency of the 2009 device. After the initial configurations, that used a liquid contact to close the circuit, the first devices that adopted a solid-state hole transport material (HTM) during 2012 appeared. Such developments were also used in DSCs but, contrary to expected behavior observed in a DSC, perovskite solar cells with the solid-state HTM reached a remarkable $\sim 10\%$ of power conversion efficiency and overcame the ephemeral stability reached using liquid electrolyte selective contact. In 2013, the first basic layer stacks and procedures to assemble the device were published. For a short history of the development of the field see Bisquert et al. (2017).

In the next few years the advancement in material engineering and interface optimization continuously pushed the power conversion efficiency of perovskite solar cells; see the dense film formed by large perovskite grains on a nanostructured TiO_2 -based electron collector in Figure 1.10. A device formed by organic contacts is shown in Figure 1.11a. A certified record efficiency of 25.2% for single-junction solar cells was reached in 2020, which is comparable to crystalline silicon solar cells and even surpasses the efficiency of thin film CIGS and CdTe solar cells.

The most attractive features for perovskite-based photovoltaic and optoelectronic technologies include a low-temperature solution-processing method, exceptional semiconductor properties, and high efficiency achieved with very thin layer (< 500 nm), as well as the

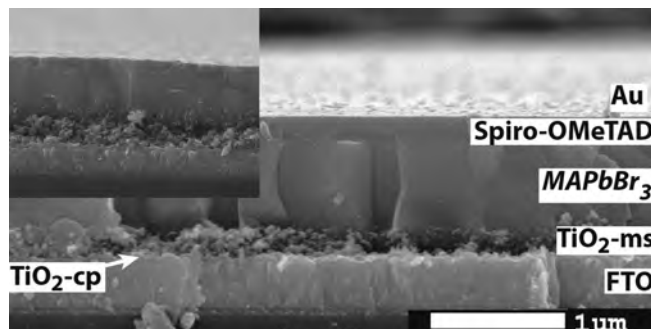


FIGURE 1.10 SEM cross-sectional view of a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite solar cell. Bottom contact (front contact of the solar cell) is nanostructured TiO_2 on top of compact TiO_2 deposited on FTO. The upper contact is Spiro-OMeTAD hole collector layer with a gold overlayer as metal contact. The inset shows the crystalline perovskite layer without top contact. (Courtesy of Clara Aranda and Antonio Guerrero.)

abundance of raw materials. These make them viable for large-scale production for lightweight, flexible devices using cost-effective methods such as roll-to-roll, screen-printing, or slot-die to facilitate low-cost solar electricity production and lighting in the future. The facile design of the bandgap obtained by modifying the compositions of the constituents makes hybrid perovskites suitable for high-efficiency LEDs, as indicated in Figure 1.12, and for the combination with other materials for high-efficiency tandem solar cells, as shown in Figure 1.11b. Note the improvement of charge collection by the application of an antireflective coating in the combined tandem arrangement shown in Figure 1.11c. The perovskite/Si two junction tandem arrangement has reached 29.1% record efficiency in 2020.

The rise of a succession of new classes of organic, inorganic, and hybrid materials with photovoltaic applications, the consequent realization and determination of their properties, and the optimization of materials and interfaces for better performance, are generally due to rather broad physical and chemical concepts and principles. The progress and understanding of the device operation of these materials has provided a pattern that will be systematically explained in this book (In addition, functionalities sometimes respond to unique and specific features).

In the pursuit of new photovoltaic conversion materials, the initial questions posed are, how can we extract charge at all, how does charge separation occur, and why do charges arrive at the electrical contact? Therefore, historically, the explanation of the functioning of a solar cell gave a heavy significance to the transport of carriers and the action of electrical fields. It has now been recognized that this approach may be highly misleading

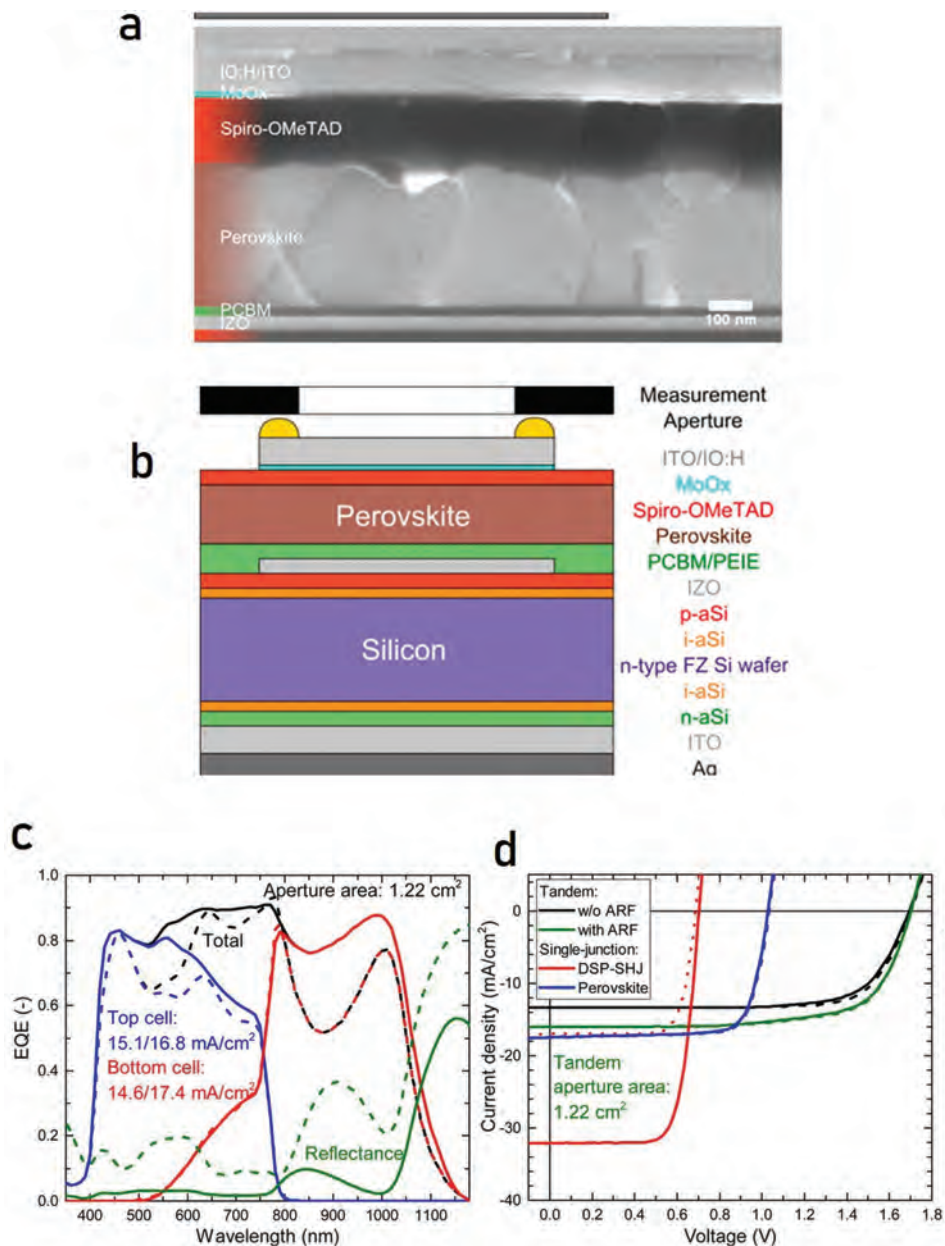


FIGURE 1.11 (a) SEM cross-sectional view of a perovskite solar cell, (b) schematic drawing of a planar monolithic perovskite/(amorphous/crystalline silicon heterojunction) tandem cell layer stack, (c) EQE spectra of a perovskite/Si monolithic tandem with (solid lines) and without (dashed lines) antireflective foil (ARF) as well as the corresponding reflectance (green curves); the integrated photocurrent for both top and bottom cells are given in the legend (without ARF/with ARF), (d) j-V measurements of the best perovskite/Si monolithic tandem with 1.22 cm² aperture area and of the single-junction perovskite and Si cells; reverse (solid lines) and forward (dashed lines) scans are shown for perovskite single-junction and tandem cells; the dotted red curve shows the j-V curve of the Si cell when illuminated at an intensity of 0.53 suns. (Reproduced with permission from Werner et al., 2016.)

about the core of the operation of photovoltaic conversion. When the material becomes better understood, carrier collection is usually not the main issue of photovoltaic cells. In most cases, the crucial issue is obtaining the maximal photovoltage allowed by the fundamental physical constraints; therefore, one begins to worry about reducing the recombination and finding the

optimized structures for selective contacts. If the technology progresses sufficiently and reaches a level of very high conversion efficiencies, the electronic operation of the device becomes reproducible and proficient, and then it is necessary to maximize the extraction of power from every photon that comes to the device surface. The researcher is then forced to attend to the photonic

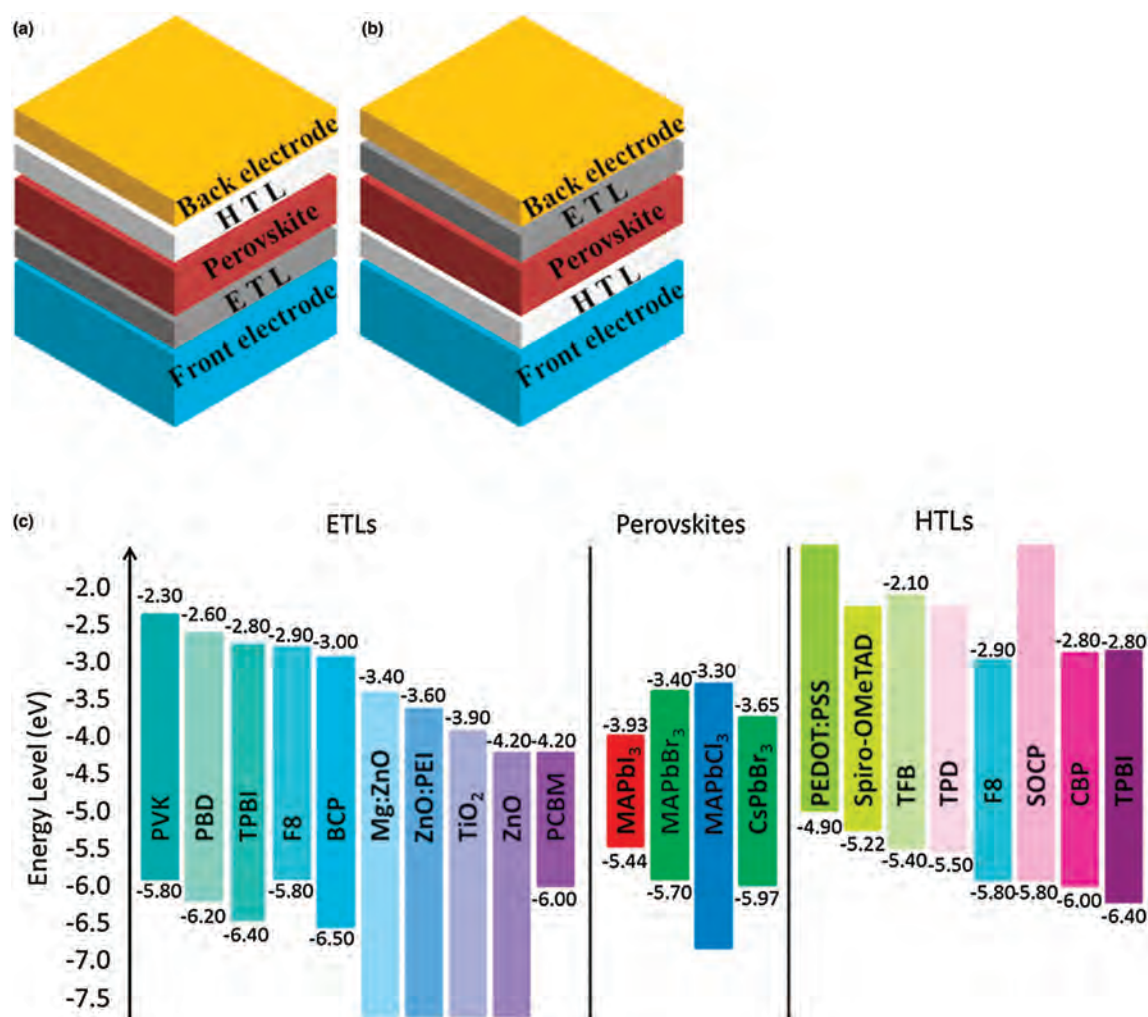


FIGURE 1.12 (a, b) Schematic diagrams of perovskite LED architectures in the conventional and inverted configuration, respectively, (c) energy level alignment of various materials used as perovskites, ETLs, and HTLs in the perovskite LEDs. (Reproduced by permission from Adjokatse et al., 2017.)

characteristics. Thereafter, schemes are developed to harvest the full solar spectrum, a task that requires a combination of absorbers. Therefore, to keep up with the pace of research, one needs to go through a wide variety of problems.

In general, this book is about understanding solar cell device operation and related devices. Device understanding usually consists of a picture of how the device operates internally, sufficient for rationalizing the outcome of different manipulations and materials variations. These tests and studies can be performed using the established array of experimental tools, as well as the new techniques that can be designed for specific problems that appear during the analysis of a new class of materials/devices. Such understanding is based on a broad range of physical principles, on the mastering of chemical features of inorganic lattices and organic molecules and

their aggregates, and on a comprehension of different classes of materials and their interfaces.

By understanding, we obtain a tool for explaining device operation that guides us in developing modifications and improvements, and opens doors for better designs of materials, structures, and interfaces. Achieving such a tool is the purpose of the forthcoming chapters.

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