# Development of Atmospheric Pressure Plasma Source with Liquid Column Interface for Plasma-Liquid Interfacial Reactions in Spatio-Temporal Dynamics

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**Abstract:** This study focuses on developing an atmospheric pressure plasma source for the plasma gas-liquid interfacial reactions. The developing experimental setup includes electrically-charged high-speed liquid jet by a nanosecond pulse plasma, measurement of the electrical charge, transversely-arranged high-frequency plasma localizing the gas-liquid interface, and schlieren visualization for liquid surface motion. Further details on the charge measurement, nitrogen species localization, and liquid dynamics will be presented.

**Keywords:** Plasma-liquid interaction, liquid column jet, electrical charge, nitrogen fixation.

## 1. Introduction

Low temperature plasmas generated exclusively with air, water, and available abundant resources have shown their potential for agricultural, medical, energy applications. Their notable characteristics can be effectively utilized in plasma nitrogen fixation, which synthesize nitrogen compounds exclusively from air and water [1,2]. The energy cost for the plasma nitrogen fixation, reaction processes from nitrogen dissociation to storable nitrogen compounds such as nitrate and ammonia, is an unresolved issue despite of its accessibility to renewable energy sources.

It has been shown that low temperature plasmas can selectively generate $O_3$, NO, $NO_2$, and $N_2O_5$, recently [3]. However, hydrogen containing species such as $NH_3$, HOONO, $HOONO_2$ have hardly been selectively and efficiently produced from air and water. Selective and efficient generation of hydrogen containing $H_xN_yO_z$ could be a ground-breaking technology, regarding the facts that green hydrogen and $NH_3$ derived from water and renewable source themselves are known sustainable energy carriers and that no concrete plan to replace current $NH_3$ production, nitrogen fixation, exists [4]. Therefore, understanding from the fundamental to applications on the plasma with liquid water is of importance.

The plasma-liquid interaction has been one of central interests in the low temperature plasma in the last decade [5]. Recent works shows that the interaction involving surface charge, surface tension, and the surface motion over a quiescent liquid in a basin [5-8]. Except some static plasma – liquid interaction phenomena [7,8], dynamics and instability development in the plasma - liquid interaction requires both sophisticated measurements and numerical analysis. In addition, since one of the major motivations in the plasma liquid interaction is the molecular flux into the liquid solution producing demanded reactive species, reaction analysis is additionally required in the plasma – liquid interaction.

We recently developed a helium plasma device with a coaxially arranged liquid column jet for OH radical reaction decay in near-liquid surface [9]. Experiments were conducted under stable liquid column surface but with flow downward. This enables the direct measurement of the reaction resulted from the plasma – liquid contact. This idea has also known as a flow-through reactor, capable of scaling the water treatment capacity [10]. Further study incorporating with surface electrical charge measurement and instability development in the liquid jet potentiate elucidation on the spatio-temporal dynamics of plasma gas-liquid interfacial reactions. Therefore, this study focuses on development of the electrical charge measurement in the liquid column jet and the measurement of the sub millimetre scale liquid surface dynamic over a liquid column jet with reaction analysis.

## 2. Experiments

Schematic of experimental setup is shown in Figure 1. The liquid column jet ejected from stainless or PEEK tube with its inner diameter of typically 0.13 to 0.25 mm is guided by coaxially arrange air or nitrogen gas jet through quadrant converging nozzle. Nanosecond pulse plasma is generated at the tip of the tube with nanosecond voltage pulse with some residual voltage generation, which realizes the electrical charge on the liquid surface flowing down with the liquid flow. The velocity sheer force in the gas - liquid interface is, therefore, controllable with both flow rates before the downstream plasma.

The electrostatic potential probe is equipped at the downstream. The electric charge motion through a ground-shielded probe ring tip induces electrical charge in the circuit capacitor, converted to voltage with high impedance amplifier. The inset figure in Figure 1 indicates example of measured voltage time-traces when a charged metal ball is free-falling through the probe ring. The electrical charge on a metal ball is managed by the applied voltage of a ball holder releasing the metal ball. The applied voltage increases the voltage amplitude of the probe output while its width is similar, inferring the same traveling speed through the ring probe tip. Owing to high-sensitivity electrical circuit, electrical charge measurement down to 10 pC has been realized.

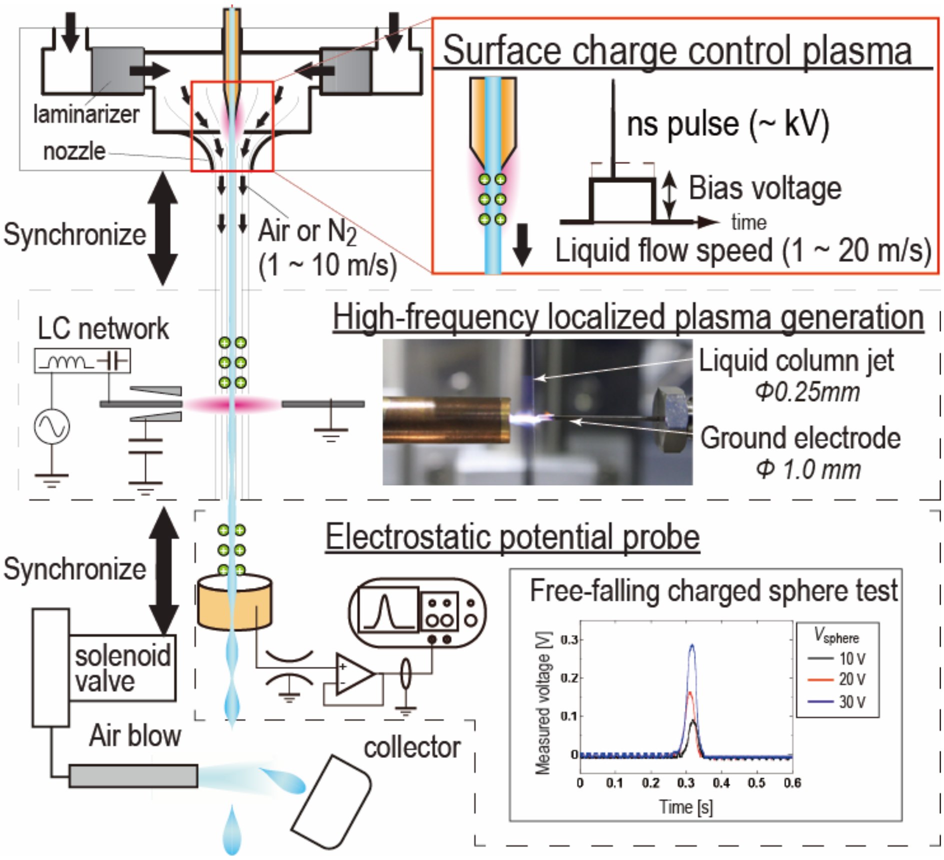


Fig.1: Schematic of experimental setup for spatio-temporal dynamics of plasma gas-liquid interfacial reactions

At the downstream of the quadrant nozzle, atmospheric pressure plasma generation, high-frequency power supply approximately 60 kHz allows localized plasma generation transversely across the gas-liquid biphasic coaxial flow. Significant specific energy input is advantageous for nitrogen atomic radical derived from nitrogen dissociation and discharge stability in transverse flow owing to less contribution of ion drift in the breakdown. Third floated electrode, capacitively coupled with the high voltage electrode, extended the breakdown gap to approximately 6 mm, longer than the converging nozzle diameter of 3.5 or 4.5 mm. Inset photo in Figure 1 indicates that the high frequency (~60 kHz) atmospheric pressure plasma discharge is transversely generated over the water column jet flow from top to bottom.

The high frequency discharge in a pulsed operation is synchronized with the nanosecond pulse for the liquid surface charge and the delay can manage the effect of the surface charge interaction with the high frequency discharge formation. A pulsed air blow synchronized with the discharges can blow out specific axial part of the gas-liquid biphasic flow and the liquid can be collected at the side. Therefore, the resultant liquid phase reactive species, generated locally on liquid column jet, can be removed from the biphasic coaxial flow (gas-jet sampling). Owing to difference in a flow speed in the biphasic flow, influence of the dissolution within the coaxial biphasic flow could be experimentally considered. Preliminary experiments of the reactive nitrogen species indicate formation of $NO_2^-$ and $NH_3/NH_4^+$. It has been suggested that those products are derived through reactions of nitrogen atom and water molecule, which may be involved in the plasma liquid interface reaction.

The liquid surface motion is visualized by schlieren method with a pulsed LED synchronized with the discharge. The pulse duration is ranged from 1 to 50 μs and the image sensor will also be exposed to the discharge emission. Figure 2(a) shows the schlieren image taken with 20 μs LED pulse with 810 μs delay after the end of the high frequency discharge. Due to the multiple exposure to the LED and the discharge emission, the exposed domain is also recoded in this imaging. The liquid column is torn at approximately 15.5 mm downstream, but was not disconnected before 450 μs. The breaking point was found rather downstream regarding the flow speed ~ 7 m/s. Further discussion and analysis on the flow instability might highlight the given phenomena.

## 3. Conclusion

Experimental schemes for plasma-liquid interfacial reactions in spatio-temporal liquid column dynamics has been developed. The experimental setup includes high-speed liquid jet with coaxially arranged gas flow, a nanosecond pulse plasma generator for liquid surface charge accumulation, measurement of the electrical charge, transversely-arranged high-frequency plasma localizing the plasma-liquid interface, and schlieren visualization for the liquid surface dynamics, and synchronized gas-jet sampling method.

Production of the reactive nitrogen species such as $NO_2^-$ and $NH_3/NH_4^+$ are experimentally detected and the localized formation is also experimentally confirmed, which indicates a success in the preliminary development of experimental schemes observing the plasma-liquid interaction from the electrical charge and the surface motion to the reaction products in the liquid phase.

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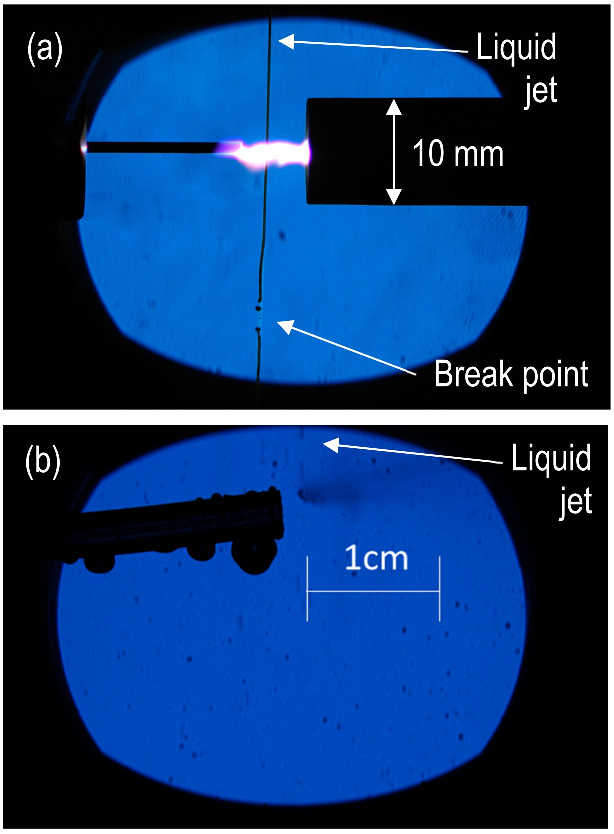


Fig.2: schlieren visualization of the liquid column jet (a) at 810 μs after the high frequency discharge and (b) at approximately 20 cm downstream.