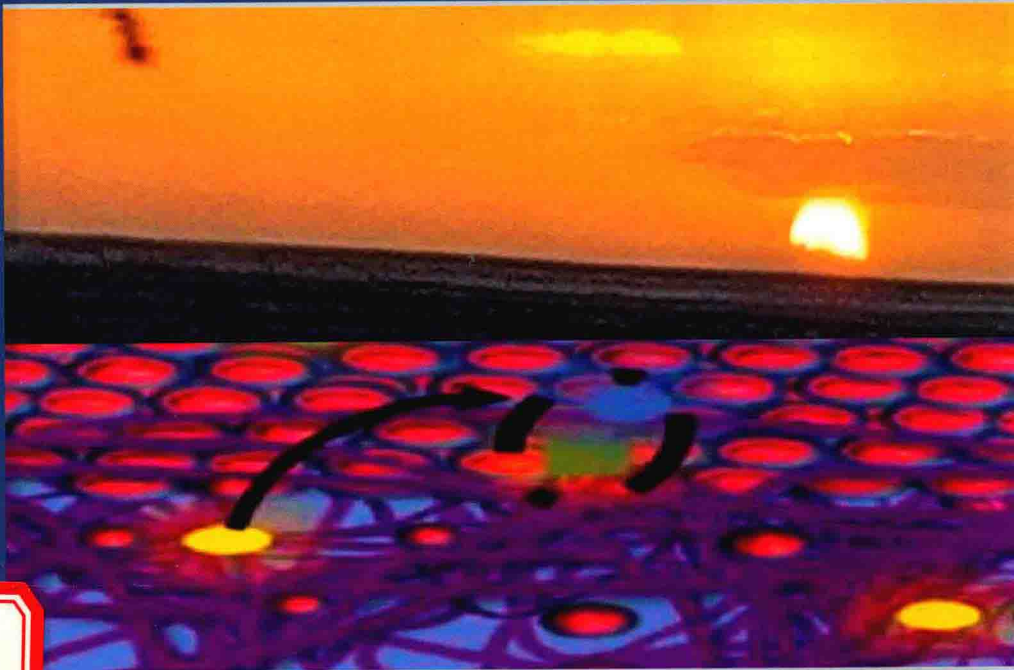
# SOLAR FUELS

## MATERIALS, PHYSICS, AND APPLICATIONS



THEODORE GOODSON, III

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## Materials, Physics, and Applications

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*To my wife Stephanie Lynn*

*and my kids Jared (Theodore IV), Elizabeth, and Sean*

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# Preface

In this book, I have attempted to provide an interesting view about solar energy production for both new and experienced scientists and engineers, as well as for enthusiasts who have a little technical background. The book is thus not intended to provide complete analytical discussions as a textbook would. Instead, I provide the key concepts and results and subsequent approaches in these areas. The book is designed for study in general for all interested thinkers to enjoy the subject without extensive background in mathematics and physics. However, the details are provided in a concise manner and the references therein will guide the reader in the direction toward learning more. Great effort has been made to make the book both very recent in content and practical in approaches and subject matter. Even more to this end, I have attempted to capture the most recent thoughts and predictions about the effect of this field on our nation's (and the world's) energy economy and market place.

In Chapter 1, the book provides a substantial introduction to the principal issues behind the goal of increasing the use and efficiency of solar cell devices in our energy economy. This chapter also outlines the basic types of solar cell devices and their positive and negative characteristics presently limiting their use in real translatable devices. This sets up chapters related to the mechanism of how present organic solar cells work, the critical organic structures used in the devices, how we measure the important parameters with a large variety of experimental techniques, modernization of organic cell design, the importance of the interfaces in organic solar cell devices, and new approaches to beat old limits to solar cells. Chapter 6 presents newer approaches with singlet exciton fission as well as with organometallic perovskite materials. In Chapter 7, I summarize and provide an outlook into what might be on the horizon for this field. The goal of these chapters is to ultimately be used as a reference point for the reader to learn the basics of the topic and to be able to come back to this topic again and remember what has already been accomplished and what are the present limitations in the field.

After much thought, I decided to concentrate mainly on organic solar cell devices. The field of solar development with inorganic devices as well as with silicon enjoyed a great deal of success and attention in other well-written texts in the past. The introductory chapters briefly review some of the approaches and successes with inorganic solar materials. The extensive reference list is straightforward and will help in finding out more concerning the physics and chemistry of these organic devices.

I am very much indebted to colleagues from around the world for the detailed discussions in this field for the preparation of writing this book. I thank Professor Luping Yu for his continued encouragement and expert advice on this subject, Professor Victor Batista for his close attention to detail and suggestions, and Professors Peter Green and Mike Wasielewski for their expert advice and work. Finally I would like to thank Pamela and Bruce Epstein as well as my parents (Exie and Theodore Goodson) for their encouragement in finishing and proofreading this book.

# Author

**Theodore Goodson III** received his BA in 1991 from Wabash College and earned his PhD in chemistry at the University of Nebraska-Lincoln in 1996. After postdoctoral positions at the University of Chicago and at the University of Oxford, he accepted a position as assistant professor of chemistry at Wayne State University in 1998. In 2004, he moved to the University of Michigan as professor of chemistry. In 2008, he was appointed as the Richard Barry Bernstein Professor of Chemistry at the University of Michigan. Dr. Goodson's research centers on the investigation of nonlinear optical and energy transfer in organic multichromophore systems for particular optical and electronic applications. His research has been translated into technology in the areas of two-photon organic materials for eye and sensor protection, large dielectric and energy storage effects in organic macromolecular materials, and the detection of energetic (explosive) devices by nonlinear optical methods. He has investigated new quantum optical effects in organic systems that have applications in discrete communication systems and sensing. Dr. Goodson's lab was also the first to investigate the fundamental excitations in small metal topologies that are now candidates for tissue and other biological imaging. In 2009, he founded Wolverine Energy Solutions and Technology Inc., a start-up company with contracts to produce high-energy-density capacitors for military, automotive, and medical devices. The company also developed a new system for the detection of IEDs remotely, with one of the patents awarded to Dr. Goodson at the University of Michigan. His awards include the Distinguished University Faculty Award, the National Science Foundation American Innovation Fellowship, the Research Young Investigator Award, National Science Foundation CAREER Award, Alfred P. Sloan Research Fellowship, the Camille Dreyfus Teacher-Scholar Award, the Lloyd Ferguson Young Scientist Award, the Burroughs Welcome Fund Award, the American Chemical Society Minority Mentorship Award, the University Faculty Recognition Award, the College of Science Teaching Award, and a National Academy of Sciences Ford Postdoctoral Fellowship. Dr. Goodson has been a senior editor for *The Journal of Physical Chemistry* since 2007. Dr. Goodson has published more than 150 scientific publications.

# Contents

# 1 Historical Background and Structure of This Book

## IN THE BEGINNING

Solar energy is the oldest form of natural energy on planet Earth (Figure 1.1). Its seemingly unlimited power has mystified cultures who have praised Ra and the Phoenix.[1] Once thought too powerful or too dangerous to harness, the sun has moved into the spotlight finally to offer a real solution to our energy needs. The use of the sun's heating potential can be traced back as far as the first century AD[2] where sun rooms appeared in Roman architecture. And as early as the 1700s, complete designs and construction of the first solar collectors were created in order to do actual work as well as cook food.[3] Indeed, the idea of utilizing the sun's energy for all its worth is not new. After all, it was in 1816 that this first solar thermal electric technology appeared, which concentrates the sun's thermal energy in order to produce power.[4] Science, ingenuity, inspiration, and timing appear to be the critical elements toward the pioneering developments in the use of solar energy. As in many paradigm shifts in technology, there comes a time when the summation of these elements comes to an uplifting cadence and the world realizes the need for something new and something better that will maintain our way of life and provide for those in the future. It has happened before; for example, the inspiration of famine and wars has galvanized the creation of new technology that has both saved and enlightened our way of living. Today's inspiration is a result of diminishing fossil fuels and the economics of a threatening new world.[5]

While the idea of utilizing solar fuels is not new, the development of the materials and the specific mechanisms that might ultimately provide the best solution have come a long way since the early days of solar thermal electric technology. Indeed, the creation and perfection of solar panels have enjoyed great success. A solar cell is any device that directly converts the energy in light into electrical energy through the process of photovoltaics.[6] The development of solar cell technology begins with the 1839 research of French physicist Antoine-César Becquerel.[7] Becquerel observed the photovoltaic effect while experimenting with a solid electrode in an electrolyte solution when he saw a voltage developed when light fell upon the electrode.[7] This photovoltaic mechanism provided the much needed insight into a possible strategy of producing useful and possibly efficient energy from the sun. It is believed that in 1883, the first functioning solar cell was made by Charles Fritts,[8] who used junctions formed by coating selenium (a semiconductor) with an extremely thin layer of gold. However, early solar cells had energy conversion efficiencies of less than 1%.[9]

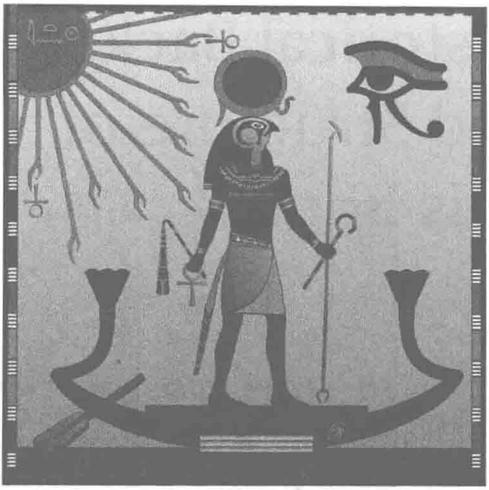

**FIGURE 1.1 (See color insert.)** The gods of ancient Egypt—Aten and Ra. Ra in the solar bark. (Credit: www.shutterstock.com, 122013538.)

In 1941, the silicon solar cell was invented by Russell Ohl.[10] And in 1954, three American researchers, Gerald Pearson, Calvin Fuller, and Daryl Chapin, designed a silicon solar cell capable of a 6% energy conversion efficiency with direct sunlight.[11] This, for the first time, gave those concerned with our world's energy economy great attention as this suggested that with further development, silicon solar cells were indeed a viable energy provider. In this invention, an array of several strips of silicon (each about the size of a razorblade) placed in sunlight captured the free electrons and turned them into electrical current.[11] They had created the first solar panels. As will be seen in this analysis of the critical points of organic solar cell technology, new materials and devices are now closer to 10% efficiency with good reproducibility.[12] It still might be a hard sale to replace silicon. The present silicon solar cells operate in the range of 15%–25% depending on the scale and operating conditions.[13] They absorb nearly 60% of solar light and their small bandgap (1.1 eV) enables photons with low energy (e.g., red light) to create the necessary electron–hole pairs that generate photocurrent.[13] However, the absorption of high-energy photons (blue light) results in "hot" electrons, which are both electronically excited and thermally activated[14] and lose most of their energy as heat without contributing to electric power.[14] Therefore, a hurdle to boosting energy conversion efficiency in organic photovoltaic solar cells is not just replacing those made from silicon, but it is also to capture the excess energy of the thermally unrelaxed electrons before it is lost as heat.

## GOALS FOR FUTURE SOLAR CELLS

In discussing the relatively broad topic of solar fuels, it is very important to know the goals of such a massive undertaking. As discussed briefly earlier, there is a long

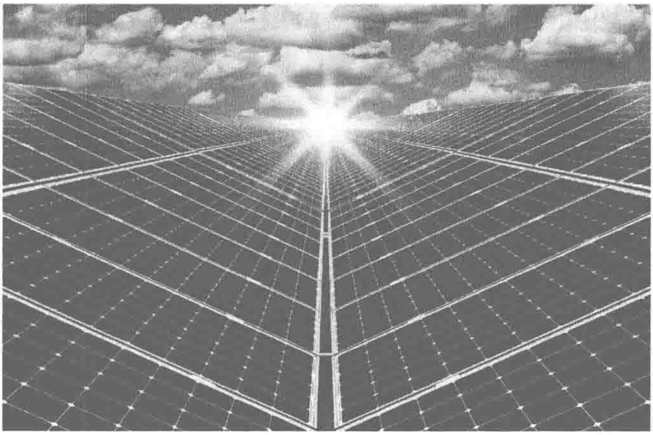

**FIGURE 1.2** **(See color insert.)** Power plant using renewable solar energy from the sun. (Credit: www.shutterstock.com, 177900254.)

history of the use of solar energy for various important applications (Figure 1.2). So it is necessary to specify particular goals for a modern analysis of this area. Thus, a major goal in this undertaking is related to the development of new materials for the construction of modern solar cells. The materials used in modern solar cells may be divided into two parts. Historically, it has been inorganic materials that first arrived on the scene in the construction of modern photovoltaic devices.[15] The use of molecular beam technology has allowed a great degree of success in this methodology as it has allowed the precise deposition of the inorganic materials on substrates to very high resolution.[16] The other kind of material used in modern solar cell development is that made of organic (made of primarily oxygen, nitrogen, carbon, and hydrogen) systems.[17] In this area of research, a virtual explosion of interest and investments has recently come to the focus of technology. From basic research to the translation of novel materials and devices, the area of organic solar cells is at the penultimate step in the development of competitive and productive materials that can one day be commercialized. Not only has the field of organic solar cell discovery enjoyed a number of great accomplishments potentially worthy of translating into the marketplace, but the field has developed a deeper understanding of the processes and science involved in their mechanisms. In many ways, the fruit of this knowledge has already begun to expose itself in other areas of science.[18] And the inspiring ideas and creative solutions illustrated by this basic research have prompted a serious consideration about the possibility of this form of solar energy consumption one day being a real alternative solution. It is because of these reasons that a major goal of this undertaking in analyzing the developments of solar fuels will focus primarily on organic solar materials. A close look at the developments in this area, some failures and many successes, as well as looking to the future for these materials will be discussed.

## MOLECULAR PROCESSES IN ORGANIC SOLAR CELLS

While the understanding of new materials is critical to one's appreciation of where the field of organic solar cells is heading, it is also important to discuss the critical lessons learned about the construction and engineering of these devices. The use of selected fabrication procedures has allotted the expertise in providing relatively efficient and reproducible results utilizing organic materials for solar devices. The earliest devices with single layers of active organic solar cell materials provided the needed standards for what was necessary in dealing with organic semiconductor solar cell materials.[19] Many of these materials were organic polymers at first, then small molecules and later other organic molecular architectures.[20] Later, after much investigation, the concept of the bulk heterojunction arrived and was initially introduced by blending two polymers having both donor and acceptor properties in solution.[21] This provided further discussions and developments in the area of mobility and diffusion of excitons and charges in such devices. The fabrication of the films and their properties became a major obstacle. A number of techniques arrived which would allow the coating of particular solutions to be homogeneous and provide less defects. For example, spin cast films from binary polymer solutions could result in solid state mixtures of both polymers with good properties but could also be optimized by the choice of polymer or particular small molecule additives.[22] The area of device and film fabrication has developed even further with other techniques such as the lamination of two polymer layers.[23] Higher power conversion efficiencies have been reported with such devices which provide a relatively diffusive interface between the donor and acceptor polymer structures. This field continues to expand in its approach toward the fabrication of solar devices utilizing solar materials.

In addition to the fascinating work carried out on bulk heterojunction organic materials, there is also considerably large effort in the field of dye-sensitized electrochemical solar cells. This area has received great attention as in its initial phase of development, there were important and very well-received accomplishments made by scientists such as Graetzel and others.[24,25] The different methods have learned from each other. For example, a number of approaches have introduced organic hole conductors in place of the liquid electrolytes in electrochemical solar cells.[26] There has also been a push to the possible exchange of the electron-conducting acceptor materials in organic heterojunction devices with inorganic nanocrystals. Thus, it appears that the electrochemical and organic photovoltaic research directions are gradually merging together in order to provide the best possible solution. Again, this puts great emphasis on the basic research nature of much of the work that has been done in organic solar cells development over the past 40 years.

## EXCITONS AND ORGANIC SOLAR CELLS

The goals of understanding the materials used in solar cells and their fabrication into devices are the first steps in obtaining a basic grasp of what and where this field is at in terms of its development. One must also understand the basic physics of how electrons and holes move throughout the material and produce efficient transfer. It is well known now that in order to create a working photovoltaic cell, the two photoactive

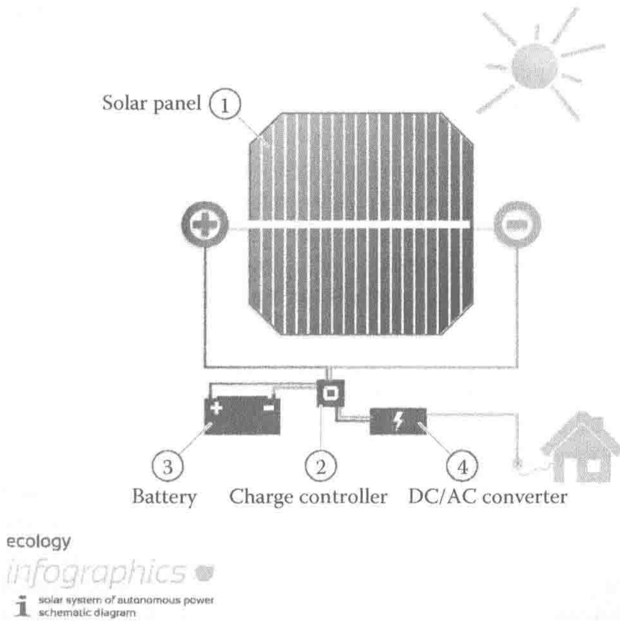


**FIGURE 1.3** **(See color insert.)** House equipped for the use of solar energy. (Credit: www.shutterstock.com, 186664391.)

materials are sandwiched between two metallic electrodes to collect the photogenerated charges. Generally, one of the electrodes is metallic and the other is transparent as to allow for good solar photon capture. After the charge separation process, the charge carriers have to be transported to these electrodes without recombination. Finally, it is important that the charges can enter the external circuit at the electrodes without interface problems. Thus, it is critical to understand the four basic steps in the solar cell function (Figure 1.3). It is now generally believed that the process of converting light into electric current in an organic photovoltaic cell is accomplished in four consecutive steps: (1) *absorption* of a photon leading to the formation of an excited state, the electron–hole pair (exciton); (2) *exciton diffusion* to a region; (3) *charge separation*; and (4) *charge transport* to the anode (holes) and cathode (electrons).[27] The potential energy stored within one pair of separated positive and negative charges is equivalent to the difference in their respective quasi-Fermi levels, or in other words it corresponds to the difference in the electrochemical potentials. The larger the quasi-Fermi level splitting that remains during charge transport through the interfaces at the contacts, the larger will be the photovoltage.[28] For ideal (ohmic) contacts, no loss is expected, and energy level offsets or band bending at nonideal contacts (that undergo energy-level alignments due to Fermi-level differences) can lead to a decrease in the photovoltage.[28] The electric current that a photovoltaic solar cell delivers corresponds to the number of created charges that are collected at the electrodes. This number depends on the fraction of photons absorbed ($\eta_{\_abs}$),