

Contents

Preface *xiii*

1	Oxygen Reduction Reaction Electrocatalysts	1
	<i>Xinwen Peng and Lei Zhang</i>	
1.1	Introduction	1
1.2	Pt-Based ORR Electrocatalysts	2
1.2.1	Facet-Controlled Catalysts	2
1.2.2	Multimetallic Nanocrystals	3
1.2.2.1	Pt Alloys	3
1.2.2.2	Supported-Enhanced Catalysts	6
1.3	Transition-Metal-Based Materials	10
1.3.1	Metals and Alloys	10
1.3.2	Transition Metal Oxides/Sulfides	12
1.4	Atomically Dispersed Metal in Carbon Materials	19
1.5	Metal-Free ORR Electrocatalysts	23
1.6	Conclusion	25
	References	26
2	Electrocatalytic Oxygen Evolution Reaction	35
	<i>Guanyu Liu and Joel W. Ager</i>	
2.1	Introduction	35
2.2	Bioinspiration: OER in Photosystem II	36
2.3	Fundamentals of Electrocatalytic OER	36
2.3.1	Electrode Substrate	37
2.3.2	Electrolyte	38
2.3.3	Onset Potential and Overpotential	38
2.3.4	Tafel Analysis of the Rate-Determining Step	38
2.3.5	pH Dependence: The Nernst Equation	39
2.3.6	Long-Term Stability	41
2.3.7	Other Parameters	41
2.4	Reaction Mechanisms	41
2.4.1	WNA Mechanism	42
2.4.2	I2M Mechanism	44
2.5	OER Catalysts	44
2.5.1	Molecular OER Catalysts	44

2.5.1.1	Ru- and Ir-Based Molecular Catalysts	45
2.5.1.2	Earth-Abundant Transition Metal-Based Molecular Catalysts	46
2.5.1.3	Stabilization Strategies for Molecular Catalysts	47
2.5.1.4	All-Inorganic Polyoxometalates	48
2.5.2	Heterogeneous OER Catalysts	48
2.5.2.1	Metal Oxides	48
2.5.2.2	(Oxy)Hydroxides and Double Hydroxides	54
2.5.2.3	Metal Chalcogenides	55
2.5.2.4	Metal Pnictides	57
2.5.2.5	Carbon-Based Materials	58
2.5.2.6	Crystalline Frameworks and Their Derivatives	59
2.6	Challenges for Practical Catalytic Electrodes for OER	62
2.6.1	Industrially Viable Fabrication Techniques	62
2.6.2	Gas Bubble Formation on the Surface of Electrodes	62
2.6.3	Novel Approaches Toward Catalyst Discovery	65
2.7	Conclusions	67
	References	68
3	Electrochemical Hydrogen Evolution Reaction	87
	<i>Guoqiang Zhao and Wenping Sun</i>	
3.1	Introduction	87
3.2	HER Mechanism	89
3.2.1	HER Mechanism in Acid Media	89
3.2.2	HER Mechanism in Alkaline Media	93
3.3	Key Parameters for Evaluating Catalytic Activity	96
3.3.1	Overpotential	96
3.3.2	Turnover Frequency	97
3.4	PGMs-Based Electrocatalysts	98
3.4.1	PGM Alloys	99
3.4.2	PGM Heterostructured Electrocatalysts	101
3.4.3	PGM Single-Atom Electrocatalysts	106
3.5	PGM-Free Materials	108
3.5.1	2D Transition Metal Dichalcogenides	108
3.5.2	Transition Metal Phosphorus/Nitrides/Carbides	111
3.5.3	PGM-Free Heterostructured Electrocatalysts	112
3.6	Summary	117
	References	118
4	Electrocatalytic Water Splitting	123
	<i>Suraj Gupta</i>	
4.1	Introduction	123
4.2	Fundamental Concepts	124
4.2.1	Electric Double Layer	124
4.2.2	Standard Electrode Potential	125
4.2.3	Overpotential	129
4.2.4	Electrode Kinetics	129
4.3	Industrial Systems for Electrocatalytic Water Splitting	133
4.3.1	Alkaline Water Electrolyzers	133
4.3.2	Proton Exchange Membrane Water Electrolyzers	135
4.3.2.1	Membrane Electrode Assembly	136

4.3.2.2	Current Collectors	137
4.3.2.3	Bipolar/Separator Plates	138
4.3.3	Zero-Gap AWE	138
4.3.4	Comparing PEMWE and AWE	139
4.3.5	Other Types of Water Electrolyzers	141
4.3.5.1	Solid Oxide Electrolyzers	141
4.3.5.2	Microbial Electrolyzers (MEs)	144
4.4	Electrocatalysts for HER and OER	145
4.5	Electrocatalytic Seawater Splitting	147
4.5.1	Demographic Analysis	147
4.5.2	Challenges in Electrocatalytic Seawater Splitting	147
4.5.3	State-of-the-Art	151
4.5.4	Prospects for Electrocatalytic Splitting of Seawater	153
4.6	Conclusions	154
	References	154
5	Electrochemical Carbon Dioxide Reduction Reaction	159
	<i>Yating Zhu, Congyong Wang, Zengqiang Gao, Junjun Li, and Zhicheng Zhang</i>	
5.1	Introduction	159
5.2	Principles	160
5.2.1	The Conversion of CO ₂ to C ₁ Products	160
5.2.2	The Conversion of CO ₂ to Multi-Carbon Products	161
5.3	Materials for Electrochemical CO ₂ RR	163
5.3.1	Metallic Materials	163
5.3.1.1	Transition Metallic Materials	163
5.3.1.2	Other Metallic Materials	165
5.3.2	Carbon Materials	165
5.3.2.1	Carbon Nanofibers	167
5.3.2.2	Carbon Nanotubes	167
5.3.2.3	Mesoporous Carbon	168
5.3.2.4	Graphene (Graphene Quantum Dots)	168
5.3.2.5	Diamond	170
5.3.3	Organic Framework Materials	171
5.3.3.1	Metal–Organic Frameworks	172
5.3.3.2	Covalent Organic Frameworks	176
5.4	Conclusion	178
	References	180
6	Electrochemical N₂ Reduction	183
	<i>Yulu Yang, Jiandong Liu, Huapin Wang, and Jianmin Ma</i>	
6.1	Introduction	183
6.2	Fundamentals of Electrocatalytic Nitrogen Reduction	184
6.3	Product Detection and Efficiency Evaluation	186
6.4	NRR Catalysts	188
6.4.1	Noble Metal Catalysts	188
6.4.1.1	Au Base Catalyst	188
6.4.1.2	Ru Base Catalyst	190
6.4.1.3	Pd Base Catalyst	191
6.4.1.4	Pt Base Catalyst	191
6.4.2	Non-noble Metal Catalyst	191

6.4.2.1	Mo Base Catalyst	194
6.4.2.2	Ni, Co and Fe Base Catalyst	197
6.4.2.3	Metal-Free Catalysts	197
6.4.3	Monatomic Catalysts	197
6.5	Conclusion and Prospects	202
	References	202
7	Photoelectrochemical Water Splitting	205
	<i>Yangqin Gao, Ge Lei, Zhijie Tian, Hongying Zhu, and Lianzheng Ma</i>	
7.1	Introduction	205
7.2	Photoelectrochemical Cells	208
7.2.1	Water Splitting	209
7.2.2	Types of Photoelectrochemical Devices	209
7.2.2.1	Photoelectrolysis Cell	210
7.2.2.2	Photo-Assisted Electrolysis Cell	210
7.2.2.3	Photovoltaic Electrolysis Cell	210
7.3	Basic Concepts in Semiconductors	211
7.3.1	Electronic Properties of Semiconductors	211
7.3.2	Optical Properties of Semiconductors	218
7.3.3	Quasi Thermal Equilibrium and Quasi Fermi Level Splitting	222
7.4	General Properties of a Semiconductor/Liquid Junction	224
7.4.1	Equilibrium State at a Semiconductor/Liquid Junction	224
7.4.2	Charge Transfer at a Semiconductor/Liquid Junction	229
7.5	The Current-Voltage Behaviours of a Semiconductor/Liquid Junction	231
7.5.1	The Current-Voltage Characteristics of a Semiconductor/Liquid Junction in Dark	231
7.5.2	The Current-Voltage Characteristics of a Semiconductor/Liquid Junction under Illumination	233
7.6	Energy Conversion Efficiency	234
7.7	Summary	235
	References	236
8	Photoelectrocatalytic Solar Water Splitting	241
	<i>Deyu Liu and Yongbo Kuang</i>	
8.1	Introduction	241
8.2	Basic Concepts of Nonbiased PEC System	242
8.2.1	Thermodynamics of PEC System	242
8.2.2	Photoelectrodes and Photoelectrochemical Cells	244
8.2.3	Unbiased PEC Solar Water Splitting Cells	245
8.2.4	Selection of Semiconducting Materials	246
8.3	Design of Photoelectrodes from System-Wide View	250
8.3.1	From Semiconductor Materials to Photoelectrodes	250
8.3.2	Parameters of the Photoelectrodes	252
8.3.3	Functionalization Layers and Cocatalysts	255
8.3.4	Testing and Operation Conditions	258
8.4	Design of Integrated PEC Systems	261
8.5	Techno-Economic Assessment	264
8.6	Summary and Overlook	268
	References	271

9	Photoelectrochemical Reduction of CO₂	275
	<i>Yuchen Qin and Haoyi Wu</i>	
9.1	Introduction	275
9.2	Fundamental Principles of PEC CO ₂ Reduction	276
9.2.1	Mechanism	276
9.2.2	Reaction Conditions	277
9.2.2.1	pH Value	277
9.2.2.2	Electrolyte Type	277
9.2.2.3	Reaction Temperature and Pressure	278
9.2.3	Evaluation Parameters for PEC CO ₂ Reduction	278
9.2.3.1	Product Evolution Rate and Catalytic Current Density	278
9.2.3.2	Faradaic Efficiency	278
9.2.3.3	Turnover Number and Turnover Frequency	278
9.2.3.4	Quantum Yield	279
9.3	Strengthen Strategies for PEC CO ₂ Reduction	279
9.3.1	Advanced Design for Photoelectrode	279
9.3.1.1	Photocathodes and Dark Anodes	279
9.3.1.2	Photoanodes and Dark Cathodes	285
9.3.1.3	Photoanodes and Photocathodes	286
9.3.1.4	PEC-Photovoltaic Cell Tandem and Wireless Monolithic Devices	286
9.3.2	PEC Reactor Configuration	287
9.3.2.1	Light Source	288
9.3.2.2	Heat Transfer	289
9.3.2.3	Utilization of CO ₂	289
9.3.2.4	Classification of Reactors	289
9.4	Summary and Perspectives	289
	References	292
10	Photoelectrochemical Oxygen Evolution	301
	<i>Hoi Ying Chung, Hao Wu, Xuelian Wu, Chenliang Su, and Yun Hau Ng</i>	
10.1	Introduction of Photoelectrochemical Oxygen Evolution	301
10.2	Working Principles of Photoelectrochemical Oxygen Evolution	302
10.3	Promising Visible Light Active Photoanode for PEC Oxygen Evolution	305
10.3.1	Tungsten Oxide (WO ₃) Photoanode	305
10.3.2	Hematite (α -Fe ₂ O ₃) Photoanode	308
10.3.3	Bismuth-Based Ternary Oxide Photoanode	311
10.3.3.1	Bismuth vanadate (BiVO ₄)	312
10.3.3.2	Bismuth Tungstate (Bi ₂ WO ₆)	319
10.3.3.3	Bismuth Molybdate (Bi ₂ MoO ₆)	322
10.3.4	Tantalum Oxynitride (TaON) and Tantalum Nitride (Ta ₃ N ₅)	324
10.4	Summary and Outlook	328
	References	329
11	Photoelectrochemical Nitrogen Reduction Reaction	339
	<i>Gnanaprakasam Janani, Subramani Surendran, Hyeonuk Choi, and Uk Sim</i>	
11.1	Introduction	339
11.2	Nitrogen Reduction Reaction	341
11.3	Photoelectrochemistry for Provision of Sustainable Energy Sources	342
11.4	Fundamentals of Photoelectrochemical Nitrogen Reduction Reaction (PEC NRR)	344

11.5	Hitches in NRR	347
11.5.1	Semiconductor Considerations	347
11.5.2	H ₂ Evolution Reaction and Selectivity	348
11.6	Mechanisms	350
11.7	Contribution of Catalysts in PEC NRR	352
11.7.1	Semiconductors	352
11.7.2	Plasmon-Induced Ammonia Synthesis	360
11.7.3	Black Phosphorus-based Catalysts	366
11.7.4	Role of Diamond	367
11.8	Beyond Conventional Catalysts	369
11.8.1	Electrolytes	370
11.8.2	Diffusion of N ₂ Gas	370
11.8.3	Prototypes	370
11.8.4	N ₂ Adsorption and Activation on the Catalyst Surface	371
11.9	Methods to Measure Ammonia	373
11.9.1	Colorimetric Method	373
11.9.2	Ion Chromatography Method	374
11.9.3	Ion-Selective Electrode Method	374
11.9.4	Fluorometric Method	375
11.9.5	Conductivity Method	375
11.9.6	Titrimetric Method	376
11.9.7	In situ Fourier Transform Infrared spectroscopy	376
11.9.8	Nuclear Magnetic Resonance	376
11.10	Formulas	377
11.11	From the Holy Grail to Practical Systems	377
11.12	Conclusion	378
	References	378
12	Photocatalytic Oxygen Reduction	389
	<i>Hai-Ying Jiang and Xianguang Meng</i>	
12.1	Formation of ROS	389
12.2	Detection of ROS	393
12.2.1	Detection of ¹ O ₂	393
12.2.2	Detection of O ₂ ^{•−}	394
12.3	Detection of H ₂ O ₂	397
12.3.1	DPD-POD Method	397
12.3.2	DMP Method	398
12.4	Detection of •OH	398
12.5	Applications of Photocatalytic Oxygen Reduction	402
12.5.1	Synthetic Applications	403
12.5.2	Environmental Applications	404
12.5.3	Photocatalytic H ₂ O ₂ Synthesis	405
	References	409
13	Photocatalytic Hydrogen Production	415
	<i>Zhen Li, Mengqing Hu, Yanqi Xu, Di Zhao, Shuaiyu Jiang, Kaicai Fan, Meng Zu, Mohammad Al-Mamun, Huajie Yin, Shan Chen, Yuhai Dou, Lei Zhang, Yu L. Zhong, Yun Wang, Shanqing Zhang, Porun Liu, and Huijun Zhao</i>	
13.1	Introduction	415

13.2	Fundamental of Heterogeneous Photocatalysis	416
13.2.1	History of Photocatalysis Hydrogen Evolution and Current Status	416
13.2.2	Thermodynamics of Photocatalytic Processes for Hydrogen Evolution	420
13.2.3	Evaluation Criteria of Efficiency for Photocatalytic Hydrogen Evolution	422
13.2.4	Key Parameters of Photocatalytic Processes	423
13.3	Enhancement for One-Step Photoexcitation for PCHER	425
13.3.1	Band Structure	425
13.3.2	Exposed Facet Engineering	427
13.3.3	Control on Microstructure and Surface Area	429
13.3.4	Doping /Vacancies/Defects	431
13.3.4.1	Metal Doping	432
13.3.4.2	Non-Metal Doping	433
13.3.4.3	Vacancies/Defects	435
13.3.5	Hole Scavenger	436
13.3.5.1	Inorganic Salts and Organic Salts	436
13.3.5.2	Organic Compounds	437
13.3.5.3	Lignocellulosic Biomass	439
13.4	Enhancement for Two-step Photoexcitation for PCHER	440
13.4.1	Surface Sensitization	442
13.4.1.1	Semiconductors Act as the Light Absorber	442
13.4.1.2	Semiconductors Act as the Reaction Sites	445
13.4.1.3	Semiconductors Act as Both Light Absorber and the Reaction Site	448
13.4.2	Type I, II, III Heterojunctions	449
13.4.3	Z-Scheme Heterojunctions	450
13.4.3.1	Z-Scheme with a Shuttle Redox Mediator	451
13.4.3.2	Z-Scheme with a Solid Mediator	453
13.4.3.3	Direct Z-Scheme	453
13.5	Enhancement with Other Operation Parameters	456
13.5.1	Backward/Side Reactions	457
13.5.2	Improved Mass Transfer	457
13.5.3	Corrosion Resistance	458
13.5.4	Temperature	459
13.5.5	Light Intensity	459
13.5.6	Solution pH	460
13.5.7	Design of Reactor	460
13.6	Summary and Perspectives	462
	References	464
14	Photocatalytic Oxygen Evolution	485
	<i>Wenzhang Li and Keke Wang</i>	
14.1	Introduction	485
14.2	Basic of Photocatalytic Water Splitting	486
14.2.1	History of Photocatalytic Water Splitting	486
14.2.2	Fundamentals of Photocatalytic Water Splitting	489
14.2.3	Half-Reactions Using Sacrificial Electron Donors and Acceptors	491
14.3	Semiconductor Photocatalysts	492
14.3.1	Brief History of Semiconductor Photocatalysts	492
14.3.2	Advancements in Photocatalyst Materials	493
14.3.2.1	Doping	493

14.3.2.2	Heterostructures	499
14.3.2.3	Morphology Control	507
14.3.2.4	Cocatalyst Loading	510
14.4	Conclusion Remarks and Future Directions	513
	References	514
15	Photocatalytic Overall Water Splitting	521
	<i>Ning Zhang</i>	
15.1	Background	521
15.2	Evaluation of Overall Water Splitting	524
15.2.1	Stoichiometric Evolved Gaseous H ₂ and O ₂	524
15.2.2	Calculation of Turnover Number	525
15.2.3	Calculation of Quantum Yield	526
15.3	Photocatalysts	526
15.3.1	Single Semiconductor	526
15.3.2	Z-Scheme System	530
15.3.3	Heterojunctions	532
15.3.4	Polymers	535
15.4	Conclusions and Prospects	538
	References	538
16	Photocatalytic CO₂ Reduction	541
	<i>Deli Jiang, Qi Song, Yuyan Xu, and Di Li</i>	
16.1	Introduction	541
16.2	Principle and Mechanism of CO ₂ Reduction	542
16.2.1	Thermodynamics of CO ₂ Reduction	542
16.2.2	Kinetics of CO ₂ Reduction	543
16.2.3	CO ₂ Adsorption Configurations	544
16.3	Strategies to Improve the Photocatalytic CO ₂ Reduction Activities	544
16.3.1	Defect Engineering	545
16.3.1.1	Anions Vacancies	545
16.3.1.2	Cations Vacancies	547
16.3.2	Loading of Metal Co-catalyst	550
16.3.2.1	Loading of Pt Nanoparticles	550
16.3.2.2	Loading of Pd Nanoparticles	551
16.3.2.3	Loading of Ag Nanoparticles	553
16.3.2.4	Loading of Alloys Nanoparticles	555
16.3.3	Construction of Heterojunctions	557
16.3.3.1	II-Typical Heterojunctions	558
16.3.3.2	Z-Scheme Heterojunction	559
16.4	Conclusions	562
	Acknowledgment	562
	References	562
	Index	569