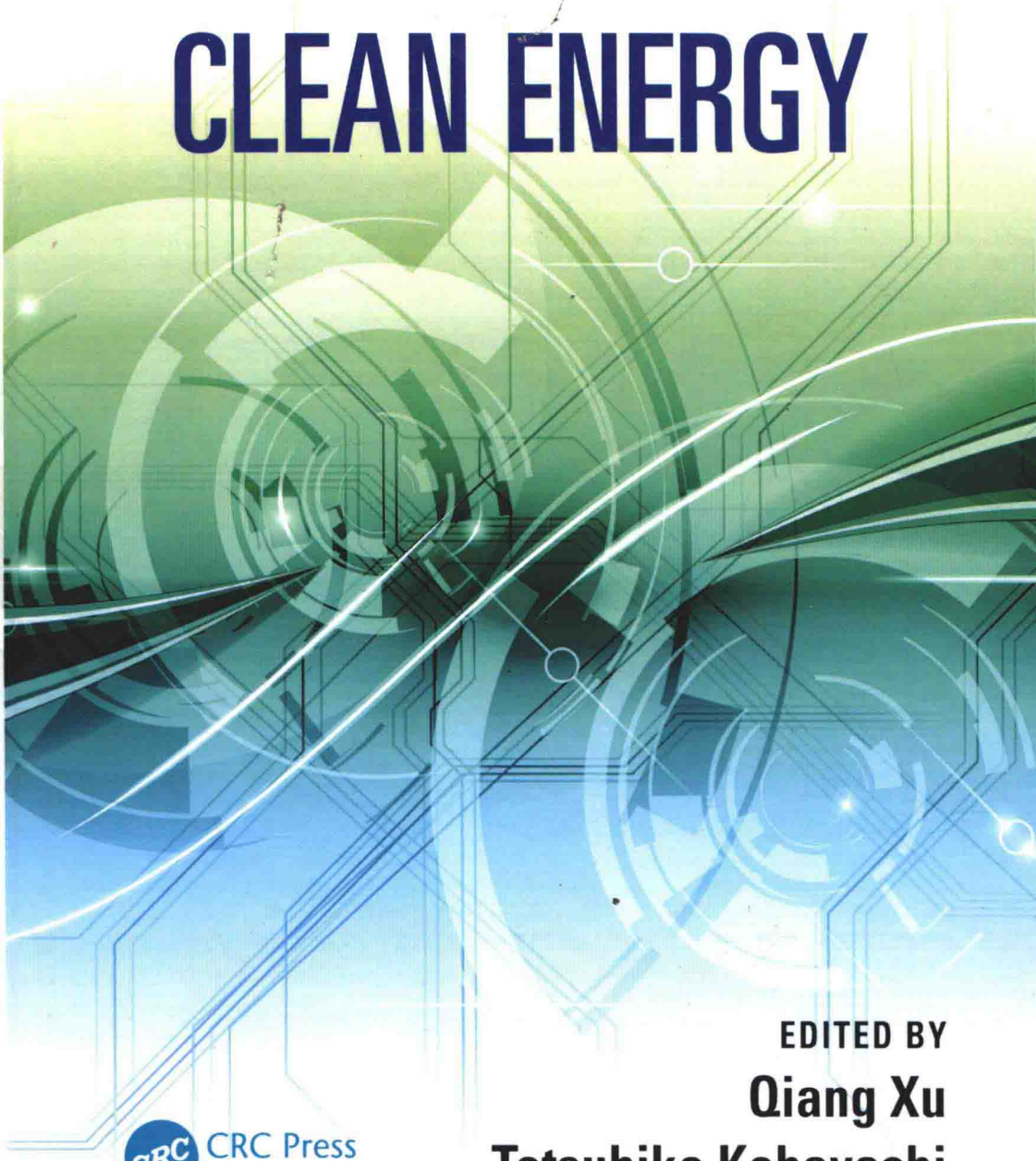
ADVANCED MATERIALS FOR CLEAN ENERGY



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Preface

Research for clean energy is in an explosive phase, driven by the rapid depletion of fossil fuels and growing environmental concerns as well as the increasing growth of mobile electronic devices. It has been the focus of a wide range of research fields to develop high-performance materials for alternative energy technologies and develop a fundamental understanding of their structure–property–performance relationship, which include materials for photovoltaics, solar energy conversion, thermoelectrics, piezoelectrics, supercapacitors, rechargeable batteries, hydrogen production and storage, and fuel cells.

After successfully organizing an international symposium on advanced materials for clean energy in 2011, an idea of publishing a book to clearly demonstrate the profound progress and provide a comprehensive recognition of advanced materials for clean energy to the researchers in this promising field was naturally conceived. It is our honor, as organizers, to invite leading scientists in this field to survey the key developments of the materials in a broad range and the important advances in their applications to date, which are outlined in the chapters as follows.

The chapters start with materials for photovoltaics. In Chapter 1, Ho and Wong provide a survey on arylamine-based photosensitizing metal complexes for dye-sensitized solar cells; in Chapter 2, Ning and Tian provide a review on p-type small electron-donating molecules for organic heterojunction solar cells; and in Chapter 3, Toyoshima gives a wide-range overview about inorganic materials for solar cell applications. In Chapter 4, Funahashi and coworkers demonstrate the development of thermoelectric technology from materials to generators. Piezoelectric materials for energy harvesting from a wide range of renewable energy sources are introduced by Maurya, Yan, and Priya in Chapter 5. In Chapter 6, Kang and Chen review the synthesis and application of various electrode materials for electrochemical capacitors focusing on the nanoarchitecture design of advanced electrodes. Being extensively investigated thus far, materials for batteries are dealt with in chapters from different directions. In Chapter 7, Inoue and Higuchi describe electrode materials for nickel/metal hydride (Ni/MH) rechargeable batteries; in Chapter 8, Casas-Cabanas and Palacín document the fabrication of electrode materials for lithium-ion rechargeable batteries; and in Chapter 9, Munakata and Kanamura review the materials for all-solid-state rechargeable batteries. A new trend in liquid electrolytes for electrochemical energy devices is highlighted by Matsumoto in Chapter 10. Recent development and future prospects of organic electrode active materials for rechargeable batteries are illustrated by Yao and Kobayashi in Chapter 11. Neburchilov and Wang present in Chapter 12 the synthesis and application of materials for metal–air batteries. Two chapters deal with solar energy/material conversion: Zhu introduces photocatalytic hydrogen production with semiconductor photocatalysts in Chapter 13, and Primo, Neaţu, and García address photocatalytic CO_2 reduction with a focus on the fundamentals behind the reaction and the photocatalysts in Chapter 14. Two chapters

are dedicated to hydrogen storage, the key technology for hydrogen economy: Zhu, Ouyang, and Wang review Mg-based hydrogen storage alloys, complex hydrides, metal amides, and imides for reversible high-capacity hydrogen storage in Chapter 15, and Kojima, Miyaoka, and Ichikawa provide an overview on ammonia and ammonia borane as chemical hydrogen storage materials in Chapter 16. Finally, three chapters are presented on fuel cells: In Chapter 17, Daimon describes cathode catalysts for polymer electrolyte fuel cell with an emphasis on the strategies for decreasing the use of the precious metal Pt; in Chapter 18, Sahai and Ma address the fundamentals and materials aspects of fuel cells directly using organic and inorganic liquids as fuels; and in Chapter 19, Merino-Jiménez, Ponce de León, and Walsh focus on the developments in electrodes, membranes, and electrolytes for direct borohydride fuel cells (DBFCs).

It is obvious that the accomplishments in materials for clean energy applications to date are exciting and the potential appears to be even greater. We are sure that this field will sustain its growth in the future.

We thank all the authors for their great contributions to this book as well as to this field. Sincere thanks to Barbara Glunn, David Fausel, and Cheryl Wolf (Taylor & Francis Group/CRC Press) for their conscientious cooperation in the editorial process.

Qiang Xu
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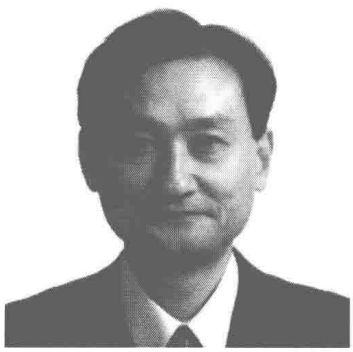

Qiang Xu received his PhD in physical chemistry in 1994 from Osaka University, Japan. After working as a postdoctoral fellow at Osaka University for a year, he started his career as a research scientist in Osaka National Research Institute (ONRI) in 1995. Currently, he is a chief senior researcher at the National Institute of Advanced Industrial Science and Technology (AIST) and adjunct professor at Kobe University, Japan. His research interests include porous materials and nanostructured materials and related functional applications, especially for clean energy.

Tetsuhiko Kobayashi received his PhD in electrochemistry in 1983 from Osaka University, Japan. After working as a Japan Society for the Promotion of Science postdoctoral fellow at Osaka University for a year, he started his career as a research scientist in the Government Industrial Research Institute of Osaka (GIRIO) in 1984. He worked as group leader in Osaka National Research Institute (ONRI) and as director of the Special Division for Green Life Technology, Research Institute for Ubiquitous Energy Devices, and Kansai Research Center in the National Institute of Advanced Industrial Science and Technology (AIST) and worked as guest professor in Kyoto University, Kobe University, and Osaka University. Currently, he is director-general for Environment and Energy Research, AIST. His research interests include electrochemistry, catalytic chemistry, and materials chemistry, especially for clean energy applications.

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Contents

1 Arylamine-Based Photosensitizing Metal Complexes for Dye-Sensitized Solar Cells

Cheuk-Lam Ho and Wai-Yeung Wong

CONTENTS

1.1 INTRODUCTION

The continuous growth of energy demand around the world and the environmental pollution resulting from global warming have triggered global research toward the exploitation of clean and renewable energy sources over the past decades as the resources of coal, oil, and natural gas are dwindling rapidly.[1] Solar energy is generally considered as the most promising way to solve the global energy crisis as it is available profusely in most of the world's regions, is inexhaustible, and can be used for direct electricity production by means of photovoltaic and photoelectrochemical cells. In this context, dye-sensitized solar cells (DSSCs) have attracted tremendous attention as an economical solar energy conversion device that offers several advantages over traditional silicon-based p–n junction devices such as low cost and simpler fabrication procedures. Furthermore, DSSCs display higher efficiencies at low light levels and the angle of the incident light has no great effect on the performance.

In DSSC, the photosensitizer plays a crucial role as it is responsible for light absorption and electron injection into the conduction band of the TiO_2 after solar light excitation to generate the photocurrent via a redox mediator. Enormous effort is being dedicated to develop efficient dyes that are suitably characterized for their modest cost, facile synthesis and modification, bulky rigid conjugation structure, large molar extinction coefficients (ε), and outstanding thermal and chemical stability. Triphenylamine (TPA) and carbazole (Cz) and their related moieties have been widely employed as active components in optoelectric devices, such as light-emitting[2] and photovoltaic devices,[3–5] because of their desirable electron-donating and hole-transport capabilities.[6,7] In recent years, a substantial number of dyes with triarylamine (e.g., TPA) or Cz as electron donor were developed for DSSCs because of their good electron-donating and electron-transporting properties, as well as their special propeller starburst molecular structure.[8] Furthermore, it was found that functional triarylamine and Cz can suppress surface dye aggregation, retard interfacial charge recombination between the electron in TiO_2 electrode and dye center, and increase the stability of dyes when exposed to light and high temperature, thereby generating high power conversion efficiency (η) and stability. Among the metal-free organic dyes, the arylamine-based organic dyes, holding the record for validated efficiency of over 10.3%, are promising candidates for highly efficient DSSCs.[9] On the other hand, the cost issue concerning the use of metalated organic photosensitizers always puts an obstacle on their applications, despite the fact that the contribution of the sensitizer to the total cell cost is indeed limited, as efficient light harvesting requires a monolayer of sensitizer molecules. Triarylamine or Cz units embedded in the metal complex can serve as the secondary electron donor moiety to enhance the light-harvesting ability, and metal complex dyes usually have higher thermal and chemical stability as compared with organic dyes. In this chapter, we present the major achievements that have been made in this field. The aim here is to provide promising design principles by using triarylamine and Cz chromophores in developing novel organometallic photosensitizing dyes for the new generation of functional molecules for DSSCs.

1.2 RUTHENIUM-CONTAINING PHOTOSENSITIZERS

A variety of transition-metal complexes and organic dyes have been successfully employed as sensitizers in DSSCs thus far; however, in terms of photovoltaic performance and long-term stability, Ru(II) polypyridyl complexes comprise the most successful family of DSSC sensitizers. They harvest visible light very efficiently with their absorption threshold being at about 800 nm. The well-known and easily tunable photophysical, photochemical, and electrochemical properties of these dyes make them excellent candidates for light-harvesting systems in energy conversion devices.[10] Since the remarkable pioneering invention of Ru(II)-based dyes, with an efficiency of 7% by O'Regan and Grätzel in 1991,[11] tremendous efforts have been expended by scientists concerning the development of DSSC technology based on Ru(II) photosensitizers. While **N3**,[11,12] **N719**,[13] and black dye[14] afford excellent DSSC performance, many research groups have attempted to modify their structures with the goal of improving photovoltaic performance that largely depends on the charge generation step (Scheme 1.1). The structure of the polypyridyl ligand determines the