Supporting Information for

"Aerosol Microdroplets Exhibit a Stable pH Gradient"

Haoran Wei,[a,b,c] Eric Vejerano,[a,b,c,d] Weinan Leng,[a,b,c] Qishen Huang,[a,b,c] Marjorie R. Willner,[a,b,c] Linsey C. Marr,[a,b,c] Peter J. Vikesland[a,b,c,1]

[a] Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia;

[b] Virginia Tech Institute of Critical Technology and Applied Science (ICTAS) Sustainable Nanotechnology Center (VTSuN), Blacksburg, Virginia;

[c] Center for the Environmental Implications of Nanotechnology (CEINT), Duke University, Durham, North Carolina;

[d] Arnold School of Public Health, University of South Carolina, Columbia, South Carolina.

[1] Corresponding author, email: pvikes@vt.edu

Materials and Methods

Materials. 4-Mercaptobenzoic acid (4-MBA), 4-aminothiophenol (4-ATP), sodium citrate tribasic dehydrate ($Na_3Citrate{\cdot}2H_2O$), gold chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), polyvinylphenol (PVP, molecular weight 10000) and 1 M phosphate buffer (PB, $C_T=[H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}]=1M$) were purchased from Sigma-Aldrich. The range of buffer capacities (β) of 1M PB solution is 0.013-0.58 for the pH range 7.2 – 12.3, which is calculated based on Equation S1 ($\alpha_0=[H_3PO_4]/C_T$, $\alpha_1=[H_2PO_4^-]/C_T$, $\alpha_2=[HPO_4^{2-}]/C_T$, $\alpha_3=[PO_4^{3-}]/C_T$). Thiolated poly(ethylene) glycol (HS-PEG, 5kDa) was purchased from Nanocs. AEROSIL®R202 (fumed silica treated with polydimethylsiloxane, average particle size: 14 nm) was purchased from Evonik Industries. Polyvinylidene fluoride (PVDF) membrane filters (0.22 μm pore size, 13 mm in diameter) and polytetrafluoroethylene (PTFE) membrane filters (0.1 μm pore size, 13 mm in diameter) were purchased from EMD Millipore.

$$\beta = 2.303([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2+C_T\alpha_2\alpha_3) \qquad \text{Equation S1}$$

pH Nanoprobe Synthesis. The synthesis of the SERS pH nanoprobes was described previously.(42) Briefly, 500 μL 4-MBA ethanol solution (100 μM) was added to 500 μL AuNP suspension (5×10^{10} NPs/mL). Following vortex mixing, the mixture was kept at room temperature for 120 min and subsequently, 100 μL HS-PEG solution (500 μM) was added to the mixture. The mixture was washed by DI water three times by centrifugation. 4-ATP-coated AuNPs were synthesized by adding 10 μL 4-ATP in ethanol (1 mM) into 500 μL AuNP suspension followed by 1 min vortex mixing. PVP-coated nanoprobes were synthesized as the following procedure: 500 μL of AuNP suspension and 500 μL of 100 μM 4-MBA ethanol solution are mixed together in a centrifuge tube and vortex for 1 min. After 30 min reaction at room temperature, 100 μL of

500 mM PVP aqueous solution was added. After 1 h reaction at room temperature, the mixture was washed by centrifugation using the same procedure as the PEG-coated probes.(42)

Generation and Collection of Aerosol Droplets. The method to generate and collect aerosol droplets is illustrated in Fig. 1A. In these experiments, 2 mL of probe suspension was added to 3 mL of 1 M PB solution followed by gentle mixing. Aerosol droplets were generated by aerosolizing this suspension with a commercial atomizer (TSI 3076, TSI Inc.) that was contained in a custom chamber designed to maintain relative humidity near 100% (Fig. S20). Aerosolized droplets were collected on a superhydrophobic filter placed ~1 cm away from the atomizer outlet. The superhydrophobic filter was produced by drop coating 100 µL of AEROSIL in acetone suspension (4 g/L) onto a PVDF filter that was then air dried. Once the aerosolized droplets were collected, the superhydrophobic filter was sealed in a flow cell that was connected to an automatic humidity controller (Fig. S21) that maintained relative humidity at 97.5%. The flow cell was then placed on the sample stage of the Raman spectrometer for analysis.

Instrumentation. Single aerosol droplets were scanned by a confocal Raman microscope using a 50× objective (WITec Alpha 500R) and a 785 nm laser. Laser spot size limits the spatial resolution of the SERS measurements. In this study, the lateral size of the laser spot was 0.68 µm, the axial size of the laser spot is 3.2 µm, and the excitation volume was 1.5 μm^3. Raman scanning was enabled by a motorized scanning table with a lateral (*X*-*Y*) travel range of 150 × 100 mm and depth (*Z*) travel range of 30 mm with a minimum step size of 0.01 µm. Each collected SERS map consists of 20 × 20 pixels and corresponds to a square area slightly larger than the droplet size. Each pixel represents a single Raman spectrum collected with an integration time of 0.1 s. Bulk solution (0.6 mL) spectra were collected using a sealed quartz cell (Starna Cells Inc.). The laser was focused 200 µm below the lid and Raman scans were collected using the same parameters as for the droplets.

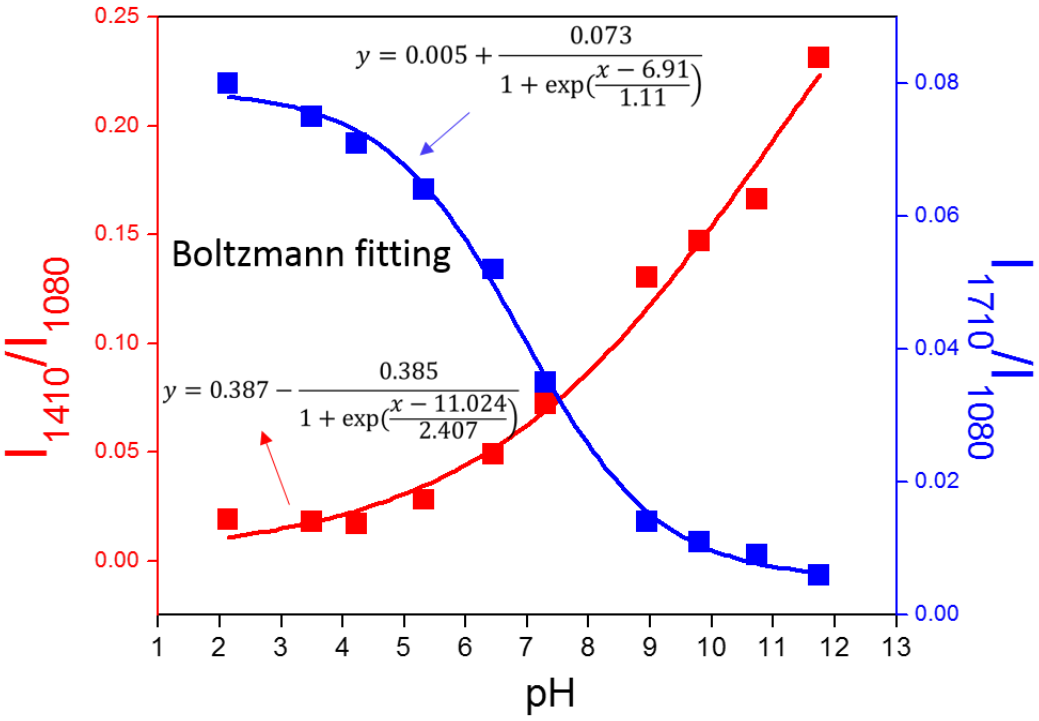

Figure S1. pH calibration curves constructed by fitting the variation of ratios I_{1410}/I_{1080} and I_{1710}/I_{1080} as a function of solution pH and then fit using the Boltzmann equation.

The Boltzmann equation as defined below has previously been applied to fit sigmoid shaped pH curves[1]:

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0)/dx}} + A_2$$

where A_1 and A_2 are low and high Y limit, respectively; x_0 is the half amplitude point and dx is the width.

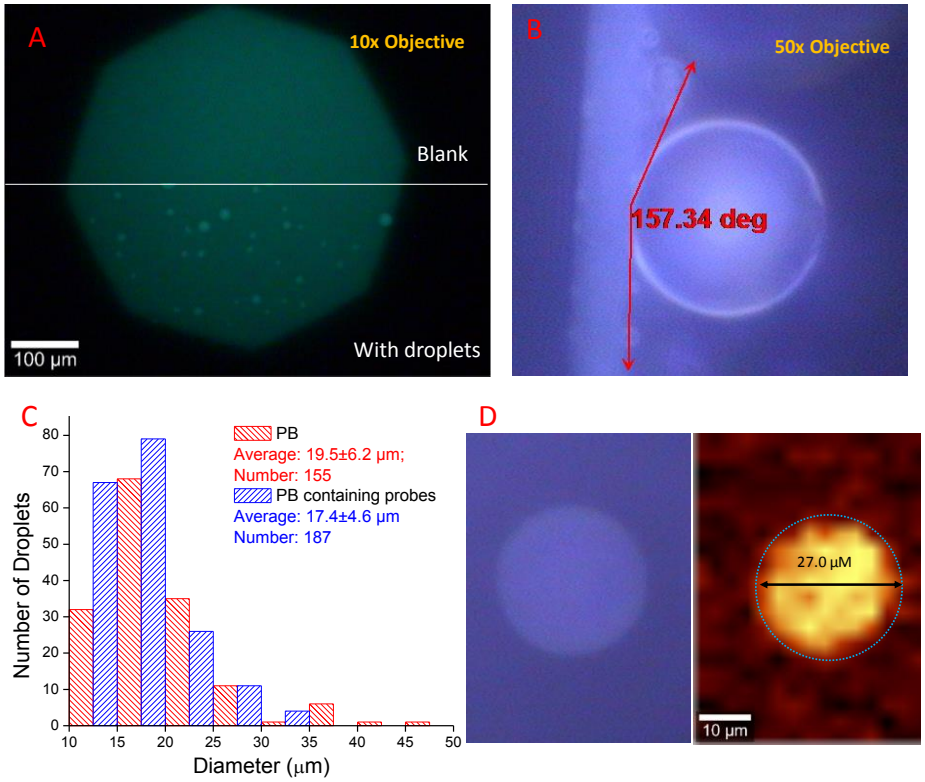

Figure S2. Generation, collection, and Raman scan of the aerosol droplets. A) Optical images of a blank superhydrophobic polyvinylidene difluoride (PVDF) filter (top) and aerosol droplets collected on a superhydrophobic PVDF filter (bottom); B) The optical image of the side view of a droplet that was used to measure contact angle; C) Distribution of droplet diameters for droplets generated from 1 M PB solution and 0.6 M PB solution + pH nanoprobes; D) Optical image and Raman map of a droplet generated from 1 M PB solution constructed by tracking the Raman band at 998 cm^{-1}.

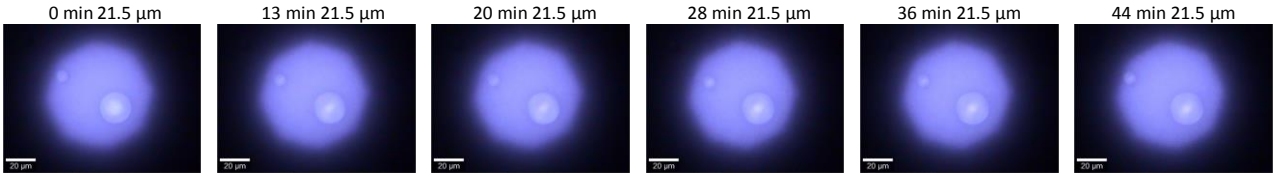

Figure S3. Optical images of one microdroplet taken at different time under well controlled RH of 97%.

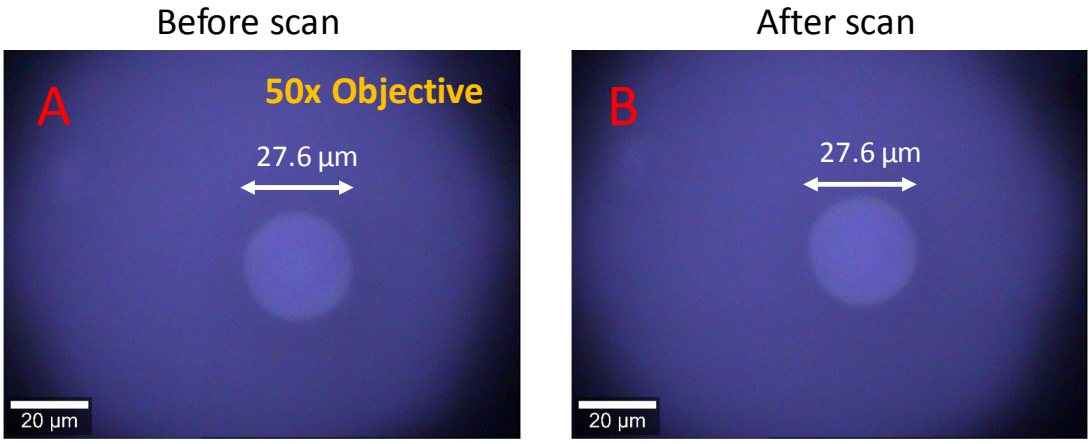

Figure S4. Optical images of one aerosol droplet under 50x objective (A) before and (B) after laser interrogation.

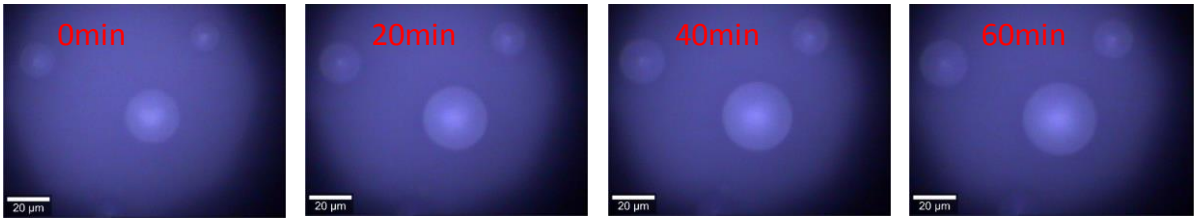

Figure S5. Optical images of one microdroplet taken at different time under oversaturated RH caused by the presence of a wet paper towel in the cell.

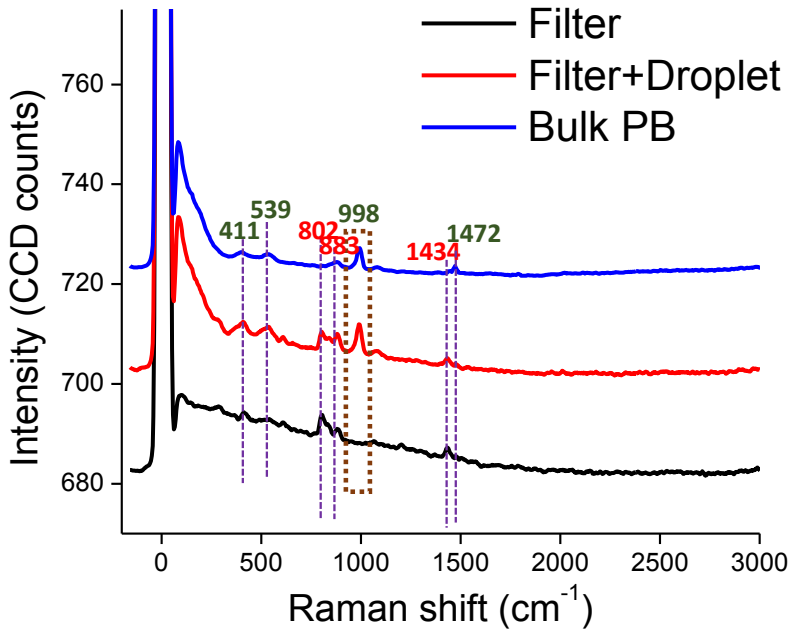

Figure S6. Raman spectra of 1M bulk PB solution, superhydrophobic PVDF filter, and 1M PB aerosol droplet on a superhydrophobic PVDF filter.

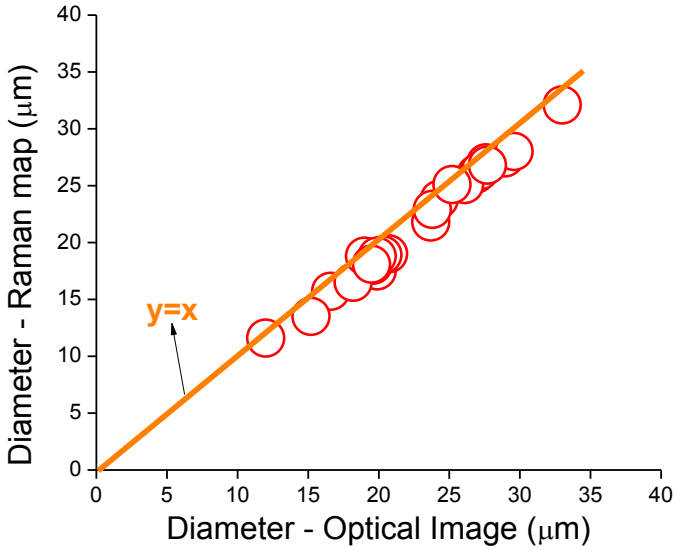

Figure S7. Relationship between droplet diameter as measured using Raman maps and optical images.

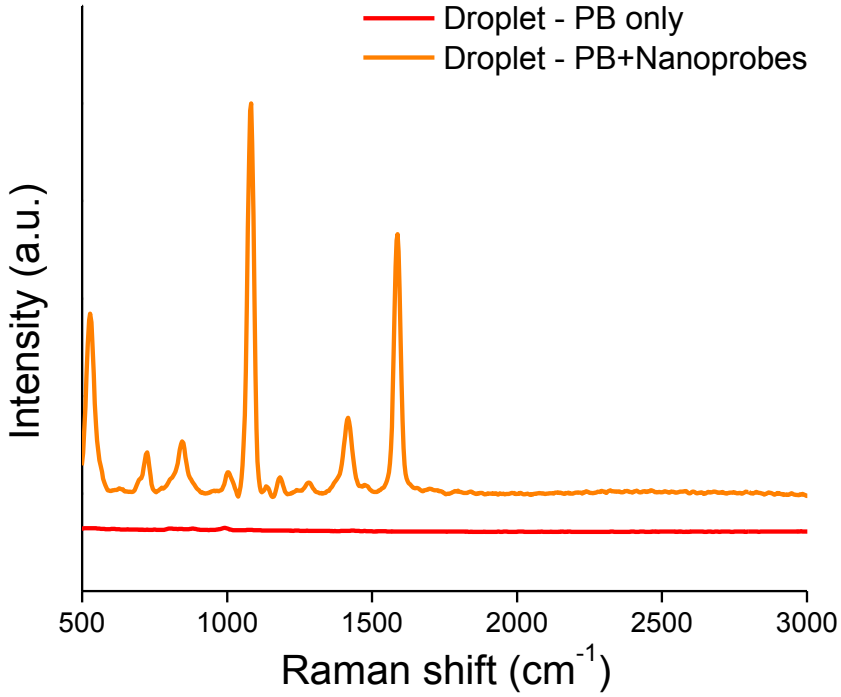

Figure S8. Raman spectra collected from aerosol droplets containing only 1 M PB and 0.6 M PB + nanoprobes.

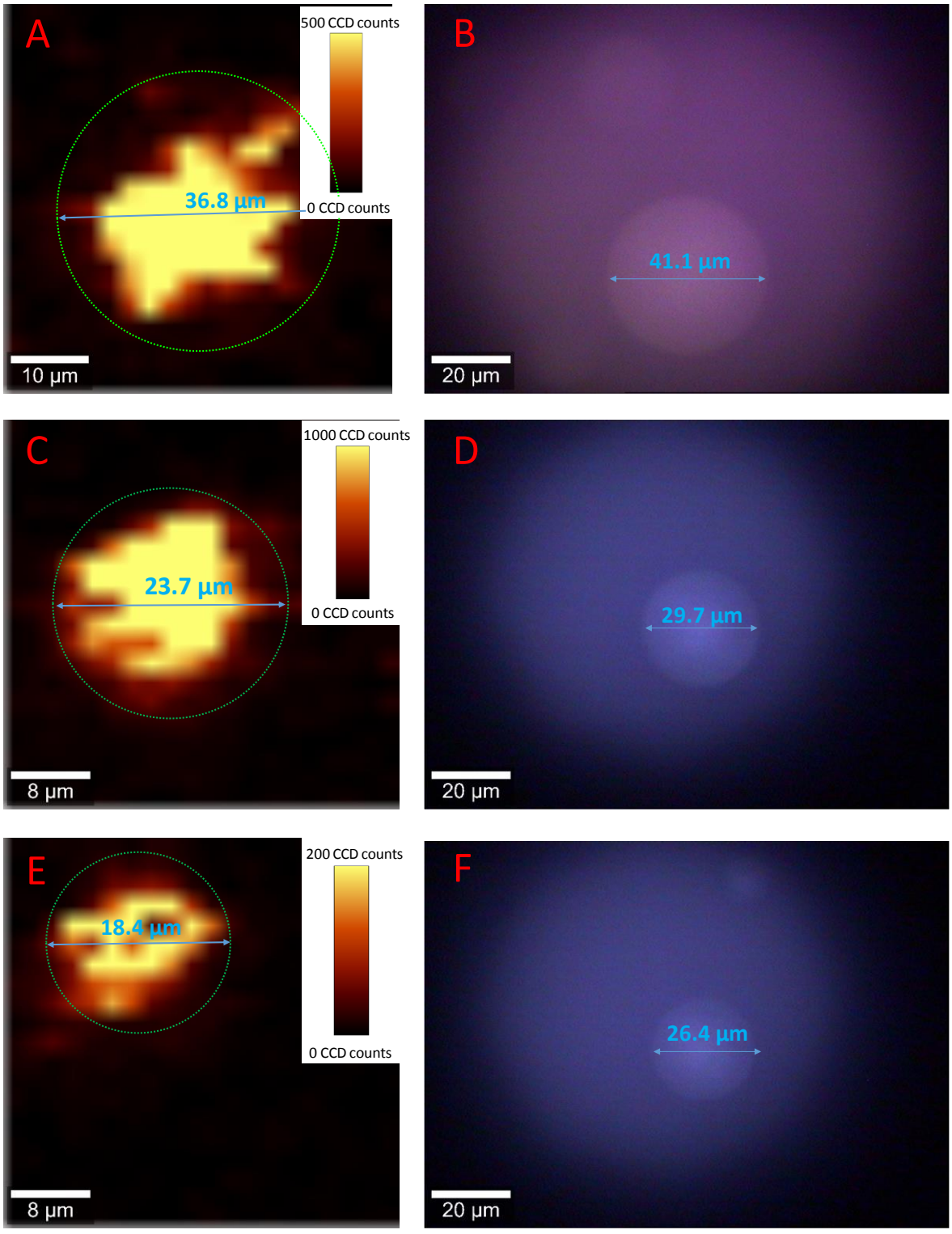

Figure S9. A, C, E) SERS maps tracking 4-MBA band at 1080 cm^{-1} of three droplets; B, D, F) Optical images of the three droplets.

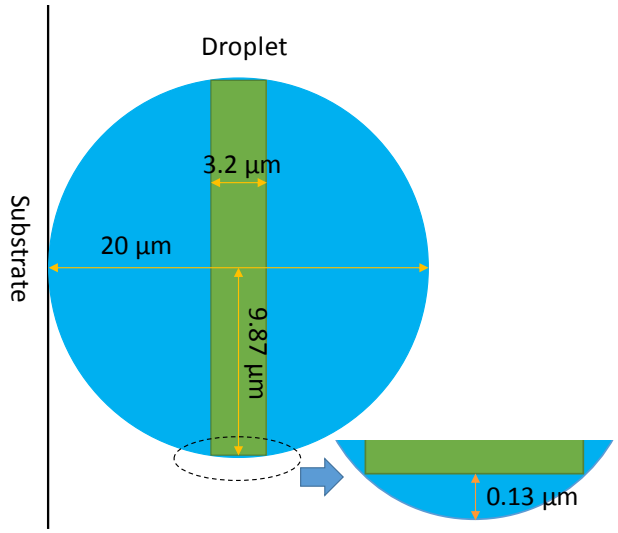

Figure S10. Schematic of the laser excited volume of a 20-µm droplet when collecting a 2D SERS map.

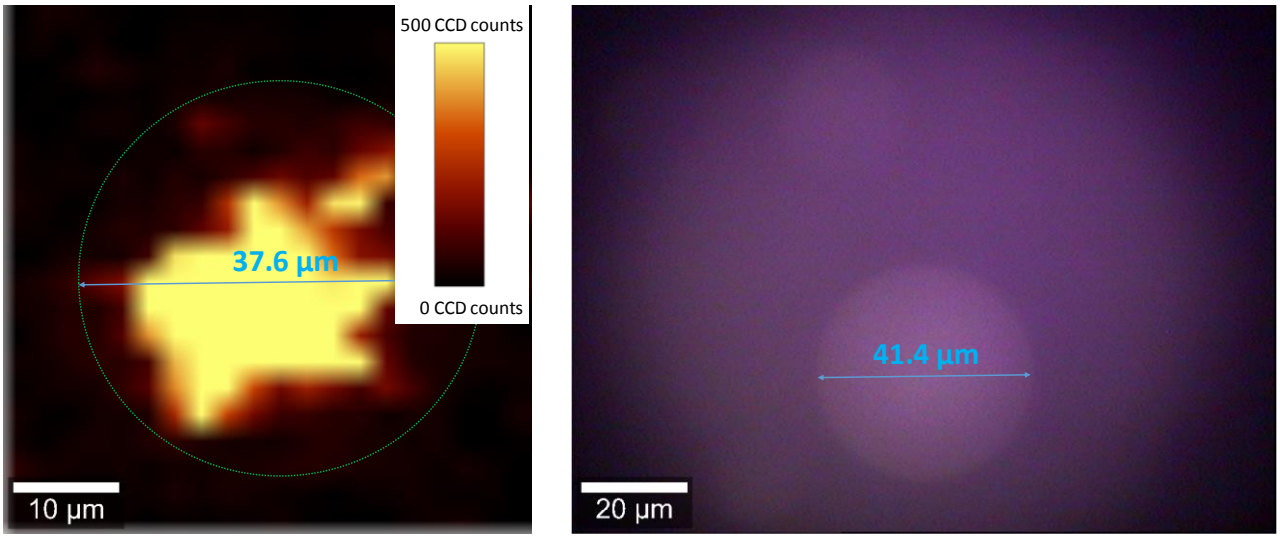

Figure S11. SERS map and optical image of a droplet containing PVP-coated pH nanoprobes.

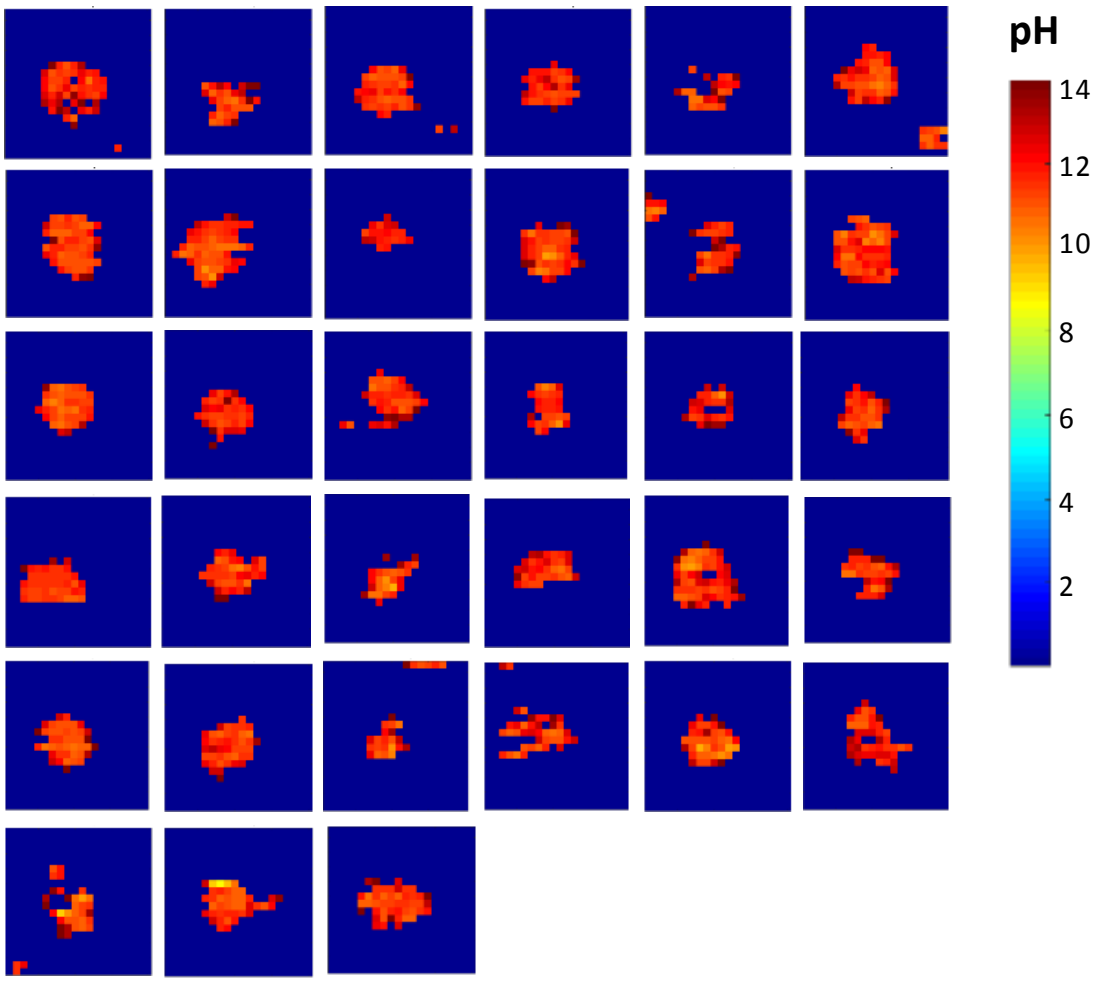

Figure S12. pH maps of 33 droplets containing 0.6 M PB and pH nanoprobes. Each map contains 400 pixels in a 50 × 50 μm^2 area.

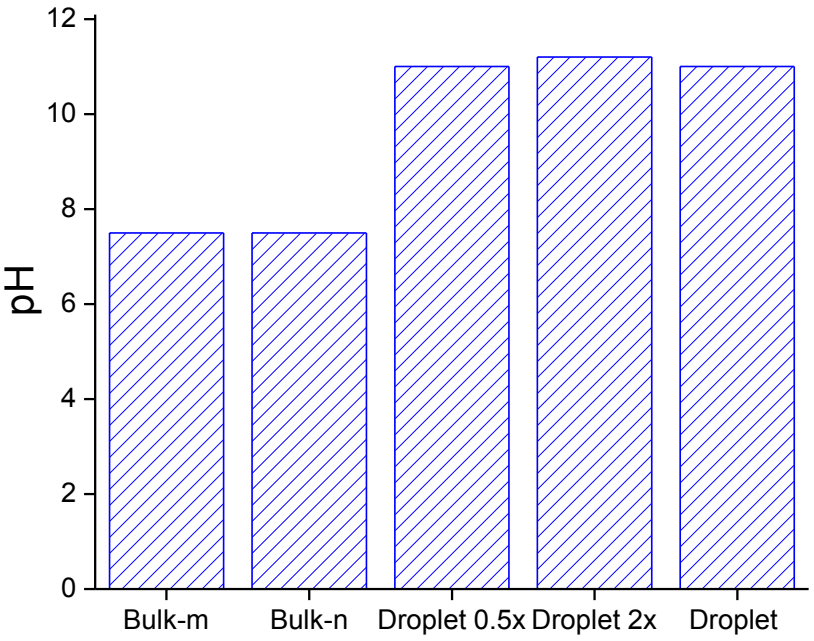

Figure S13. pH values at the centroid of droplets containing 0.5× and 2× the normal probe concentration. Bulk-m: bulk solution pH measured using a commercial pH meter; Bulk-n: bulk solution pH measured using pH nanoprobes; Droplet 0.5×: droplet containing half probe concentration; Droplet 2×: droplet containing twice probe concentration.

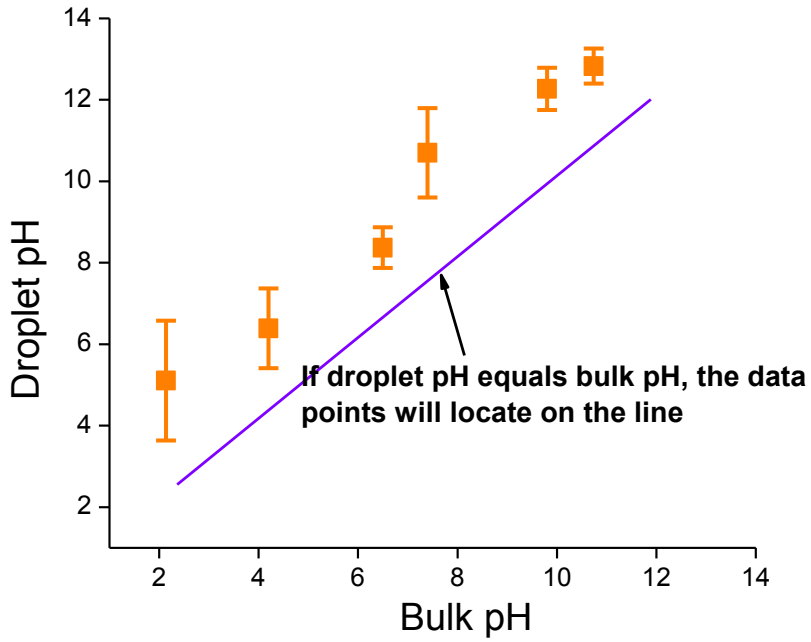

Figure S14. pH of droplets (supported on a superhydrophobic substrate in a petri dish, but without RH control) generated from bulk solution with different initial pH.

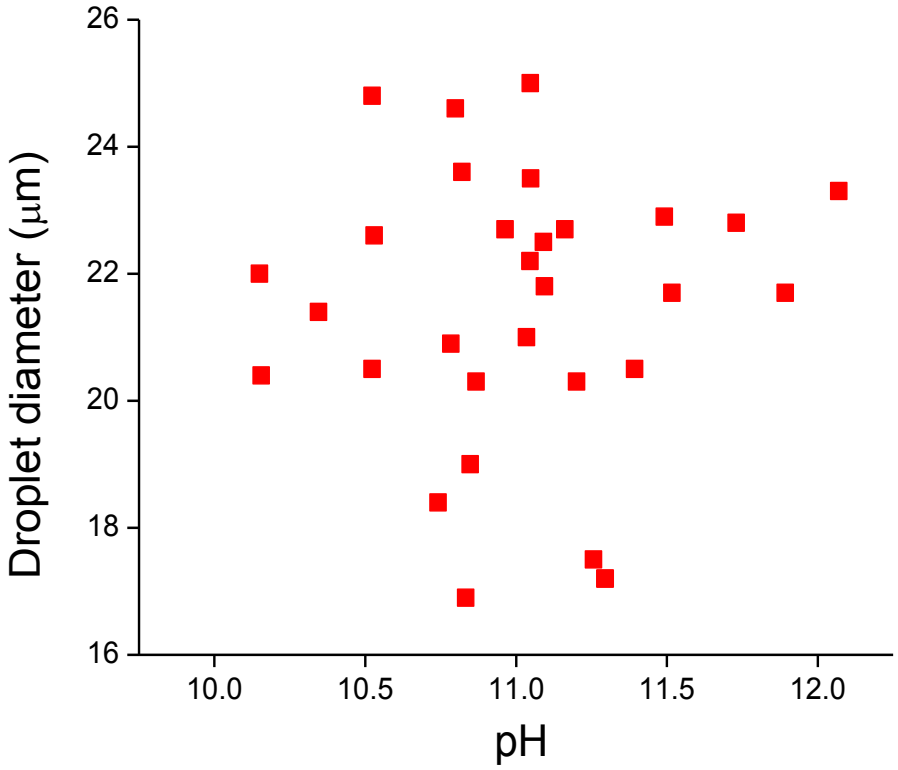

Figure S15. pH values at the centroid of 31 droplets as a function of droplet diameter.

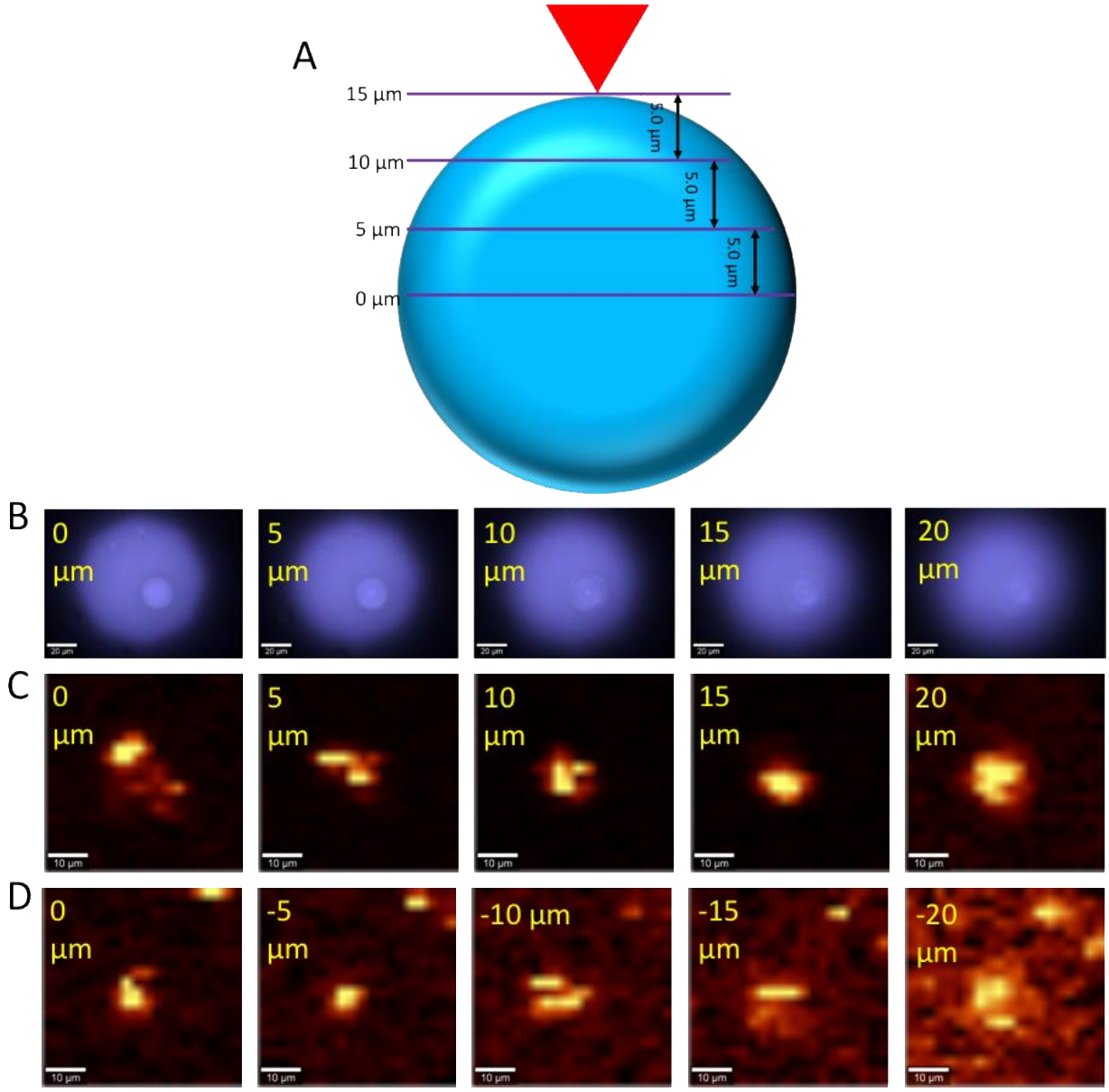

Figure S16. 3D characterization of the pH inside aerosol droplets. A) Schematic of the 3D scan of the droplet. B) Optical images of droplets containing nanoprobes collected by focusing the light beam at different Z above the middle (0 µm); C) SERS maps of droplets containing nanoprobes collected by focusing the laser beam at different Z above the middle (0 µm); D) SERS maps of droplets containing nanoprobes collected by focusing the laser beam at different Z below the middle (0 µm);

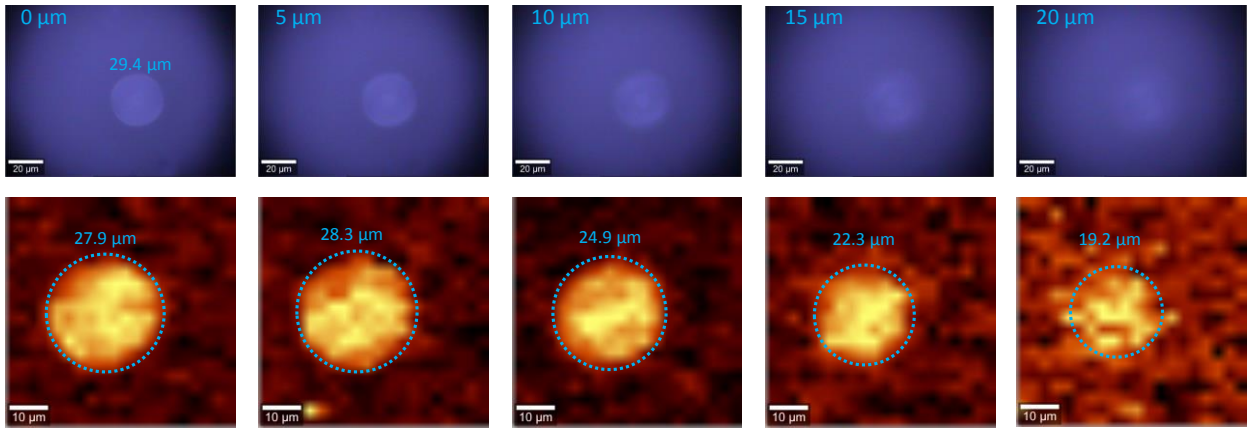

Figure S17. Variation in the optical images and SERS maps (tracking 998 cm^{-1}) collected from a droplet generated from 1M PB solution as a function of Z (0 µm = droplet centroid, 20 µm = top of droplet).

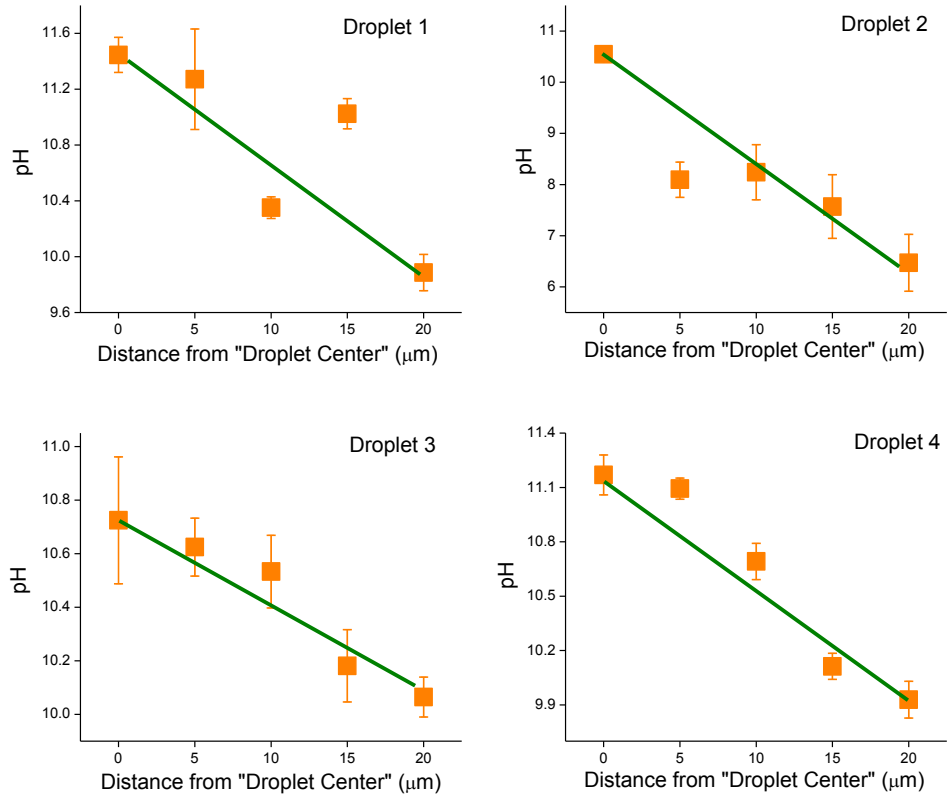

Figure S18. Variation of pH at the centroid of Raman maps as the objective is moved upward (Each data point is the average of four pixels within a 5 × 5 $µm^2$ area at the droplet center with the error bars reflecting the standard deviation of the four pixels).

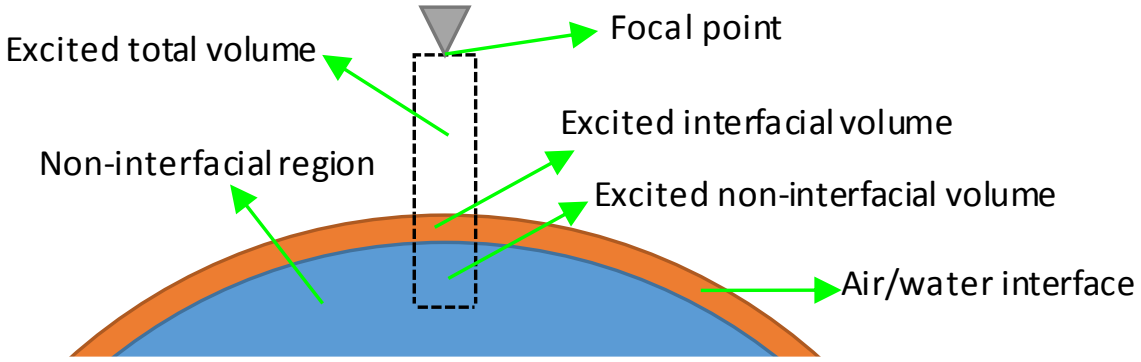

Figure S19. Schematic for the laser excited interfacial/non-interfacial volume when the focal point is above the top of the droplet.

Figure S20. Photo of the commercial atomizer contained in a homemade humidity chamber.

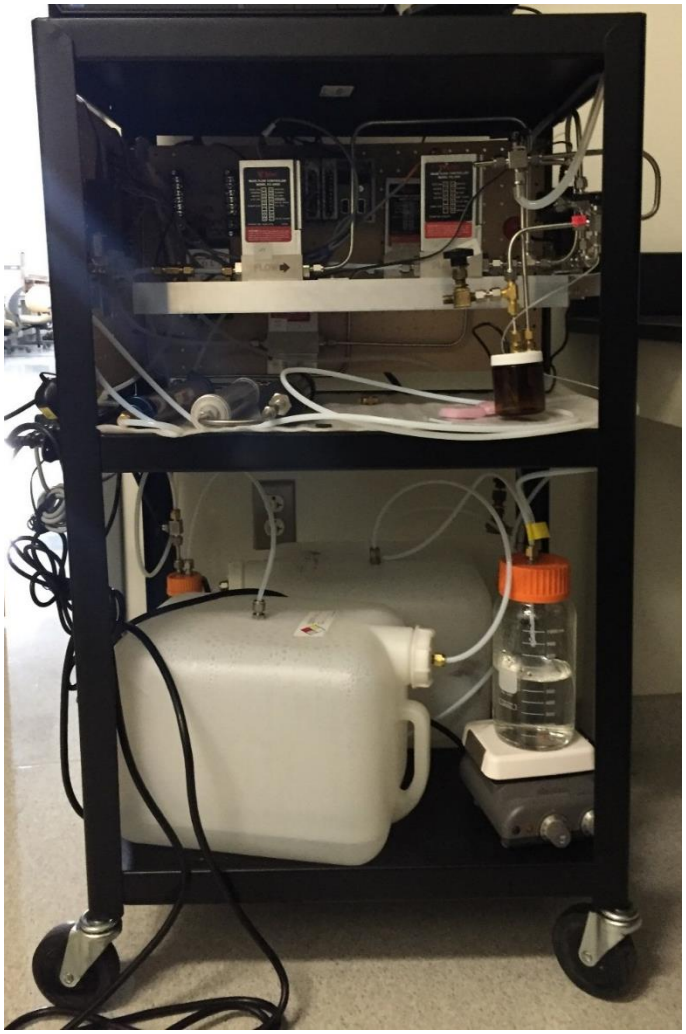

Figure S21. Photo of the homemade humidity controller.

Reference

1. Jamieson, L. E.; Jaworska, A.; Jiang, J.; Baranska, M.; Harrison, D.; Campbell, C., Simultaneous intracellular redox potential and pH measurements in live cells using SERS nanosensors. *Analyst* **2015,** *140*, (7), 2330-2335.