

Contents

Preface IX

1	Electron Transfer Theories	1
1.1	Introduction	1
1.2	Theoretical Models	1
1.2.1	Basic Two States Models	1
1.2.1.1	Landau–Zener Model	1
1.2.1.2	Marcus Model	3
1.2.1.3	Electronic and Nuclear Quantum Mechanical Effects	5
1.2.2	Further Developments in the Marcus Model	7
1.2.2.1	Electron Coupling	7
1.2.2.2	Driving Force and Reorganization Energy	9
1.2.3	Zusman Model and its Development	17
1.2.4	Effect of Nonequilibrium on Driving Force and Reorganization	21
1.2.5	Long-Range Electron Transfer	24
1.2.6	Spin Effects on Charge Separation	28
1.2.7	Electron–Proton Transfer Coupling	29
1.2.8	Specificity of Electrochemical Electron Transfer	33
1.3	Concerted and Multielectron Processes	38
	References	40
2	Principal Stages of Photosynthetic Light Energy Conversion	45
2.1	Introduction	45
2.2	Light-Harvesting Antennas	46
2.2.1	General	46
2.2.2	Bacterial Antenna Complex Proteins	47
2.2.2.1	The Structure of the Light-Harvesting Complex	47
2.2.2.2	Dynamic Processes in LHC	48
2.2.3	Photosystems I and II Harvesting Antennas	49
2.3	Reaction Center of Photosynthetic Bacteria	53
2.3.1	Introduction	53
2.3.2	Structure of RCPB	56
2.3.3	Kinetics and Mechanism of Electron Transfer in RCPB	58

2.3.4	Electron Transfer and Molecular Dynamics in RCPB	64
2.4	Reaction Centers of Photosystems I and II	68
2.4.1	Reaction Centers of PS I	69
2.4.2	Reaction Center of Photosystem II	72
2.5	Water Oxidation System	76
	References	84
3	Photochemical Systems of the Light Energy Conversion	91
3.1	Introduction	91
3.2	Charge Separation in Donor–Acceptor Pairs	92
3.2.1	Introduction	92
3.2.2	Cyclic Tetrapyrroles	93
3.2.3	Miscellaneous Donor–Acceptor Systems	101
3.2.4	Photophysical and Photochemical Processes in Dual Fluorophore–Nitroxide Molecules (FNO)	106
3.2.4.1	System 1	107
3.2.4.2	Systems 2	109
3.3	Electron Flow through Proteins	113
3.3.1	Factors Affecting Light Energy Conversion in Dual Fluorophore–Nitroxide Molecules in a Protein	116
3.3.2	Photoinduced Interlayer Electron Transfer in Lipid Films	118
	References	121
4	Redox Processes on Surface of Semiconductors and Metals	127
4.1	Redox Processes on Semiconductors	127
4.1.1	Introduction	127
4.1.2	Interfacial Electron Transfer Dynamics in Sensitized TiO ₂	127
4.1.3	Electron Transfer in Miscellaneous Semiconductors	130
4.1.3.1	Single-Molecule Interfacial Electron Transfer in Donor–Bridge–Nanoparticle Acceptor Complexes	130
4.1.4	Redox Processes on Carbon Materials	133
4.2	Redox Processes on Metal Surfaces	136
4.3	Electron Transfer in Miscellaneous Systems	144
	References	147
5	Dye-Sensitized Solar Cells I	151
5.1	General Information on Solar Cells	151
5.2	Dye-Sensitized Solar Cells	153
5.2.1	General	153
5.2.2	Primary Grätzel DSSC	155
5.3	DSSC Components	158
5.3.1	Sensitizers	158
5.3.1.1	Ruthenium Complexes	158
5.3.1.2	Metalloporphyrins	159
5.3.1.3	Organic Dyes	161

5.3.1.4	Semiconductor Sensitizes	167
5.3.2	Photoanode	168
5.3.3	Injection and Recombination	171
5.3.4	Charge Carrier Systems	175
5.3.5	Cathode	182
5.3.6	Solid-State DSSC	185
	References	189
6	Dye-Sensitized Solar Cells II	199
6.1	Optical Fiber DSSC	199
6.2	Tandem DSSC	202
6.3	Quantum Dot Solar Cells	208
6.4	Polymers in Solar Cells	211
6.5	Fabrication of Solar Cell Components	219
6.6	Fullerene-Based Solar Cells	223
	References	229
7	Photocatalytic Reduction and Oxidation of Water	235
7.1	Introduction	235
7.2	Photocatalytic Dihydrogen Production	236
7.2.1	Photocatalytic H ₂ Evolution over TiO ₂	236
7.2.2	Miscellaneous Semiconductor Photocatalysts for H ₂ Evolution	237
7.2.3	Photocatalytic H ₂ Evolution from Water Based on Platinum and Palladium Complexes	240
7.3	Water Splitting into O ₂ and H ₂	241
7.3.1	Thermodynamics and Feasible Mechanism of the Water Splitting	241
7.3.2	Mn Clusters as Water Oxidizing Photocatalysts	242
7.3.2.1	Structure and Catalytic Activity of Cubane Manganese Clusters	242
7.3.2.2	Catalytic Activity and Mechanism of WOS in Manganese Clusters	244
7.3.3	Heterogeneous Catalysts for WOS	248
7.3.3.1	General	248
7.3.3.2	Photocatalysts Based on Titanium Oxides	250
7.3.3.3	Miscellaneous Semiconductors for the WOS Catalysis	251
	References	256
	Conclusions	261
	References	263
	Index	265

