LEIBNIZ-
WISSENSCHAFTSCAMPUS
PHOSPHORFORSCHUNG
ROSTOCK

Final Report

Funding number:	SAS-2015-IOW-LWC
Grantee:	Institut für Plasmaforschung und Technologie
Cooperation partner:	Universität Rostock (AUF)
Project title:	Processing of alternative P sources for fertilization in agriculture
Project duration:	1 May to 30 June
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* z.B. Conference contributions, publications (with status), funding applications (with status)

1. Summary

The aim of the project was the investigation of atmospheric pressure plasma discharges for utilization of bone char as fertilizer in agriculture.

Bone char is a promising candidate that involves the element phosphor. The treatment of bone char could convert the surface characteristics to improved phosphor uptake by plants and enhance the adsorption capability for additional loading with nutrients. Plasma technology is known as an innovative method for surface and material processing but so far no attempts on the modification of bone char has been made.

Barrier corona (BC) arrangements are employed in different plasma-based applications such as material surface and exhaust gas treatments. Due to the geometry and material of the arrangement, the discharge behaviour depends significantly on the two polarities of the applied sinusoidal voltage. The investigation of this behaviour was an important issue of the project. For the voltage amplitude being applied, mostly two micro discharges (MD) appear in the anodic pin half-cycles. It is observed that the breakdown mechanism in both MDs is a positive streamer starting near the anode, similar to the single MDs in symmetric dielectric barrier discharges (DBDs). However, the second MDs have different properties, such as longer duration of the bulk plasma and broader current pulses. It is considered that the differences are mainly due to the positive surface charges deposited by the first MDs on the dielectric. It is proposed, for the first time, that the current pulse derivative maximum corresponds to the arrival of the streamer head at the cathode surface. This is used to synchronize the spatio-temporal development of the MDs with their current pulses. The accuracy of the synchronization is limited to the rise-time of the current probe (350 ps). In each cathodic pin half-cycle, only one major MD appears. The appearance and amplitude of the MDs are more erratic compared to the anodic pin polarity. The TC-SPC recordings show that the MDs appearing at low applied voltages have a similar spatio-temporal development to the MDs of the anodic pin polarity. On the other hand, at high applied voltages a development similar to transient sparks, i.e. a double-streamer starting near the tip of the pin (cathode), is observed. The statistical study shows that in DBD-like MDs the current pulse amplitude is not dependent on the appearance phase (or applied voltage), but this is not the case for the transient sparks.

2. Introduction and aim of the project

Bone char is conventionally produced from bone granulate by pyrolysis at 700 °C. In the past, this material was used as a pigment for black paint. Today, fertilizers, filters in the sugar industry, water filters, color pigment, homeopathic medication as an application are in the foreground.

The chemical composition of bone char is ~80 % $Ca_5(PO_4)_3OH$, ~10 % activated carbon, ~8 % $CaCO_3$, 0,17 % $CaSO_4$, 0,12 % Fe_2O_3, 0,34 % SiO_2, 0,35 % alkaline salts.

Atmospheric pressure plasmas was used for the treatment of bone charcoal. Cold atmospheric pressure plasmas (CAPPs) are already being employed in various industrial and medical applications, and have a great potential for various new application [1-6]. Plasma technology is able to address environmental concerns by two approaches, first by offering more environmental friendly alternatives for the hazardous chemical processes being employed in the industry, and second as an effective tool for destroying the hazardous by-products of these processes [7]. Therefore, due to the increased environmental concerns and more strict laws against polluting and harming the environment, the importance of plasma technology, in particular CAPPs, is growing. Atmospheric pressure plasmas do not require costly vacuum facilities, which are essential for low-pressure plasmas. This is making them attractive for various applications [7].

Dielectric barrier discharges (DBDs) are an important type of CAPPs, which have been employed for applications such as ozone generation and water cleaning since the nineteenth century [8, 9]. Despite of the long history, the diagnostics and investigation of the discharge Development and properties are still a challenge. This is due to the small discharge dimensions (gap distance of some millimetres) and short duration of the microdischarges (MDs) (ns to µs range).

The main aim of the present dissertation is to conduct a comprehensive experimental study of the properties and development mechanisms of single microdischarges in a BC arrangement. The results of this study are planned to be employed in the improvement and optimization of plasma devices such as the “stacked DBD reactor” or “RotDBD reactor”. Especially the “RotDBD reactor” provide the possibility for carbon treatment.

3. Results and discussion

Untreated bone granulate was subjected to plasma pyrolysis. A microwave excited atmospheric pressure plasma with nitrogen as working gas was used. Gas temperatures of 700 - 1000 °C are reached in the centre of the plasma. In the plasma nitrogen radicals, atoms and excited nitrogen species are generated. It was possible to pyrolyse the bone granulate. The used plasma source is shown in Figure 1. Figure 2 shows a similar source Plexc under working conditions. The problem was that this kind of plasma sources corrodes in nitrogen atmosphere. Normally air is a suitable working gas for these kind of plasma sources however for pyrolysis an oxygen free working gas is necessary.

The result of the treatments is shown in Figure 3. The plasma-pyrolysed bone particles can be recognized by their black colour (Fig. 3b).

Figure 1 Atmospheric pressure air

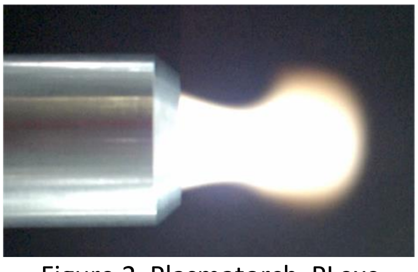
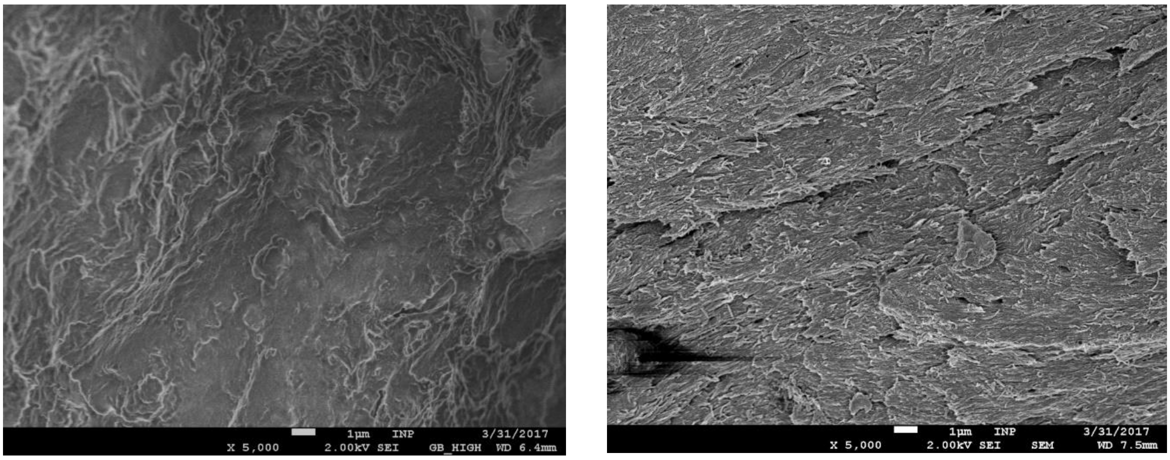


Figure 2 Plasmatorch PLexc

Figure 3 Untreated (a) und plasma treated (b) bone particles



a) Bone granules b) Plasma-pyrolysised bone granules

Figure 4 Scanning electron microscopy (SEM) results

The surfaces of the untreated and plasma treated bone particles were examined in the SEM (Fig. 4). The structures differ significantly from each other. The treatment roughens the surface and a layer structure becomes visible (Fig. 4b).

The chemical composition of the surface was investigated with the aid of the XPS (Fig. 5). The difference between the two samples is mainly in the carbon concentrations. The pyrolysis may cause fat layers on the bone splinters to be removed. By reducing the carbon content, the proportions of the other elements automatically increase. In contrast to commercially available bone char, the nitrogen content of the plasma treated one is higher (Fig. 5 inset).

Due to the problems that arose regarding the corrosion phenomena of the plasma source used, an alternative was sought. Dielectric barrier discharges (Fig. 6) show significantly higher stability. For this purpose, however, it appeared necessary to carry out more detailed investigations of the discharge mechanisms.

The single micro discharges has been investigated in a sinusoidally driven barrier corona (BC) discharge (Fig. 7). The hemispherical electrode is covered with alumina (Al_2O_3, $\varepsilon_r \approx 9$, tip thickness: 0.5 mm). The radius of curvature of this electrode is 2 mm. The metal pin electrode is made of stainless-steel and its radius of curvature at the tip is 0.2 mm. The gap distance between the electrodes is 1 mm. The discharge is operated at atmospheric pressure. Dry air at 300 sccm flowrate is used to flush the cell from the bottom to the top. A sinusoidal voltage at 7.5 kHz (period: 134 µs) is applied to the dielectric-covered electrode and the metal pin is grounded. The minimum applied voltage for the operation of a stable plasma is 11.5 $kV_{p\text{-}p}$.

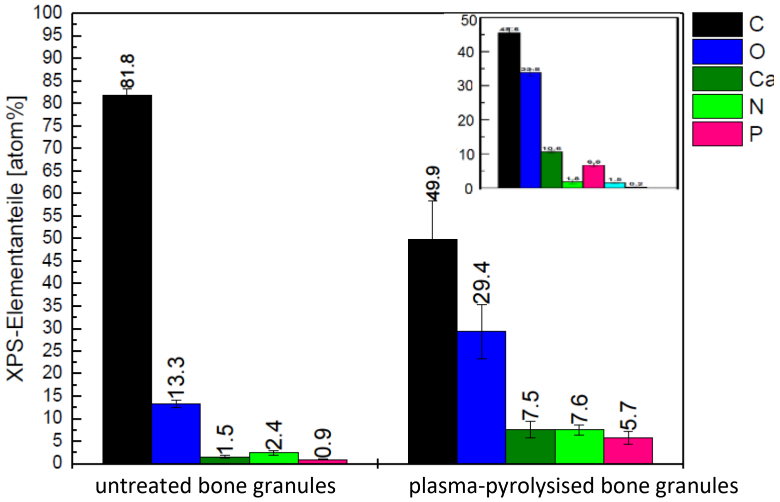


Figure 5. XPS investigation of untreated and plasma pyrolysed bone granules; inset: commercially available bone char

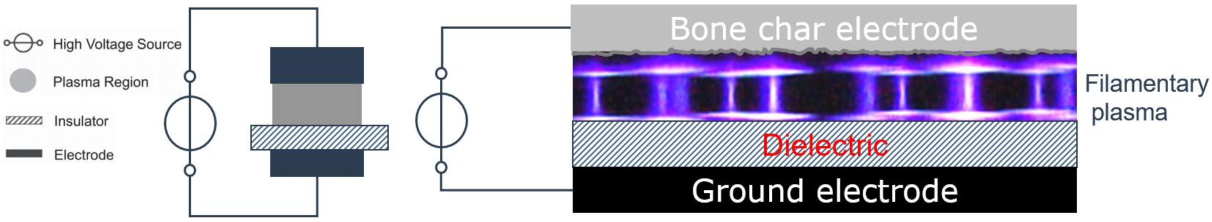


Figure 6. Schematics and image of dielectric barrier arrangenment

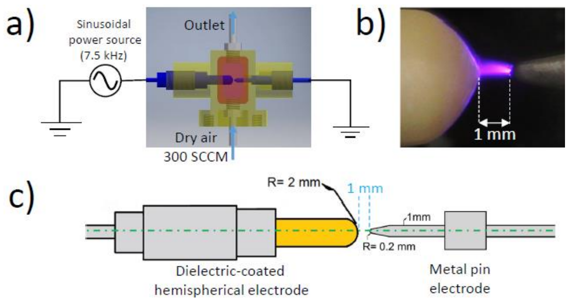


Figure 7. a) 3D drawing of the discharge cell together with the power and gas connections, b) Photo of the discharge during the experiments, c) 2D drawings of the electrodes.

Due to the asymmetric geometry of the barrier corona arrangement, the behavior of the discharge in the two polarities of the applied ac voltage is significantly different. An accumulated current-voltage oscillogram of the discharge is shown in Figure 8. The micro discharges (MD) in the anodic pin half-cycle appear in two separated groups and the variation in the amplitude of the current pulses is not significant. However, the appearance of MDs in the cathodic pin half-cycle is significantly erratic and the variation of the current pulse amplitudes is clearly seen, reaching much higher values compared to the MDs of anodic pin half-cycle.

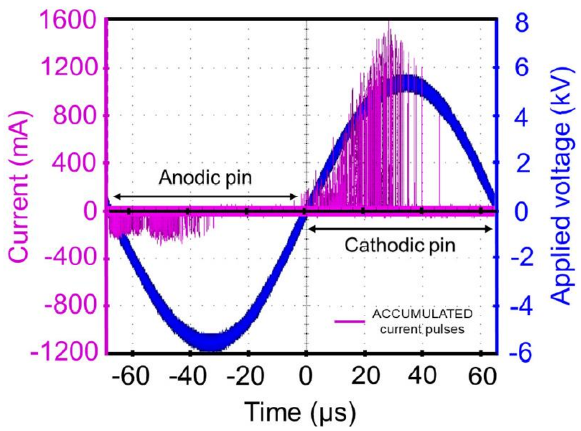


Figure 8.: Accumulated (for 1 second) current-voltage oscillogram of the BC discharge

It is proposed, for the first time, that the maximum of the current pulse derivative corresponds to the arrival of the positive streamer on the cathode surface. The idea originates from focusing on the physics of positive streamer propagation in the gap. By further propagation of the streamer, the streamer head velocity and electric field increase, resulting in an increasing ionization rate. However, this is hindered by the impact of the streamer on the cathode surface. Hence, the derivative of the current reaches its maximum value when the streamer arrives on the cathode surface. This finding is used to synchronize the spatio-temporal development of the MDs (obtained using the TC-SPC technique see appandix) and their averaged current pulses (Fig. 9).

It is shown that the formation and expansion of the bulk plasma and also the increase of external current are correlated with the dynamics of the surface streamer. This is done by a detailed investigation of spatio-temporal development of subsequent MDs (second group MDs) in the anodic pin half-cycle and its synchronization with the averaged current pulse. When the positive residual surface charges, deposited by first group MDs, decelerate the propagation of the surface streamer in the second group MDs, the bulk plasma cannot expand in the gap and the external current does not rise. These become only possible when the surface streamer overcomes the barrier of positive residual surface charges and starts to propagate with much higher velocities. These findings show the benefits of high-resolution and phase-resolved current measurements in filamentary discharges, which can give information about the spatio-temporal development of MDs.

The TC-SPC results show that when an MD appears at lower applied voltage in cathodic pin polarity, the breakdown mechanism is based on positive streamer breakdown near the anode (dielectric) similar to single DBDs. On the other hand, when an MD appears at higher voltages, the breakdown mechanism is based on double-streamer breakdown near the cathode (pin) tip, similar to transient sparks. The phase-resolved current pulse amplitude histograms (CPAH) indicate that in the phase intervals where single DBDs appear, the CPAHs do not change significantly by the increased applied voltage. However, in the phase-intervals where the transient sparks appear, the CPAHs are dependent on the applied voltage and are shifted to higher values by the increased applied voltage. These results shows that such studies can give a hint about the breakdown mechanisms of the MDs.

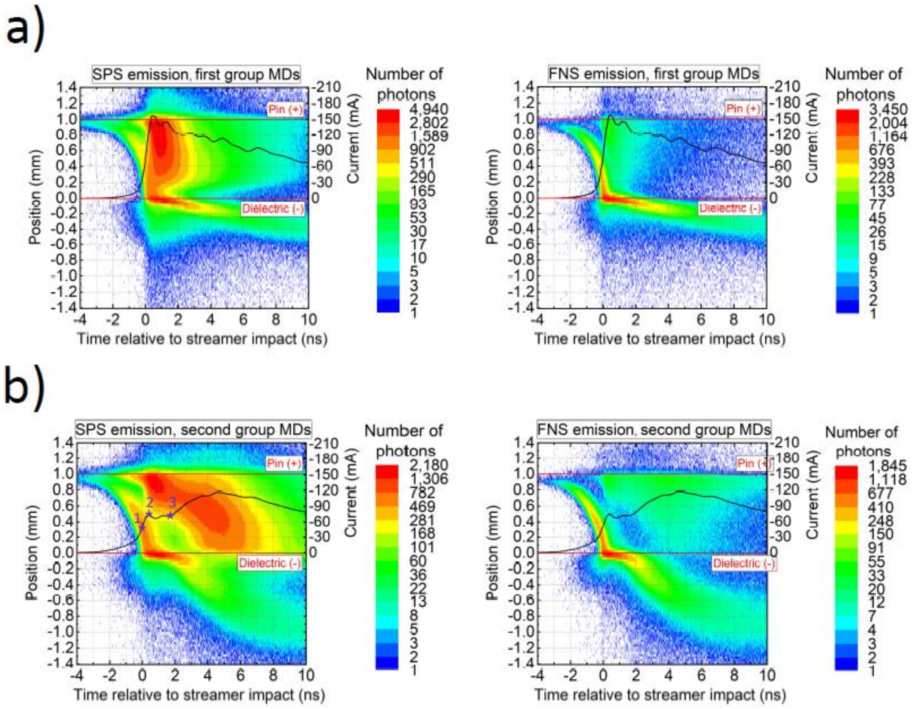


Figure 9: The averaged current pulses synchronized with TC-SPC recordings for the a) first and b) second group MDs (0-0 transitions of the molecular bands of the second positive system (SPS) λ_C = 337 nm, excitation energy: 11 eV and the first negative system (FNS) (λ_B = 391 nm, ionization-excitation energy: 18.7 eV)
At the beginning, the surface streamers of the two MD groups propagate with the same velocities and are decelerated for approximately 500 ps (points 1 to 2, figure b left).

Furthermore, it is demonstrated that the statistical study of appearance phase and amplitude of current pulses can help to understand the interactions between the preceding and following MDs. The investigation of the pre-conditions leading in appearance of the MDs at different phase of cathodic pin half-cycle showed that if a second group MD in an anodic pin half-cycle appears at later phases and has a higher current pulse amplitude, the MD in the following cathodic pin half-cycle will most probably appear at earlier phases and will have a DBD-like spatio-temporal development. On the other hand, when a second group MD appears earlier and has a lower current pulse amplitude, the MD in the following catholic pin half-cycle will most probably appear later and will have spatio-temporal development similar to transient sparks. These methods can also be employed in applicational multi-filament reactors, which can possibly result in better understanding and control of the processes.

The experiments of this dissertation are conducted in a single set of operational conditions and discharge geometry. First experiments at 14 kV in dry air shows that by the appearance of third MDs in the anodic pin half-cycle, the discharge appearance in the cathodic pin half-cycle is concentrated in earlier phases of the applied voltage and the high-current pulses become rare. As a future work, it is important to study the effects of operational parameters such as the applied voltage and frequency and the gas composition and flowrate. Study of effects of pin geometry (radius of curvature) and the gap distance can be helpful for the optimization of the applicational plasma reactors.

It is also planned to employ the findings and the methods developed in this dissertation to study the discharge behavior and characteristics in a DBD reactor with a metal knife and a rotating dielectric-covered electrode, named as “RotDBD” reactor. This concept of DBD enables the removal of the surface charges by the rotation of the dielectric-covered electrode and employing a surface charge neutralization process. When the surface charges are removed effectively, the discharge can be operated with a DC applied voltage and the influence of surface charges on the discharge development can be neglected [10, 11].

In this project the multi-dimensional TC-SPC technique is firstly employed together with optical and electrical diagnostics and statistical studies in order to investigate single MDs in a metal pin to dielectric-covered electrode (barrier corona) arrangement. Different types of micro discharges, e.g. DBDs and transient sparks, and streamer breakdowns, e.g. positive streamer and double-streamer breakdowns, are observed and investigated in the barrier corona (BC) discharge.

In general, the obtained results contribute to a better understanding of the effects of volume and surface memory effects on the spatio-temporal development of different types of streamer discharges. In addition, this study gives a more precise view about the relation between the spatio-temporally resolved photon emission (or spatio-temporal development) of the MDs and their external current and morphology. These finding can be of interest for different applications of atmospheric pressure plasmas and streamer discharges, e.g. for the optimization of the CAPP reactors. The results can also be useful for the understanding of partial discharges, which are an important problem in the insulation of high-voltage electrical devices, such as transformers.

4. Further achievements / benefit from the project

Three publications have appeared in the project:

- S. Jahanbakhsh, V. Brüser, R. Brandenburg; "Single microdischarges in a barrier corona arrangement with an anodic metal pin: discharge characteristics in subsequent breakdowns." Plasma Sources Science and Technology **27**(11): 115011. (2018)

- S. Jahanbakhsh, T. Hoder, R. Brandenburg; "Correlation between electric field, current and photon emission in subsequent barrier corona microdischarges." Journal of Applied Physics **126**(19): 193305. (2019)

- S. Jahanbakhsh, V. Brüser, R. Brandenburg;"Experimental investigation of single microdischarges in a barrier corona arrangement with a cathodic metal pin." Plasma Sources Science and Technology **29**(1): 015001. (2020)

5. References

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Appendix

Diagnostic setup

A schematic of the diagnostic setup is shown in Figure 10. The employed diagnostics techniques are:

- *Electrical measurements:* current and voltage are measured using a voltage probe (Tektronix P6015A) placed at the high-voltage side, and a current probe (Tektronix CT1, bandwidth: 1 GHz, rise time: 350 ps) placed at the grounded side. Both signals are recorded by an oscilloscope (Tektronix DPO4104, bandwidth: 1 GHz, samplerate: 5 GS/s).
- **ICCD imaging:** using an intensi_ed charge-coupling device (ICCD) camera (Andor iStar DH334T-18U-A3), the morphology of the microdischarges is recorded at different phases of the applied voltage. A mirror guides the light from the discharge to the ICCD camera through a lens. The spatial resolution of the images is 7.5 µm. The ICCD camera is triggered via a signal delivered from the delay generator (DG, Princeton Instruments DG535) and the ICCD-gate is delivered as a TTL signal to the oscilloscope. The ICCD images are recorded in two modes: single-shot and accumulated. In single-shot images, which are taken for individual MDs, it is possible to record the corresponding current pulses by triggering the oscilloscope via the ICCD-gate signal. The exposure time of all accumulated ICCD images is set to 10 ms, which corresponds to 74 applied voltage cycles.

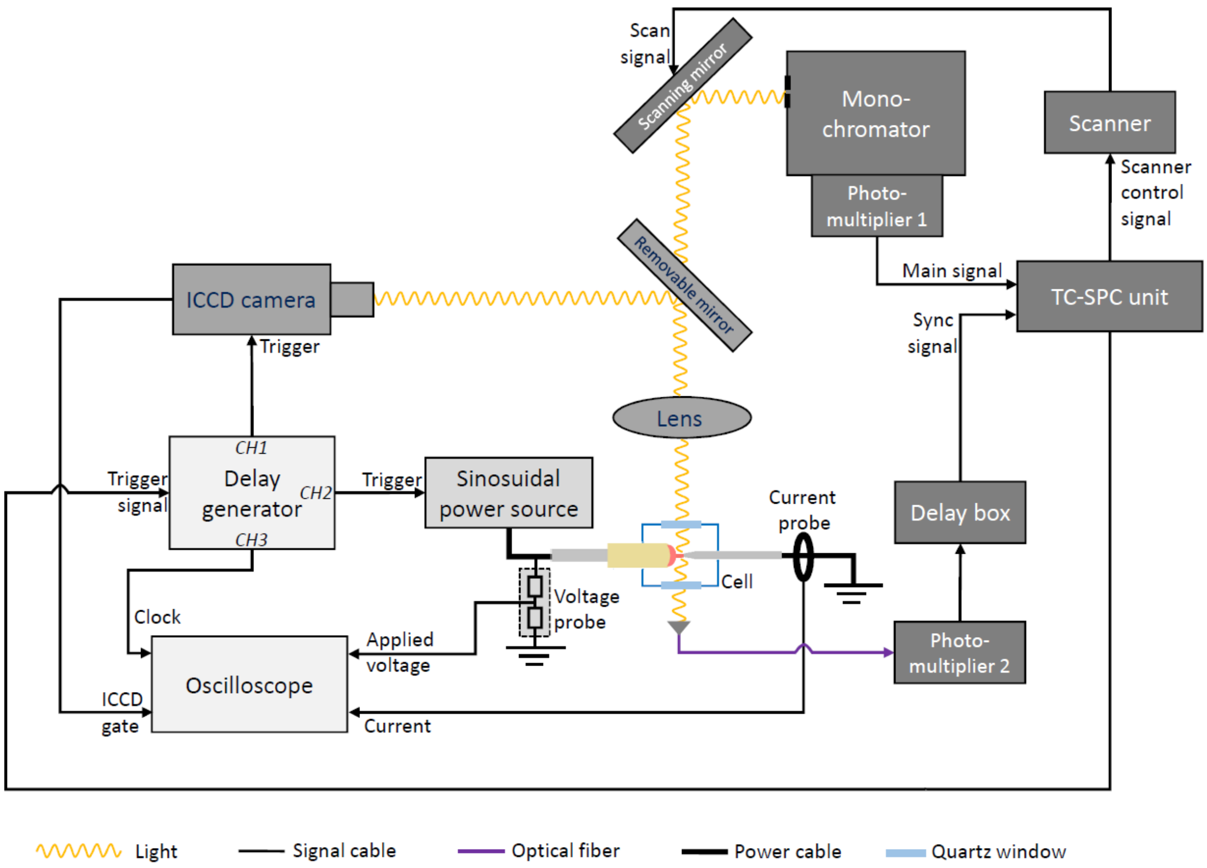

Figure 10: Schematic of the diagnostic setup.

- *Time-correlated single photon counting:* spatio-temporally resolved light emission from the microdischarges are recorded using TC-SPC technique (spatial resolution: 25 µm, temporal sampling: 12 ps). These recordings are also resolved over the applied voltage cycle in 128 channels, resulting in phasial resolution of 134/128 µs = 1.05 µs. For the TCSPC measurements, light goes trough the lens and a scanning mirror to a monochromator (MC) (Princeton Instrument SP2300) entrance slit. The magnification of the lens at the MC entrance is 4x. The scanning mirror is controlled by a scanner box and enables the one-dimensional spatial resolution of the measurements along the axis of the electrodes, i.e the recordings are not radially resolved. Based on the height of the MC entrance slit and the lens magni_cation, the height of the TC-SPC recordings is 1 mm around the central axis. The MC determines the wavelength of the photons being detected by the photomultiplier 1 (PMT1) (Becker & Hickl PMC-100-04). The electrical signals generated by PMT1 are then delivered to the TC-SPC module as the “main signal”. The light from the microdischarges goes through a second pathway, which is for the synchronization signal (sync signal) of the TC-SPC unit. This signal is for determining the time information of photons being detected in the main signal. In this pathway, the photons are carried with an optical fiber to PMT2. The electrical signal generated in PMT2 is carried through a delay box to the TC-SPC module as the so-called “sync signal”. The discharge is kept at the same conditions during the long accumulation times of TS-SPC measurements.