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Role of reactive oxygen species in ultra-weak photon emission in biological systems

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ABSTRACT

Ultra-weak photon emission originates from the relaxation of electronically excited species formed in the biological systems such as microorganisms, plants and animals including humans. Electronically excited species are formed during the oxidative metabolic processes and the oxidative stress reactions that are associated with the production of reactive oxygen species (ROS). The review attempts to overview experimental evidence on the involvement of superoxide anion radical, hydrogen peroxide, hydroxyl radical and singlet oxygen in both the spontaneous and the stress-induced ultra-weak photon emission. The oxidation of biomolecules comprising either the hydrogen abstraction by superoxide anion and hydroxyl radicals or the cycloaddition of singlet oxygen initiate a cascade of oxidative reactions that lead to the formation of electronically excited species such as triplet excited carbonyl, excited pigments and singlet oxygen. The photon emission of these electronically excited species is in the following regions of the spectrum (1) triplet excited carbonyl in the near UVA and blue–green areas (350–550 nm), (2) singlet and triplet excited pigments in the green–red (550–750 nm) and red-near IR (750–1000 nm) areas, respectively and (3) singlet oxygen in the red (634 and 703 nm) and near IR (1270 nm) areas. The understanding of the role of ROS in photon emission allows us to use the spontaneous and stress-induced ultra-weak photon emission as a non-invasive tool for monitoring of the oxidative metabolic processes and the oxidative stress reactions in biological systems *in vivo*, respectively.

1. Introduction

Reactive oxygen species (ROS) are formed either during the metabolic processes linked to life-sustaining enzyme-catalyzing reactions or during the response to stress reactions when microorganisms, plants and animals including humans are exposed to biotic and abiotic stress factors. When ROS are effectively scavenged by the antioxidant defense system, the oxidative effect of ROS on biomolecules such as lipids, proteins and nucleic acids is fully prevented [1]. However, under circumstance, when the formation of ROS exceeds the capacity of antioxidant defense system, biomolecules are oxidized by ROS. The oxidation of lipids, proteins and nucleic acids leads to the formation of high-energy intermediates [2]. The decomposition of high-energy intermediates generates the electronically excited species which undergo the electronic transition from either the singlet or the triplet excited state to the singlet ground state [3]. The electronic transition of electronically excited species from the singlet or the triplet excited state to the ground state is accompanied by photon emission. As merely few photons are emitted per second per square centimeter, the photon emission is ultra-weak in nature. In order to envision the role of ultra-weak photon emission, the propagation of ultra-weak photons in biological system via through specialized primo vascular channels was hypothesized [4].

Based on the process during which ROS are formed comprising either metabolic processes or stress reactions, two types of ultra-weak photon emission are well described in the literature [5–7]. Spontaneous ultra-weak photon emission originates from the relaxation of electronically excited species formed in the biological systems during the oxidative metabolic process that are associated with the production of ROS during normal metabolic processes [5,6,8,9]. Stress-induced ultra-weak photon emission originates from relaxation of electronically excited species formed under abiotic (physical and chemical) and biotic (virus, bacteria, fungi) stress reactions.

Abbreviations: SOD, superoxide dismutase; NADPH, nicotinamide adenine dinucleotide phosphate; PMT, photomultiplier tube; UV, ultraviolet; ROS, reactive oxygen species.

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This review is focused on the involvement of ROS formed either during the oxidative metabolic processes or during the oxidative stress reactions in spontaneous and stress-induced ultra-weak photon emission, respectively. It is stated that ROS oxidize lipids, proteins and nucleic acids and thus initiate a cascade reactions that leads to the formation of electronically excited species responsible for the photon emission in near UVA, visible and near IR regions of the spectrum.

2. Reactive oxygen species production

Reactive oxygen species are formed either by the sequential one-electron reduction of molecular oxygen or by the triplet–singlet energy transfer from triplet excited pigments to molecular oxygen. The sequential one-electron reduction of molecular oxygen leads to the formation of superoxide anion radical ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($HO^{\cdot}$), each of which possess a differential redox potential and thus bears a varied degree of reactivity [10]. The triplet–singlet energy transfer from the triplet excited pigment to molecular oxygen results in the formation of singlet oxygen ($^1O_2$). Reactive oxygen species formed during the metabolic processes play an important role in the defense against infection, cell signaling, apoptosis and ageing [11]. On the other hand, ROS are able to oxidize biomolecules such as lipids, proteins and nucleic acids [1,10]. To prevent the dangerous effect of ROS on biomolecules, the non-enzymatic and the enzymatic antioxidant defense systems have been developed in the cells. The non-enzymatic antioxidant defense system comprises of the low molecular weight components such as carotenoids, coenzyme Q10, glutathione, lipoic acid, melanin, urocanic acid, porphyrin, bilirubin, flavins and pterins and vitamins (A, B, C, D and E) [1]. The enzymatic antioxidant defense is maintained by various types of antioxidant enzymes comprising superoxide dismutase (SOD), various types of peroxidases (glutathione peroxidase, ascorbate peroxidase, cytochrome c peroxidase), catalase and glutathione reductase [12–14]. Under the normal metabolic processes, the cells unceasingly produce ROS which exceed the threshold under the abiotic and the biotic stress as described in the next sections.

2.1. Metabolic production of reactive oxygen species

Metabolic processes (e.g. cellular respiration, photosynthesis) are the essential chemical reactions known to occur inside microbial, plant and animal cells. It is well known that metabolic processes are associated with the formation of radical ($O_2^{\cdot-}$, $HO^{\cdot}$) and non-radical (H_2O_2, $^1O_2$) ROS (Fig. 1). Superoxide anion radical is formed by the one-electron reduction of molecular oxygen or by the one-electron oxidation of H_2O_2. In animal cells, the one-electron reduction of molecular oxygen to $O_2^{\cdot-}$ occurs in the mitochondria during the cellular respiration. Electron donation to molecular oxygen is maintained by the complex I and the complex III located in the inner mitochondrial membrane [13,15]. Apart to mitochondria, the one-electron reduction of molecular oxygen is catalyzed by NADPH oxidase during the respiratory burst in the phagocytic cells, xanthine oxidase in the cytoplasm [16]. The one-electron oxidation of H_2O_2 catalyzed by flavin oxidases in peroxisomes is another source of $O_2^{\cdot-}$ in animal cells [17]. In plants, $O_2^{\cdot-}$ is formed by one-electron reduction of molecular oxygen by the stromal side of photosystem I [18] and photosystem II [19]. Hydrogen peroxide is formed either by the one-electron reduction of $O_2^{\cdot-}$ or by the two-electron reduction of molecular oxygen. The one-electron reduction of $O_2^{\cdot-}$ to H_2O_2 occurs either spontaneously or is catalyzed by SOD located in the mitochondria, chloroplast and cytoplasm [20]. The two-electron reduction of molecular oxygen occurs during the reaction in which specific substrates are oxidized by the various types of oxidases in the mitochondria and peroxisomes [10,21]. Hydroxyl radical formed by the one-electron reduction of H_2O_2 catalyzed by metal in the reaction known as Fenton reaction. Several types of metal ions such as iron, copper, manganese, zinc, chromium, cobalt, nickel and vanadium have been shown to reduce H_2O_2 to $HO^{\cdot}$ [22]. It is well known that metals are coordinated to the active enzyme site in metalloproteins or stored in a ubiquitous protein called ferritin, hemosiderin, transferrin and lactoferrin [12,23]. Singlet oxygen is formed by the triplet–singlet energy transfer from the triplet excited chlorophyll to molecular oxygen in chloroplast. The triplet chlorophyll is formed by the intersystem crossing from the singlet excited chlorophyll formed upon the light absorption in the light-harvesting complex in photosystem II [19].

2.2. Stress-induced production of reactive oxygen species

Various types of abiotic (physical and chemical stress factors) and biotic (virus, bacteria, fungi) stresses are known to significantly enhance ROS formation. Under such circumstances, the formation of ROS exceeds the capacity of antioxidant system and the hazardous ROS are inadequately eliminated. The inconsistency between the formation and the elimination of ROS causes the oxidation of lipids, proteins and nucleic acids. Below, the formation of ROS initiated by physical, chemical and biological stimuli is outlined.

2.2.1. Physical production of reactive oxygen species

It well known that both UV radiation and visible light results in the formation of radical ($O_2^{\cdot-}$, $HO^{\cdot}$) and non-radical ($^1O_2$) ROS by Type I and Type II reactions, respectively (Fig. 2) [24–28]. Endogenous pigments in plants, animals and humans such as porphyrins, bilirubins, melanins, pterins and urocanic acid are known to act as photosensitizers [27]. The absorption of UV radiation or visible light by photosensitizers leads to the formation of the singlet state of photosensitizer which forms the triplet excited state via intersystem crossing. The excited photosensitizer undergoes either the electron transport forming $O_2^{\cdot-}$, H_2O_2 and $HO^{\cdot}$ (Type II reaction) or the energy transfer forming $^1O_2$ (Type II reaction) [27,29–31]. In Type I reaction, the electron transport leads to the formation of $O_2^{\cdot-}$ via the formation of photosensitizer anion radical and substrate cation radical or vice versa [30,32]. The spontaneous or enzymatically driven dismutation of $O_2^{\cdot-}$ leads to the formation of H_2O_2 which subsequently forms $HO^{\cdot}$ via Fenton reaction or other metals catalyzed reactions [14,30,32–34]. In Type II reaction, the triplet–singlet energy transfer from the excited photosensitizer to molecular oxygen forms $^1O_2$.

2.2.2. Chemical production of reactive oxygen species

Reactive oxygen species can be produced via different chemical systems either exogenously (independently to cell components) or endogenously (dependently to cell components). The exogenous source of ROS comprises of xanthine/xanthine oxidase system producing $O_2^{\cdot-}$, Fenton reagent (H_2O_2 and transition metal ions) known to generate $HO^{\cdot}$ and photosensitizer such as rose bengal, radachlorin and benzoporphyrin derivative known to produce $^1O_2$ upon photosensitization [10,35–37]. Besides the exogenous ROS production, ROS are also produced endogenously in the association with cell components. Paraquat anion radical formed by the reduction of paraquat by NAD(P)H reduces molecular oxygen to $O_2^{\cdot-}$ [38]. The addition of H_2O_2 to the cells can lead to the formation of $HO^{\cdot}$ upon reaction with endogenous metal ions coordinated to active enzyme site in metalloproteins or released from a ubiquitous protein called ferritin, hemosiderin, transferrin and lactoferrin [23]. Singlet oxygen is formed from lipid and DNA hydroperoxides in the presence of metal ions, cytochrome c, peroxynitrite, chloroperoxide and