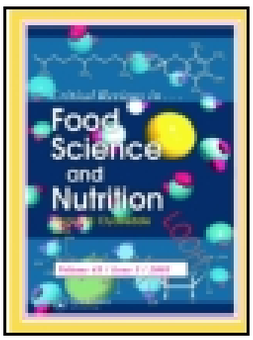

Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: https://www.tandfonline.com/loi/bfsn20

Diagnostics of plasma reactive species and induced chemistry of plasma treated foods

Kexin Zhang, Camila A. Perussello, Vladimir Milosavljević, P. J. Cullen, Da-Wen Sun & Brijesh K. Tiwari

To cite this article: Kexin Zhang, Camila A. Perussello, Vladimir Milosavljević, P. J. Cullen, Da-Wen Sun & Brijesh K. Tiwari (2019): Diagnostics of plasma reactive species and induced chemistry of plasma treated foods, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2018.1564731

To link to this article: https://doi.org/10.1080/10408398.2018.1564731

Published online: 24 Jan 2019.

CRITICAL REVIEWS IN FOOD SCIENCE AND NUTRITION
https://doi.org/10.1080/10408398.2018.1564731

Taylor & Francis
Taylor & Francis Group

REVIEW

Diagnostics of plasma reactive species and induced chemistry of plasma treated foods

Kexin Zhang[a,b], Camila A. Perussello[a], Vladimir Milosavljević[c], P. J. Cullen[c,d], Da-Wen Sun[b], and Brijesh K. Tiwari[a]

[a]Department of Food Chemistry and Technology, Teagasc Food Research Centre, Dublin, Ireland; [b]Food Refrigeration and Computerized Food Technology (FRCFT), School of Biosystems and Food Engineering, University College Dublin, National University of Ireland, Dublin, Ireland; [c]BioPlasma Group, School of Food Science and Environmental Health, Dublin Institute of Technology, Dublin, Ireland; [d]School of Chemical and Biomolecular, University of Sydney, Australia

ABSTRACT

Cold plasma is a promising technique that has been tested as a process technology for a range of food commodities, mainly to destroy microorganisms, but also aimed at toxin degradation, enzyme inactivation, residual pesticide degradation and functionalization of food properties. Plasma has already been employed by industry for food packaging material sterilization and surface modification. As most of the current literature on cold plasma in the field of food science is focused on microbial inactivation efficacy, the information about its chemical influences on food is sparse. To better understand the chemical interactions of with plasma, this review focuses on plasma chemistry diagnostics techniques available to characterize the plasma reactive species generated. Equally important is the detection of induced chemistry in the food and here we present approaches to analyze likely reactions with key food bio-molecules. Such analysis will support mechanistic insights involved in these complex chemical reactions (i.e., DNA, lipid and protein) along with potential physical modifications of the food structure. For successful adoption of plasma as a food processing aid it is critical to elucidate these interactions as they have an important role in demonstrating the technology's safety as a food processing technique along with understanding any effect on food nutrients.

KEYWORDS

Absorbance spectroscopy; diagnostics; emission spectroscopy; lipid oxidation; plasma; protein destruction; reactive plasma species

Introduction

Plasma, the fourth state of matter, is a promising non-thermal food processing technology composed of highly excited species, such as molecular, atomic, ionic and radical species (Surowsky, Schlüter, and Knorr 2015). Due to the collisions between gas molecules and electrons, the gas dissociates to gas atoms, which become positively or negatively charged by losing or gaining electrons. If a significant portion of the gas agents is ionized, this substance is referred to as plasma (Akhiezer, Akhiezer, and Polovin 2017).

Within current food research, plasma has gained popularity as a non-thermal decontamination treatment, and has been tested for a wide range of food products (e.g. lettuce, mushroom, potato, tomato, apple, strawberry, egg, beef, and ground nuts), generally for postharvest preservation (Lee et al. 2015a; Xu et al. 2016; Ziuzina et al. 2014; Mir et al., 2016; Misra et al., 2014). When foods are exposed to plasma or the resultant afterglow, the various reactive species in plasma can react with both the food components and residing microorganisms, resulting in food properties changes and microbial inactivation (Kim, Lee, and Min 2014; Misra et al. 2015; Misra et al. 2014a). Chemical reactions between food components and plasma reactive species might also be responsible for food surface modification and functionality changes, as in the case of packaging materials (Misra et al. 2014b; Li et al. 2017a). Plasma-food reactions may preserve food postharvest quality during storage, for example by improving color retention (Ramazzina et al. 2015), and can slow down tissue metabolism (Tappi et al. 2014). However, food components (such as DNA, lipids and proteins) are susceptive to react with various chemical reactive species in plasma, in particular biomolecular oxidation may occur during the plasma treatment, which may cause DNA damage, produce undesirable flavors and potentially harmful compounds (Gavahian et al. 2018; Han et al. 2014; Sarangapani et al. 2017; Takai et al. 2012; Nowicka et al. 2013).

Most of the research to date on plasma in food science has focused on microbiological interactions (Lee et al. 2015b; Xu et al. 2016; Lacombe et al. 2015; Georgescu, Apostol, and Gherendi 2017; Fernandez, Noriega, and Thompson 2013). There is a lack of information in the literature on the mechanisms involved in changing food biomolecules. Therefore, the current review provides an overview of available diagnostic techniques for both plasma reactive species and possible induced chemistry in the target food.

Plasma diagnostics

Plasma chemistry

The reactivity of plasma depends on the type of plasma source used and processing variables employed, such as gas

CONTACT Da-Wen Sun dawen.sun@ucd.ie Food Refrigeration and Computerized Food Technology (FRCFT), School of Biosystems and Food Engineering, University College Dublin, National University of Ireland, Belfield, Dublin 4, Ireland.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/bfsn.

frequency, pressure, and degree of ionization (Surowsky, Schlüter, and Knorr 2015). Free radicals and reactive species in plasma are responsible for biomolecule oxidation, surface modification, functionality changes, and postharvest preservations (Sarangapani et al. 2017; Takai et al. 2012). The extent of influence of these factors also depends on the operation parameters of plasma, such as power, frequency, gas agents, and gas flow rate (Cheng et al. 2014). Various feeding gases (e.g. air, oxygen, hydrogen, nitrogen and argon) can be used in plasma generation, leading to different antimicrobial effects and different extents of biomolecule modification (Attri et al. 2015). Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are often cited for their roles in applications, such as the observed antimicrobial effects (Cullen et al. 2018; Graves 2012). Where ROS normally refers to radicals O_2^-, OH, HO_2, CO_3^-, CO_2^-, $^1O_2$ and radicals H_2O_2, O_3, O_2 1 Dg, HOBr, HOCL, HOI; RNS normally refers to radicals NO, NO_2, NO_3, and non-radicals HNO_2, NO^+, NO^-, N_2O_3, N_2O_4, N_2O_5 (Graves 2012). Moreover, given the scale of food processing operations and its typically low value-added nature, use of atmospheric air as the inducer gas is highly desirable if not the only feasible option. Indeed, examination of the rapidly expanding literature shows a clear trend towards the use of air as the operational gas of choice (Pignata et al. 2017).

A vast array of reactive species are generated by atmospheric air plasmas, as shown in Table 1 (Klämpfl et al. 2012). However, as the lifetimes for most of the excited species are very short, they will reach a stable state quickly by emitting a photon (Gorbanev and Bogaerts 2018). As reported by Klämpfl et al. (2012), the dominant active species in atmospheric air plasma are O_3, NO_2, NO_3, N_2O, N_2O_5, H_2, H_2O_2, HNO_2, and HNO_3. Based on the charge properties of particles, these active species can be divided into positively charged particles (N^+, N_2^+, N_3^+, N_4^+, O^+, O_2^+, O_4^+, NO^+, N_2O^+, NO_2^+, H^+, H_2^+, H_3^+, OH^+, H_2O^+, H_3O^+), negatively charged particles (e, O^-, O_2^-, O_3^-, O_4^-, NO^-, N_2O^-, NO_2^-, NO_3^-, H^-, OH^-), and neutral species ($N(^2D)$, N_2 ($A\ ^3\sum$), $N_2(B\ ^3\prod)$, O (^1D), H, N, O, O_2 ($a^1\Delta$), O_3, NO, N_2O, NO_2, NO_3, N_2O_3, N_2O_4, N_2O_5, H_2, OH, HO_2, H_2O_2, HNO, HNO_2, HNO_3, N_2, O_2, H_2O).

Table 1. Chemical reactions involved in the generation of reactive species in plasma, sourced from Klämpfl et al. (2012).

Reaction Substances	Reaction Products
$e + N_2$	$N(^2D) + N + e$
	$N_2\ (A\ ^3\sum) + e$
	$N_2(B\ ^3\prod) + e$
	$N_2^+ + e + e$
$e + N$	$N(^2D) + e$
	$N_2^+ + e + e$
$e + O_2$	$O + O + e$
	$O(^1D) + O + e$
	$O_2(a^1\Delta) + e$
	$O_2^+ + e + e$
$e + O_3$	$O + O_2 + e$
$e + O$	$O(^1D) + e$
	$O^+ + e + e$
$e + H_2O$	$H_2O^+ + e + e$
	$OH^+ + H + e + e$
	$H^+ + OH + e + e$
	$O^+ + H_2 + e + e$
	$H_2^+ + O + e + e$
	$OH + H + e$
	$H_2 + O(^1D) + e$
	$O^- + OH$
	$OH^- + H$
$e + H_2$	$H + H + e$
	$H_2^+ + e + e$
$e + NO_2$	$O^- + NO$
$e + NO_2 + M$	$NO_2^- + M$
$e + NO_3 + M$	$NO_3^- + M$

Note: M = any gas molecule.

Diagnostics techniques

Most of the plasma applications in food depend on the chemical reactions between plasma reactive species and food components such as DNA, protein, lipid and carbohydrates over physical effects such as etching which is important for numerous plasma material applications (Attri et al. 2015). Therefore, to better understand the mechanisms involved in plasma processing, the detection of process reactive species is essential. Optical spectroscopy is a group of popular non-destructive techniques studying the interaction between a substance (molecules and atomic reactive species) and electromagnetic radiation, providing important information about their excited and ionization states, and other process parameters (Surowsky, Schlüter, and Knorr 2015; Friedl and Fantz 2012; Patil et al. 2014). Non-optical techniques, such as mass spectroscopy and electron spin trapping are the alternatives (van Ham et al. 2014; Gorbanev and Bogaerts 2018). The advantages and disadvantages for different diagnostics techniques for plasma reactive species are summarized in Table 2.

Optical emission spectroscopy

Optical emission spectroscopy (OES) has been used for characterization and diagnostic of the reactive oxygen species and reactive nitrogen species excited during plasma for decades (Misra et al. 2015). The occurrence of emission profiles in plasmas is due to the transfer of energy through collisional and radiative processes. These transfers of energy can cause an electron to undergo excitation to a higher energy state (i), which it then falls back to a lower and more stable state (j) due to the relaxation transition, showed in Figure 1a. By undergoing this relaxation transition, a photon is emitted to preserve the conservation of energy. This emission is of light energy which corresponds to a particular wavelength. The wavelength is dependent on the energy emitted and varies between every atom and molecule, allowing the use of OES to identify the species present within a plasma discharge (Misra et al. 2014b). After implementing OES, the data that is acquired can be analyzed to give the absolute emission intensity for each spectral line observed. Each of these emission lines has their own constant (Einstein coefficient) associated with their spontaneous emission. There are several representative spectral lines or bands that correspond to specific chemical compositions. For N and O, the representative spectral lines are at 760.9 nm and 844.6 nm, respectively; for Ar, the

Table 2. Comparison of advantages and disadvantages of different diagnostics techniques for plasma reactive species.

Diagnostics techniques		Advantages	Disadvantages	References
Optical	Optical emission spectroscopy	Experimental simply for characterization of plasma reactive species	Difficult to interpret the measured spectra to yield the absolute values of non-equilibrium plasma	Bruggeman et al. 2014; Nikiforov et al. 2015
	Optical absorption spectroscopy	The simples and the most direct way to detect the absolute density of reactive species without the need of calibration	Can only deliver line or sight densities of reactive species, the sensitivity are relatively low	Reuter et al. 2015
	Laser-induced florescence	Can detect population density and energy state of reactive species, and can be used for the interactions with living cells and tissues with high spatial and time resolution	Rely on model assumptions and lack accuracy or the possibility to probe to detect gas temperature and electron parameters	Lu et al. 2016
Non-optical	Mass spectroscopy	Can detect charged and neutral atomic and molecular reactive species	Cannot deliver absolute or relative densities for reactive species without calibration	Dünnbier et al. 2013; Schmidt-Bleker, Reuter, and Weltmann 2014b
	Scattering techniques	Can detect density for reactive species, electron temperature, gas temperature, partial air pressure with high spatial resolution and calibration	Relays on several assumptions and model calculations	van Gessel et al. 2012; Hübner et al. 2017
	Electron spin trapping	Can be used to detect short-lived reactive species in water-based media.	Requires further care to choose appropriate spin trap and used liquid which may influence the measurements result.	Novák et al. 2013

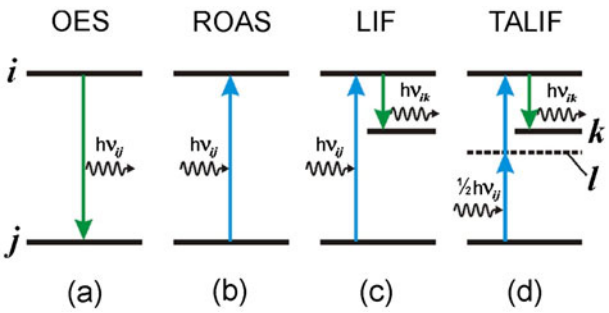

Figure 1. Schematic diagram of optical diagnostics of plasma (a) optical emission spectroscopy; (b) optical absorption spectroscopy; (c) laser induced fluorescence; (d) two photon absorption laser induced fluorescence. I, j and k are quantum states; h is plank constant; and v is frequency.

representative spectral lines are at 696.5, 750.4, 772.4, 811.5, 826.5 and 912.3 nm (Chiper et al. 2011).

As reported by Friedl and Fantz (2012), the absolute intensity of the spectral lines is dependent on plasma operation conditions, such as electron temperature (Te), gas temperature (Tg) and electron density (ne). When using atmospheric-pressure low-temperature plasma, the effective Te and Tg were found in a particularly narrow range of 1–2 eV and 300–600 K, respectively. So, it is assumed that the changes in ne have the largest impact on the population density (Np) of each species, compared to Te and Tg. Therefore, any changes seen in Np can be attributed to the changes in ne. Chung, Ra Kang, and Keun Bae (2012) combined OES with a rf-compensated Langmuir probe to investigate the physical properties of inductively coupled Ar, O_2, Ar/O_2 mixture plasma. Detected by OES models, there was a decrease trend of electron temperature with increasing power and pressure. When increasing the Ar content, temperature decreased. OES was also used to estimate the dissociation fraction of O_2 in an Ar/O_2 discharge. An increased dissociation fraction was observed with increasing power and Ar content. By using OES, Walsh et al. (2010) investigated the characteristics of reactive species in a plasma that was generated by different mechanisms (sub-microsecond pulsed atmospheric air and atmospheric pressure helium oxygen glow plasma). Relatively low intensity peaks, corresponding to excited oxygen species O(5p) and O(3p), were observed in the sub-microsecond pulsed atmospheric air plasma at 777 and 856 nm, which means that the concentration of excited oxygen atoms in sub-microsecond pulsed atmospheric air plasma is lower compared with the concentration in the atmospheric pressure helium oxygen glow plasma. Strong intensities of emission from reactive nitrogen species in the air plasma was observed below 400 nm (especially for the nitrogen second positive system but also for nitric oxide). The high emission of the N_2 secondary system in air plasma might be caused by the greater N_2 concentration in air than in He/O_2 mixture gas. Misra et al. (2014b) used OES and observed the OH peak around 300 nm and peaks of atomic oxygen with optical transitions at 725.4 nm (from $5s^3S$ to $3p^3P$), 533.0 nm (from $5d^5D$ to $3p^5P$), and 777.47 nm (from $2s^22p^33p^5P$ to $2s^22p^33s^5S$).

Optical absorption spectroscopy

If there is a lack of or low spectral radiation, optical absorption spectroscopy (OAS) is a better option to be employed instead of OES. In OAS, particles inside of the plasma are regarded as absorbers for the electromagnetic waves (transmitted through or reflect at the plasma boundary) so as to estimate the level of reactive species in the plasma, as shown in Figure 1b. Similar to OES, OAS typically employs fiber optical cables and a spectrometer, in addition to a Deuterium-Tungsten lamp which provides the light source, as shown in Figure 2.

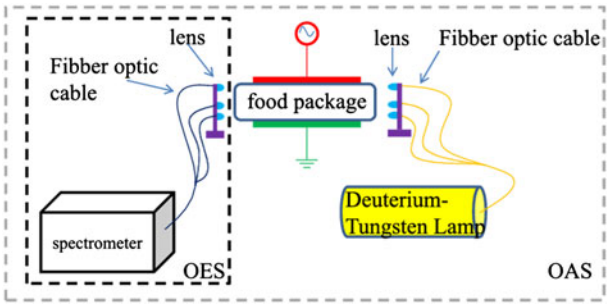

Figure 2. Schematic diagram of OES system and OAS system for plasma diagnostics of a food package.

As reported by Reuter et al. (2015), the diagnostics of plasma by absorption spectroscopy are from the vacuum ultraviolet (VUV) to mid infrared (MIR) range. In the VUV spectral region, O and, N atoms and singlet delta oxygen O_2 (a1Δg) exhibit absorption features, but VUV absorption radiation is normally operated under vacuum conditions to control the ambient gas due to its strong absorption with humid air species. UV absorption spectroscopy is a relatively sensitive method to detect ozone and the hydroxyl radical, but measurements have to be done to avoid misinterpretation of species density. In the visible and near infrared range, argon metastables and helium metastables can be measured respectively. For MIR absorption spectroscopy, Fourier transform infrared spectroscopy and mid-infrared laser induced absorption spectroscopy (MIR-LAS) can be used to provide fingerprint information for plasma species.

Patil et al. (2014) used OAS to quantify the concentration of NO_2 and O_3 for plasma discharges generated within the confines of food packages based on their absorbance in the wavelength range of 385–415 and 250–160 nm, respectively. The presence of N_2O_5, H_2O_2 and HNO_4 is indicated by the absorbance bands in the wavelength range from 220 to 240 nm. For OH and water-bonded OH complexes, the absorbance bands showing their presence are in the 290–340 nm range. However, the absorption peak for the presence of OH radicals at 308 nm was not observed clearly, which might due to their fast reaction rates. The post discharge gas composition was also assessed by UV-Vis absorption spectroscopy after the package gas was exposed to plasma for 15–20 s (Moiseev et al. 2014). The findings showed that the concentration of nitrogen oxides and ozone in the contained gas increased with increasing relative humidity. However, both the levels of O_3 and the abundance of nitrogen oxides in the closed container decreased with increasing relative humidity. Similarly, Brayfield et al. (2016) used OAS to quantify the species created by high voltage cold atmospheric plasma from 70 to 88 kV. The concentrations of these reactive species were shown as a function of applied plasma voltage and gas humidity.

By combining absorption spectroscopy with a simple modeling approach, Schmidt-Bleker, Reuter, and Weltmann (2014b) investigated the long living species of a cold atmospheric plasma jet with varies mixtures of oxygen and nitrogen at different humidity levels. Result showed that clear absorptions were obtained are in the regions corresponding to ozone and nitrogen dioxide, although the absorption of HNO_3 and H_2O_2 were also identified, the quantitative evaluations were not feasible due to the weak signals. The ozone density drops significantly with increasing humidity, which is about $1.75 \times 10^{14}\,cm^{-3}$ with the dry gas and $1.25 \times 10^{14}\,cm^{-3}$ with 36% relative humidity, but it rises continuously with the oxygen content in gas mixture. The density of nitrogen dioxide is about $8 \times 10^{12}\,cm^{-3}$ with a gas of 18% relative humidity, it has a maximum value with the gas mixture of 30% oxygen. The density of H_2O_2, HNO_3 and OH generated by atmospheric pressure plasma jet has been successfully detected by OES, which is about $5 \times 10^{12}\,cm^{-3}$, $3 \times 10^{12}\,cm^{-3}$ and in the of $10^{14}\,cm^{-3}$, respectively (Winter et al. 2013).

Laser-induced fluorescence

Laser-induced fluorescence (Jiang, Feng, and Li 2012) is a commonly used plasma diagnostic technique providing high spatial and temporal resolutions, which can measure both the density and temperature of ground-state plasma active species. As shown in Figure 1c, LIF is the process of light emission by a substance which has absorbed energy from a dye laser, the fluorophore absorbs the energy from light at a specific wavelength (at ultraviolet or visible regions) which then emits energy in the form of light at a higher wavelength. LIF has been successfully used in the investigation of the density distribution and temporal behaviors of oxygen reactive species (OH and O radicals) generated by helium plasma jets (Yonemori and Ono 2014). Similarly, two-photon absorption laser-induced fluorescence (TALIF) is widely used to obtain the absolute atomic oxygen or hydrogen density in the effluent of plasma systems (Schmidt et al. 2017). As shown in Figure 1d and a distinction from LIF is the retirement of a comparative measurement TALIF with the same laser on a calibration gas (with a known density) so as to derive the absolute density of the target atom. Reuter et al. (2012) investigated the atomic oxygen density (calibrated by xenon gas) in the effluent of argon/oxygen atmospheric pressure plasma jet using TALIF spectroscopy. Two photons (225.65 nm) are used to excite the $2P^4\ ^3P_2$ state (ground state) oxygen atoms into the $3P\ ^3P_J$ state, the resulting fluorescence radiation is detected in the infrared range (844.87 nm). Results showed that the atomic oxygen density was about $3.75 \times 10^{15} cm^{-1}$ at the nozzle of plasma jet and decreases with increasing distance to plasma jet nozzle.

For in cellular plasma diagnostics, dichlorodihydrofluorescein diacetate is the most popular fluorescent used in the detection of intracellular H_2O_2 and oxidants; hydroethidine probe is widely used in the measurement of O_2^-; and dihydrorhodamine is the most frequently used probe in the evaluation of $ONOO^-$(Kalyanaraman et al. 2012).

Molecular beam mass spectrometry

Molecular Beam Mass Spectrometry (MBMS) is another important plasma diagnostic technique providing information on the absolute density of reactive oxygen species (ROS).

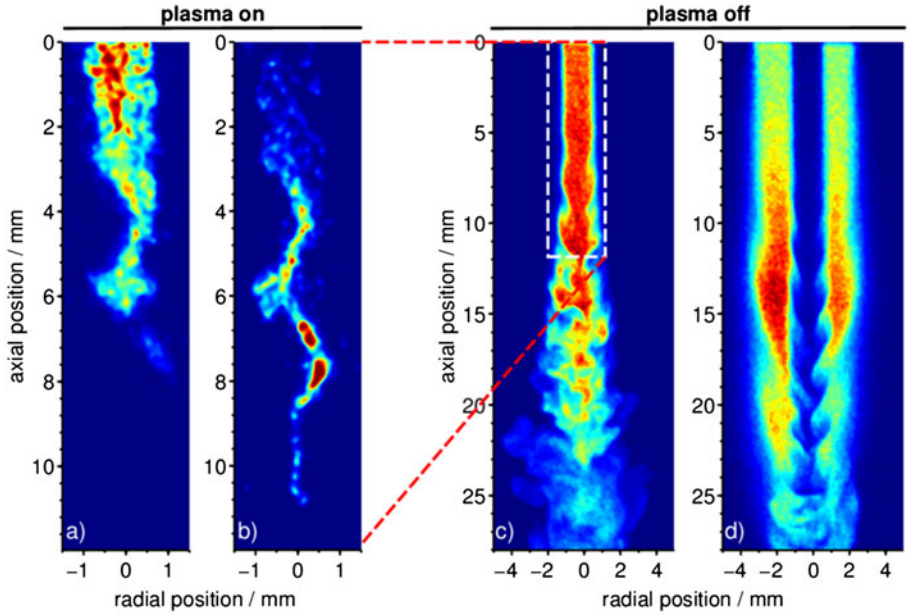

Figure 3. Plasma distribution and concentration diagram detected by mass spectroscopy.

A MBMS system is commonly composed of two or three pumping stages that interconnect with each other via small grounded orifices. A gas ionizer is placed in the line-of-sight with the sampling orifices in a mass spectrophotometer. In the working state, the gas mixture in the high-pressure chamber is allowed to pass through small orifices towards a low pressure chamber, forming the molecule beam (molecules, atoms, ions, and free radicals), which is captured and analyzed by mass spectroscopy to detect the plasma distribution and concentration (based on the color difference) showed in Figure 3. Therefore, the reactive species involved in the process can be evaluated. Ellerweg et al. (2010) placed the first orifice on the axis of the plasma jet with a diameter about 100 µm in order to extract the gas mixture for further analysis. The gas flow passing the first sampling orifice is much lower than the gas flow in the jet, causing a stagnation of the flow. Different to conventional gas sampling methods, only the pulsed gas flow (realized by a rotating skimmer) from the atmosphere is allowed through the system. The rotating skimmer is a stainless-steel disk with fine embedded skimmers. The molecular beam can penetrate the second stage when the skimmer is aligned with the orifice or are blocked by the disk when the skimmer is in blocking position. The density of reactive species detected in a MBMS system is a combination of the species density in the molecular beam and the background density related to the background pressure of the MS pumping system (Benedikt, Ellerweg, and Von Keudell 2009).

The effluent of a microscale helium atmospheric plasma jet operated with a small proportion of O_2 was qualitatively measured by Ellerweg et al. (2010) using a MSMB system. In the effluent, the density of ozone was recorded to be as high as $4.7 \times 10^{15}\,cm^{-3}$ and O_2 depletion of up to 10% was measured. The ozone density showed a continuous increase with higher O_2 proportions in the input gas. By increasing the distance from the jet nozzle, ozone density decreased and saturated at a distance of 40 mm. Similarly, absolute atomic nitrogen (N) density in the effluent of a microscale atmospheric plasma jet operated in helium with small admixture of N_2 were measured by MSMB under different plasma operation conditions (Schneider et al. 2014). The N density increases approximately linearly with applied voltage and decreases continuously with increasing distance between the jet nozzle and the sample orifice of the mass spectrometer. When varying the proportion of N_2, the maximum density of N was about $1.5 \times 10^{14} cm^{-3}$, reaching about 25% of the N_2 admixture. Moreover, van Ham et al. (2014) also measured the concentrations of nitric acids and ozone in a radio frequency driven cold atmospheric pressure plasma jet operated with argon by MSMB.

Others

Electron spin resonance (ESR) spectroscopy, also called electron paramagnetic resonance (EPR) spectroscopy is also used in the identification of short-lived radical reactive species in water based media (such as O_2^-, ·OH, ·OOH and ·NO). The technique has been widely applied in structural biology and quantum physics based on the detection of unpaired electrons (free radicals transition metal ions) (Gorbanev and Bogaerts 2018). The commonly used spin traps for plasma diagnostics are 5,5-dimethyl-pyrroline N-oxide, alpha-phenyl N-tertiary-butyl nitrone, and 5,5-dimethyl-pyrroline N-oxide (DMPO) (Uchiyama et al. 2015). Furthermore, scattering techniques (such as Rayleigh scattering, Thomson and Raman scattering) and non-optical techniques (such as low visualization) are alternatives (Lu et al. 2016).

Induced chemistry in plasma treated food

As a novel process, plasma has been successfully applied to a wide range of food products, such as cabbage, lettuce,

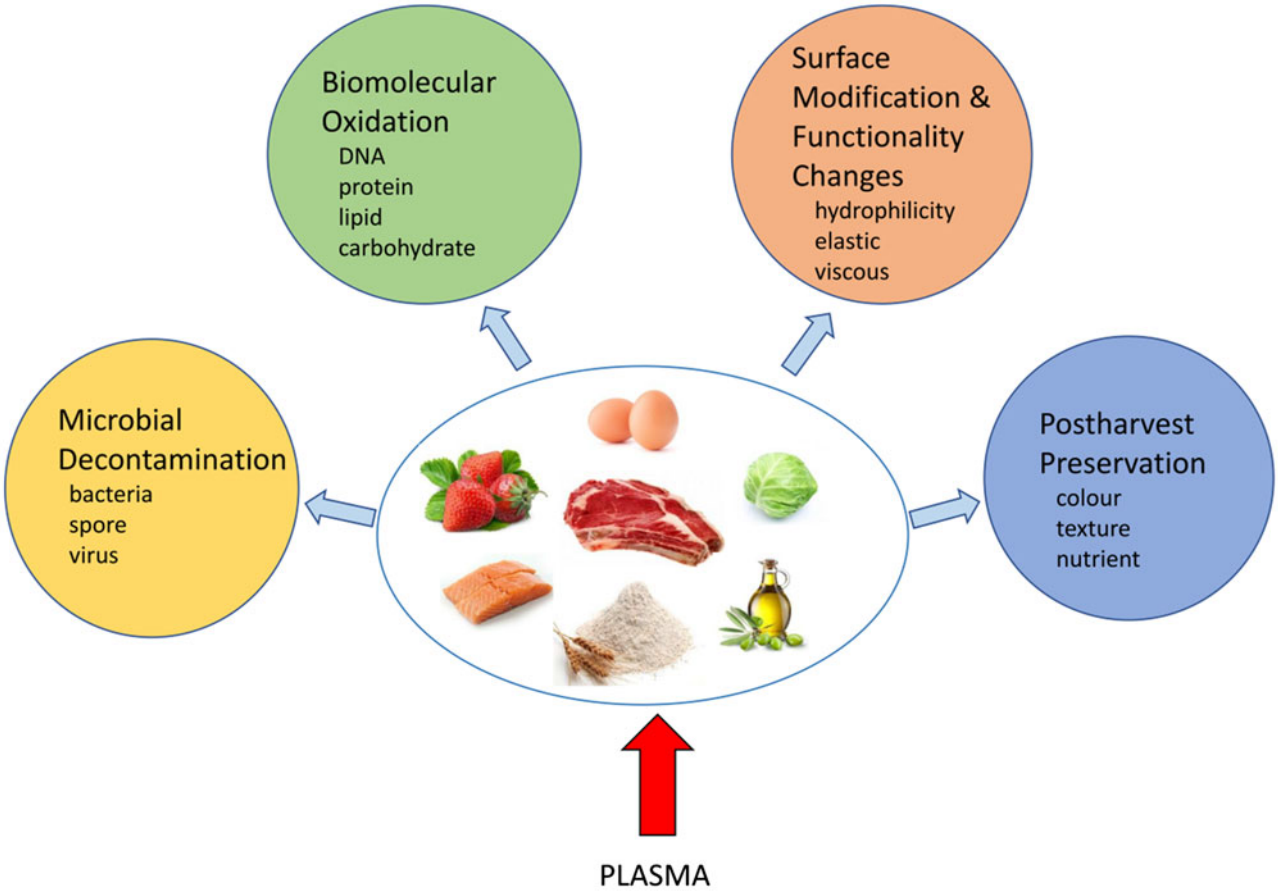

Figure 4. Potentials of plasma for food applications.

potato, cherry tomato, strawberry, milk and seafood (Ma et al. 2017; Ekezie et al. 2018, 2019; Han et al. 2019). The applications of plasma in food processing can be mainly classified into microbial inactivation, biomolecular oxidation, surface modification and functionality changes, and postharvest preservations, as shown in Figure 4.

Based on recent research, plasma has demonstrated useful decontamination efficacy for a wide range of bacteria, spores and viruses (Julák et al. 2011; Klämpfl et al. 2012). To further investigate the mechanisms of action in microbial decontamination, Laroussi and Leipold (2004) studied the reaction between plasma species and microorganisms. They demonstrated that the hydroxyl radical (OH*) compromises the function of microbial membranes by direct interaction with the outermost membranes of microorganisms. As shown in Figure 5, microorganisms' membranes are structured by lipid bilayers, mainly composed of lipids and proteins, and small amounts of carbohydrates. Regarding lipids, unsaturated fatty acids play an important role in forming gel-like membranes, and act as a barrier against the transportation of ions and polar compounds across the cell membrane. When in contact with OH*, the unsaturated fatty acids in the membranes are attacked and lose function (Laroussi and Leipold 2004). In addition, proteins (linear chains of amino acids) that are imbedded in the membrane lipid bilayer are susceptible to oxidation when they react with radicals in the plasma. As a result, proteins lose the ability of controlling the passage of compounds and the integrity of the microbial cell is compromised, leading to the microorganisms' destruction (Laroussi and Leipold 2004).

Biomolecular oxidation

Radicals (such as ROS and RNS) work as intermediate species in a wide range of biochemical reactions, causing oxidative stress in living tissues (Cullen et al. 2018; Graves 2012). Lipids, proteins (such as heme pigments, and various oxidative enzymes) and DNA in food (especially in muscle food) are prone to be oxidized by free radicals (Attri et al. 2015; Sarangapani et al. 2017; Misra et al. 2016). Therefore, biomolecular oxidation occurred during plasma process.

DNA damage

DNA is susceptible to chemical oxidation by reactive oxygen and nitrogen species (Hepel et al. 2012). Plasma can lead to oxidative DNA damage through breaking down single and double DNA strands, generating different base oxidation and base modification products, blocking the DNA replication process and leading to cell death (Attri et al. 2015). Among all DNA bases (Adenine, Guanine, Cytosine and Thymine), guanine is the most sensitive to oxidation damage (Hepel et al. 2012). As shown in Figure 6, the oxidation products of guanosine exist either in keto or enol form (Lunec and Griffiths 2000), which means the 2'deoxyguanosine in DNA could be oxidized to 8-oxo-2'-

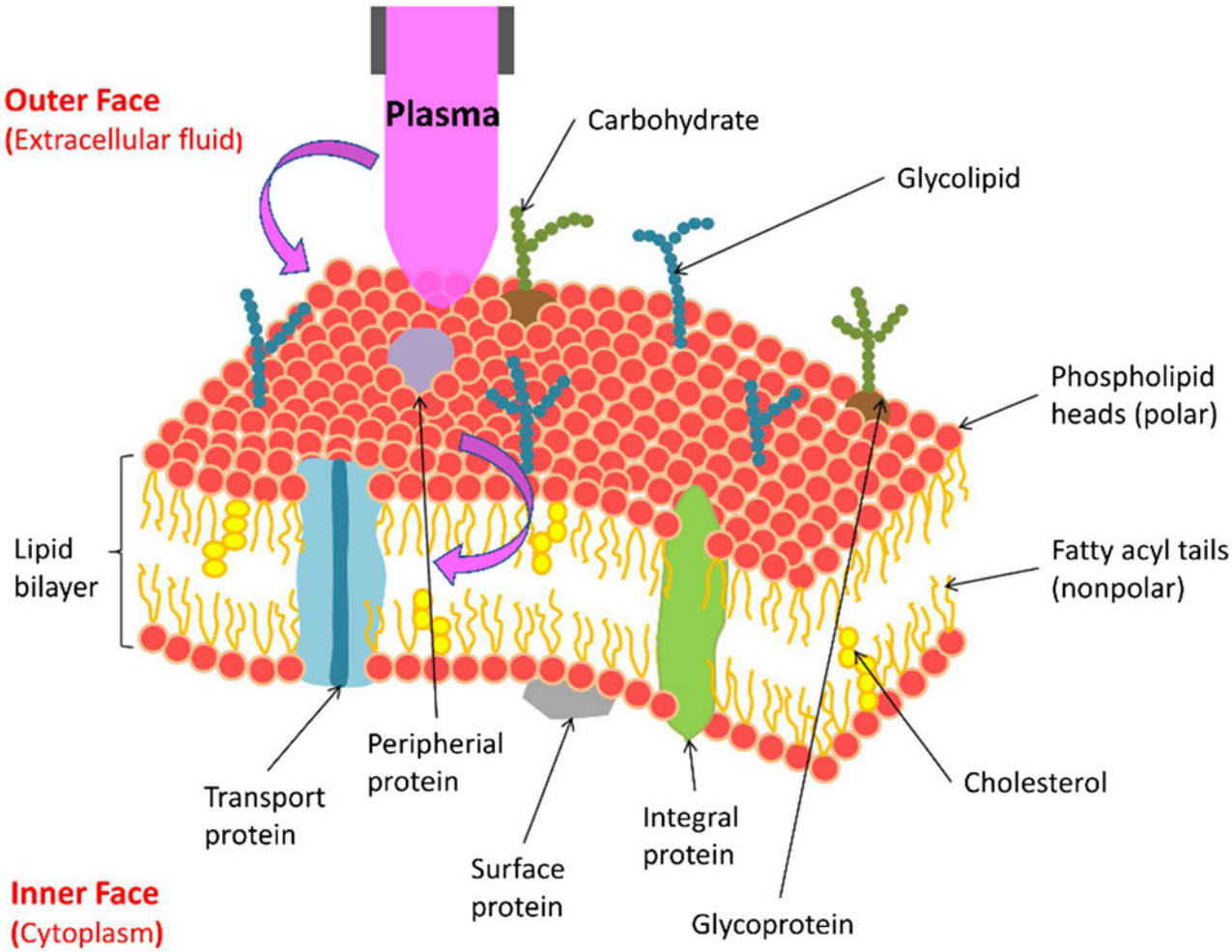

Figure 5. Schematic diagram of cell membranes in microorganisms with direct plasma attack.

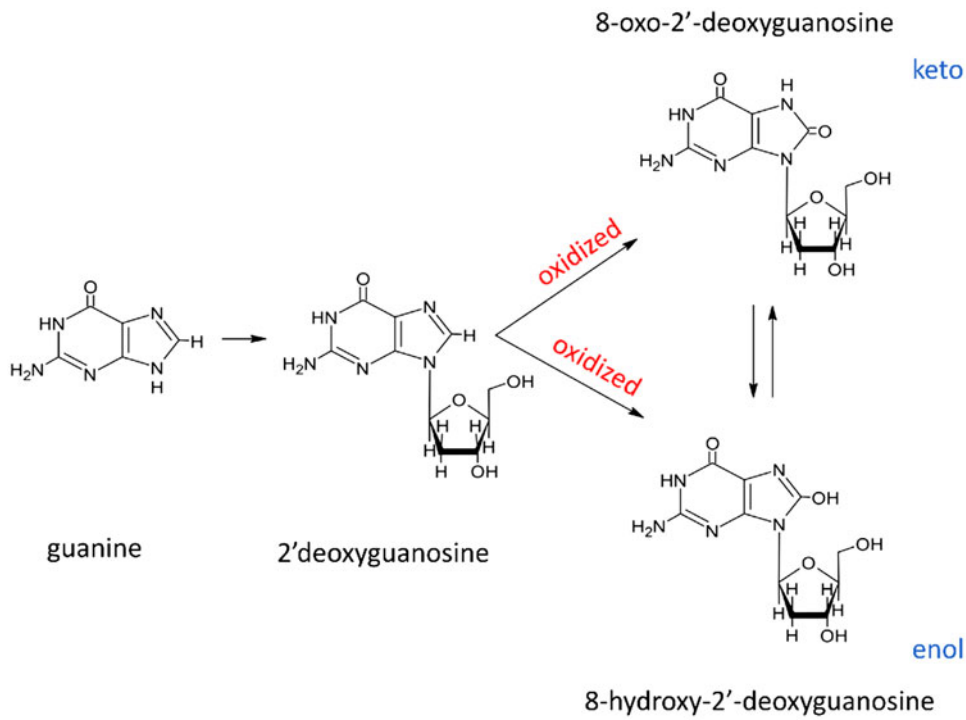

Figure 6. Formation of 8-xox-2′-deoxyguanosine (8oxodG) and 8-hydroxy-2′-deoxygyanosine (8OHdG) in DNA.

deoxyguanosine (8oxodG) or 8-hydroxy-2'-deoxyguanosine (8OHdG). Therefore, an oxidative product of guanine is usually regarded as an indicator of oxidative DNA damage. Currently, the determinations of oxidative DNA damage usually involve high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), and mass spectroscopy (Dizdaroglu, Coskun, and Jaruga 2015).

Regarding the DNA damage in atmospheric-pressure glow discharges (APGDs), Li et al. (2008) demonstrated that chemical active species are responsible for the breakdown of double chains in the DNA, rather than heat, intense electric field, charged particles and ultraviolet radiation. The extent of the damage depends on the plasma operating conditions, such as gas flow rate, power input, process distance, and exposure time. DNA strand breaks increase when the distance between plasma nozzle and DNA samples decrease, or by increasing exposure time (Han et al. 2014).

To further understand the mechanisms of DNA damage by plasma, Ptasińska et al. (2010) studied the effect of different plasma activated species (excited atoms, charged particles, electrons and UV light) on molecular DNA. Extrachromosomal plasmid DNA was extracted from *E. coli* and then purified to only a small amount of residual protein. After that, DNA was dissolved in autoclaved ultra-pure water (200 ng μL^{-1}) and every 2 µg of DNA solution was deposited on mica plates and dried at room temperature. Samples of DNA were exposed perpendicularly to a cold plasma jet of helium (He) for different periods. The total percentage damage to the DNA by positive ions, electrons, negative ions, excited and reactive species, and UV light, after 1 min-exposure to plasma were 8, 20, 62 and 10%, respectively. The result is in agreement with the study of Li et al. (2008), who attributed the breakdown to the chemical active species. O'Connell et al. (2011) used gel electrophoresis to further analyze the plasmid DNA damage process. A rate equation was fitted to quantify the rate of strand break formation (single and double strand). The density of atomic oxygen in the plasma correlated well with the formation of double strand breaks, and the neutral components can effectively induce double-strand breaks. Hepel et al. (2012) used the formation of guanine to 9-oxoguanine (8-oxoG) as an indicator to assess calf-thymus DNA damage. They reported that under physiological conditions both H_2O_2 and O_2^- in the plasma do not react directly with DNA components. However, the OH radical formed from H_2O_2 can easily penetrate cell membranes. The role of OH radicals in plasma DNA damage was studied by Nowicka et al. (2013). The attack of OH radicals on calf thymus DNA was investigated from biochemical and biosensor points of view. Radical activities corresponding to different nanomolar concentrations of H_2O_2 were detected by techniques such as UV – vis spectroscopy, atomic force microscopy (AFM), square wave voltammetry (SWV), electrochemical quartz crystal microbalance (EQCM) and circular dichroism (CD). The sensitivities of these techniques to radical concentrations and thickness of DNA layers were different. EQCM is the most sensitive in monitoring the actions of OH radicals. When the concentrations of H_2O_2 were higher than 1 µM, AFM and SWV could also detect the responses. As detected by EQCM, DNA strands were disintegrated locally under relatively high H_2O_2 concentrations (higher than 1 µM). This damage caused by OH radicals can be practically prevented in the presence of α-tocopherol, which is a strong antioxidant. DNA structure changes from a atmospheric pressure plasma jet (APPJ) was also investigated (Yan et al. 2009). With the use of agrose gel electrophoresis, DNA topology alteration after plasma treatment was observed. The percentage of supercoiled plasmid DNA was reduced, and the percentage of pen circular and linearized plasmid DNA forms increased. However, the genes of plasmid DNA were not affected by APPJ. The deformation effect of plasma with different feeding gases (air, N_2 and Ar) on calf thymus DNA was also investigated by Attri et al. (2015), and the results showed that N_2 has a stronger deformation effect on DNA compared to other plasma gases.

Lipid oxidation

Lipid oxidation in food can produce undesirable flavors and potentially toxic and harmful compounds (Gavahian et al. 2018). This oxidation is known to be proceeded by free radical chain reactions, where the molecular oxygen reacts with unsaturated lipids to form lipid peroxides. As reported by Decker, Faustman, and Lopez-Bote (2000), four stages are involved in these reactions: initiating, propagation, branching and termination. When a hydrogen atom is abstracted from a fatty acid molecule (LH) to form a lipid radical (L*), the initiation of lipid oxidation occurs. For example, high reactive OH* produced by high energy irradiated aqueous solutions can initiate lipid peroxidation (Hall et al. 2016). Then L* reacts with molecular oxygen (O_2) to form a lipid peroxy radical (LOO*), LOO* abstracts a hydrogen atom from another unsaturated LH and propagates the reaction. The formation of lipid hydroperoxides (LOOH) may undergo homolytic scission forming alkoxyl (LO*) and hydroxyl radicals (OH*) that can propagate further oxidation, leading to chain branching. After that, in the termination stage, the reaction of free radicals (LOO* and L*) forms non-initiation and non-propagating products. The free radical chain reaction is terminated by chain-breaking antioxidants (AH) by donating hydrogen atoms to free radical species and forming less reactive products.

To understand the interaction of plasma with food lipids and the critical parameters governing lipid oxidation, Sarangapani et al. (2017) studied cold plasma induced lipid (dairy and meat fat) oxidation using (FTIR), 1 H NMR and chromatographic techniques. After plasma treatment of 30 min, the oxidative damage in the lipids were found as to be a function of the applied voltage level. Reactive species (such as singlet oxygen and hydrogen peroxide-like species) in non-thermal DBD plasma were responsible for the membrane lipid peroxide in *Escherichia coli* (Joshi et al. 2011), and the extent of lipid peroxide was significantly inhibited by ROS scavengers (such as α-tocopherol/vitamin E).

Table 3. Possible protein reactive reactions as catalyzed by oxidizing lipids (Decker, Faustman, and Lopez-Bote 2000).

Stages		Reactions
Stage 1	Initiation	$L \rightarrow L^*$
Stage 2	Propagation	$L^* + O_2 \rightarrow LOO^*$
Stage 3	Hydrogen Abstraction	$LOO^* + P \rightarrow LOOH + P^*$ (CH)
Stage 4	Addition	$LOO^* + P \rightarrow {}^*LOOP$
Stage 5	Complex	$^*LOOP + P + O_2 \rightarrow {}^*POOLOOP$
Stage 6	Polymerization	$P\text{-}P^* + P^* + P \rightarrow P\text{-}P\text{-}P^* + P\text{-}P\text{-}P$

Note: L = lipid, P = protein.

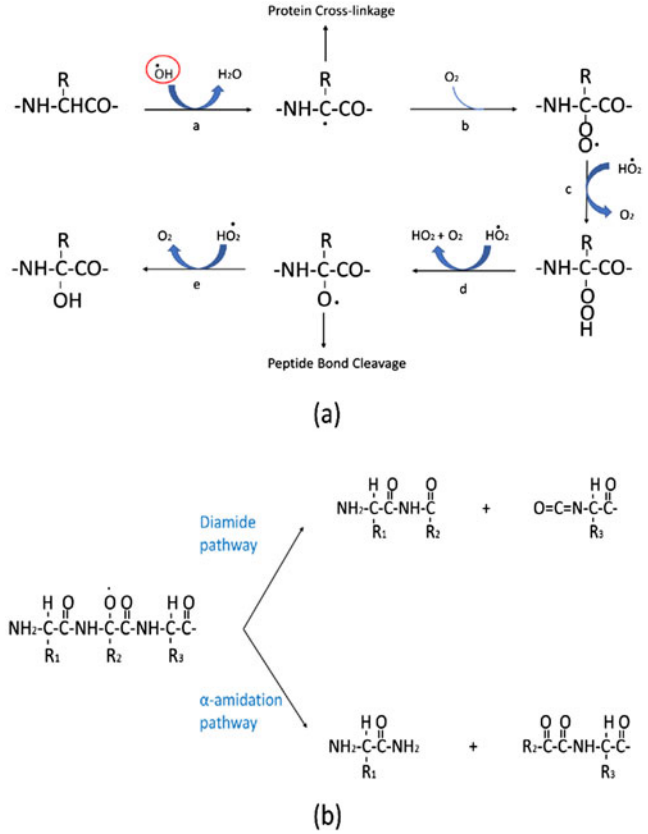

Figure 7. Mechanisms of protein oxidation: (a) oxidative attach by oxygen free radical on polypeptide backbone (b) peptide bond cleavage.

Protein and enzyme oxidation

In the presence of oxidizing lipids, protein oxidation is manifested by free radical chain reactions (Table 3) similar to those for lipid oxidation. As reported by Amos et al. (2015), amino acids of proteins are subject to attack from free radicals and non-free radicals, however, each amino acid is not equality susceptible to the reactive species. Free radicals attack proteins amino acids side chains and the peptide backbone. The amino acids with reactive side chains (such as sulfoxide, methionine, amino group, imidazole ring and indole ring) are particularly susceptible to oxidation initiated by oxidized lipids and their products (Soladoye et al. 2015). Therefore, cysteine, methionine, lysine, arginine, histidine and tryptophan are the common target amino acids of ROS in protein oxidation.

Peptide scission is a general pathway of ROS-initiated protein oxidation. As shown in Figure 7a, *OH abstracts hydrogen atoms from the α-carbon of the polypeptide backbone. The resulting alkyls radicals react with O_2 to form alkyl radicals, which are converted to alkyl peroxide via reaction with free peroxy radicals or abstraction of a hydrogen atom from another source. The protein alkyl peroxide is then converted to alkoxy protein derivatives via different mechanisms: dismutation, reaction with free peroxy radical or reaction with Fe^{2+}. The alkoxy radical then converts to hydroxyl derivatives, which undergo peptide bond scission either by α-amidation pathway or by diamide pathway, as shown in Figure 7b (Davies 2016; Oh and Moon 2015).

Yasuda et al. (2008) observed the prominent protein denaturation activity in *E. coli* in the early stage of DBD treatment, which is regarded as playing an important role in the inactivation of plasma bacteria and bacteriophages. The irreversible denaturation of the protein tertiary structure or chemical modifications were caused by oxidation or reduction but did not relate to the degradation of peptide bonds. In the protein reduction process, the plasma gas mixture and the thickness of the protein sample directly influenced the inactivation rate. According to Deng, Shi, and Kong (2007), different amounts of oxygen additions to helium gas in atmospheric pressure glow discharges (APGD) can achieve different protein reduction rates, up to 4.5 log CFU/g. Typical biphasic reduction kinetics of surface protein is highly affected by the protein thickness. A synergistic effect between these two factors is possibly responsible for the most effective reduction of protein. Attri et al. (2015) also studied the effect of different feeding gases in plasma on the modification of proteins hemoglobin (Hb) and myoglobin and amino acids. Results showed that N_2 has a stronger deformation effect on protein compared to other plasma gases.

Plasma processes can also influence the activities of enzymes. Misra et al. (2016) concluded that the inactivation of enzymes by cold plasma depends mainly on the power input of the discharge, exposure to reactive species, characteristics of the enzymes (structural complexity and stability), and mass transfer between the liquid and plasma phase. By myriad action, chemical constituents in the plasma are able to break down specific bonds or modify side chains, leading to the loss of protein secondary structure and accordingly inactivating enzymes. As demonstrated by Takai et al. (2012), the changes of protein secondary structure are caused by the increased molecular weight of enzyme within chemical reactions. The results suggested that reactive species produced in plasma affect the lysozyme instead of the UV light or plasma heat. Li et al. (2011) studied the sublethal effect of radio-frequency and atmospheric-pressure glow discharge plasma jet on the activities of lipase. After treatment using a plasma jet for one minute, the lipase activity significantly increased. Compared with heat, charged particles, UV radiation, intensified electric field, and ozone, the chemically reactive species in the plasma jet are the main factors attributed to the secondary and tertiary structure changes of lipase. In the inactivation process of soybean trypsin inhibitor (which is an important anti-nutritional factor in soybeans) by dielectric-barrier discharge (DBD) plasma, the enzyme activity was reduced by 86.1% after exposure for 21 min at 51.4 W (Li et al. 2017b).

Surface modification and functionality changes

Initially, the effect of plasma on surface modification was widely investigated for organic polymers and textile fabrics (Tsougeni et al. 2009). By modifying the material's surface energy, plasma treatments can produce different surface characteristics.

In food applications, the surface properties are usually expressed as hydrophilicity or hydrophobicity. Misra et al. (2014a) investigated the potential of non-thermal dielectric barrier discharge (DBD) plasma on the modification of surface hydrophobicity or hydrophobicity on freshly baked biscuits. By using a digital image analysis technique to measure the spread area of individual oil drops on the biscuit surface, the spread area was shown to exponential increase with respect to exposure time at 80 kV. Li et al. (2017b) showed that after the plasma treatment, the surface hydrophobicity of Kunitz-type trypsin inhibitor from soybean was reduced. However, the surface energy and the hydrophilicity of starch granules were increased by plasma treatment (Thirumdas, Kadam, and Annapure 2017a).

The effect of dielectric barrier discharge atmospheric pressure cold plasma (ACP) on the properties of wheat flour was also studied (Misra et al. 2015). Reactive oxygen species and reactive nitrogen spices excited during the process were evaluated by OEM and ozone measurement. Based on mixographs, the dough strength and optimum mixing time for flour showed an important improvement after the plasma treatment. With increased treatment time and voltage, the elastic and viscous moduli of wheat flour increased gradually. On the other hand, the changes of the secondary structure in protein were detected by FTIR spectroscopy. In wheat flour (both strong and weak), an increases of α-helix and β-turns and a decrease in β-sheet were observed.

Starch modification is another application of plasma that has been investigated. Due to the reactions of depolymerization and cross lining of amylose and amylopectin side chains, viscosity, molecular weight, and gelatinization temperatures of treated starch are changed (Thirumdas, Kadam, and Annapure 2017a). After rice starch treated by radio frequency powered air plasma at 40 and 60 W, an increase in the pasting viscosity and final viscosity of the treated starch was examined using a Rapid Visco Analyser, and a decrease in the retrogradation tendency of starch gels was observed from the G; and G" modulus (Thirumdas, Kadam, and Annapure 2017a).

Food quality preservations

Chemical reactions between reactive species and food components in plasma process can lead to positive effects on food postharvest quality preservation.

Ramazzina et al. (2015) investigated the effect of atmospheric DBD cold plasma on the postharvest quality preservation of kiwifruits. Each side of the fresh-cut kiwifruits were treated by air plasma (voltage from 2 to 9 V) for 10 and 20 min, and then their quality (visual appearance, texture, chlorophyl, and content of carotenoids and polyphenols) were evaluated during 4 days of storage. Results showed that the plasma process positively influenced the postharvest quality of kiwifruit by improving color retention, reducing dark area formation and not inducing any textural changes during 4 days of storage, although a slight pigment loss was observed. The influence of atmospheric air DBD plasma on fresh-cut Pink Lady apples was also investigated by treating the samples for 10, 20, and 30 min (Tappi et al. 2014). Their corresponding changes of qualitative and metabolic parameters were evaluated during 24 h storage. With the treatment for 30 min, a 65% decrease of the browning area in fresh-cut apples were observed, compared to the control after 4 h of storage. The total reductions of PPO activity ranged from 12 to 58%. By increasing treatment times, polyphenol oxidase activity decreased linearly. Additionally, the metabolic activity of the apple tissue was also slowed down. The effect of plasma was studied on apple juice as well. Rodríguez et al. (2017) investigated the effect of indirect cold plasma processing (carried out at flow rate of 10, 20, 30 mL/min, with treatment time of 5, 10, 15 min, respectively) on the quality of apple juice. The plasma treatment increased the contents of vitamin C, polyphenols and flavonoids content, as well as the polyphenol activities of the product.

Knowledge gaps and future trends

Plasma as a new state of matter has been discovered only about 100 years ago. Although it has been proposed to be a potential non-thermal alternative of traditional food microbial decontamination process, there are many unknowns which require further studies.

First, although plasma has been applied in a wide range of food products, these current applications are dominated by microbial inactivation. Given the effective microbial decontamination effect demonstrated using cold plasma, this technology is regarded as a potential alternative to conventional thermal-based technologies, such as pasteurization and sterilization (Ekezie, Sun, and Cheng 2017). It has been scientifically proved that plasma can provide effective inactivation of food microorganisms, both for bacteria, spores and viruses (Julák et al. 2011; Dirks et al. 2012). However, the interactions between the chemical reactive species of plasma and bacteria/biomolecules still require further elucidation (Klämpfl et al. 2012; Takai et al. 2012). For instance, there are a number of mechanisms of microbial inactivation that still needed to be elucidated: physical damage of the microbial cell, direct destruction of microbial DNA and modification of microbial genes (blocking expression process of protein). Investigations on microbial DNA changes after plasma processing can be approached from several points of view: DNA structure, sequence and quantification. Currently, 8oxodG and 8OHdG are commonly used as biomarkers in the evaluation of DNA damage (Han et al. 2014). HPLC, GC-MS and LC-MC and mass spectroscopy have also been employed to detect these biomarkers (Dizdaroglu, Coskun, and Jaruga 2015).

Second, chemical analysis of reactive species is essential to understand plasma's mechanisms of action. Currently, the

reactive species (such as ROS and RNS) during plasma treatment are regarded as the most responsible factors in microbial inactivation, biomolecular oxidation, surface modification and functionality changes. However, the lifetimes of most of the reactive species (such as singlet oxygen, hydroxyl radical, and peroxynitrite) are quite short, which introduces difficulties in plasma chemical analysis (Uchiyama et al. 2015). As described in Section 2.4.2, optical spectroscopy methods (such as OES, MBMS, EPR and fluorescent probe) are available techniques for this purpose. As OES is based on the measurement of the intensity of the radiation emission spectra, it can be utilized to detect the concentration of these chemical reactive species. The correspondent spectra line or bands for N, O, Ar (Chiper et al. 2011) and the reactive oxygen species and reactive nitrogen species in different plasma systems have been successfully evaluated (Misra et al. 2015; Walsh et al. 2010; Chung, Ra Kang, and Keun Bae 2012). MBMS is composed of a pumping stage system and a gas ionizer. The gas mixture at high-pressure chamber passes through small orifices towards a low-pressure chamber to form a molecule beam of particles which will be analyzed by mass spectroscopy. This method can provide information about both qualitative and quantitative aspects of the ROS in the stream (Ellerweg et al. 2010). EPR spin trapping can detect the reactive spices with very short lifetimes. Also, fluorescent probes are alternatives in the measurement of both ROS and RNS in the plasma stream (Kalyanaraman et al. 2012). Further studies about the effect of some specific plasma reactive species in food microbial decontamination process might be interesting. As some of these reactive species have very short lifetimes, and can react with others, it is hard to connect the decontamination effect to either individual reactive species if the food sample was treated by the gas mixture during the process. It is better to use chemical solutions or radical filters (e.g., UV filter) to remove the disturbing reactive species before the sample treatment and before the evaluation of other reactive species with minor oxidation effects.

Third, the effect of plasma process on food nutritional properties changes and on food chemical components modifications is also uncertain (Misra et al. 2014a). As food nutrients are susceptible to reactive species, the effects of plasma on food biomolecule modification can be investigated by chemical-based detection methods. In lipid peroxidation, OH * is regarded as the reactive species responsible for process initiation, which could be produced both by the decomposition of peroxynitrite and by the reaction of transition-metal with H_2O_2. Thiobarbituric acid (TBA) test is one of the most commonly available assays in lipid peroxidation through the measurement of malondialdehyde (MDA) formed during the process. The test sample is heated with TBA at low pH, and the absorbance of the pink chromogen (TBA2-malondialdehyde adduct) is measured (Frankel 2014). HPLC is another approach that can provide specific chemical information about the real occurrence of lipid oxidation, and it is available for the detection of lipid peroxides and cytotoxic aldehydes (Runas and Malmstadt 2015). Protein oxidation is also believed to be initiated mainly by reactions with OH*. Although various kinds of ROS have an effect on the modification of biological molecules, only OH*, O_2^{-}* and the mixture of both are made available (the oxidation process is determined by the accessibility of O_2, O_2^{-}* and HO_2*) (Davies 2016). Further studies in plasma induced protein oxidation should refer to the detailed oxidation pathways, such as the oxidation of amino acid side chains, oxidation of the protein backbone, and the formation of protein-protein cross-link-ages.

Conclusions

Plasma is a novel technique that has attracted a great deal of attention by researchers. In this paper, the interactions of plasma species with food components have been reviewed from a chemical aspect. Plasma reactions include; biomolecule oxidation, surface properties and functionality changes, as well as overall food quality indices. Additionally, the detection methods for reactive species are also mentioned as it is significant for plasma chemical components analysis. Strategies for further studies of the plasma process in the food industry are also proposed. In conclusion, there is a recommendation for further mechanistic studies of cold plasma processing based on chemical reactions, which would have a profound impact on our understanding of plasma processes.

Acknowledgments

The authors also wish to acknowledge the financial support by the JPI project ProHealth (Ref: 15/HDHL/1 PROHEALTH) “Innovative processing to preserve positive health effects in pelagic fish products”. The authors would like to acknowledge UCD-CSC Scholarship Scheme supported by University College Dublin (UCD) and China Scholarship Council (CSC) for this study.

References

Akhiezer, A. I. I., I. Akhiezer, and R. Polovin. 2017. *Collective oscillations in a plasma: International series of monographs in natural philosophy*. Pergamon: Elsevier.

Amos, R. I., B. Chan, C. J. Easton, and L. Radom. 2015. Hydrogen-atom abstraction from a model amino acid: dependence on the attacking radical. *The Journal of Physical Chemistry. B* 119 (3): 783–8.

Attri, P., N. Kumar, J. H. Park, D. K. Yadav, S. Choi, H. S. Uhm, I. T. Kim, E. H. Choi, and W. Lee. 2015. Influence of reactive species on the modification of biomolecules generated from the soft plasma. *Scientific Reports* 5 (1):8221.

Benedikt, J., D. Ellerweg, and A. Von Keudell. 2009. Molecular beam sampling system with very high beam-to-background ratio: The rotating skimmer concept. *Review of Scientific Instruments* 80 (5): 055107. doi: 10.1063/1.3133804.

Brayfield, R. S., S. M. Sanders, A. Jassem, M. Lauria, A. L. Garner, and K. M. Keener. 2016. *Optical absorption spectroscopy of high voltage, cold atmospheric pressure plasmas. Plasma Science (ICOPS), 2016 IEEE International Conference on, IEEE*, 1.

Bruggeman, P., N. Sadeghi, D. Schram, and V. Linss. 2014. Gas temperature determination from rotational lines in non-equilibrium plasmas: a review. *Plasma Sources Science and Technology* 23 (2): 023001. doi: 10.1088/0963-0252/23/2/023001.

Cheng, X., J. Sherman, W. Murphy, E. Ratovitski, J. Canady, and M. Keidar. 2014. The effect of tuning cold plasma composition on glioblastoma cell viability. *PloS One* 9 (5):e98652.

Chiper, A. S., W. Chen, O. Mejlholm, P. Dalgaard, and E. Stamate. 2011. Atmospheric pressure plasma produced inside a closed package by a dielectric barrier discharge in Ar/CO2 for bacterial inactivation of biological samples. *Plasma Sources Science and Technology* 20 (2):025008. doi: 10.1088/0963-0252/20/2/025008.

Chung, T., H. Ra Kang, and M. Keun Bae. 2012. Optical emission diagnostics with electric probe measurements of inductively coupled Ar/O2/Ar-O2 plasmas. *Physics of Plasmas* 19 (11):113502. doi: 10.1063/1.4765357.

Cullen, P. J., J. Lalor, L. Scally, D. Boehm, V. Milosavljević, P. Bourke, and K. Keener. 2018. Translation of plasma technology from the lab to the food industry. *Plasma Processes and Polymers* 15 (2):1700085. doi: 10.1002/ppap.201700085.

Davies, M. J. 2016. Protein oxidation and peroxidation. *The Biochemical Journal* 473 (7):805–25.

Decker, E. A., C. Faustman, and C. J. Lopez-Bote. 2000. *Antioxidants in muscle foods: Nutritional strategies to improve quality*. New York: John Wiley & Sons.

Deng, X., J. Shi, and M. G. Kong. 2007. Protein destruction by a helium atmospheric pressure glow discharge: Capability and mechanisms. *Journal of Applied Physics* 101 (7):074701. doi: 10.1063/1.2717576.

Dirks, B. P., D. Dobrynin, G. Fridman, Y. Mukhin, A. Fridman, and J. J. Quinlan. 2012. Treatment of raw poultry with nonthermal dielectric barrier discharge plasma to reduce Campylobacter jejuni and Salmonella enterica. *Journal of Food Protection* 75 (1):22–8. doi: 10.4315/0362-028X.JFP-11-153.

Dizdaroglu, M., E. Coskun, and P. Jaruga. 2015. Measurement of oxidatively induced DNA damage and its repair, by mass spectrometric techniques. *Free Radical Research* 49 (5):525–48. doi: 10.3109/10715762.2015.1014814.

Dünnbier, M., A. Schmidt-Bleker, J. Winter, M. Wolfram, R. Hippler, K. Weltmann, and S. Reuter. 2013. Ambient air particle transport into the effluent of a cold atmospheric-pressure argon plasma jet investigated by molecular beam mass spectrometry. *Journal of Physics D: Applied Physics* 46 (43):435203. doi: 10.1088/0022-3727/46/43/435203.

Ekezie, F.-G, C. D.-W. Sun, and J.-H. Cheng. 2017. A review on recent advances in cold plasma technology for the food industry: current applications and future trends. *Trends in Food Science & Technology* 69:46–58.

Ekezie F.-G. C, J.-H. Cheng and D.-W. Sun. 2018. Effects of Mild Oxidative and Structural Modifications Induced by Argon-Plasma on Physicochemical Properties of Actomyosin from King Prawn (*Litopenaeus Vannamei*). *Journal of Agricultural and Food Chemistry* 66 (50):13285–13294.

Ekezie F.-G. C, J.-H. Cheng and D.-W. Sun. 2019. Effects of Atmospheric Pressure Plasma Jet on the Conformation and Physicochemical Properties of Myofibrillar Proteins from King Prawn (*Litopenaeus vannamei*). *Food Chemistry* 276:147–156.

Ellerweg, D., J. Benedikt, A. VON Keudell, N. Knake, and V. Schulz-Von Der Gathen. 2010. Characterization of the effluent of a He/O2 microscale atmospheric pressure plasma jet by quantitative molecular beam mass spectrometry. *New Journal of Physics* 12 (1):013021. doi: 10.1088/1367-2630/12/1/013021.

Fernandez, A., E. Noriega, and A. Thompson. 2013. Inactivation of Salmonella enterica serovar typhimurium on fresh produce by cold atmospheric gas plasma technology. *Food Microbiology* 33:24–9. doi: 10.1016/j.fm.2012.08.007.

Frankel, E. N. 2014. *Lipid oxidation*. UK: Elsevier.

Friedl, R., and U. Fantz. 2012. Spectral intensity of the N2 emission in argon low-pressure arc discharges for lighting purposes. *New Journal of Physics* 14 (4):043016. doi: 10.1088/1367-2630/14/4/043016.

Gavahian, M., Y.-H. Chu, A. M. Khaneghah, F. J. Barba, and N. Misra. 2018. A critical analysis of the cold plasma induced lipid oxidation in foods. *Trends in Food Science & Technology* 77:32–41.

Georgescu, N., L. Apostol, and F. Gherendi. 2017. Inactivation of Salmonella enterica serovar typhimurium on egg surface, by direct and indirect treatments with cold atmospheric plasma. *Food Control* 76:52–61.

Gorbanev, Y., and A. Bogaerts. 2018. *Chemical detection of short-lived species induced in aqueous media by atmospheric pressure plasma. Atmospheric Pressure Plasma*. London, UK: IntechOpen.

Graves, D. B. 2012. The emerging role of reactive oxygen and nitrogen species in redox biology and some implications for plasma applications to medicine and biology. *Journal of Physics D: Applied Physics* 45 (26):263001. doi: 10.1088/0022-3727/45/26/263001.

Hall, E. D., J. A. Wang, J. M. Bosken, and I. N. Singh. 2016. Lipid peroxidation in brain or spinal cord mitochondria after injury. *Journal of Bioenergetics and Biomembranes* 48 (2):169–74.

Han, X., W. A. Cantrell, E. E. Escobar, and S. Ptasinska. 2014. Plasmid DNA damage induced by helium atmospheric pressure plasma jet. *European Physical Journal D* 68:1–7.

Han Y.-X., J.-H. Cheng and D.-W. Sun. 2019. Activities and Conformation Changes of Food Enzymes Induced by Cold Plasma: A Review. *Critical Reviews in Food Science and Nutrition*. doi: 10.1080/10408398.2018.1555131.

Hepel, M., M. Stobiecka, J. Peachey, and J. Miller. 2012. Intervention of glutathione in pre-mutagenic catechol-mediated DNA damage in the presence of copper (II) ions. *Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis* 735 (1–2):1–11. doi: 10.1016/j.mrfmmm.2012.05.005.

Hübner, S., J. S. Sousa, J. VAN DER Mullen, and W. G. Graham. 2017. Thomson scattering on non-thermal atmospheric pressure plasma jets. *Plasma Sources Science and Technology* 24 (5):054005. doi: 10.1088/0963-0252/24/5/054005.

Jiang, T., L. Feng, and J. Li. 2012. Changes in microbial and postharvest quality of shiitake mushroom (Lentinus edodes) treated with chitosan–glucose complex coating under cold storage. *Food Chemistry* 131 (3):780–6. doi: 10.1016/j.foodchem.2011.08.087.

Joshi, S. G., M. Cooper, A. Yost, M. Paff, U. K. Ercan, G. Fridman, G. Friedman, A. Fridman, and A. D. Brooks. 2011. Nonthermal dielectric-barrier discharge plasma-induced inactivation involves oxidative DNA damage and membrane lipid peroxidation in Escherichia coli. *Antimicrobial Agents and Chemotherapy* 55 (3):1053–62. doi: 10.1128/AAC.01002-10.

Julák, J., O. Janoušková, V. Scholtz, and K. Holada. 2011. Inactivation of prions using electrical DC discharges at atmospheric pressure and ambient temperature. *Plasma Processes and Polymers* 8 (4):316–23. doi: 10.1002/ppap.201000100.

Kalyanaraman, B., V. Darley-Usmar, K. J. Davies, P. A. Dennery, H. J. Forman, M. B. Grisham, G. E. Mann, K. Moore, L. J. Roberts, and H. Ischiropoulos. 2012. Measuring reactive oxygen and nitrogen species with fluorescent probes: challenges and limitations. *Free Radical Biology and Medicine* 52 (1):1–6. doi: 10.1016/j.freeradbiomed.2011.09.030.

Kim, J. E., D.-U. Lee, and S. C. Min. 2014. Microbial decontamination of red pepper powder by cold plasma. *Food Microbiology* 38:128–36.

Klämpfl, T. G., G. Isbary, T. Shimizu, Y.-F. Li, J. L. Zimmermann, W. Stolz, J. Schlegel, G. E. Morfill, and H.-U. Schmidt. 2012. Cold atmospheric air plasma sterilization against spores and other microorganisms of clinical interest. *Applied and Environmental Microbiology* 78 (15):5077–82. doi: 10.1128/AEM.00583-12.

Lacombe, A., B. A. Niemira, J. B. Gurtler, X. Fan, J. Sites, G. Boyd, and H. Chen. 2015. Atmospheric cold plasma inactivation of aerobic microorganisms on blueberries and effects on quality attributes. *Food Microbiology* 46:479–84. doi: 10.1016/j.fm.2014.09.010.

Laroussi, M., and F. Leipold. 2004. Evaluation of the roles of reactive species, heat, and UV radiation in the inactivation of bacterial cells by air plasmas at atmospheric pressure. *International Journal of Mass Spectrometry* 233 (1–3):81–6. doi: 10.1016/j.ijms.2003.11.016.

Lee, H., J. E. Kim, M.-S. Chung, and S. C. Min. 2015. Cold plasma treatment for the microbiological safety of cabbage, lettuce, and dried figs. *Food Microbiology* 51:74–80.

Li, G., H.-P. Li, L.-Y. Wang, S. Wang, H.-X. Zhao, W.-T. Sun, X.-H. Xing, and C.-Y. Bao. 2008. Genetic effects of radio-frequency,

atmospheric-pressure glow discharges with helium. *Applied Physics Letters* 92 (22):221504. doi: 10.1063/1.2938692.

Li, H. P., L. Y. Wang, G. Li, L. H. Jin, P. S. Le, H. X. Zhao, X. H. Xing, and C. Y. Bao. 2011. Manipulation of lipase activity by the helium radio-Frequency, Atmospheric-Pressure glow discharge plasma jet. *Plasma Processes and Polymers* 8 (3):224–9. doi: 10.1002/ppap.201000035.

Li, J. G., Q. S. Xiang, X. F. Liu, T. Ding, X. S. Zhang, Y. F. Zhai, and Y. H. Bai. 2017. Inactivation of soybean trypsin inhibitor by dielectric-barrier discharge (DBD) plasma. *Food Chemistry* 232:515–22. doi: 10.1016/j.foodchem.2017.03.167.

Lu, X., G. Naidis, M. Laroussi, S. Reuter, D. Graves, and K. Ostrikov. 2016. Reactive species in non-equilibrium atmospheric-pressure plasmas: Generation, transport, and biological effects. *Physics Reports* 630:1–84. doi: 10.1016/j.physrep.2016.03.003.

Lunec, J., and H. R. Griffiths. 2000. *Measuring in vivo oxidative damage: a practical approach*. Chichester: Wiley.

Ma, L., M. Zhang, B. Bhandari, and Z. Gao. 2017. Recent developments in novel shelf life extension technologies of fresh-cut fruits and vegetables. *Trends in Food Science & Technology* 64:23–38.

Mir, S.A., M. A. Shah, and M. M. Mir. 2016. Understanding the role of plasma technology in food industry. *Food and Bioprocess Technology* 9:734–750.

Misra, N., T. Moiseev, S. Patil, S. Pankaj, P. Bourke, J. Mosnier, K. Keener, and P. Cullen. 2014. Cold plasma in modified atmospheres for post-harvest treatment of strawberries. *Food and bioprocess technology* 7:3045–3054.

Misra, N., S. Kaur, B. K. Tiwari, A. Kaur, N. Singh, and P. Cullen. 2015. Atmospheric pressure cold plasma (ACP) treatment of wheat flour. *Food Hydrocolloids* 44:115–21. doi: 10.1016/j.foodhyd.2014.08.019.

Misra, N., S. Pankaj, A. Segat, and K. Ishikawa. 2016. Cold plasma interactions with enzymes in foods and model systems. *Trends in Food Science & Technology* 55:39–47. doi: 10.1016/j.tifs.2016.07.001.

Misra, N., C. Sullivan, S. Pankaj, L. Alvarez-Jubete, R. Cama, F. Jacoby, and P. Cullen. 2014a. Enhancement of oil spreadability of biscuit surface by nonthermal barrier discharge plasma. *Innovative Food Science & Emerging Technologies* 26:456–61.

Misra, N. N., K. M. Keener, P. Bourke, J.-P. Mosnier, and P. J. Cullen. 2014. In-package atmospheric pressure cold plasma treatment of cherry tomatoes. *Journal of Bioscience and Bioengineering* 118 (2):177–82. doi: 10.1016/j.jbiosc.2014.02.005.

Moiseev, T., N. Misra, S. Patil, P. Cullen, P. Bourke, K. Keener, and J. Mosnier. 2014. Post-discharge gas composition of a large-gap DBD in humid air by UV–Vis absorption spectroscopy. *Plasma Sources Science and Technology* 23 (6):065033. doi: 10.1088/0963-0252/23/6/065033.

Nikiforov, A. Y., C. Leys, M. Gonzalez, and J. Walsh. 2015. Electron density measurement in atmospheric pressure plasma jets: Stark broadening of hydrogenated and non-hydrogenated lines. *Plasma Sources Science and Technology* 24 (3):034001. doi: 10.1088/0963-0252/24/3/034001.

Novák, I., A. Popelka, A. S. Luyt, M. M. Chehimi, M. Špírková, I. Janigová, A. Kleinová, P. Stopka, M. Šlouf, V. Vanko, et al. 2013. Adhesive properties of polyester treated by cold plasma in oxygen and nitrogen atmospheres. *Surface and Coatings Technology* 235:407–16. doi: 10.1016/j.surfcoat.2013.07.057.

Nowicka, A. M., A. Kowalczyk, S. Sek, and Z. Stojek. 2013. Oxidation of DNA followed by conformational change after OH radical attack. *Analytical Chemistry* 85 (1):355–61.

O'Connell, D., L. Cox, W. Hyland, S. Mcmahon, S. Reuter, W. Graham, T. Gans, and F. Currell. 2011. Cold atmospheric pressure plasma jet interactions with plasmid DNA. *Applied Physics Letters* 98:043701. doi: 10.1063/1.3521502.

Oh, H. B., and B. Moon. 2015. Radical-driven peptide backbone dissociation tandem mass spectrometry. *Mass Spectrometry Reviews* 34 (2):116–32. doi: 10.1002/mas.21426.

Patil, S., T. Moiseev, N. N. Misra, P. J. Cullen, J. P. Mosnier, K. M. Keener, and P. Bourke. 2014. Influence of high voltage atmospheric cold plasma process parameters and role of relative humidity on inactivation of Bacillus atrophaeus spores inside a sealed package. *Journal of Hospital Infection* 88 (3):162–9. doi: 10.1016/j.jhin.2014.08.009.

Pignata, C., D. D'Angelo, E. Fea, and G. Gilli. 2017. A review on microbiological decontamination of fresh produce with nonthermal plasma. *Journal of Applied Microbiology* 122 (6):1438–55. doi: 10.1111/jam.13412.

Ptasińska, S., B. Bahnev, A. Stypczyńska, M. Bowden, N. J. Mason, and N. S. J. Braithwaite. 2010. DNA strand scission induced by a non-thermal atmospheric pressure plasma jet. *Physical Chemistry Chemical Physics* 12 (28):7779–81. doi: 10.1039/c001188f.

Ramazzina, I., A. Berardinelli, F. Rizzi, S. Tappi, L. Ragni, G. Sacchetti, and P. Rocculi. 2015. Effect of cold plasma treatment on physico-chemical parameters and antioxidant activity of minimally processed kiwifruit. *Postharvest Biology and Technology* 107:55–65. doi: 10.1016/j.postharvbio.2015.04.008.

Reuter, S., J. S. Sousa, G. D. Stancu, and J.-P. H. van Helden. 2015. Review on VUV to MIR absorption spectroscopy of atmospheric pressure plasma jets. *Plasma Sources Science and Technology* 24 (5):054001. doi: 10.1088/0963-0252/24/5/054001.

Reuter, S., J. Winter, A. Schmidt-Bleker, D. Schroeder, H. Lange, N. Knake, V. Schulz-von der Gathen, and K. Weltmann. 2012. Atomic oxygen in a cold argon plasma jet: TALIF spectroscopy in ambient air with modelling and measurements of ambient species diffusion. *Plasma Sources Science and Technology* 21 (2):024005. doi: 10.1088/0963-0252/21/2/024005.

Rodríguez, Ó., W. F. Gomes, S. Rodrigues, and F. A. Fernandes. 2017. Effect of indirect cold plasma treatment on cashew apple juice (Anacardium occidentale L.). *LWT-Food Science and Technology* 84:457–463.

Runas, K. A., and N. Malmstadt. 2015. Low levels of lipid oxidation radically increase the passive permeability of lipid bilayers. *Soft Matter* 11 (3):499–505. doi: 10.1039/C4SM01478B.

Sarangapani, C., D. R. Keogh, J. Dunne, P. Bourke, and P. Cullen. 2017. Characterisation of cold plasma treated beef and dairy lipids using spectroscopic and chromatographic methods. *Food Chemistry* 235:324–33. doi: 10.1016/j.foodchem.2017.05.016.

Schmidt-Bleker, A., S. Reuter, and K.-D. Weltmann. 2014b. Non-dispersive path mapping approximation for the analysis of ambient species diffusion in laminar jets. *Physics of Fluids* 26 (8):083603. doi: 10.1063/1.4893573.

Schmidt, J. B., S. Roy, W. D. Kulatilaka, I. Shkurenkov, I. V. Adamovich, W. R. Lempert, and J. R. Gord. 2017. Femtosecond, two-photon-absorption, laser-induced-fluorescence (fs-TALIF) imaging of atomic hydrogen and oxygen in non-equilibrium plasmas. *Journal of Physics D: Applied Physics* 50 (1):015204.

Schneider, S., M. Dünnbier, S. Hübner, S. Reuter, and J. Benedikt. 2014. Atomic nitrogen: a parameter study of a micro-scale atmospheric pressure plasma jet by means of molecular beam mass spectrometry. *Journal of Physics D: Applied Physics* 47 (50):505203. doi: 10.1088/0022-3727/47/50/505203.

Soladoye, O., M. Juárez, J. Aalhus, P. Shand, and M. Estévez. 2015. Protein oxidation in processed meat: mechanisms and potential implications on human health. *Comprehensive Reviews in Food Science and Food Safety* 14:106–22. doi: 10.1111/1541-4337.12127.

Surowsky, B., O. Schlüter, and D. Knorr. 2015. Interactions of non-thermal atmospheric pressure plasma with solid and liquid food systems: a review. *Food Engineering Reviews* 7 (2):82–108. doi: 10.1007/s12393-014-9088-5.

Takai, E., K. Kitano, J. Kuwabara, and K. Shiraki. 2012. Protein inactivation by low-temperature atmospheric pressure plasma in aqueous solution. *Plasma Processes and Polymers* 9 (1):77–82. doi: 10.1002/ppap.201100063.

Tappi, S., A. Berardinelli, L. Ragni, M. Dalla Rosa, A. Guarnieri, and P. Rocculi. 2014. Atmospheric gas plasma treatment of fresh-cut apples. *Innovative Food Science & Emerging Technologies* 21:114–22. doi: 10.1016/j.ifset.2013.09.012.

Thirumdas, R., D. Kadam, and U. Annapure. 2017a. Cold plasma: an alternative technology for the starch modification. *Food Biophysics* 12 (1):129–39. doi: 10.1007/s11483-017-9468-5.

Tsougeni, K., N. Vourdas, A. Tserepi, E. Gogolides, and C. Cardinaud. 2009. Mechanisms of oxygen plasma nanotexturing of organic polymer surfaces: from stable super hydrophilic to super hydrophobic surfaces. *Langmuir* 25 (19):11748–59. doi: 10.1021/la901072z.

Uchiyama, H., Q.-L. Zhao, M. A. Hassan, G. Andocs, N. Nojima, K. Takeda, K. Ishikawa, M. Hori, and T. Kondo. 2015. EPR-spin trapping and flow cytometric studies of free radicals generated using cold atmospheric argon plasma and X-ray irradiation in aqueous solutions and intracellular milieu. *Plos One* 10 (8):e0136956. doi: 10.1371/journal.pone.0136956.

van Gessel, A., E. Carbone, P. Bruggeman, and J. van der Mullen. 2012. Laser scattering on an atmospheric pressure plasma jet: disentangling Rayleigh, Raman and Thomson scattering. *Plasma Sources Science and Technology* 21 (1):015003. doi: 10.1088/0963-0252/21/1/015003.

van Ham, B., S. Hofmann, R. Brandenburg, and P. Bruggeman. 2014. In situ absolute air, O3 and NO densities in the effluent of a cold RF argon atmospheric pressure plasma jet obtained by molecular beam mass spectrometry. *Journal of Physics D: Applied Physics* 47 (22):224013. doi: 10.1088/0022-3727/47/22/224013.

Walsh, J. L., D. X. Liu, F. Iza, M. Z. Rong, and M. G. Kong. 2010. Contrasting characteristics of Sub-microsecond pulsed atmospheric air and atmospheric pressure helium–oxygen glow discharges. *Journal of Physics D: Applied Physics* 43 (3):032001. doi: 10.1088/0022-3727/43/3/032001.

Winter, J., K. Wende, K. Masur, S. Iseni, M. Dünnbier, M. Hammer, H. Tresp, K. Weltmann, and S. Reuter. 2013. Feed gas humidity: a vital parameter affecting a cold atmospheric-pressure plasma jet and plasma-treated human skin cells. *Journal of Physics D: Applied Physics* 46 (29):295401. doi: 10.1088/0022-3727/46/29/295401.

Xu, Y., Y. Tian, R. Ma, Q. Liu, and J. Zhang. 2016. Effect of plasma activated water on the postharvest quality of button mushrooms, Agaricus bisporus. *Food Chemistry* 197:436–44. doi: 10.1016/j.foodchem.2015.10.144.

Yan, X., F. Zou, X. P. Lu, G. He, M. J. Shi, Q. Xiong, X. Gao, Z. Xiong, Y. Li, F. Y. Ma, et al. 2009. Effect of the atmospheric pressure nonequilibrium plasmas on the conformational changes of plasmid DNA. *Applied Physics Letters* 95 (8):083702. doi: 10.1063/1.3212739.

Yasuda, H., M. Hashimoto, M. Rahman, K. Takashima, and A. Mizuno. 2008. States of biological components in bacteria and bacteriophages during inactivation by atmospheric dielectric barrier discharges. *Plasma Processes and Polymers* 5 (6):615–21. doi: 10.1002/ppap.200800036.

Yonemori, S., and R. Ono. 2014. Flux of OH and O radicals onto a surface by an atmospheric-pressure helium plasma jet measured by laser-induced fluorescence. *Journal of Physics D: Applied Physics* 47 (12):125401. doi: 10.1088/0022-3727/47/12/125401.

Ziuzina, D., S. Patil, P. J. Cullen, K. Keener, and P. Bourke. 2014. Atmospheric cold plasma inactivation of Escherichia coli, Salmonella enterica serovar typhimurium and Listeria monocytogenes inoculated on fresh produce. *Food Microbiology* 42:109–16. doi: 10.1016/j.fm.2014.02.007.