

Introduction

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Increasing worldwide demand on energy and the limited amounts of nonrenewable fossil fuels have stimulated intense research and development efforts on renewable energy, in the areas of solar cells, energy storage, fuel cells, and water splitting, to name a few. However, widespread applications of renewable energy have not been very successful mainly due to the high cost of materials and underdeveloped processing and fabrication techniques. When compared to their bulk counterparts, nanomaterials possess well-defined nanostructures and exceptional physical and chemical properties. They exhibit great potential for developing low-cost, high performance renewable energy sources. For example, rational engineering on the nanostructure of photoanodes in dye-sensitized solar cells (DSSCs) has led to largely enhanced device performance; quantum dots that show multiple exciton generation (MEG) capability may offer great promise in the fabrication of solar cells with power conversion efficiency exceeding the Shockley–Queisser limit; development of advanced synthetic methods for pyrite nanoparticles has led to solution-based fabrication of low-cost, environmental friendly thin film solar cells; investigation on the Indium tin oxide (ITO)-free transparent conductive films will help realize the commercialization of flexible electronic devices; design and fabrication of nanostructured electrodes have provided the opportunity for developing high performance, low-cost fuel cells, efficient water splitting, high density hydrogen storage, high performance batteries, and supercapacitors; and the development of nanoscale phase change materials (PCMs) has contributed to the preparation of more efficient heat transfer fluids. Despite tremendous efforts on incorporating nanomaterials into a variety of renewable energy sources, the high

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fabrication cost, small synthesis scales, and underdeveloped processing methods associated with nanomaterials prevent them from progressing to commercial scale applications. How to go about affecting this transition from lab bench to industrial scales will be the primary research focus of future work in this field. Clearly, it is necessary to have a comprehensive collection of review chapters covering the current state-of-art research progresses, ongoing challenges, and possible future directions in which to apply nanomaterials for renewable energy applications.

In this book, researchers actively working on renewable energy contribute their views on how nanomaterials would be beneficial for the development of high performance yet low-cost renewable energy sources. With comprehensive coverage of fundamental knowledge, in-depth background information, status of current research and development, and an outlook for future directions, this book aims to provide general information for undergraduate and graduate students interested in nanomaterials and their applications in renewable energy, and serves as a handbook and reference for advanced readers such as materials scientists and researchers working on renewable energy or related fields.

An overview of each chapter included in this book is given in the following paragraphs under different categories, which we expect to provide readers with a brief idea about the content of this book and help them navigate to areas of interest.

1 Dye-Sensitized Solar Cells

Solar cells, also known as photovoltaic devices (PVs), directly convert incident solar photons to electricity, and are one of the most studied solar energy systems because they employ clean and abundant resources and show great potential to satisfy future global energy demands. The current PV market is dominated by single crystal silicon-based solar cells that deliver power conversion efficiencies of 15 % or higher. However, these first-generation solar cells still suffer from several inherent deficiencies, such as high fabrication cost, heavy weight, and inevitable use of toxic chemicals. DSSCs, a new generation of high performance and low-cost solar cells, have attracted tremendous attention in the past decades owing to several advantages such as low fabrication cost, low toxicity, and high power conversion efficiency. A typical DSSC consists of several key components, including an electrically conductive support (e.g., transparent conductive film), a nanostructured semiconductor film (e.g., TiO_2), a sensitizer (e.g., ruthenium dye N719), an electrolyte (e.g., iodide/triiodide couple), and a counter electrode (e.g., Pt-coated electrode). In order to develop DSSCs with sufficiently high performance for commercial scale fabrication, optimization on the above-mentioned components should be carried out to achieve higher light absorption, better charge collection and transport, minimal recombination, and long-term device stability. Among all semiconductors studied for DSSCs, TiO_2 has been regarded as the most promising material for photoanodes in DSSCs due to its appropriate electronic

band structure, photostability, chemical inertness, and well-established synthesis methods. Modification of TiO_2 has been extensively investigated in recent years. The aim is to improve charge collection and charge transport in DSSCs, including the development of TiO_2 nanostructures with high surface area and unique morphologies and the preparation of doped TiO_2 nanostructures with improved optical and electronic properties.

In the chapter by Lin et al., various synthetic methods for the preparation of nanostructured TiO_2 are presented, including sol-gel, hydrothermal/solvothermal, electrochemical anodization, and electrospinning/electrospray methods. These methods produce a wide range of TiO_2 nanostructures that meet the requirements of many different applications. In the second section of this chapter, an overview of how the modification of TiO_2 influences its chemical/physical properties in different optoelectronic devices is presented.

In the chapter by Ma et al., nitrogen-doped TiO_2 nanostructures and their effect on the performance of DSSCs are described. Various doping methods, nanostructures, the resulting physiochemical properties of N-doped TiO_2 , and the effect of N-doped TiO_2 photoanode on the performance of DSSCs devices are discussed in detail. In the last section of this chapter, an analysis of the electron kinetic behaviors (i.e., charge transport, electron lifetime, and charge recombination) in DSSCs based on N-doped TiO_2 photoanodes is presented.

In another chapter contributed by Ma et al., recent progress on the development of Pt-free counter electrodes for DSSCs is comprehensively reviewed. Platinum-based counter electrodes are commonly used in current DSSCs. However, its high cost has motivated the search for low-cost, high performance alternatives, including carbon materials, conductive polymers, transition metal compounds, and composite catalysts. The advantages and disadvantages of each Pt-free counter electrode alternative are subsequently reviewed.

An analog to DSSCs, quantum dot-sensitized solar cells (QDSSCs) in which quantum dots play the role of “dye” in DSSCs have been extensively explored in recent years primarily due to the exceptional optoelectronic properties of quantum dots (e.g., size-dependent optical properties and MEG characteristics) and the well-established synthetic methods for the preparation of high quality quantum dots with tuneable morphologies and compositions. In a chapter by Mora-Seró et al., recent advances in the development of QDSSCs are presented with a focus on highlighting the differences between quantum dot- and dye-sensitized solar cells (QDSSCs vs. DSSCs) in several aspects, including the preparation of sensitizers, nanostructured electrodes, hole transporting materials, counter electrodes, and recombination and surface states. Through such comparisons, further improvements on QDSSCs can be envisioned. One example is the recent breakthrough in photovoltaics with organometallic halide perovskites which came about through the intensive study on QDSSCs. This is presented in detail in the last section of this chapter.

2 Pyrite Solar Cells

Pyrite (iron disulfide (FeS_2), also known as fool's gold) has long been proposed as a green solar cell material owing to its optimum band gap (i.e., 0.95 eV), high optical absorption coefficient (i.e., greater than 10^5 cm^{-1} , two orders of magnitude greater than the absorption coefficient of silicon), and abundance on earth, making it possible to fabricate highly efficient thin film solar cells with largely decreased consumption of raw materials. However, unanswered questions about the effects of defects and techniques to grow pure crystalline material still remain. In the chapter by Ren et al., the crystal structure and fundamental properties of pyrite are first introduced to offer an overview as to why it is a promising material for photovoltaics, followed by the detailed review on various synthetic methods for the preparation of nanostructured pyrite with a focus on the most recently developed solution phase synthesis of pyrite nanoparticles. In the last section of this chapter, the applications of nanostructured pyrite for photovoltaics and photodetectors are presented.

3 Polymer-Based Solar Cells

Many organic semiconductors exhibit the electronic properties of their inorganic counterparts while carrying the advantages of plastic processing and low fabrication cost through well-established polymeric materials processing techniques, thereby yielding a variety of organic-based electronic devices such as organic photovoltaic devices (OPVs), organic light emitting diodes (OLEDs), organic thin film transistors, etc. Organic photovoltaic devices have been regarded as promising technologies for the conversion of solar energy to electricity due to their light weight, flexibility, and cost-effective processibility. Additional advantages of OPVs also include short energy payback time compared to existing photovoltaic devices, non-toxic, and abundance on earth. In a chapter contributed by Fang-Chung Chen et al., the fundamentals of OPVs are presented in detail, followed by a comprehensive review on the recent progress on conjugated polymer-based OPVs. Effects of thermal annealing, solvent annealing, and interface engineering on the performance of OPVs are also discussed. In the last section of this chapter, common optical methods used to improve light absorption in OPVs are summarized, followed by an overview of the development of low-band gap conjugated polymers for more efficient light harvesting.

Indium tin oxide is the most commonly used transparent conductive materials for a wide range of electronic devices such as OPVs. However, ITO usage is diminished due to high material cost and poor flexibility. Clearly, the development of a low-cost replacement for ITO is crucial for the commercial feasibility of OPVs and other organic-based electronic devices. In this regard, a variety of nanomaterials have been investigated that have shown great potential as an ITO replacement by providing comparable or better electronic and optical properties. In the chapter by Krebs et al., the development of ITO-free polymer solar cells is

reviewed, which should help to realize commercially feasible OPV devices. In the first section of this chapter, various nanomaterials showing the possibility to substitute ITO are discussed, including metal nanogrids, metal nanowires, carbon nanotubes, and graphene; followed by a discussion on the very recent progress in the scale-up experiments on ITO-free OPVs modules.

Solution-based processing methods have been recognized as the most appropriate techniques for the fabrication of polymer-based electronic devices such as OPVs and OLEDs. However, technical challenges, including large-area processing technologies, coating quality, and long-term stability toward scalable and low-cost polymer electronics, still remain. In a chapter by Guo et al., recent advances in low-cost fabrication of OPVs and OLEDs are reviewed. Various scalable processing methods are presented by focusing on the coating quality and the resulting device performance in polymer-based electronics. This can ultimately lead to conclusions on how appropriate coating techniques can be selected based on the thickness requirement of each functional layer in polymer electronics. In the last section of this chapter, ITO-free electrodes based on polymer materials are introduced by evaluating their mechanical and optical properties, and a hybrid ITO-free transparent conductive film based on metal mesh and conjugated polymers is also introduced for the fabrication of large-area devices.

4 Hydrogen Energy and Fuel Cells

Hydrogen represents a clean and high gravimetric energy density fuel that could potentially replace fossil fuels in many applications. However, the widespread adoption of hydrogen fuels is stymied by a lack of efficient hydrogen generation and high density hydrogen storage methods. Current technology for hydrogen generation is based on the steam methane reforming and water–gas shift reaction which still relies on fossil fuels. Obviously, it is important to develop efficient, low-cost, and scalable techniques to generate hydrogen in a sustainable manner. In this context, photoelectrochemical water splitting has been considered as one of the most promising approaches as presented thoroughly in the chapter by Li et al. The most recent achievement in this area is comprehensively reviewed in this chapter, and the key factor for efficient photoelectrochemical water splitting has been identified to be the development of low-cost and efficient nanostructured photoelectrodes. In another chapter by Prieto et al. on the development of hydrogen storage materials, nanostructured magnesium and doped magnesium are described. This includes the size and shape controllable synthesis of these nanostructures, the kinetics of efficient hydrogen storage based on experimental observation and modeling, and the theoretical models that could guide experimental efforts.

Fuel cells that convert the chemical energy stored in fuels into electricity through electrochemical reactions with oxygen or other oxidizing agents have been receiving considerable attention in the past few decades. However, the widespread commercialization of fuel cells is still challenging due in part to the low catalytic

performance and high cost of Pt-based electrocatalysts. In addition, efficient hydrogen storage is also critical for the commercialization of hydrogen-powered fuel cells. In the chapter by Wei Chen et al., the development of one-dimensional (1D) palladium (Pd)-based nanomaterials as efficient electrocatalysts for fuel cells is presented. Among all Pt-free catalysts, Pd has been found to be a promising substitute owing to its excellent catalytic properties and lower material cost compared to Pt. Moreover, Pd-based materials exhibit high hydrogen storage capability which is desirable for hydrogen-powered fuel cells. This chapter reviews the most recent progress in the synthesis of 1D Pd-based nanomaterials for fuel cell applications. Areas addressed include controllable synthesis of Pd-based nanostructures through various synthetic routes, their high catalytic performance for electro-oxidation of small organic molecules and oxygen reduction reaction (ORR), and the high capacities for hydrogen storage exhibited in 1D Pd-based nanomaterials.

In another chapter on fuel cells contributed by Kumar and Pillai, the development of low-cost nanomaterials for high performance polymer electrolyte fuel cells is reviewed. Proton exchange membrane fuel cells (PEMFCs) utilize a polymer electrolyte membrane to transport protons from the anode to the cathode and restrict electrons from directly going to cathode from anode. They have garnered great interest due to their easy start-up and flexible design. A typical PEMFC consists of several critical components: Pt electrocatalysts, catalyst support (e.g., carbon), gas diffusion layer or backing layer, bipolar plate, and polymer electrolyte membrane. The successful operation of PEMFCs relies on the formation of effective triple phase boundary (reactant gases, electrocatalysts, and polymer electrolyte membrane) to facilitate efficient electrochemical reactions at both anode and cathode. However, the commercialization of PEMFCs is facing obstacles due to the high materials cost associated with Pt electrocatalysts and the poor performance of existing polymer electrolyte membranes. This chapter provides the most recent progress on the development of nanomaterials for PEMFCs in both fundamental and technological aspects with special emphasis on carbon-based nanostructures such as carbon nanotubes, graphene, nanostructured Pt electrocatalysts, and bio-inspired catalysts development, followed by a sound conclusion and perspective on the future activities in developing low-cost, high performance PEMFCs.

5 Batteries

Electrochemical energy storage (EES) technologies, including flow redox batteries, super capacitors, and rechargeable batteries (Pb–acid, Ni–Cd, Na–S, and Li–ion batteries, etc.), have demonstrated significant advantages including high efficiency, low-cost, and flexibility. Li–ion batteries in particular are currently considered as one of the most promising technologies due to their long lifetime and high energy density. However, for widespread EES applications, there is an increasing concern about the costs and the limitations of natural lithium reserves. As a result, efforts have been made to explore low-cost and reliable EES

technologies, among which Na-ion batteries are seen as a promising alternative due to the abundance of natural sodium resources and its similar electrochemical properties when compared with lithium. However, the realization of the Na-ion intercalation/deintercalation mechanism remains challenging as Na ions are 40 % larger in radius than Li ions. Thus, suitable host materials with high storage capacity, rapid ion uptaking rate, and long cycling life need to be developed for Na-ion batteries. In the chapter by Liu et al., the very recent progress on the development of promising electrode materials for Na-ion batteries is reviewed and discussed. The aim is to provide an overview of existing problems and future research directions in this area.

There is an ever-increasing demand for flexible portable electronic devices such as roll up displays, wearable devices, and implanted medical devices. This requires the development of flexible batteries or supercapacitors as their power sources. Typical batteries and supercapacitors are composed of several major components including electrodes (i.e., positive electrode and negative electrode), separator, and electrolyte. The two electrodes are spaced apart by a separator and all these components are soaked in solution or gel electrolyte. In order to fabricate flexible batteries and supercapacitors, electrodes with desired flexibility should be developed. In a chapter by Xue et al., the chemical routes to graphene-based flexible electrodes are discussed for applications in EES. Graphene is of interest due to its superior electronic properties and low-cost fabrication by chemical reduction. In this chapter, utilization of graphene for flexible electrodes is presented in detail by analyzing the structure–property relationships. This includes the use of graphene as dominant constituent of electrodes, the use of graphene as a conductive matrix in flexible electrodes, and the use of graphene as a functional additive to improve the performance of cellulose and carbon nanofiber papers. Evidenced by experimental examples, the development of graphene-based flexible electrodes offers new opportunities to further reduce the fabrication cost. A perspective on the future development of graphene-based flexible electrodes is presented at the end of this chapter.

6 Thermal Energy

Thermal energy storage and transfer have been two of the hottest research topics in renewable energy owing to the large abundance of thermal energy from the sun or the earth (geothermal). PCMs have garnered considerable attention for use in thermal energy storage and transfer due to their high heat storage capability during phase transitions. They offer the potential to reduce energy consumption, and in turn lower the related environmental impact. In the chapter by Yang et al., the development of nanoscale PCMs for applications in high performance heat transfer fluids is reviewed with special attention on the material synthesis and property characterizations of phase changeable fluids.