Contents

Series Editor Preface XVII Preface XIX About the Series Editor XXIII About the Volume Editor XXV List of Contributors XXVII

Part I Fundamentals: Active Species, Mechanisms, Reaction Pathways 1

- 1 Identification and Roles of the Active Species Generated on Various Photocatalysts 3 Yoshio Nosaka and Atsuko Y. Nosaka Key Species in Photocatalytic Reactions 3 1.1 1.2 Trapped Electron and Hole 6 1.3 Superoxide Radical and Hydrogen Peroxide $(O_2^{\bullet-} \text{ and } H_2O_2)$ 7 1.4 Hydroxyl Radical (OH[•]) 9 1.5 Singlet Molecular Oxygen $({}^{1}O_{2})$ 12 1.6 Reaction Mechanisms for Bare TiO₂ 15 1.7 Reaction Mechanisms of Visible-Light-Responsive Photocatalysts 17 Conclusion 1.8 20 References 21 2 Photocatalytic Reaction Pathways - Effects of Molecular Structure, Catalyst, and Wavelength 25 William S. Jenks 2.1 Introduction 25 2.2 Methods for Pathway Determination 27 2.3 Prototypical Oxidative Reactivity in Photocatalytic Degradations 29
- 2.3.1 Oxidation of Arenes and the Importance of Adsorption 30
- 2.3.1.1 Hydroxylation and the Source of Oxygen 30
- 2.3.1.2 Ring-Opening Reactions 32

VII

VIII Contents

2.3.1.3	Indicators of SET versus Hydroxyl Chemistry in Aromatic		
2.3.2	Systems 32 Carbonylic Acida 35		
2.3.2	Carboxylic Acids 35		
2.3.3	Alcohol Fragmentation and Oxidation 36 Oxidation of Alkyl Substituents 37		
2.3.4	•		
	Apparent Hydrolysis Reactions 38		
2.3.6	Sulfur-Bearing Compounds 39		
2.4 2.5	Prototypical Reductive Reactivity in Photocatalytic Degradations 39 The Use of Organic Molecules as Test Probes for Next-Generation Photocatalysts 41		
2.6	Modified Catalysts: Wavelength-Dependent Chemistry of Organic Probes 42		
2.7	Conclusions 44		
	References 45		
3	Photocatalytic Mechanisms and Reaction Pathways Drawn from Kinetic and Probe Molecules 53		
	Claudio Minero, Valter Maurino, and Davide Vione		
3.1	The Photocatalyic Rate 53		
3.1.1	Other Kinetic Models 55		
3.1.2	Substrate-Mediated Recombination 57		
3.2	Surface Speciation 60		
3.2.1	Different Commercial Catalysts 60		
3.2.2	Surface Manipulation 61		
3.2.3	Crystal Faces 62		
3.2.4	Surface Traps for Holes 64		
3.3	Multisite Kinetic Model 65		
3.4	Conclusion 68		
	References 68		
	Part II Improving the Photocatalytic Efficacy 73		
4	Design and Development of Active Titania and Related		
	Photocatalysts 75		
	Bunsho Ohtani		
4.1	Introduction – a Thermodynamic Aspect of Photocatalysis 75		
4.2	Photocatalytic Activity: Reexamination 77		
4.3	Design of Active Photocatalysts 78		
4.4	A Conventional Kinetics in Photocatalysis: First-Order Kinetics 79		
4.5	A Conventional Kinetics in Photocatalysis: Langmuir–Hinshelwood		
	Mechanism 80		
4.6	Topics and Problems Related to Particle Size of Photocatalysts82		
4.7	Recombination of a Photoexcited Electron and a Positive Hole 85		
4.8	Evaluation of Crystallinity as a Property Affecting Photocatalytic		
	Activity 86		

Contents IX

4.9	Electron Traps as a Possible Candidate of a Recombination Center 87	
4.10	Donor Levels – a Meaning of n-Type Semiconductor 89	
4.11	Dependence of Photocatalytic Activities on Physical and Structural	
	Properties 90	
4.11.1	Correlation between Physical Properties and Photocatalytic	
	Activities 90	
4.11.2	Statistical Analysis of Correlation between Physical Properties and	
	Photocatalytic Activities – a Trial 92	
4.11.3	Common Features of Titania Particles with Higher Photocatalytic	
	Activity 94	
4.11.4	Highly Active Mesoscopic Anatase Particles of Polyhedral Shape 95	
4.12	Synergetic Effect 96	
4.13	Doping 97	
4.14	Conclusive Remarks 98	
	Acknowledgments 99	
	References 99	
-	Madified Dhate satelysts 102	
5	Modified Photocatalysts 103 Nurit Shaham-Waldmann and Yaron Paz	
5.1		
5.1 5.2	Why Modifying? 103 Forms of Modification 104	
5.2 5.3		
5.3.1	Modified Physicochemical Properties 106 Crystallinity and Phase Stability 106	
5.3.2	Surface Morphology, Surface Area, and Adsorption 107	
5.3.3	Adsorption of Oxygen 111	
5.3.4	Concentration of Surface OH 111	
5.3.5	Specificity 112	
5.3.5.1	- · ·	
5.3.5.2	TiO ₂ Surface Overcoating 115 Composites Comprised of TiO ₂ and Metallic Nanoislands 116	
5.3.5.2		
	1 8	
5.3.5.4	Utilizing the "Adsorb and Shuttle" Mechanism to Obtain Specificity <i>117</i>	
5.3.5.5	Mesoporous Materials 119	
5.3.5.6	Molecular Imprinting 120	
5.3.6	Products' Control 122	
5.3.6.1	Surface Modification by Molecular Imprinting 123	
5.3.6.2	Composites Comprised of TiO_2 and Metallic Nanoislands 124	
5.3.6.3	Doping with Metal Ions 124	
5.3.6.4	Nonmetallic Composite 125	
5.3.6.5	TiO ₂ Morphology and Crystalline Phase 125	
5.3.7	Reducing Deactivation 125	
5.3.8	Recombination Rates and Charge Separation 126	
5.3.8.1	Structure Modification 127	
5.3.8.2	Composites–Metal Islands 127	
5.3.8.3	Composites Comprising Carbonaceous Materials 128	
5.5.0.5	Composites Comprising Carbonaccous Materials 120	

X Contents

5.3.8.4 5.3.8.5 5.3.8.6 5.3.8.7 5.3.9 5.3.10 5.3.11 5.3.12	Composites Composed of TiO ₂ and Nonoxide Semiconductors 128 Composites Composed of TiO ₂ and Other Oxides 129 Doping with Metals 131 Doping with Nonmetals 132 Visible Light Activity 132 Charging–Discharging 132 Mass Transfer 133 Facilitating Photocatalysis in Deaerated Suspensions 134 Summary 134 References 134
6	Immobilization of a Semiconductor Photocatalyst on Solid Supports: Methods, Materials, and Applications 145 Didier Robert, Valérie Keller, and Nicolas Keller
6.1	Introduction 145
6.2	Immobilization Techniques 147
6.3	Supports 152
6.3.1	Packed-Bed Photocatalytic Materials 153
6.3.2	Monolithic Photocatalytic Materials 155
6.3.3	Optical Fibers 164
6.4	Laboratory and Industrial Applications of Supported Photocatalysts 168
6.5	Conclusion171References172
7	Wastewater Treatment Using Highly Functional Immobilized TiO ₂ Thin-Film Photocatalysts 179
	Masaya Matsuoka, Takashi Toyao, Yu Horiuchi, Masato Takeuchi, and Masakazu Anpo
7.1	Introduction 179
7.2	Application of a Cascade Falling-Film Photoreactor (CFFP) for the Remediation of Polluted Water and Air under Solar Light Irradiation 180
7.3	Application of TiO ₂ Thin-Film-Coated Fibers for the Remediation of Polluted Water 184
7.4	Application of TiO_2 Thin Film for Photofuel Cells (PFC) 186
7.5	Preparation of Visible-Light-Responsive TiO ₂ Thin Films and Their Application to the Remediation of Polluted Water 187
7.5.1	Visible-Light-Responsive TiO ₂ Thin Films Prepared by Cation or Anion Doping 188
7.5.2	Visible-Light-Responsive TiO ₂ Thin Films Prepared by the Magnetron Sputtering Deposition Method 190
7.6	Conclusions 195 References 195

Contents XI

8	Sensitization of Titania Semiconductor: A Promising Strategy to Utilize
0	Visible Light 199
	Zhaohui Wang, Chuncheng Chen, Wanhong Ma, and Jincai Zhao
8.1	Introduction 199
8.2	Principle of Photosensitization 200
8.3	Dye Sensitization 201
8.3.1	Fundamentals of Dye Sensitization 202
8.3.1.1	Geometry and Electronic Structure of Interface 202
8.3.1.2	Excited-State Redox Properties of Dyes 203
8.3.1.3	Electron Transfer from Dyes to TiO_2 205
8.3.2	Application of Dye Sensitization 208
8.3.2.1	Nonregenerative Dye Sensitization 208
8.3.2.2	Regenerative Dye Sensitization 211
8.4	Polymer Sensitization 213
8.4.1	Carbon Nitride Polymer 213
8.4.2	Conducting Polymers 214
8.5	Surface-Complex-Mediated Sensitization 214
8.5.1	Organic Ligand 215
8.5.2	Inorganic Ligand 217
8.6	Solid Semiconductor/Metal Sensitization 218
8.6.1	Small-Band-Gap Semiconductor 219
8.6.1.1	*
8.6.1.2	Category in Terms of Charge Transfer Process 219
8.6.2	Plasmonic Metal 222
8.6.2.1	Basic Concepts 222
8.6.2.2	Proposed Mechanisms 224
8.6.2.3	Critical Parameters 225
8.7	Other Strategies to Make Titania Visible Light Active 226
8.7.1	Band Gap Engineering 226
8.7.1.1	Metal Doping 226
8.7.1.2	Nonmetal Doping 227
8.7.1.3	Codoping 227
8.7.2	Structure/Surface Engineering 228
8.8	Conclusions 230
	Acknowledgment 231
	References 231
9	Photoelectrocatalysis for Water Purification 241
	Rossano Amadelli and Luca Samiolo
9.1	Introduction 241
9.2	Photoeffects at Semiconductor Interfaces 242
9.3	Water Depollution at Photoelectrodes 245
9.3.1	Morphology and Microstructure 245
9.3.2	Effect of Applied Potential 247
9.3.3	Effect of pH 247

XII Contents

9.3.4	Effect of Oxygen 248
9.3.5	Electrolyte Composition 249
9.4	Photoelectrode Materials 249
9.4.1	Titanium Dioxide 249
9.4.1.1	Cation Doping 250
9.4.1.2	Nonmetal Doping 250
9.4.2	Other Semiconductor Photoelectrodes 251
9.4.2.1	Zinc Oxide and Iron Oxide 251
9.4.2.2	Tungsten Trioxide 251
9.4.2.3	Bismuth Vanadate 251
9.4.3	Coupled Semiconductors 251
9.4.3.1	n-n Heterojunctions 253
9.4.3.2	p–n Heterojunctions 254
9.5	Electrodes Preparation and Reactors 255
9.6	Conclusions 256
	References 257
	Part III Effects of Photocatalysis on Natural Organic Matter and
	Bacteria 271
10	Photocatalysis of Natural Organic Matter in Water Characterization

10	Photocatalysis of Natural Organic Matter in Water: Characterization
	and Treatment Integration 273
	Sanly Liu, May Lim and Rose Amal

- 10.1 Introduction 273
- 10.2 Monitoring Techniques 274
- 10.2.1 Total Organic Carbon 275
- 10.2.2 UV-vis Spectroscopy 275
- 10.2.3 Fluorescence Spectroscopy 277
- 10.2.4 Molecular Size Fractionation 278
- 10.2.5 Resin Fractionation 280
- 10.2.6 Infrared Spectroscopy 280
- 10.3 By-products from the Photocatalytic Oxidation of NOM and its Resultant Disinfection By-Products (DBPs) 281
- 10.4 Hybrid Photocatalysis Technologies for the Treatment of NOM 284
- 10.5 Conclusions 287 References 289

11	Waterborne Escherichia coli I	nactivation by TiO ₂ Photoassisted
	Processes: a Brief Overview	295

Julián Andrés Rengifo-Herrera, Angela Giovana Rincón, and Cesar Pulgarin

- Introduction 295 11.1
- Physicochemical Aspects Affecting the Photocatalytic E. coli 11.2 Inactivation 296
- 11.2.1 Effect of Bulk Physicochemical Parameters 296

- 11.2.1.1 Effect of TiO₂ Concentration and Light Intensity 296
- 11.2.1.2 Simultaneous Presence of Anions and Organic Matter 297
- 11.2.1.3 pH Influence 298
- 11.2.1.4 Oxygen Concentration 298
- 11.2.2 Physicochemical Characteristics of TiO₂ 299
- 11.3 Using of N-Doped TiO₂ in Photocatalytic Inactivation of Waterborne Microorganisms 299
- 11.4 Biological Aspects 302
- 11.4.1 Initial Bacterial Concentration 302
- 11.4.2 Physiological State of Bacteria 302
- 11.5Proposed Mechanisms Suggested for Bacteria Abatement by
Heterogeneous TiO2 Photocatalysis303
- 11.5.1 Effect of UV-A Light Alone and TiO₂ in the Dark 303
- 11.5.2 Cell Inactivation by Irradiated TiO₂ Nanoparticles 304
- 11.6 Conclusion 304 References 305

Part IV Modeling. Reactors. Pilot plants 311

- Photocatalytic Treatment of Water: Irradiance Influences 313 David Ollis
 Introduction 313
- 12.1.1 Chapter Topics 313
- 12.1.2 Photon Utilization Efficiency 313
- Reaction Order in Irradiance: Influence of Electron–Hole Recombination and the High Irradiance Penalty 314
- 12.3 Langmuir–Hinshelwood (LH) Kinetic Form: Equilibrated Adsorption 315
- 12.4 Pseudo-Steady-State Analysis: Nonequilibrated Adsorption 317
- 12.5 Mass Transfer and Diffusion Influences at Steady Conditions 321
 12.6 Controlled Periodic Illumination: Attempt to Beat Recombination 323
- 12.7 Solar-Driven Photocatalysis: Nearly Constant nUV Irradiance 324
- 12.8 Mechanism of Hydroxyl Radical Attack: Same Irradiance Dependence 326
- 12.9 Simultaneous Homogeneous and Heterogeneous Photochemistry 327
- 12.10 Dye-Photosensitized Auto-Oxidation 328
- 12.11 Interplay between Fluid Residence Times and Irradiance Profiles *329*
- 12.11.1 Batch Reactors 329
- 12.11.2 Flow Reactors 329
- 12.12 Quantum Yield, Photonic Efficiency, and Electrical Energy per Order 331

XIV Contents

12.13	Conclusions 332
	References 332
13	A Methodology for Modeling Slurry Photocatalytic Reactors for
	Degradation of an Organic Pollutant in Water 335
	Orlando M. Alfano, Alberto E. Cassano, Rodolfo J. Brandi, and
12.1	Maríia L. Satuf
13.1	Introduction and Scope 335
13.2	Evaluation of the Optical Properties of Aqueous TiO ₂ Suspensions 337
13.2.1	Spectrophotometric Measurements of TiO ₂ Suspensions 338
13.2.2	Radiation Field in the Spectrophotometer Sample Cell 339
13.2.3	Parameter Estimation 341
13.3	Radiation Model 342
13.3.1	Experimental Set Up and Procedure 343
13.3.2	Radiation Field Inside the Photoreactor 344
13.4	Quantum Efficiencies of 4-Chlorophenol Photocatalytic
13.4	Degradation 346
13.4.1	Calculation of the Quantum Efficiency 346
13.4.2	Experimental Results 347
13.4.2	Kinetic Modeling of the Pollutant Photocatalytic Degradation 348
13.5.1	Mass Balances 348
13.5.2	Kinetic Model 349
13.5.3	Kinetic Parameters Estimation 350
13.5.5	Bench-Scale Slurry Photocatalytic Reactor for Degradation of
15.0	4-Chlorophenol 352
13.6.1	Experiments 352
13.6.2	Reactor Model 352
13.6.2.1	Radiation Model 352
13.6.2.1	
13.6.2.2	
13.6.3	Mass Balances in the Tank and Reactor 354 Results 355
	Conclusions 356
13.7	Acknowledgments 357
	References 357
	References 557
14	Design and Optimization of Photocatalytic Water Purification
	Reactors 361
	Tsuyoshi Ochiai and Akira Fujishima
14.1	Introduction 361
14.1.1	Market Transition of Industries Related to Photocatalysis 361
14.1.2	Historical Overview 361
14.2	Catalyst Immobilization Strategy 363
14.2.1	Aqueous Suspension 363
14.2.2	Immobilization of TiO ₂ Particles onto Solid Supports 365
	* *

Contents XV

- 14.3 Synergistic Effects of Photocatalysis and Other Methods 366
- 14.3.1 Deposition of Metallic Nanoparticles onto TiO₂ Surface for Disinfection 366
- 14.3.2 Combination with Advanced Oxidation Processes (AOPs) 367
- 14.4 Effective Design of Photocatalytic Reactor System 369
- 14.4.1 Two Main Strategies for the Effective Reactors 369
- 14.4.2 Design of Total System 371
- 14.5 Future Directions and Concluding Remarks 372 Acknowledgments 373 References 373
- 15 Solar Photocatalytic Pilot Plants: Commercially Available Reactors 377

Sixto Malato, Pilar Fernández-Ibáñez, Maneil Ignacio Maldonado, Isabel Oller, and Maria Inmaculada Polo-López

- 15.1 Introduction 377
- 15.2 Compound Parabolic Concentrators 379
- 15.3 Technical Issues: Reflective Surface and Photoreactor 382
- 15.4 Suspended or Supported Photocatalyst 386
- 15.5 Solar Photocatalytic Treatment Plants 388
- 15.6 Specific Issues Related with Solar Photocatalytic Disinfection 390
- 15.7 Conclusions 394

Acknowledgments 395

References 395

Index 399