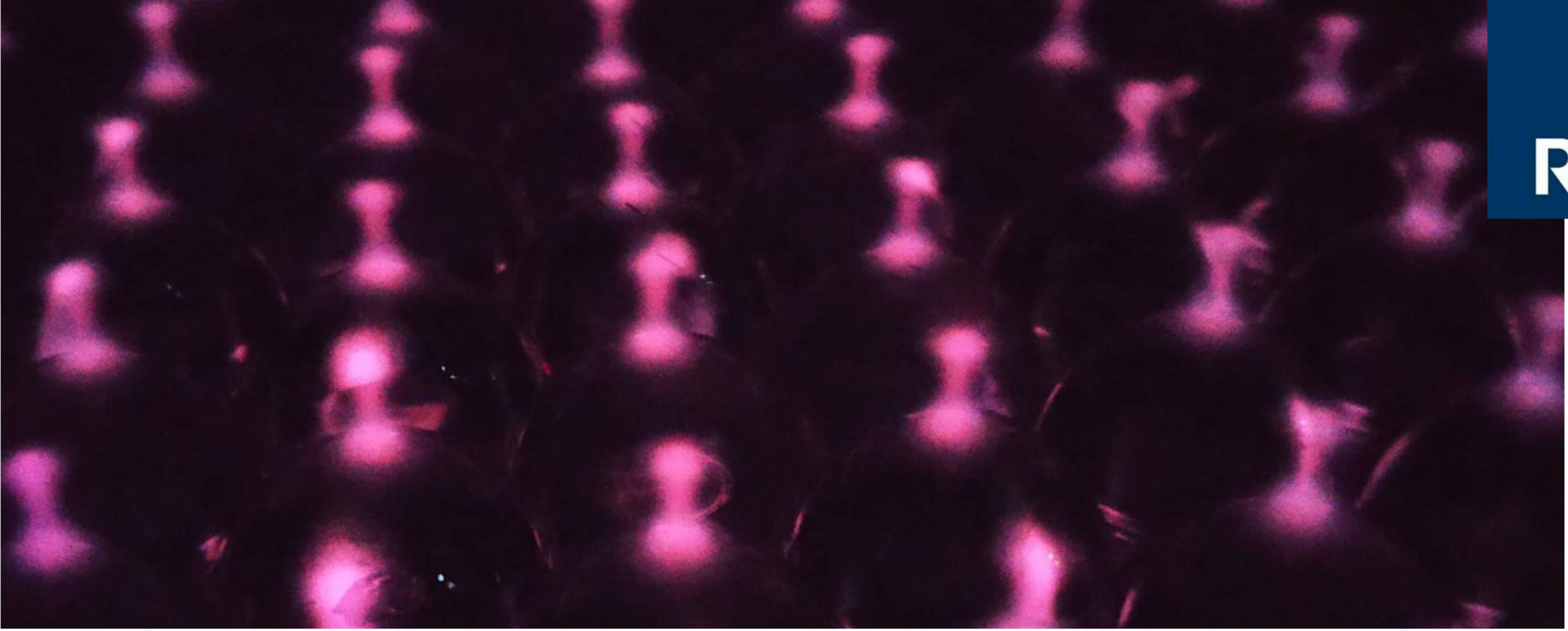


Plasma propagation in a patterned dielectric barrier discharge at different length scales

Zaka-ul-Islam Mujahid

RUHR UNIVERSITY Germany

Deutsche Forschungsgemeinschaft
German Research Foundation

Outline

- Introduction - Packed bed plasma reactor (PBPR)
- Patterned DBD (pDBD)

- Length scales in a pDBD
- Experimental system
- Results

- Chemical reactions in pDBD

- Conclusion

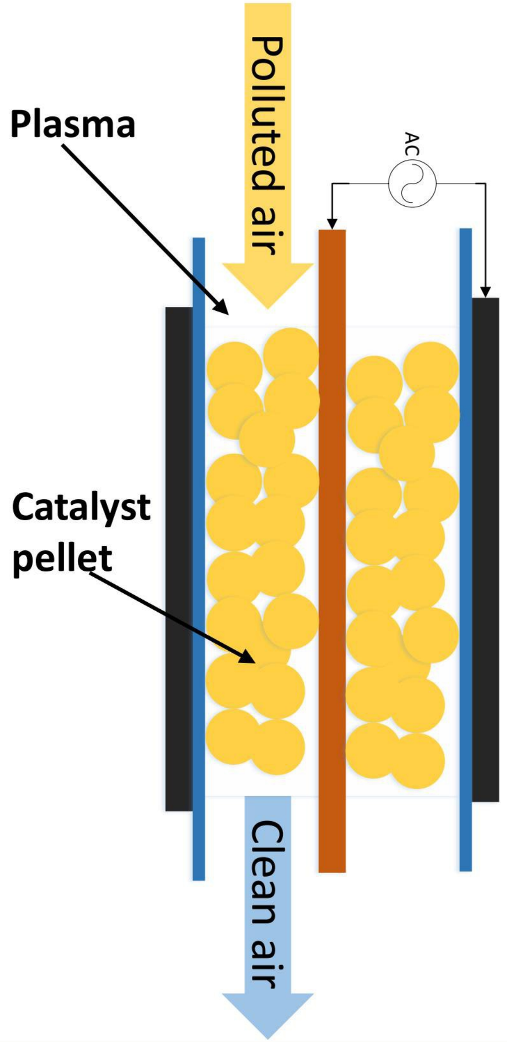
Packed bed plasma reactor (PBPR)

- Various plasma sources are used for gas reprocessing applications
  – Air purification - Odor and VOC removal
  – CO_2 and CH_4 valorization
  – NH_3 production

- Plasma Catalysis

- Packed bed plasma reactor (PBPR) – volume DBD packed with dielectric pellets loaded with catalyst

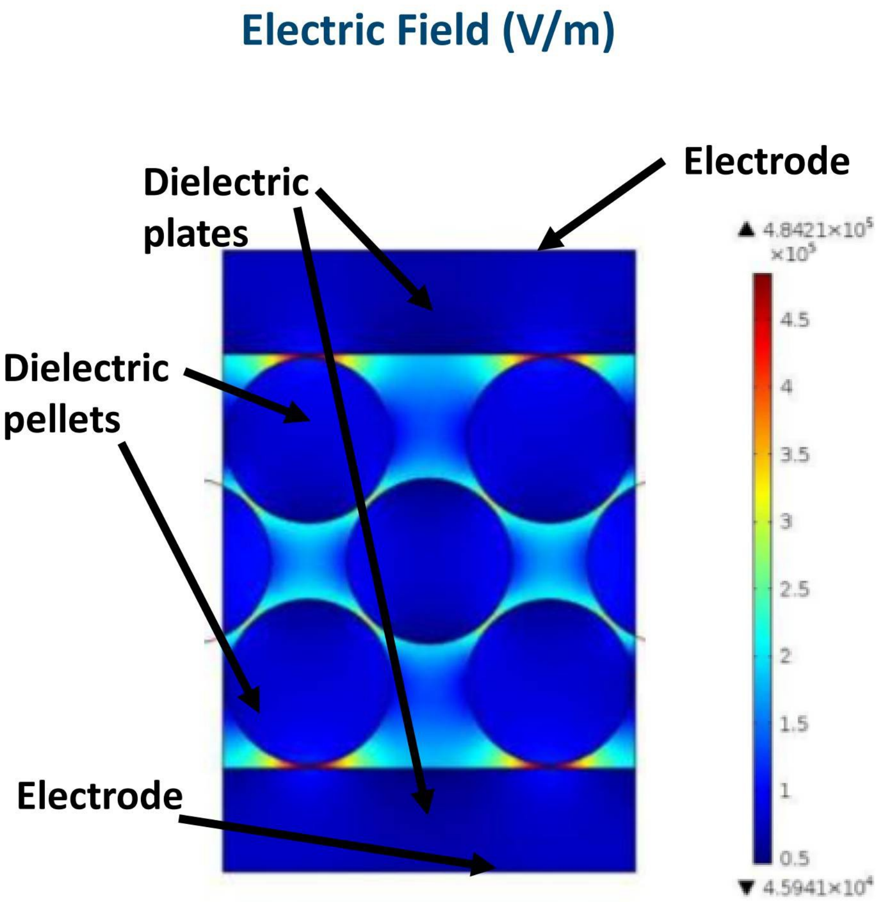
- Plasma is generated in the voids - proximity of the catalyst



Conventional PBPR

- Surface aspect
  - Adsorb – increase interaction time
  - Catalytic effects – chemical reactions on the surface
- Plasma – linked to design
  - Multiple voids between these pellets
  - Curved boundaries
  - Pellets (dielectric), stronger electric field is produced where more than one dielectric meets – contact point
- This talk will focus on the plasma aspect

Z. Abd Allah, J. C. Whitehead, P. Martin, *Environ. Sci. Technol.* 2014, **48** (1), 558–565

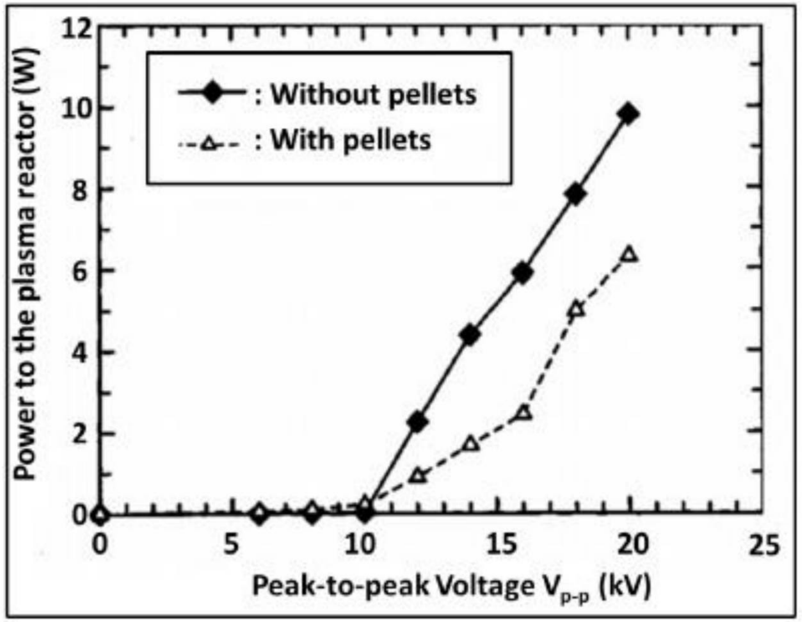


ZakaulIslam M, Van Laer K and Bogaerts A 2013 Proc. 33rd Int. Conf. Phenomena Ionized Gases

Performance of PBPR is also linked to the design

- Influence of packing on plasma
  - Modifies the plasma
- Energy effectiveness (g VOC removed / kWh) of a PBPR is 1.5 times higher when compared to the unpacked reactor. [Lin et al 2001]
- The specific energy density required for the non-packed reactor is quite higher than the packed bed to obtain similar decomposition efficiency. [Lin et al 2001]

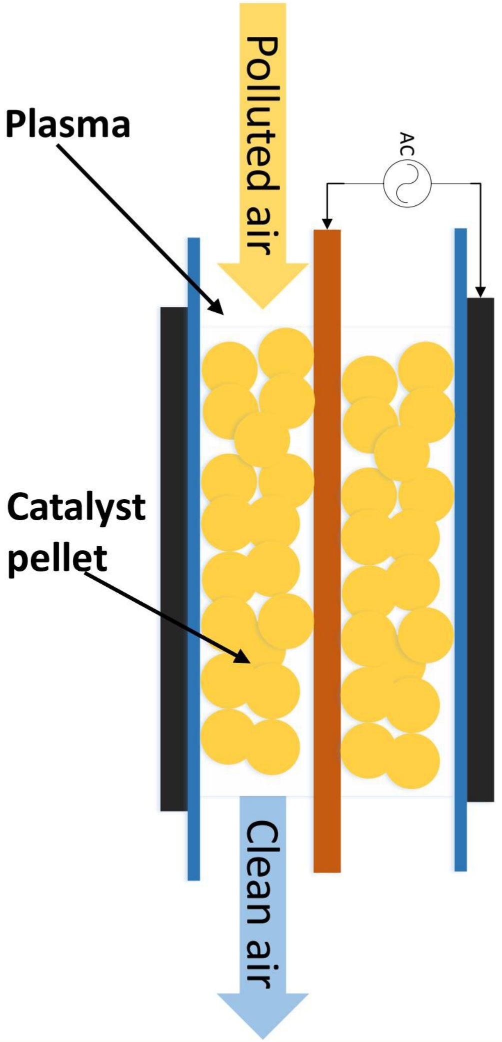
- Effect of dielectric constant



[Lin et al 2001]

Conventional PBPR limitations

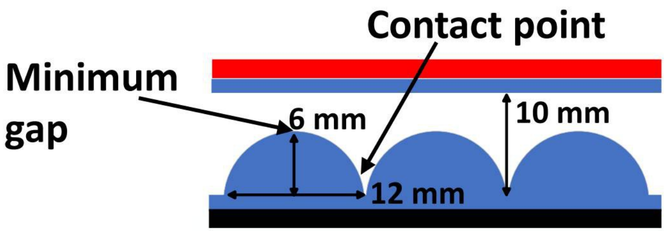
- Space and time averaged performance – widely investigated
- Complex design
  - Irregular packing of pellets
- Difficult to probe experimentally or model
- Simplified/organized design is required
  - Easier to investigate experimentally and model

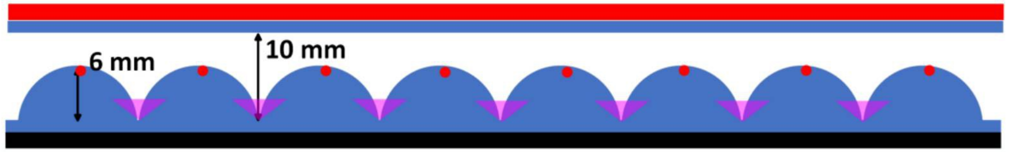


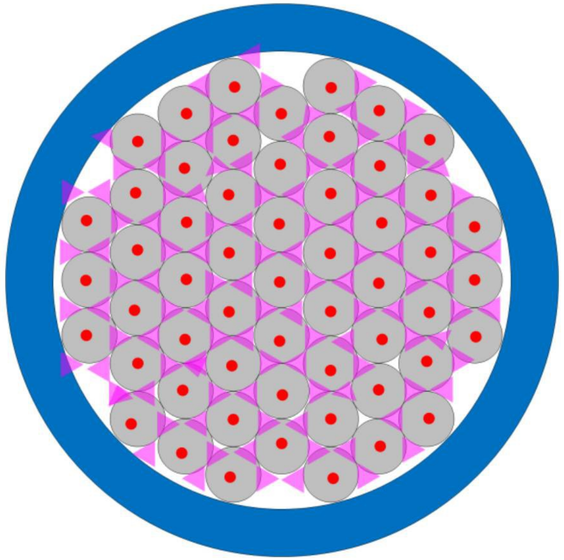
Patterened Dielectric barrier discharge (pDBD)

- Single layer of hemispherical pellets
- Regularly arranged
- Incorporates the design elements of a conventional PBPR
  - Curved boundaries
  - Contact point
- Parallel plate geometry with transparent electrode
  - Quasi-3D view of the discharge
  - View discharge formation at the contact points

- pDBD – Similar discharge conditions at multiple locations
- Enables study through diagnostics requiring averaging over multiple cycles
- Experimentally understand and model the same geometry







pDBD vs conventional PBPR

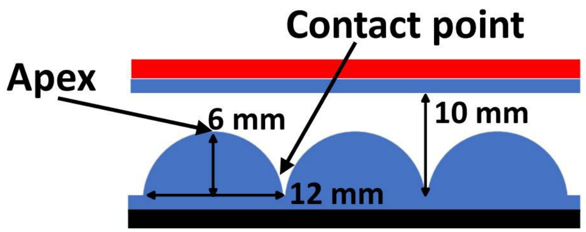
- 100 mm diameter and 10 mm gap cell
- Filled with 55 12 mm diameter hemispherical pellets

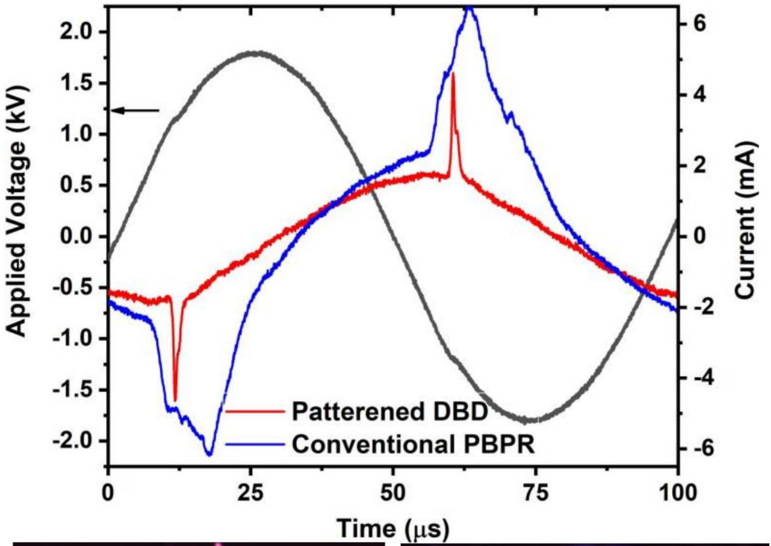
- Patterned Dielectric barrier discharge (pDBD)
  – Regularly arranged in hexagonal

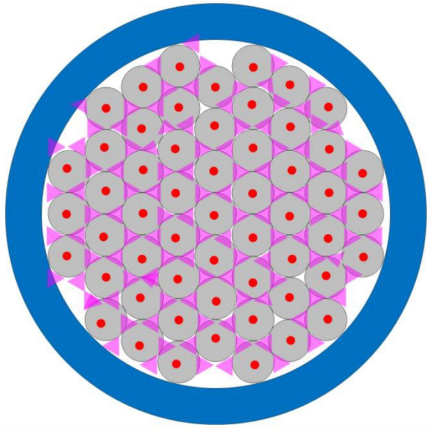
- Conventional PBPR
  – Irregularly filled

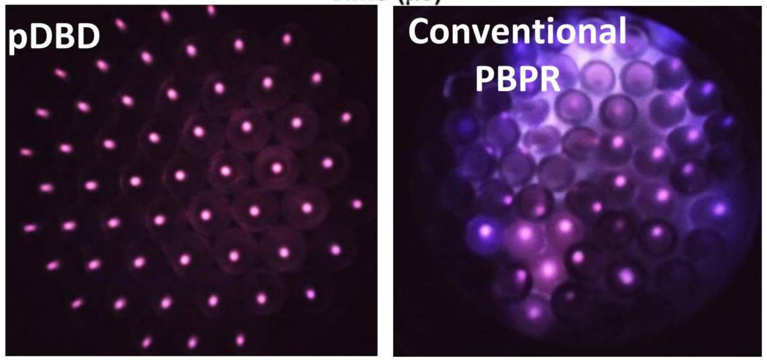
- pDBD -Filaments generated at minimum gap positions
  - Time synchronized – sharp current peak

- Conventional PBPR
  - Broad current peak







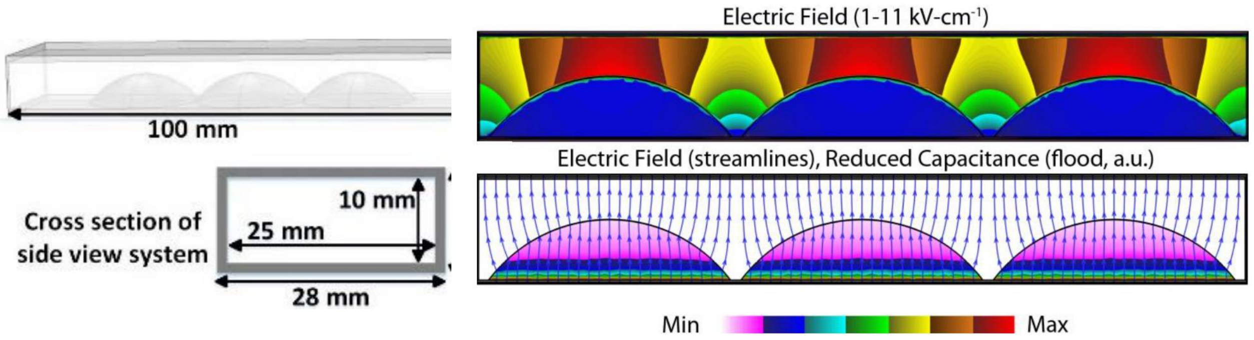


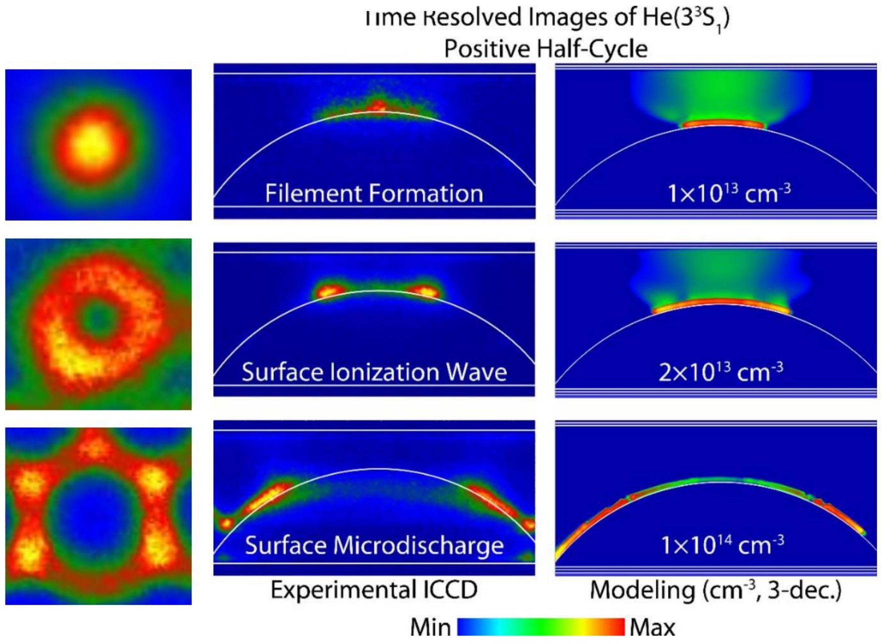
Qualitative agreement between experiment and modelling

- 100 mm diameter and 10 mm gap cell
- 24 mm diameter and 6 mm height pellets

- Positive polarity

- Three discharge mechanisms
  - Filaments at the minimum gap
  - Surface ionization waves
  - Surface microdischarge





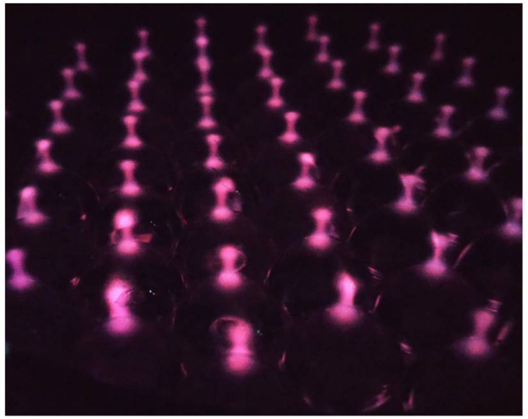
[1] Z. Mujahid, A. Hala, J. Kruszelnicki M. Kushner Chemical Engineering Journal 382, 123038 (2020)

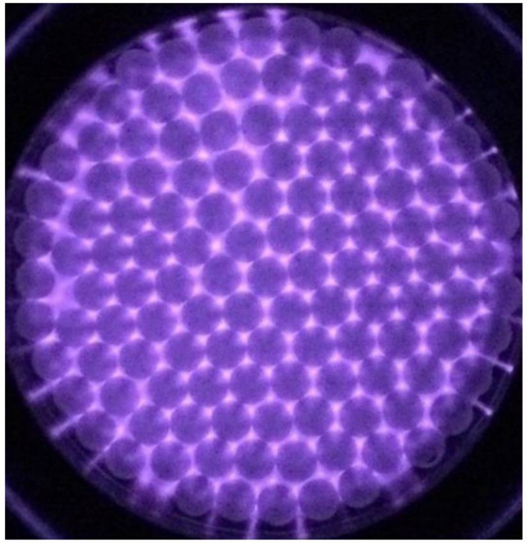
Length scales in a pDBD

- Array of segmented or connected microdischarges

- Size of plasma reactor – macroscale (cm)
- Size of the pellet – macro/meso scale (cm – mm)
- Contact point and surface pores – meso/micro scale (mm – µm)

- Plasma propagation at these different length scales is important to improve their performance

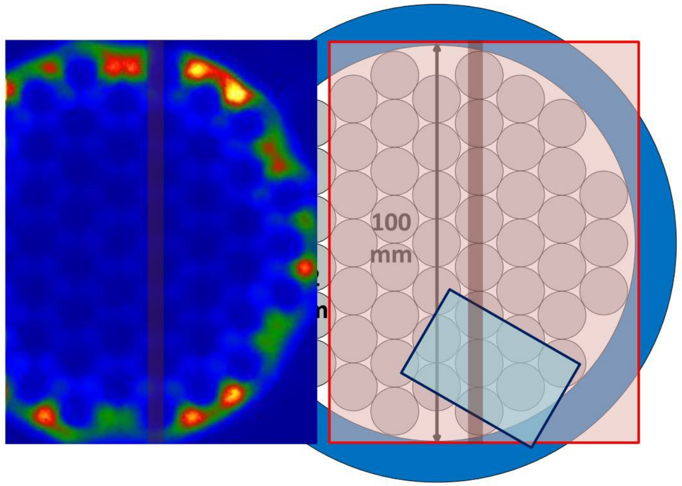


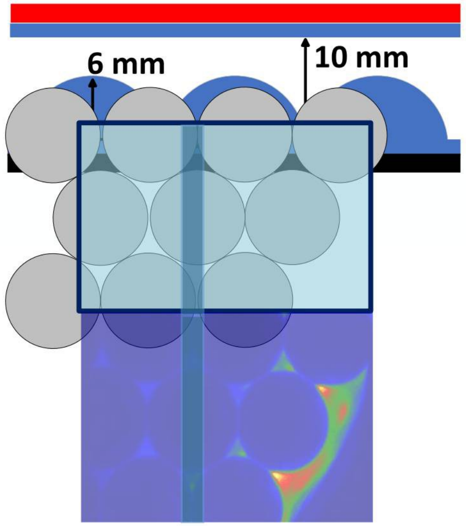


Experimental system

- 100 mm diameter and 10 mm gap parallel plate DBD operated in Helium
- 12 mm diameter hemispherical pellets
- 55 pellets arranged in a hexagonal pattern*

- Powered by 10 kHz, sinusoidal HV power supply
- Powered transparent electrode at top (outside flat dielectric)
- Grounded electrode (behind structured dielectric)
- He 706 nm through transparent electrode





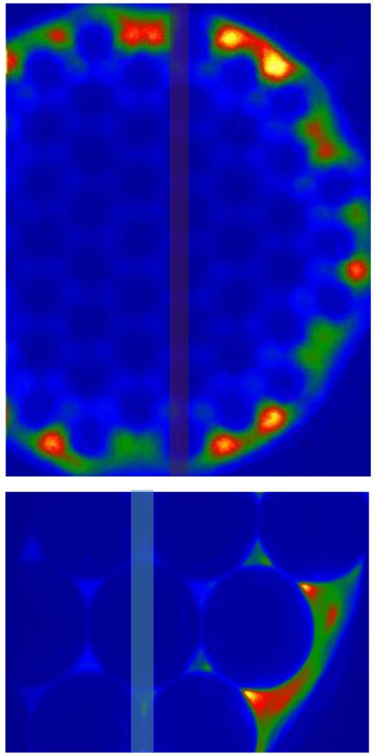
- Two different areas
  – full view of the reactor diameter (red rect.)
  – zoomed view of few pellets (blue rect.)

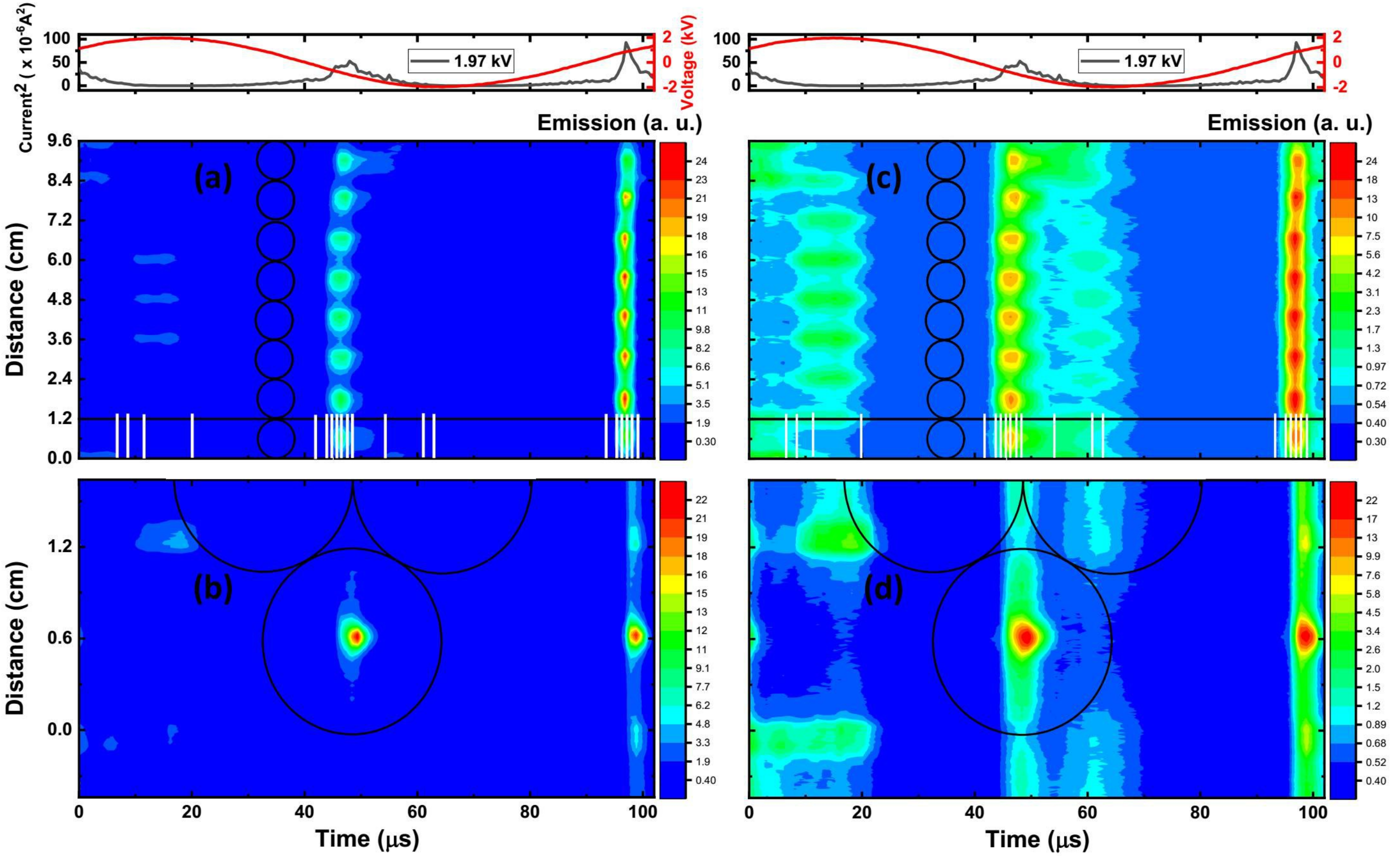
*Plasma propagation dynamics in a patterned dielectric barrier discharge at different length scales Z. Mujahid and J. Schulze (submitted) 2020

Time resolved measurements

- Time resolved measurements for the two regions in similar conditions
- The successive peaks can only be observed simultaneously in log scale

- First structure - emission in the center of dielectric structure
- Second structure - emission between the dielectric structures





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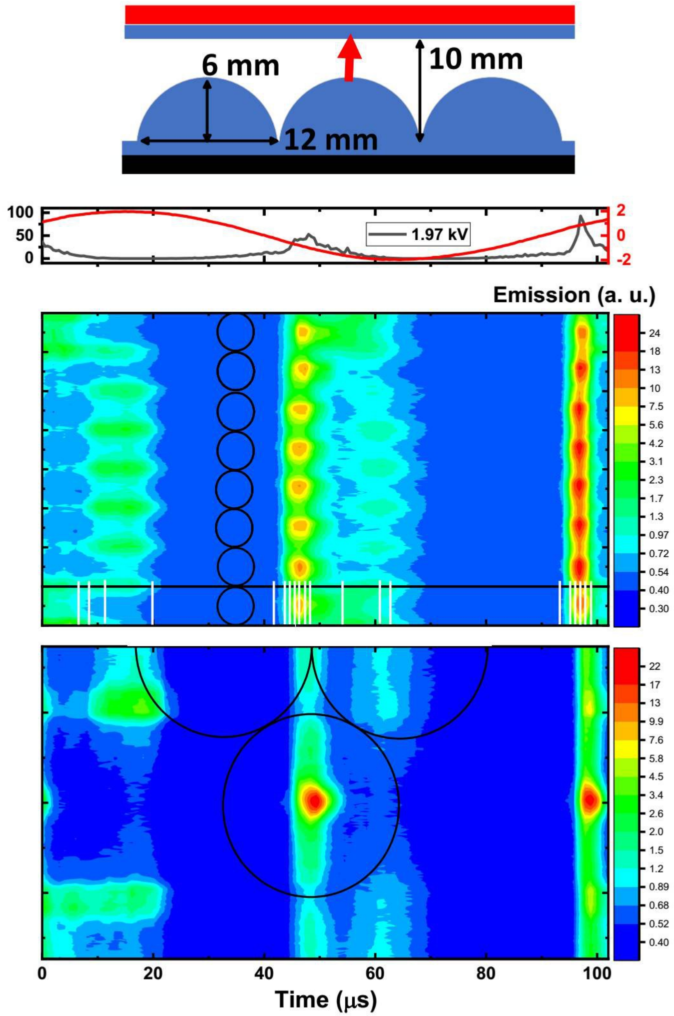
Filamentary and surface microdischarge (Neg half)

- First emission structure

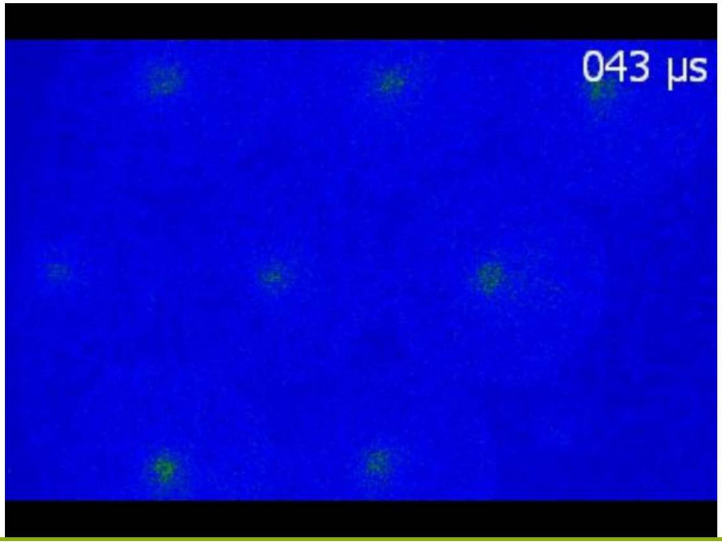
Cathode directed positive streamer → filamentary microdischarge (FMD).

- Second emission structure

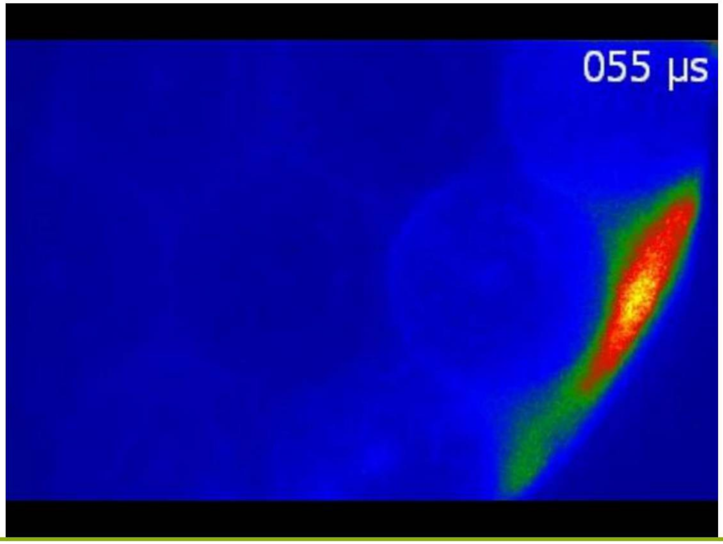
Surface microdischarges (SMDs)



First Structure



Second structure



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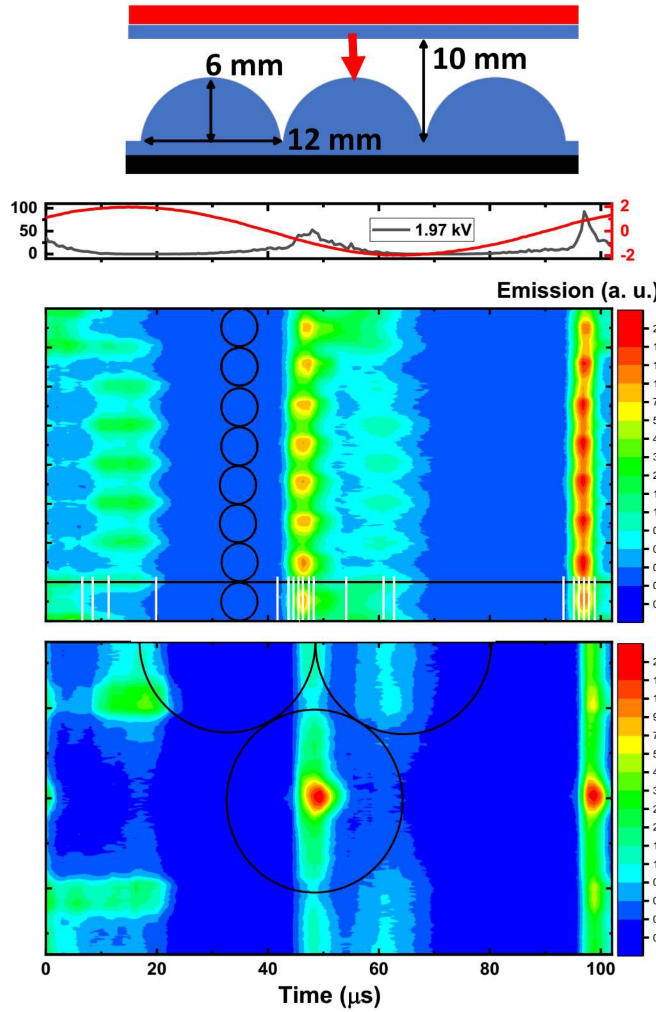
Filamentary and surface microdischarge (Pos half)

- First emission structure

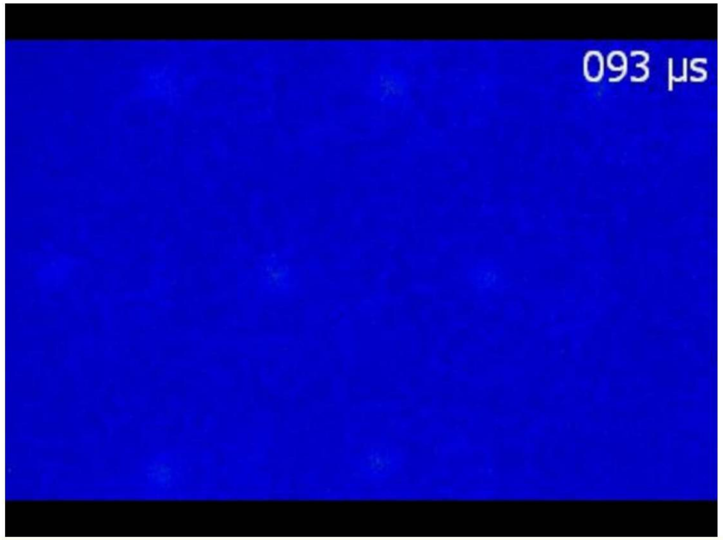
Cathode directed positive streamer → filamentary microdischarge (FMD) → surface microdischarges (SMD).

- Second emission structure

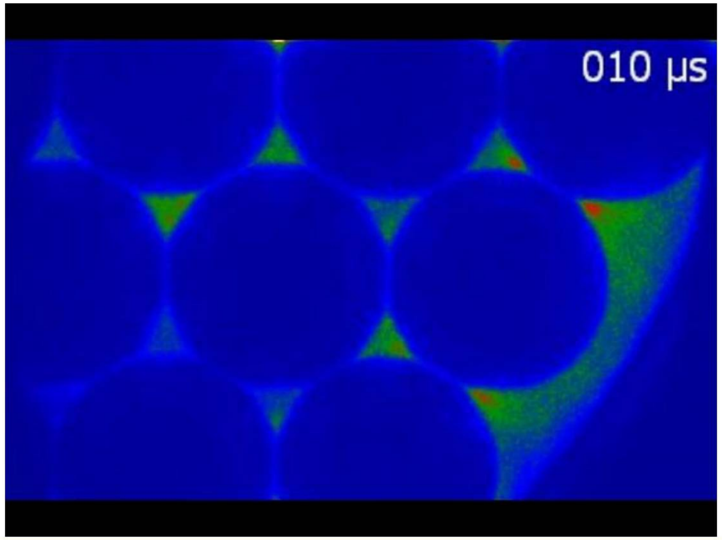
Surface microdischarges (SMDs)



First Structure



Second structure



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What happens at the contact point?

- In both halves, higher emission is generated at the contact point position
- The structures become sharper with the increase of voltage amplitude
- During the positive half, each SMD is formed as multiple microscopic structures

2nd structure

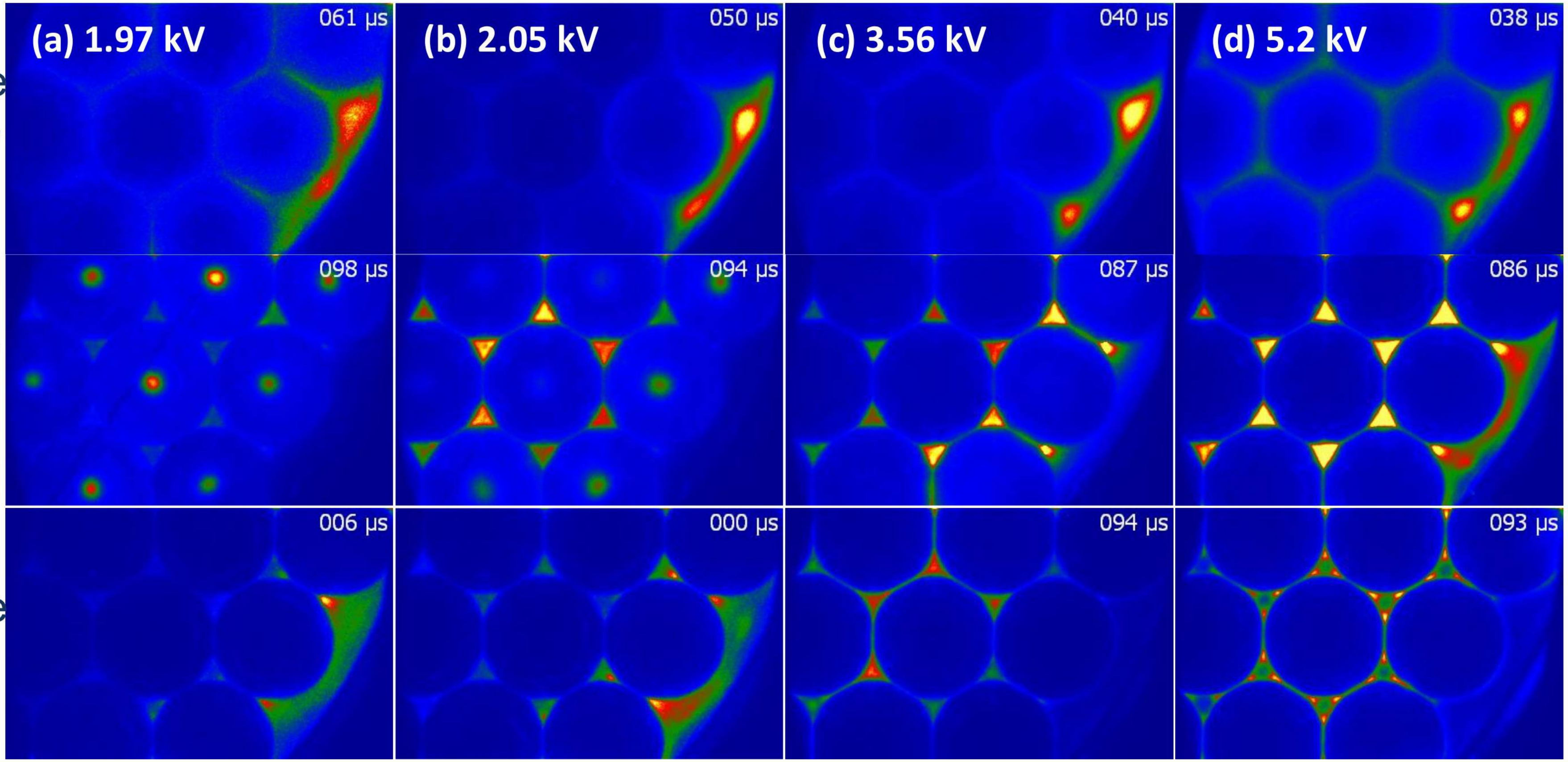
Neg. half

1st structure

Pos. half

2nd structure

Pos. half



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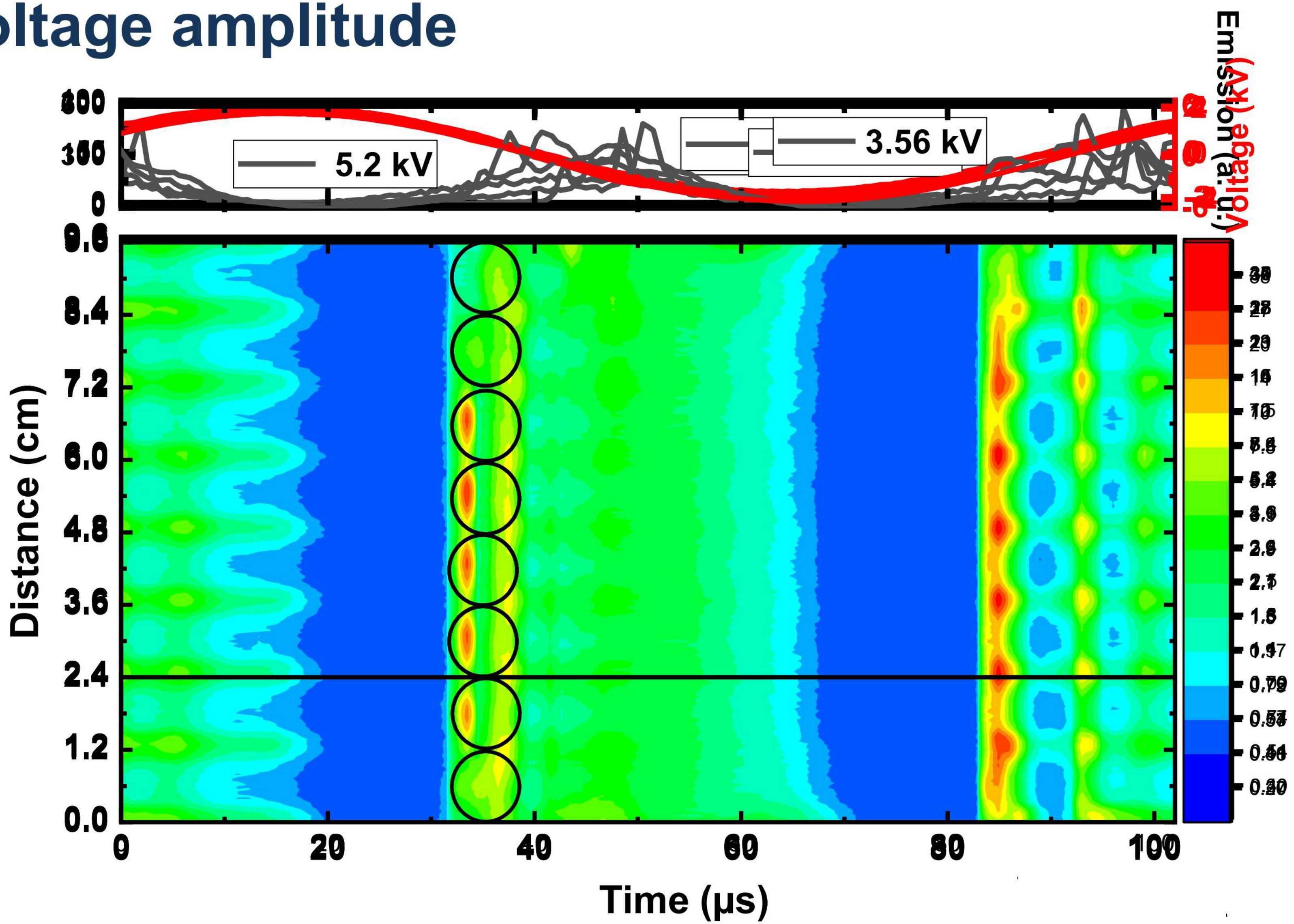
Influence of applied voltage amplitude

- The number of discharge pulses increase in both positive and negative halves
- Comparatively, the emission structures are much sharper in the positive half as the effect of electric field is much stronger
- All the emission structures are not equally bright due to wave-like propagation.

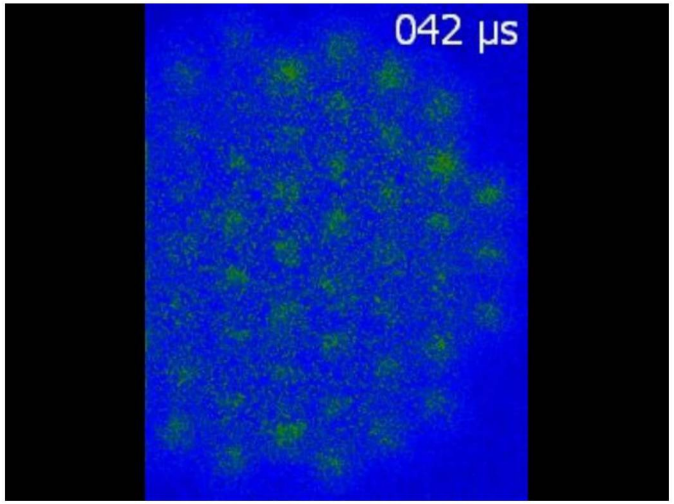


Wave-like propagation of emission intensity

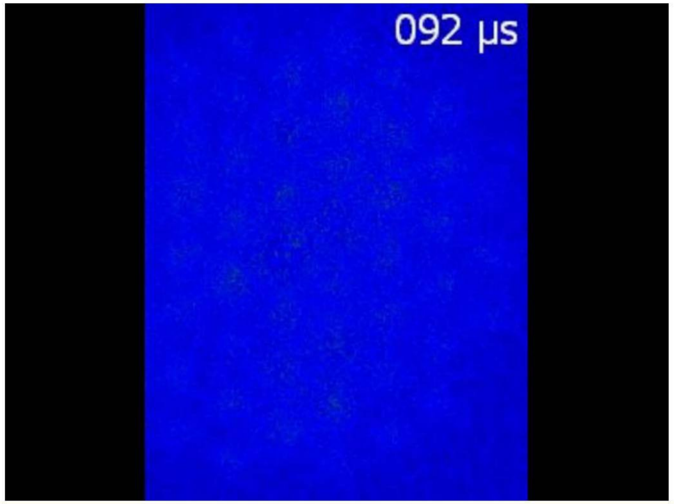
- The discharge ignition is initially uniform as a PS
- The emission later becomes brighter in the center and spreads radially, and finally extinguish from the center
- Wave propagation velocity is faster at higher voltages
- Similar wave-like propagation happens during successive emission structures
- Such interaction has consequences for the size of PBP

1.97 kV

Negative half

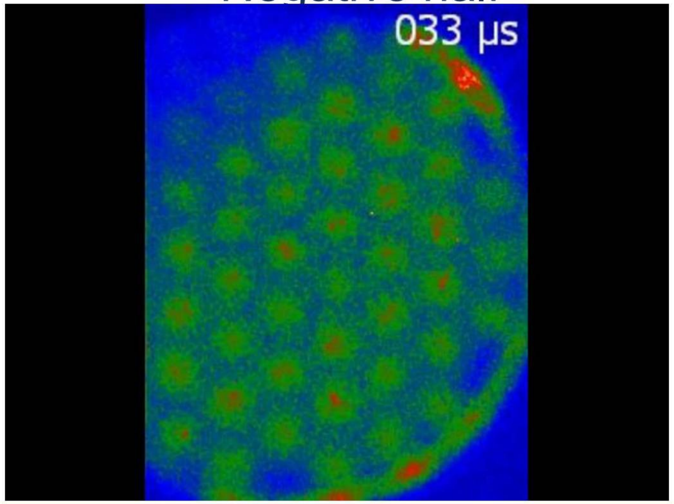


Positive half

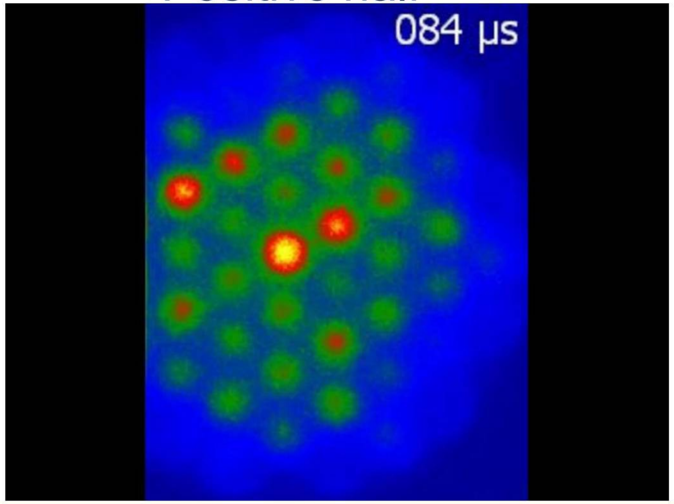


3.56 kV

Negative half



Positive half



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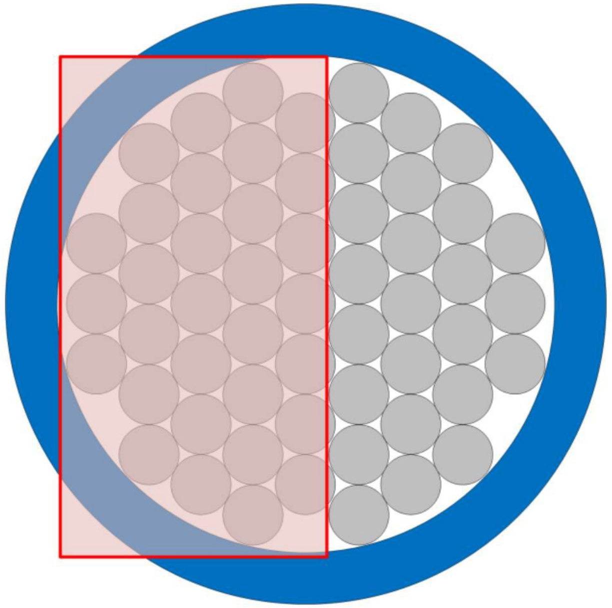
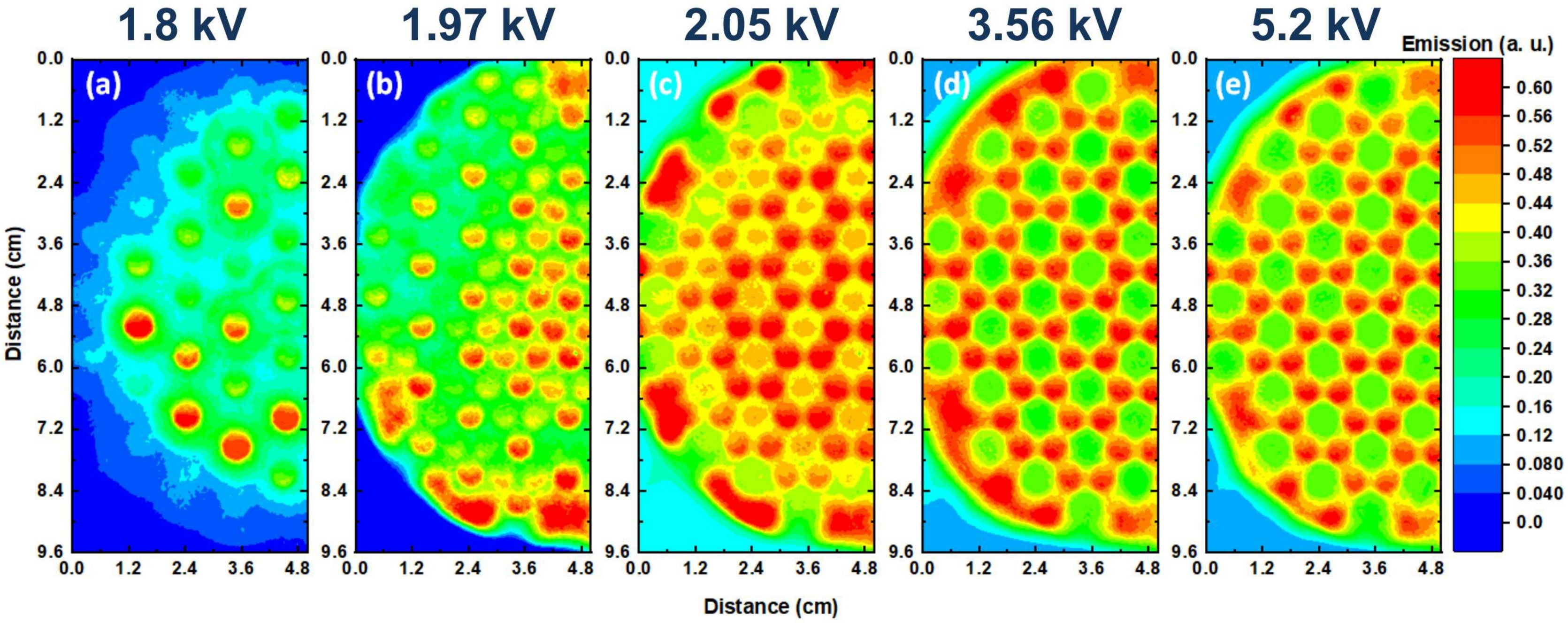
Time averaged measurements

- Time averaged measurements as a function of applied voltage are obtained using ICCD camera.
- At low voltages, the emission is maximum at the positions of minimum gap or apex of pellets. With the increase of voltage amplitude, the emission increases at the contact points.





Deposition of oxygenated hydrocarbons in a packed-bed plasma reactor during the oxidation of toluene: Influence of applied voltage Z Mujahid, M D. Y. Oteef, Xin Tu, Julian Schulze (submitted) 2021

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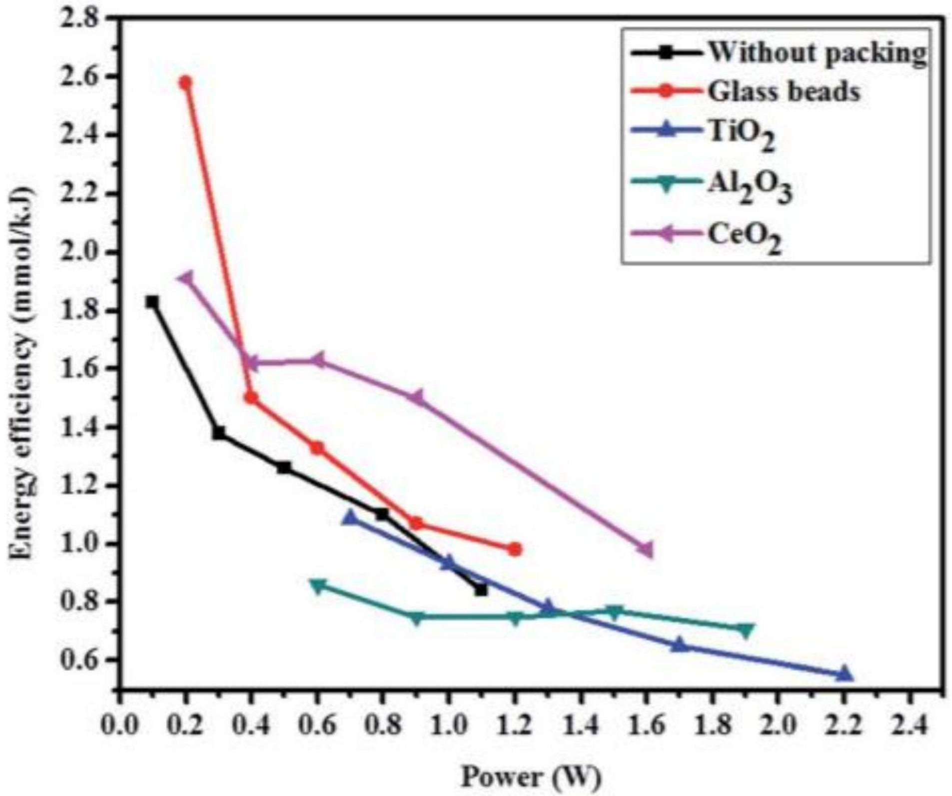
Influence of applied voltage on performance and plasma emission position

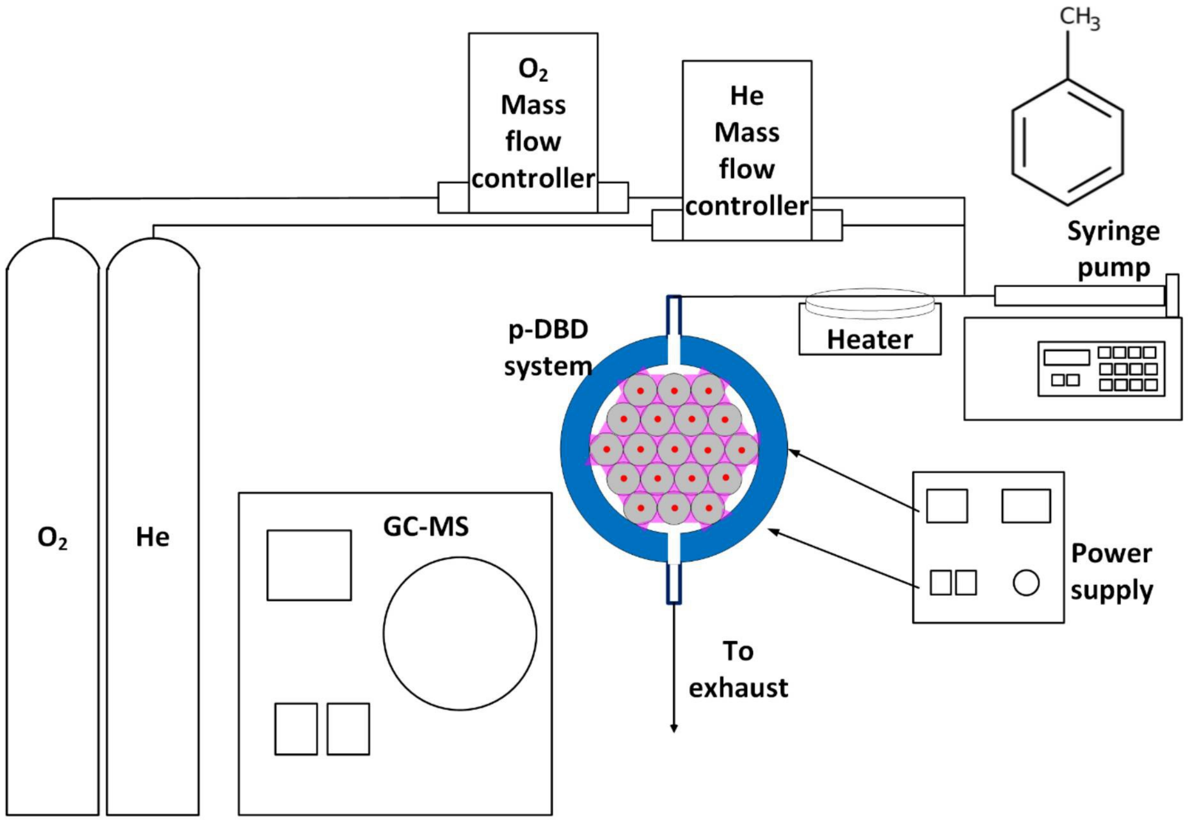
- Applied voltage (or power) is an important parameter with regards to PBPR's performance such as conversion and energy efficiency [1-2]. The origin of such change is not yet understood.
- Previous experimental results and modelling showed that the plasma emission position, discharge mechanisms and parameters change with the applied voltage amplitude [3].
- Here, we have tailored the conditions to increase the intermediate reaction products deposition/condensation.
- The deposition of intermediate reaction products position is used as a trace of reaction position.



[1] Ray, D. and C.J.R.A. Subrahmanyam, 2016 RCS Advances 6(45): p. 39492-39499.
[2] Xu, S., et al., 2018 Plasma Sources Science and Technology 27(7): p. 075009.
[3] Mujahid Z, Kruszelnicki J, Hala A and Kushner M J 2019 Chemical Engineering Journal 382 123038

Experimental system - depositon

- Second p-DBD system (similar to the first system) with hexagonal packing except smaller chamber diameter (62 mm) and number of pellets (19), operated in almost similar operating conditions with 2 slm flow rate.
- In this system 2.5 % oxygen is admixed in Helium and toluene injection rate is 48 µl/min.
- Gas line heated to ~ 250^{o} C to avoid toluene condensation.
- Discharge is generated for 30 minutes to obtain the deposition profile images.
- For the GC-MS analysis, discharge is operated for only 5 minutes to avoid complete degradation of deposited compounds.



Deposition of oxygenated hydrocarbons in a packed-bed plasma reactor during the oxidation of toluene: Influence of applied voltage Z Mujahid, M D. Y. Oteef, Xin Tu, Julian Schulze (submitted) 2021

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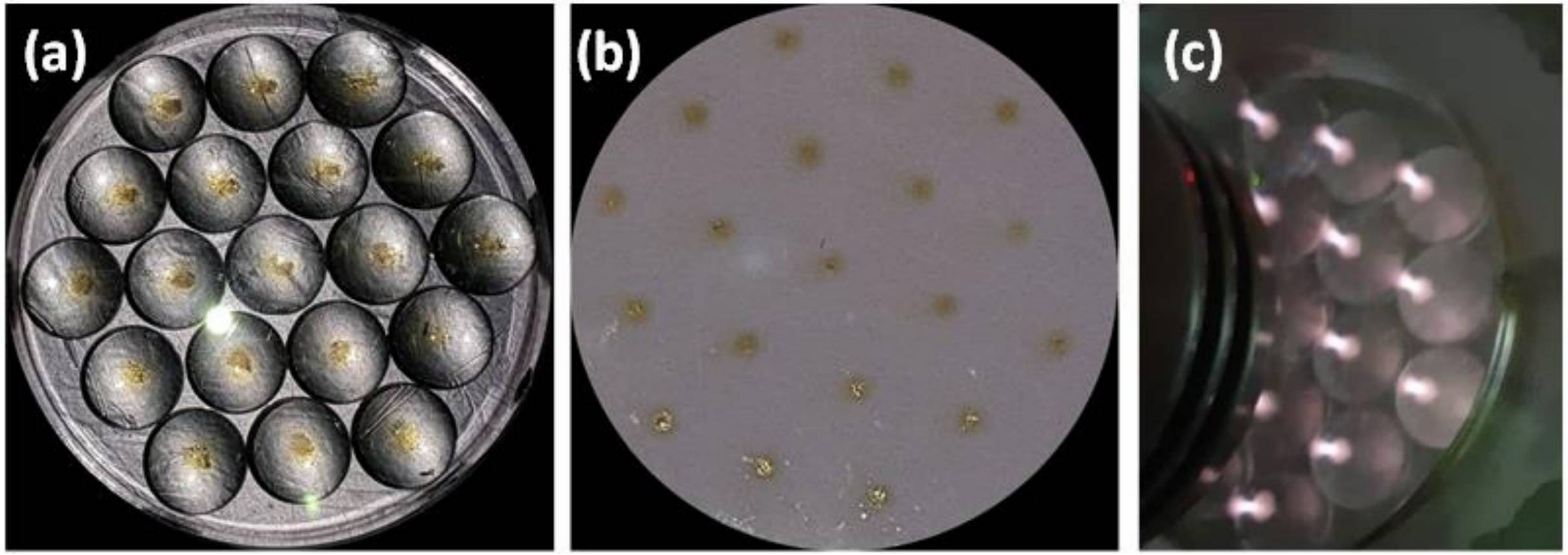
Deposition/condensation position at low power

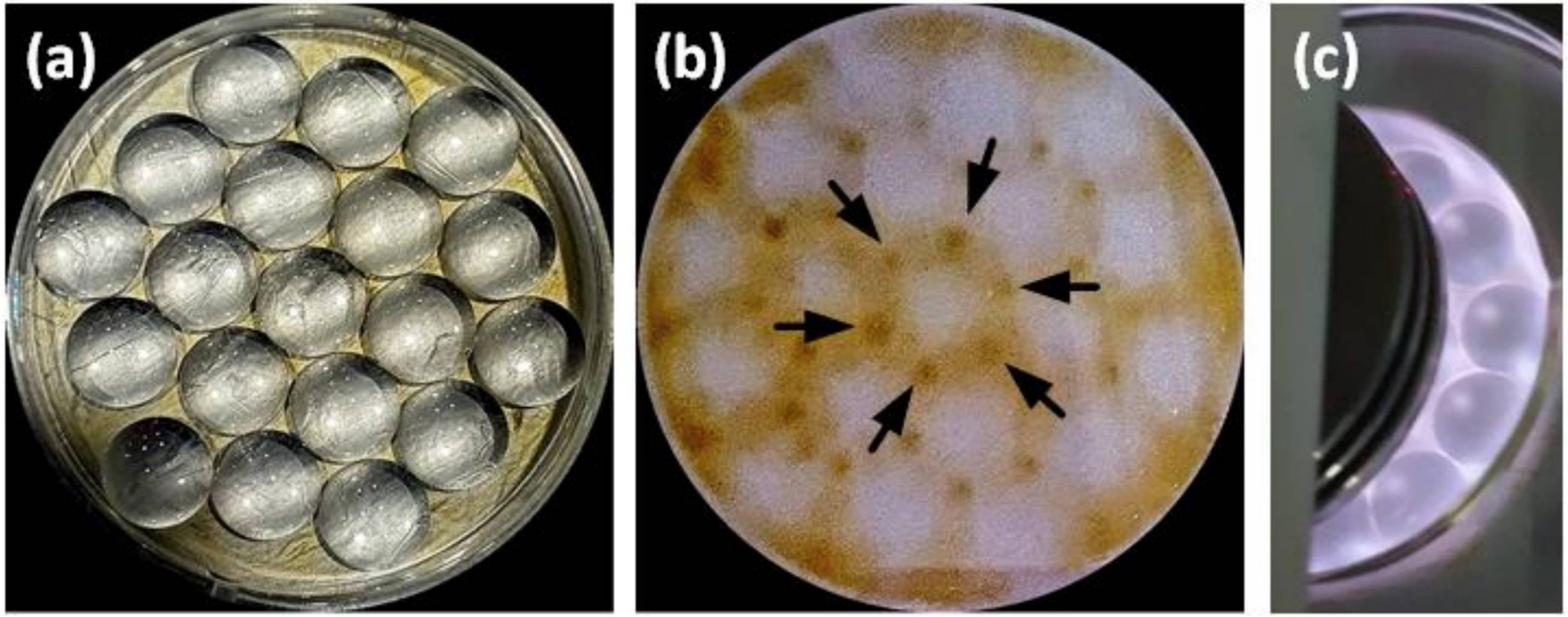
- The plasma is operated at the lowest voltage 3.67 kV where a stable filamentary discharge can be sustained (observed through a single current peak in each half cycle).
- Plasma is operated continuously for 30 minutes and then deposition over both the flat and the curved dielectric are imaged.
- The deposition is mostly in the center of the dielectric structures, i.e. below the active plasma region, which indicates that the reactions are caused by the short duration species such as O, OH and electrons.



Deposition of oxygenated hydrocarbons in a packed-bed plasma reactor during the oxidation of toluene: Influence of applied voltage Z Mujahid, M D. Y. Oteef, Xin Tu, Julian Schulze (submitted) 2021

Deposition/condensation position at high power

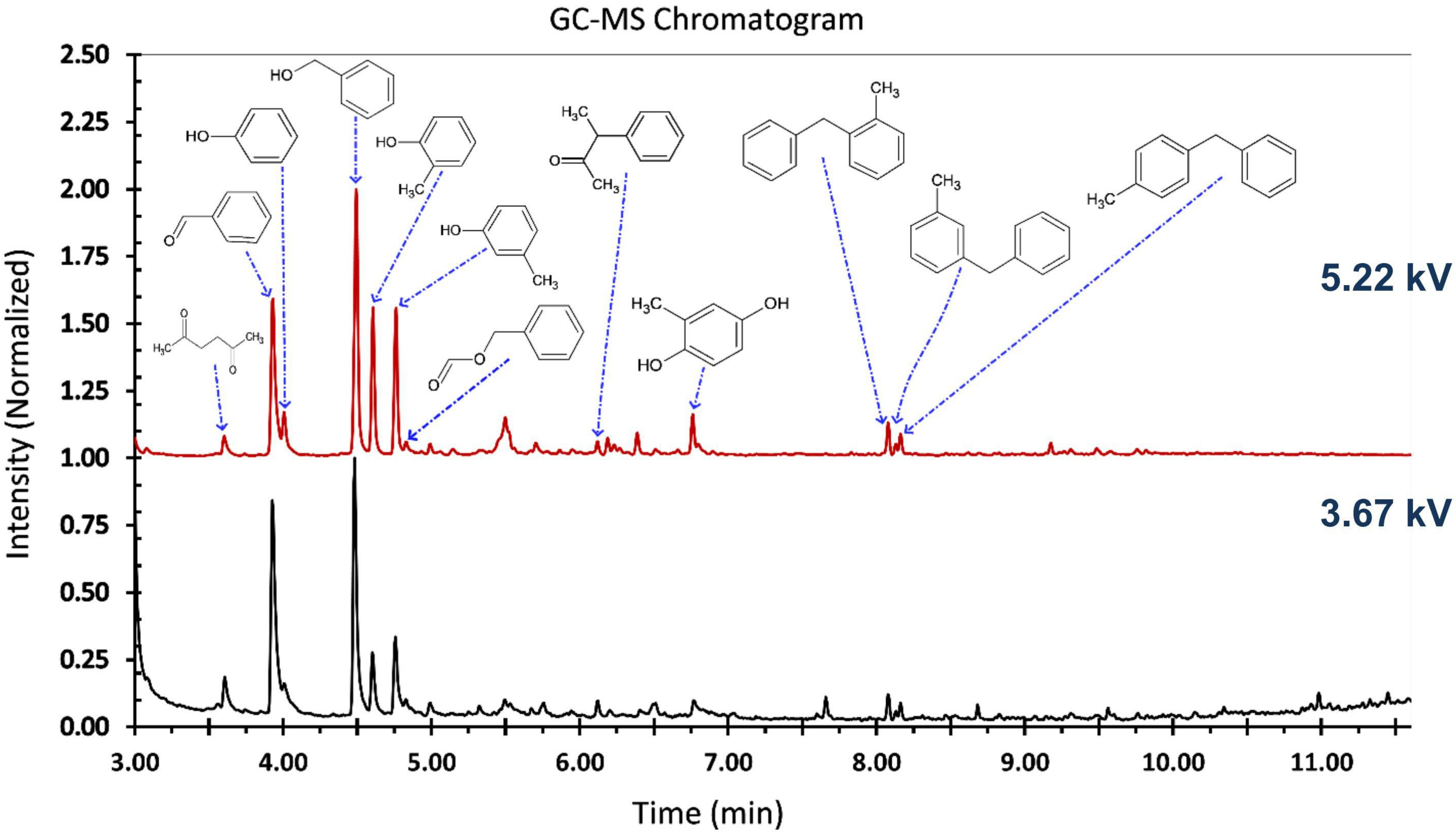
- The plasma is operated at the high voltage (observed through two current peaks in each half cycle) at 5.22 kV.
- Plasma is operated continuously for 30 minutes and then deposition over both the flat and the curved dielectric are imaged.
- The deposition reflects the plasma emission profile at high voltage amplitudes, which shows maximum emission between the dielectric structures and is maximum at the contact points.



Deposition of oxygenated hydrocarbons in a packed-bed plasma reactor during the oxidation of toluene: Influence of applied voltage Z Mujahid, M D. Y. Oteef, Xin Tu, Julian Schulze (submitted) 2021

GC-MS of the deposited products

- The deposited products were analyzed five minutes after plasma operation.
- Most of the reactive products have an addition of an OH group while few have the addition of the O radical. There is also recombination two Toluene molecules.



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Rate coefficients of important radicals

- Electrons, metastable O, O, OH and ozone have lifetimes lifetimes of ~ 10 ns, 10 ns, 50 µs, 100 µs and 10 min [1]
- Rate coefficients of important radicals O_3, O and OH.
- 1) $C_7H_8 + O_3 \rightarrow$ products k ~ 1×10^{-21} cm³/s [2]
- 2) $C_7H_8 + O \rightarrow$ products k ~ 8×10^{-14} cm³/s [3]
- 3) $C_7H_8 + OH \rightarrow$ products k ~ 3×10^{-12} cm³/s [3]
- OH has the highest rate coefficient, which supports the presence of an OH group in most of the deposited products.

[1] Kim H-H, Teramoto Y, Negishi N and Ogata A 2015 Catalysis Today 256 13-22

[2] Pate, C., et al., 1976 Journal of Environmental Science 11(1): p. 1-10.

[3] Blin-Simiand, N., et al., 2008. Plasma Chemistry and Plasma Processing 28(4): p. 429-466.

CONCLUSIONS

- Plasma is generated as multiple segmented filamentary microdischarges at the minimum gap and connected surface microdischarges at the contact points
- The interaction between the adjacent microdischarges generates a wave like propagation of emission from the center towards the edges
- Zooming into each surface discharge reveals microscopic structures which are more pronounced at higher voltage amplitude
- Using Toluene as a representative VOC, the location of the chemical reactions is investigated.
- It is observed that the chemical reactions in the considered chemistry happened at the location of the dominant plasma generation, which changes with power/voltage.
- At low power/voltage time averaged emission and deposition happen at the minimum gap. At higher power/voltage, both the time averaged emission and deposition are predominantly in the void between dielectrics (or contact points).
- The analysis of the life times and rate coefficients of the expected reactive species, reaction products and deposition location indicate that electrons, OH and O play the dominant role in toluene conversion. The comparison of the products at low and high power show that the product formation rate changes with voltage possibly due to change of the plasma parameters [1].

Acknowledgement

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- Mohammed Oteef
- Mukul Sharma
- Xin Tu

Deutsche Forschungsgemeinschaft

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THANK YOU

How is OH generated and how it can react with Toluene?

- The source of the OH, is still not known. The reactivity of Toluene with OH can be enhanced by the following electron induced reactions (with unknown rate coefficients) [1].

- 4) $C_7H_8 + e \rightarrow H + C_7H_7$ [1]

- 5) $C_7H_8 + e \rightarrow CH_3 + C_6H_5$ [1]

[1] Blin-Simiand, N., et al., Plasma reactivity and plasma-surface interactions during treatment of toluene by a dielectric barrier discharge 2008 Plasma Chemistry and Plasma Processing 28(4): p. 429-466.