Sixto Giménez · Juan Bisquert *Editors*

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From Basic Principles to Advanced Devices

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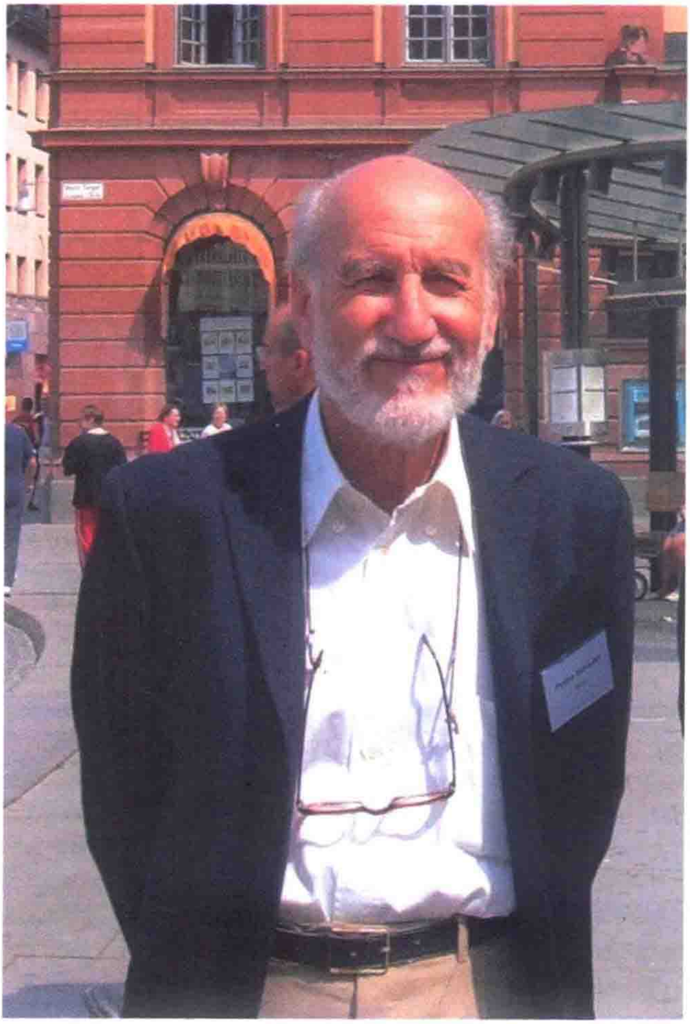

To Professor Pedro Salvador, a pioneer of photoelectrochemistry

Preface

The supply of water, food, and energy on a global scale constitutes the most relevant challenge to sustain humankind development in the twenty-first century. Focusing on energy, the wide availability of resources is essential to meet the needs of a growing world population with increasing living standards and hence high energy demand. In this context, chemical fuels constitute a key energy vehicle in the global scheme, since energy is available in a form that can be easily stored and used upon demand. Fossil fuels are excellent for transportation and generation of electricity and heat, but they arise from finite reserves that will be depleted in a few decades. In addition, burning oil and natural gas produces heavy pollution and greenhouse effect, leading to progressive warming of the earth crust with the concomitant risks of climate change. Consequently, we urgently need chemical fuels that can be derived from a widely available source, and that yield a benign residue when converted into other energy vectors. The production of a green and renewable chemical fuel is a major challenge for science and technology.

Water and sunlight are abundant and decentralized natural resources, which constitute ideal candidates for fuel production. Sunlight is the largest readily available source of energy in the world, and water can be split into O_2 and H_2, the latter being one of the most valuable energy vectors due to its high energy density and its clean combustion in fuel cells. Turning solar photons into a convenient fuel that stores energy as chemical bonds, either H_2 gas or a hydrocarbon derived by further dark reactions, has been a longstanding goal of research, particularly at those times when conventional energy sources experienced trouble. Inspired by natural photosynthesis, the process satisfying the energy needs of all living matter on earth, we can prepare inorganic or organic semiconductor materials that absorb photons and convert them into energetic electronic carriers. These carriers endowed with excess free energy can launch desired chemical and electrochemical reactions, provided that their forward pathway probability is larger than recombination rates.

Semiconductor materials have demonstrated their ability to split water into separate O_2 and H_2 gases, or to reduce CO_2, and have been investigated for over

40 years in the scientific field of photoelectrochemistry. The oil scarcity during the supply crisis in the 1970s was a major driving force to search for a semiconductor material capable of extensive energy generation based on the photoelectrochemical properties of the semiconductor/electrolyte interface. In principle one could employ abundant materials processed by low-cost synthetic procedures (as titanium dioxide or iron oxide) for the large-scale production of solar fuels. However, in practice, these semiconductors face important limitations, rendering the conversion efficiency from solar photons to hydrogen very low. It is well recognized that these materials are useful model systems but far from a technologically viable solution.

There exist a number of stringent requirements for a semiconductor to transform water into hydrogen at high performance, assisted only by the solar radiation. A principal factor impeding the viability of such device is the difficult balance between two opposing properties. The first is the necessity of a narrow semiconductor bandgap to realize the optical absorption of a large portion of the solar spectrum, as photons with energy less than the bandgap cannot be absorbed. On the other hand, in order to drive water oxidation and reduction reactions involving significant overpotential, a separation of valence and conduction band in the semiconductor quite in excess of the water splitting free energy of 1.23 eV is needed. Furthermore, in order to efficiently realize all the functions of charge separation, collection, and charge transfer across a semiconductor/electrolyte interface, excellent semiconductor properties are needed, including high conductivity, low recombination rates, and excellent surface catalytic properties. Another important drawback is related to the fact that some materials with the required properties lack the necessary stability under photoelectrochemical operation due to decomposition caused by the photogenerated carriers. All in all, the "artificial photosynthesis" based on a single successful semiconductor photoelectrode could not be realized.

Nevertheless, the demand for renewable primary energy vectors such as solar-based H_2 or hydrocarbon fuel constitutes an urgent priority in the near future global energy context. Recently, the research community has started a sustained effort towards the realization of the photoelectrochemical solar fuel production, adopting new avenues of research and shaping a dynamic and rapidly growing field. The current activity has benefited from the basic "classical" knowledge on semiconductor photoelectrochemistry established in the last century, combined with an expanded array of innovative tools and scientific directions, and together with the technological research needed for the demonstration of viable device engineering methods. The present research on solar fuel production applies and develops new methods of nanomaterials production, incorporates advanced photovoltaic devices, designs original catalytic materials and coatings, and introduces new semiconductor materials, as well as new nanoscale, electrochemical, optoelectronic, computational, and surface characterization techniques. This development of the field adopts a broad perspective with respect to the candidate materials and device configurations to target a low-cost high-conversion-efficiency and durable device. A combination of mixed metal oxides, nonoxide conventional semiconductors, and molecular systems is exploited in order to find the most suitable materials and interfaces. The use of combinatorial methods for high-throughput studies involves the investigation of ternary or quaternary compositions, maximizing the possibilities to optimize optical, electronic, and catalytic properties contributing to efficient solar fuel production.

The combination of photoelectrochemical and photovoltaic concepts, catalysis, advanced materials and nanostructuring strategies, facilitates a variety of routes, which may produce important progress towards effective applications. Indeed, different approaches towards reliable technological devices coexist in the research arena, which show potential advantages as well as drawbacks. As mentioned earlier, it is well established that capturing sunlight with a single junction material is a too demanding task for a high voltage application as water splitting. Consequently, one of the most promising approaches involves the combination of different light absorbing materials with complementary spectral properties adding up the voltages in *tandem* connection. The strategy to separate device functions in different materials and interfaces relaxes the stringent conditions that a single semiconductor must satisfy to perform all water splitting steps. Therefore light active semiconductors can be coupled with suitable catalysis layers. However, when different junctions, parts, and connections are required, there is a price to pay in terms of increased complexity and decreased integration. Therefore charge separation at semiconductor/electrolyte junctions, where electrochemical reactions also occur, continues to be a favorite research topic. On the other extreme, one may couple effective PV cells with dark catalysis. As a compromise, a photovoltaic cell can supply additional voltage to a photoelectrochemical cell.

In summary, a wide variety of approaches exists towards the established goal and often involves device configurations that use different types of fundamental properties. However, a strong connection occurs between the different methods. The innovations and discovery obtained in the massive research effort towards the solar fuel production eventually may become of broader interest and significance. Advances in one particular topic of research are likely to fertilize others. This is why it appears useful for students and researchers to present a general perspective of the field on a unified basis, starting from the fundamental knowledge set of established photoelectrochemical and catalysis concepts, and moving to a variety of materials and devices that constitute the vanguard of investigation in this field. This is the general purpose of this book, aiming at introducing the main trends of current research in photoelectrochemical solar fuel production from the standpoint of a firm scientific basis.

The book is organized in three topical parts, starting with fundamentals, followed by the experimental protocols and characterization techniques. The final and larger part explains the main types of materials and devices applications. The introductory chapter by L. M. Peter is a summary of the thermodynamics and kinetics properties of the semiconductor/electrolyte interface, which provides an understanding of how band bending combined with electron transfer model explains the photocurrent. This analysis shows the central role of surface catalysis in all fuel production cells; hence two chapters examine the central reactions that are considered today for solar fuel production. Doyle and Lyons explain the properties of the oxygen evolution reaction, which slow kinetics is a major barrier for the expansion of solar fuel production. Sudhagar, Nakata, and coworkers discuss the materials and properties for catalytic photoreduction to form hydrogen gas or to reduce CO_2.

The second part of the book addresses the experimental methods that are used to understand and guide the development of solar fuels materials, interfaces, and devices. First W. Smith provides a broad and detailed view of the main types of devices that are currently investigated, and he describes their parts, principles of operation, as well as the methods of measurement for the characterization of operational properties. Jaegermann, Kaiser, and coworkers critically discuss the different alternatives of solar fuel production approaches. The second part of the chapter gives fundamental insights into the structure of the critical interfaces, like the formation of semiconductor/passivation layer/co-catalyst/electrolyte interfaces. A detailed view of such properties is obtained by extensive application of photoelectron spectroscopies. Bisquert, Giménez, and coworkers describe the recent advances in the application of impedance spectroscopy technique in photoelectrochemical system, aiming to develop a profound characterization of kinetic steps that occur in the formation of photocurrent, with particular attention to the role of surface states in the competition between charge transfer and recombination. These previous two chapters recognize the complexity of the catalyzed interface and the many interactions and effects that determine the dynamics of the photoelectrochemical behavior. Subsequently Lin and Boettcher address this central problem and describe advanced characterization methods able to examine separate components of the interface during operation.

The last part of the book is devoted to the description of relevant materials and devices for photoelectrochemical solar fuel production. The first four chapters provide a detailed panorama of the most advanced materials developed in the last years. Abdi, Berglund, and Van de Krol describe the current research status of multinary metal oxides and discuss the main challenges of using these materials as photoelectrode materials along with future outlook for their application. Fujii provides an extensive description of nonoxide materials, particularly nitrides, chalcogenides, and arsenides, emphasizing the controllability of their electronic properties and the strategies needed to enhance the stability of these materials under solar fuel production conditions. Skorupska and Parkinson review the main advances on combinatorial synthesis and screening of oxide-based materials providing a detailed overview of the experimental methods employed for high-throughput combinatorial studies, focusing on oxygen evolution photoanodes, hydrogen evolution photocathodes, and electrocatalysts for both oxygen and hydrogen evolution. Thorne, He, and Wang discuss how the nanoscale synthesis of materials entails both advantages and disadvantages for the performance of semiconductor photoelectrodes. They describe the morphologies of nanostructured materials as well as some of the most relevant synthetic methods and critically discuss the performance of nanostructured photoelectrodes compared with their bulk counterparts. The last two chapters of this part illustrate how optimized materials can be integrated in advanced devices, based on different principles, targeting technological exploitation of photoelectrochemical solar fuel production. Sivula extensively describes how the use of tandem devices, combining two or more semiconductor junctions, can lead to efficient devices with up to 30 % conversion efficiency even assuming large losses. Particularly, key examples of tandem cells are discussed, taking into account the choice of semiconductor material, the design geometry of the device with respect to resistance losses due to membranes and ionic conduction, and techno-economic considerations. Finally, Coggins and Meyer provide an overview of the dye-sensitized photoelectrosynthesis cell devices, covering the fundamentals of the device concept, as well as the different strategies employed to achieve competitive efficiencies in prototype device.

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List of Acronyms

AACVD	Aerosol-assisted chemical vapor deposition
AAO	Anodized aluminum oxide
ABPE	Applied bias photon to current conversion efficiency
AEM	Anion exchange membrane
AIST	(National Institute of)Advance Industrial Science and Technology
ALD	Atomic layer deposition
AM	Air mass
APCE	Absorbed photon to current conversion efficiency
APCVD	Atmospheric pressure chemical vapor deposition
APT	Atom-proton transfer
ARUPS	Angle-resolved UPS
AZO	Aluminum doped zinc oxide
bb	Band bending
BPM	Bipolar membrane
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$
CB	Conduction band
CBD	Chemical bath deposition
CE	Counter electrode
CEM	Cation exchange membrane
CHT	Combinatorial high throughput
CNL	Charge neutrality level
CoBi	Cobalt-based catalysts deposited from borate electrolytes
Co-OEC	Co oxygen evolved complex
CoPi	Cobalt-based catalysts deposited from phosphate electrolytes
CUS	Coordinately unsaturated
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DC	Direct current
DFT	Density functional theory
DI	Distillate water

DOE	U.S. Department of Energy
DOS	Density of states
DSPEC	Dye-sensitized photoelectrosynthesis cells
DSSC	Dye-sensitized solar cell
DWE	Dual-working-electrode
EATP	Electron-atom-proton transfer
EC	Electrochemically prepared amorphous oxide
EC	Electrochemical converter
EC	Equivalent circuit
EC	Electrocatalyst
ECR	Electron cyclotron resonance
EDX	Energy dispersive X-ray spectroscopy
EFRC	Energy Frontier Research Center
EPR	Electron paramagnetic resonance
EQE	External quantum efficiency
ESCA	Electron spectroscopy for chemical analysis
eV	Electron volts
FF	Fill factor
FTO	Fluorine doped tin oxide
FVD	Flame vapor deposition
FWHM	Full width at half-maximum
g	Gaseous
HArPoON	Heterogeneous anodes rapidly perused for oxygen overpotential neutralization
HBE	Hydrogen binding energy
HEC	Hydrogen evolution catalyst
HER	Hydrogen evolution reaction
HF	Hydrofluoric acid
HOMO	Highest occupied molecular orbital
HTE	High-throughput experimentation
IMPS	Intensity-modulated photocurrent spectroscopy
IPCE	Incident photon to current conversion efficiency
IQE	Internal quantum efficiency
IS	Impedance spectroscopy
ITO	Indium doped tin oxide
JCAP	Joint Center for Artificial Photosynthesis
l	Liquid
LCAO	Linear combination of atomic orbitals
LED	Light-emitting diode
LMMR	Light-modulated microwave reflectance
MBE	Molecular beam epitaxy
MCC	Molecular cobaltate clusters
MD	Molecular dynamics
MeCN	Acetonitrile

MIGS	Metal-induced gap states
MIS	Metal insulator semiconductor
MLCT	Metal to ligand charge transfer
MOCVD	Metal-organic chemical vapor deposition
MOS	Metal oxide semiconductor
MPP	Maximum power point
NHE	Normal hydrogen electrode
oc	Open circuit
occ	Occupied
OCP	Open circuit potential
OEC	Oxygen evolution catalyst
OEC	Oxygen evolving complex
OER	Oxygen evolution reaction
OHP	Outer Helmholtz plane
op	Operational
ORR	Oxygen reduction reaction
OSDC	Optical scanning droplet cell
ox	Oxidized
PC	Propylene carbonate
PCET	Proton-coupled electron transfer
PDS	Potential determining step
PEC	Photoelectrochemical/photoelectrochemistry
PECVD	Plasma-enhanced chemical vapor deposition
PEM	Proton exchange membrane
PES	Photoelectron spectroscopy
ph	Photo
PL	Photoluminescence
PLD	Pulsed laser deposition
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
PSII	Photosystem II
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
QD	Quantum dot
QDSSC	Quantum dot sensitized solar cell
RDS	Rate determining step
RE	Reference electrode
red	Reduced
RHE	Reversible hydrogen electrode
SC	Semiconductor
SCE	Standard calomel electrode
SCLI	Semiconductor electrolyte interface
SCR	Space charge region
SEAL	Solar Energy Activity Laboratory

SECM	Scanning electrochemical microscopy
SEM	Scanning electron microscopy
SETI	Search for Extraterrestrial Intelligence
SHArK	Solar hydrogen activity research kit
SHE	Standard hydrogen electrode
SLJ	Semiconductor liquid junction
SoLiAS	Solid/liquid analysis system
SPM	Scanning probe microscope
STFCE	Solar-to-fuel conversion efficiency
STH	Solar-to-hydrogen conversion efficiency
STHCE	Solar-to-hydrogen conversion efficiency
SWE	Single-working-electrode
SXPS	Soft X-ray photoelectron spectroscopy
TC	Thermally prepared crystalline oxide
TCO	Transparent conducting oxide
TEM	Transmission electron microscopy
UHV	Ultra-high vacuum
UNC	University of North Carolina at Chapel Hill
UNC EFRC	University of North Carolina at Chapel Hill Energy Frontier Research Center
unocc	Unoccupied
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
UV–vis	Ultraviolet–visible (spectroscopy)
vac	Vacuum level
VB	Valence band
VLS	Vapor-liquid-solid
WE	Working electrode
XANES	X-ray absorption near edge spectroscopy
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRC	X-ray rocking curve
XRD	X-ray diffraction
YAG	Yttrium aluminum garnet

Contents