

Advances in plasma-driven solution electrochemistry

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ABSTRACT

Energetic species produced by gas-phase plasmas that impinge on a liquid surface can initiate physicochemical processes at the gas/liquid interface and in the liquid phase. The interaction of these energetic species with the liquid phase can initiate chemical reaction pathways referred to as plasma-driven solution electrochemistry (PDSE). There are several processing opportunities and challenges presented by PDSE. These include the potential use of PDSE to activate chemical pathways that are difficult to activate with other approaches as well as the use of renewable electricity to generate plasmas that could make these liquid-phase chemical conversion processes more sustainable and environmentally friendly. In this review, we focus on PDSE as an approach for controlled and selective chemical conversion including the synthesis of nanoparticles and polymers with desired but currently uncontrollable or unattainable properties as the next step in the use of PDSE. The underpinning redox chemistry and transport processes of PDSE are reviewed as many PDSE-driven processes are transport-limited due to the many short-lived highly reactive species involved.

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I. INTRODUCTION

Electricity-driven chemical reactions have the potential to provide low-carbon footprint processes for the chemical and manufacturing industry. Electrochemical, photochemical, electrocatalytic, sonochemical, electric heating, and plasma-based approaches are being investigated to fulfill this promise.¹ Plasmas have been investigated to initiate and sustain non-equilibrium gas-phase chemistry (such as for the synthesis of O₃)² or thermal chemistry.³ When combined with catalysts, these plasma-initiated processes may selectively enhance the synthesis of a range of chemicals.⁴ A less investigated process in the context of chemical synthesis is

plasma-driven solution electrochemistry (PDSE),⁵ a method where a plasma is sustained in the gas phase, producing energetic species that impinge on a liquid surface, initiating physicochemical processes at the gas/liquid interface and in the liquid phase.⁶ The energetic species include high-energy electrons, ions, photons, and radicals. Their interactions with the liquid phase can trigger chemical reaction pathways that result in their consumption and/or the generation of new species through cascading reactions. There are several processing opportunities and challenges presented by PDSE. These include the potential use of PDSE to activate chemical pathways that are difficult to activate with other approaches, as well as the use of renewable electricity to generate plasma which could

make these chemical conversion processes more sustainable and environmentally friendly.

While the plasma-induced gas-phase chemistry in humid air, as an example, can contain more than 100 different species and involve 1000+ reactions,⁷ all of which can potentially impact the resulting liquid-phase chemistry, many studies suggest that plasma produced $\cdot\text{OH}$ radicals and electrons, which quickly solvate, play important roles in aqueous chemistry.⁸ Conventionally, $\cdot\text{OH}$ radicals have been produced by radiolysis,⁹ photolysis,¹⁰ and Fenton chemistry,¹¹ while solvated electrons have been produced by radiolysis,¹² dissolving an alkali metal in ammonia,¹³ photo-detachment of negative ions in solution such as iodide¹⁴ or from plasmons.¹⁵ In PDSE, these species are produced at ambient pressure and temperatures at the interface of the plasma and liquid water without the need for vacuum equipment, complex potentially toxic and harmful carcinogenic solvents, precursor chemicals, or expensive catalysts.

Research into the interaction of plasma and liquids in the context of electrochemistry dates back to the 19th century.¹⁶ Applications of PDSE have remained mainly focused on the decomposition of harmful compounds in water including per- and polyfluoroalkyl substances (PFAS) removal,¹⁷ using PDSE to sample analytes in solution in analytical chemistry¹⁸ and PDSE-derived plasma-liquid activation for medical and agricultural applications.¹⁹ The current understanding of plasma-liquid interactions, based on research that is often focused on these applications, has been reviewed in a roadmap⁶ and discussed in several review papers.^{5,20–23} There have been fewer studies that have investigated the cascading reactions of these high-energy oxidizing, and reducing species can lead to a range of highly desirable chemical transformations in liquid water solutions.²⁴

In this review, we focus on PDSE as an approach for controlled and selective chemical conversion and the synthesis of nanoparticles (NP) and polymers with desired but currently uncontrollable or unattainable properties. Achieving these goals would represent a transformative step in the use of PDSE. While PDSE has been previously investigated,²⁵ fundamental research into PDSE-enabled chemical conversion is now focused on the synthesis of high value materials, such as the use of PDSE for polymerization,²⁶ organic synthesis such as pinacol coupling,²⁷ nanoparticles synthesis,²⁸ ammonia synthesis,²⁹ and peroxidation reactions such as propylene to propylene oxide.³⁰

The tuning and controlling of selective reaction outcomes benefits from a detailed understanding of the reactions and transport processes in PDSE, which is an emphasis of this review. A subgroup of the authors wrote a 2021 perspective in which ten questions were proposed to guide fundamental research in PDSE.⁵ This paper reviews progress in addressing these proposed questions. While most of the reviews and perspectives related to PDSE have been written from a physics perspective, this review is intended for the physical chemistry and electrochemistry community.

The underpinning redox chemistries of PDSE important transport phenomena are reviewed as many PDSE-driven processes are highly transport-limited due to the many short-lived highly reactive species involved. Recent advances in organic and inorganic synthesis are reviewed and promising PDSE control approaches are described that can be used to enable selective and desired reaction products. As the past decade has seen a rapidly emerging understanding of

PDSE through significant advances in diagnostics and modeling of these highly complex systems, key advances and further needs are highlighted. When a new approach is developed, efficiency metrics are often adapted from other fields, which is not different for PDSE. In this regard, the advantages and limitations of the use of Faradaic efficiency (FE) for PDSE are discussed.

II. REDUCING AND OXIDIZING PROCESSES

Despite the promise of PDSE for synthesis, our understanding of underlying chemical processes that initiate most of the PDSE driven chemical reactions is largely based on recent developments. One approach that can offer insights into PDSE is to compare PDSE with conventional electrochemical systems that are driven by current from solid electrodes. In a conventional electrochemical system, the direction of the electron flow between the solid electrode and the solution (oxidation or reduction of the solution species) is determined by a difference in the electrochemical potential of the electrode electrons and the redox potential of the solution redox couples (solution potential).^{31,32} Depending on the electrochemical potential difference, a solid electrode will produce either oxidation or reduction reactions of the species in solution. In general, an electrode will not concurrently induce both processes. In PDSE, the cascading reactions in the liquid phase are initiated by energetic species produced by and delivered from the plasma onto the plasma-liquid interface. These species can include both oxidative and reductive agents and, therefore, trigger oxidative or reductive reactions. Consequently, in PDSE, it is possible to have concurrently reductive and oxidative chemical pathways, and the prevalence of these pathways is governed by the flux of each species along with the rate constants for their reactions with an individual redox couple (Fig. 1).

To understand chemical transformations in PDSE, a closer look into the reducing and oxidizing species formed in the process of the plasma impinging on the liquid phase is required. Research has shown that at the plasma-liquid interface, the reactive species that enter the liquid phase will have a lifetime and penetration depth that is a function of the liquid environment.³³ For the plasma/water system, solvated electrons are often assumed to be the initial reducing agent while hydroxyl ($\cdot\text{OH}$) radicals are usually the initial oxidizing agent.³⁴ The $\cdot\text{OH}$ radicals are mainly formed in the process of electrons colliding with water molecules close to the plasma-liquid interface. It has been demonstrated that as the energetic plasma electrons enter the aqueous environment, they are slowed down and solvated by water molecules.^{22,35} There have been attempts to quantify the ratio of solvated electrons and hydroxyl radicals that enter the plasma/water interface.^{36,37} For example, Yue *et al.* measured the spatial distributions of electrons and $\cdot\text{OH}$ radicals close to the plasma-liquid interface in a pulsed atmospheric-pressure glow-like plasma with an aqueous liquid anode.³⁶ (The plasma discharge configuration which optimally drives plasma produced electron fluxes into the liquid surface is to have the plasma electrode be negatively charged and the liquid serve as the anode, often by having a grounded electrode in contact with the conductive solution.) The time-resolved number density measurements of electrons and $\cdot\text{OH}$ radicals indicated that when the plasma was active, the electron flux at the plasma/liquid interface was approximately two orders of magnitude higher than the flux of the $\cdot\text{OH}$ radicals. For these conditions,

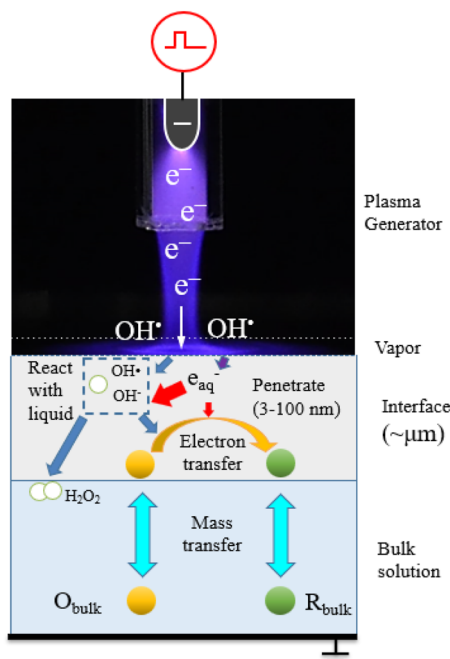
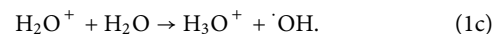
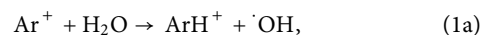


FIG. 1. Schematic representation of selected redox processes underpinning PDSE.

an overall reductive environment was being produced. When the plasma is off (the *afterglow* of the discharge), the electron flux into the liquid terminates (or decreases by many orders of magnitude) $\cdot\text{OH}$ radicals remaining in the gas phase may continue to solvate into the liquid. This continuing flux of $\cdot\text{OH}$ radicals onto the liquid surface and the longer lifetime of the $\cdot\text{OH}$ radicals relative to that of solvated electrons, $\cdot\text{OH}$ radicals would dominate during the afterglow and result in the aqueous environment to be overall oxidative. This dichotomy between coexisting oxidation and reduction reactions (or separated in time) is a feature of plasma/water interactions that could be exploited for creative chemical transformations. When the liquid is the cathode, $\cdot\text{OH}$ radicals are still a dominant gas-phase species, but instead of electrons, positive ions will dominantly

impinge on the liquid. Positive ions incident onto water will typically undergo hydration reactions which likely will result in the formation of $\cdot\text{OH}$ radicals and lead to a more dominant oxidizing environment through, for example, the following charge exchange reactions in an argon plasma, which may also acidify the solution:



The resulting liquid-phase chemistry can, therefore, be highly polarity-dependent. Solvated electrons have a reduction potential of -2.88 V vs NHE (normal hydrogen electrode), and $\cdot\text{OH}$ radicals have an oxidation potential of 2.8 V vs NHE,³⁸ resulting in reaction rate coefficients with most species that are diffusion-limited (10^9 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Hence, the reactions enabled by these species will occur near the plasma-liquid interface. Their lifetimes depend on the solution composition leading to finite penetration depths on the order of 10s of nm to a few micrometers.^{33,39} The redox processes in PDSE can lead to distinctive differences between conventional electrochemistry and PDSE, which are highlighted in Table I.

III. SPECIES UNDERPINNING PDSE

When plasmas interact with liquid-like water, species that can result in both oxidation and reduction of the water as well as dissolved species are produced.^{5,6} These processes are complex and can significantly vary depending on the nature of the plasma, the species dissolved in the solvent, distance in the solvent relative to the plasma-solvent interface, and as a function of time. Further investigations that we discuss here provide additional insights into redox chemistry initiated not only by solvated electrons and $\cdot\text{OH}$ but also by the potentially important role of anions in driving reduction reactions, nonthermal processes, and (vacuum) ultraviolet (V)UV-induced processes in PDSE.

A. Solvated electrons and $\cdot\text{OH}$

Recent modeling by Raisanen *et al.*⁴⁰ has examined the evolution of gaseous species coming from a plasma into water. While the

TABLE I. Comparison of conventional electrochemistry with PDSE.

	Conventional electrochemistry	PDSE
Charge transfer driven by	Difference in Fermi level between electrode and solution	Plasma-generated high-energy species (electrons, ions, photons, radicals, etc.)
Penetration depth and lifetime	Generally, not considered due to charge transfer only occurring at the electrode solution interface	Determined by the liquid environment, the nature and energy of the energetic species, the transport and lifetime of species
Reaction rate for a given redox couple	Determined by the electrode potential, the electrode material, diffusion, and the nature of the redox couple in the solution	Determined by the flux of high-energy species, transport and rate constants of the redox reaction

precise results depend on details of the plasma and on whether the plasma species are exposed to air and water vapor before entering the plasma, several experiments show that the highest concentration species capable of causing significant redox after entering the water layer are electrons and the $\cdot\text{OH}$ radical.^{33,36} The electrons are often at high energies/temperatures in non-equilibrium plasmas, with kinetic energies above 1 eV. However, the mean free path of these electrons in the liquid is less than 10 nm,⁴¹ during which the electrons are thermalized, forming e_{aq}^- in less than 1 ps.⁴² Electrons above about 6.5 eV are capable of directly reacting with water as hot electrons can lead to dissociation; this will be discussed in Subsection IV. Other processes associated with the hot electron regime, such as dissociation of neutral water that arises from electronic excitation, and the formation of H_2O^+ by electron impact/ionization have been described in a review by Garrett *et al.*⁴³ Electrons that survive to become thermalized, as well as thermalized secondary electrons, can participate in aqueous kinetics as hydrated electrons that can survive for microseconds.⁴⁴ When these electrons do react with water, $\text{H}^\cdot$, H_2 , and OH^- are produced. In addition, H_2O^+ disproportionates through charge exchange reactions in solution to produce H_3O^+ and $\cdot\text{OH}$.

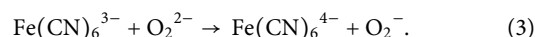
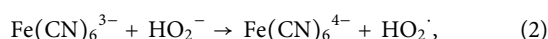
$\cdot\text{OH}$ radicals from the plasma, if above the temperature of the liquid, should equilibrate after hitting the water surface to the thermal temperature of the liquid in a few fs. The $\cdot\text{OH}$ radicals can participate in many kinetic processes, such as the recombination of two $\cdot\text{OH}$ radicals to produce hydrogen peroxide, H_2O_2 . In basic solutions, H_2O_2 can ionize to produce hydroperoxide (HO_2^-) and peroxide (O_2^{2-}), both of which are reducing agents, as discussed in Subsection III B. There is another active species, superoxide ($\text{O}_2^{\cdot-}$), which can be directly produced from the gaseous plasma in the presence of O_2 or produced in a solution by reaction of solvated electrons with solvated O_2 . There is also a significant flux of $\text{H}^\cdot$ from the gas-phase incident onto the liquid (for example, resulting from electron impact dissociation of water forming $\cdot\text{OH}$ and $\text{H}^\cdot$). While $\text{H}^\cdot$ can serve to reduce species such as Ag^+ , $\text{H}^\cdot$ atoms do not

react directly with water. $\text{H}^\cdot$ has a small Henry's law constant and is likely produced by other processes if present in the liquid phase (see Subsection III D). There are dozens of kinetic processes that are routinely used in modeling these processes.^{40,45}

B. Redox involving HO_2^- , O_2^{2-} , and $\text{O}_2^{\cdot-}$

Although the role of thermalized hydrated electrons and $\cdot\text{OH}$ in PDSE has been extensively studied, there are other species coming from the gaseous plasma or which are produced when the plasma species interact with water whose role in redox processes during PDSE is not known in as much detail. These include the three anions HO_2^- , O_2^{2-} , and $\text{O}_2^{\cdot-}$. HO_2^- is potentially of interest in PDSE as it has an estimated lifetime in alkaline solution of 1 h.⁴⁶ One way to describe redox processes involving these species when they interact with other species in solution (and where the kinetic processes are not so fast that the reactions are diffusion controlled) is to use Marcus theory⁴⁷ (see schematic in Fig. 2). For most practical cases, Marcus theory provides an accurate semiclassical middle ground in the description of electron-driven reactions.

Recent experiments operating at high pH or in thin liquid films in which the plasma significantly increases the pH due to solvated electron recombination, have shown increased conversion of formate and increased reduction of ferricyanide.⁴⁸ The latter observation could potentially be explained by



The calculated ferricyanide reduction rate coefficient of reaction (2) with Marcus theory is sufficiently fast to explain these results. The rate coefficient of O_2^{2-} was found to be significantly slower than that of HO_2^- , making it an unlikely reductant consistent with previous studies.⁴⁸ The ferricyanide reduction rates were also found

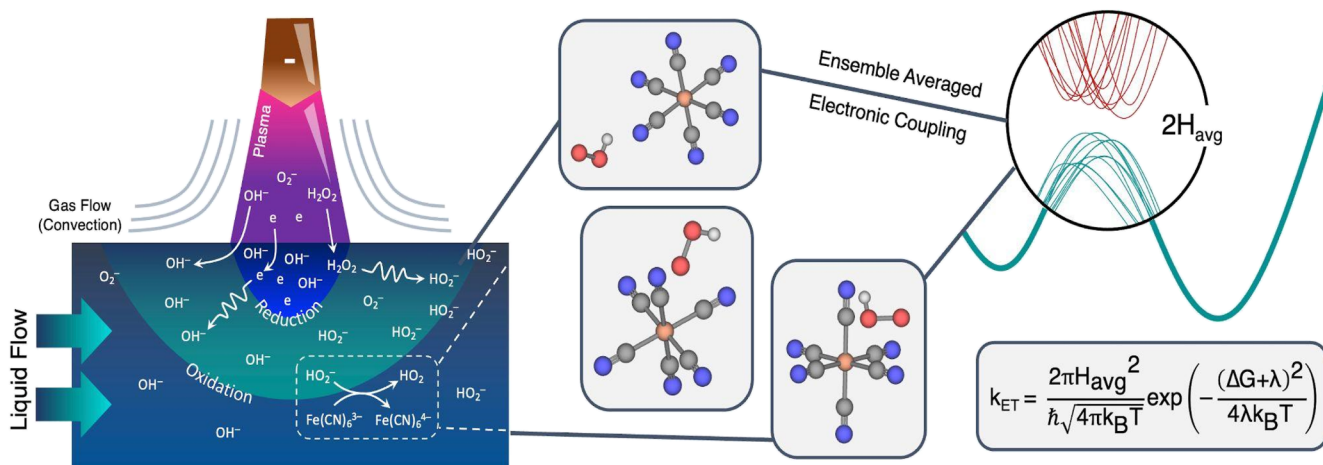


FIG. 2. Left panel: schematic cross section of the liquid film and plasma illustrating the distribution of $\cdot\text{OH}$ radicals, solvated electrons and other species, and including locations of oxidation and reduction in the liquid film. Right panel: schematic of Marcus theory evaluation of electron transfer rate coefficients, including averaging over potential curves for many possible geometries. Reproduced from Srivastava *et al.*, J. Chem. Phys. **160**(9), 094201 (2024) with the permission of AIP Publishing.

to be faster than ferrocyanide oxidation rates by $\text{HO}_2^\cdot$, consistent with the experimental results. Recently, the important role of O_2^- in PDSE, particularly for the oxidation and oligomerization of aniline, has been studied.⁴⁹

C. Hot electrons and other non-thermal processes

To date, most PDSE models have only considered thermalized electrons. However, electrons in gas-phase plasmas near the liquid surface can have average electron energy of several eV (Fig. 3). While recognizing that the near interfacial electron energy at the surface is challenging to measure and might require more research, the electron energy distribution function that produces this average energy may contain electrons with energies much greater than 10 eV. Plasma electrons that have energies >6 eV, and perhaps as low as

4 eV, can readily react with water to form a variety of products. As reviewed previously,⁵ the nature of these hot electron reactions is complex, and their reactions can take place on very short timescales (<1 ps), so there is little known from the experiments about these reactions. At high enough energy (>10 eV), ionization can occur, leading to secondary electrons that can become solvated. At lower energy, reaction with water can give $\text{H}^\cdot + \text{OH}^\cdot$, $\text{H}^- + \cdot\text{OH}$, and $\text{O}^- + \text{H}_2$ and neutral species such as $\text{H}^\cdot$, $\text{O}^\cdot$, and $\cdot\text{OH}$ but the yields of these products are not known.

Electron fluxes produced by negative discharges incident onto water contaminated with surfactant-like molecules, such as PFAS, have been shown to efficiently dissociate those molecules.¹⁷ Direct electron impact reactions from the gas phase with surface resident molecules are likely one of the contributing processes in that dissociation. Multi-dimensional modeling of atmospheric pressure argon

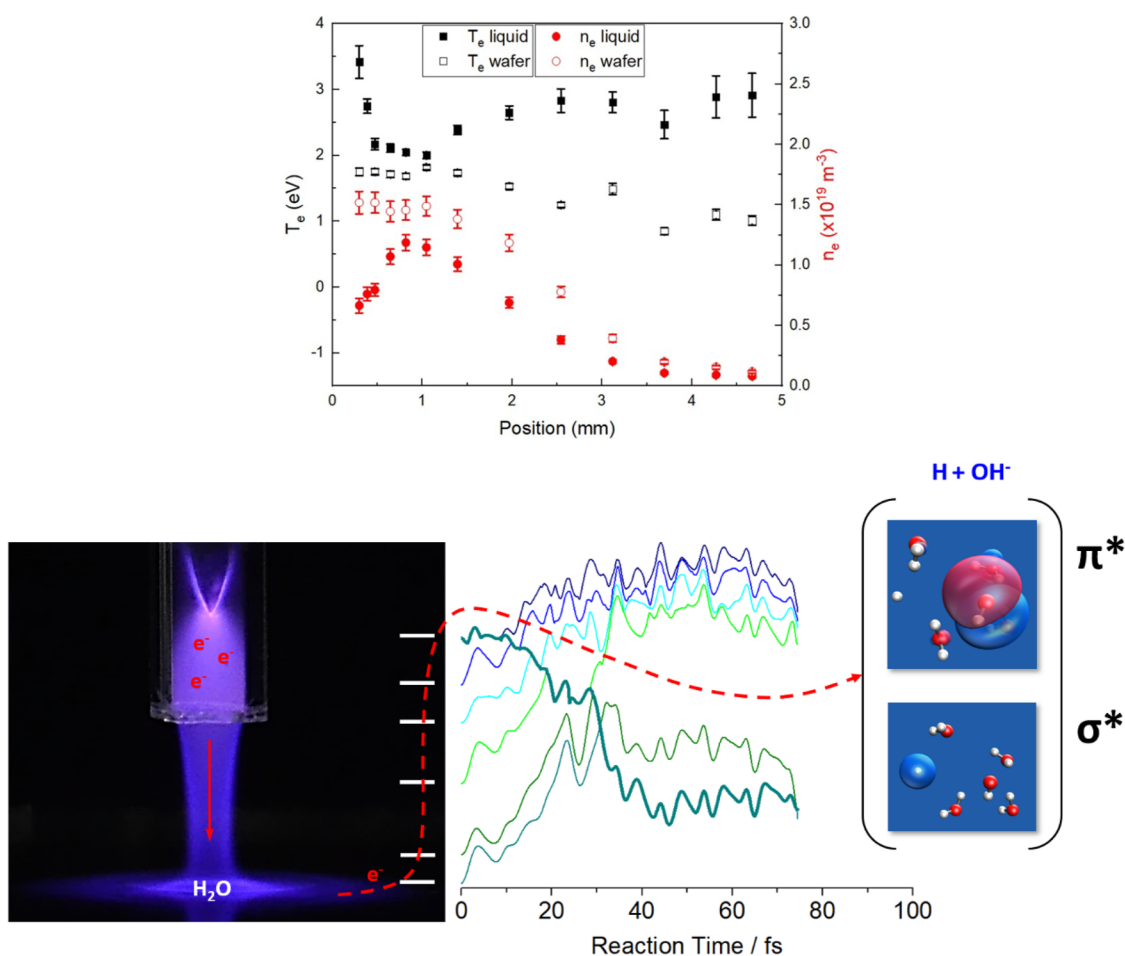


FIG. 3. Top panel: measurement of electron density and temperature near a plasma–liquid water interface and semiconductor wafer in a pulsed discharge. Reproduced with permission from Y. Yue and P. J. Bruggeman, *Plasma Sources Sci. Technol.* **31**(12), 124004 (2022). Copyright 2022 IOP Publishing. A significant increase in electron temperature was found in the case of the liquid interface. An electron temperature of 3.4 eV corresponds to a mean electron energy of 5.1 eV. In the case of Maxwell–Boltzmann distribution and the maximum measured electron energy being maintained up to the liquid interface, 30% of the impinging electrons would have an energy above the 6.5 eV threshold. Bottom panel: evolution of the excited states after a hot electron is added to a water cluster, including surface-hopping that leads to $\text{OH}^\cdot + \text{H}_2$, with $\text{OH}^\cdot$ initially produced in the σ^* excited state.

plasmas incident onto PFAS contaminated water have demonstrated that direct electron impact inelastic processes on surface resident molecules are likely important, as shown in Fig. 4.⁵¹ The results shown in Fig. 4 used electron impact cross sections for electrons interacting with gas phase PFAS molecules.⁵² Fundamental data for direct electron impact processes with aqueous species, as discussed in the following, are lacking for most complex processes. Developing a database for such electron impact on aqueous species is a high priority in understanding these complex systems.

Addressing this need for fundamental data describing the interaction of hot electrons with aqueous species, Jones and Schatz⁵³ have studied hot electron reactions with water, using theory methods to determine the threshold electron energy for dissociative electron attachment (DEA) in solution (see Fig. 3). To study the dynamics, it is necessary to describe the motions of nuclei with Born–Oppenheimer molecular dynamics, wherein one evolves the nuclei in time using forces obtained from an electronic structure calculation and also incorporates transitions between potential energy surfaces that arise because of nonadiabatic coupling using the fewest switches surface hopping (FSSH) technique. To treat this problem, the DEA of water clusters with 2–12 water molecules was considered and the threshold energy as a function of cluster size was determined. The dynamics was modeled assuming that an electron is added to a neutral cluster in a state that corresponds to a Feshbach resonance associated with electron + cluster scattering, and then, the system is evolved for many 10s of fs, ultimately leading to reaction. Figure 3 shows one such trajectory for a cluster of five water molecules that leads to the $\text{H}^- + \text{OH}^-$ product. Numerous hops

take place during the first 30 fs of the trajectory, with the spin density transitioning from highly delocalized initial excitation to more localized orbitals where the electron spin is on the dissociating H atom. Similar simulations for an ensemble of initial conditions and different excited states show that the threshold for dissociation is at about 6.5 eV, with little variation across cluster size (increasing to 6.9 eV for 12 molecule clusters), and that the only product is $\text{H}^- + \text{OH}^-$.

The only exception is with the water monomer that leads to $\text{H}^- + \text{OH}^-$, as has previously been established.⁵⁴ Autoionization of the clusters can also occur, but this is generally a slower process than nonadiabatic dissociation, which is a point that was not apparent until the work of Jones and Schatz. These results are related to what has been studied in cluster experiments and existing theory work, but the previous theoretical studies did not consider nonadiabatic dynamics. Given that the probability of hot electrons reacting with water is very high, as illustrated by the measurement of the electron temperature near the liquid interface with Thomson scattering shown in Fig. 3 (top), the reaction identified here is likely only significant in the top few nm of water exposed to plasma, which corresponds to the penetration depth but might have the potential to significantly impact the overall electron-induced chemistry. Balcerzyk *et al.*⁵⁵ reported pulsed radiolysis experiments for which diffusion-controlled rate coefficients for e^-_{aq} with Ag^+ are found although with an additional fast recombination on a time scale of a few 100 fs for electrons with Ag^+ where the electron is not hydrated. (The electron hydration time is 250 fs.)

D. Chemistry with VUV photons

An earlier review examined the importance of UV and VUV radiation in PDSE involving aqueous solutions,⁶ where it was noted that a significant fraction (28%) of the power dissipated by underwater plasmas can be converted into UV light that can induce photochemical reactions.⁶ Certain gaseous plasmas have been reported to produce VUV with an efficiency of up to 60% of the total energy deposition into the plasma.⁵⁶ The work by Troe and co-workers has suggested that the threshold for photoionization of water is at 6.5 eV,⁵⁷ but several processes (electron transfer, dissociation, and proton transfer) are possible, and the importance of these as a function of photon energy is a subject of ongoing interest.

Recent studies by Kortshagen and co-workers (Fig. 5, and also Ref. 58) at low pressures have demonstrated that under conditions where plasma electrons, ions, and neutrals are blocked from entering a solution of silver nitrate in glycerol solvent, the rate of Ag precursor reduction to Ag nanoparticles depends on the optical filter used to block radiation above a threshold energy during PDSE. Noticeably, less than 1% of the Ag^+ ions were reduced with the irradiation of UV at wavelengths longer than 280 nm, corresponding to an excitation energy of 4.4 eV.

As shown in Fig. 5, exciting the glycerol solvent to energies of ~5 eV can lead to its dissociation, with C–H and C–C bond breaking requiring a little less energy than for breaking O–H and C–O bonds. Especially for C–H and O–H bond breakage, this leads to the formation of H atoms, which, as noted earlier, can reduce Ag^+ through the electron transfer process, $\text{Ag}^+ + \text{H} \rightarrow \text{Ag}^0 + \text{H}^+$. Moreover, the more complex radicals that are also produced in these processes (involving an unpaired electron on carbon in many cases) are also able to

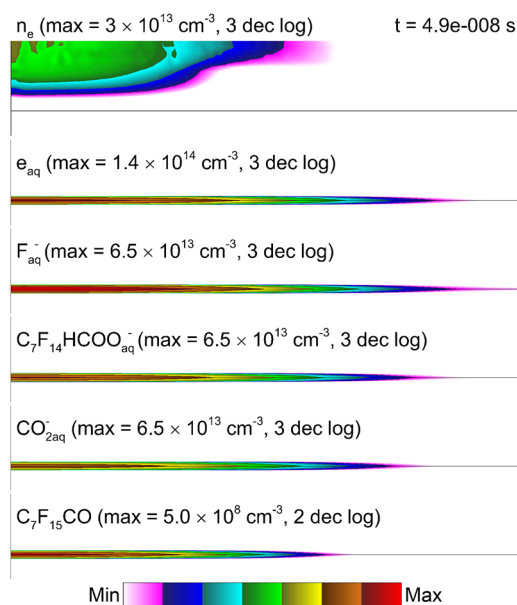


FIG. 4. Results from two-dimensional computational modeling of an atmospheric pressure argon plasma incident onto a water surface contaminated with PFAS molecules. Densities of solvated electrons and electron impact dissociation products are shown after 50 ns of plasma exposure.

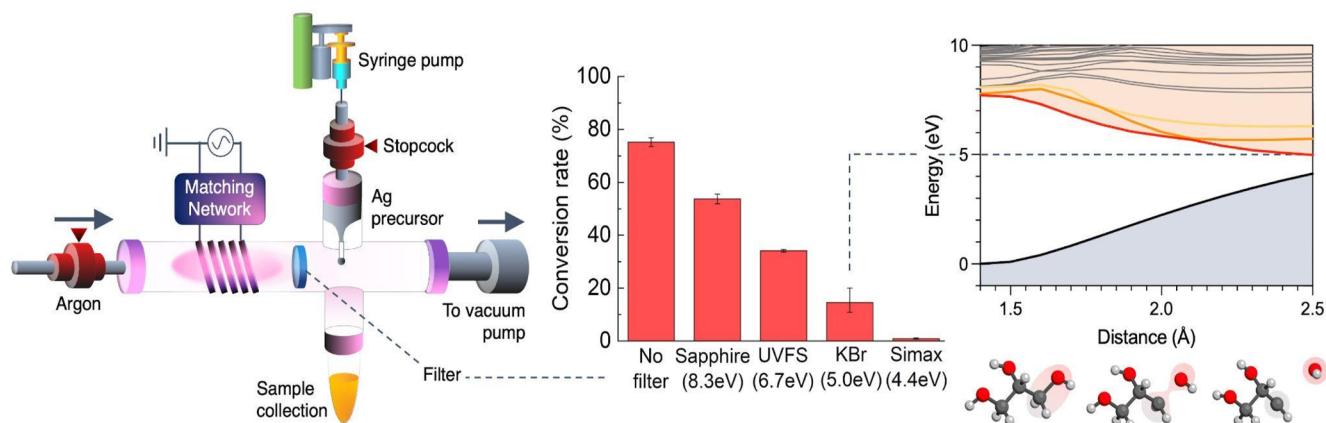


FIG. 5. Left panel: schematic of apparatus used for studying VUV effects on PDSE. Middle panel: conversion rate for several choices of optical filter separating plasma source and droplet. Right panel: Potential curves for ground and excited states potential curves of glycerol, showing states that would be accessed by UV/VUV excitation. Reproduced with permission from Xu *et al.*, J. Phys. Chem. Lett. **14**(44), 9960–9968 (2023). Copyright 2023 ACS.

provide reducing (or in some cases oxidizing) power that can play a role in silver nanoparticle formation. This points to the importance of UV and VUV in PDSE, and the results reported in Ref. 58 suggest that a substantial fraction of the reducing/oxidizing power associated with PDSE in this experiment can be due to UV/VUV. Similarly, several studies of the interaction of plasmas with liquid water have indicated that VUV can play a role in the production of radicals.⁵⁹

When atmospheric pressure plasmas interact with liquid surfaces, the discharge often transitions into a surface ionization wave (SIW). The SIW is an intense plasma that may have the thickness of several hundred micrometers to a mm and is essentially in direct contact with the liquid.⁶⁰ As a result, UV/VUV photons produced in the SIW can directly intersect the liquid prior to being absorbed by gas phase species. As discussed in Sec. IX, this proximity can produce fluxes of VUV photons onto the surface of the liquid that are commensurate with the electron flux.

E. Other primary sources of PDSE reactivity

While we have introduced the main species and recent new insights into the primary species responsible for PDSE above, several other sources of plasma-induced reactivity have been reported. In the case of oxygen plasmas, this involves O_3 , singlet delta oxygen, and atomic oxygen ($O^{\bullet}$). Ozone and singlet delta oxygen have been shown to be important to plasma-induced inactivation of bacteria and viruses.⁶¹ Plasma-produced $O^{\bullet}$ has been shown to be responsible for plasma-induced chlorine chemistry in saline solutions through the formation of $OCl^{\bullet}$ and to facilitate direct reactions with hydrocarbons.⁶² In air containing plasmas, this chemistry is further enhanced with the generation of highly reactive nitrogen chemistry, including peroxyxynitrate chemistry.⁶³ Plasmas have been used as an approach to synthesize H_2O_2 , which can accumulate over time in the plasma-treated solution. The species that have been investigated are a small subset of the plasma-produced gas-phase species that can be produced. Reported synthetic results illustrating selective ammonia generation suggest a possible role of $N^{\bullet}$ ⁶⁴ and

some nanoparticle synthesis studies have suggested a role of $H^{\bullet}$.⁶⁵ Nonetheless, further studies are required to elucidate the importance of these and potentially other important plasma-produced gas-phase species in PDSE.

IV. TRANSPORT PROCESSES

Transport phenomena associated with PDSE play a key role in chemical transformations and the final reaction products, particularly as many reactions are driven by short-lived plasma-produced radicals near the plasma-liquid interface. These multi-phase transport processes can be divided into three categories: gas-phase transport, gas-liquid interfacial transport, and liquid-phase transport. Convective gas flow, caused by externally applied gas flow in plasma jets and thermal and density gradients in the plasma contribute to the transport of reactive species.⁶ As already described above, the short-lived species have a limited penetration depth through the liquid from the gas-phase, generally concentrated within a thin region near the plasma-liquid interface.^{66–68} Primary reactions induced by plasma-produced $^{\bullet}OH$ radicals and solvated electrons are confined to distances of 10s of nanometers to a few micrometers.^{33,69} Therefore, in applications involving PDSE, the species dissolved in the liquid phase typically need to be transported to the near-interfacial plasma-liquid region with a large concentration of plasma-produced short-lived species that can readily react species in solution. This transport of species can either be due to induced or natural convection, diffusion, or drift. Transport in the liquid phase can be exceedingly complex and can be impacted by externally applied gas flows by the concentration and the nature of the compound dissolved in liquid (whether it is a surfactant or not)⁷⁰ and by the electrohydrodynamic (EHD) forces induced by the plasma.⁷¹ Gas-liquid interfacial transport involves bi-directional mass transfer including evaporation, sputtering, solute transfer, and diffusion of reactive and non-reactive plasma-produced species from the gas to the liquid phase. To first order, the steady state densities of neutral species at the gas-liquid interface are determined

by Henry's law equilibrium. It is common to think of gas phase species solvation into the liquid. However, super-saturated species in the liquid will de-solvate into the gas phase. The de-solvation process is potentially important in pulsed PDSE systems. For example, a gas phase species with a small Henry's law constant such as O_3 will quickly saturate the surface layers of the liquid during a plasma pulse. In the afterglow of the plasma pulse, advective gas motion may clear the surface of gas phase O_3 , leaving the liquid super-saturated. At that point, O_3 will de-solvate from the liquid into the gas phase.

As many plasma-produced species have a lifetime that is shorter than typical transport timescales, transport processes can significantly contribute to, if not even dominate, PDSE. The chemistry in the liquid phase can be limited due to the amount of reactive species transferred across the plasma-liquid interface⁷² and is, therefore, limited due to gas phase species production and/or transport. However, typical transport timescales in the liquid phase are slower than the gas phase,⁷² resulting in many plasma-induced liquid-phase reactions to be limited by liquid-phase transport. These transport limitations can significantly reduce the performance and efficiency of plasma-liquid reactor systems.⁵ Referring to Henry's law limitations to neutral long-lived transport into the liquid, this limitation applies only to the interface. Rapid transport of otherwise saturated aqueous species away from the surface will work toward de-saturating the surface, which then enables more gas phase species to solvate into the liquid. Although transport limitations are exceedingly important, there are few quantitative studies of transport phenomena in plasma-liquid systems and even fewer studies reporting "canonical" reactor geometries, allowing for a highly simplified description of transport phenomena. We highlight some key studies covering these aspects in the following.

While few studies report detailed direct measurement of gas phase reactive species fluxes to the liquid phase (see also Sec. X), an alternative indirect approach to assess gas phase species fluxes is to measure the chemical conversion of a liquid-phase chemical as a function of concentration. The goal in such an experiment is to increase the concentration of the liquid phase compound until the gas phase reactive species flux to the liquid phase becomes rate

limiting (instead of liquid phase transport), therefore, enabling the assessment of the amount of gas phase reactive species entering the liquid phase and reacting with the compound. An example of such a study is the work of Jirasek and Lukes⁷³ that reported on hypochlorite formation from Cl^- oxidation with plasma delivered $O^\bullet$ atoms. They found that at high concentrations of NaCl solution, the limiting reaction rate corresponds to the delivery rate of $O^\bullet$ atoms from the plasma gas phase (see Fig. 6). At increasing solution concentrations, the replenishing of Cl^- to the liquid surface via liquid-phase convection and diffusion becomes orders of magnitude greater than the flux of $O^\bullet$ atoms arriving from the gas phase, and the formation of OCI^- becomes independent of the Cl^- concentration. A complementary study was reported by Nayak *et al.*,⁷⁴ which focused on the conversion of formate by $^\bullet OH$ for plasma-droplet interactions. In this study, the $^\bullet OH$ density (and, therefore, $^\bullet OH$ flux to the droplet) was varied by adjusting the water concentration in the plasma. The results show that for a gas phase $^\bullet OH$ density in excess of $2.5 \times 10^{14} \text{ cm}^{-3}$, the conversion is limited by liquid phase transport of formate in a $40 \mu\text{m}$ droplet (see Fig. 6). In this case, it was shown that the conversion can be predicted by solving a diffusion equation for formate in the droplet with the assumption that the formate concentration at the interface is in good approximation negligible due to the very fast reactions of formate at the interface with the abundantly available $^\bullet OH$ radicals.

While plasma-driven reactions in the bulk of the liquid have been extensively reported, they often involve secondary reactions, such as peroxyxynitrite chemistry.⁶³ For example, coupled gas phase and liquid phase modeling (see Fig. 7) shows that when a plasma jet impinges on a solution, a reverse vortex is formed at the plasma-liquid interface near the edge of the liquid vessel alongside vortex formation in the bulk liquid. The plasma-generated reactive species accumulate in this reverse vortex, in which the short-lived species are quickly consumed to form long-lived species and do not penetrate into the bulk liquid even in the presence of convection.⁷⁵ This modeling result is supported by the experimental study of Taghvaei *et al.*⁷² They found that crystal violet dye decomposition timescales were consistent with convective solution mixing times.

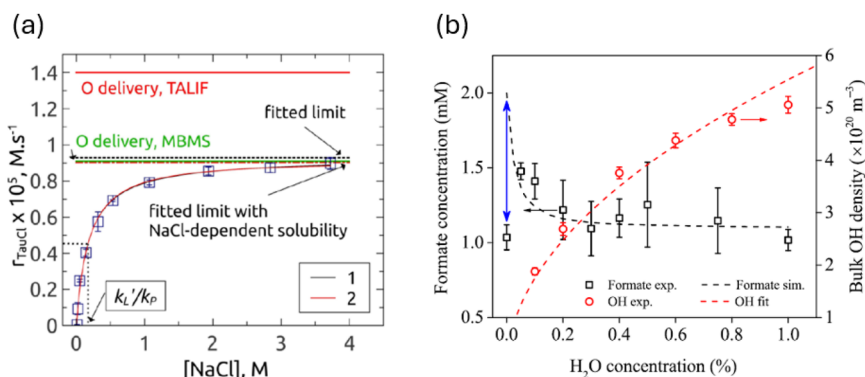


FIG. 6. (a) Production rate of TauCl (used to detect the amount of OCI^- formed in solution), and $O^\bullet$ atom delivery estimate, green line, as a function of the initial NaCl solution concentration. Reproduced with permission from V. Jirasek and P. Lukeš, *J. Phys. D: Appl. Phys.* **53**(50), 505206 (2020). Copyright 2020 IOP Publishing. (b) Average formate concentration in plasma-treated droplets as a function of water concentration in $\text{He}/\text{H}_2\text{O}$ plasma (and hence, varying gas-phase $^\bullet OH$ concentration) compared to the 1D reaction-diffusion modeling result. Reproduced with permission from Nayak *et al.*, *Plasma Sources Sci. Technol.* **30**(11), 115003 (2021). Copyright 2021 IOP Publishing.

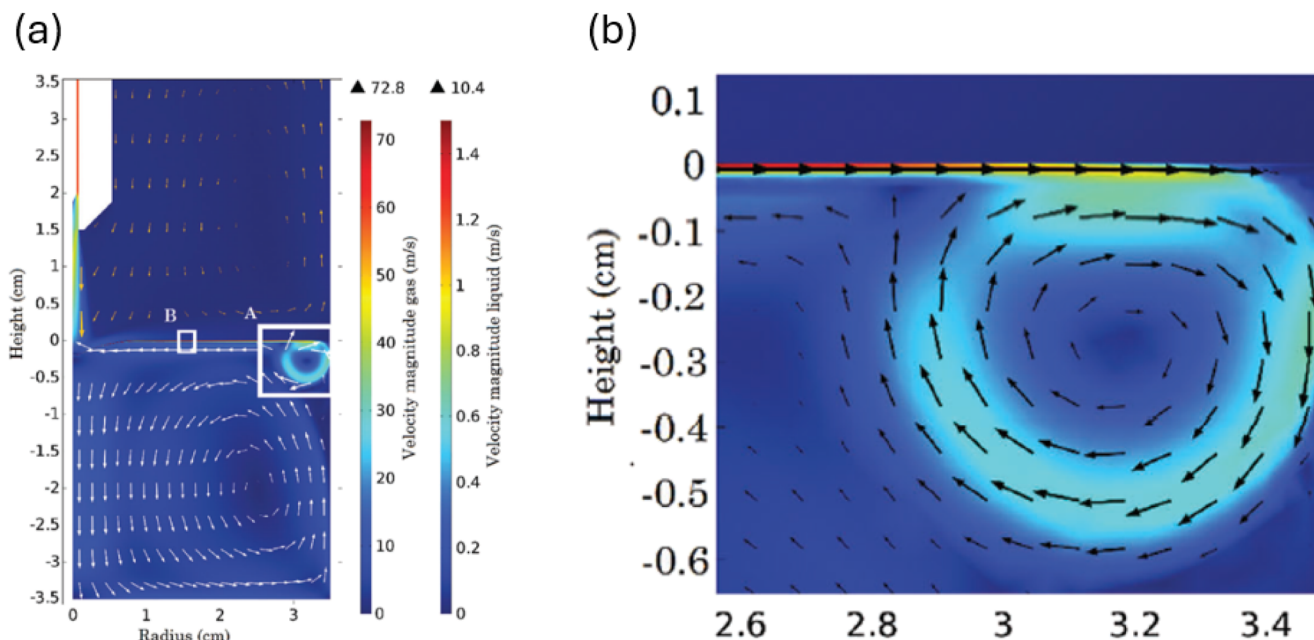


FIG. 7. (a) 2D modeling of the velocity magnitude in both gas and liquid phases for a jet-liquid configuration, and (b) close-up of the reverse vortex formed at the plasma-liquid interface. Reproduced with permission from Verlackt, Van Boxem, and Bogaerts, *Phys. Chem. Chem. Phys.* **20**(10), 6845–6859 (2018). Copyright 2018 RSC Publishing.

Kondeti and Bruggeman⁷⁶ showed that the dynamics of the liquid interface can further enhance the impact of liquid-phase convection. Other than liquid phase flows caused by the transfer of momentum from gas-phase convection, the roles of electrodynamic and Marangoni forces have been identified. Thagard *et al.*⁷⁰ reported that for a surfactant compound (e.g., perfluorooctanoic acid), the liquid flow at the interface reversed, flowing toward the plasma discharge due to Marangoni stress (flow induced by surface tension gradient). Lai *et al.*⁷⁷ found Marangoni effects during plasma-streamer interactions, which caused circulation patterns and capillary waves at the interface enhancing the transfer of highly reactive species into the bulk liquid. While all these processes could enhance transport, their timescales remain typically significantly longer than *fast* reaction timescales at the plasma-liquid interface.

When the majority of the reactions occur at the plasma-liquid interface, one needs to enhance the timescales of replenishment of the near interfacial plasma-liquid layer with compounds dissolved in solution to enhance the chemical conversion of compounds in solution. Delgado *et al.*⁷⁸ have shown through numerical modeling that in order for the bulk liquid species with a concentration of 1 mM to continuously replenish the near plasma-liquid interface (with a plasma diameter at the interface of a few millimeters on a timescale commensurate with plasma induced reactions), a minimum convective flow velocity of 10^2 – 10^4 m/s would be needed, which is not feasible. Nonetheless, plasma reactors having flowing liquid films have been shown to be able to reach improved conversion efficiencies of dissolved compounds compared to bulk reactors.^{79,80} This improvement is likely enhanced by increasing surface to volume

ratio, which enhances the flux of plasma-produced reactive species to the solution as was also found for microdroplets.^{81–83} Further improvement of conversion efficiency can be obtained by modulating the plasma discharge on a timescale similar to transport timescales although a more detailed understanding of the coupled transport-reaction processes might be required to achieve the full potential of PDSE.

Transport limitations are not only inherently difficult to overcome but they also lead to major challenges to quantitatively describe PDSE due to the complex coupling of multi-dimensional transport and reactions over a large range of time and length scales. Only recently, canonical reactors have been developed that allow for a simplified description of transport phenomena. One such reactor is a falling-thin liquid film plasma reactor developed by leveraging the work of Tauber *et al.*,⁸⁴ which enables the study of plasma-liquid interactions for liquid film thickness down to 50 μm , with liquid flow velocities on the order of 0.5–2 m/s. The liquid-phase transport in this reactor can be described by convection in the direction of the liquid flow and diffusion in the direction perpendicular to the main liquid flow. A model of transport-limited conversion of formate at the plasma-liquid interface shows excellent agreement with the experiments and describes the conversion as a function of the dimensionless equivalent of a Peclet number, with convection and diffusion occurring in directions perpendicular to each other.⁴⁸

Another highly simplified transport condition occurs in situations where diffusive transport dominates convection. This can be the case, for example, for thin static liquid films, which have

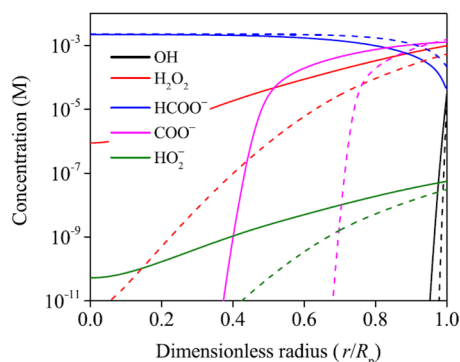


FIG. 8. Radial profile of species in a microdroplet after 10 ms plasma treatment for droplet diameters of 36 μm (solid line) and 56 μm (dashed line). Reproduced with permission from Oinuma *et al.*, Plasma Sources Sci. Technol. **29**(9), 095002 (2020). Copyright 2020 IOP Publishing.

been studied by modeling⁸⁵ but are experimentally difficult to implement. Microdroplets are another case, at least for short interaction times. Oinuma *et al.*³⁹ utilized this approach to achieve a quantitative understanding of the reactivity transfer of $\cdot\text{OH}$ radicals from the plasma gas phase into the liquid phase with formate droplets. It was found that for a 10 ms plasma treatment duration, H_2O_2 was able to penetrate the entire 36 μm droplet, while the $\cdot\text{OH}$ radical only penetrated up to 2 μm into the droplet, as shown in Fig. 8. The formate in the bulk of the droplet, therefore, needs to diffuse to the interface before it can be decomposed by the plasma-produced $\cdot\text{OH}$ radicals.

While significant progress has been made to quantify transport in recent years, there remains a lack of detailed studies of multiphase transport during plasma–liquid interactions. The characterization of canonical plasma–liquid interaction reactors for which the transport can be easily described for a broader range of chemistries is important to advance the field of PDSE and ultimately achieve the goal of controlling selective PDSE.

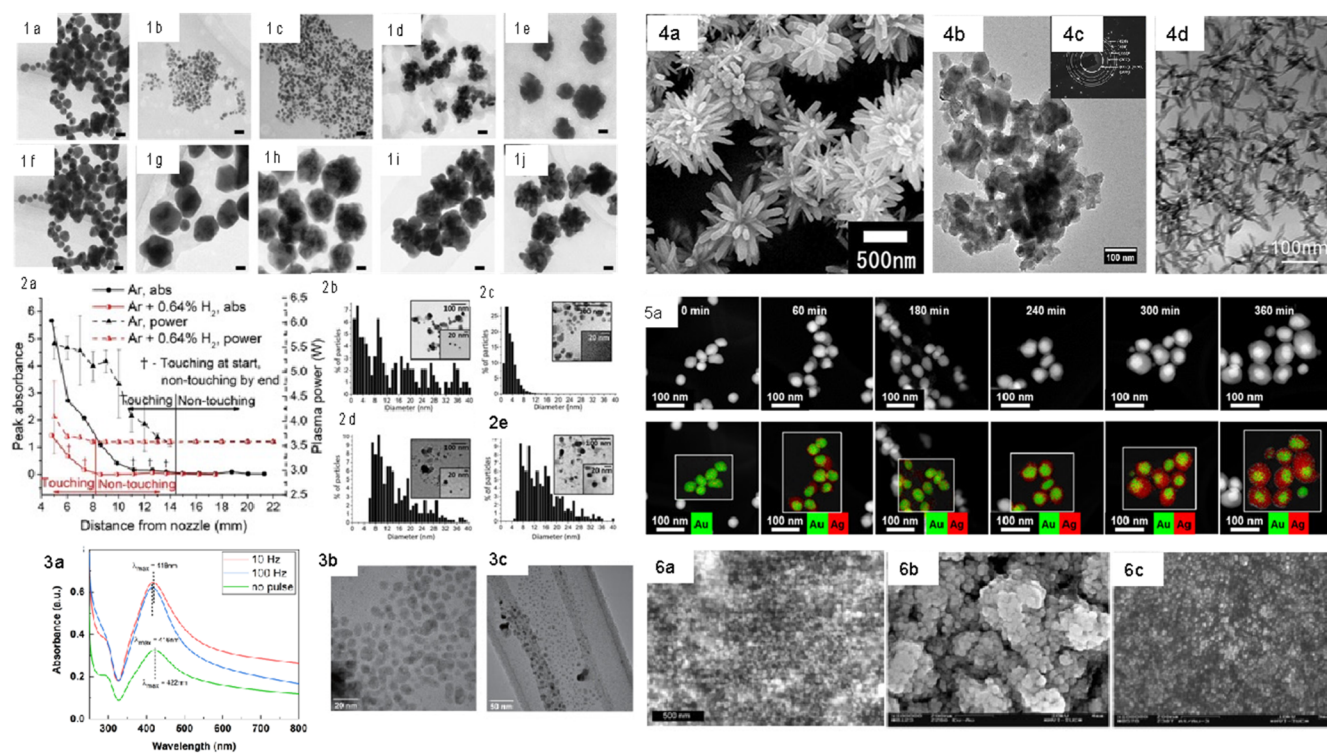


FIG. 9. Synthesis of unique nanostructures through PDSE. TEM images of morphology and size tuning of Au nanoparticles using varied concentrations of guanine [(1a)–(1e)] and cytosine [(1f)–(1j)]. Adapted from Ref. 94. Maximum absorbance at 420 nm of Ag nanoparticles synthesized via plasma treatment as a function of the distance between the plasma jet nozzle and solution (2a) as well as TEM images and particle sizes for feed gas and treatment distances as follows: Ar, 5 mm (2b); Ar + 0.64% H_2 , 5 mm (2c); Ar, 20 mm (2d); and Ar + 0.64% H_2 , 15 mm (2e). Adapted from Ref. 65. UV–vis spectra (3a) and TEM images of synthesized Ag nanoparticles with 10 Hz (3b) and 100 Hz pulse modulation frequency in a low-pressure glycerol droplet system. Adapted from Ref. 95. TEM images of metal oxides synthesized via PDSE: ZnO nanoflowers (4a), WO_{3-x} nanoparticles (4b) and (4c), and CuO nanoparticles (4d). Adapted from Refs. 96–98 respectively. HAADF images and elemental maps of Au and Au@Ag core-shell nanoparticles with varied times (5a). Adapted from Ref. 99. SEM images of Ag (6a), Cu (6b), and Al (6c) nanoparticles in low-pressure plasma-ionic liquid systems. Adapted from Refs. 100 and 101, respectively.

V. NANOPARTICLE SYNTHESIS

There has been a growing interest in synthesizing nanoparticles (NPs) through PDSE. The diverse reducing species in PDSE not only increase the complexity of analyzing the synthesis mechanism but also expand the routes available to tune the synthesis process.^{28,86–88} PDSE in both aqueous and non-aqueous solutions has been explored. Several review papers have reviewed the research in recent years.^{87,89–93} Some unique results are summarized in Fig. 9, and a list of different NPs synthesized by PDSE is provided in Table II in the Appendix, with some systems described in more detail in the following.

A. Aqueous solutions

Aqueous media have been widely used for the synthesis of NPs in atmospheric pressure PDSE. Synthesis of Ag nanowires using an arc discharge generated over an aqueous solution of NaNO_3 with two Ag filaments was reported in 1999.¹⁰² In 2005, Koo *et al.* investigated the synthesis of Pt NPs by exposing an aqueous solution of H_2PtCl_6 to atmospheric pressure alternating current (AC) H_2/He plasma.¹⁰³ Following these initial studies, the synthesis of many varieties of metal and metal oxide NPs was demonstrated, including Au,^{104–106} Ag,^{65,107,108} Pt,^{109,110} Pd,^{111,112} Ni,¹¹³ Fe and FeO_x ,¹¹⁴ Cu and its oxides,⁹⁸ ZnO ,¹¹⁵ defect induced black titanium oxide (H-TiO_{2-x}),¹¹⁶ tungsten oxide (WO_{3-x}),⁹⁷ and nanocomposites including Au-Ag,⁹⁹ Pd-Ru,¹¹¹ and Fe-Pt.¹¹⁴ By using arc discharges with carbon electrodes, carbon related materials including multi-walled C nanotubes, carbon NPs, and graphene nanosheets, were synthesized.²⁸ It was found that properties of NPs can be tuned by varying plasma parameters such as discharge voltage and current, treatment time, and pulse frequency.^{28,88} Chemical parameters

such as the solvent, type, and concentration of metal precursors, pH value, and the use of surfactants also play a crucial role for the morphology and chemical composition of NPs. Narrow size particle distributions have been obtained by PDSE without the use of capping agents.¹¹⁷ The voltage polarity impacts plasma properties and the types of reducing species for NP synthesis as well. For example, Thai and co-workers examined the formation of gold NPs for different discharge polarities. They found that if the liquid served as the anode, gold NPs were synthesized under the plasma-liquid interface via the reduction of solvated electrons. In contrast, when the liquid was the cathode, NPs were mainly generated at the Pt wire where H_2O_2 was proposed to reduce gold ions.¹¹⁸

Maguire *et al.*, have shown that Au NPs can be produced in micrometer-sized droplets with plasma contact times on the order of milliseconds.¹²⁰ They compared the rate of nanoparticle synthesis in their approach with radiolysis and electron beam approaches. The electron dose rate for the plasma conditions of their work is moderate compared to electron beams, but the Au^{3+} reduction rate per unit time and volume was two orders of magnitude larger. Nam *et al.*¹¹⁹ recently investigated this process in more detail. They showed that the ion precursor conversion exceeded by 300 times the maximum Faradaic efficiency and were able to identify important roles of both short-lived reducing species such as solvated electrons likely complemented with VUV photon-induced reactions and H_2O_2 in the reduction of Au^{3+} . A model involving burst nucleation driven by reduction of the precursor ion, Au^{3+} , during the millisecond plasma exposure and subsequent autocatalytic growth facilitated by H_2O_2 after the plasma exposure was able to reproduce the experimental findings. Autocatalytic growth mainly determines the particle size and is responsible for the majority of the ion precursor conversion in the model while also explaining the excessively large Faradaic efficiency found in the experiment (Fig. 10). While this

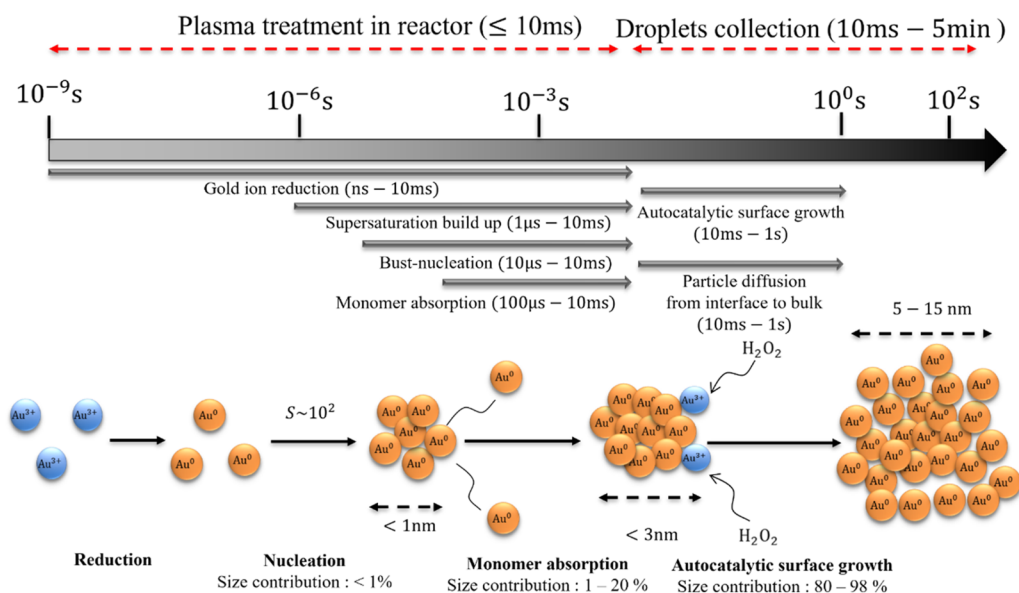


FIG. 10. Schematic representation of PDSE-enabled Au NP synthesis as found through the investigation of plasma-droplet interactions. Reproduced with permission from Nam *et al.*, Chem. Sci. **15**, 11643 (2024). Copyright 2024 RSC Publishing.

model remains highly simplified, it underlines the complexity of PDSE-enabled processes that are likely facilitated by a multitude of plasma produced species. The recent work of Raisanen *et al.*⁴⁰ presents an attempt to model the growth of nanoparticles one atom or ion at a time up to a critical size related to the nucleation threshold. The details of this model are described in Sec. IX. While this model seems to capture the essential growth elements for modeling nanoparticle growth, details of the model remain to be verified by the experiment.

B. Non-aqueous solutions

While aqueous solutions are suitable for PDSE at atmospheric pressure, the high vapor pressure of water limits its applicability for low-pressure PDSE. Ionic liquids (ILs) with low vapor pressures are an attractive alternative for low-pressure PDSE.¹⁰¹ The groups of Endres and Janek conducted the first synthesis of Ag NPs in 1-butyl-3-methylimidazolium trifluoromethylsulfonate,¹⁰⁰ which was followed by the synthesis of other metals such as Au¹⁸⁹ and Cu¹⁰¹ as well as semiconductors such as Si and Ge.¹²¹ While ILs are capable of surface passivation and stabilization of NPs, the low solubility of metal salts in ILs, contamination of NPs by derivatives of decomposed ILs, and high viscosity limiting diffusion of reducing species pose critical issues for NP synthesis in ILs in low-pressure PDSE.^{122,123}

Glycerol, a major co-product of biodiesel production with a low vapor pressure, was recently investigated as an electrolyte solvent.⁹⁵ Size tuning of Ag NPs in a droplet-based low-pressure PDSE system was demonstrated. Plasma generates reactive species, including electrons and UV photons. After they reach the liquid surface, the solvated electrons and glycerol fragmentation radicals generated by photodissociation become reducing species, which are consumed in reduction reactions with Ag⁺. Reducing the droplet residence time and plasma power caused the geometric standard deviation of the nanoparticles to decrease from 1.8 to 1.4, with a geometric mean diameter of 14.9 nm. With an extended droplet residence time and higher power with increased plasma species fluxes, the continuous reduction of silver ions likely leads to continued nucleation of Ag NPs that can coalesce and increase in size through surface growth, leading to larger NPs and a broader size distribution. The size of synthesized silver NPs decreased to less than 10 nm and a geometric standard deviation of 1.3 for pulsed power operation at 10 and 100 Hz and 20% duty cycle, compared to continuous wave (CW) plasma under the same average power. The proposed mechanism is during the plasma-on period, when silver ions are first reduced to atoms, following the nucleation of Ag clusters and their coalescence to form Ag NPs. However, during the plasma-off period, the reduction of silver ions to atoms is significantly suppressed, without enough plasma reactive species. In this case, the low frequency pulsing (long inter-pulse period) attenuated the replenishment of newly formed NPs and thus the diffusion of adjacent NPs to grow into larger ones in the liquid phase. Tuning plasma parameters may present an effective way for tuning NP properties.

The interactions between non-aqueous solvents and metal salt precursors, combined with the rapid reduction processes facilitated by atmospheric PDSE, also enable unique applications, particularly in synthesizing alloy nanomaterials that are difficult to fabricate using alternative approaches. Chen *et al.* demonstrated

this approach through the synthesis of bimetallic nanoparticles composed of Ag and Pt atoms.¹²⁴ Their mechanistic studies indicated that a unique feature of plasma/solvent systems was high reduction rates, triggered by solvated electrons, which resulted in the kinetic trapping of Ag and Pt metals in alloy nanoparticles. It was also observed that well-mixed Ag–Pt alloy nanoparticles [Figs. 11(a)–11(c)] were produced when ethylene glycol (EG) was used as the solvent. In contrast, using water as the solvent led only to the formation of monometallic Ag nanoparticles [Figs. 10(d)–10(f)]. The differences were attributed to the large discrepancies in the reduction rates of Pt and Ag precursors in water compared to the discrepancies in ethylene glycol.

VI. ORGANIC SYNTHESIS

Previous work on PDSE has shown that plasma–solution interactions drive the production of many reactive chemical species such as oxygen and nitrogen radicals, solvated electrons, high-energy photons, and peroxides. However, most of the research in the space of plasma-driven reactions has focused on gas-phase chemistry or plasma–solid interfacial reactions. Plasma–liquid chemical reactions are potentially an avenue to novel synthesis methods, particular in organic chemistry. The current work in PDSE is looking to control these species to drive organic reactions, ideally in solvents such as water. The opportunity to harvest and use radicals and high-energy species that are not available as standard reagents potentially opens a large number of possible reaction pathways. Solution-based plasma-driven reactions also open a possibility to remove the need for more environmentally damaging solvents or metal-containing oxidants by substituting them with water solvent and transient aqueous reactive radicals. This section will discuss some currently known reactions and polymerizations driven through plasma–solution interactions and provide insight into the potential for future control of plasma-driven chemistry in solutions.

Organic molecule modifications are an intriguing use of plasma–liquid interfaces to produce useful functional changes to existing molecules. An overview of reported organic chemistries is provided in Table III in the Appendix. The current understanding of what reactions can be driven, especially selective reactions, in a plasma solution interaction is limited due to the complex mixture of active chemical species produced through the interaction; however, the field is rapidly growing. Studies reporting on selective chemical reactions of small molecules begin to illustrate potential reaction targets for future research. Ahmadi *et al.* identified a preferential oxidation of the terminal aldehyde of *D*-glucose in water to convert the molecule into *D*-gluconic acid.¹²⁵ They showed that the key species for driving the oxidation was likely short-lived radical oxygen species formed by the plasma. The reaction was also selectively driven by altering the feed gas composition, increasing product formation with the addition of oxygen into the argon gas and a nitrogen shield gas. These findings imply that selective oxidation of chemical species can be tuned through feed gas alterations, as well as selective trapping of reactive radicals. In a study performed by Gorbanev *et al.*, they found that the process of dehalogenation of aromatic compounds can also be in part controlled by the identity of the feed gas.¹²⁶ Recently, PDSE was leveraged for carbon–carbon bond

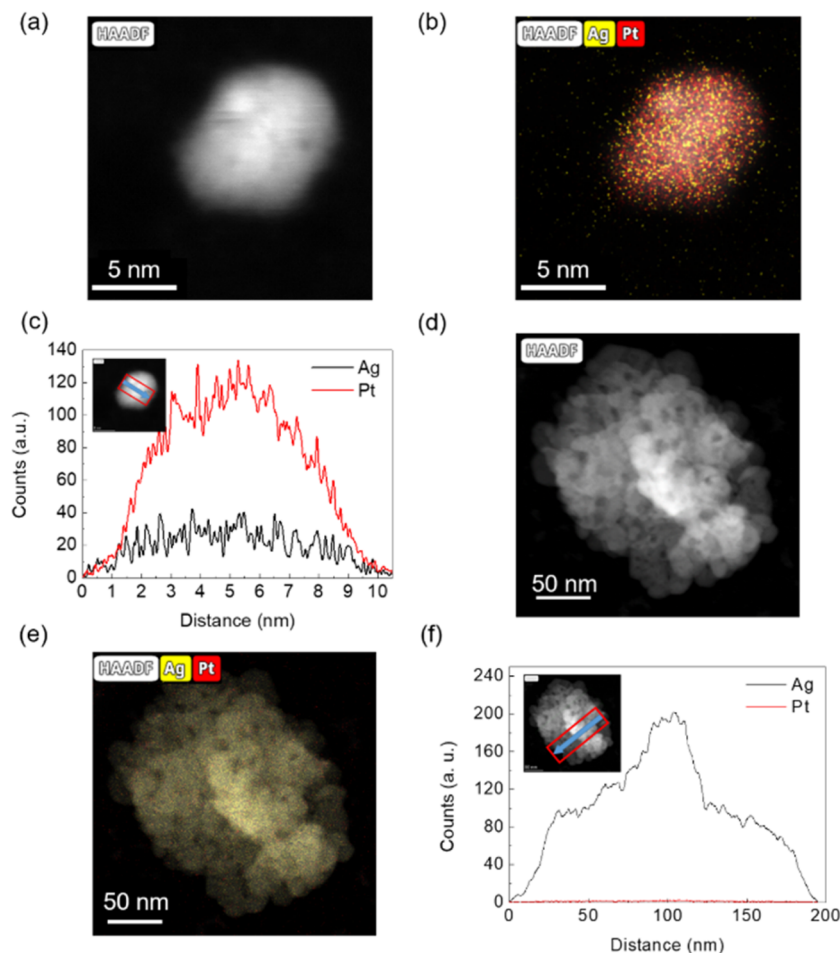


FIG. 11. (a) Dark-field scanning transmission electron microscopy (STEM) image, (b) overlapping Ag and Pt energy-dispersive x-ray spectroscopy (EDS) mapping data with the STEM image, and (c) EDS line scan of the Ag and Pt net signals of $\text{Ag}_{0.2}\text{Pt}_{0.8}\text{-NP}_{(\text{EG})}$ synthesized in EG. (d) The dark-field STEM image, (e) overlapping Ag and Pt EDS mapping data with the STEM image, and (f) EDS line scan of the Ag and Pt net signals of a nanoparticle synthesized in aqueous solution. The dark-field STEM images were acquired by the high-angle annular dark-field detector (HAADF). Reproduced with permission from Chen, Lee, and Linic, *Chem. Mater.* **35**(16), 6557–6565 (2023). Copyright 2023 ACS.

formation via pinacol coupling.²⁷ This process was ascribed to solvated electrons with Faradaic efficiencies up to 80% (Fig. 12) and was studied for methyl-4-formylbenzoate reporting yields of 40%. This work was generalized to benzaldehydes, benzyl ketones, and furfural. Another biological molecule target study performed by Takai *et al.* showed that selective organic oxidation can be performed on amino acid targets.¹²⁷ The conversion of a terminal amine into a conjugated aldehyde was reported. They observed the formation of disulfide bonds between cysteines, which quickly converted to sulfonic acid. The range of functional groups across the amino acids and the range in selectivity found in this study show merit for more research to identify chemical moieties that show selective reactivity under plasma–solution reaction conditions.

Lee *et al.* have shown the ability to drive partial oxidation catalytic processes as demonstrated in the synthesis of propylene oxide ($\text{C}_3\text{H}_6\text{O}$) through selective propylene epoxidation³⁰ (Fig. 12). These studies showed that hydrogen peroxide (H_2O_2), which is formed near or at the water/plasma interface from $\cdot\text{OH}$ radicals, served as a selective oxidizing agent to epoxidize the dissolved propylene (C_3H_6) over a titanium silicate-1 (TS-1) catalyst dispersed in water solution with a carbon-based selectivity of more than 98%.

This was the first demonstration of a partial oxidation reaction where oxygen atoms were derived from H_2O . These studies show that plasma can be used, when interfacing with water solutions, to modify small molecules for the addition of some functional groups such as aldehydes or double bonds while leaving much more room to study a broad range of chemical moieties for further chemical modification.

Plasma solution interfaces have also been shown to drive polymerization reactions.^{26,128} The work by Lee *et al.* showed that a polyaniline–metal complex can be synthesized in a solvated water droplet to form polyaniline films used for phosphate detection.¹²⁹ The work by Gangal *et al.* found that the addition of metal salts in a solution of acrylamide amplified the production of polyacrylamide by complexing with the metallic nanoparticles formed in tandem.¹³⁰ Both studies indicate a trend of polymer formation being enhanced by the addition of nanoparticle formation. However, much remains unclear about why these interactions are symbiotic, and how plasma can be tuned to better drive these reactions. Polymerizations are also not limited to metallic interactions. Tan *et al.* show that atmospheric pressure plasma can be used on liquid styrene to polymerize styrene into polystyrene, while also identifying some oxidized

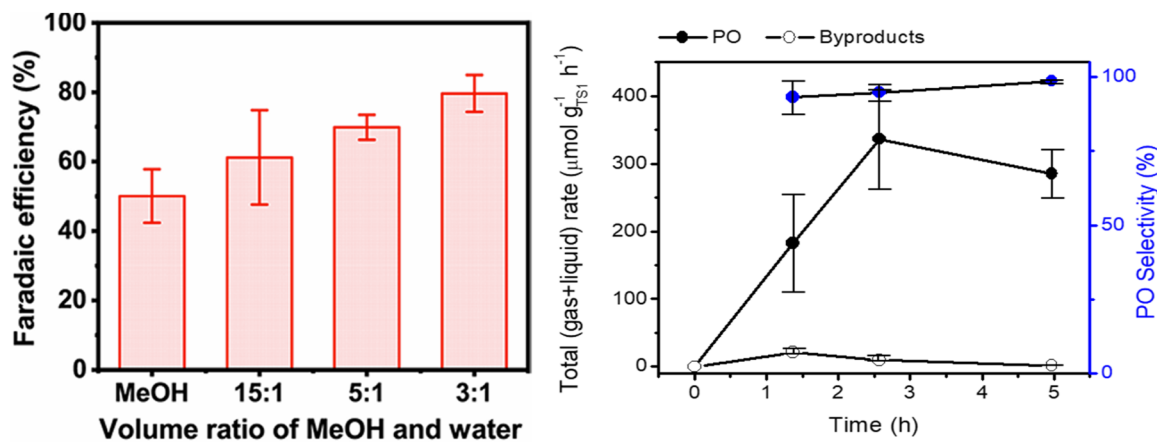


FIG. 12. Left panel: Faradaic efficiency of pinacol-coupling product methyl-4-formylbenzoate by PDSE as a function of methanol/water volume ratio. Reproduced with permission from Wang *et al.*, J. Am. Chem. Soc. **145**(19), 10470–10474 (2023). Copyright 2023 ACS. (right) The total production rates (gas and liquid phase) of propylene oxide (PO) by PDSE (black filled circle) and by-products (black empty circle). PO selectivity is illustrated by the blue circles. Reproduced with permission Lee, Chen, and Linic, JACS Au **3**(4), 997–1003 (2023). Copyright 2023 ACS.

styrene species.¹³¹ Clay *et al.* found that superoxide mediates the oligomerization of aniline, ruling out significant contributions from other plasma-generated oxidizing species.⁴⁹ A thorough discussion of plasma–liquid interaction polymerizations can be found in the review by Jang *et al.*⁹⁰ Each of these studies has shown that polymerization can be driven by plasma interfacing with the solution. Many of these reactions differ in their PDSE polymerization mechanism compared to conventional polymerization mechanisms, implying possible advantages for PDSE for controlled polymerization. The potential for driving redox driven and radical chain growth polymers in plasma–solution interactions opens a large space for future research in unique polymerization possibilities.

The potential for plasma-driven chemistries in solution provides a route of study for future control of organic reactions. Many of these reactions can substitute toxic metals and harmful chemicals for less environmentally impactful transient plasma products. However, there is still much work to be done to make plasma a readily available, chemically selective, synthetic tool. Little is known about the mechanisms that drive many of the reactions. Experiments, such as radical trap measurements, can begin to show whether a reaction is driven by short-lived radical species, of which there are many, or long-lived peroxides and acids that form.⁴⁹ However, these experiments can only provide limited information toward understanding the reaction mechanisms. Since many of these reactions seem to be driven by transient species, time-resolved experiments must be developed to identify the short-lived intermediates that drive reactions. Development of more selective radical trap experiments and sequestration reactions can also be used to identify radicals at play in redox chemistries driven by plasma at the solution interface, such as the use of superoxide dismutase to sequester superoxide.⁴⁹ These findings can help identify the means of controlling the production of wanted reagents in the liquid and removing or muting the interfering reactive reagents to selectively drive useful organic reactions.

VII. CONTROL OF PDSE

Controlling PDSE remains a major challenge because the experimentally controllable parameters typically only indirectly control reactive species fluxes and hence PDSE. Controlling the electron flux onto a liquid in a plasma reactor typically involves controlling the electron density, which in DC plasmas is proportional to the power deposition. For pulsed discharges, this can be achieved by controlling the applied voltage. Changing power or applied voltage will also result in changes in radical densities and (V)UV photon generation. Therefore, any change made to the plasma will typically impact multiple aspects of the PDSE process, making advanced control approaches challenging. The most obvious control for PDSE is temporal control of the plasma-produced radical initiators, supplied in a repetitive burst mode or modulated radio frequency (RF) plasmas. Choice of solvent can significantly impact PDSE and this is a logical additional tuning parameter toward controlling PDSE.

Pulsed electric fields are a common way of controlling discharge properties. By tuning operating conditions, such as discharge polarity, voltage amplitude and pulse duration, plasma properties, including electron density and gas temperatures can be manipulated. Since plasmas produce a wide range of short-lived and long-lived species, parameters such as pulse frequency, applied peak voltage, gas flow rate, and polarity may have a significant impact on the plasma chemistry.^{123,132–134} It is well-established that pulsed excitation can enhance the energy efficiency of plasma processes;¹³⁵ however, few studies have been reported that link these parameter changes in a holistic way to PDSE or synthesis outcomes. Yue *et al.* reported the impact of pulse width on the reduction of ferricyanide.³⁶ This result showed that the Faradaic efficiency for ferricyanide increased from 15% by DC excitation to 40% by pulsed excitation (0.5 μs pulse width). Liu *et al.* investigated the impact of the pulse width on the formation of H₂O₂, NO₂[−], and NO₃[−] in

solution showing distinctive trends for these three species as a function of the pulse width, suggesting the possibility to control reactive species compositions.¹³⁷

Modulation of the RF power is a technique to control ion energies and fluxes to surfaces, which is widely used in semiconductor processing.^{139–142} Modulating RF power leads to a rapid relaxation of the electron energy in the plasma afterglow. This also causes the plasma sheath potential to decay thus leading to reduced ion energies between plasma pulses and possible extraction of negative ions from the decaying plasma. Limited work has been done on exploiting RF modulation to actively control PDSE processes. Dzimitrowicz *et al.* studied the formation of silver NPs using AC voltage (50 kHz) modulated at frequencies within 500–1500 Hz with duty cycles of 30%–70%.¹⁴³ The authors found that increasing either the pulse modulation frequency or its duty cycle led to a larger size of Ag NPs. In recent work on PDSE under low-pressure conditions, using glycerol as a solvent, Xu *et al.* found that the size of synthesized silver NPs can be changed by RF power modulation⁹⁵ as described above. In these cases, both the treatment time variations and transport of the produced NPs during the plasma off time away from the interface could impact the results.

pH values have a significant impact on PDSE-driven processes,¹⁴⁴ particularly as many plasma-driven reactions are sensitive to pH. For example, recent studies demonstrated the potential of manipulating pH values to control the NP formation and morphologies in aqueous solutions. Wu *et al.* studied the formation of silver NPs in aqueous solutions with argon DC plasmas within a pH range of 1.99–10.71.¹⁴⁵ No observable Ag NPs were obtained from silver nitrate at a pH value of 1.99. The authors concluded that while most of the solvated electrons will be consumed upon reaction with protons. Sun *et al.* similarly reported the synthesis of gold NPs using HAuCl₄ as the precursor with pH of 2, 7, and 12.¹⁴⁶ The results showed that gold NPs with relatively uniform size distribution were obtained at a pH of 2. The authors concluded that reduction of gold salt by H₂O₂ is enhanced at neutral pH and larger numbers of reduced Au atoms available per nucleation site at high pH value contributing to large clusters. pH values can also also significantly

impact the reactive species formation. Recently, Nam and Brugge-man qualitatively explained pH effects in plasma-enabled gold NP synthesis with a one-dimensional film reaction-diffusion model.¹⁴⁷ Wang *et al.* showed that H₂O₂ and NO₂[−] formation are favored under alkaline conditions (pH = 9) in atmospheric discharges (see Fig. 13) compared to neutral (pH = 7) and acidic (pH = 5) solutions.¹³⁸

While the pH change was used as an analytical signal, to gain insight into competing and synergetic effects of various reducing species in water, pH was shown to be a key parameter that can impact the reaction paths in organic solvents as well. For example, Padmanaban *et al.* observed a pH decrease and acidolysis of ethanol with increasing plasma treatment time.¹⁴⁸ A detailed understanding of pH-controlled reaction pathways will help in devising PDSE reactions.

The choice of solvent in PDSE can have a notable impact on the overall process, affecting the formation and stability of the plasma, as well as the characteristics of reactive species produced, ultimately determining the final outcome of the process. Chen *et al.* showed that when pulsed discharge plasma was formed between two Cu rods in ethylene glycol, spherical Cu NPs were synthesized.¹⁴⁹ However, under similar conditions with an ethylene glycol–water mixture, the products were needle-like CuO NPs or polygon and square Cu₂O NPs, which were tunable by fractional water content. These different morphologies were attributed to the different thermal conductivities of ethylene glycol–water solutions. Similarly, solvents can impact the reduction potential and enable the synthesis of bimetallic particles, as discussed above.

The chemical structure of ILs also influences the properties of NPs. Brettholle *et al.* reported that the size of Cu NPs can be modified by the cation of ILs. While [EMIm]Tf₂N yielded 11 nm Cu NPs, [Py1,4]Tf₂N produced larger 26 nm Cu NPs when exposed to a low-pressure glow discharge argon plasma.¹⁵⁰ Size tunability of Cu NPs was ascribed to variations in the chemical surface composition of the NPs, which were determined by the chemical composition of the ionic liquid. The impact of solvent structure on NP synthesis in PDSE requires further exploration.

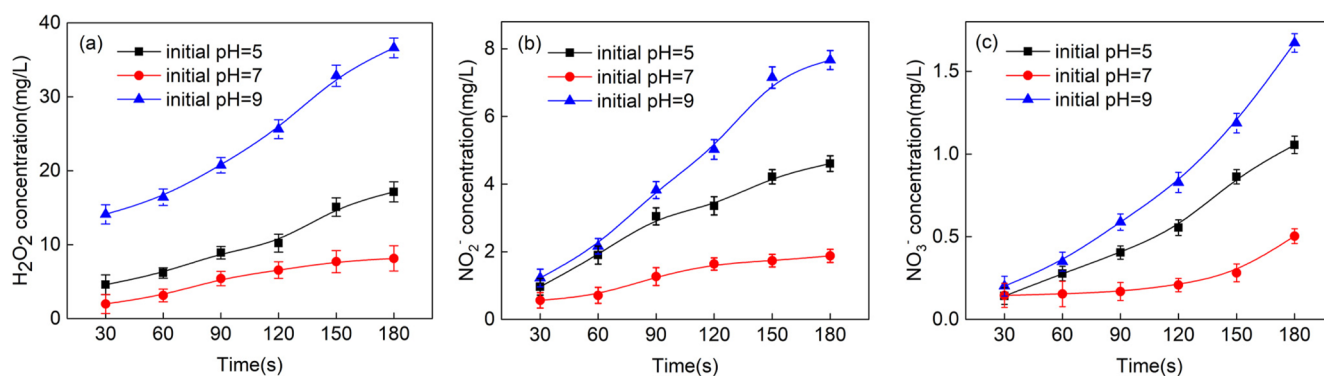


FIG. 13. Concentration of aqueous reactive species varies with discharge durations controlled by different initial pH values: (a) H₂O₂, (b) NO₂[−], and (c) NO₃[−]. Reproduced with permission from Wang *et al.*, J. Appl. Phys. **130**(10), 103302 (2021). Copyright 2021 AIP Publishing.

VIII. ON THE USE OF ELECTROCHEMICAL METRICS
FOR PDSE

The concept of Faradaic efficiency (FE) is extensively used in electrolysis as an efficiency measure. As chemical reactions in electrolysis are often enabled by an applied voltage of the order of 1 or 2 V, the energy efficiency of the system shows a strong correlation with the FE and both parameters are often used interchangeably. In electrochemistry, the term FE is defined as the ratio of charge carriers that drive a desired reaction relative to the total number of charge carriers. It is basically a measure of the selectivity to different products driven by charge carriers (for example, electrons). In the case of PDSE, due to the high energy of incident electrons onto the liquid, non-Faradaic reactions can also take place. These non-Faradaic reactions can be induced by electrons without consuming them, by thermal processes; by VUV, UV, or visible photons; or even by sequential reactions induced by different intermediates formed during initial electron-molecule collision. Therefore, it might be misleading to apply the concept of classical Faradaic efficiency in PDSE since these efficiencies will often exceed 100%.²⁵ It might be more useful to use total energy efficiency as a figure of merit. For example, the energy efficiency of producing $\cdot\text{OH}$ radicals from H_2O can be expressed by multiplying the mole number of the produced $\cdot\text{OH}$ radicals to the bond dissociation enthalpy of a H-OH bond in H_2O ^{151,152} (498 kJ/mol, or 5.2 eV, at standard conditions) divided by the total energy input. This energy efficiency indicates the fraction of energy input into a specific reaction pathway.

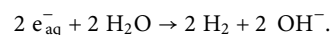
The situation for PDSE is, however, different and significantly more complex. The electrons are generated in the gas phase due to an ionization event. Most common gases used in PDSE have ionization energy between 12 eV (O_2) and 24.6 eV (He). However, additional non-ionizing electron-induced collisions also need to be considered in these energy considerations. In atmospheric pressure plasmas, nearly all electrical energy is transferred to the electrons and subsequently transferred to the heavy species (atoms and molecules) in elastic and inelastic collisions. As the average electron energy in most plasmas is a few eV, most inelastic collisions are not producing ionization events but lead to vibrational excitation, dissociation, or electronic excitation, which usually have significantly lower activation energy thresholds than ionization. The total power loss from electrons resulting from these collisions is typically significantly larger than the power spent in producing ionization in the plasma. Consequently, even if each electron created in the gas phase is lost at the plasma-liquid interface and is available to drive an electrochemical reaction in the solution, the effective energy cost to create the electron-ion pair will typically be between 100 and 1000 eV, depending on the gas composition, the plasma excitation, and the average electron energy of the plasma. As an example, it was shown that PDSE can synthesize NH_3 from N_2 and water with an FE of 100%, significantly larger than for typical equivalent electrolysis processes.⁶⁴ However, the reported energy efficiency corresponded to 500 eV/electron (assuming the formation of NH_3 requires three electron-driven reduction reactions).

This analysis would suggest that the potential of PDSE lies in the generation of chemicals and materials that are difficult to synthesize by conventional electrolysis-driven processes, which has been one of the key focus areas of the PDSE research to date. Examples include the generation of nanoparticles and electrodeless

polymerization, as discussed above. In the case of polymerization, the efficiency of the PDSE process can be intrinsically enhanced when exploiting PDSE as a source of primary radicals, which through propagation reactions form polymers. If conditions can be found that discourage chain-termination reactions, one radical formed by PDSE could lead to many chain propagation reactions.

The above-mentioned discussion has not considered that PDSE is intrinsically not limited by 100% FE as is conventional electrolysis, which then opens a broader range of opportunities. While non-ionizing collisions are an energy sink, they are also a source of (V)UV photons and neutral reactive species, which can be transferred to the liquid phase and drive chemical reactions. In noble gasses, the electrical energy conversion efficiency into VUV excimer radiation can reach values of 50% for optimized conditions, although these are likely not obtained for PDSE.¹⁵³ Nonetheless, PDSE could enable photolysis (photodissociation) or photoionization, which could significantly complement or enhance electron-driven reactions. An example is discussed in Sec. III D, concerning the role of UV in the synthesis of silver nanoparticles in glycerol.

In addition, gas-phase dissociation reactions lead to the generation of radicals that can transfer to the liquid phase or convert into long-lived reactive species that are absorbed in the liquid phase. Recent studies have shown the ability to achieve Faradaic efficiencies of up to 600%⁴⁸ for the reduction of ferricyanide. While this result requires the injection of electrons to enable the reduction chemistry, most reduction reactions are caused by species formed from the precursor molecule H_2O_2 produced in the gas phase. H_2O_2 can contribute to liquid-phase reactions without contributing to the electrical current into the liquid. In this case, it may be more efficient to drive reduction reactions when electrons form a high pH boundary layer near the plasma-liquid interface due to the following recombination reaction:



This high pH boundary layer converts H_2O_2 into HO_2^- , which can act as a reducing agent for ferricyanide and has a significantly longer lifetime at high pH compared to solvated electrons. This longer lifetime results in a significantly deeper penetration into the solution and a reduction reaction that is less limited by transport compared to solvated electrons. H_2O_2 plays a similar role in the growth of AuNP for which 300 times the maximum FE was found,¹¹⁹ as discussed in more detail above. While these novel reactions allowing for an FE significantly more than 100% show significant promise, fully exploiting these unique conditions will require a detailed understanding of the kinetics and transport in PDSE systems, which is only just starting to emerge.

In the case of DC-driven plasmas, FE can be determined from a measurement of the electrical current and overall conversion, although this is not necessarily always the case, particularly for AC excited plasmas. When, for example, radio frequency plasmas are used, it is difficult to measure the electron current through the liquid. These systems can drive electrochemical reactions without electrical conduction current when the positive ion flux is equal to the electron flux (ignoring displacement current). Determining the FE for such systems is usually done indirectly and may often require models. Nonetheless, the FE remains a valuable parameter for describing

the efficiency of PDSE, at least for the conditions that FE can unambiguously be calculated. However, one needs to be careful in the interpretation of FE as it does not account for contributions of all gas-phase induced electrochemistry. One should consider energy efficiency of the process independently of FE.

One approach to obtain a metric of chemical reactivity that describes PDSE without having to make a distinction between the species producing the reactivity might be the effective oxidation potential. This concept has been explored for characterizing plasma-activated water (PAW), which is used for medical applications, including disinfection of wounds and cancer treatment.¹⁵⁴ Oxidation potential is being discussed as a potential approach toward a treatment dose–biological response relationship on typical timescales of minutes. A similar approach might be applied to PDSE. Attempts have been made to link to *in situ* measurements of electrochemical potential.¹⁵⁵

Nonetheless, the question remains what limits the reduction reaction rate. Specific studies have shown that several PDSE-enabled reactions are determined by reactant transport to the plasma–liquid interface and in this case, the conversion efficiency is better described by a transport mode if the plasma-produced species have a very large redox potential. For example, in thin film flowing reactors, the conversion scales with the dimensionless Peclet number.⁴⁸ In this viewpoint, the energy needed to sustain sufficient reactive species density at the plasma–liquid determines the energy cost and is also species-agnostic. The conversion rate is fully determined by transport.

IX. MODELS OF PDSE

Modeling and simulation of PDSE have the synergistic goals of advancing our fundamental understanding of plasma–solution interactions and providing a platform for system studies and scaling. Modeling PDSE is, to a large degree, a subset of simulations of plasma–liquid interactions. These processes include gas-phase plasma chemistry and transport, neutral flow dynamics, radiation transport, gas-to-liquid (and liquid-to-gas) transport, and within-liquid chemistry and transport. Underlying these models is a robust reaction mechanism of gas-phase and liquid-phase processes and the data required for those mechanisms.

Perhaps one of the greatest uncertainties in the current models of plasma–liquid interactions is the transport of neutral and charged species from the gas phase into the liquid. In most models, as in the one by Liu *et al.*,^{156,157} neutral species densities are constrained by Henry's law equilibrium at the interface, with charged particle transport being unconstrained. They found that if the dominant loss for the gas-phase species is solvation into the liquid, the densities of the resulting in-liquid reactive species are not particularly sensitive to uncertainties in Henry's law constants. The gas-phase densities adjust to the change in Henry's law constant so that the flux into the liquid is constant. However, species that are reactive in the gas phase, having loss processes other than solvation, will produce in liquid densities that are sensitive to Henry's law constants.

Kenley *et al.* developed a one-dimensional plasma Henry's law equilibrium liquid transport model for a DC discharge sustained in argon.¹⁵⁸ Neutral species enter the liquid having a density given by Henry's law equilibrium at the surface. The boundary condition for

all charged species is their immediate solvation at the interface. The sum of the flux of (positive) cations equals the flux of water ions at the interface, assuming rapid charge exchange, while the fluxes of individual (negative) anions, including electrons, are equal across the interface.

The polarity of water with respect to the plasma producing electrode clearly has a large influence on the transport of charged species into the liquid. Although the transport of gas-phase fluxes of neutral species onto the liquid are not terribly sensitive to polarity, the generation of these species is sensitive due to the polarity-dependent structure of the discharge. That being said, differences in in-liquid processes are largely attributed to fluxes of charged species. There are few computational investigations that are addressing, in a systematic and comprehensive manner, these complexities.

Most experiments investigating these processes, as well as models, will buffer the liquid to control its conductivity. This constraint on conductivity then reduces the feedback between solution electrical properties and plasma generation of species as well as their transport into the liquid. With molarity of the solution being an important variable in PDSE materials synthesis, the coupling between solution electrical and plasma properties needs to be accounted for in models. For example, the electron density is shown in Fig. 14 following -15 kV discharge pulse in a plasma jet incident onto an AgNO_3 solution of varying molarity.¹⁵⁹ The plasma spreads on the solution as a surface ionization wave (SIW). For pure water, current through the liquid is essentially all displacement current while the top of the water charges negatively. At the upper range of molarity, the conductivity of the solution is able to transmit conduction current through the liquid, which decreases the spreading of the SIW across the solution.

These plasma dynamics can have a major impact on the electron and VUV fluxes incident into the solution. For example, the computed fluences of electrons and VUV photons incident onto the surface of the AgNO_3 solution are shown in Fig. 15 along the surface of the solution (position 0 is on axis) for the conditions and geometry of Fig. 14. The high conductivity of the 50 mM solution produces narrow on-axis centered electron fluence. Lower molarity solutions having lower conductivity spread the discharge along the surface of the solution, producing more extended fluences of electrons onto the surface. The differences in fluences at a given position are a factor of ten or more. The VUV fluences are commensurate with those of electrons, with the ratio of electron to VUV flux varying by large factors as a function of position and molarity. Incident electrons in negative discharges arrive with energies sufficient to undergo inelastic dissociative and ionization collisions with surface resident species prior to solvation. VUV penetration distances are tens of nm (much deeper than electrons), resulting in roughly half photolysis and half photoionization of water. VUV photolysis processes of non-water species important to PDSE and their interaction with materials being synthesized (e.g., NPs and polymers) are generally unknown. These physical and computational issues are common to plasma–liquid interactions regardless of the material processing aspects of PDSE and can have a significant impact on the liquid-phase chemistry.

The distinguishing aspect of models for PDSE is the in-liquid reaction mechanism. The development of that reaction mechanism is discussed in other sections of this paper. Most models for conventional electrolysis are not based on microkinetics or a series

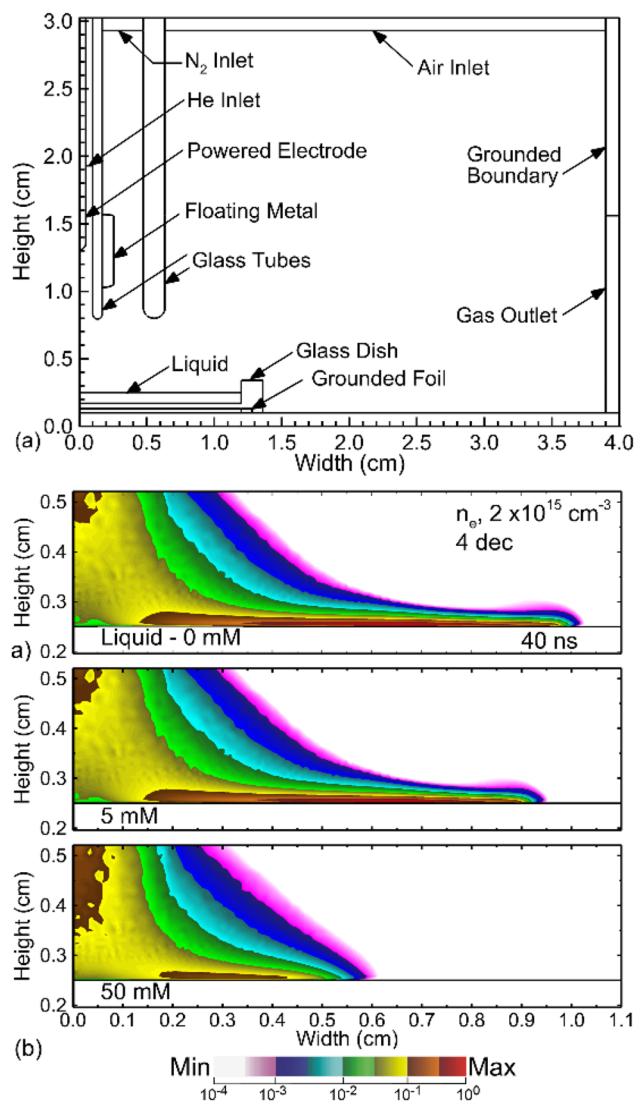


FIG. 14. Electron density following -15 kV pulsed He/O_2 plasma jet onto a thin AgNO_3 solution of different molarities. Electron densities are shown at ~ 40 ns. (a) Schematic of geometry showing central He nozzle and N_2 shield flowing into ambient air. (b) Electron densities for molarities of (b) 0 mM (pure water) and 50 mM. These results were produced with a two-dimensional plasma hydrodynamics model. The 1 mm thick solution is in contact with electrical ground with molarities from 0 to 50 mM.

of elementary reactions as is common practice in plasma-liquid interaction models. The microkinetic approach for modeling conventional electrolysis face the same challenges as for PDSE—the reaction mechanism that transitions from solute components to complex molecules or even nm to micrometer-sized particles.¹⁶⁰ While several reaction sets have been developed based on the work from adjacent fields for small molecules (e.g., formate and phenol etc),^{161,162} there have been few models of coupled plasma-and-liquid-phase chemistry that also address, for example, the material

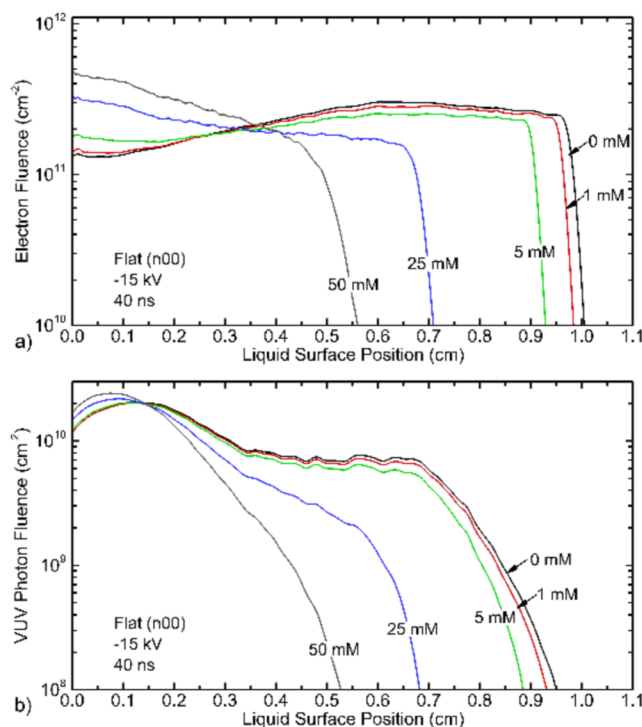


FIG. 15. Computed fluences of (a) electrons and (b) VUV photons onto the AgNO_3 solution for discharge conditions of Fig. 13. The fluences are for different molarities of the solution at about 60 ns during the negative discharge pulse. High molarity conductive solutions concentrate electron fluence on axis, whereas low molarity solutions produce a discharge that spreads along the surface, with more distributed electron fluence. VUV photon fluences are generally peaked on axis.

processing capabilities of PDSE. The most comprehensive model to date addresses silver nanoparticle synthesis from plasma exposed AgNO_3 solutions using a plug-flow plasma transport model and a global liquid model.⁴⁰ The results from this investigation highlighted several key research issues that need to be addressed to produce predictive, multidimensional models for PDSE. These issues will be highlighted in the context of Ag NP synthesis but generally apply to material synthesis PDSE systems.

Hierarchical reactions: the formation of NPs of only few nm in radius involves several thousand atoms, requiring a sequence of reactions that begin with the clustering of Ag^+ with neutral Ag^0 , the latter of which is produced by reduction reactions. Higher order clusters are formed, Ag_n^{m+} , that undergo similar reactions as the original mono-cation reduction by solvated electrons (e_{aq}^-) hydrogen and, in specialized cases, anions. When achieving a critical cluster size, the addition of atoms to the cluster transitions to an accretion or surface-growth mode, increasing the size of the now nanoparticle (NP). A systematic method of representing this hierarchical set of sequence of reactions is required, for example, $\text{Ag}_n^{m+} + e_{aq}^- \rightarrow \text{Ag}_n^{(m-1)+}$, $\text{Ag}_n^{m+} + \text{H} + \text{H}_2\text{O} \rightarrow \text{Ag}_n^{(m-1)+} + \text{H}_3\text{O}^+$, or $\text{Ag}_n^{m+} + \text{Ag}_k^{l+} \rightarrow \text{Ag}_{(n+k)}^{(m+l)+}$. In each case, the hierarchical reactions extend to replacing Ag_n^{m+} with a NP.

Efforts to characterize these Ag–Ag reactions, both experimentally and theoretically, have a significant history. Experimentally, the spectral overlap of small Ag clusters makes identification of individual species larger than five atoms intractable, although the primary growth mechanism up to that point has been well-characterized.^{163,164} While theoretical investigations do not suffer from the same limitations, efforts on that front have also largely been restricted to the initial stages of growth or to processes occurring after the critical nucleation radius has been reached. It has been shown that the growth up to five Ag atoms is driven by the formation of highly stable clusters that exhibit sigma aromaticity—the delocalization of $4N + 2$ valence electrons, where N is the number of atoms, through a sigma type HOMO.¹⁶⁵ To address the missing steps between the initial atomistic growth and nucleation, Mueller and Schatz developed the *PathTree* method for employing data trees to systematically map the growth reactions for metallic clusters up to an arbitrarily selected cluster size.¹⁶⁶ *PathTree* uses free energies of reaction from electronic structure calculations to rank possible reactions, allowing for the ready pruning of the full reaction set to include only the most favorable reactions, which can then be implemented in other models. Raisanen *et al.* employed both a full and a pruned reaction set generated by *PathTree* to investigate the plasma-driven growth of Ag clusters up to nine atoms and subsequent nucleation events.⁴⁰

Role of anions in reduction processes: the densities of plasma-produced anions in solution are typically much larger than solvated electrons. Under typical PDSE conditions, plasma produced anions in solution exceed the density of solvated electrons by 10^4 – 10^5 . As such, even small rate coefficients for reduction of Ag_n^{m+} by these anions can play an important role in the synthesis process. It is likely that as the cluster size increases, the reduction probability increases, in analogy to charge dynamics of nanoparticles. Nanoparticles maintain their charge state and a floating electrical potential by having equal currents of anions and cations to their surface. These conditions require the inclusion of reduction processes by those

anions. The hierarchical nature of these processes is at best poorly understood.

Photolysis and photoionization: PDSE differs from conventional electrolysis in that the surface of the solution receives significant fluxes of UV and VUV photons, as discussed above. These photons penetrate only a few nm to tens of nm for those absorbed by water, however, in doing so are capable of producing low pH surface layers through photoionization (and subsequent rapid formation of H_3O^+) and large concentrations of $\text{H}^\cdot$ and $\text{OH}^\cdot$ through photolysis. Longer wavelength photons (having energies below the photolysis threshold for water) penetrate distances of hundreds of micrometers to cm, while having sufficient energy to photo detach electrons from most anions. The consequences of photolysis reactions, particularly for photo detachment, are poorly understood in large part due to lack of fundamental data.

Representing non-equilibrium processes: photoionization of aqueous species by VUV photons may produce electrons with energies of up to 15 eV. Following photolysis, Franck–Condon processes can produce atomic and molecular dissociation fragments that may have energies of up to 5 eV. Electrons incident onto the surface of anodic solutions may arrive with energies of 10s eV even at atmospheric pressures. These energetic particles introduce the possibility of non-equilibrium kinetics, processes that are largely absent from current models.

Transients: conventional electrolysis is usually a continuous process or, at best, is slowly time-varying. PDSE using pulsed discharges (e.g., plasma jets and dielectric barrier discharges) can introduce charged reactants and photons to the solution over periods as short as tens of ns and repetition rates as high as tens of kHz. Delivery of neutral reactants occurs with successively less modulation as the lifetimes of these species exceed the pulse period or gas residence time. Since plasma typically does not uniformly deliver reactants to the solution, the transients are spatially dependent. These are difficult conditions to model (times from sub-ns to seconds, spatial scales of nm to cm) but also provide an opportunity

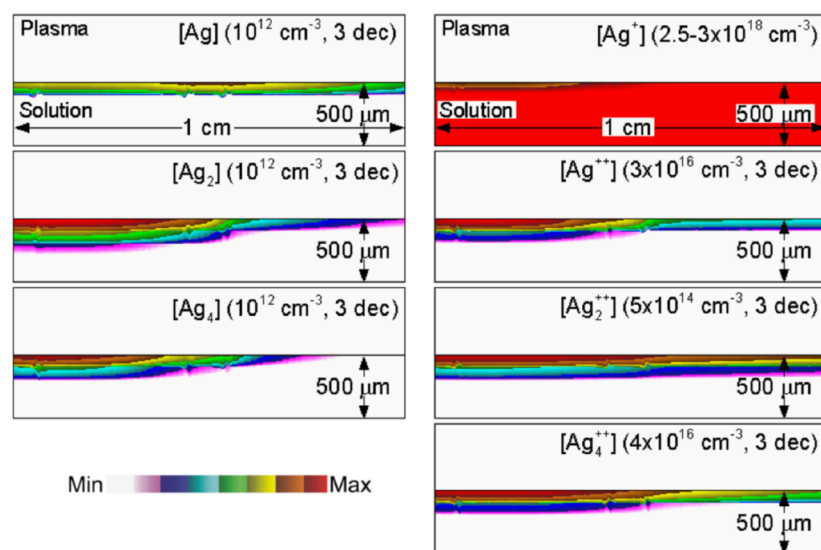


FIG. 16. Ag_n^{m+} densities at the surface of a 5 mM AgNO_3 predicted by a combined plasma–liquid hydrodynamics model¹⁵⁹ using the geometry shown in Fig. 1. The solution has been treated with 30, 1.4 μs at a repetition rate of 1 kHz. Ag^0 is produced on a pulse-by-pulse basis by delivery of reducing species (primarily electrons and $\text{H}^\cdot$), mildly reducing Ag^+ at the surface. Ag^0 is rapidly depleted by a reaction with Ag^+ forming Ag_2^{2+} and Ag_2^{2+} , which are similarly transient. Ag_2 , Ag_4 , and Ag_4^{2+} accumulate over pulses.

to leverage kinetic pathways to produce unique materials. For example, the model results shown in Fig. 16 (produced with the model described in Ref. 159) show small Ag_n^{m+} species following exposure of the plasma to 30 pulses of a negative Atmospheric Pressure Plasma Jet (APPJ) having pulse lengths of $1.4\ \mu\text{s}$ and a repetition rate of 1 kHz. The transient production and depletion of species produces a different distribution than the same reactants delivered continuously.

X. DIAGNOSTICS

A. Plasma/gas-phase diagnostics

To gain insights into the underlying mechanisms of plasma–liquid interaction, it is necessary to employ *in situ* diagnostic techniques that enable probing the spatial and often temporal variations in plasma properties and both long-lived and short-lived reactive species densities that are critical in plasma–liquid interactions. Under typical atmospheric pressure conditions, sheaths and boundary layers have length scales of $100\ \mu\text{m}$ or less requiring high spatial resolution measurements.¹⁶⁷ A high temporal resolution of diagnostics techniques will be required to understand rapid processes, especially as nanosecond pulsed-discharges have been increasingly utilized for plasma–liquid interaction.^{168,169} A detailed understanding of the flux of reactive species transported onto and into the liquid phase is critical for a quantitative understanding of interfacial chemistry. This is exceedingly challenging, in particular, for the usual dynamic nature of the liquid interface, which can include displacements of the interface on a length scale similar or even larger than the desired spatial resolution. A major effort needed to enable detailed diagnostics of plasma–liquid interactions often involves the development of highly stable plasma systems with a well-defined and controlled liquid interface.¹³⁶

Many diagnostics techniques have been implemented to probe the properties and species densities of gas-phase plasmas. Diagnostics include passive, non-intrusive methods, such as optical emission spectroscopy (OES), enabling the accurate measurement of gas temperature¹⁷⁰ and electron densities and temperatures.¹⁷¹ A broad range of absorption spectroscopy methods have been developed and implemented to measure species concentrations in gas-phase plasmas.¹⁷² Nonetheless, these techniques yield line integrated measurements and require assumptions such as imposing cylindrical symmetry to deduce spatially resolved species densities through Abel inversion, which can be a significant limitation, particularly for plasmas interacting with liquids. While mass spectrometry has been instrumental to measure species fluxes or densities during interactions of plasmas with solid surfaces for a broad range of both neutral and ionic species,¹⁷³ it requires intrusive sampling, which remains challenging to implement at the plasma–liquid interface without affecting the plasma–liquid interface.

Laser-based diagnostics remain the preferred approach to probe near interfacial plasma–liquid interactions not only because many laser-based techniques provide highly selective measurements of plasma properties and species densities but also because they can be non-invasively applied near the liquid interface. The most common laser diagnostics that have also been applied to study plasma–liquid interactions include Thomson scattering for measuring electron densities and temperatures,¹³⁶ laser induced fluorescence (LIF) for the measurement of diatomic radicals such as

$\cdot\text{OH}$, gas temperatures³⁶ and two-photon absorption LIF (TALIF) for measuring atomic radicals such as $\text{O}\cdot$ and $\text{H}\cdot$,¹⁷⁴ Raman scattering to measure the gas composition,¹⁷⁵ and Rayleigh scattering to measure gas temperatures.¹⁷⁶

Most of the gas-phase diagnostic studies in the context of plasma–liquid interactions have focused on the bulk concentration of species of interest.¹⁷⁷ While valuable, bulk concentration is not always representative of the species flux impinging onto the liquid surface, which is critical to gaining an understanding of the plasma-induced liquid-phase chemistry. Evaporation from the liquid to the gas phase can lead to significant gradients in vapor concentrations and cause major changes in near-interfacial plasma properties compared to bulk plasma properties. These changes have been shown in several studies. For example, Riès *et al.*¹⁷⁸ and Yagi *et al.*¹⁷⁹ measured spatially and temporally resolved distributions of plasma produced $\cdot\text{OH}$ radicals as well as water vapor densities using LIF. They showed a significant enhancement of $\cdot\text{OH}$ densities and water concentrations near the plasma–liquid interface compared to the bulk of the plasma. Similarly, Yonemori and Ono¹⁸⁰ measured $\cdot\text{OH}$ and $\text{O}\cdot$ densities and fluxes onto three types of surfaces: dry, wet, and rat skin, showing the key impact of the (humidity) of the substrate on the near interfacial gas-phase species densities and fluxes. Yue and Bruggeman⁵⁰ reported the measurement of electron density and temperature near the liquid anode (NaCl solution) surface using Thomson scattering and showed that the local increase in water vapor near the liquid surface can lead to a significant local increase in the electron temperature. Similarly, gas temperature gradients near the plasma–liquid interface have also been reported.⁵⁰

A study of plasma properties surrounding microdroplets is another illustration of the impact of the liquid phase on the local plasma properties, as shown in Fig. 17. These variations have been reflected in spatially resolved $\cdot\text{OH}$ radical and water concentration measurements by LIF and electron densities measurements using absolute continuum radiation.¹⁸¹ While these studies have provided significant insights into the local variations of plasma properties and species densities, the spatial resolution near the interface was often insufficient to deduce accurate species fluxes. For example, in the case of the droplet, a diffusion model was used to account for the anticipated decrease in $\cdot\text{OH}$ density near the droplet.⁷⁴ The formation of sheaths (electrical boundary layers) around the droplet can warp the local electric field and divert current, in addition to being a physical barrier to current flow. For example, Fig. 17 shows a decrease in plasma density in the vicinity of the particle due to obscuration of electron current by the droplet.¹⁸² Electrical or optical diagnostics capable of resolving these perturbations are challenging due to both the transient nature of the phenomena and the small spatial scales.

Despite ongoing research, quantifying the flux of plasma-produced species to the liquid surface remains a challenge. Yue *et al.*³⁶ recently reported the measured flux of $\cdot\text{OH}$ radicals and electrons produced by gas-phase plasma at the liquid anode. The density of $\cdot\text{OH}$ near the interface was measured by 2D planar LIF with a spatial resolution of $30\ \mu\text{m}$. This resolution was enabled by using a stabilized convex liquid interface formed at the end of a vertical tube with a continuous flowing solution allowing for optical access at the plasma–liquid interface. The fluence of electrons and $\cdot\text{OH}$ radicals were determined based on the measurements, which

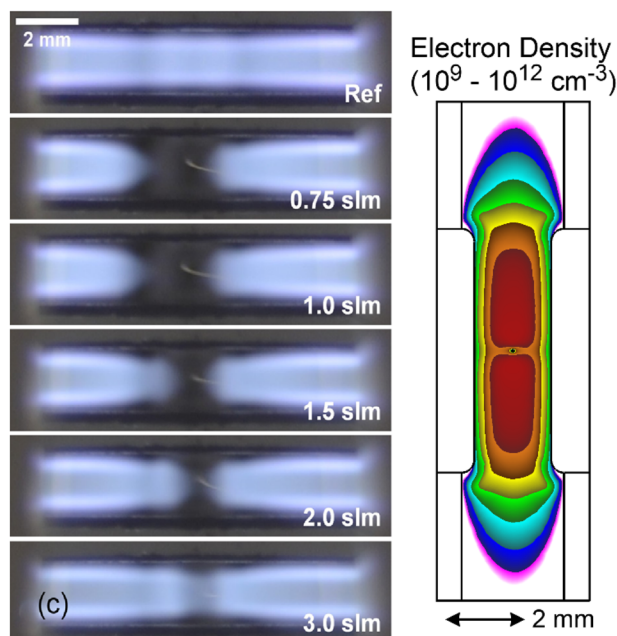


FIG. 17. Left panel: images of an RF capacitive glow discharge in He + 17% Ar through which a train of droplets with a diameter of $40\ \mu\text{m}$ are dispensed in the middle of the discharge in the direction perpendicular of the image. The droplets lead to an accumulation of water vapor for the lower flow rates and can locally even quench the plasma. Reproduced with permission from Nayake *et al.*, *Plasma Processes Polym.* **20**(5), 2200222 (2023). Copyright 2023 Wiley.¹⁸¹ Right panel: predictions for plasma density in the same reactor with a dielectric droplet, showing perturbations resulting from charging and discharging of the capacitance of the droplet. Reproduced with permission from Meyer *et al.*, *J. Appl. Phys.* **132**(8), 083303 (2022). Copyright 2022 AIP Publishing.

enabled prediction of the plasma-induced liquid conversion of a redox indicator. Recent measurements using photo-fragmentation LIF extended these methods to imaging H_2O_2 density distributions.¹⁸³ There are species of interest such as O_2^- ¹⁸⁴ known to be responsible for silver ion reduction for which there are no real-time diagnostics of sufficient accuracy and spatial resolution to address these science challenges. Extending such measurements to a broader range of plasma conditions and different reactive species that are believed to play critical roles in applications involving plasma–liquid interactions would be beneficial for the field.

B. *In situ* liquid-phase diagnostics

The tunability of the flux, energy, and composition of atmospheric plasmas is promising for controllably driving chemical reactions in solution. However, the plasma–liquid interface is a highly non-equilibrium system, with spatially dependent composition, dynamics, and energy. Similar to long-standing questions regarding the nature of the double-layer at the electrochemical interface, there are fundamental questions regarding the nature of the time-dependent and spatially-varying plasma–liquid interface. In order to accurately understand, predict, and ultimately control this

dynamic reactive environment, quantitative and versatile *in situ* probes are urgently needed.

Ideal *in situ* probes of PDSE would measure the transient and spatial evolution of chemical composition and dynamics at the liquid interface and deeper as needed, mapping how solvated electrons and other plasma-derived species react and evolve in the liquid environment. Spectroscopic probes are ideally suited for *in situ* measurements, as they are readily interfaced with the multiphase plasma–liquid environment. Here, we will discuss how spectroscopic probes can be used to quantify the yield and lifetime of plasma-derived species with the incorporation of high spatial and temporal resolution to track reaction evolution.

Laser scattering approaches have been successful for *in situ* monitoring of the evolution of liquid-phase properties during PDSE. Processes such as Raman scattering have a number of advantages for these measurements, as they provide insight into chemical composition, are compatible with water and other solvents, and can be interfaced with a number of geometries, such as liquid film reactors. Recent work by Pai *et al.*,¹⁸⁵ (Fig. 18) who used light sheet microscopy to monitor plasma-derived species, was able to monitor composition with micrometer-scale resolution. This work demonstrates the capability of Raman spectroscopy to probe plasma-derived long-lived reactive species, although this particular technique was limited to detection limits of about 1 mM.

Quantifying of properties of reactive solvated electrons species is a needed capability of *in situ* probes of PDSE. Rumbach *et al.*³³ monitored solvated electron formation using a total internal reflection optical absorption system [Fig. 19(a)]. Given that solvated electrons have a broad absorption spanning the visible and near infrared regions of the spectrum, it is possible to directly measure these signals despite the low absorption cross sections and experimental uncertainties [Fig. 19(b)]. The authors also used scavengers to modify the absorption signals and were able to extrapolate kinetic values and penetration depths, finding that plasma-derived solvated electrons react quickly (rate constants on the order of $10^9\text{M}^{-1}\text{s}^{-1}$) and within the first nanometers of the interface. Recently, Sasaki applied laser-induced desolvation to detect solvated electrons in a liquid cathode.¹⁸⁶ The experimental quantum yield was significantly larger than predicted by Monte Carlo simulations, suggesting the possibility that the detected solvated electrons might have much lower

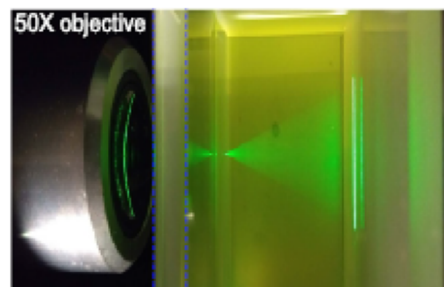


FIG. 18. Light sheet Raman spectroscopy to probe species concentrations near the plasma–liquid interface. Reproduced with permission from D. Z. Pai, *J. Phys. D: Appl. Phys.* **54**(35), 355201 (2021). Copyright 2021 IOP Publishing.

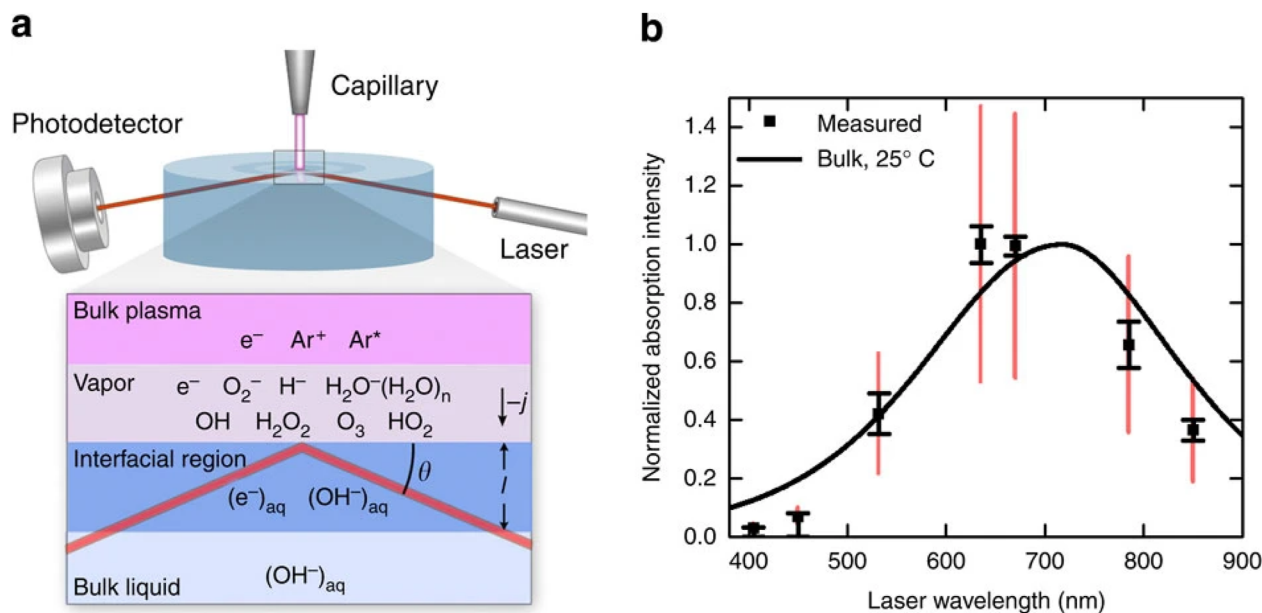


FIG. 19. Quantification of plasma-derived solvated electrons by optical absorption measurements. (a) Schematic representation of the total reflection absorption technique. (b) Example of a measured solvated electron absorption spectrum. Reproduced with permission from Rumbach *et al.*, Nat. Commun. 6(1), 7248 (2015). Copyright 2015 Authors, licensed under a Creative Commons 4.0 Attribution License.

hydration energies than well-known solvated electrons, pointing again at possible non-equilibrium effects in PDSE.

Many methods have been developed and implemented to measure radical species indirectly through turn-on colorimetric and/or spin-trapping methods.¹⁸⁷ Both colorimetric and spin-trapping methods use stable chemical probes that are transformed through reactions with radical species. As currently implemented, this is a time-integrated measurement technique as opposed to a time-resolved technique. The use of optically active scavengers to probe reactive intermediates formed in PDSE can be advantageous as these probes can have strong absorption cross sections in the visible region, increasing signal to noise ratios and decreasing experimental complexity. Optically active scavengers can be used to monitor local pH conditions as well as the formation of reactive intermediates. The use of such indirect measurements need to be considered with caution in a PDSE environment as (1) the complex mixture of short-lived and long-lived reactive species leads to inherent unselective chemical reactions or potentially even decomposition of the probe molecules and (2) gradients in radical species are inherently present in PDSE and could significantly impact the number of products being formed through transport-limited reactions.

A falling liquid film plasma reactor setup enabling time-resolved *in situ* optical absorption measurements of PDSE has been reported.⁴⁸ This approach leverages controlled flow conditions and thin films to probe chemical processes enabled by PDSE near the plasma-liquid interface on millisecond timescales. For example, this technique indicated a pathway for PDSE-enabled reduction reactions facilitated by plasma-produced HO_2^- that was

previously ascribed to be dominated by solvated electrons (as discussed above).

Surface sensitive techniques, such as second harmonic generation (SHG) or sum-frequency generation (SFG), are also promising to investigate plasma-liquid interactions perhaps even enabling accurate measurements of species residing in the first few nm of the plasma-liquid interface. Nonetheless, efforts have been limited in this area. Kondo *et al.* applied vibrational SFG to probe the interfacial water structure and showed the significant impact of the transfer of reactive gas-phase species on the SFG signal on long timescales.¹⁸⁸ The inherent time-dependent capabilities of the technique have not been exploited to date.

Overall, spectroscopic probes are increasingly being used for *in situ* probing of PDSE as a means for characterizing and quantifying the reactants, products, and intermediates involved as well as the corresponding thermodynamics of the gas-liquid interface. To date, this work has focused on optical absorption measurements and spontaneous Raman measurements, as these techniques are ideally suited to monitoring chemical composition. However, more advanced spectroscopic methods could provide greater insight into the dynamics of plasma-liquid interfacial chemistry and physics of PDSE.

XI. CONCLUSION AND OUTLOOK

Plasma-liquid interactions have been studied for a variety of different applications; however, an understanding of PDSE-induced chemical modifications has only recently started to emerge. The

power flow in non-equilibrium plasmas leads to a complex range of cascade reactions enabling the production of a large variety of reactive species. This rich chemistry coupled with the strong, non-linear, bi-directional feedback between the gas and liquid-phase processes challenges our current understanding of PDSE. Ten scientific questions for the research field were proposed in 2021.⁵ While the field has made significant progress in the past four years on addressing these questions, further understanding of the properties of the interfacial layer between the plasma and liquid that remain is needed to translate PDSE research to applications. This interface has unique properties that might impact, for example, the double layers at the plasma–liquid interface and the solvation structure of species. This review is intended to motivate further interest from the physical chemistry community in these interesting fundamental questions whose resolution may lead to the development of chemical reaction pathways and products that are currently not considered.

Several examples of opportunities for selective green chemical transformations have been reported in this review, which leverage our emerging understanding of PDSE for specific cases and/or highly controlled experimental conditions. The current understanding of these processes is rooted in solvated electron and $\cdot\text{OH}$ -driven chemistry although recently other chemical pathways involving, for example, H_2O_2 , O_2^- , and HO_2^- have emerged. These pathways suggest the potential to leverage PDSE for a broader range of green synthesis capabilities that have not yet been explored. The large majority of PDSE studies have utilized aqueous solutions compared to other solvents. The example of the bi-metallic particle synthesis leading to a non-miscible alloy is an example of how a well-chosen solvent can enable control of the ratio of the reduction rate of two species and enable unique synthesis conditions.

Electricity-driven chemical reactions are gaining significant interest as a promising pathway to a low-carbon footprint chemical and manufacturing industry. An increase in the understanding of PDSE will develop its potential and contribute to meeting this goal, particularly in areas of chemical conversion and the synthesis of nanoparticles and polymers with desired but currently uncontrollable or unattainable properties. Successful applications of PDSE processes will likely leverage (1) higher conversion rates and/or multiple species produced by PDSE (for example, gold nanoparticle synthesis), (2) highly energetic reactions not possible with conventional electrolysis (for example, bi-metallic nanoparticle synthesis), or (3) conditions under which non-specific radical-driven reactions can be scavenged (for example, peroxidation of propylene oxide). Nonetheless, a broader applicability will require more comprehensive quantitative studies of the composition of plasma-derived species in order to provide pathways to increased selectivity and reaction efficiency including more detailed insight on processes underpinning particle growth, such as the role of potential charging effects.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: SUMMARY OF REPORTED SYNTHESIS RESULTS

List of different NPs synthesized by PDSE (Table II). Overview of reported organic chemistries enabled by PDSE (Table III).

TABLE II. List of different NPs synthesized by PDSE, including information about the precursors and ligands used, plasma discharge treatment time, and the average size of the NP.

	Precursor	Plasma type	Discharge time (min)	Ligand	Average size (nm)	References
Gold (Au)	HAuCl ₄ in water	Atmospheric pressure DC glow discharge	25	Sodium dodecylsulfonate (SDS)	~50	104
	HAuCl ₄ in water	Atmospheric pressure glow discharge	1–50	SDS	20–150	105
	HAuCl ₄ in water	Atmospheric pressure glow discharge		Hexadecyltrimethylammonium chloride (CTAC)	1–10	106
	HAuCl ₄ in water	Atmospheric pressure microplasma discharge	10		5	117
	HAuCl ₄ in water	Low-pressure microplasma discharge	2	DNA (guanine)	20–30	94
Silver (Ag)	HAuCl ₄ in 1-butyl-3- methyl-imidazolium tetrafluoroborate	Low-pressure DC glow discharge	15, 45			123 and 189
	Ag wires in water	Atmospheric discharge	5–20		~13–53	107
	AgNO ₃ in water	Atmospheric pressure RF plasma jet	5–10	Fructose	~2–40	65
	AgNO ₃ in water	Atmospheric pressure DC microplasma	15	Fructose	~5–40	190
	AgNO ₃ in water	Atmospheric pressure glow discharge	2–10		~10–16	191
Platinum (Pt)	AgNO ₃ and a AgCF ₃ SO ₃ in 1-butyl- 3-methylimidazolium trifluoromethylsul- fonate	Low-pressure DC glow discharge	5–10		~8–30	100 and 101
	AgNO ₃ in glycerol	Low-pressure RF ICP discharge	0.06–0.2		~6–20	58 and 95
	Pt wires in ethanol, water, and carbon black	Atmospheric pressure solution plasma sputtering	5–20		2–5	109
	H ₂ PtCl ₆	Atmospheric pressure AC discharge			~2–5	103
	PtCl ₂ in water	Low-pressure DC discharge	15		1–2	123

TABLE II. (Continued.)

	Precursor	Plasma type	Discharge time (min)	Ligand	Average size (nm)	References
Palladium (Pd)	Pd wires in water	Atmospheric pressure DC discharge	3		~4–8	112
	Pd electrode in water	Atmospheric pressure pulsed discharge	60			111
Nickel (Ni)	Ni needle in NaOH	Atmospheric pressure glow discharge			~220	113
Copper (Cu)	Cu ⁺ in [EMIm]Tf ₂ N and [Py _{1,4}] Tf ₂ N	Low-pressure glow discharge	30		~11–26	150
Copper oxide (CuO and Cu ₂ O)	Cu electrode in water	Atmospheric pressure arc discharge	10		~30–80	98 and 192
Zinc and Zinc oxides (Zn and ZnO)	Zn wire in K ₂ CO ₃	Atmospheric pressure glow discharge	60		~13–42	96 and 115
Titanium oxide (TiO _{2-x})	Ti electrode in aqueous KCl	Atmospheric pressure discharge	15			116
Tungsten oxide (WO _{3-x})	W electrodes in water	Atmospheric pressure DC discharge	5–15		~12–19	97
Tin and Tin oxide (Sn and SnO ₂)	Sn electrodes in water	Atmospheric pressure pulsed discharge	40		~3–25	193
Au–Ag	Au core particles (HAuCl ₄) and AgNO ₃ in water	Atmospheric pressure microplasma	60–360	Fructose	~30–120	99
Pd–Ru	Pd–Ru electrode in water	Atmospheric pressure pulsed discharge	60		~4–6	111
Fe–Pd	Pd–Fe electrode in ethanol	Atmospheric pressure pulsed discharge	60		~4–6	194
Ag–Cu	Ag–Cu electrodes in Xylene	Atmospheric pressure pulsed discharge	120		2	195
Ag–Pt	AgNO ₃ and Pt(NH ₃) ₄ (NO ₃) ₂ in water	Atmospheric pressure DC discharge	10		~10	124
Fe–Pt	Fe and PtCl ₂ in molten salt	Atmospheric pressure DC discharge			~100–260	114

TABLE III. Overview of the reported organic chemistries enabled by PDSE, including plasma type, gas, and solvent used.

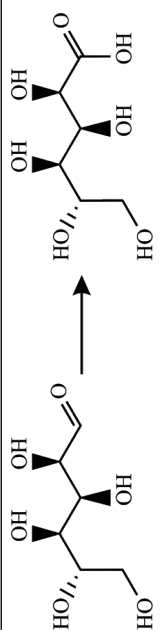
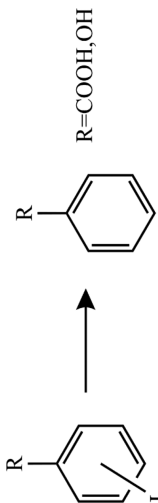
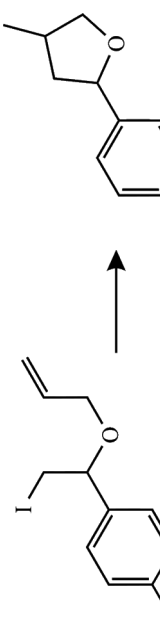
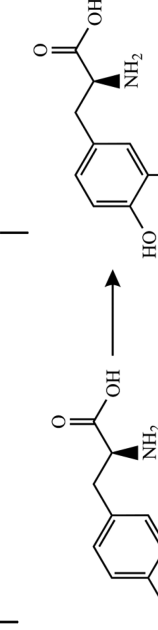
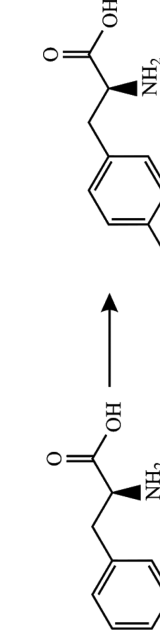
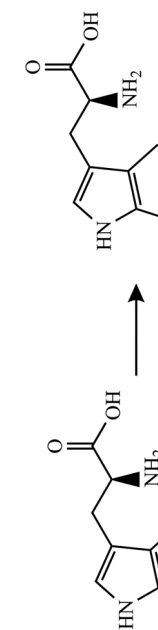
Reaction	Plasma type	Feed gas	Solvent	References
	kINpen	Argon Argon + 0.5% O ₂	Water	125
	3.5 kHz, 40 kV, nanosecond pulse widths	Nitrogen Helium	Water	126
	3.5 kHz, 40 kV, nanosecond pulse widths 25 kHz, 18 kV, AC	Nitrogen Helium	Water	126
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127

TABLE III. (Continued.)

Reaction	Plasma type	Feed gas	Solvent	References
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	13.9 kHz, -3.5–5.0 kV, AC	Helium	Water	127
	1.0 kHz, -2.51 kV, 1 μ s pulse width	Helium	Water	49
	1 kHz, -2.4 kV, 0.5 μ s pulse width	Helium	Titanium silicate-1 dispersed in water	30
	-2.0 kV, DC	Argon	Water:MeOH	27
	200 W, AC	Nitrogen	Water	129
	13.3 MHz, 4.5–6.6 W, RF	Argon	Water:MeOH	130
	60 Hz, 15 kV, AC	Argon	Water Styrene	131

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