

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
 - 1.1 Key Species in Photocatalytic Reactions 3
 - 1.2 Trapped Electron and Hole 6
 - 1.3 Superoxide Radical and Hydrogen Peroxide ($O_2^{\bullet-}$ and H_2O_2) 7
 - 1.4 Hydroxyl Radical (OH^\bullet) 9
 - 1.5 Singlet Molecular Oxygen (1O_2) 12
 - 1.6 Reaction Mechanisms for Bare TiO_2 15
 - 1.7 Reaction Mechanisms of Visible-Light-Responsive Photocatalysts 17
 - 1.8 Conclusion 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

2.3.1.3	Indicators of SET versus Hydroxyl Chemistry in Aromatic Systems	32
2.3.2	Carboxylic Acids	35
2.3.3	Alcohol Fragmentation and Oxidation	36
2.3.4	Oxidation of Alkyl Substituents	37
2.3.5	Apparent Hydrolysis Reactions	38
2.3.6	Sulfur-Bearing Compounds	39
2.4	Prototypical Reductive Reactivity in Photocatalytic Degradations	39
2.5	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
	<i>Claudio Minero, Valter Maurino, and Davide Vione</i>	
3.1	The Photocatalytic 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
	<i>Bunsho Ohtani</i>	
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 Photocatalysts	82
4.7	Recombination of a Photoexcited Electron and a Positive Hole	85
4.8	Evaluation of Crystallinity as a Property Affecting Photocatalytic Activity	86

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
5	Modified Photocatalysts	103
	<i>Nurit Shaham-Waldmann and Yaron Paz</i>	
5.1	Why Modifying?	103
5.2	Forms of Modification	104
5.3	Modified Physicochemical Properties	106
5.3.1	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	TiO ₂ Surface Overcoating	115
5.3.5.2	Composites Comprised of TiO ₂ and Metallic Nanoislands	116
5.3.5.3	Doping with Metal Ions and Oxides	116
5.3.5.4	Utilizing the “Adsorb and Shuttle” Mechanism to Obtain Specificity	117
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

5.3.8.4	Composites Composed of TiO ₂ and Nonoxide Semiconductors	128
5.3.8.5	Composites Composed of TiO ₂ and Other Oxides	129
5.3.8.6	Doping with Metals	131
5.3.8.7	Doping with Nonmetals	132
5.3.9	Visible Light Activity	132
5.3.10	Charging–Discharging	132
5.3.11	Mass Transfer	133
5.3.12	Facilitating Photocatalysis in Deaerated Suspensions	134
	Summary	134
	References	134
6	Immobilization of a Semiconductor Photocatalyst on Solid Supports: Methods, Materials, and Applications	145
	<i>Didier Robert, Valérie Keller, and Nicolas Keller</i>	
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	Conclusion	171
	References	172
7	Wastewater Treatment Using Highly Functional Immobilized TiO₂ Thin-Film Photocatalysts	179
	<i>Masaya Matsuoka, Takashi Toyao, Yu Horiuchi, Masato Takeuchi, and Masakazu Anpo</i>	
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

8 Sensitization of Titania Semiconductor: A Promising Strategy to Utilize 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 Basic Concepts 219
 - 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

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 and Treatment Integration	273
	<i>Sanly Liu, May Lim and Rose Amal</i>	
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 <i>Escherichia coli</i> Inactivation by TiO₂ Photoassisted Processes: a Brief Overview	295
	<i>Julián Andrés Rengifo-Herrera, Angela Giovana Rincón, and Cesar Pulgarin</i>	
11.1	Introduction	295
11.2	Physicochemical Aspects Affecting the Photocatalytic <i>E. coli</i> Inactivation	296
11.2.1	Effect of Bulk Physicochemical Parameters	296

11.2.1.1	Effect of TiO_2 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 TiO_2	299
11.3	Using of N-Doped TiO_2 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
11.5	Proposed Mechanisms Suggested for Bacteria Abatement by Heterogeneous TiO_2 Photocatalysis	303
11.5.1	Effect of UV-A Light Alone and TiO_2 in the Dark	303
11.5.2	Cell Inactivation by Irradiated TiO_2 Nanoparticles	304
11.6	Conclusion	304
	References	305

Part IV Modeling. Reactors. Pilot plants 311

12	Photocatalytic Treatment of Water: Irradiance Influences	313
	<i>David Ollis</i>	
12.1	Introduction	313
12.1.1	Chapter Topics	313
12.1.2	Photon Utilization Efficiency	313
12.2	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

12.13	Conclusions	332
	References	332
13	A Methodology for Modeling Slurry Photocatalytic Reactors for Degradation of an Organic Pollutant in Water	335
	<i>Orlando M. Alfano, Alberto E. Cassano, Rodolfo J. Brandi, and Mari�a L. Satuf</i>	
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 Degradation	346
13.4.1	Calculation of the Quantum Efficiency	346
13.4.2	Experimental Results	347
13.5	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
13.6	Bench-Scale Slurry Photocatalytic Reactor for Degradation of 4-Chlorophenol	352
13.6.1	Experiments	352
13.6.2	Reactor Model	352
13.6.2.1	Radiation Model	352
13.6.2.2	Reaction Rates	354
13.6.2.3	Mass Balances in the Tank and Reactor	354
13.6.3	Results	355
13.7	Conclusions	356
	Acknowledgments	357
	References	357
14	Design and Optimization of Photocatalytic Water Purification Reactors	361
	<i>Tsuyoshi Ochiai and Akira Fujishima</i>	
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

14.3	Synergistic Effects of Photocatalysis and Other Methods	366
14.3.1	Deposition of Metallic Nanoparticles onto TiO ₂ 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
	<i>Sixto Malato, Pilar Fernández-Ibáñez, Maneil Ignacio Maldonado, Isabel Oller, and Maria Inmaculada Polo-López</i>	
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