White paper on the future of plasma science in environment, for gas conversion and agriculture

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Climate change, environmental pollution control, and resource utilization efficiency, as well as food security, sustainable agriculture, and water supply are among the main challenges facing society today. Expertise across different academic fields, technologies, and disciplines is needed to generate new ideas to meet these challenges. This "white paper" aims to provide a written summary by describing the main aspects and possibilities of the technology. It shows that plasma science and technology can make significant contributions to address the mentioned issues. The paper also addresses to people in the scientific community (inside and outside plasma science) to give inspiration for further work in these fields.

KEYWORDS
clean food, nonthermal plasma, plasma-agriculture, plasma chemistry, plasma technology, pollution control

1 INTRODUCTION

Climate change, environmental pollution control, and resource utilization efficiency, as well as food security,
sustainable agriculture, and water supply are among the main challenges facing society today. Expertise across different academic fields, technologies, and disciplines is needed to generate new ideas to meet these challenges.\[^1\] The purpose of the present paper is to show that plasma science and technology can make significant contributions to address these issues.

In general, plasma processes can already be considered as inherently environmental technologies.\[^2\] Plasma processes enable resource saving through high energy utilization efficiency and thus, are environmentally friendly technologies, e.g., in surface cleaning and activation (e.g., for solvent-less painting). These surface treatment processes already make significant contributions to the economic prosperity and development of industrialized societies, as described and illustrated with different examples and commercial areas in the consensus paper.\[^3\] In addition, the direct use of plasmas in environmental technologies is established or under development and research. This white paper was prepared after comprehensive discussions among plasma scientists from all over the world during the “Future in Plasma Science” workshops. Figure 1 shows the graphical summary of the discussions prepared by a visual facilitator during the second meeting in 2016. The advantages and shortcomings of plasmas for environmental purposes (e.g., cleaning of water and air), and in agriculture were elucidated. New topics like solar fuel production and the possible role of plasma processes in sustainable product cycles were also considered. This “white paper” aims to provide a written summary to legislative and funding bodies by describing the main aspects and possibilities of the technology. Therefore, only short explanations of the physics, chemistry, or technologies are given, but the possible benefits and problems to be solved are addressed. However, the paper also addresses to people in the scientific community (inside and outside plasma science) to give inspiration for further work in these fields.

Plasmas have a large potential for the decontamination of gases and water. For example, technologies have been developed for the deodorization of gases and the removal of residues from drinking water supplies. This manuscript will focus on nonthermal plasmas, i.e., plasmas where thermal equilibrium is not reached and, thus, the different components are characterized by different mean kinetic energies. Since the gas temperature can remain moderate (e.g. at room temperature)
because the protection of the environment and natural resources are also requirements for sustainable agriculture, there is a strong link between these two fields. However, the topic “plasma and/or agriculture” has to be considered in a wider context. Plasma treatment of seeds can increase their germination rates and efficiencies and plasma can enhance plant growth. Seeds, food, and food processing tools can be protected from or decontaminated of fungi or bacteria. Furthermore, plasma chemistry may help to produce fertilizers or to enable sustainable material life cycles with its unique nonthermal character.

In the following text an introductory overview on the prospects and possibilities for plasma-based treatment of gases, liquids, seeds, fresh products, and soil, including decontamination and production of desirable chemical species in the context of environmental and agricultural challenges will be given. The state-of-the-art on plasma technology utilized in different fields is summarized, and an outlook on the future needs for fundamental and applied research is given. The paper will close with a general conclusion regarding the overriding important scientific challenges.

2 | PROCESS GAS AND WASTE GAS CLEANING

Plasma processes are used to clean gases containing a wide range of contaminants including particulate matter, microorganisms and viruses, and chemical compounds. The starting point of plasma-based technologies for gas cleaning was the development of electrostatic precipitators. In electrostatic precipitators, corona discharges are used for the removal of dust from flue gases by means of physical mechanisms, namely electrostatic charging, ion migration, and electrohydrodynamic effects. Electrostatic precipitators are still one of the most important gas cleaning technologies since they enable high efficiency treatment and collection efficiency (99.9%) of large volumetric gas flows with lower pressure drops than alternative technologies (e.g., cyclones or bag filters).

The degradation of chemical pollutants in gas streams as well as the removal of particulate matter (e.g., soot) and aerosols is possible with nonthermal plasmas. Much research has been devoted to the removal of nitrogen oxides (NOx) and sulfur oxides (SOx) from flue gases exiting combustion processes and of volatile organic compounds (VOCs) from off gases in manufacturing processes. The conversion of hydrogen sulfide (H2S), ammonia (NH3), and other toxic waste gases into less harmful or more easily removed products was also investigated, and some of this research has resulted in pilot- and large-scale installations based on dielectric barrier discharges (DBDs) and packed bed reactors, corona discharges, plasma torches, plasma-based UV-lamps, and electron beam-generated plasmas. A few of these discharge types are shown schematically in Figure 2. The successful application of nonthermal plasma to large industrial gas flows was realized for deodorization, e.g., in food production.

The degradation of chemical compounds by nonthermal plasmas is based on the collision of the pollutant molecules with free radicals and ions generated by the plasma. If oxygen and/or water vapor are significant constituents of the gas, the oxidizing reactions are dominant. For example, organic molecules and nitrogen oxides react with these oxidizing species (e.g., O, ·OH, HO2, O3) which can also start chemical chain processes involving other radicals. For example, the treatment of NOx results in higher oxides like N2O5, and in the presence of water can lead to acids. The efficacy and selectivity of the mentioned chemical processes are affected by the humidity, temperature, and the chemical composition of the gas mixture. The reduction of NO to N2 and O2 is also possible, but is of minor importance in the presence of oxygen and water. Hydrocarbon additives (e.g., unburned fuel) enhance the oxidation of NO to NO2 by the introduction of additional reaction pathways, while the formation of by-products (SO3 from SO2, HNO2, HNO3) is suppressed.

Oxidation of pollutants can be realized also by the injection of ozone (O3), which is most efficiently generated by DBD-reactors. This process is often called low-temperature oxidation and is also established in the industry for the removal of pollutants from waste gas streams (e.g., gas, coal and petcoke fired boilers and metals furnaces). This end-of-pipe process removes the non-water soluble compounds, including NO and NO2, from the waste gas by reaction with ozone. The resulting N2O5 is effectively removed e.g., by wet or semi-dry scrubbers, or wet electrostatic precipitation. This technology is used in stand-alone treatment systems, when inlet NOx levels are moderate, or in conjunction with combustion modification processes (low NOx burners or selective non-catalytic reduction) in the case of higher pollution levels. The capture of nitrogen oxides in wet scrubbers results in dilute nitric acid, a valuable by-product in large industrial and utility systems, e.g., for the production of fertilizers. Gas volumes treated range from about 6000 and 600 000 Nm3 h−1 with NOx concentrations...
from 30 to 3000 ppm, and more than 16 500 tons of NOx are removed each year with this ozone injection process in USA.[17]

In the so-called plasma enhanced selective catalytic reduction (PE-SCR), the oxidative conversion of NO into NO2 by means of plasma with the addition of ammonia (NH3) is realized. The process results in the formation of solid salt particles, which are precipitated, and, can be used as fertilizer.

Due to the limited density and selectivity of radicals, the applicability of nonthermal plasma treatment is restricted to slightly contaminated gas flows (typically contaminant concentrations of less than 1000 ppm).[10,18–20] Substantially less energy is required in such cases than in thermal processes (incineration, thermal-plasma treatment, catalytic decomposition).[13] Since contamination of exhaust gases occurs in many industrial processes, food production, and animal farms, there is a large number of potential applications. Many installations have been realized within the last 15 years for gas volumes between 300 and 80 000 Nm³ h⁻¹ and specific energy consumption between 50 and 0.3 kWh/(10³ · m³).[13]

The waste gas is either directly processed in the plasma reactor (mostly DBDs) or plasma-treated air is injected into the waste gas (indirect treatment). In most cases, the plasma as the oxidizing stage is combined with other processes such as adsorption, absorption, catalytic reactors, or biological treatment systems.[21–23] There are several synergies possible with these combinations, in particular with catalysts,[24–28] which require further analysis and elucidation of the key mechanisms.

An important advantage of nonthermal plasma is that it can be used “on-demand.” Thus, the power consumption can be adapted to the specific, and possibly variable, contamination load of the gas to be treated. The limiting factors for industrial application are selectivity and efficiency. Efficiency (characterized as the energy yield, i.e., the mass of removed or converted reactant per dissipated energy) is often too low, in particular when the contamination level exceeds the hundreds of ppm-level. Selectivity, as a measure of the fraction of the desired reaction products (e.g., CO₂ from hydrocarbons), is also often not sufficient, and the formation of unwanted (or even harmful) by-products prohibit industrial application in many situations. Concluding the description of the state-of-the-art applications and the status of research activities, one can summarize that plasma in combination with other processes are niche environmental technologies for low-contaminated waste gas streams. These processes are already established in the industry but can be further advanced. Furthermore, the applicability and potential of these processes as well as their limitations have to be broadly communicated and disseminated to stakeholders in industry, politics, and governmental and environmental agencies, as well as incorporated in the education on environmental technologies. A deeper fundamental knowledge about the synergies between plasmas and catalysts and other technologies could enable more reliable, more selective, more efficient
and lower maintenance environmental technologies. The risks lies in the complex chemistry and in the fact that the given environmental conditions determine the basic plasma parameters, which are very challenging to measure in these plasmas.

The principles and characteristics of plasma-based air cleaning and depollution technologies are not only suitable for large facilities. Smaller systems for the deodorization of exhaust gas or recirculating cooking stove air have entered the market. Systems for gastronomy as well as private households are established. Furthermore, indoor air cleaning devices are commercialized and supply a large market, particularly in Asia.\[9\]

### 3 | CONVERSION OF CARBON DIOXIDE AS THE MAIN GREENHOUSE GAS

Since global warming is one of the most important climate issues, the dissociation and conversion of CO\(_2\) as the main greenhouse gas has been considered in the context of carbon capture and utilization (CCU) approaches. CCU is the sequestration of CO\(_2\) and its following conversion into energy carriers or bulk, value-added chemicals. Many different ways are under development and investigation including CO\(_2\) fixation (inorganic carbonates), to growing bio-fuel forming algae, and the direct conversion of CO\(_2\) into hydrocarbons. Most often, the overall techniques are affected by low energy efficiencies and poor chemical selectivity.

The dissociation of CO\(_2\) in plasma has been studied for a wide range of applications ranging from carbon nanomaterial formation to CO\(_2\) lasers.\[^{10,29,30}\] DBDs and gliding arc discharges (both mainly at atmospheric pressure), microwave (mainly at reduced pressure), radio frequency discharges, atmospheric pressure glow discharges, corona discharges, spark discharges, and nanosecond-pulsed discharges have been used.\[^{31–33}\] Microwave plasmas and DBDs operating in CO\(_2\) are shown in Figure 3. CO\(_2\) molecules are dissociated into carbon monoxide (CO) and valuable oxygen (O\(_2\)). While dissociation by electrons dominates in DBDs and coronas, it is the electron impact vibrational excitation, followed by chemical reactions, that is important in gliding arcs and microwave plasmas. The thermal dissociation mechanism can be predominant in microwave plasmas.\[^{34}\] The highest yield and best energy efficiency are obtained by microwave plasmas at reduced pressure and supersonic flow conditions. Further processing of CO through the water-gas shift reaction results in the production of syngas, an important chemical feedstock.

**FIGURE 3** Examples of CO\(_2\)-conversion with microwave plasmas (1 kW and 2.45 GHz; left) and DBDs (right). Microwave plasmas (1 kW, 2.45 GHz) are (a) full-height waveguide configuration with forward vortex flow at 130 mbar, (b) half-height waveguide configuration with forward vortex flow at 150 mbar, and (c) same configuration than (a) with additional water-cooled brass quencher in the exhaust at 130 mbar. The plasma is seen through a metal grid, which acts as a short-circuit in the waveguide resonator and the gas is tangentially injected from the top.\[^{34}\] The DBDs are operated in cylindrical configuration at (a) 1.3 bar and (b) 2.1 bar. A glass tube surrounded by a mesh acts as the outer electrode.\[^{35}\]
In the 1990s different approaches to CO₂ reforming by means of plasmas, also combined with catalyst have been studied,[30–33,36] but noneconomic energy yields were obtained. Nevertheless, energy from renewable sources is not uniformly available and the temporary energy surpluses require storage methods of this excess energy. The electrolysis of water and subsequent delivery of hydrogen to the natural gas system is not feasible or desirable because of lower volumetric heating values. In this context, renewable energy can be seen as a cheap source of electrical energy for plasma operation to realize plasma-based energy-to-gas conversion since it can be switched on/off whenever needed.

However, plasma technology has to compete with solar-powered CO₂ conversion technologies, such as electrolytic, photocatalytic, and solar thermochemical conversion.[33] A critical overview of processes that consume CO₂ as feedstock was recently published.[37] The key performance indicator for the comparison with other approaches is the solar-to-fuel energy conversion efficiency.[33,38] This efficiency is currently less than 2%[39] in the case of photocatalytic conversion and has a theoretical limit of 17% due to the band gap energy of photocatalysts.[40] For solar-powered thermochemical conversion, theoretical solar-to-fuel efficiencies exceeding 30% have been reported, but demonstration of experimental values above 10% are still pending with robust and scalable solar reactors,[39,41,42] while a value of 20% is required for solar fuels to become cost competitive.[43] When using photovoltaic cells, which currently have an efficiency of 25%, solar-to-fuel efficiencies of 7–10% are reported for water electrolysis.[39] In a recently published review,[38] comparisons of numerical simulations and experimental results on different plasma sources for CO₂ conversion demonstrate that there is still room for enhancement of the energy efficiency with plasmas. Assuming that the electrical energy for the plasma generation is produced by solar panels, with an efficiency of 25%, an energy efficiency of 50% for CO₂ conversion in the plasma would yield a solar-to-fuel efficiency of 12.5%. This value is at least competitive to other emerging technologies, but selectivity and efficiency of plasma processes still need to be improved in order to be competitive and economical.

4 | NONTHERMAL PLASMAS FOR OTHER GAS CONVERSIONS

Molecular hydrogen (H₂) and methane (CH₄) are considered to be the most important fuels for the future because they have a tremendous potential to reduce environmental pollution. Holladay et al.[44] divided the technologies for H₂ generation into reforming and non-reforming H₂ production methods. Mainly three hydrocarbon reforming technologies are currently in use in industry, namely steam reforming, partial oxidation, and autothermal reforming. The main drawback of these methods is the massive production of CO₂. All the other remaining reforming technologies are still at pilot plant/demonstration stage or are under fundamental investigation. The non-reforming technologies are divided into H₂ from biomass and H₂ from water, depending on the source of production. With H₂ from biomass it is possible to obtain H₂ from direct gasification of the organic material and thus, biological hydrogen. The gasification technology is commercially used in many other processes like coal gasification. The biologically derived hydrogen includes several emerging technologies where H₂ is ultimately obtained indirectly from water through the biological materials such as algae and other microorganisms. The technologies to obtain H₂ directly from water are electrolysis, thermochemical water splitting, and photoelectrolysis.

Currently, worldwide there are major investments in R&D programs on H₂ technology and fuel cells. One of the most advanced assessments of the present H₂ policy has been made by the U.S. Department of Energy (DOE).[45] The aim of this policy is to identify research pathways leading to H₂ production technologies that produce near-zero net greenhouse gas emissions and use renewable energy sources, nuclear energy, and coal (with carbon dioxide capture and storage). Therefore, the development of systems for efficient H₂ production is important. There currently exist several conventional mass-scale H₂ production methods with acceptable costs. However, since H₂ has transport and storage problems the development of small-scale technology is needed. Nevertheless, according to the statements of the U.S. DOE, all H₂ production technologies have to meet the requirement of producing H₂ with a production cost of 1–2 $/kg (H₂) (or 60 g(H₂)/kWh) by 2020. Plasma technologies were not considered in the DOE report as economically competitive for H₂ production. In a following update by the DOE the technologies most suitable for H₂ production are, in order, electrolysis, photoelectrochemical, solar thermochemical hydrogen, biogas, and microbial.[46] Several research programs working on the development and improvement of these technologies are now funded, but support for plasma-based technology is excluded. Thus, there is a need to disseminate the prospects of plasmas to this community.

At the present stage, some plasma technologies have met the DOE’s energy yield requirement foreseen for 2020. In plasma reforming the chemical reactions involved are the same as with the traditional reforming processes. However, the reactive species are generated with electricity (both thermal and nonthermal plasmas) or heat (only thermal plasmas). The plasma reforming process has some advantages compared to the traditional technologies, namely, reduced cost and degradation of the catalyst, lower size and weight requirements, less sluggish response, and less limitations on hydrogen production when utilizing heavy hydrocarbons.
Plasma processes can be operated at lower temperatures than the thermal technology, and when no catalyst is needed the plasma can tolerate higher sulfur content. Disadvantages include the need for specific power supplies and electricity as well as high electrode erosion at elevated pressure.

In the case of distributed H₂ production from gaseous and liquid fuels, gliding arcs, plasmatrons, nozzle arcs, and microwave discharges are included. These methods have yet to meet the requirements for high H₂ production rates, high reliability, and low investment cost. Therefore, significant progress has to be made to develop plasma H₂ production systems. More technical progress and cost reduction have to be realized to compete with traditional reforming technologies. Plasma H₂ production has been considered, just as biohydrogen, thermochemical and photoelectrochemical water splitting, and photoelectrolysis, to be a longer term technology.

Nitrogen is one of the basic elements responsible for the growth of living organisms on earth. At the beginning of the last century, a chemical process was developed to obtain fixed nitrogen from the atmosphere to fulfill the demand of a growing population: the Haber-Bosch ammonia synthesis process, which is considered as one of the most important discoveries of the 20th century. Nowadays the annual amount of nitrogen fixed by the Haber-Bosch process has reached 130 million tons per year (about 29% of the global fixation). The Haber-Bosch process consumes almost 1–2% of the world’s total energy production and ~3–5% of the total natural gas output, and in total it feeds ~40% of the world’s population. The International Energy Agency (IEA) and its member countries published a Technology Roadmap focusing on energy and greenhouse gas (GHG) reduction in the chemical industry via catalytic processes. Ammonia has been identified among the 18 chemicals which consume 80% of the energy demand of the chemical industry and contribute to 75% of the GHG emissions from this industry. Ammonia has been demonstrated to be the chemical compound with the highest potential to reduce energy and GHG emissions by 2050 through improvements in its production efficiency including improvements of the current catalyst and the catalytic process. Furthermore, ammonia is an important chemical feedstock in addition to its large scale use for fertilizer production. Ammonia is also considered as a hydrogen capture substance for the upcoming hydrogen fuel cell economy (see previous section), e.g., in Japan.

Ammonia can be more safely transported than high-pressureized H₂, and it is easily converted back to H₂ and N₂. Ammonia is just one chemical that results from nitrogen fixation. There are several other ways to obtain nitrogen fixation including the production of nitric oxide (NO), hydrogen cyanide (HCN), and nitric acid (HNO₃). These compounds have also been the subject of investigations during the last century. For example, Birkeland and Eyde successfully developed the electric arc process in Norway in 1903 to produce HNO₃. In this process, N₂ and O₂ are fixed into NO in the plasma and in a following stage NO is absorbed into water and converted to HNO₃.

The chemical fixation of nitrogen directly under plasma conditions is very challenging and requires fundamental knowledge of the plasma and chemical processes. Plasma offers several advantages such as a simple one step process that can be operated and stopped instantaneously, and it provides high energy density for very fast reactions. Plasma nitrogen fixation is generally accomplished by the reaction of N₂ with O₂ or H₂ to produce NO or NH₃, respectively. In the case of plasma NO synthesis, the raw materials are abundantly available at low cost. The reactions to produce NO are favored by high-temperature processing, owing to the high dissociation energy of nitrogen (binding energy of 9.77 eV). However, another route, consisting of electron impact vibrational excitation of N₂ followed by the Zeldovich mechanism with oxygen atoms or molecules is quite efficient in gliding arcs working in a temperature range of 1000–1500 K.

The first industrial application of a plasma-based nitrogen fixation technology, the already mentioned Birkeland-Eyde process utilizes electric arc furnaces. This method uses deflection of the arc by a magnetic field to help the spreading of the arc through the gas. The Schönerr furnace uses a steady and long slender arc and the Pauling furnace operates on the principle of a spreaded arc.

In addition to gliding arcs, plasma NO synthesis was also investigated with several different types of plasma sources such as MW and DBDs. Initially, no additional catalysts were used, but more recently different kinds of catalysts were tested to increase the nitrogen fixation as well as the energy efficiency. Recently, a pure plasma electric arc reactor for NO production was patented. The reactor is fed with air and a magnetic field is applied to expand the plasma volume. The reactor is operated at a pressure below 1 bar and a temperature in the range 3000–5000 K. The effluent is cooled with spayed water or by simple dilution with air to obtain a gas temperature below 2000 K. They reported an energy consumption of below 30 GJ/ton N. For a residence time of 0.1 s the NO concentration was 8 vol%, and for 0.001 s it was 12 vol%. By raising the NO yield from 2 to 10%, the energy consumption per ton of N₂ was reduced by 80%.

Alternatively, the performance of a small-scale gliding arc discharge at atmospheric pressure revealed an energy consumption of 77 GJ/ton N.

The plasma ammonia synthesis uses expensive H₂ along with readily available N₂. The kinetics favor high temperature for higher reaction rates and dissociation of N₂. However, the thermodynamics favor low temperature processing to achieve higher yields. Until now, there has been no plasma ammonia synthesis process developed at the industrial or pilot scale.
Nevertheless, several efforts have been made on a lab scale to develop and improve a process that could be competitive with the existing technology. Over the years different plasma sources with or without the combination of heterogeneous catalysis have been investigated. The industrial Haber-Bosch process demands around 30–35 GJ/ton NH₃, depending on the hydrogen source. The plasma ammonia synthesis process must have an energy consumption less than 33.6 GJ ton⁻¹ NH₃ (9333 kWh ton of NH₃⁻¹) in order to be competitive. Plasma has the main advantage to be an “on demand” technology; thus, it could be switched on/off whenever there is the need.

In order to demonstrate the possibility to implement “portable” ammonia synthesis processes depend only upon renewable energy a different approach to produce on-site ammonia has been developed recently. The first small-scale ammonia plant running on wind energy and using air and water as feed was realized in these contributions. The wind energy is used to produce H₂ from water splitting and N₂ from air purification, and then the two compounds produce NH₃ in a classic chemical process. The energy consumption of this plant is reported to be 60 GJ/ton NH₃, which is still higher than the Haber-Bosch process. However, the Haber-Bosch process has been optimized over the past 100 years. These new concepts of modular plants and de-centralized chemical production facilities are gaining rapid acceptance in the chemical industry and could be very relevant to plasma-based technology for ammonia synthesis. Additionally, the commercialization of solar and wind technologies for energy production combine very well with the application of plasma processes. Considerable opportunities exist in revisiting the plasma nitrogen fixation with a renewed toolbox of advances in plasma physics, plasma chemistry, catalysis, process engineering and electrical engineering, and unique interdisciplinary collaborations.

A high potential for increased efficiency of ammonia generation is seen in the combination of low temperature plasma (e.g., DBD) with catalytic materials. Using ruthenium and manganese on an alumina carrier and a N₂–H₂ gas mixture in the DBD, an energy yield up to 120–144 GJ/ton NH₃ could be reached, which is almost an order of magnitude bigger than the Haber-Bosch process, but on the same order of magnitude as the Birkeland-Eyde process. The combination of a nonthermal plasma (packed bed DBD) in N₂–H₂ gas mixtures combined with catalytic monodisperse-nanodiamond and diamond-like carbon coatings on the filling material (α-Al₂O₃ spheres) also revealed a significant effect on the production yield of ammonia. The authors found that carbonyl groups on the surface promote the adsorption of H₂ and thus, increase ammonia generation. Increased understanding of surface processes will be the driving force for further improvements of such ammonia generation processes.

In fact, there are specific challenges to developing larger scale plasma processes. The knowledge required for the scale-up of the plasma sources is relatively underdeveloped. Since nitrogen fixation is a much bigger industry than ozone production, it not only requires more scale-up than ozone generation, it also may provide a very large potential market for plasma technology. Therefore, it is very likely that one of the plasma chemical synthesis processes discussed above in this paragraph could be utilized on industrial scale in the next few decades.

Methane is a cleaner and more abundant primary energy and carbon source than coal or oil. Methane combustion emits 50–60% less CO₂ when burned in new efficient natural gas power plants compared with emissions from a typical new coal plant. Recent explorations have discovered an abundance of conventional and unconventional gas reserves rich in methane, mostly located at decentralized areas, far away from the market. A solution to overcome the transportation problem is to convert methane into a liquid product, to avoid leakage and loss of raw materials in gas transport, as well as to contribute to a reduction of the greenhouse effects. To accomplish this purpose several methane reforming technologies have been studied: nonoxidative methane coupling, pyrolysis, partial oxidation, and dry and steam reforming. One of the formed products is syngas, an important chemical feedstock. However, this is just a first step, because the syngas has to overcome another process to be transformed into a liquid fuel, e.g., methanol.

Syngas (abbreviated from “synthesis gas”) is a mixture of CO and H₂ and an intermediate for various synthesizing chemicals and environmentally clean fuels, such as ammonia, methanol, acetic acid, methyl formate, dimethyl ether, synthetic gasoline, and diesel (via the Fischer-Tropsch process). Various techniques including steam reforming of methane (SRM, reaction with water), partial oxidation of methane (POM, reaction with oxygen), and dry reforming of methane (DRM, reaction with carbon dioxide) can be applied to convert methane into syngas. SRM is a commercialized technique to generate syngas or H₂, however, the endothermic reaction needs a high temperature (usually higher than 700 °C) to activate the reforming reaction. POM is an exothermic reaction, which is favorable to be operated at lower temperatures (300–500 °C), leading to lower energy consumption. Unfortunately, the ratio of O₂/CH₄ needs to be controlled precisely, otherwise full oxidation to CO₂ and overheating of the reaction bed would happen. DRM was invented by Fischer and Tropsch (the inventors of the Fischer-Tropsch process) in 1928 to convert CH₄ and CO₂ simultaneously. DRM has received much attention, since the reactants of DRM are two important GHGs. Since DRM is highly endothermic, catalysts are needed to reduce the operating temperature.
Plasma-assisted methane reforming is currently considered a promising alternative solution\(^\text{[66]}\) overcoming most of the issues that thermal processes face. The active species resulting from electron-neutral collisions rapidly undergo several chemical reactions under atmospheric pressure and mild temperature (\(<\sim1000\, \text{K}\)). Relatively low reaction volumes are needed due to the fast reactions and high energy density. Finally, \(\text{CO}_2\) emissions diminish if the electricity input would be taken from renewable energy sources. On the downside, plasma is not selective and usually generates a wide product distribution. This problem could be overcome by combining plasma with a heterogeneous catalyst.

In the last two decades, numerous plasma-assisted processes have been investigated and proposed for direct \(\text{CH}_4\) reforming to added value products.\(^\text{[63]}\) Thermal arc plasma is the only process which has industrially been applied for \(\text{CH}_4\) coupling (Hüls process\(^\text{[70]}\)). In this process, all species (ions, electron, and molecules) are at thermal equilibrium; thus, it can be considered as a conventional thermal process. It has been specifically developed for acetylene and carbon production. The efficiency reaches 40\% and the energy cost for acetylene production is about 1080 \text{kJ mol}^{-1}. DBD yields the lowest efficiencies. An effective way to increase the efficiency, as proposed in Ref. \(^{[71]}\), is to apply nanosecond pulsed voltage (<10–100 ns) to suppress the undesired energy losses caused by ion current generation (resulting in gas heating). However, the most effective solution is the placement of tailored catalysts inside the discharge zone; a part of the thermal losses is efficiently utilized in catalytic reactions, thus increasing the efficiency.\(^\text{[72]}\)

There are only two published papers reporting a higher efficiency and comparable or lower energy cost than the thermal process. Microwave-sustained (MW) plasma at medium pressure (80 mbar)\(^\text{[73]}\) and a pulsed discharge at atmospheric pressure\(^\text{[74]}\) were used. The MW discharge reached 61\% efficiency and an energy cost of 604 \text{kJ (mol C}_2\text{H}_2)^{-1}. For the pulsed discharge, the efficiency was 46\% with an energy cost of 860 \text{kJ mol}^{-1} \text{C}_2\text{H}_5.

Many efforts have been carried out to integrate plasma and catalysis into one process. It has been observed that plasma-catalyst interaction leads to synergies, i.e., the conversion and the energy efficiency are higher than the sum of both individual processes (i.e., plasma-alone and catalyst-alone) and different products are formed, as compared to plasma or thermal catalytic processing alone. However, hybrid plasma-catalytic systems still face several challenges. Some of them are of technical nature (i.e., coke formation and deposition resulting in catalyst deactivation, catalyst instability, and decomposition); others of scientific nature (diffusion and surface chemistry enhancement by the electric field, effect of catalyst presence on the electric field pattern, nature of the reactive species that are produced by plasma interact with catalyst surface). All these challenges force the researchers to search for optimal catalysts in a plasma environment, which might be different from typically classical (thermal) catalysts.

The strong motivation for efficient valorization of methane in various forms and feedstocks in combination with the increasing utilization of renewable electricity renders plasma a worthy technology to further investigate and develop for methane valorization.

## 5 | TREATMENT OF WATER

The supply of fresh water to humans and other living organisms is one of the most important global problems due to the limited fraction of available fresh water relative to the total water present on earth and the demands of a growing population, climate change, and aquifer depletion.\(^\text{[75]}\) The introduction of harmful contaminants such as organic chemicals or microbes into freshwater sources reduces the water quality. Therefore, managing fresh water scarcity and developing innovative depollution, cleaning, and remediation technologies have become high priorities. Of particular concern are emerging contaminants (e.g., pharmaceuticals, industrial solvents, volatile organic compounds, and personal care products) in drinking water, ballast water contamination of ecosystems, wastewater production in industry, and drought-induced freshwater supply stress. Recent studies have shown that conventional drinking water treatment processes (e.g., coagulation and filtration followed by disinfection) are not able to remove many of the relevant contaminants.

Advanced conventional water treatment methods include the combination of reverse osmosis and advanced oxidation (e.g., processes that generate highly oxidizing OH radicals through such means as UV irradiation or ultrasound, and the addition of other chemicals such as ozone and hydrogen peroxide). Advanced oxidation (AO) means the decomposition of toxins in water by means of these OH radicals, which undergo a series of chemical reactions with the contaminants. This leads to the conversion of organic compounds in solution into water, carbon dioxide, and harmless mineral acids and salts (termed mineralization). Most AO processes require the addition of chemicals. For example, ozone and hydrogen peroxide are used alone or in various combinations with UV light. Therefore, the infrastructure to generate or store these precursors can lead to higher investment and treatment costs compared to the conventional methods.

The interest and study of nonthermal atmospheric pressure plasmas in and in contact with liquids including water has increased significantly within the last 20 years although the first investigations on this topic can be dated back to the early 20th century.\(^\text{[76]}\) The high complexity of the
physical and chemical processes involved present new scientific challenges, while the potential of this emerging technology has been identified. Due to the generation of different agents that can degrade and inactive biological and chemical contaminants, such as UV radiation, shock waves and radicals, plasmas in and with liquids are particularly suitable for decontamination and sterilization purposes.

Ozonation of water is fully established and commercialized. The most efficient way to generate ozone is via nonthermal plasma ("remote plasma treatment of liquids"). Ozonation is increasingly replacing conventional chlorination processes. Ozone is a stronger oxidizing and disinfectant than chlorine and it produces less byproducts. However, the costs of ozonation processes are high[77] and ozone does not directly react with many chemical species. Hence, further work is still desired and ongoing to increase the efficiency of ozone generation, to enhance the dispersion of ozone in water, and to increase the conversion of ozone into free radicals (e.g., by the combined use of UV and H2O2 with ozone).[78,79]

Generally speaking, plasmas in and in contact with liquids can be generated in three different ways.[80] First, a discharge can be generated directly in the liquid as streamer-like or corona discharge, or as an underwater arc discharge. A streamer-like or corona discharge is almost always generated by pulsed excitation in a pin-to-plate configuration, where the short-pulsed excitation keeps the plasma in the nonthermal regime. Thus, these processes are significantly different from the underwater arc, which is considered a thermal plasma. Second, discharges in the gas phase can be generated with combined gas and liquid electrodes. Although the main principle is similar to a classical gas discharge, its properties can be much different. The discharge current is transported through the water to the electrode by ions. The ions in water have a much smaller mobility than the electrons in metal electrodes. Furthermore, the secondary electron emission coefficient of most liquids (e.g., water) is much smaller than that of metals. Third, plasma can be generated in bubbles or cavities in the liquid. This can be achieved in many different configurations as reviewed in Ref. [80]. Examples of plasmas in and in contact with water are given in Figure 4. Indeed, the method of generation has a distinct effect on the type of active agents formed and, thus on the efficiency of the desired process. However, plasmas with liquid electrodes can be generated with the classical or established high voltage power technologies. Pulsed power voltage supplies are more sophisticated to design but enable much higher power densities and, thus higher densities of reactive species in the liquid.

These plasmas are a source of high electric fields, energetic charged particles, ultrasound, UV light, and shockwaves, which can also drive the production of radicals in the water without the addition of further consumables.[8,81] The plasma chemistry driven by free electrons and excited species in the gas phase produces large quantities of reactive oxygen species, e.g., OH radicals, hydrogen peroxide, ozone, singlet oxygen, nitrate radicals, and super oxide (O2\(^-\)). These reactive atomic and molecular species transport into the water by interfacial diffusion and can be limited by solubility (e.g., Henry's law). The plasma also interacts with the water surface, directly generating reactive species at the interface. For example, electrons are rapidly thermalized and captured in the potential wells formed by clusters of water molecules. These solvation complexes are reactive and lead to the decomposition of water molecules into OH radicals.

The efficacy of plasmas for water decontamination has been demonstrated in numerous studies on a wide array of chemical and biological contaminants[75,78] Early tests were focused on recalcitrant dyes as they show directly observable effects by transforming a colored solution to a clear one; although it should be clearly noted that decoloration does not imply degradation or even detoxification. Meanwhile, organic pollutants, e.g., phenol and other hazardous chemicals

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**FIGURE 4** Principles for the generation of plasmas in and in contact with liquids: discharge directly in the liquid (left), discharge in the gas phase with liquid electrode (middle), and plasma in bubbles (right), adapted from Ref. [80]
(including pesticides, dioxin, PCP, TNT, BPA) have also been demonstrated to be removed and partially or completely degraded by plasma-based AO. The cell membrane and cellular genetic material of bacteria are also attacked by the reactive oxygen and reactive nitrogen species. However, it is also necessary to identify the intermediates formed in these processes. Complete mineralization of the compounds is not always achieved and the plasma-induced chemical reactions are not selective. It can be noted that complete mineralization is not always necessary, in particular if the target compounds can be converted to easily biodegradable and non-hazardous compounds.

In some cases the decomposition rates of plasma-based water treatment have been demonstrated to be superior to chemical methods, the AO capability enables micro-contaminant removal as well as disinfection, and its application can be used as a finishing stage in a conventional water treatment system. The literature reports about up to 99% of degradation for treated volumes of 20 mL to 150 L with concentrations of polluting substances in the range 36–100 mg L\(^{-1}\), yielding energy removal yields between 0.7 and 450 mg kWh\(^{-1}\).[82] Obviously, the most efficient way for decomposition of dyes and surface active compounds is the interaction of thin layers of water or water mist with the plasma.[77] However, such concepts of water treatment will not enable systems with high throughput of water.[75] The key indicator for the comparison of plasma-based methods with other AO technologies is the electrical energy required to reduce a contaminant by one order of magnitude (so-called electrical energy per order, EEO given in kWh m\(^{-3}\)).[75] The energy yield for the degradation of 90%, the so-called G-value given in g kWh\(^{-1}\), of a substance is then calculated for an assumed first order removal kinetics.[83] In the work,[82] the EEO of different pharmaceutical residues is reported in the range 27–430 kWh m\(^{-3}\) resulting in G-values of 3–45 mg kWh\(^{-1}\). However, the comparison should not be made only by such values, but the costs for capital investments and operation should be included. The unique selling points of plasma-based methods could be the absence of the infrastructure for the handling of chemical precursors, the on-demand simultaneous regulation of the removal efficiency for different pollutant loads, and, the fact that only electricity is needed.

Another area for development include combination of atmospheric pressure plasma and TiO\(_2\) photocatalyst for control of microorganisms in aqueous solutions.[84]

6 | PLASMA TECHNOLOGY FOR AND IN AGRICULTURE

Due to the world population growth there is a demand for increasing food production. The agricultural industry needs to work more efficiently and resource and habitat conservation needs to be promoted. Furthermore, the quality and safety of food and other agricultural products must be enhanced. These challenges require the exploration of new technologies in all sectors of the food production chain (“From Farm to Fork”).

Plasma technologies have demonstrated their potential for agricultural production in many different aspects, including the chemical and biological decontamination of processing tools and packaging, the cleaning of air and water, and the production of fertilizers (also see previous sections). These mentioned aspects address the resource and habitat conservation as well as the safety and shelf life of agricultural products in pre- and postharvest applications. A need for plasma processes will arise if more insect pests develop resistances against pesticides, fumigants, and other agro-chemicals. An increase of concentration of toxic and hazardous pesticides will not be the solution since overuse of pesticides is known to affect the other organisms in the environment. The major advantages of plasmas have already been discussed above. However, it must be taken into account that agricultural products usually serve mass markets with limited profit margins when transferring technologies from other application areas to the agricultural industry. In the following, the sole topics for agriculture, namely the effects of plasma on plant biology, increase of plant growth and output, soil remediation, and the use for new agricultural products are considered. Food safety aspects are discussed in the following section.

The decontamination of seeds and the enhancement of their germination by treatment with nonthermal plasmas have been demonstrated in several studies. Atmospheric pressure plasmas such as DBDs, RF- and MW-sustained plasmas, and gliding arcs under different conditions (mostly operating in air, but also in other gases) have been applied, either directly to the seeds or by remotely using the products of the gas discharge. Figure 5 shows the treatment of dill seeds with a surface DBD.

The effects of plasma treatment in seeds are assumed to be induced by the plasma-generated reactive oxygen and nitrogen species (RONS). The decontamination of seeds, e.g., the removal of pathogenic fungi[86,87] and bacteria[88,89] as well as the insecticidal activity against larval and pupal stages of pests[90] have been achieved. This can increase the cleanliness of seeds, during storage and sowing, grains, during processing in food production (e.g., brewing, malting, weaning, instant food). Furthermore, several effects of RONS on the physiological and biochemical properties of seeds have been reported. The change of wetting properties and structure of the coat increases the water uptake,[91–93] the permeability of nutrients,[94] or it accelerates the root formation.[95,96] Furthermore, several effects on plant hormones, enzymes such as catalase, proteins, soluble sugar, and antioxidants are possible.[93,94,97–99] The plasma treatment is not only
affecting the seeds, but it also affects the environmental conditions, such as the pH-value or the introduction of nitrate and nitrous species into the surrounding water. All of these changes result in increasing the sprouting and germination rates, and faster initiation of germination. Finally, application of plasmas may also lead to an enhanced plant growth. Even the use of plasma-activated water (e.g., clean water treated with air-plasma), rather than the direct plasma treatment, with its possible effects on the plant as well as the chemical fertilizer action might be a feasible approach. However, more research is needed to demonstrate the full feasibility of these approaches. Furthermore, the performance and other process requirements should be compared with alternative approaches (e.g., ultrasound, pulsed electric fields). In particular, the energy requirements (determined by the reduction of a specific contaminant) per mass of treated seed volume must be provided to compare different plasma sources, but also to compare plasmas with alternative or already existing approaches. These comparisons of plant growth are complicated due to the very complex and often hard to define or fix environmental conditions.

In addition to the decontamination of seeds and water, the remediation of soil is an important issue because of the overuse of chemicals in agriculture and contamination by other industrial processes. Remediation processes like washing, phytoextraction, solidification, and bioremediation are expensive. Plasmas could provide an alternative or supporting low-cost technology for such applications. The first attempts with in-direct plasma on soil remediation were performed by using ozonation to reduce plant diseases, and significant bactericidal effects were obtained. The challenge of such an approach is to enable selective treatment to reduce fungi and detrimental bacteria while preserving the activity of nitrogen-fixing bacteria. Further studies used direct plasma treatment of soil and demonstrated significant reduction of chemical species, e.g., dyes and chloride-containing contaminants. Degradation degrees of more than 90% and high degrees of mineralization of the contaminants were achieved. The effects of plasmas are moisture and soil material dependent. The latter might be due to the different diffusion behavior of the active species. Moisture and natural organic matter influence the overall chemistry and the concentration of reactive species needed for oxidizing reaction of the contaminants. The number of studies is still very small and more work is needed. Furthermore, the plasma processes must be quantified regarding the degradation per energy input and per mass unit of soil. The field of plasma-agriculture has been growing over the last few years and it is still too early to determine the future economic impact. This topic is extremely interdisciplinary because it includes aspects of plant and cell biology, biotechnology, engineering, and logistics. Fundamental processes of cell stimulation and redox-based plant cell biology and plant physiology and the mechanisms of inactivation have to be investigated. Furthermore, there are possibilities to develop new biotechnologies or agricultural products with plasma processes. The experiences on gas cleaning and pollutant degradation in exhaust gas treatment being described in Section 2 can also be very useful for the field of plasma agriculture. Plasma offer new prospects to increase the indoor air quality and thus, potential of airborne contamination in facilities with livestock or for food processing. The possibilities and prospects are so manifold that it is worth to be investigated within the coming years. On its way to understand and optimize the fundamental processes and effects, and to develop new technologies, the plasma community has to face many technological and economical challenges. In particular, reliable and controllable plasma sources operating in air are needed. Here, the community can profit from the large knowledge in the field of ozone generation, pollutant degradation, and other plasma-chemical reactions.

7 | NONTHERMAL PLASMAS FOR FOOD SAFETY, FOOD SUSTAINABILITY, AND IN FOOD PROCESSING

Within the last decade, the potential of nonthermal plasma as a food processing aid has been demonstrated for a range of processes and products. One distinctive driving force of these activities derives from the need in food processing and food safety for successful technologies. Food borne pathogens pose a serious threat to health and food production efficiency. Thus, a large fraction of plasma applications to agriculture concerns post-harvest processes. Investigated
are various decontamination procedures at different stages of food processing. Plasma decontamination of food produce exhibits similarities to the field of plasma medicine, but also distinct differences can be described, deriving from the specific requirements of food processing. The requirements for bacterial log-reduction of colony forming units are not as strong as they need to be in medicine, but the treated products are sometimes even more sensitive than human tissue or medical devices and processing volumes are much larger than in medicine.

Plasma has the ability to inactivate bacterial contaminants even from sensitive food produce. The need for novel techniques in food safety arises from the increase in resistant pathogen strains, their high infectiousness and the increasing demand for food production efficiency. Food safety is relevant, where food-borne pathogens can cause serious illnesses or even death. Plasma has been shown to not cause antibacterial resistance and acts on a broad variety of pathogens. Studies for plasma pathogen inactivation include highly hazardous bacterial strains such as EHEC. Several studies have shown that plasma can decontaminate e.g., strawberries, lettuce, meat, fish, tomatoes, chicken, and eggs. Using plasma for decontamination of food produce is a matter of food safety on the one hand and increasing shelf life on the other. Especially with the rise of convenience food with a high level of “ready to eat” preparation such as in fresh cut fruit and vegetable, food safety aspects are of increasing importance.

A key requirement for safe food processing is clean water. This aspect has already been discussed in Section 5. Additionally, plasma-activated water is used with many beneficial aspects. Many food processing lines employ a wet process. Thus, implementing plasma liquid technology in already existing wet process steps is easier than developing new process steps altogether. Recently, a plasma-activated water process for lettuce treatment on an industrial scale has been proven. Washing food with plasma-treated water could be an alternative to chlorine-treated water that is increasingly being banned.

Increasing shelf life has been shown for a variety of food products. Roughly 30% of food is wasted worldwide. Increasing the shelf life of food produce largely contributes to reduction of food waste, which is both beneficial environmentally and economically.

Apart from direct treatment of food produce, treatment of packaging or treatment of food in packaging has been proven to improve shelf life. Applications range from salad and meat to tomatoes and other freshly prepared or freshly cut products. It has to be noted that plasma treatment of packaging material has a long history, and the decontamination of bottles and improvement of gas permeation of polymer bottles have been reported. Especially, the treatment of fresh food directly in the package shows great technological and economic potential and successful commercialization has been reported. While in some approaches, packages are adapted to have an electrode imprinted on the inside of the package or on the label, another economical approach is to operate a DBD inside the polymer package (i.e., the package material acts as a dielectric and the electrode assembly is on the outside) in the production line. Ignition of the discharge generates ozone inside the package and the contents are subjected to a decontaminating atmosphere.

Plasma treatment of meat and fish products has been shown to reduce seeping and discoloration through aging. The product stays fresh longer with an overall better appearance in time. A large portion of research is on the topic of meat and lettuce decontamination. This has to be attributed to four facts: 1) the large demand for safe food from the fast food companies; 2) the high hazard level for meat; 3) the high incidence level due to optimal pathogen growth conditions in lettuce; and 4) the large product volumes required by the fast food and convenience food companies. Plasma is used not only for direct decontamination of food products but is also used to clean and decontaminate surfaces and tools in contact with food products, thus reducing the need for hazardous and polluting wet chemicals.

In an unconventional approach in food production plasma treatment was used to simulate aging of vegetable oil. Common aging tests involve thermal treatment. However, these conventional tests do not mimic aging very well and cause thermal denaturation of proteins. Plasma seems to be a promising approach to mimic oxidation through aging in air.

Plasma is also used for ethylene reforming for improved logistics during transportation of fruits. Ethylene gas accelerates the ripening process of fruit. Plasma can decompose the ethylene produced by the fruit. A Japanese company (Energy Support Corporation) together with the University of Iwate currently performs field studies to investigate the efficiency of this approach in a real scale experiment.

In summary, plasma can support new developments in post-harvest processes involving food treatment. Food industry is a multi-billion dollar market with a high growth potential. Currently, food industry faces two challenges in global markets. Logistics of transport of sensitive food produce and increasing legislative restrictions to achieve a more sustainable and environmentally friendly food economy.

Up to date most of the studies are at laboratory scale, but a considerable progress on transferring the technology to the industry can be seen, although the demonstration of product/process specific efficacies, the scale-up, the effective process control and validation as well as the regulatory approval are still big challenges in the field. Finally, the consumer acceptance must be realized.
Nonthermal plasma will compete with other processes that keep the quality attributes of a product close to that of its “fresh” state. The competing processes include thermal pasteurization, use of high hydrostatic pressures, pulsed electric fields, radiofrequency waves, and UV radiation. From a legislative point of view, foods treated by plasma have to meet the novel food directive. This directive states that all new food items that have not been consumed before or that are produced by a method that has not been used for preparation of food previously falls under the category of novel food and must be authorized under the novel food directive.\textsuperscript{[139]}

If these challenges are met, plasma has the potential to meet above issues in food production as it leaves no contaminants and harmful residues in treated foods and has been shown to drastically increase shelf life of food products allowing longer and thus cheaper transportation times. With this in mind, it becomes clear that plasma is on position 11 of the top 25 future preserving food technologies with a potential for commercialization in the next few years.\textsuperscript{[140]}

8 | SCIENTIFIC AND TECHNOLOGICAL CHALLENGES

Nonthermal plasmas offer a multitude of processes in the environmental sector and in agriculture. Figure 6 summarizes the advantages of nonthermal plasmas for different fields of applications and their respective industries.

There are several examples where plasma science has led to new industrial applications for the depollution of gases and the cleaning of water. However, several fields, like gas reforming, have not reached the status of commercialization. The potential benefits of the technology are the extension of product shelf-life, lower food processing and storage losses, low operational and maintenance costs with high environmental sustainability and, an enhanced chemical safety of foods.

Plasma science is developing into a highly interdisciplinary field.\textsuperscript{[2]} A general challenge is to present the basic knowledge and concepts of gas discharges, its physics and chemistry to a broader and more heterogeneous community, but also to bring it into other scientific and engineering communities and to convince them about the advantages of plasmas. Plasmas in gases and water will usually not be the technology of first choice, and even with the given success stories discussed in the previous sections, plasma is still regarded as a niche field. For example, cleaning of low-contaminated gases is more efficient by means of plasmas than by other technologies, discharges in water are able to reduce some substances, which cannot be removed by other techniques, and the conversion of carbon dioxide will only become economic, if “cheap” surplus energy is available from renewable sources. Before considering a plasma process for a given problem, one should be aware of the conventional or alternative technologies and determine the (potential) unique selling points of a plasma process.

Some of the main concerns are the monitoring, control, and tuning of the plasma chemistry in order to ensure as efficient and selective process as possible. The efficiency and energy requirements must compete with those of the alternative processes. Common measures of these aspects

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure6.png}
\caption{The advantages of nonthermal plasmas with its different fields of applications and their respective industries}
\end{figure}
should be defined by the community and become mandatory in all scientific reports in the field. While this is already established for the depollution of gases, this still needs to be developed in the fields of water treatment and agriculture.

For most of the mentioned applications, the handling of large volumes (gas, water, seed, soil, etc.) must be considered, and this is a great technological and economical challenge. Therefore, similarity parameters must be identified and, scalability concepts must be developed. Furthermore, plasma sources, preferably working in air, must be reliable and controllable under different surrounding conditions, and should allow for a high power input into small volumes. This includes the availability of sustainable high-voltage or microwave power sources with sufficient lifetime. Semiconductor based and stackable modules can lead to a significant progress in this regard.\textsuperscript{[34]} The combination with flow chemistry must be taken into account and the fact that industrial processes often run under high pressure must be considered (>1 atm).

Another key factor is the understanding of the fundamentals of plasma-surface interactions. Such knowledge will give new inspiration for the design of plasma sources and reaction schemes. Plasma processes will also require sophisticated gas separation techniques. Separation is based on differences in solubility and/or diffusivity and consequently permeability of the gases to be separated. Mixed matrix membranes, comprising embedded gas selective particles in a continuous polymeric matrix and operating at moderate temperatures (<300 °C), attract much interest for separation of CO\textsubscript{2} from exhaust gases.\textsuperscript{[141]} The dispersion of selective particles, metal organic frameworks (MOFs), enhances the separation properties resulting in increased selectivity and productivity. MOFs show very high adsorption capacities and are attractive for use as the dispersed phase enhancing CO\textsubscript{2} and CO separation. In general MOFs show a high pore volume and surface area are easily tuneable in terms of pore size and functionality. Because of the relatively low pressure (100 mbar to 1 bar) of the gas produced by plasmolysis, the use of MOFs with open metal sites (e.g., IRMOFs, Zn-based) are essential as these favor electrostatic interactions between the MOF and CO\textsubscript{2}.\textsuperscript{[142]} Another framework structure that can be used is ZIF-68 or ZIF-70 (also Zn-based). This material belongs to the class of Zeolitic Imidazolate frameworks (ZIFs). The structural topologies of ZIFs resemble the traditional zeolite cage topologies, while the chemical functionalization potential of MOFs is retained. Pure ZIF-70 shows one of the highest CO\textsubscript{2} over CO sorption selectivities reported in literature.\textsuperscript{[143,144]}

The transfer of plasma technology into some industrial processes will further require improved selectivity. To improve selectivity, as well as the efficiency, the combination with other technologies and processes, in particular with catalysts, must be studied in more detail.

If these problems can be solved, plasmas will have a more significant impact on the solution for the main societal challenges mentioned at the beginning, in particular environmental protection, for gas conversion and electrical energy supply, and safe and sustainable food production.

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