

Contents

Preface *xvii*

Part I Visible-Light Active Photocatalysis – Research and Technological Advancements 1

1 **Research Frontiers in Solar Light Harvesting 3**
Srabanti Ghosh
1.1 Introduction 3
1.2 Visible-Light-Driven Photocatalysis for Environmental Protection 4
1.3 Photocatalysis for Water Splitting 8
1.4 Photocatalysis for Organic Transformations 11
1.5 Mechanistic Studies of Visible-Light-Active Photocatalysis 13
1.6 Summary 14
References 15

2 **Recent Advances on Photocatalysis for Water Detoxification and CO₂ Reduction 27**
Carlotta Raviola and Stefano Protti
2.1 Introduction 27
2.2 Photocatalysts for Environmental Remediation and CO₂ Reduction 30
2.2.1 Undoped TiO₂ 30
2.2.2 Undoped Metal Oxides Different from TiO₂ 32
2.2.3 Carbon Modified Metal Oxides as Photocatalysts 33
2.2.4 Doped Metal Oxides 34
2.2.5 Perovskites 35
2.2.6 Metal Chalcogenides 36
2.2.7 Other Catalysts 37
2.3 Photoreactors for Solar Degradation of Organic Pollutants and CO₂ Reduction 38
2.3.1 Non Concentrating (Low Concentration or Low Temperature) Systems 39
2.3.2 Medium Concentrating or Medium Temperature Systems 40

2.3.3	High Concentrating or High-Temperature Systems	42
2.3.4	Parameters of a Solar Reactor	43
2.4	Conclusion	44
	Acknowledgment	44
	References	45
3	Fundamentals of Photocatalytic Water Splitting (Hydrogen and Oxygen Evolution)	53
	<i>Sanjib Shyamal, Paramita Hajra, Harahari Mandal, Aparajita Bera, Debasis Sariket, and Chinmoy Bhattacharya</i>	
3.1	Introduction	53
3.2	Strategy for Development of Photocatalyst Systems for Water Splitting	54
3.3	Electrochemistry of Semiconductors at the Electrolyte Interface	56
3.4	Effect of Light at the Semiconductor–Electrolyte Interface	58
3.5	Conversion and Storage of Sunlight	62
3.6	Electrolysis and Photoelectrolysis	63
3.7	Development of Photocatalysts for Solar-Driven Water Splitting	65
3.8	Approaches to Develop Visible-Light-Absorbing Metal Oxides	66
3.9	Conclusions	68
	References	68
4	Photoredox Catalytic Activation of Carbon—Halogen Bonds: C—H Functionalization Reactions under Visible Light	75
	<i>Javier I. Bardagi and Indrajit Ghosh</i>	
4.1	Introduction	75
4.2	Activation of Alkyl Halides	77
4.3	Activation of Aryl Halides	91
4.4	Factors That Determine the Carbon–Halogen Bond Activation of Aryl Halides	108
4.5	Factors That Determine the Yields of the C—H Arylated Products	109
4.6	Achievements and Challenges Ahead	109
4.7	Conclusion	110
	References	110

Part II Design and Developments of Visible Light Active Photocatalysis 115

5	Black TiO₂: The New-Generation Photocatalyst	117
	<i>Sanjay Gopal Ullattil, Soumya B. Narendranath, and Pradeepan Periyat</i>	
5.1	Introduction	117
5.2	Designing Black TiO ₂ Nanostructures	118
5.3	Black TiO ₂ as Photocatalyst	122
5.4	Conclusions	123
	References	123

6	Effect of Modification of TiO₂ with Metal Nanoparticles on Its Photocatalytic Properties Studied by Time-Resolved Microwave Conductivity	129
	<i>Hynd Remita, María Guadalupe Méndez Medrano, and Christophe Colbeau-Justin</i>	
6.1	Introduction	129
6.2	Deposition of Metal Nanoparticles by Radiolysis and by Photodeposition Method	130
6.3	Electronic Properties Studied Time-Resolved Microwave Conductivity	132
6.3.1	Surface Modification of Titania with Monometallic Nanoparticles	133
6.3.1.1	Surface Modification of Titania with Pt Clusters	133
6.3.1.2	Surface Modification of TiO ₂ with Pd Nanoparticles	135
6.3.1.3	Modification of TiO ₂ with Ag Nanoparticles	136
6.4	Modification of TiO ₂ with Au Nanoparticles	138
6.5	Modification of TiO ₂ with Bi Clusters	144
6.6	Surface Modification of TiO ₂ with Bimetallic Nanoparticles	146
6.6.1	Surface Modification with Au–Cu Nanoparticles	146
6.6.2	Surface Modification with Ag and CuO Nanoparticles	148
6.6.3	Comodification of TiO ₂ with Ni and Au Nanoparticles for Hydrogen Production	150
6.6.4	TiO ₂ Modified with NiPd Nanoalloys for Hydrogen Evolution	153
6.7	The Effect of Metal Cluster Deposition Route on Structure and Photocatalytic Activity of Mono- and Bimetallic Nanoparticles Supported on TiO ₂	155
6.8	Summary	156
	References	157
7	Glassy Photocatalysts: New Trend in Solar Photocatalysis	165
	<i>Bharat B. Kale, Manjiri A. Mahadadalkar, and Ashwini P. Bhirud</i>	
7.1	Introduction	165
7.2	Fundamentals of H ₂ S Splitting	166
7.2.1	General	166
7.2.2	Thermodynamics of H ₂ S Splitting	166
7.2.3	Role of Photocatalysts	167
7.3	Designing the Assembly for H ₂ S Splitting	168
7.3.1	Standardization of H ₂ S Splitting Setup	168
7.3.2	Interaction of Photocatalyst and Reagent System	169
7.4	Chalcogenide Photocatalysts	170
7.5	Limitations of Powder Photocatalysts	170
7.6	Glassy Photocatalyst: Innovative Approach	171
7.6.1	Semiconductor–Glass Nanocomposites and Their Advantages	171
7.7	General Methods for Glasses Preparation	172
7.7.1	Glass by Melt-Quench Technique	172
7.8	Color of the Glass – Bandgap Engineering by Growth of Semiconductors in Glass	174

7.9	CdS–Glass Nanocomposite	174
7.10	Bi ₂ S ₃ –Glass Nanocomposite	178
7.11	Ag ₃ PO ₄ –Glass Nanocomposite	179
7.12	Summary	183
	Acknowledgments	184
	References	184
8	Recent Developments in Heterostructure-Based Catalysts for Water Splitting	191
	<i>J. A. Savio Moniz</i>	
8.1	Introduction	191
8.1.1	Band Alignment	193
8.2	Visible-Light-Responsive Junctions	195
8.2.1	BiVO ₄ -Based Junctions	195
8.2.1.1	BiVO ₄ /WO ₃	197
8.2.1.2	BiVO ₄ /ZnO	197
8.2.1.3	BiVO ₄ /TiO ₂	199
8.2.1.4	BiVO ₄ /Carbon-Based Materials	199
8.2.2	Fe ₂ O ₃ -Based Junctions	199
8.2.3	WO ₃ -Based Junctions	201
8.2.4	C ₃ N ₄ -Based Junctions	202
8.2.5	Cu ₂ O-Based Junctions	204
8.3	Visible-Light-Driven Photocatalyst/OEC Junctions	207
8.3.1	BiVO ₄ /OEC	207
8.3.2	Fe ₂ O ₃ /OEC	207
8.3.3	WO ₃ /OEC	208
8.4	Observation of Charge Carrier Kinetics in Heterojunction Structure	209
8.4.1	Transient Absorption Spectroscopy	209
8.4.2	Electrochemical Impedance Spectroscopy	211
8.4.3	Surface Photovoltage Spectroscopy	213
8.5	Conclusions	215
	References	216
9	Conducting Polymers Nanostructures for Solar-Light Harvesting	227
	<i>Srabanti Ghosh, Hynd Remita, and Rajendra N. Basu</i>	
9.1	Introduction	227
9.2	Conducting Polymers as Organic Semiconductor	228
9.3	Conducting Polymer-Based Nanostructured Materials	231
9.4	Synthesis of Conducting Polymer Nanostructures	231
9.4.1	Hard Templates	232
9.4.2	Soft Templates	232
9.4.3	Template Free	233
9.5	Applications of Conducting Polymer	233
9.5.1	Conducting Polymer Nanostructures for Organic Pollutant Degradation	233

9.5.2	Conducting Polymer Nanostructures for Photocatalytic Water Splitting	237
9.5.3	Conducting Polymer-Based Heterostructures	242
9.6	Conclusion	245
	References	246

Part III Visible Light Active Photocatalysis for Solar Energy Conversion and Environmental Protection 253

10	Sensitization of TiO₂ by Dyes: A Way to Extend the Range of Photocatalytic Activity of TiO₂ to the Visible Region	255
	<i>Marta I. Litter, Enrique San Román, the late María A. Grela, Jorge M. Meichtry, and Hernán B. Rodríguez</i>	
10.1	Introduction	255
10.2	Mechanisms Involved in the Use of Dye-Modified TiO ₂ Materials for Transformation of Pollutants and Hydrogen Production under Visible Irradiation	256
10.3	Use of Dye-Modified TiO ₂ Materials for Energy Conversion in Dye-Sensitized Solar Cells	260
10.4	Self-Sensitized Degradation of Dye Pollutants	262
10.5	Use of Dye-Modified TiO ₂ for Visible-Light-Assisted Degradation of Colorless Pollutants	265
10.6	Water Splitting and Hydrogen Production using Dye-Modified TiO ₂ Photocatalysts under Visible Light	269
10.7	Conclusions	270
	Acknowledgement	271
	References	271
11	Advances in the Development of Novel Photocatalysts for Detoxification	283
	<i>Ciara Byrne, Michael Nolan, Swagata Banerjee, Honey John, Sheethu Jose, Pradeepan Periyat, and Suresh C. Pillai</i>	
11.1	Introduction	283
11.2	Theoretical Studies of Photocatalysis	285
11.2.1	Doping and Surface Modification of TiO ₂ for Bandgap Engineering	285
11.2.2	Alignment of Valence and Conduction Band Edges with Water Oxidation and Reduction Potentials	291
11.2.3	Electron and Hole Localization	293
11.3	Metal-Doped Photocatalysts for Detoxification	296
11.3.1	High-Temperature Stable Anatase TiO ₂ Photocatalyst	296
11.3.2	Main Group Metal Ions on Anatase Stability and Photocatalytic Activity	296
11.3.3	Effect of Transition Metals on Anatase Stability and Photocatalytic Activity	296

11.3.4 Effect of Rare Earth Metal Ions on Anatase Stability and Photocatalytic Activity 297

11.4 Graphene-TiO₂ Composites for Detoxification 299

11.5 Commercial Applications of Photocatalysis in Environmental Detoxification 303

11.5.1 Self-Cleaning Materials 303

11.5.2 Bactericidal 307

11.5.3 Wastewater Detoxification 308

11.6 Conclusions 313

References 313

12 Metal-Free Organic Semiconductors for Visible-Light-Active Photocatalytic Water Splitting 329
S. T. Nishanthi, Battula Venugopala Rao, and Kamalakannan Kailasam

12.1 Introduction 329

12.2 Organic Semiconductors for Photocatalytic Water Splitting and Emergence of Graphitic Carbon Nitrides 331

12.3 Graphitic Carbon Nitrides for Photocatalytic Water Splitting 332

12.3.1 Precursor-Derived g-CN 334

12.3.2 Nanoporous g-CN by Templating Methods 336

12.3.2.1 Hard Templating 337

12.3.2.2 Soft Templating 339

12.3.2.3 Template-Free 340

12.3.3 Heteroatom Doping 341

12.3.3.1 Metal Doping 341

12.3.3.2 Nonmetal Doping 342

12.3.4 Metal Oxides/g-CN Nanocomposites 344

12.3.5 Graphene and CNT-Based g-CN Nanocomposites 345

12.3.6 Structural Modification with Organic Groups 345

12.3.7 Crystalline Carbon Nitrides 347

12.3.8 Overall Water Splitting and Large-Scale Hydrogen Production Using Carbon Nitrides 348

12.4 Novel Materials 349

12.4.1 Triazine and Heptazine-Based Organic Polymers 349

12.4.2 Covalent Organic Frameworks (COFs) and Beyond 350

12.5 Conclusions and Perspectives 351

References 352

13 Solar Photochemical Splitting of Water 365
Srinivasa Rao Lingampalli and C. N. R. Rao

13.1 Introduction 365

13.2 Photocatalytic Water Splitting 366

13.2.1 Fundamentals of Water Splitting 366

13.2.2 Light-Harvesting Units 367

13.2.3 Photocatalytic Activity 369

13.2.4 Effect of Size of Nanostructures 369

13.3	Overall Water Splitting	371
13.3.1	One-Step Photocatalytic Process	371
13.3.2	Two-Step (Z-Scheme) Photocatalytic Process	374
13.4	Oxidation of Water	376
13.5	Reduction of Water	380
13.5.1	C_3N_4 and Related Materials	380
13.5.2	Semiconductors	382
13.5.3	Multicomponent Heterostructures	383
13.6	Coupled Reactions	386
13.7	Summary and Outlook	387
	Acknowledgments	387
	References	387
14	Recent Developments on Visible-Light Photoredox Catalysis by Organic Dyes for Organic Synthesis	393
	<i>Shounak Ray, Partha Kumar Samanta, and Papu Biswas</i>	
14.1	Introduction	393
14.2	General Mechanism	393
14.3	Recent Application of Organic Dyes as Visible-Light Photoredox Catalysts	396
14.3.1	Photocatalysis by Eosin Y	396
14.3.1.1	Perfluoroarylation of Arenes	396
14.3.1.2	Synthesis of Benzo[<i>b</i>]phosphole Oxides	397
14.3.1.3	Direct C—H Arylation of Heteroarenes	398
14.3.1.4	Synthesis of 1,2-Diketones from Alkynes	399
14.3.1.5	Thiocyanation of Imidazoheterocycles	401
14.3.2	Photocatalysis by Rose Bengal	402
14.3.2.1	Aerobic Indole C-3 Formylation Reaction	402
14.3.2.2	Decarboxylative/Decarbonylative C3-Acylation of Indoles	404
14.3.2.3	Oxidative Annulation of Arylamidines	405
14.3.2.4	Cross-Dehydrogenative Coupling of Tertiary Amines with Diazo Compounds	406
14.3.2.5	C—H Functionalization and Cross-Dehydrogenative Coupling Reactions	407
14.3.2.6	Oxidative Cross-Coupling of Thiols with P(O)H Compounds	408
14.3.3	Photocatalysis by Methylene Blue	409
14.3.3.1	Oxidative Hydroxylation of Arylboronic Acids	409
14.3.3.2	Radical Trifluoromethylation	410
14.3.4	Photocatalysis by 3,6-Di(pyridin-2-yl)-1,2,4,5-tetrazine	411
14.3.4.1	Synthesis of 2-Substituted Benzimidazole and Benzothiazole	411
14.3.4.2	Oxidation of Alcohols to Carbonyl Derivatives	413
14.3.5	Photocatalysis by Phenothiazine Dyes: Oxidative Coupling of Primary Amines	414
14.4	Conclusion	415
	Abbreviations	415
	References	415

15	Visible-Light Heterogeneous Catalysts for Photocatalytic CO₂ Reduction	421
	<i>Sanyasinaidu Boddu, S.T. Nishanthi, and Kamalakannan Kailasam</i>	
15.1	Introduction	421
15.2	Basic Principles of Photocatalytic CO ₂ Reduction	422
15.2.1	Thermodynamic Favorability of the Reactions	423
15.3	Inorganic Semiconductors	424
15.3.1	Metal Oxides	424
15.3.2	Sulfides	428
15.3.3	Oxynitrides	429
15.4	Organic Semiconductors	430
15.4.1	Carbon Nitride and their Composites	430
15.4.2	Metal Organic Frameworks (MOFs)	434
15.4.3	Covalent Organic Frameworks	435
15.5	Semiconductor Heterojunctions	436
15.6	Conclusion and Perspectives	437
	References	438

Part IV Mechanistic Studies of Visible Light Active Photocatalysis 447

16	Band-gap Engineering of Photocatalysts: Surface Modification versus Doping	449
	<i>Ewa Kowalska, Zhishun Wei, and Marcin Janczarek</i>	
16.1	Introduction	449
16.2	Doping	451
16.2.1	Metal Ion Doping	451
16.2.2	Nonmetal Ion Doping	453
16.2.3	Codoping	455
16.2.4	Self-Doping	457
16.3	Surface Modification	458
16.3.1	Metals	458
16.3.2	Nonmetals	464
16.3.3	Organic Compounds (Colorless and Color)	464
16.4	Heterojunctions	468
16.4.1	Excitation of One Component	468
16.4.2	Excitation of Both Components	469
16.5	Z-Scheme	470
16.6	Hybrid Nanostructures	471
16.7	Summary	473
	References	473

17	Roles of the Active Species Generated during Photocatalysis	485
	<i>Mats Jonsson</i>	
17.1	Introduction	485
17.2	Mechanism of Photocatalysis in TiO_2 /Water Systems	486
17.3	Active Species Generated at the Catalyst/Water Interface	486
17.4	Oxidative Degradation of Solutes Present in the Aqueous Phase	490
17.5	Impact of H_2O_2 on Oxidative Degradation of Solutes Present in the Aqueous Phase	492
17.6	The Role of Common Anions Present in the Aqueous Phase	493
17.7	Summary of Active Species Present in Heterogeneous Photocatalysis in Water	494
	References	495

18	Visible-Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications	499
	<i>Ramachandran Vasant Kumar and Michael Coto</i>	
18.1	Introduction	499
18.2	Historical Background	499
18.3	Basic Concepts	501
18.4	Structure of TiO_2	504
18.5	Photocatalytic Reactions	506
18.6	Physical Architectures of TiO_2	507
18.7	Visible-Light Photocatalysis	509
18.8	Ion Doping and Ion Implantation	510
18.9	Dye Sensitization	513
18.10	Noble Metal Loading	514
18.11	Coupled Semiconductors	518
18.12	Carbon– TiO_2 Composites	518
18.13	Alternatives to TiO_2	520
18.14	Conclusions	521
	References	522

Part V Challenges and Perspectives of Visible Light Active Photocatalysis for Large Scale Applications 527

19	Quantum Dynamics Effects in Photocatalysis	529
	<i>Abdulrahiman Nijamudheen and Alexey V. Akimov</i>	
19.1	Introduction	529
19.2	Computational Approaches to Model Adiabatic Processes in Photocatalysis	531

19.3	Computational Approaches to Model Nonadiabatic Effects in Photocatalysis	532
19.4	Quantum Tunneling in Adiabatic and Nonadiabatic Dynamics	535
19.5	The Mechanisms of Organic Reactions Catalyzed by Semiconductor Photocatalysts	541
19.5.1	Methanol Photooxidation on Semiconductor Surfaces	541
19.5.2	Water-Splitting Reactions on Semiconductor Surfaces	544
19.5.3	Carbon Oxide Redox Reactions on Semiconductor Surfaces	546
19.6	Conclusions and Outlook	547
	References	549
20	An Overview of Solar Photocatalytic Reactor Designs and Their Broader Impact on the Environment	567
	<i>Justin D. Glover, Adam C. Hartley, Reid A. Windmiller, Naoma S. Nelsen, and Joel E. Boyd</i>	
20.1	Introduction	567
20.2	Materials	568
20.3	Slurry-Style Photocatalysis	569
20.4	Deposited Photocatalysts	569
20.5	Applications	570
20.5.1	Gas Phase and Self-Cleaning Applications	570
20.5.2	Water Purification Applications	571
20.5.3	Inclined Plate Collectors	571
20.5.4	Parabolic Trough Concentrator	572
20.5.5	Compound Parabolic Concentrator Reactor	573
20.5.6	The Environmental Impact of Nanoscale Titania	574
20.5.7	Detecting and Quantifying Nanoparticles	574
20.5.8	Transformation of Nanoparticles in the Environment	575
20.5.9	Toxicity of Nanoparticles	576
20.6	Conclusion	577
	References	577
21	Conclusions and Future Work	585
	<i>Srabanti Ghosh</i>	