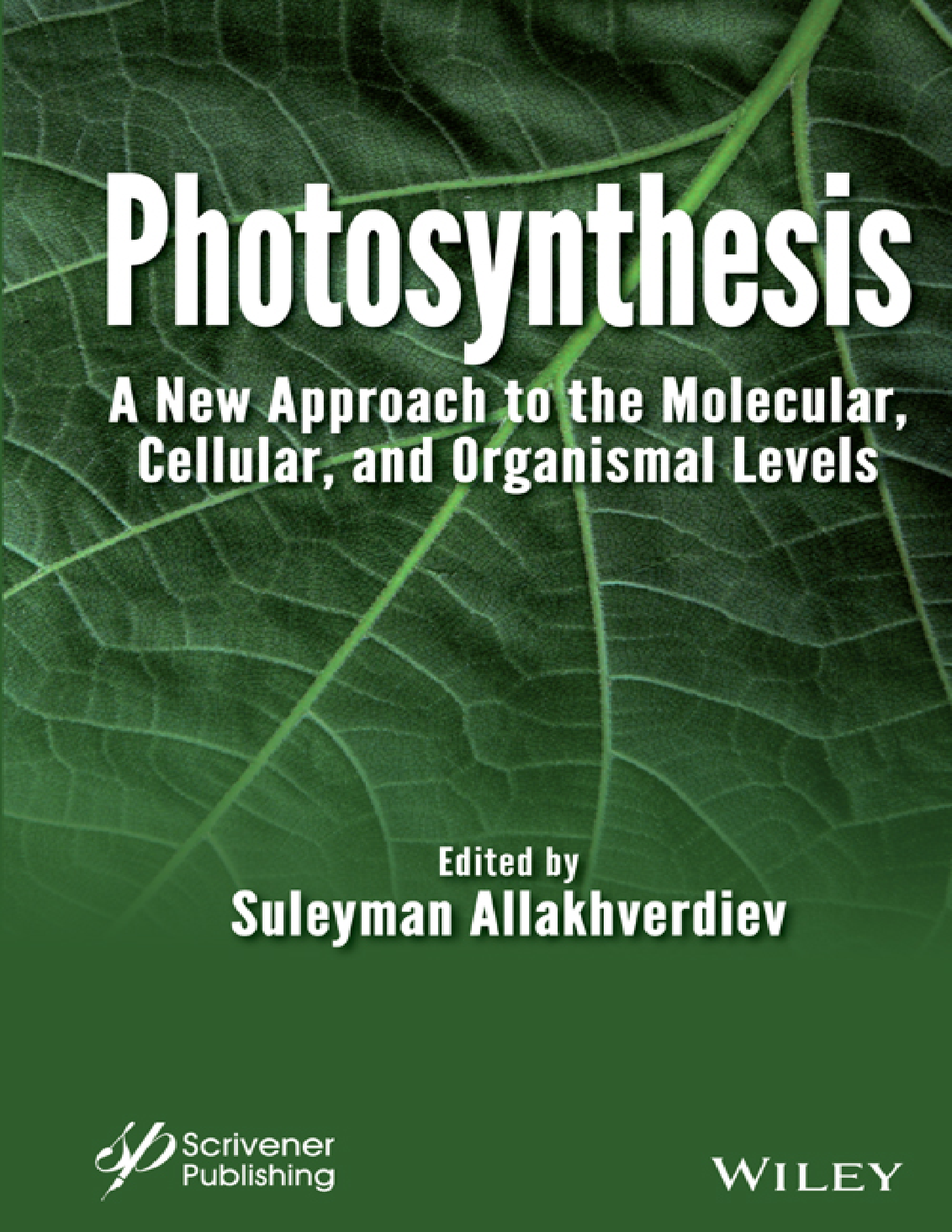
Photosynthesis
A New Approach to the Molecular, Cellular, and Organismal Levels
Edited by
Suleyman Allakhverdiev
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Abstract

This book is written by Russian and international authors in the field of photosynthesis research. It is dedicated to investigations of the problems of photosynthesis at different levels of organization: molecular, cellular and organismal. The book describes the multiple roles of various reactive oxygen species in photosynthetic organisms. Further, we have presented here a discussion of the structure and function of water oxidation complex (WOC) of PS II, and a possible role of Mn-bicarbonate complex in WOC. Other important topics in this book are: the structural and functional organization of the pigment-protein complexes, the structure and regulation of chloroplast ATP-synthase, the participation of molecular hydrogen in microalgae metabolism, the current concepts on the evolution and the development of photosynthetic carbon metabolism, and the adaptive changes of photosynthesis at increased CO_2 concentrations, as well as the photosynthetic machinery response to low temperature stress. The material available in this book is a unique report on the state of this trend in modern science. This book will be helpful not only for biophysicists, biochemists and experts in plant physiology, but also for a wider group of biologists; in addition, it is expected to be used in ongoing and future research work in the field. Lastly, and most importantly, it will serve to educate undergraduate, graduate and post-graduate students around the world.

Preface

Existence of life on the Earth is supported by photosynthetic organisms which provide production of organic substances and oxygen evolution. In general, photosynthesis includes primary light reactions and secondary dark reactions. Light reactions begin with absorption of photons by light harvesting photosynthetic pigments, resulting in the formation of their singlet exited states. This process is followed by excitation energy transfer from one pigment molecule to the other. Then, charge separation occurs in the photosynthetic reaction centers. Excited electrons are transferred via the photosynthetic electron transport chain (ETC), providing production of the reducing power in the form of reduced nicotinamide adenine dinucleotide phosphate (NADPH). In anoxygenic phototrophs, external hydrogen compounds are a source of the electrons, and the light is absorbed in a single photosystem. The ETC of oxygenic photosynthetics contains two photochemical systems – PS II (water-plastoquinone oxido-reductase) and PS I (plastocyanin-ferredoxin oxido-reductase) – which transfer electrons from water to NADP, using one more complex, the cytochrome-*b*6*f*-complex. The source of electrons in this case is water molecules which are decomposed by water-oxidizing complex (WOC) of the PS II. Oxygen as a “waste” product of photosynthetic water cleavage led to the present-day aerobic atmosphere. From the very first moment the interaction with oxygen generated a new condition for the existing organisms starting an evolutionary adaptation process to this new oxydizing environment. Reactive oxygen species (ROS) became a powerful selector and generated a new hierarchy of life forms from the broad range of genetic mutations represented in the biosphere. During the electron transfer

from water to NADP, protons are transferred from the stroma side (the positive (p) side) to the lumen side (the negative (n) side), and when this proton gradient is dissipated through the ATP-synthase, ATP is produced.

The next stage includes biochemical processes of fixation and reduction of CO_2 in photosynthetic carbon metabolism with using NADPH, and ATP. To date, the known metabolic pathways of carbon in photosynthesis can be classified into the 3-hydroxypropionat bicycle; the reductive citrate cycle, i.e., the Arnon-Buchanan cycle; C_3 or the reductive pentose phosphate cycle, i.e., the Benson-Bassham-Calvin cycle; C_4 or cooperative photosynthesis; Crassulacean acid metabolism (CAM); C_3/C_4 photosynthesis; and C_4-CAM photosynthesis. Some of them, for example the 3-hydroxypropionat bicycle and the Arnon-Buchanan cycle, are specific to anoxygenic phototrophs, others, such as C_4, CAM, and so on, have been in the evolution of higher plants. The most important way of carbon in photosynthesis – the Benson-Bassham-Calvin cycle – is widespread in phototrophic organisms of different taxa. Eventually, fixation and reduction of CO_2 during photosynthesis leads to the formation of sugars and other organic compounds.

The present book has 8 chapters written mainly by the researchers of the Institute of Basic Biological Problems of the Russian Academy of Sciences (formerly the Institute of Photosynthesis). The each chapter describes photosynthesis at different levels of organization: molecular, cellular, and organismic. Among discussed problems in this book are: the structural and functional organization of the pigment-protein complexes; the evolutionary origin of the water-oxidizing complex of PS II; the hydrogen photoproduction coupled with photosynthesis; the structure and regulation of chloroplast ATP synthase; the formation, decay and signaling of reactive oxygen species in oxygen-evolving

photosynthetic organisms during exposure to oxidative stress; the strategy of adaptation of photosynthetic carbon metabolism; the adaptive changes of photosynthesis under enhanced CO_2 concentration, and the photosynthetic machinery response to low temperature stress.

The material presented here reflects, mainly, the research interests and views of the authors. We do not claim to have produced all-inclusive views of the entire field. The book is intended for a broad range of researchers and students, and all who are interested in learning the most important global process on our planet – the process of photosynthesis.

We should like to believe that this book will stimulate future researchers of photosynthesis, leading to progress in our understanding of the mechanisms of photosynthesis and in its practical use in biotechnology and human life.

We express our sincere appreciation to the 17 authors for their outstanding contribution to this book. We are extremely grateful to Academician of the Russian Academy of Sciences (RAS) V.A. Shuvalov, Academician of the Azerbaijan National Academy of Sciences J.A. Aliyev, Corresponding Member of RAS A.B. Rubin, Corresponding Member of RAS Vl.V. Kuznetsov, and Professors D.A. Los, A.M. Nosov, V.Z. Paschenko, T.E. Krendeleva, A.N. Tikhonov, V.V. Klimov, A.A. Tsygankov, Dr. I.R. Fomina, and J. Karakeyan for their permanent help and fruitful advices.

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Chapter 1

The Multiple Roles of Various Reactive Oxygen Species (ROS) in Photosynthetic Organisms[1]

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Abstract

This chapter provides an overview on recent developments and current knowledge about monitoring, generation and the functional role of reactive oxygen species (ROS) – H_2O_2, $HO_2^{\bullet}$, $HO^{\bullet}$, OH^- ^{1},O_2 and $O_2^{-\bullet}$ – in both oxidative degradation and signal transduction in photosynthetic organisms including a summary of important mechanisms of nonphotochemical quenching in plants. We further describe microscopic techniques for ROS detection and controlled generation. Reaction schemes elucidating formation, decay and signaling of ROS in cyanobacteria as well as from chloroplasts to the nuclear genome in eukaryotes during exposure of oxygen-evolving photosynthetic organisms to oxidative stress are discussed that target the rapidly growing field of regulatory effects of ROS on nuclear gene expression.

Keywords: photosynthesis, plant cells, reactive oxygen species, ROS, oxidative stress, signaling systems, chloroplast, cyanobacteria, nonphotochemical quenching, chromophore-activated laser inactivation, sensors

1.1 Introduction

About 3 billion years ago the atmosphere started to transform from a reducing to an oxidizing environment as evolution developed oxygenic photosynthesis as key

mechanism to efficiently generate free energy from solar radiation (Buick, 1992; Des Marais, 2000; Xiong and Bauer, 2002; Renger, 2008; Rutherford *et al.*, 2012; Schmitt *et al.*, 2014a). Entropy generation due to the absorption of solar radiation on the surface of the Earth was retarded by the generation of photosynthesis, and eventually a huge amount of photosynthetic and other organisms with rising complexity developed at the interface of the transformation of low entropic solar radiation to heat. The subsequent release of oxygen as a “waste” product of photosynthetic water cleavage led to the present-day aerobic atmosphere (Kasting and Siefert, 2002; Lane, 2002; Bekker *et al.*, 2004), thus opening the road for a much more efficient exploitation of the Gibbs free energy through the aerobic respiration of heterotrophic organisms (for thermodynamic considerations, see (Nicholls and Ferguson, 2013; Renger, 1983).

From the very first moment this interaction with oxygen generated a new condition for the existing organisms starting an evolutionary adaptation process to this new oxydizing environment. Reactive oxygen species (ROS) became a powerful selector and generated a new hierarchy of life forms from the broad range of genetic mutations represented in the biosphere. We assume that this process accelerated the development of higher, mainly heterotrophic organisms in the sea and especially on the land mass remarkably.

The efficient generation of biomass and the highly selective impact of ROS lead to a broad range of options for complex organisms to be developed in the oxydizing environment. The direct, mostly deleterious impact of ROS on the biosphere is thereby just a minor facet in the broad spectrum of consequences. Important and more complex side effects are for example given by the fact that the molecular oxygen led to generation of the stratospheric ozone layer, which is the indispensable protective shield

against deleterious UV-B radiation (Worrest and Caldwell, 1986). ROS led to new complex constraints for evolution that drove the biosphere into new directions – by direct oxidative pressure and by long-range effects due to environmental changes caused by the atmosphere and the biosphere themselves as energy source for all heterotrophic organisms.

For organisms that had developed before the transformation of the atmosphere the pathway of redox chemistry between water and O_2 by oxygenic photosynthesis was harmful, due to the deleterious effects of ROS. O_2 destroys the sensitive constituents (proteins, lipids) of living matter. As a consequence, the vast majority of these species was driven into extinction, while only a minority could survive by finding anaerobic ecological niches. All organisms developed suitable defense strategies, in particular the cyanobacteria, which were the first photosynthetic cells evolving oxygen (Zamaraev and Parmon, 1980).

The ground state of the most molecules including biological materials (proteins, lipids, carbohydrates) has a closed electron shell with singlet spin configuration. These spin state properties are of paramount importance, because the transition state of the two electron oxidation of a molecule in the singlet state by $^3\Sigma^-_gO_2$ is “spin-forbidden” and, therefore, the reaction is very slow. This also accounts for the back reaction from the singlet to the triplet state.

In contrast to this majority of singlet ground state molecules the electronic configuration of the O_2 molecule in its ground state is characterized by a triplet spin multiplicity described by the term symbol $^3\Sigma^-_gO_2$. This situation drastically changes by two types of reactions which transform $^3\Sigma^-_gO_2$ into highly reactive oxygen species

(ROS): i) Electronic excitation leads to population of two forms of singlet O_2 characterized by the term symbols $^1\Delta_g$ and $^1\Sigma^+_g$. The $^1\Sigma^+_g$ state with slightly higher energy rapidly relaxes into $^1\Delta_g O_2$ so that only the latter species is of physiological relevance (type I). ii) Chemical reduction of $^3\Sigma^-_g O_2$ (or $^1\Delta_g O_2$) by radicals with non-integer spin state (often doublet state) leads to formation of $O^{-\bullet}_2$, which quickly reacts to $HO_2^\bullet$ and is subsequently transferred to H_2O_2 and $HO^\bullet$ (*vide infra*) (type II). In plants, the electronic excitation of $^3\Sigma^-_g O_2$ occurs due to close contact to chlorophyll triplets that are produced during the photoexcitation cycle (Schmitt *et al.*, 2014a) (see Figure 1.1, Figure 1.2). Singlet oxygen is predominantly formed via the reaction sensitized by interaction between a chlorophyll triplet (^{3}Chl) and ground state triplet $^3\Sigma^-_g O_2$:

Figure 1.1 Production of ROS by interaction of oxygen with chlorophyll triplet states (type I) to $^1O_2$ or chemical reduction of oxygen to $O^{-\bullet}_2$ (type II)

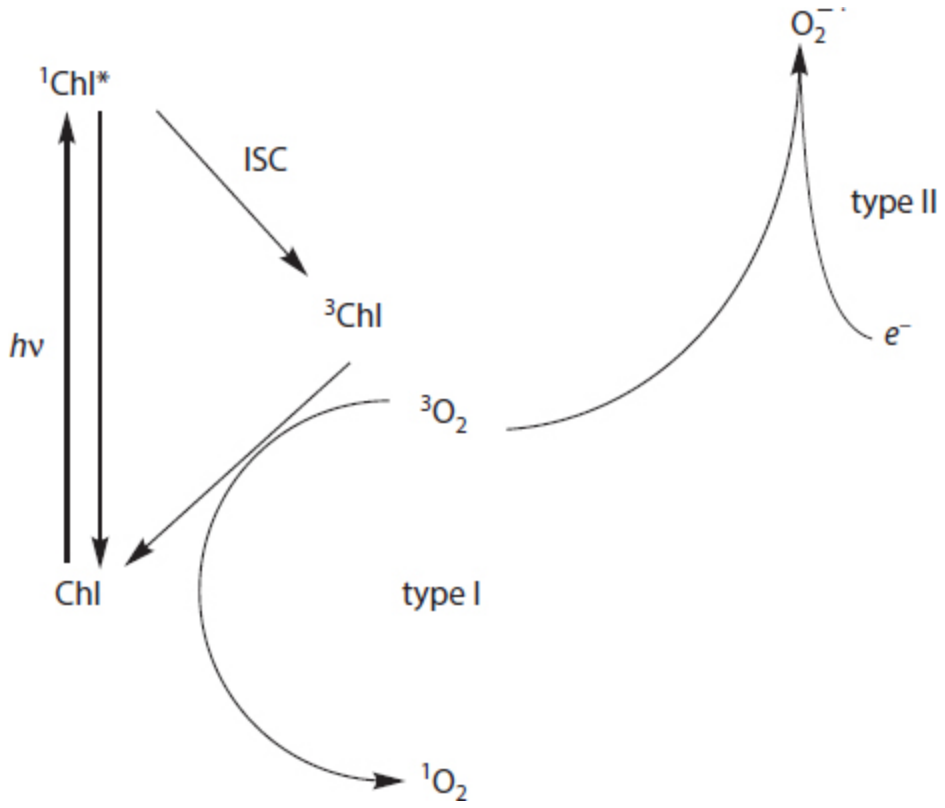
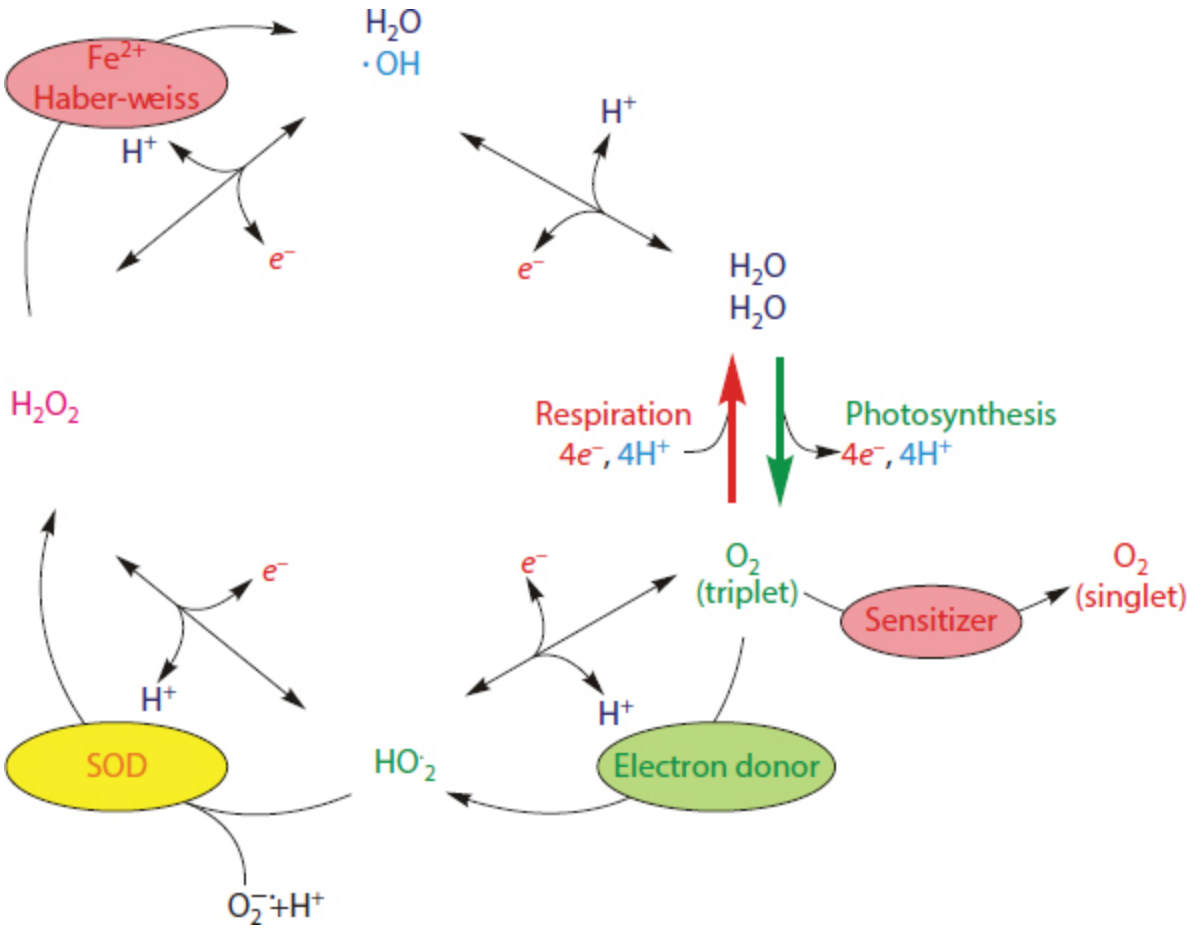


Figure 1.2 Scheme of ROS formation and water redox chemistry (water-water cycle, for details, see text)



(1) $^3\text{Chl} + {}^3\Sigma_g^- O_2 \rightarrow {}^1\text{Chl} + {}^1\Delta_g O_2$

^{3}Chl can be populated either via intersystem crossing (ISC) of antenna Chls or via radical pair recombination in the reaction centers (RCs) of photosystem II (PS II) (for reviews, see Renger, 2008; Vass and Aro, 2008; Rutherford *et al.*, 2012; Schmitt *et al.*, 2014a). Alternatively, $^1\Delta_g O_2$ can also be formed in a controlled fashion by chemical reactions, which play an essential role in programmed cell death upon pathogenic infections (e.g. by viruses).

Figure 1.2 schematically illustrates the pattern of one-electron redox steps of oxygen forming the ROS species $HO^\bullet$, H_2O_2 and $HO^\bullet_2/O^{-\bullet}_2$ in a four-step reaction sequence with water as the final product. The sequence comprises the water splitting, leading from water to O_2 + $4H^+$ and the

corresponding mechanism *vice versa* of the ROS reaction sequence. The production of $^1\Delta_g$ O_2 is a mechanism next to that.

In biological organisms, the four-step reaction sequence of ROS is tamed and energetically tuned at transition metal centers, which are encapsulated in specifically functionalized protein matrices. This mode of catalysis of the “hot water redox chemistry” avoids the formation of ROS. In photosynthesis, the highly endergonic oxidative water splitting ($\Delta G° = + 237.13$ kJ/mol, see Atkins, 2014) is catalyzed by a unique Mn_4O_5Ca cluster of the water-oxidizing complex (WOC) of photosystem II and energetically driven by the strongly oxidizing cation radical $P680^{+\bullet}$ (Klimov *et al.*, 1978; Rappaport *et al.*, 2002) formed via light-induced charge separation (for review, see Renger, 2012).

Correspondingly, the highly exergonic process in the reverse direction is catalyzed by a binuclear heme iron-copper center of the cytochrome oxidase (COX), and the free energy is transformed into a transmembrane electrochemical potential difference for protons (for a review, see Renger, 2011), which provides the driving force for ATP synthesis (for a review, see Junge, 2008). In spite of the highly controlled reaction sequences in photosynthetic WOC and respiratory COX, the formation of ROS in living cells cannot be completely avoided. The excess of ROS under unfavorable stress conditions causes a shift in the balance of oxidants/antioxidants towards oxidants, which leads to the intracellular oxidative stress (Kreslavski *et al.*, 2012b). Formation of ROS (the production rate) as well as decay of ROS (the decay rate) with the latter one determining the lifetime, both bring about the concentration distribution of the ROS pool (Kreslavski *et al.*, 2013a). The activity of antioxidant enzymes, superoxide dismutase