

## Contents

### Preface *xi*

### 1 Photocatalytic Hydrogen Production in the Context of Sustainable Energy 1

*Alberto Puga*

- 1.1 The Transition to Sustainable Energy 1
- 1.1.1 Trends in Primary Energy Production 1
- 1.1.2 Fossil Reserves 2
- 1.1.3 Carbon Dioxide Emissions and Global Warming 3
- 1.1.4 Strategic Low-carbon Goals and Energy Sustainability 4
- 1.2 Hydrogen as Renewable Energy Carrier 5
- 1.2.1 The Colors of Hydrogen: Toward Clean Hydrogen 5
- 1.2.2 Costs of Hydrogen Production 6
- 1.2.3 Solar Fuels and Synthetic Fuels 7
- 1.3 The Opportunity for Photocatalytic Hydrogen 8
- 1.3.1 Photoelectrocatalytic Water Splitting 9
- 1.3.2 Photocatalytic Water Splitting 10
- 1.3.3 Photocatalytic Hydrogen from Various Feedstocks by Photoreforming 11
- 1.3.4 Photobiocatalytic Hydrogen 13
- 1.4 Outlook 14
- Acknowledgments 15
- References 15

### 2 Fundamentals and Concepts of Photocatalytic Hydrogen Evolution 19

*Bunsho Ohtani, Fitri R. Amalia, Mahbub A. Akanda, and Mai Takashima*

- 2.1 Heterogeneous Photocatalysis 19
- 2.2 Thermodynamic Description 19
- 2.3 Standard Electrode Potential 22
- 2.4 Photocatalysts for Hydrogen Evolution 23
- 2.5 Co-catalysts for Hydrogen Evolution 24
- 2.6 Role of Platinum 26
- 2.7 Anatase and Rutile 29

2.8	Outlooks on Photocatalytic Hydrogen Evolution	31
	References	32
<b>3</b>	<b>Isotopic Substitution to Unravel the Mechanisms of Photocatalytic Hydrogen Production</b>	<b>35</b>
	<i>Mariano Curti, Yamen AlSalka, Osama Al-Madanat, and Detlef W. Bahnemann</i>	
3.1	Introduction	35
3.2	Isotopic Substitution on the Solvent or Substrate	36
3.2.1	Water	36
3.2.2	Alcohols	38
3.2.3	Carbonyl Compounds	41
3.2.4	Aromatic Compounds	45
3.3	Isotopic Substitution on the Photocatalyst	47
3.3.1	Ti Substitution	47
3.3.2	O Substitution	49
3.3.3	H Substitution	51
3.3.4	Substitution in Materials Other than TiO <sub>2</sub>	53
3.4	Concluding Remarks	54
	Acknowledgments	55
	References	55
<b>4</b>	<b>Photocatalytic Overall Water Splitting and Related Processes for Strategic Energy Storage into Hydrogen</b>	<b>63</b>
	<i>Alberto Puga</i>	
4.1	Photocatalysis as a Water Splitting Technology Option	63
4.1.1	What Is (and What Is Not) Photocatalytic Overall Water Splitting?	63
4.1.2	Comparison to Competing Technologies: Photoelectrochemical and Photovoltaic-Electrochemical	64
4.2	Basics and Fundamentals of Photocatalytic Water Splitting	66
4.2.1	Water Splitting Thermodynamics, Energy Balance and Metrics	66
4.2.2	Photophysics of Heterogeneous Semiconductor Photocatalysts	67
4.2.3	The Challenging Kinetics of Water Splitting and Co-Catalyst Requirements	69
4.2.4	Photoreactor Engineering and Process Conditions	69
4.3	Materials for Photocatalytic Overall Splitting of Pure Water into H <sub>2</sub> and O <sub>2</sub>	71
4.3.1	Single Light Absorber Configuration Based on Metal Oxide Semiconductors	73
4.3.2	Doped Metal Oxides Improve Single Absorber Photocatalysts	75
4.3.3	Modifications of Single Light Absorber Photocatalysts: (Oxy)nitrides, (Oxy)sulfides	76
4.3.4	Organic or Metal–Organic Semiconductors for Photocatalytic Water Splitting	78
4.3.5	Bioinspired Two-Absorber Z-Scheme Configurations toward Artificial Chloroplasts	79

4.3.6	Artificial Leaves Based on Semiconductor Junctions	81
4.4	Photocatalytic Splitting of Seawater	82
4.5	Photocatalytic Overall Water Splitting into $H_2O_2$ and $H_2$	84
4.6	Beyond Water Splitting: Photocatalytic Hydrogen from $NH_3$ or Other Binary Hydrogen Substances	85
4.7	Outlook and Prospects	86
	Acknowledgments	86
	References	86
<b>5</b>	<b>Photoelectrocatalytic <math>H_2</math> Production</b>	<b>95</b>
	<i>Levente Nagy, Roberto González-Gómez, Gunasekaran Kumaravel Dinesh, and Pau Farràs</i>	
5.1	Introduction	95
5.2	Parameters Affecting PEC $H_2$ Production	96
5.2.1	Solar-to- $H_2$ Conversion Efficiency	96
5.2.2	Incident Photon to Current Efficiency	98
5.2.3	Photocurrent Density	98
5.2.4	Reactor Setup	98
5.2.4.1	Type of Photocell	99
5.2.4.2	Incident Light	100
5.2.4.3	Photocell Window Material	100
5.3	Photoelectrochemical Semiconductor Materials	101
5.3.1	Morphologies of Semiconductor Materials	101
5.3.2	Photoelectrode Modification	102
5.3.2.1	Bilayer Structure	103
5.3.2.2	Z-Scheme Multilayer	103
5.3.2.3	Co-Catalyst Layer	104
5.3.2.4	Surface Passivation Coating	105
5.4	Photoelectrochemical Reactor Configurations	106
5.4.1	Single Photoelectrochemical Cells	106
5.4.2	Tandem Photoelectrochemical Cells	107
5.4.3	PEC-DSSC Systems	108
5.4.4	Integrated PEC Systems	109
5.5	Design Considerations for Water Splitting	109
5.5.1	Theoretical Studies and Models	110
5.5.2	Temperature Effects	112
5.5.3	Semiconductor Features	112
5.5.4	Technical Challenges	113
5.6	Conclusion	114
	References	114
<b>6</b>	<b>Hydrogen Production from Water Using Thermal and Photo-Driven Systems. An Overview of Research Activity on Catalysts-Based Multi-junction Solar Cells</b>	<b>123</b>
	<i>Hicham Idriss</i>	
6.1	Introduction	123
6.1.1	Thermal Water Splitting Using Metal Oxides	124

6.1.1.1	Principle	124
6.1.1.2	Application	125
6.1.1.3	Limitation	126
6.1.2	Electrocatalytic Water Splitting	128
6.1.3	Photocatalytic and Photoelectrocatalytic Water Splitting	128
6.1.3.1	Principle	128
6.1.3.2	Application	128
6.1.3.3	Limitation	129
6.2	A Case Study	129
6.2.1	Photoelectrocatalytic (PEC) Systems, Stability, and Performance	130
6.3	Conclusions	133
	Acknowledgments	134
	References	134
<b>7</b>	<b>Photocatalytic Hydrogen Generation by Metal–Organic Frameworks</b>	<b>141</b>
	<i>Josep Albero and Hermenegildo García</i>	
7.1	Introduction	141
7.2	Photocatalysis	142
7.3	Photocatalysts	145
7.4	Metal–Organic Frameworks (MOFs)	147
7.5	MOFs as Photocatalysts	149
7.6	MOFs as Photocatalysts for H <sub>2</sub> Generation	153
7.7	MOFs as Photocatalysts for Overall Water Splitting	156
7.8	Conclusions	160
	References	161
<b>8</b>	<b>Organic Transformations Involving Photocatalytic Hydrogen Release</b>	<b>165</b>
	<i>Miriam Marchi, Michele Melchionna, and Paolo Fornasiero</i>	
8.1	Introduction	165
8.2	Fundamental Principles of Photocatalytic Systems for H <sub>2</sub> Evolution	167
8.3	Photocatalytic Organic Transformations Integrated with H <sub>2</sub> Generation	170
8.3.1	Photocatalytic Organic Oxidation Coupled with H <sub>2</sub> Production	170
8.3.1.1	Oxidation of Alcohols	170
8.3.2	Oxidation of Biomass-Derived Intermediates	173
8.3.3	Photocatalytic Oxidative Coupling Reactions Integrated with H <sub>2</sub> Formation	175
8.3.3.1	Formation of C—C Coupled Products	175
8.3.3.2	Formation of C—N Coupled Products	180
8.3.3.3	Formation of S—S Coupled Products	181
8.3.4	Integration of H <sub>2</sub> Production with Oxidative Cross-Coupling	182
8.4	Conclusions and Perspectives	184
	Acknowledgments	185
	References	185

<b>9</b>	<b>Photocatalytic Hydrogen Production by Biomass Reforming</b>	<b>191</b>
	<i>Thangjam I. Singh, Shuya Li, Gyu Leem, and Seunghyun Lee</i>	
9.1	Introduction	191
9.2	General Principles of Photocatalysis	192
9.3	Photocatalytic Reforming of Biomass	193
9.4	Metal-Based Photocatalytic Reforming of Biomass	193
9.4.1	TiO <sub>2</sub> -Based Photocatalysts and Effect of Co-catalysts	193
9.4.1.1	Platinized TiO <sub>2</sub> (Pt/TiO <sub>2</sub> ) Photocatalysts	194
9.4.1.2	Pd/TiO <sub>2</sub> Photocatalysts	195
9.4.1.3	Au/TiO <sub>2</sub> Photocatalysts	196
9.4.2	Non-precious Metals/TiO <sub>2</sub> Photocatalysts	198
9.4.3	Nonmetals/TiO <sub>2</sub> Photocatalysts	200
9.4.4	CdS-Based Photocatalysts and Co-catalyst Loading	201
9.4.4.1	Au/CdS Photocatalysts	202
9.4.4.2	Ni/CdS Photocatalyst	202
9.4.4.3	NiS/CdS Photocatalyst	202
9.4.5	Metal Sulfides Other than CdS	203
9.4.6	Metal Oxides Other than TiO <sub>2</sub> -Based Photocatalysts	204
9.5	Metal–Organic Framework (MOFs)-Based Photocatalysts	206
9.6	Metal-Free Photocatalysts	209
9.7	Dye-Sensitized TiO <sub>2</sub> Photocatalysts	211
9.8	Conclusion	213
	Acknowledgment	213
	References	214
<b>10</b>	<b>Photocatalytic Hydrogen Production from Aqueous Solutions of Organic Substances – Biomass Components – Over CdS-based Photocatalysts Under Visible Light</b>	<b>219</b>
	<i>Anna Y. Kurenkova and Ekaterina A. Kozlova</i>	
10.1	Introduction	219
10.2	Comparison of Various Biomass Processing Methods	221
10.3	Photocatalytic Hydrogen Production from Biomass Components	221
10.4	The Use of CdS-Based Photocatalysts for Hydrogen Evolution from Biomass Components	223
10.5	The Synthesis of Novel Photocatalysts Cd <sub>1-x</sub> Zn <sub>x</sub> S–Cd <sub>1-y</sub> Zn <sub>y</sub> S for Photocatalytic Hydrogen Evolution from Biomass Components	226
10.5.1	Hydrogen Evolution from Low-soluble Biomass Components	232
10.5.1.1	Photocatalytic Hydrogen Evolution from Cellulose Aqueous Suspensions	232
10.5.1.2	Photocatalytic Hydrogen Evolution from Starch Aqueous Suspensions	235
10.6	Concluding Remark and Outlook	237
	Acknowledgment	238
	References	238

<b>11</b>	<b>Photocatalytic Hydrogen Production from Waste</b>	<b>245</b>
	<i>Sandra Y. Toledo-Camacho and Sandra Contreras Iglesias</i>	
11.1	Introduction	245
11.2	Municipal Wastewater (MWW)	247
11.3	Industrial Wastewater (IWW)	251
11.3.1	Effect of Oxidic or Anoxic Conditions and Hydrogen Precursor	252
11.3.2	Dyes-containing Wastewaters	256
11.3.3	Biodiesel Production-derived Wastewater	258
11.4	Pharmaceutical Wastewater (PWV)	261
11.4.1	Pharmaceutical Compounds	261
11.5	Conclusions	265
	References	267
<b>12</b>	<b>Catalysts and Photoreactors for Photocatalytic Solar Hydrogen Production: Fundamentals and Recent Developments at Pilot Scale</b>	<b>275</b>
	<i>Alba R. Aguirre, Alejandro C. Reina, José P. Pérez, Gerardo Colon, and Sixto Malato</i>	
12.1	Materials for Solar Photocatalytic Hydrogen Production	275
12.1.1	General Considerations on the H <sub>2</sub> Production Reaction	275
12.1.2	Photoreforming	278
12.2	Factors that Influence Photocatalyst Activity	279
12.2.1	Catalyst Structure and Morphology	280
12.2.2	Light Intensity	281
12.2.3	Temperature	282
12.2.4	pH	284
12.3	Current Photoreactors and Pilot Plants	284
12.3.1	Pilot Solar Photoreactors for Photocatalytic Hydrogen Production: CPCs	286
12.3.2	Pilot Solar Photoreactors for Photocatalytic Hydrogen Production: Other Collectors	288
12.4	Advances in Photoreactors	289
12.4.1	Slurry Photoreactors	289
12.4.2	Fixed Catalyst Photoreactors	291
12.5	Photocatalytic Wastewater Treatment with Simultaneous Hydrogen Production	293
12.6	Future Outlook	296
	References	296
	<b>Index</b>	<b>305</b>