Artificial Photosynthesis

From Basic Biology to Industrial Application

Edited by
Anthony F. Collings and Christa Critchley
Contents

Foreword V
Preface IX
List of Contributors XXIII

Part I The Context 1

1 Artificial Photosynthesis: Social and Political Issues 3
Ian Lowe
1.1 Introduction 3
1.2 The Need for a Transition to Artificial Photosynthesis 4
1.3 Some Associated Social and Political Issues 6
1.4 Using the Available Photons: Towards Sustainability Science 9
1.5 Conclusions 11
References 11

2 An Integrated Artificial Photosynthesis Model 13
Ron J. Pace
2.1 Introduction 13
2.2 Natural Photosynthesis 13
2.3 Artificial Photosynthesis: An Integrated Strategy 17
2.4 A Technological Approach to Photosynthesis 19
2.5 Program 1: Biomimetic Photoelectric Generation 20
2.5.1 Milestones 24
2.6 Program 2: Electrolytic Hydrogen 24
2.6.1 Milestones 28
2.7 Programs 3 and 4: Waterless Agriculture 28
2.7.1 Program 3: Bioenergetic Converters 29
2.7.1.1 Milestones 30
2.7.2 Program 4: The CO₂-fixing Enzyme Reactor 31
2.7.2.1 Milestones 32
2.8 Conclusions 33
References 33

Artificial Photosynthesis: From Basic Biology to Industrial Application
Edited by Anthony F. Collings and Christa Critchley
Copyright © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 3-527-31090-8
<table>
<thead>
<tr>
<th>Part II</th>
<th>Capturing Sunlight</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Broadband Photon-harvesting Biomolecules for Photovoltaics</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Paul Meredith, Ben J. Powell, Jenny Riesz, Robert Vogel, David Blake, Indriani Kartini, Geff Will, and Surya Subianto</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>37</td>
</tr>
<tr>
<td>3.2</td>
<td>The Photoelectrochemical Grätzel Cell (Dye-sensitized Solar Cell)</td>
<td>39</td>
</tr>
<tr>
<td>3.3</td>
<td>Typical Components and Performance of a DSSC</td>
<td>41</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Construction and Mode of Operation</td>
<td>41</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Typical DSSC Performance</td>
<td>45</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Device Limitations</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Melanins as Broadband Sensitizers for DSSCs</td>
<td>48</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Melanin Basics</td>
<td>48</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Melanin Chemical, Structural, and Spectroscopic Properties</td>
<td>50</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Melanin Electrical and Photoconductive Properties</td>
<td>58</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Melanins as Broadband Photon-harvesting Systems</td>
<td>61</td>
</tr>
<tr>
<td>3.4.5</td>
<td>A DSSC Based Upon Synthetic Eumelanin</td>
<td>62</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusions</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>64</td>
</tr>
</tbody>
</table>

4 The Design of Natural Photosynthetic Antenna Systems | 67 |
| Nancy E. Holt, Harsha M. Vaswani, and Graham R. Fleming |
| 4.1     | Introduction | 67 |
| 4.2     | Confined Geometries: From Weak to Strong Coupling and Everything in Between | 68 |
| 4.2.1   | Conventional Förster Theory: B800 to B800 Intra-band Energy Transfer | 69 |
| 4.2.2   | Generalized Förster Theory: B800 to B850 Inter-band Energy Transfer | 69 |
| 4.2.3   | Generalized Förster Theory with the Transition Density Cube Method: Car to Bchl Inter-pigment Energy Transfer | 70 |
| 4.2.4   | Modified Redfield Theory: Intra-band B850 Exciton Dynamics | 72 |
| 4.3     | Energetic Disorder Within Light-harvesting Complexes | 73 |
| 4.3.1   | From Isolated Complexes to Membranes: Disorder in LH2 | 73 |
| 4.3.2   | Photosystem I | 75 |
| 4.4     | Photochemistry and Photoprotection in the Bacterial Reaction Center | 78 |
| 4.5     | The Regulation of Photosynthetic Light Harvesting | 79 |
| 4.6     | Concluding Remarks | 83 |
|         | References | 83 |
5 Identifying Redox-active Chromophores in Photosystem II by Low-temperature Optical Spectroscopies 87
Elmars Krausz and Sindra Peterson Årsköld

5.1 Introduction 87
5.2 Experimental Methods 89
5.2.1 Sample Preparation 89
5.2.2 Illumination 90
5.2.3 Spectra 90
5.3 Results and Discussion 91
5.3.1 Absorption and CD Signatures: Plant PSII Cores and BBYs 91
5.3.2 Absorption and CD Signatures: Plant and Cyanobacterial PSII Cores 94
5.3.3 Absorption Signatures: The Native and Solubilized Reaction Center 94
5.3.4 MCD Signatures: P680 and Chl$_Z$ 96
5.3.5 Electrochromic Signature: Pheo$_{D1}$ in Active PSII 99
5.4 Conclusions 103
5.4.1 Low-temperature Precision Polarization Spectroscopies 103
5.4.2 Signatures of P680 and Chl$_Z$ 103
5.4.3 Electrochromism Signature of Pheo$_{D1}$ 104
5.4.4 Coupling and Robustness in P680 and Biomimetic Systems 104

References 105

6 The Nature of the Special-pair Radical Cation Produced by Primary Charge Separation During Photosynthesis 109
Jeffrey R. Reimers and Noel S. Hush

6.1 Introduction 109
6.2 The Special Pair 109
6.3 The Hole-transfer Band 113
6.4 Initial Investigations of the Hole-transfer Band 116
6.5 Identification of the SHOMO to HOMO Band 118
6.6 Full Spectral Simulations Involving all Bands 119
6.7 Predicting Chemical Properties Based on the Spectral Analysis 121
6.8 Conclusions 125
References 125

7 Protein-based Artificial Photosynthetic Reaction Centers 127
Reza Razeghifard and Thomas J. Wydrzynski

7.1 Introduction 127
7.2 Natural Reaction Centers 127
7.2.1 Structure and Function 127
7.2.2 Creation of a Charge-separated State 129
7.2.3 Mutational Studies 129
8 Novel Geometry Polynorbornane Scaffolds for Chromophore Linkage and Spacing 147
Ronald N. Warrener, Davor Margetic, David A. Mann, Zhi-Long Chen, and Douglas N. Butler

8.1 Introduction 147
8.2 Results and Discussion 151
8.2.1 Reaction at Carbonyl Groups to Form Unsymmetrical Type III Dyads 151
8.2.2 Extended-frame Dyads 154
8.3 Preliminary Results 155
8.3.1 The Use of Multicarbonyl Reagents for Dyad Formation 155
8.4 Conclusions 157
8.5 Dyad Nomenclature 158
References 165

Part III Feeding the Grid from the Sun 167

9 Very High-efficiency in Silico Photovoltaics 169
Martin A. Green

9.1 Introduction 169
9.2 Silicon Wafer Approach 171
9.3 Thin-film Approaches 173
9.4 Third-generation Technologies 178
9.5 Conclusions 183
References 184

10 Mimicking Bacterial Photosynthesis 187
Devens Gust, Thomas A. Moore, and Ana L. Moore

10.1 Introduction 187
10.2 Natural Photosynthesis 188
10.3 Artificial Photosynthesis 190
10.3.1 Artificial Antenna Systems 190
10.3.2 Artificial Reaction Centers 194
10.3.3 Antenna–Reaction Center Complexes 199
10.3.4 Transmembrane Proton Pumping 201
10.3.5 Synthesis of ATP 204
10.3.6 Transmembrane Calcium Transport 206
10.4 Conclusions 208
References 209

Part IV Photohydrogen 211

11 Development of Algal Systems for Hydrogen Photoproduction:
Addressing the Hydrogenase Oxygen-sensitivity Problem 213
Maria L. Ghirardi, Paul King, Sergey Kosourov, Marc Forestier,
Liping Zhang, and Michael Seibert

11.1 Introduction 213
11.2 Sulfur Deprivation and Hydrogen Photoproduction 214
11.2.1 Background 214
11.2.2 Model of the Interactions Between Different Metabolic Pathways in Sulfur-deprived Cells 215
11.2.3 Confirmation of the Model 217
11.2.4 Limiting Factors for H$_2$ Photoproduction under Sulfur Deprivation 218
11.2.5 Mechanism of Regulation 220
11.3 Molecular Engineering of the Algal Hydrogenase 221
11.3.1 Algal Hydrogenases and H$_2$ Production 221
11.3.2 Cloning and Sequencing of the Two C. reinhardtii [FeFe]-Hydrogenases 221
11.3.3 Anaerobic Expression of the two C. reinhardtii Hydrogenases 223
11.3.4 Oxygen Inhibition of Hydrogenase Activity and Molecular Engineering for Increased O$_2$ Tolerance 224
References 226

12 Bioengineering of Green Algae to Enhance Photosynthesis and Hydrogen Production 229
Anastasios Melis

12.1 Introduction 229
12.2 Rationale and Approach 230
12.3 Physiological State of the Chl Antenna Size in Green Algae 231
12.4 The Genetic Control Mechanism of the Chl Antenna Size in Green Algae 232
12.5 Effect of Pigment Mutations on the Chl Antenna Size of Photosynthesis 233
12.6 Genes for the Regulation of the Chl Antenna Size of Photosynthesis 235
12.7 Conclusions 237
Acknowledgements 237
References 237
Part V  The Carbon Connection  241

13  Manipulating Ribulose Bisphosphate Carboxylase/Oxygenase in the Chloroplasts of Higher Plants  243
    T. John Andrews and Spencer M. Whitney

13.1  Introduction  243
13.2  Why Manipulate Rubisco in Plants?  243
13.2.1  Genetic Manipulation of Higher-plant Rubisco Is Now Feasible  243
13.2.2  The Advantages of “Ecological” Studies of Rubisco “at Home” in Its Physiological Context  244
13.2.3  A Compelling Example of Genome–Phenome Interactions  244
13.2.4  An Improvement in the Resource-use Efficiency of Photosynthesis?  245
13.3  What Constitutes an Efficient Rubisco?  245
13.3.1  Key Kinetic Parameters  245
13.3.2  Physiological Consequences of Rubisco Efficiency  246
13.3.3  Regulatory Properties  247
13.3.4  Evolution of Rubisco Efficiency  248
13.4  How to Find a Better Rubisco?  248
13.4.1  In Nature?  248
13.4.2  By Rational Design?  248
13.4.3  By in Vitro Evolution?  249
13.5  How to Manipulate Rubisco in Plants?  250
13.5.1  Nuclear Transformation  250
13.5.2  Plastid Transformation  252
13.6  What Have We Learned So Far?  252
13.6.1  Both Nuclear and Plastidic Genomes Are Able to Express Both \textit{rbcL} and \textit{RbcS} Genes  252
13.6.2  Photosynthesis and Growth Can Be Supported by a Foreign Rubisco  254
13.6.3  The Properties of a Mutated or Foreign Rubisco Are Reflected in the Leaf’s Gas-exchange Properties  254
13.6.4  The Requirements for Folding and Assembly of the Subunits of Red-type, Form-I Rubisco Are Not Accommodated in Chloroplasts  255
13.6.5  A Better Strategy for Directed Mutagenesis of \textit{rbcL}  256
13.6.6  Subunit Hybrids Can Be Formed \textit{in vivo}  256
13.7  Priorities for Future Manipulation of Rubisco \textit{in vivo}  257
13.7.1  The Structural Foundations of Efficient Properties  257
13.7.2  Regulation of Rubisco Gene Expression  258
13.7.3  Folding and Assembly of Rubisco Subunits  258
13.8  Conclusions  259

References  260
14 Defining the Inefficiencies in the Chemical Mechanism of the Photosynthetic Enzyme Rubisco by Computational Simulation 263

Jill E. Gready

14.1 Introduction 263
14.1.1 Catalytic Inefficiencies 263
14.1.2 Evolutionary Constraints? 264
14.1.3 Experimental Limitations 265
14.1.4 Goals of Simulations 265
14.1.5 Simulation Options 266
14.2 Computational Methods 267
14.2.1 Computational Programs 267
14.2.2 Enzyme Models 268
14.2.3 Active-site Fragment Complexes 268
14.2.4 QM/MM Simulations 269
14.3 Results and Discussion 271
14.3.1 Fragment-complex Calculations 271
14.3.1.1 Enolization Step 271
14.3.1.2 Carboxylation Step 273
14.3.1.3 Hydration Step 275
14.3.1.4 Sequential Addition of CO₂ and H₂O 275
14.3.1.5 Alternative Conformations of the Gem-diol 275
14.3.1.6 C2-C3 Bond Cleavage: Pathway I 276
14.3.1.7 C2-C3 Bond Cleavage: Pathway II 276
14.3.1.8 Protonation of C2 276
14.3.1.9 Dissociation of Products 277
14.3.2 Summary of Main Findings 277
14.3.3 QM/MM+MD Calculations 277
14.3.3.1 CO₂ Addition: Early vs. Late Protonation of the Carboxylate 278
14.3.3.2 Hydration of the β-Keto Acid 280
14.3.3.3 His294 Protects Intermediates from Decarboxylation 280
14.3.3.4 The Tightly Coupled Active-site Environment 280
14.4 Conclusions 281

References 281

15 Carbon-based End Products of Artificial Photosynthesis 283

Thomas D. Sharkey

15.1 Introduction 283
15.2 What Are the End Products of Plant Chloroplast Photosynthesis? 284
15.3 Does End-product Synthesis Ever Limit Photosynthesis? 285
15.4 What Would Be a Desirable Carbon-based End Product of Photosynthesis? 286

References 289
The Artificial Photosynthesis System: An Engineering Approach
Dilip K. Desai

16.1 Introduction 291
16.2 Engineering Approach to APS 291
16.3 Elements of the Engineering Approach 292
16.3.1 Economic Value 292
16.3.2 Limitations of Natural Photosynthesis Systems (NPS) 292
16.3.2.1 Speed of NPS 292
16.3.2.2 Energy Efficiency of NPS 292
16.3.2.3 Water Requirements of NPS 293
16.3.2.4 Land Use for NPS 293
16.3.3 Scale of Operation 293
16.3.4 Functional Specification 294
16.4 Elements of Envisaged System 294
16.5 Cyanobacteria 295
16.6 Photo-bioreactor 296
16.7 Theory 296
16.8 Results 298
16.9 Conclusions 299
References 299

Greenhouse Gas Technologies: A Pathway to Decreasing Carbon Intensity
Peter J. Cook

17.1 Introduction 301
17.2 CO₂ Capture 301
17.3 Storing CO₂ 303
17.4 Australian Initiatives: Capture and Storage Technologies 306
17.5 Conclusions 307
References 308

Subject Index 309