

## Contents

### Preface *xi*

|          |   |           |
|----------|---|-----------|
| <b>1</b> | <b>Kinetic and Thermodynamic Considerations for Photocatalyst Design</b>          | <b>1</b>  |
|          | <i>Frank E. Osterloh</i>  |           |
| 1.1      | Introduction  | 1         |
| 1.2      | Mechanistic Aspects of Photochemical Reaction Systems                             | 2         |
| 1.3      | Common Parameters of Photochemical Reaction Systems                               | 10        |
| 1.4      | Differences Between Photocatalytic and Photosynthetic Reaction Systems            | 13        |
| 1.5      | Conclusion  | 17        |
|          | Acknowledgment  | 18        |
|          | References  | 18        |
| <b>2</b> | <b>Design of Reliable Studies on Photocatalysis: Logic, Concepts, and Methods</b> | <b>29</b> |
|          | <i>Bunsho Ohtani</i>  |           |
| 2.1      | Photocatalysis  | 29        |
| 2.2      | Reliability in Scientific Studies   | 30        |
| 2.2.1    | Reliability in Science  | 30        |
| 2.2.2    | Truth in Science: Unambiguousness Text  | 30        |
| 2.2.3    | Logic in Scientific Studies   | 30        |
| 2.2.4    | Examples of Propositions  | 31        |
| 2.2.5    | Counter (Contrary) Evidence: Killer Card  | 32        |
| 2.2.6    | Reliability in Scientific Studies   | 34        |
| 2.3      | Methods in Photocatalysis Studies   | 34        |
| 2.3.1    | Bandgap Determination by Tauc Plots   | 34        |
| 2.3.2    | Action Spectrum Analysis  | 36        |
| 2.3.3    | Light Intensity-Dependent Analysis  | 39        |
| 2.3.4    | Photocatalytic Activity Evaluation  | 41        |

|          |  |           |
|----------|--|-----------|
| 2.3.5    | Correlation Between Photocatalytic Activity and Physical/Structural Properties                   | 44        |
| 2.4      | Design of Reliable Studies on Photocatalysis   | 46        |
|          | References   | 46        |
| <b>3</b> | <b>In Situ Spectroscopy for Mechanistic Studies in Semiconductor Photocatalysis</b>              | <b>51</b> |
|          | <i>Jan P. Hofmann</i>  |           |
| 3.1      | Introduction   | 51        |
| 3.2      | Challenges in In Situ and <i>Operando</i> Characterization in Photocatalysis                     | 52        |
| 3.3      | Overview of Methods and Examples from the Literature   | 54        |
| 3.3.1    | (Transient) UV/Vis/NIR Electronic Spectroscopies   | 57        |
| 3.3.2    | Vibrational Spectroscopies   | 59        |
| 3.3.2.1  | Infrared Spectroscopy  | 59        |
| 3.3.2.2  | Raman Spectroscopy and Microscopy  | 63        |
| 3.3.2.3  | Nonlinear Spectroscopies: Second-harmonic Generation and Sum Frequency Generation Spectroscopies | 64        |
| 3.3.3    | Electron Paramagnetic Resonance  | 65        |
| 3.3.4    | (Synchrotron) X-ray Spectroscopies   | 66        |
| 3.3.4.1  | Photoelectron Spectroscopy   | 66        |
| 3.3.4.2  | X-ray Absorption Spectroscopy (XAS, XANES, and EXAFS)  | 68        |
| 3.4      | Outlook and Future Perspectives  | 68        |
|          | References   | 69        |
| <b>4</b> | <b>Principles and Limitations of Photoelectrochemical Fuel Generation</b>                        | <b>77</b> |
|          | <i>Bastian Mei and Kasper Wenderich</i>  |           |
| 4.1      | Introduction   | 77        |
| 4.2      | Photoelectrochemical Energy Storage  | 78        |
| 4.2.1    | Thermodynamic Requirements and Driving Forces  | 78        |
| 4.2.2    | Basics of Semiconductors and the Semiconductor/Electrolyte Interface                             | 80        |
| 4.2.3    | Semiconductor/Electrolyte Interface Under Illumination   | 84        |
| 4.2.4    | Devices and Efficiencies   | 86        |
| 4.2.4.1  | Device Configurations  | 86        |
| 4.2.4.2  | Device Figures of Merit and System Efficiencies  | 87        |
| 4.2.4.3  | Theoretical Limitations of PEC Solar Fuel Production   | 90        |
| 4.2.4.4  | Theoretical Limitations of PEC Solar Fuel Production – Beyond Water Splitting                    | 93        |
| 4.2.5    | Surface Modification   | 94        |
| 4.2.5.1  | Integration of Electrocatalysts  | 95        |
| 4.2.5.2  | Stability of PEC Device – Protection Layers/Surface Coatings                                     | 96        |
| 4.2.6    | Short Summary  | 97        |
|          | References   | 98        |

|          |   |            |
|----------|---|------------|
| <b>5</b> | <b>Photocatalysis – The Heterogeneous Catalysis Perspective</b>             | <b>101</b> |
|          | <i>Pawel Naliwajko and Jennifer Strunk</i>                                  |            |
| 5.1      | Introduction  | 101        |
| 5.1.1    | General Function of Classical Heterogeneous Catalysts                       | 102        |
| 5.1.2    | Comparison of Classical Catalysis and Photocatalysis                        | 103        |
| 5.2      | Examples of Relevant Catalytic Properties of Photocatalysts                 | 109        |
| 5.2.1    | Consideration of Active Sites   | 109        |
| 5.2.2    | Nanosized Gold in Alcohol Oxidation   | 109        |
| 5.2.3    | Vanadium Oxide (Sub)monolayer Catalysts in Photocatalytic Alcohol Oxidation | 113        |
| 5.3      | Conclusions   | 117        |
|          | References  | 118        |
| <b>6</b> | <b>Insights into Photocatalysis from Computational Chemistry</b>            | <b>127</b> |
|          | <i>Stephen Rhatigan and Michael Nolan</i>                                   |            |
| 6.1      | Introduction  | 127        |
| 6.2      | Computational Descriptors   | 128        |
| 6.2.1    | Light Absorption  | 128        |
| 6.2.2    | Charge Carrier Separation   | 130        |
| 6.2.3    | Surface Reactivity  | 134        |
| 6.3      | Examples of Computational Studies of Photocatalyst Materials                | 138        |
| 6.3.1    | Metal Oxides  | 138        |
| 6.3.2    | Noble Metal Loading   | 139        |
| 6.3.3    | Metal Chalcogenides and Metal Phosphides                                    | 142        |
| 6.3.4    | Hetero- and Nanostructuring   | 144        |
| 6.3.5    | Charge Localization Models  | 146        |
| 6.4      | Conclusion  | 147        |
|          | References  | 149        |
| <b>7</b> | <b>Selected Aspects of Photoreactor Engineering</b>                         | <b>155</b> |
|          | <i>Dirk Ziegenbalg</i>  |            |
| 7.1      | Fundamentals of Photochemical Reaction Engineering                          | 155        |
| 7.2      | Radiation Field and Rate of Reaction  | 160        |
| 7.3      | Light Sources   | 166        |
| 7.4      | Particularities of Different Types of Photocatalysts                        | 173        |
| 7.5      | Types of Photoreactors  | 176        |
| 7.6      | Conclusions and Outlook   | 181        |
|          | Symbols and Abbreviations   | 182        |
|          | References  | 184        |
| <b>8</b> | <b>Defects in Photocatalysis</b>  | <b>187</b> |
|          | <i>Greta Haselmann and Dominik Eder</i>                                     |            |
| 8.1      | Introduction  | 187        |
| 8.1.1    | Definition and Thermodynamics   | 187        |

|         |  |     |
|---------|--|-----|
| 8.1.2   | Classification   | 188 |
| 8.1.2.1 | Dimensionality   | 188 |
| 8.1.2.2 | Location: Surface, Subsurface, and Bulk                  | 189 |
| 8.1.3   | Concepts in Defect Chemistry                             | 190 |
| 8.1.3.1 | Charge Neutrality  | 190 |
| 8.1.3.2 | Intrinsic and Extrinsic Defect Pairs                     | 190 |
| 8.1.3.3 | Nonstoichiometry vs. Substoichiometry                    | 190 |
| 8.1.3.4 | Kröger–Vink Notation and Defect Diagrams                 | 191 |
| 8.1.3.5 | Diffusion and Segregation                                | 192 |
| 8.1.4   | How Are Defects Created?                                 | 192 |
| 8.1.4.1 | Intrinsic Defects  | 192 |
| 8.1.4.2 | Extrinsic Defects  | 193 |
| 8.1.5   | Characterization of Defects                              | 194 |
| 8.1.5.1 | Quantification   | 196 |
| 8.1.5.2 | In Situ  | 196 |
| 8.1.6   | Effect of Defects on Material Properties                 | 197 |
| 8.1.6.1 | Structural Changes/Physical Structure                    | 197 |
| 8.1.6.2 | Electronic Changes/Electronic Structure                  | 197 |
| 8.2     | Influence of Defects on the Photocatalytic Performance   | 199 |
| 8.2.1   | Location of the Defect                                   | 200 |
| 8.2.1.1 | Bulk: Charge Carrier Generation and Migration            | 200 |
| 8.2.1.2 | Surface: Adsorption Sites and Charge Transfer            | 202 |
| 8.2.1.3 | Optimized Treatment Conditions and Surface-to-bulk Ratio | 204 |
| 8.2.1.4 | Subsurface Defects in Photocatalysis                     | 206 |
| 8.2.2   | Deep vs. Shallow Trap States                             | 206 |
| 8.2.3   | Strain-Induced Photocatalysis                            | 207 |
| 8.2.4   | Dynamic Defects  | 208 |
| 8.2.5   | Defects of Higher Dimensionalities in Photocatalysis     | 208 |
| 8.2.5.1 | Black TiO <sub>2</sub>                                   | 210 |
| 8.3     | Concluding Remarks                                       | 213 |
|         | References   | 213 |

## 9 Photocarrier Loss Pathways in Metal Oxide Absorber Materials for Photocatalysis Explored with Time-Resolved Spectroscopy: The Case of BiVO<sub>4</sub> 221

*Rainer Eichberger and Sönke Müller*

|     |   |     |
|-----|---|-----|
| 9.1 | Introduction  | 221 |
| 9.2 | Photodynamics of BiVO <sub>4</sub> – Carrier Trapping and Polaron Formation | 224 |
| 9.3 | Conclusions   | 238 |
|     | References  | 238 |

## 10 Metal-free Photocatalysts 245

*Josefine P. Hundt, Marco Weers, Vanessa Lühns, Dereje H. Taffa, and Michael Wark*

|      |                           |     |
|------|---------------------------|-----|
| 10.1 | Introduction              | 245 |
| 10.2 | Graphitic Carbon Nitrides | 246 |

|           |   |            |
|-----------|---|------------|
| 10.2.1    | Structure and Properties of g-C <sub>3</sub> N <sub>4</sub>   | 246        |
| 10.2.2    | Application as Photocatalytic Active Material   | 249        |
| 10.2.2.1  | Photocatalytic Hydrogen Production  | 249        |
| 10.2.2.2  | Photocatalysis-Assisted Organic Synthesis   | 250        |
| 10.2.2.3  | Photocatalytic Reduction of CO <sub>2</sub>   | 252        |
| 10.2.2.4  | Photocatalytic Degradation of (Organic) Pollutants  | 254        |
| 10.3      | Covalent Organic Frameworks   | 254        |
| 10.4      | Conjugated Polymers   | 257        |
| 10.4.1    | Synthesis Strategies of Nanostructured Conducting Polymers  | 258        |
| 10.4.2    | Application as a Photocatalytic Active Material   | 260        |
| 10.4.2.1  | Hydrogen Evolution  | 261        |
| 10.4.2.2  | Pollutant Degradation   | 261        |
| 10.5      | Conclusions   | 263        |
|           | Acknowledgments   | 264        |
|           | References  | 264        |
| <b>11</b> | <b>Photocatalytic Water Splitting: Fundamentals and Current Concepts</b>                              | <b>269</b> |
|           | <i>Kazuhiro Takanabe</i>  |            |
| 11.1      | Solar Energy Conversion   | 269        |
| 11.2      | Photocatalyst: Fundamental Concept  | 270        |
| 11.3      | Reporting Protocol  | 272        |
| 11.4      | Photon Absorption   | 276        |
| 11.5      | Exciton Separation  | 276        |
| 11.6      | Carrier Transport   | 277        |
| 11.7      | Electrocatalysis  | 279        |
| 11.8      | Mass Transfer: Electrolyte  | 280        |
| 11.9      | Suppression of Back Reaction  | 280        |
| 11.10     | Photocatalytic Overall Water Splitting: State of the Art  | 281        |
| 11.11     | Concluding Remarks  | 283        |
|           | References  | 284        |
| <b>12</b> | <b>Photocatalytic CO<sub>2</sub> Reduction and Beyond</b>   | <b>287</b> |
|           | <i>Minoo Tasbihi, Michael Schwarze, and Reinhard Schomäcker</i>                                       |            |
| 12.1      | Introduction  | 287        |
| 12.2      | Photocatalytic Reactions Utilizing CO <sub>2</sub>  | 290        |
| 12.2.1    | Photocatalytic Reduction of CO <sub>2</sub> by CH <sub>4</sub> (Dry Reforming)                        | 292        |
| 12.2.2    | Photocatalytic Reduction of CO <sub>2</sub> by CH <sub>4</sub> and H <sub>2</sub> O (Steam Reforming) | 296        |
| 12.2.3    | Other Photocatalytic Reactions with CO <sub>2</sub>   | 298        |
| 12.3      | Summary   | 298        |
|           | References  | 299        |
| <b>13</b> | <b>Photocatalytic NO<sub>x</sub> Abatement</b>  | <b>303</b> |
|           | <i>Jonathan Z. Bloh</i>   |            |
| 13.1      | Introduction  | 303        |
| 13.2      | Basic Principle   | 304        |

|           |   |            |
|-----------|---|------------|
| 13.3      | Reaction Pathway  | 305        |
| 13.3.1    | Intermediates, Selectivity  | 307        |
| 13.4      | Reaction Kinetics   | 308        |
| 13.4.1    | Guidelines for Accurate Performance Determination   | 310        |
| 13.5      | Strategies to Improve the Performance   | 312        |
| 13.5.1    | Strategies to Improve the Photocatalytic Activity   | 312        |
| 13.5.2    | Strategies to Improve the Spectral Response   | 314        |
| 13.5.3    | Strategies to Improve the Selectivity   | 317        |
| 13.5.4    | Summary of Material Developments  | 319        |
| 13.6      | Strategies to Incorporate the Catalysts into Building Materials                                     | 319        |
| 13.7      | Results from Field Tests and Simulations  | 321        |
|           | References  | 323        |
| <b>14</b> | <b>Photoactive Nanomaterials: Applications in Wastewater Treatment and Their Environmental Fate</b> | <b>331</b> |
|           | <i>Jang S. Chang and Meng N. Chong</i>  |            |
| 14.1      | Introduction  | 331        |
| 14.2      | Photoactive Semiconductor Nanomaterials and Their Applications in Wastewater Treatment              | 332        |
| 14.2.1    | Nano-TiO <sub>2</sub>   | 332        |
| 14.2.2    | Nano-ZnO  | 334        |
| 14.2.3    | Nano-Fe <sub>2</sub> O <sub>3</sub>   | 336        |
| 14.2.4    | Nano-WO <sub>3</sub>  | 337        |
| 14.3      | Environmental Fate and Behavior of Photoactive Nanomaterials in Wastewater Treatment Processes      | 338        |
| 14.3.1    | Prevalence, Occurrence, and Routes of Nanomaterials into the Environment                            | 338        |
| 14.3.2    | Fate and Transformation Processes of Nanomaterials  | 339        |
| 14.3.2.1  | Aggregation and Agglomeration   | 339        |
| 14.3.2.2  | Photochemical Transformation  | 342        |
| 14.3.2.3  | Redox Reactions   | 342        |
| 14.3.2.4  | Adsorption of Macromolecules  | 343        |
| 14.3.2.5  | Biotransformation   | 344        |
| 14.4      | Environmental Effects of Nanomaterials Toward Wastewater Treatment Processes                        | 344        |
| 14.5      | Conclusion  | 345        |
|           | References  | 346        |
|           | <b>Index</b>  | <b>351</b> |