Atmospheric Pressure Dielectric Barrier Discharges in Air: Chemistry and Antimicrobial Effects

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Surface Mirodischarge Air Plasma Disinfection

- Plasma-generated reactive oxygen and nitrogen species (RONS) are biologically significant
- Use *E. coli* disinfection as a ‘biological proxy’
- Key parameters: plasma/(photon) power/fluence per area
Schematic diagram of experimental air plasma system: SMD adjacent to vial with *buffered* water/E. coli bacteria; UVA exposed to water after plasma.
Nitrite Photochemistry

\[
\text{NO}_2^- + \text{H}_2\text{O} + h\nu \rightarrow \text{NO} + \text{OH} + \text{OH}^- 
\]

Black: nitrite absorbance

Blue: UVA-LED emission spectrum (our data)
UVA (LED ~ 1 W/cm²) applied to bottom of glass vial and higher power (5 mins @ 0.30 W/cm²) plasma treatment.

(O): expected additive effect; (■): UVA followed by 5 minutes of plasma treatment; (▲): UVA following 5 minutes of plasma treatment.
Air plasma forms RONS including nitrogen dioxide (NO$_2$) and nitric oxide (NO). NO$_2$ and NO, through a series of reactions, dissolve in water and hydrolyze to yield nitrite (NO$_2^-$).
(2) In aqueous solution, nitrite is photolyzed at 369 nm to yield nitric oxide (NO), hydroxyl (OH), and hydroxide (OH⁻).
When the 369 nm LED is turned off, in the absence of other reactants, NO and OH recombine into nitrous acid (HNO$_2$). Nitrous acid dissociates at neutral pH to nitrite and hydrogen ion (H$^+$), and H$^+$ and OH$^-$ recombine to water (H$_2$O).
(4) In the presence of *E. coli*, OH damages biomolecules to inactivate the bacteria: *postulated key antimicrobial effect*
(5) In the presence of both *E. coli* and ascorbate (a strong OH scavenger), OH scavenged by ascorbate, abrogating antimicrobial effect.
(6) Nitrite alone does not fully account for observed plasma-UVA synergy, but combining NO$_2^-$ and H$_2$O$_2$ does. H$_2$O$_2$ also produced in plasma, enters aqueous phase, reacts with NO$_2^-$ to form (perhaps) ONOO$^-$. 
Surface Microdischarge Air Plasma Disinfection

- Frequency: 10 kHz
- Voltage: 10 kV $V_{pk-pk}$
- Power consumption: ~5 W
- Distance to sample: varies
- Plasma on: 0.5-5 min

- Diameter: 50 mm
- Bacteria: E. coli K12
- Material: SS, silicon, pig skin

E. coli

- Rinse
- Diluted specimen
- Agar plate
- Count #CFU

Overnight
Gas Phase Measurement and Surface Disinfection

Goal: Measure gas phase species as a function of time and correlate with antibacterial killing at surface
FTIR Spectrum: Quantify via HITRANS Database

Typical FTIR measurements as a function of time:
2, 8 and 16 minutes; power ~ 0.3 W/cm².
Nitric Oxide (NO) vs. Time and Power Density
Ozone (O$_3$) vs. Time and Power Density
Nitrogen Dioxide (NO$_2$) vs. Time and Power Density
Bacterial (E. coli) Killing vs. Time and Power Density
Conclusions

• UVA and plasma water treatment have a synergistic antimicrobial effect
  – Only in high-power (‘NO\textsubscript{x}’) mode
  – Seen most clearly under buffered conditions (not acidified water)
  – Only when plasma treatment happens first
• Plasma treatment of water creates active precursor species
  – Nitrite (NO\textsubscript{2}\textsuperscript{-}) is the most important species
  – But it doesn’t account for all the synergy; H\textsubscript{2}O\textsubscript{2} also important; NO\textsubscript{3}\textsuperscript{-} relatively inactive
• Generation of OH radical is an important step
  – Synergistic effect nearly eliminated with OH scavenger added (ascorbate)
Conclusions

• Confined SMD shows clearly distinct modes: low power results in O$_3$; higher power gives NO$_x$.

• SMD surface antibacterial results imply that NO and NO$_2$ are more effective than O$_3$ in gas phase (recall that O$_3$ is much more effective when dissolved in water)

• Consistent with other published results for O$_3$; very few data for NO/NO$_2$.

• LR considerably higher when bacteria grow on moist agar plates.
UVA and plasma treatment exhibit synergy...

- 5 minutes of plasma treatment in high-power mode $\rightarrow 0.20$ log reduction
- Expected additive: UV effect + 0.20
- UV then plasma: additive effect
- Plasma then UV: synergistic effect
...but only under the right conditions.

- 30 seconds of plasma treatment in low-power mode $\rightarrow$ 0.50 log reduction
- Expected additive: UV effect + 0.50
- UV then plasma: additive effect
- Plasma then UV: still only additive effect
PAW components reproduce some synergy…

- UVA with 5 mM nitrite in water added: *synergistic* (but not full effect)
- UVA with 5 mM nitrate: additive
- UVA with 100 uM hydrogen peroxide: additive

- 5 mM nitrite, 5 mM nitrate, 100 uM hydrogen peroxide
- Measured from plasma-treated PBS
...and their combination recovers the full effect.

- UVA with nitrite: some synergy
- UVA with nitrite plus hydrogen peroxide: full synergy
- Adding nitrate does not increase effect

- 5 mM nitrite, 5 mM nitrate, 100 uM hydrogen peroxide
- Measured from plasma-treated PBS
OH is likely an important antimicrobial species

- Plasma treatment with ascorbate added to water: little or no synergy

\[ \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \cdot\text{O} + \text{OH}^- + \cdot\text{NO} \]

- Ascorbate, or Vitamin C
- OH radical scavenger
Air Plasma + UVA Photons
Synergistically Antimicrobial

- Antimicrobial effect from combined UVA (LED ~ 1 W/cm²) applied to bottom of glass vial and higher power (5 mins @ 0.30 W/cm²) plasma treatment.

- UVA first, followed by plasma: no synergy

- Plasma first, followed by UVA: synergy