Final Report of

Collaborative Research:

Collaborative Research: Atmospheric Pressure Microplasma Chemistry-Photon Synergies

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Executive Summary

Combining the effects of low temperature, atmospheric pressure microplasmas and microplasma photon sources shows greatly expanded range of applications of each of them. The plasma sources create active chemical species and these can be activated further by addition of photons and associated photochemistry. There are many ways to combine the effects of plasma chemistry and photochemistry, especially if there are multiple phases present. The project combines construction of appropriate test experimental systems, various spectroscopic diagnostics and mathematical modeling.

Mathematical modeling at UC Berkeley led to key insights. In one mode, a set of about 600 reactions was assembled from the literature and used to predict the time evolution of the chemical species in the plasma and downstream regions. Successfull comparisons were made between measured and predicted gas phase species and liquid (water) species that arose from the gas phase species. The model (qualitatively and/or semi-quantitatively) for low power conditions successfully predicted the rise of the following species: O_3, N_2O, NO_2, NO_3, HNO_2 and HNO_3. Interestingly, the model also predicted the formation of N_2O_5 and that was not observed.

Corresponding experiments conducted at UIUC have demonstrated that microcavity plasma technology is capable of realizing compact lamps of UV/VUV radiation and arrays of plasma jets. Chemical analysis of the radicals generated by arrays of microchannel plasmas were conducted with a residual gas analyzer (RGA) in proximity to the array. In addition, microcavity plasma lamps capable of generating more than 20 mW/cm2 at 172 nm (Xe dimer) have been fabricated with a custom form factor to mate to the plasma chemistry setup, The lamp was installed by the Berkeley team so as to investigate plasma chemistry-photon synergies at a higher photon energy (~7.2 eV) as compared to the UVA treatment that is afforded by UV LEDs operating at 365 nm.

The UC Berkeley team showed that the air plasma device operates either in an O_3-rich mode (low power) or NOx-rich mode (higher power). The NOx mode is more effective in inactivating dried bacteria on surfaces. This device was then used in the next stage by combining with UVA and UVC photons to test the effectiveness of gas phase photochemistry synergy with plasma chemistry. The combined device was highly effective against dried bacteria at surfaces and in water. This work was extended to include cow hoof as a model for human nail. The combined plasma-UVA exposure was shown to be highly effective acting through the hoof/nail material. The UC Berkeley team also explored additional applications - the first used air plasma plus UVA photons to disinfect contact lens solution, lens material and lens cases. This work showed that the combination has many attractive advantages - disinfection is rapid and material damage was undetectable.

Year 1 Progress Report, May 2013: Activities and Findings

Overview

Combining the effects of low temperature, atmospheric pressure microplasmas and microplasma photon sources offers the promise of greatly expanding the range of applications of each of them. The plasma sources create active chemical species and these can be activated further by addition of photons and associated photochemistry. There are many ways to combine the effects of plasma chemistry and photochemistry, especially if there are multiple phases present. The project combines construction of appropriate test experimental systems, various spectroscopic diagnostics and mathematical modeling.

The **Project Participants** include at

a) **University of California at Berkeley**, Profs. ***D. B. Graves and D. S. Clark***, along with Research Associate Y. Sakiyama, and graduate students M. Pavlovich and S. Karim.
b) **University of Illinois** Profs. ***J. G. Eden and S.-J. Pa***rk, along with graduate students P. Sun and Y. Ho

The collaboration has produced promising results during the first year of performance. We have had periodic discussions between the collaborative partners to help define the types of devices to build and test. At the University of Illinois, various microcavity photon devices were built, focusing on the vacuum ultraviolet wavelength (172 nm Xe dimer sources). The first photon source was designed, tested and delivered for testing and analysis to UC Berkeley in April 2013. These relatively high-energy photons are most likely to interact strongly with adjacent liquid or gas phase chemical species created by plasma. Preliminary work at UC Berkeley focused on initial tests using light emitting diodes in the near-ultraviolet region (UVA; 365 nm). These tests focused on a synergy between air plasma-generated species that dissolve into water and the applied UV photons. The effects of the synergy were tested by measuring rates of killing E. coli bacteria in water from the combined plasma and photon flux. A clear synergy was observed. In addition, mathematical modeling was coupled with various spectroscopic diagnostics to better understand the nature of the synergy. [1-4]

Plasma Chemistry and Photon Synergies at the University of California at Berkeley (UCB)

The goal of this project was to characterize the photochemical and antimicrobial synergy between chemical species generated by ambient air plasma in water and ultraviolet photons at 365 nm. We considered the interaction of UVA photons, produced by a UVA-emitting LED source, with reactive aqueous-phase species under different discharge power densities. Next, we characterized the synergy between UVA treatment and solution containing individual plasma-associated species to determine which species is most responsible for the synergistic effect. Finally, we considered the effects of adding a radical scavenger (ascorbate), effectively preventing the synergy from occurring.

This project has reached three major conclusions. First, we examined the difference between treating solution with plasma before and after UVA treatment under both low-power (i.e., ozone-rich) and high-power (i.e., nitrogen oxides-rich) modes. In low-power mode, the main specie detected is ozone (O_3). In the high-power mode, the main chemical species that we were able to identify (although there may be others) were nitrite (NO_2^- ~ 5 mM concentration), nitrate (NO_3^- ~ 5 mM concentration) and hydrogen peroxide (H_2O_2, ~ 0.1 mM concentration).

As illustrated ion Fig. 1, the experimental system consists of a 'surface microdischarge' (SMD) plasma device crates a plasma in air in a thin (~ 1mm) region around a grounded mesh. This grounded mesh is separated from the powered electrode (~ 5 kV sinusoidal input at 10 kHz) by a thin (~ 2 mm thick) quartz plate. Inside the acrylic enclosure is placed a small vial containing 150 μL water with E. coli bacteria suspended in it. After plasma exposure at a given power and length of time, the vial is removed from the container, vortexed (i.e. thoroughly mixing the gas above the liquid and the liquid/bacteria mixture). The bottom of the vial is then exposed to a set of 4 light emitting diodes (LEDs), generating light at about 0.8 W/cm^2 at ~365 nm.

When an aqueous suspension of E. coli was treated with high-power air plasma for 5 minutes followed by UVA for 60 seconds, the antimicrobial effect was at least a 4.5 log reduction in bacterial load, as shown in Fig. 2. Under the same conditions, the expected additive effect of plasma treatment alone plus UVA treatment alone was a 2-log reduction in load. In contrast, we show that under other conditions, such as treating with UVA first or using low-power plasma, the combined antimicrobial effect matches the expected additive effect. Therefore, plasma in the high-power mode is "priming" the treated solution for UVA synergy by manipulating the aqueous chemistry.

Of the species that are known to be created in high-power air plasma treatment of aqueous solution, nitrite (NO_2^-) appears to influence the observed synergy the most. Nitrite is also known to absorb and photolyze in the UVA range to form NO and OH. These species are much more chemically and biologically active than nitrite. To support this hypothesis, we show that the addition of nitrite to aqueous solution increases the synergistic antimicrobial effect when treated with UVA. Finally, ascorbate (or Vitamin C) is known to be a potent scavenger of OH radical. When both nitrite and ascorbate are added to aqueous solution, the synergistic effect is not observed. Fig. 3 shows the effects of adding nitrite and ascorbate to the treated solution.

Although adding nitrite to buffered water at the concentration observed to form after air plasma exposure creates a solution that reproduces some of the synergistic effect, it does not account for the entire effect observed after plasma exposure. We therefore tested combinations of nitrite, nitrate and hydrogen peroxide. Nitrate did not appear to contribute to the effect, but mixtures of nitrite and hydrogen peroxide at the same concentration as made by air plasma exposure reproduced very similar plasma-photon synergy. This is illustrated in Fig. 4. Not shown is the effect of adding ascorbate to the nitrite/hydrogen peroxide mixture – the same elimination of the antibacterial effect was observed for this mixture as was observed for the others.

Therefore, we suggest the following mechanism for plasma/UVA synergy. High-power plasma most strongly contributes to the synergistic effect by adding nitrite and hydrogen peroxide to aqueous solution. UVA photolyzes nitrite and hydrogen peroxide, possibly to form peroxynitrite ($ONOO^-$), which reacts rapidly with bacterial cells to inactivate them. The interaction of UVA photons with plasma-generated chemical species has the potential to increase the speed and efficacy of both ambient-plasma disinfection and UV-based disinfection methods. Furthermore, our results suggest the possibility of a wider application of ambient-condition plasma chemistry coupled with photochemistry to produce unique chemical and biological effects. For example, there are many potential biomedical applications that could exploit the unique characteristics of nitric oxide (NO).

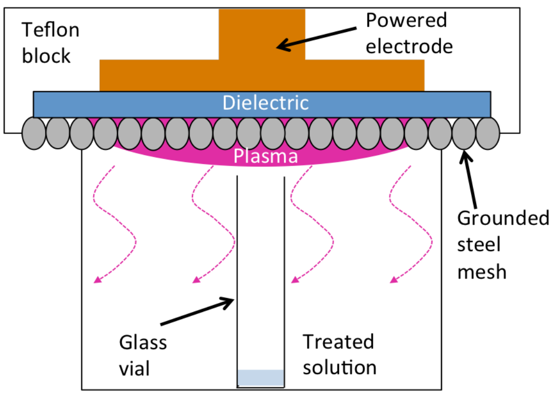


Figure 1.Schematic of the air DBD device with glass vial containing water and E. coli.

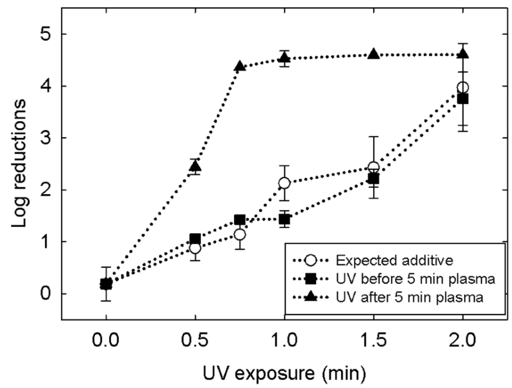


Figure 2. Plasma treatment in high-power mode, followed by UVA treatment, produces a stronger antimicrobial effect than would be expected by performing both treatments alone. In contrast, UVA treatment followed by plasma treatment shows no enhancement of the antimicrobial effect above the expected additive inactivation.

In the interests of space, we briefly summarize the results of the mathematical models developed during the first year of the project. More details are provided in references [1] and [2]. The plasma region was assumed to be well-mixed and coupled by diffusion to a 'downstream' region to match the experimental system. A set of about 600 reactions was assembled from the literature and used to predict the time evolution of the chemical species in the plasma and downstream regions. We made preliminary comparisons between measured and predicted gas phase species and also measure liquid (water) species that arose from the gas phase species. The model (qualitatively and/or semi-quantitatively) for low power conditions successfully predicted the rise of the following species: O_3, N_2O, NO_2, NO_3, HNO_2 and HNO_3. Interestingly, the model also predicted the formation of N_2O_5 and that was not observed. In addition, the model was unable to predict the transition from low power mode in which O_3 dominates and high power mode in which N_xO_y species dominate. Various attempts to account for these differences due to gas heating effects and/or vibrational excitation of molecular nitrogen were so far unsuccessful.

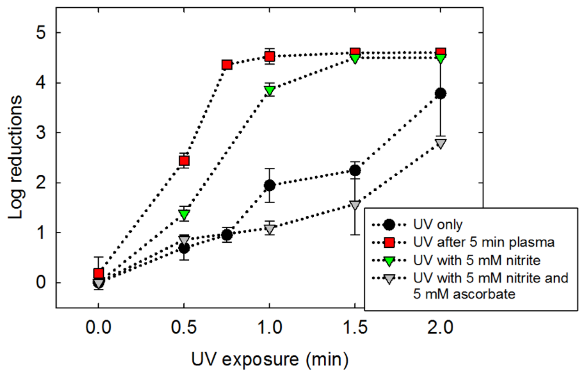


Figure 3. Adding nitrite to a bacterial suspension then exposing it to UVA photons increases the antimicrobial effect, but adding ascorbate (a radical scavenger) removes that enhancement. These data support the hypothesis that the photolysis of nitrite to NO and OH is a critical step in the observed synergy.

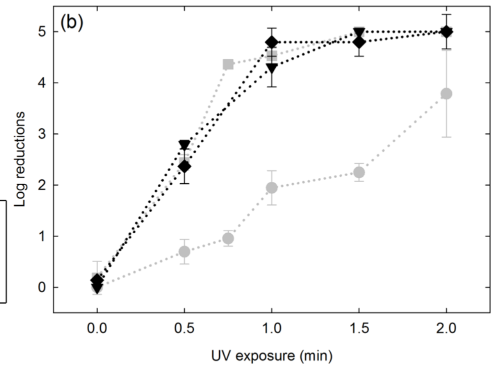


Figure 4. Antimicrobial effect from UVA treatment with multiple added species. Open circles: UVA only; open squares: UVA after 5 minutes plasma. Closed inverted triangles: 5 mM nitrite plus 100 μM hydrogen peroxide; closed diamonds: 5 mM nitrite plus 100 μM hydrogen peroxide plus 5 mM nitrate. The combination of nitrite and hydrogen peroxide at the concentrations observed after plasma treatment appears to reproduce the plasma-UVA synergy.

Plasma Chemistry and Photon Synergies at the University of Illinois at Urbana-Champaign (UIUC)

The focus of the work being conducted at the University of Illinois (UIUC) under this DOE program is the investigation, under carefully-controlled conditions, of the synergistic interaction of photons and plasma-produced radicals with a surface. Of particular interest is the use of vacuum ultraviolet (VUV)/UV photons in conjunction with plasma-generated molecular or atomic species, to deactivate bacteria or cells in a spatially-selective manner. The work being conducted at UIUC is being devoted initially to realizing microcavity plasma lamps capable of: 1) efficiently generating photons at discrete wavelengths over the VUV/UV (100-400 nm) spectral region, and 2) being integrated with a microscopic plasma source.

The lower half of Fig. 5 is a diagram in cross-section of a microchannel plasma lamp design that has been fabricated and tested successfully. An array of linear microchannels is fabricated into an alumina or ceramic substrate by a micropowder ablation process, and a wafer of quartz, Pyrex glass, or sapphire serves as the output window. Electrodes in the form of a wire mesh are embedded into both the upper and lower substrates which are bonded by a high temperature sealing agent. Lastly, the appropriate gas or gas mixture is introduced to the lamp through a feed tube that is hard-sealed.

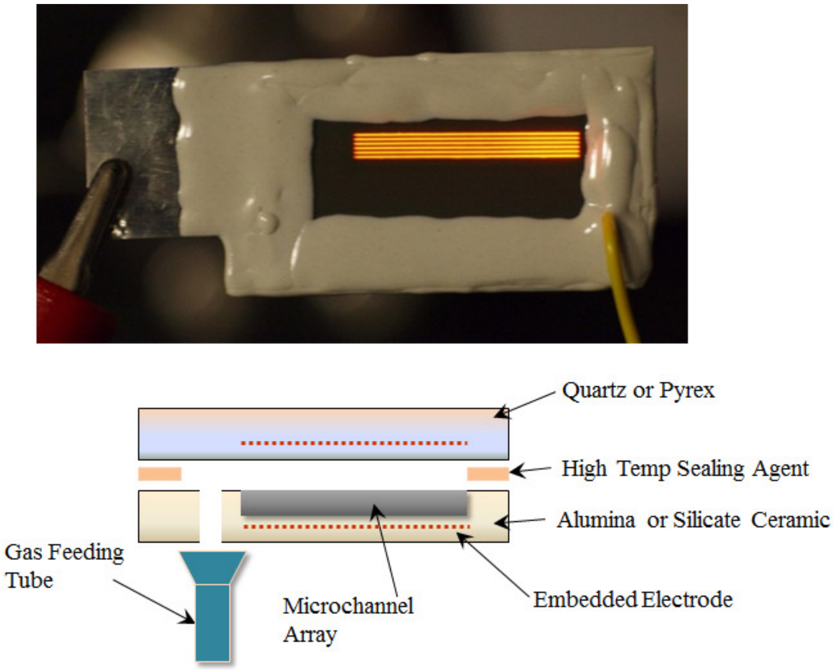


Fig. 5 (Bottom) Diagram in cross-section of a representative microchannel plasma lamp design developed at UIUC; (Top) Photograph of a ten microchannel lamp operating in 1 atm. of Ne to the lower substrate. The photograph in the upper portion shows a prototype microchannel plasma lamp operating at a pressure of 1 atmosphere of neon gas. These first lamps comprise 10 linear channels, each having a length of ~4 cm and an aperture (width of the channel at the top) of, typically, 200-400 μm.

The process developed at Illinois for fabricating the microchannels has been successfully applied to a wide range of materials, and Fig. 6 shows photographs of material combinations that have already been shown to be well-suited to producing and transmitting (into ambient air) visible or UV photons. As indicated in Fig. 6, microchannels of high quality can be produced in various ceramics, alumina, and borosilicate glass. By mating such arrays to windows having high transmission in the deep UV or VUV (100-200 nm), lamps targeting various spectral regions and, therefore, generating a specific range of photon energies, can be realized.

As an example of the short wavelength emission that can be produced with this first generation of lamps, Fig. 7 presents fluorescence spectra recorded in the 160-190 nm region when a lamp having the design of Fig. 5 is operated with pure Xe at pressures ranging from 100 to 450 Torr.

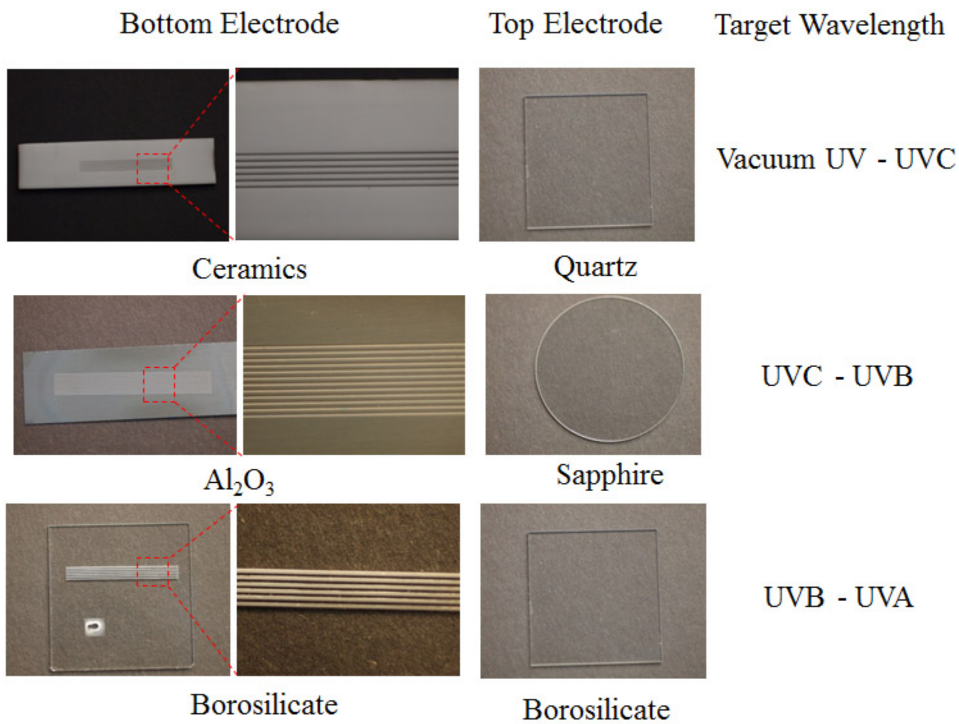


Fig. 6 Photographs of materials combinations demonstrated to date for the window and microchannel host for the lamps of Fig. 5.

The decline of the relative emission intensity of the Xe dimer at 450 Torr is the result of collisional quenching of the molecule. Notice that the lamp spectrum is free of absorption on the Schumann-Runge transition of the homonuclear oxygen molecule.

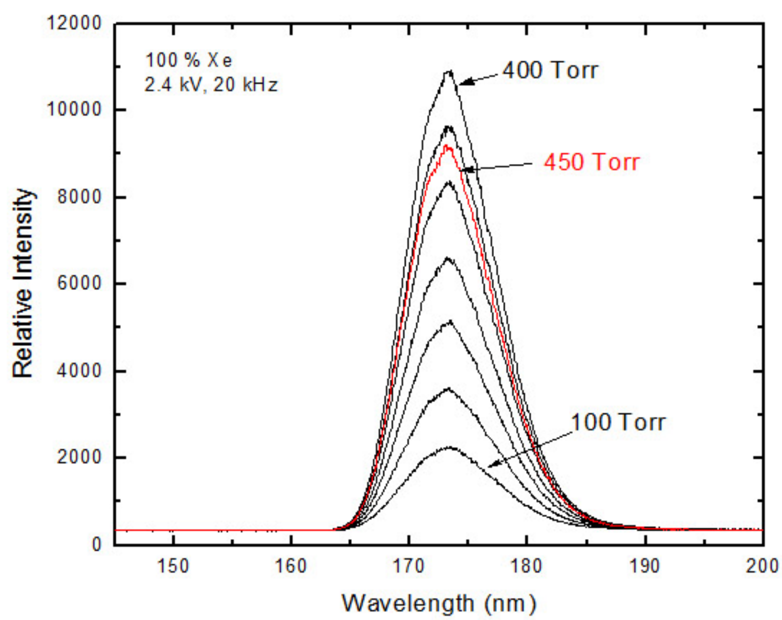
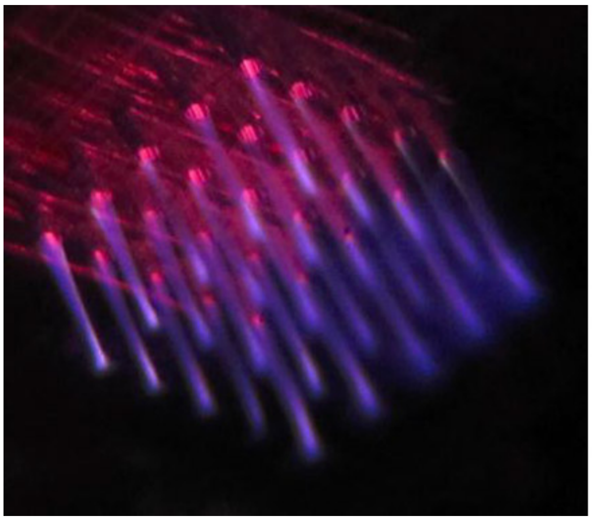


Fig. 7 Emission spectra in the 160-190 nm spectral region, produced by the Xe excimer molecule when a lamp having the design of Fig. 5 is operated with 100-450 Torr of Xe.

Microplasma jet arrays developed at UIUC provide simultaneously both optical radiation and plasma-produced radicals, as exemplified by the results of Fig. 8. The photograph at left shows a 5x5 array of plasma jets produced in helium feedstock gas by cylindrical electrodes embedded within a block of moldable polymer. These 25 plasma jets interact with ambient air to produce an obvious violet glow that is emitted by the nitrogen molecular ion. A representative spectrum of the emission produced by the array is shown at right in Fig. 8 - emission from the molecular ion at 391.4 nm clearly dominates the spectrum. These data demonstrate that specific ions (or radicals) can be produced by microplasma sources, thereby enabling a surface to be dosed selectively with a particular species.



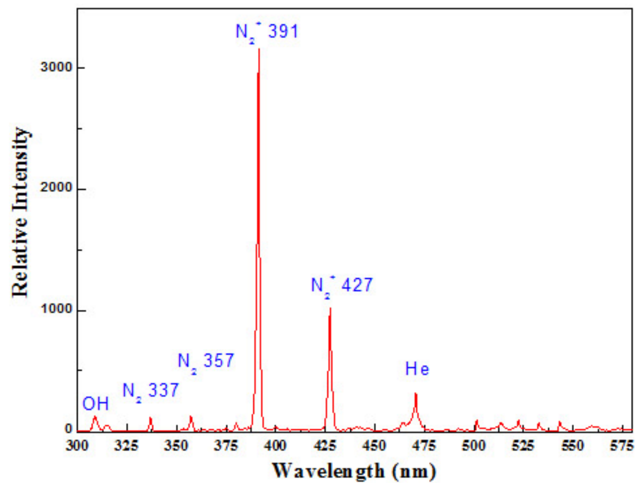


Fig. 8 (Left) Photograph of a 5x5 array of microchannel plasma jets, produced in He feedstock gas and expanding into ambient air; (Right) Representative spectrum (in the visible and UV) of the emission shown at left. The dominant features originate from the nitrogen dimer ion.

In summary, experiments conducted at UIUC have demonstrated that microcavity plasma technology is capable of realizing compact lamps of UV/VUV radiation and arrays of plasma jets. Our next goals include demonstrating emission at a variety of different (discrete) wavelengths in the VUV/deep UV region and to supply lamps to our colleagues at UC Berkeley. Chemical analysis of the radicals generated by arrays of microchannel plasmas (such as those of Fig. 8) will be conducted with a residual gas analyzer (RGA) in proximity to the array.

Year 2 Progress Report, May 2014: Activities and Findings

Overview

Combining the effects of low temperature, atmospheric pressure microplasmas and microplasma photon sources offers the promise of greatly expanding the range of applications for each of them. The plasma sources create active chemical species and these can be activated further by the addition of photons and the associated photochemistry. There are many ways to combine the effects of plasma chemistry and photochemistry, especially if there are multiple phases present. This project combines the construction of appropriate test experimental systems, various spectroscopic diagnostics and mathematical modeling.

Through a continuous discussion and co-design process with the UC-Berkeley Team, we have successfully completed the preparation of all components for a microplasma array-assisted system designed for the photon-activated plasma chemistry research. Microcavity plasma lamps capable of generating more than 20 mW/cm2 at 172 nm (Xe dimer) have been fabricated with a custom form factor to mate to the plasma chemistry setup, and a lamp is current being installed by the Berkeley team so as to investigate plasma chemistry-photon synergies at a higher photon energy (~7.2 eV) as compared to the UVA treatment that is afforded by UV LEDs operating at 365 nm. In particular, motivated by the promising results from the Berkeley team with UVA treatment, we have started to develop microplasma devices that can generate photons in the 300-370 nm wavelength range. Despite technical difficulties in the development, we all are highly motivated because these devices will have a high uniformity of irradiation on the surface of samples and are expected to be quite efficient in photon utilization for the treatment. We believe that a series of microplasma lighting sources operating in various wavelengths will create a synergy in the efficiency of the treatment, and furthermore, will enable the design of controlled environments for manipulating specific biochemical reactions at a target system.

Plasma Chemistry and Photon Synergies at the University of Illinois at Urbana-Champaign (UIUC)

The goal of the work being conducted at the University of Illinois (UIUC) under this DOE program is the investigation, under carefully-controlled conditions, of the synergistic interaction of photons and plasma-produced radicals with a surface. Toward this goal, during the past year, we have been in continuous discussions with the Berkeley team concerning the optimization of the treatment system. Figure 9 shows the current design for the VUV treatment system. One of the greatest challenges in the design was the efficient delivery of VUV photons into the target samples without significant loss. In particular, the VUV transmission at the liquid cell is very critical to the photon interaction that can explored. We had to redesign the specific reaction cell and it is constructed entirely from VUV compatible material (fused silica). To increase the treatment surface area, the diameter of the liquid cell was increased to ~19 mm and the vertical wall of the cell is also constructed with VUV transparent quartz. Figure 1 shows in cross-section the current design of the treatment system for plasma chemistry-VUV photon synergy experiments. At present, the UV emitting microplasma device and the atmospheric pressure plasma generator unit (top of Fig. 9) are being operated with separate power supply units in the same way as has been done previously with UVA LED treatment tests, but we expect that it can be operated with a single power supply to ignite both the plasma reactor and the microcavity arrays if the discharge operating points of both units are adjusted. This is an important property that not only is a benefit to the simplicity of the system operation, but allows us to operate the system in a synchronized manner so as to maximize the interaction of reactive species with UV photons in the sub-microsecond regime. Figure 10 is a photograph of the operation of a microcavity array which is connected to the newly-designed, VUV-compatible liquid reaction cell. The device is being operated in 500 Torr of a Xe/Ne gas mixture.

Another key research activity during the past year was the design and development of UV lamps in the UVB-UVA wavelength region (290-370 nm). The range matches that for the UVA experiments that were carried out by the Berkeley team. This device will provide more versatility and efficiency in the utilization of photons while interacting with target surfaces due to the flat, uniform nature of the microcavity plasma arrays. Also, because there are several emitter candidates available, we can simply tune the irradiation wavelengths through the selection of different gas mixtures. The only negative aspect of our current down conversion (phosphor-based) lamps is that the intensity of UV still remains to be improved, and we expect the range of intensity to be sub- to a few mW/cm2. During this research period, we have investigated a window materials other than quartz and have identified glass materials to be used. Also, the proper vacuum sealing method and materials have been investigated thoroughly, all of which consumed significant time and efforts on the trial of several sealing processes and optimization. Figure 11 shows a microcavity array fabricated in a functional glass substrate which transmits UVA-UVB photons efficiently, we should report that a successful hermetic seal was demonstrated recently. It is our intention to adopt several gas emitter candidates for this device structure so as to operate the lamp in different regions of the UV and measure the light output along with the corresponding optical spectra.

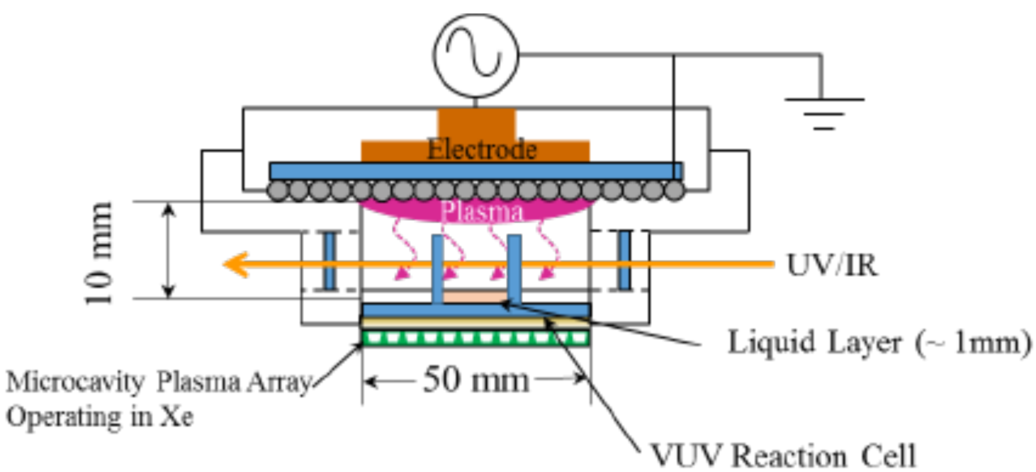


Fig. 9 Diagram of optimized design for the atmospheric pressure plasma reactor with VUV treatment system driven by a flat microcavity plasma device. Power connection into the array of microcavity plasma devices is not shown in this diagram.

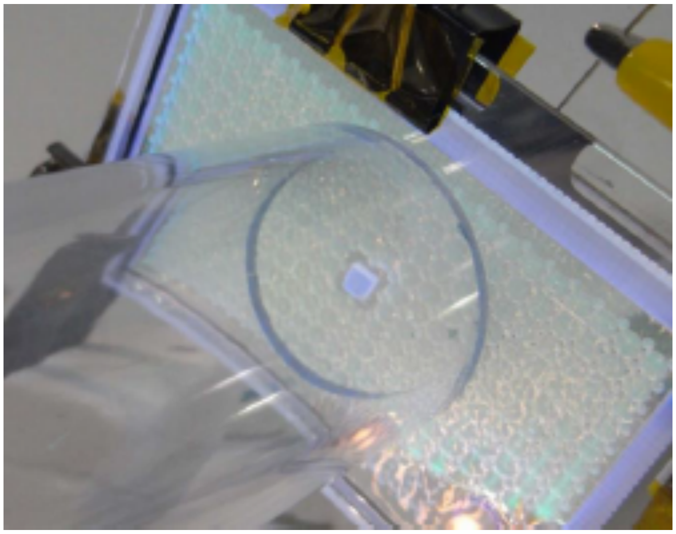


Fig. 10 A Photograph of a VUV transmission test in an ultraviolet-compatible cell designed with a microcavity array operated in Xe. The array of microcavity plasma devices was operated in a Xe/Ne mixture at a pressure of 500 Torr.

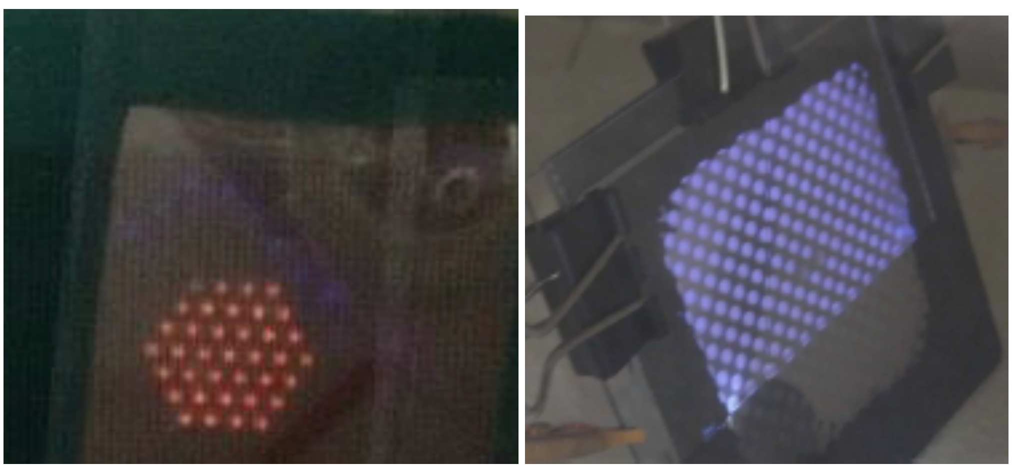


Fig. 11 Photographs showing the new microcavity structure fabricated on a functional glass which can transmit UVA-UVB photons. The left image shows the development work of the sealing methodology with new materials and demonstration of the hermetic seal in vacuum
(image shows the discharge in Ne). The right image shows the test of one molecular emitter for UVB region which emits photons in the range of 290-370 nm.

In summary, experiments conducted at UIUC have successfully demonstrated a series of lamp systems suitable for tests of the VUV photon-plasma chemistry synergy. With the optimized design, chemical analysis on the active species in the plasma and their interaction with VUV photons will be investigated. Furthermore, the Illinois group has developed and successfully demonstrated a new microcavity plasma structure that can generate uniformly distributed photons in the in UVB (and A) spectral region. Our next goal is to pursue, with the Berkeley team, the systematic study of the interaction of VUV or UV radiation with the plasma and various samples.

Emphasis will be placed on the alternation of the surface chemistry that can be realized with the addition of photons having energies in the $3.5 \lesssim \hbar\omega \lesssim 7.5$ eV range.

Plasma Chemistry and Photon Synergies at the University of California at Berkeley (UCB)

The initial goal of the second year of the project was to identify the synergistic mechanism through which UVA photons (365 nm) and air plasma treatment of aqueous solution inactivated suspended *E. coli* bacteria. The system schematic and previous results are shown in Figs 2 and 13 for clarity.

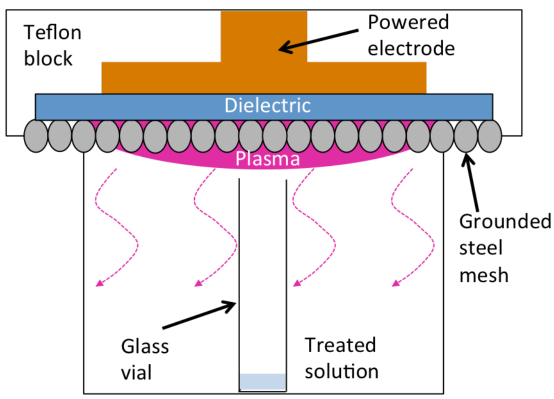


Figure 12. Schematic of the air DBD device with glass vial containing water and *E. coli*.

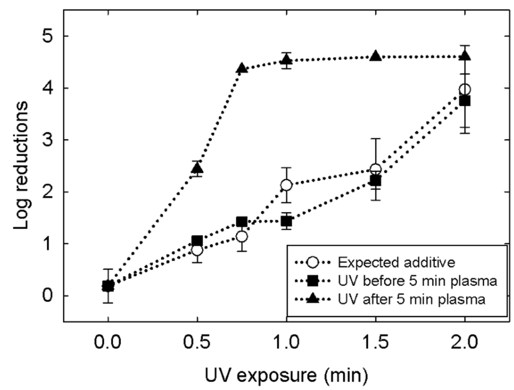


Figure 13. Plasma treatment in high-power mode, followed by UVA treatment, produces a stronger antimicrobial effect than would be expected by performing both treatments alone. In contrast, UVA treatment followed by plasma treatment shows no enhancement of the antimicrobial effect above the expected additive inactivation.

Of the species that are known to be created in high-power air plasma treatment of aqueous solution, nitrite (NO_2^-) was shown to influence the observed synergy the most. Nitrite is also known to absorb and photolyze in the UVA range to form NO and OH. These species are much more chemically and biologically active than nitrite. We also showed that the presence of hydrogen peroxide (H_2O_2) enhanced this synergy.

The proposed mechanism is diagramed and described in Fig. 14.

A second major focus of effort in the second year at UCB was the characterization of the antimicrobial effects of the SMD in air on dried bacteria at surfaces. The device is illustrated in Fig. 15. (Pavlovich et al., 2014) In the interests of brevity, the essential results from this first stage study are that the device operates either in an O_3-rich mode (low power) or NOx-rich mode (higher power). The NOx mode is more effective in inactivating dried bacteria on surfaces. This device will be used in the next stage by combining with UVA and UVC photons to test the effectiveness of gas phase photochemistry synergy with plasma chemistry.

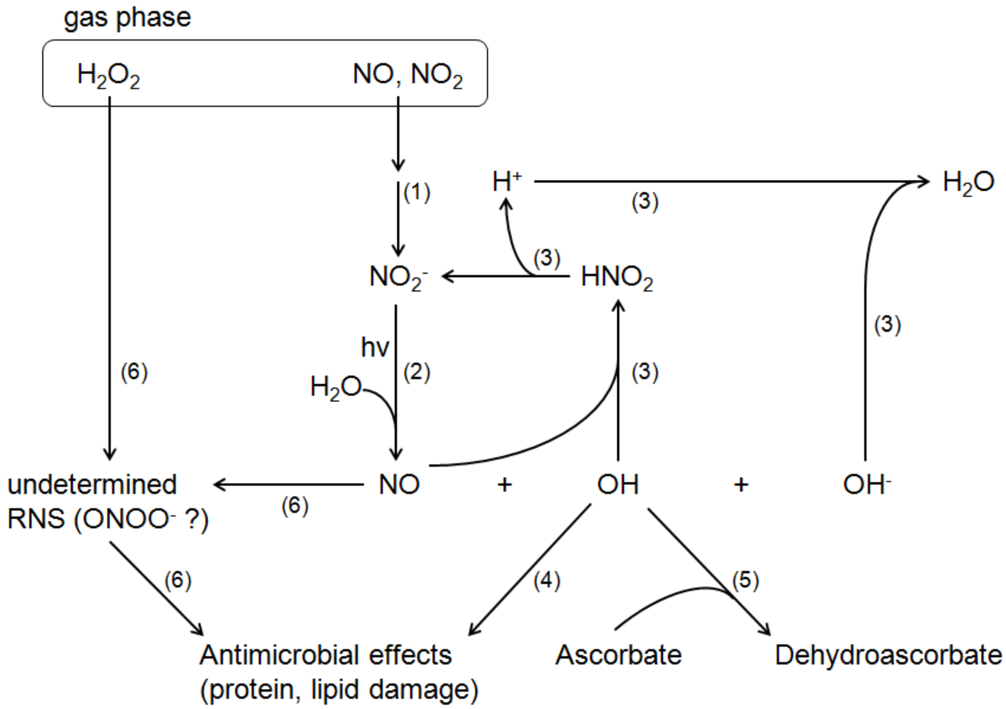


Figure 14. Summary of reaction pathways in the antimicrobial synergy between air plasma species and UVA photons. (1) Air plasma forms RONS including nitrogen dioxide (NO_2) and nitric oxide (NO). NO_2 and NO, through a series of reactions, dissolve in water and hydrolyze to yield nitrite (NO_2^-). (2) In aqueous solution, nitrite is photolyzed at 369 nm to yield nitric oxide (NO), hydroxyl (OH), and hydroxide (OH^-). (3) 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_2O). (4) In the presence of E. coli, OH damages biomolecules to inactivate the bacteria. (5) In the presence of both E. coli and ascorbate (a strong antioxidant), OH preferentially reacts with ascorbate, diminishing the antimicrobial effect. (6) Nitrite alone does not account for the full synergy between plasma and UVA, but the combination of nitrite and hydrogen peroxide (H_2O_2) does. Hydrogen peroxide is also produced in the plasma and dissolves into the aqueous phase, where it may react with NO to form another antimicrobial compound, probably peroxynitrite ($ONOO^-$).

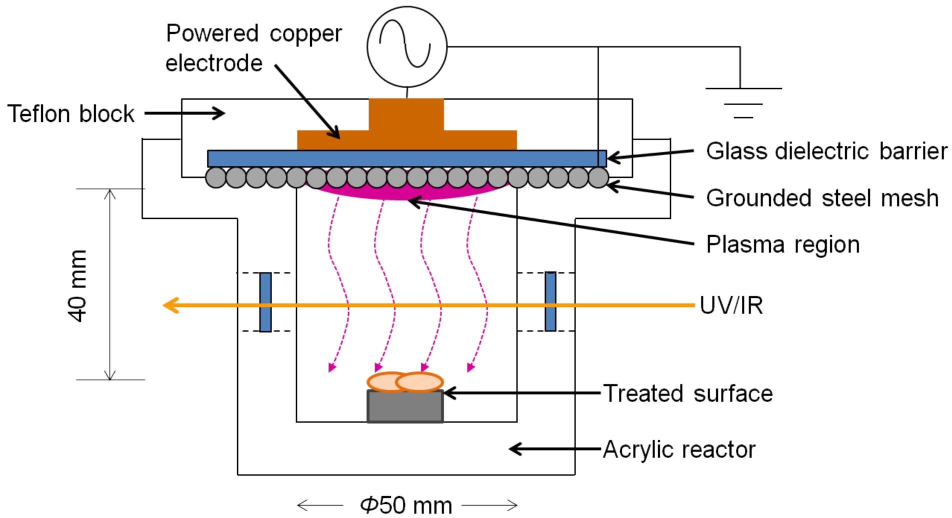


Figure 15. Schematic of the air DBD device with gas phase characterization by FTIR and UV absorption spectroscopy and simultaneous surface disinfection analysis. This system can be used to test the effects of photons on gas phase and/or surface chemistry

A third focus was exploration of two novel applications of the combination of UVA and air plasma chemistry. The first application involves the use of air plasma plus UVA photons to disinfect contact lens solution, lens material and lens cases. The initial work has involved building and characterizing an appropriate plasma source device enclosure. The device utilizes a similar surface

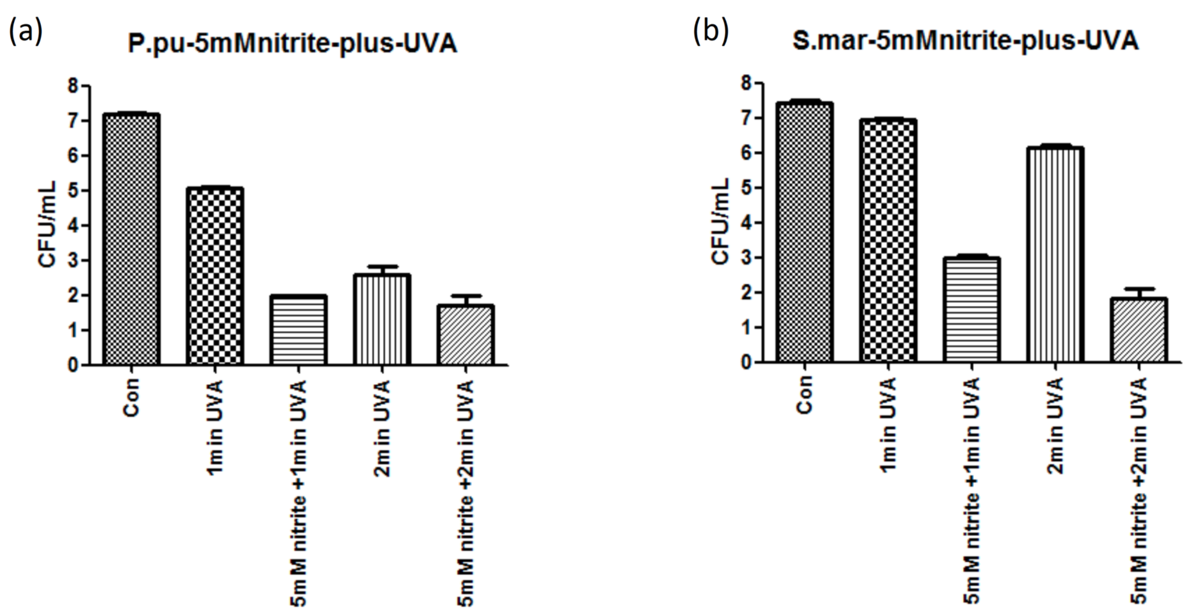


Figure 16. (a) Log reductions from control (Con ~ 7 logs initially) of Pseudomonas putida using UVA for 1 or 2 minutes, with or without added nitrite at 5 mM; (b) Analogous measurements using Serratia marcescens as target bacteria. The role of both UVA and nitrite can be seen in both cases. S. marcescens is known to be UV-resistant.

microdischarge design as the one illustrated in Fig.12. The gas– and liquid–phase compositions generated by the device have both been characterized. Preliminary antibacterial studies have been initiated by examining the effects of combining 5 mM nitrite in buffered (PBS) solution with bacteria and exposing this solution to UVA. The results from treating two additional strains (*Pseudomonas putida* and *Serratia marcescens*) are illustrated in Fig. 16.

The second application involves the treatment of infected toenails. Preliminary results have shown that plasma alone – either He/O_2 plasma jets or air DBD plasmas, will reduce bacterial contamination by between 1.5-2 logs on the backside of a several-mm thick bovine hoof nail simulant in about 20 minutes of exposure. The combination of UVA with the plasma is in its preliminary stages and will be reported in greater detail in the subsequent report.

Finally, a study of the photochemical effects of the microplasma UVC source provided by UIUC on atmospheric plasma systems has been initiated. UV photons can activate and photolyze species produced by the plasma; we can monitor photochemistry-induced alterations in the time-dependent evolution of species in adjacent gas and liquid phases using FT-IR and UV-Vis.

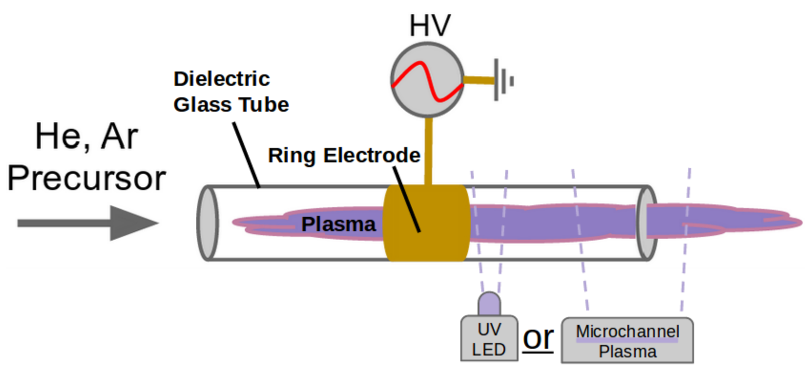


Figure 17. Schematic of the plasma jet device used for plasma-assisted polymer deposition and surface functionalization. UV photochemistry may assist in precursor fragmentation, altering the chemical and physical properties of the resulting polymer film.

Photons of appropriate wavelengths may also aid in intensifying and stabilizing an atmospheric pressure plasma by contributing photolysis products to the gas phase, and may assist in fragmenting the gas-phase polymer precursors used in plasma-assisted polymer deposition and surface functionalization. We are developing equipment for coupling photons from LED and microplasma photon sources into an atmospheric pressure plasma dielectric barrier jet–based polymer deposition system. Photochemical effects on the deposition process will be monitored by optical emission spectroscopy of the plasma, and the impact on the properties of the resulting polymer films will be evaluated using ATR-FTIR, SIMS, and other surface analytical techniques.

Year 3 Progress Report, May 2015: Activities and Findings

Plasma Chemistry and Photon Synergies at the University of California at Berkeley (UCB)

In the third year of the project, we continued to examine the effects of UVA on bovine hoof samples. A schematic of the experimental system is shown in Fig. 18. The bacteria preparation protocol used in these experiments is as follows: 100ul E.coli in LB broth was centrifuged and LB broth was removed. 10ul PBS or PBS with 5mM NO_2^- and 100uM H_2O_2 was added. Solution was shaken to re-suspend the bacteria solution. 10ul E.coli suspension was added onto one side of hoof disk and sprayed to a diameter of 5mm.

In these experiments, the hoof thickness was 0.2mm; the distance from UVA-LED: 1.1cm; the power density under hoof disk: 270~280mW; and the measured power density through hoof disk and bacteria suspension: 200~220mW.

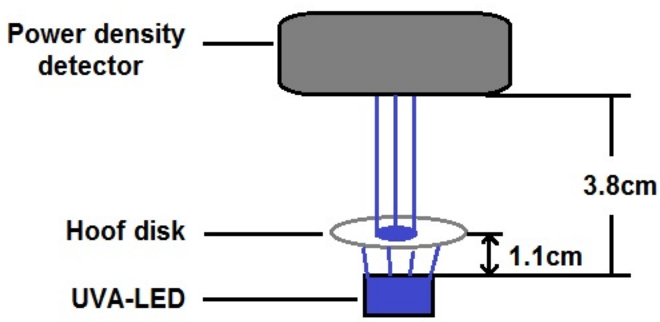


Fig. 18 Schematic of the experimental system testing the effects of UVA exposure on contaminated hoof disks.

The major result of the study is illustrated in the Fig. 19. There is a significant effect of the combination of nitrite and hydrogen peroxide with the UVA exposure, and this is shown in the Figure. However, if the power density is reduced and/or if the distance between the UVA LED and sample surface is increased, the effects are significantly reduced. We tested power densities below 100 mW and distances of over 2 cm, and the results were that the bacterial counts were not significantly reduced. We do not show those results here.

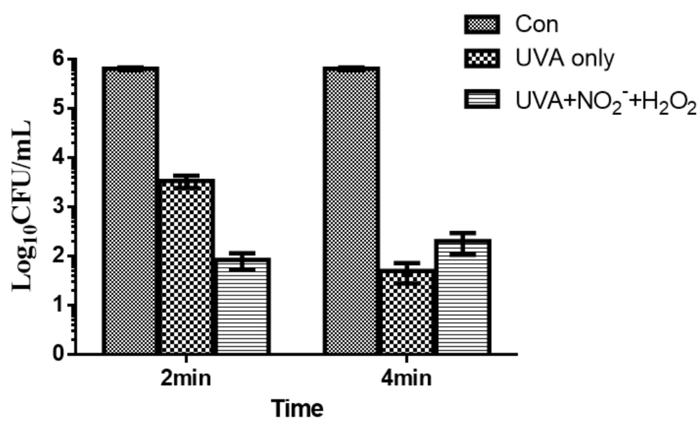


Fig. 19 Results from the study of the antimicrobial effects of using UVA alone and the combination of UVA with a solution of nitrite (NO_2^-) and hydrogen peroxide (H_2O_2). Exposure times of 2 minutes and 4 minutes are shown. There appears to be an effect of exposure time for the UVA only case, but less of an effect with the combined system.

Year 4 Progress Report, August 2016: Activities and Findings

Plasma Chemistry and Photon Synergies at the University of California at Berkeley (UCB)

In the final year of the project, we studied the effects of UVA on polymer contact lens samples. We used atmospheric pressure plasma and UVA radiation for disinfection of contact lens in this investigation. The combination of atmospheric pressure air surface micro-discharge operating in NOx mode with UVA (365nm) exposure shows remarkable increased anti-bacteria effect (another 3~4.5 log reduction comparing to UVA exposure) against 4 kinds of testing bacterium involved in eye infection caused by wearing contact lens and shows no selectivity on bacteria strains, such as gram positive or negative, UVA resistant or drug resistant, etc. Material properties of 4 commercial brands of contact lens after treatment including Young's modulus, water contact angle, surface morphology, and UV transparency, are nearly the same comparing to the control group, which demonstrates that this method would not bring any damage to the lens material. The mechanism of the synergic effect of this atmospheric pressure plasma and UVA radiation is mainly proved to be the photodecomposition of nitrite by UVA exposure, and partly by peroxynitrite formation through reaction between NO and H_2O_2 in neutral buffered solution.

The four bacterial strains studied here were: Pseudomonas putida (ATCC 12633); Serratia marcescens (ATCC 13880); Staphylococcus epidermidis (ATCC 35984); and Staphylococcus warneri (ATCC 27836).

This research provides an alternative faster, easy operating and more efficient method for contact lens disinfection, and seems promising for the future commercial use. Further works are remaining to do such as: the efficacy on fungi and Acanthamoeba; the impact of treatment on lens case biofilm build-up, the cytoxicity/ biocompatility of treated fluid and lenses, etc.

The experimental setup is sketched in Fig. 20.

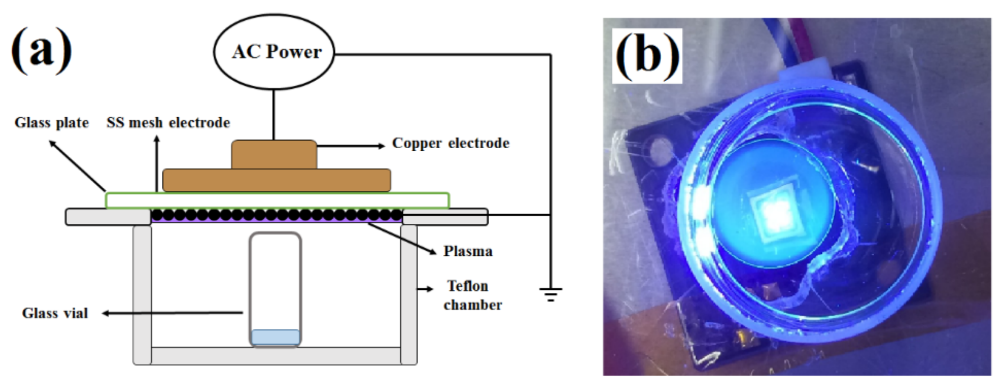


Fig.20 Experimental set-up of the UVA-plasma exposure study. (a) Sketch of SMD treatment; (b) Photograph of UVA exposure of contact lens in PBS Through the bottom of a glass contact lens case.

Figure 21 illustrates the major results of the study: the combination of plasma plus UVA is a promising method to disinfect contact lens material with minimal if any material damage.

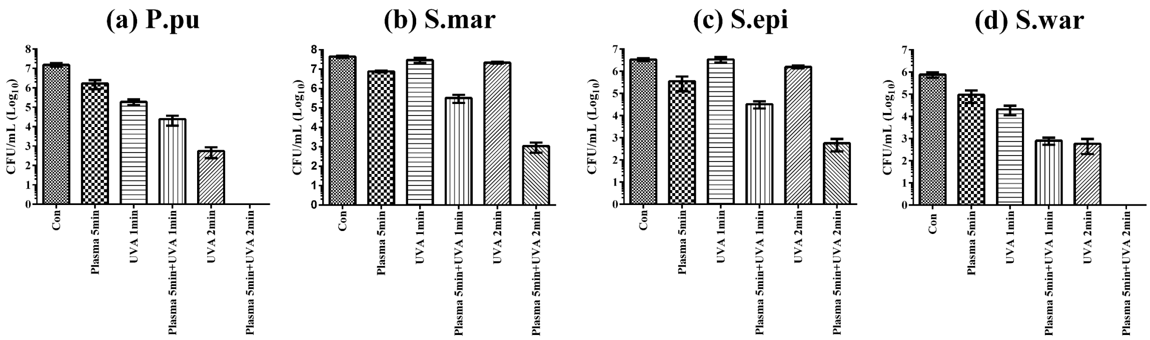


Fig. 21 Anti- bacterial effect comparison of 5 min plasma treatment, UVA-LED treatment and 5 min plasma plus UVA-LED treatment for the tested bacterium. (a) Pseudomonas putida; (b) Serratia marcescens; (c) Staphylococcus epidermidis; (d) Staphylococcus warneri. These results show the effectiveness of combining the plasma + UVA exposure for the different bacterial strains.

UC Berkeley Publications:

[1] Y. Sakiyama et al., Plasma chemistry model of surface microdischarge in humid air and dynamics of reactive neutral species, Journal of Physics D: Applied Physics, 45(42), article no. 425201, 2012.

[2] Y. Sakiyama and D.B. Graves, Efficient modeling of atmospheric pressure surface micro-discharge plasma chemistry, Plasma Sources Science Technology, 22, 012003, 2013.

[3] M.J. Pavlovich et al., Ozone correlates with antibacterial effects from indirect air dielectric barrier discharge treatment of water, Journal of Physics D: Applied Physics, 46, 145202, 2013.

[4] M.J. Pavlovich, Y. Sakiyama, D.S. Clark, and D.B. Graves, Antimicrobial Synergy Between Ambient-Gas Plasma and UVA Treatment of Aqueous Solution, Plasma Processes and Polymers, 10, 1051-1060, 2013.

[5] Z. Xiong et al., Anti-bacteria effect by UVA and UVA plus NO2-/H2O2 through hoof disk, in preparation, 2017.

[6] Z. Xiong et al., Synergetic effects of atmospheric pressure plasma and UVA treatment for contact lens disinfection, in preparation, 2017.

Broader Impacts.

The central contribution of the work in this project has been to establish the clear promise of synergistic effects obtained by combining low temperature, atmospheric pressure microplasmas and microplasma photon sources to generate chemical species useful for disinfection applications as well as other biological applications. Plasma sources create active chemical species and these can be activated further by addition of photons and associated photochemistry. There are many ways to combine the effects of plasma chemistry and photochemistry, especially if there are multiple phases present. The project combined construction of appropriate test experimental systems, various spectroscopic diagnostics and mathematical modeling.

The successful application of the techniques to a variety of different areas demonstrates the versatility of the idea. We showed that bacteria in aqueous solution could be effectively killed using this approach. In addition, bacteria and fungus can be effectively killed on and through bovine hoof (a model for human nail). Finally, the techniques was shown to be effective in killing four different types of bacteria on various commercial polymers used for contact lenses.

This project contributed to the **graduate education** of two UC Berkeley PhD students, both now graduated, and several postdoctoral scholars. Matt Pavlovich (UCB) and Carly Anderson (UCB) graduated in 2014 and 2016, respectively, from UC Berkeley with a PhD. Research Associate Dr. Yuki Sakiyama worked on this project in its first several years. Also contributing were Dr. Zilan Xiong, a postdoctoral scholar who is currently a visiting scholar at UC Berkeley, and Dr. X. Pei, another visiting scholar from China.

Additionally, several undergraduate students were involved on a continuous basis in this project.