

Supporting Information for

**"Highly Stable SERS pH Nanoprobes Produced by Co-Solvent
Controlled AuNP Aggregation"**

Haoran Wei, Marjorie R. Willner, Linsey C. Marr, and Peter J. Vikesland*

Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA, USA.

Institute for Critical Technology and Applied Science (ICTAS) Center for Sustainable
Nanotechnology (VTSuN), Virginia Tech, Blacksburg, VA, USA.

NSF-EPA Center for the Environmental Implications of Nanotechnology (CEINT).

*Corresponding author E-mail: pvikes@vt.edu; 540-231-3568; Fax: 540-231-791

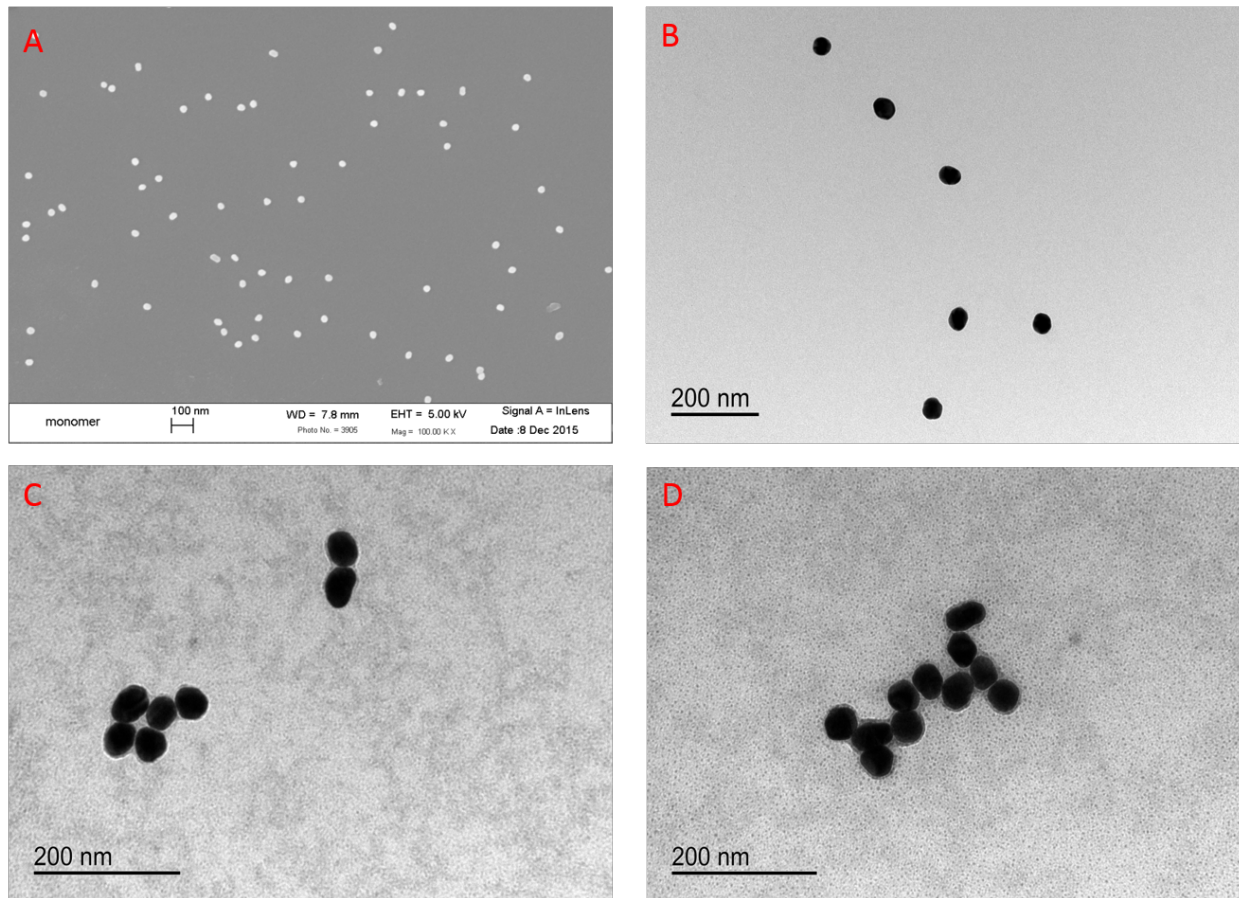


Figure S1 A) Scanning electron microscopy image of the pristine AuNPs spin coated on a silicon wafer; Transmission electron microscopy images of pristine AuNP monomer (B), and PEG-coated AuNP aggregates (C&D).

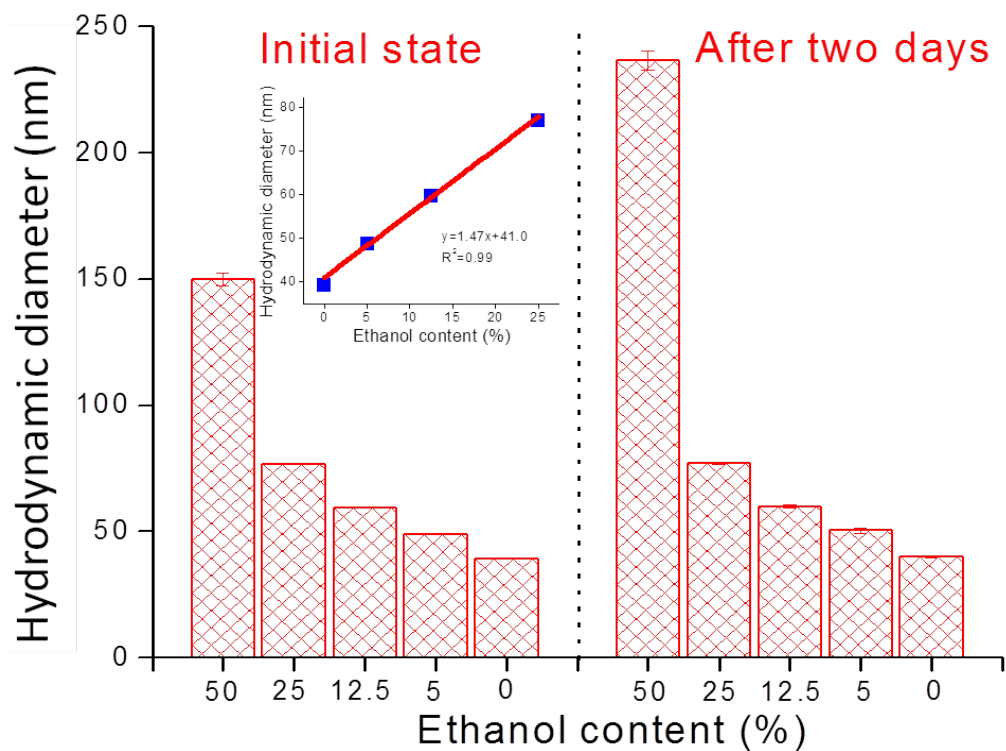


Figure S2 Size of AuNPs dispersed in water/ethanol mixture with different ethanol content; Inset figure shows the linear relationship between AuNP size and the ethanol content when it is below 25%.

AuNPs dispersed in a series of water:ethanol mixture with ethanol contents from 0-50% were prepared. When the ethanol content was below 25%, AuNP size increased linearly with ethanol content and remained constant after two days (Fig. S-1), thus indicating mild and stable aggregation occurred. These mild aggregations cannot generate enough "hot spots" for SERS applications (data not shown).

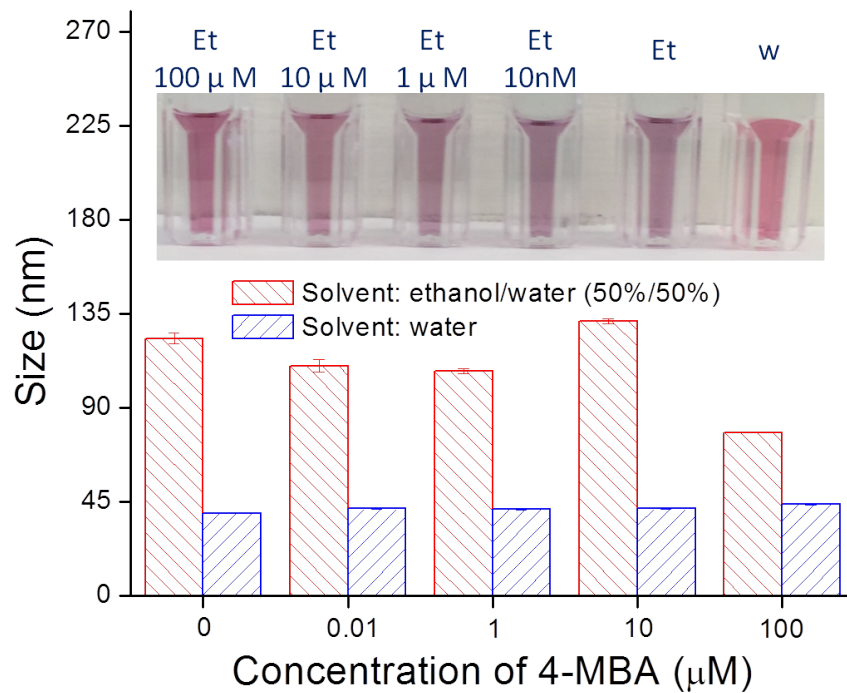


Figure S3 Size of 4-MBA coated AuNPs in water and water:ethanol co-solvent with different 4-MBA concentrations; Insets are photos of MBA coated AuNPs in water and water:ethanol co-solvent with different 4-MBA. All the results are at time = 0 h.

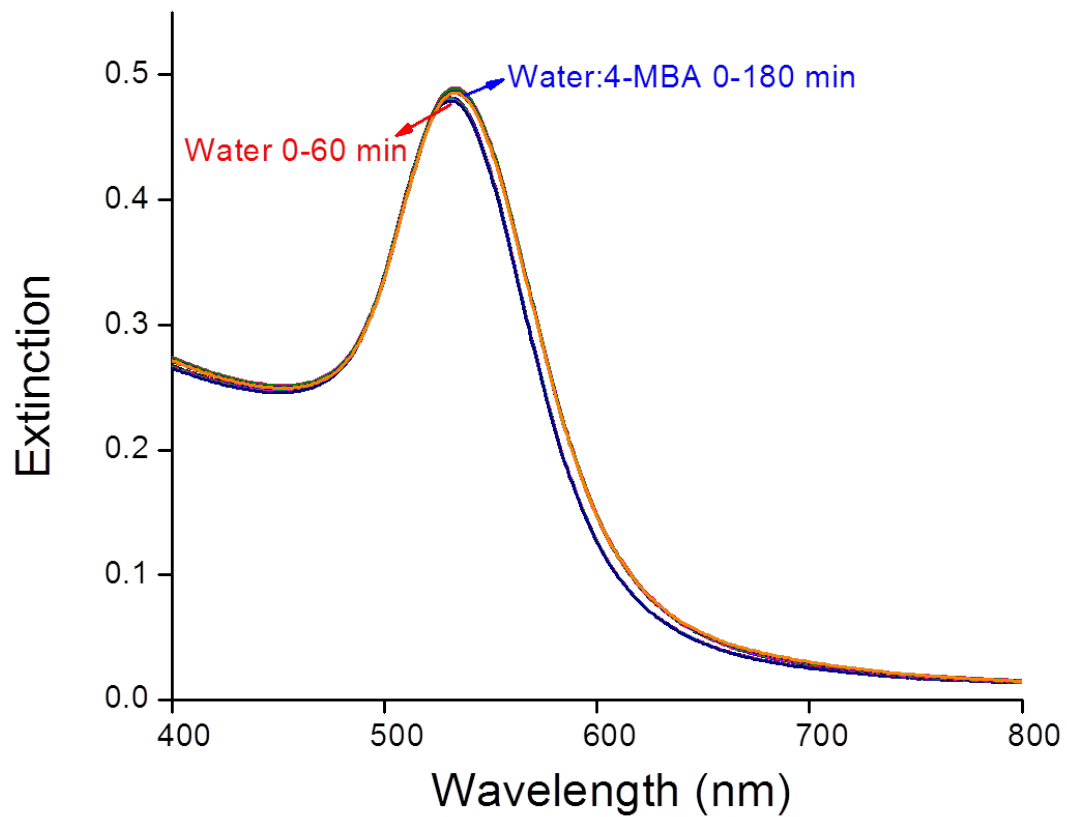


Figure S4 Extinction spectra of AuNPs and 4-MBA coated AuNPs in water as a function of time.

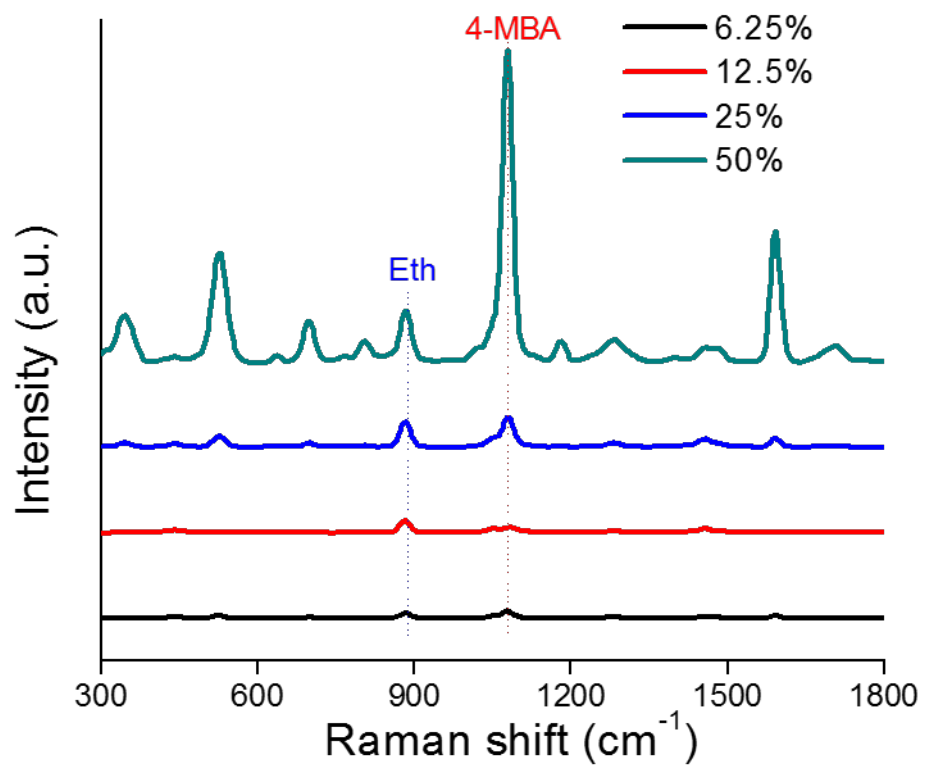


Figure S5 SERS spectra of 4-MBA coated AuNPs in solutions with different ethanol contents.

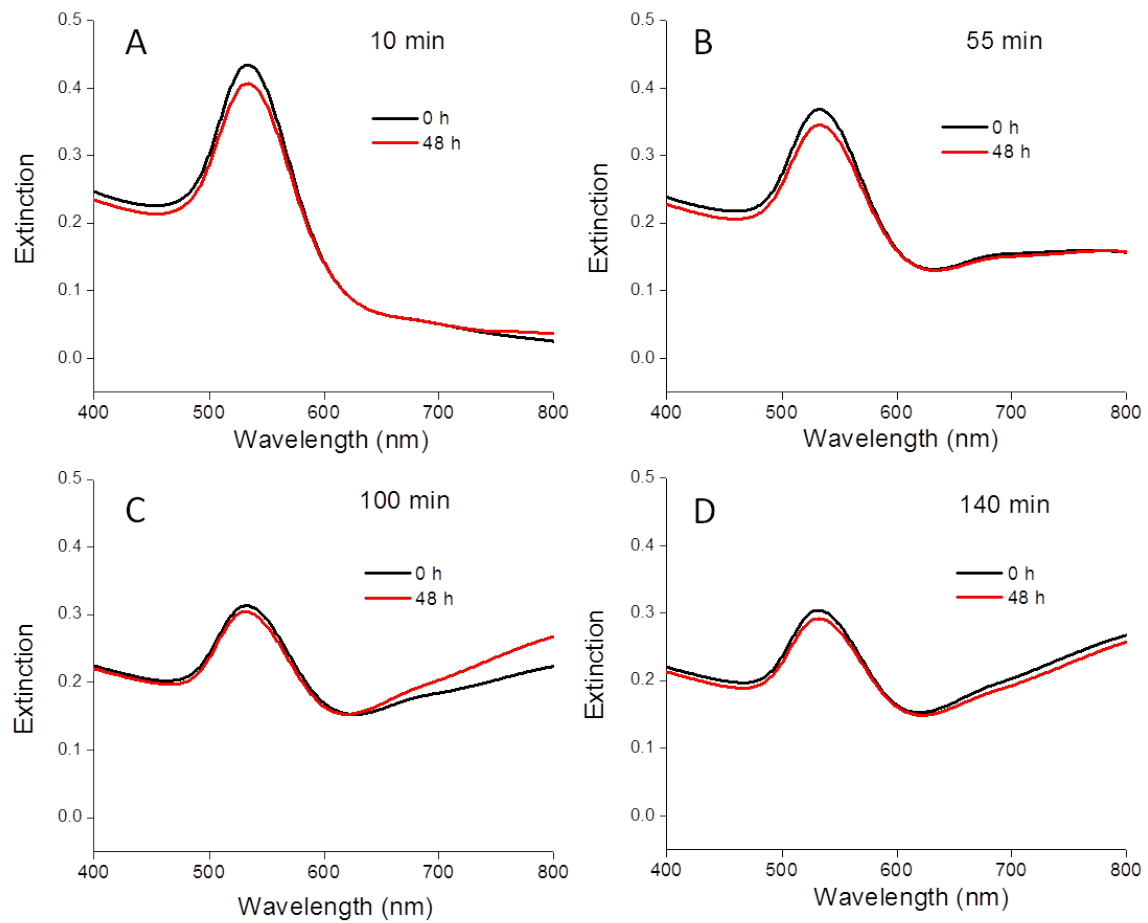


Figure S6 UV-VIS extinction spectra of 4-MBA coated AuNPs in water/ethanol co-solvent 0 h and 48 h after adding HS-PEG.

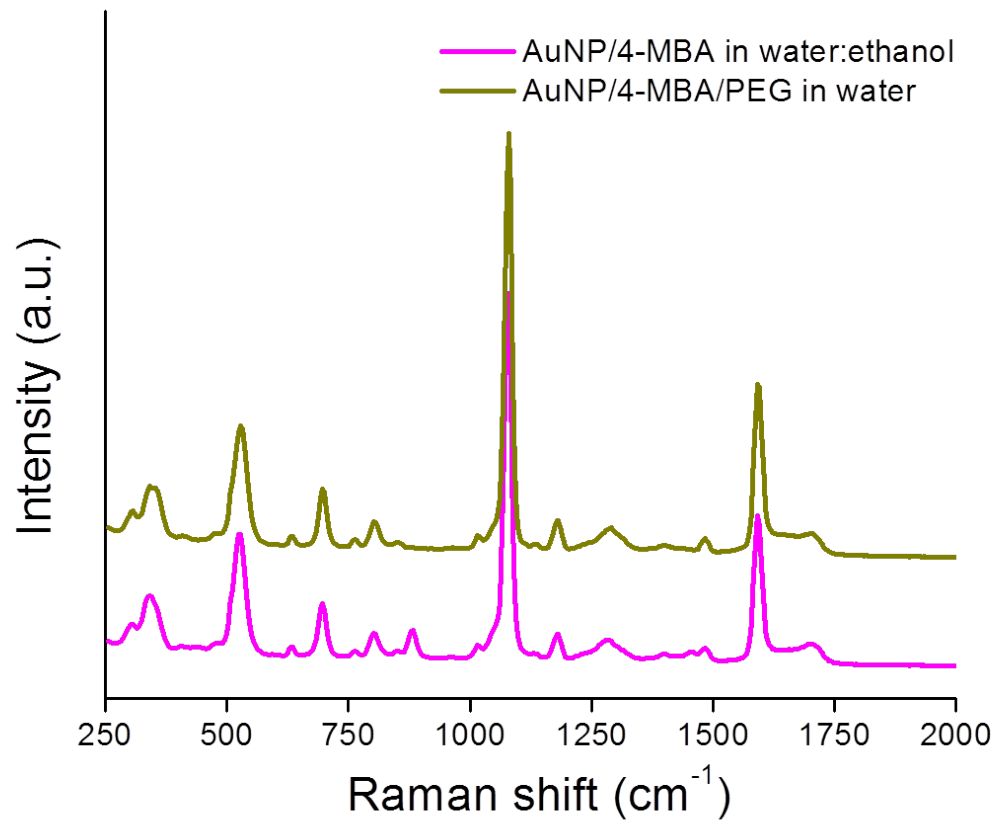


Fig. S7 SERS spectra of AuNP/MBA in water:ethanol co-solvent and AuNP/4-MBA/PEG in water at 100 min.

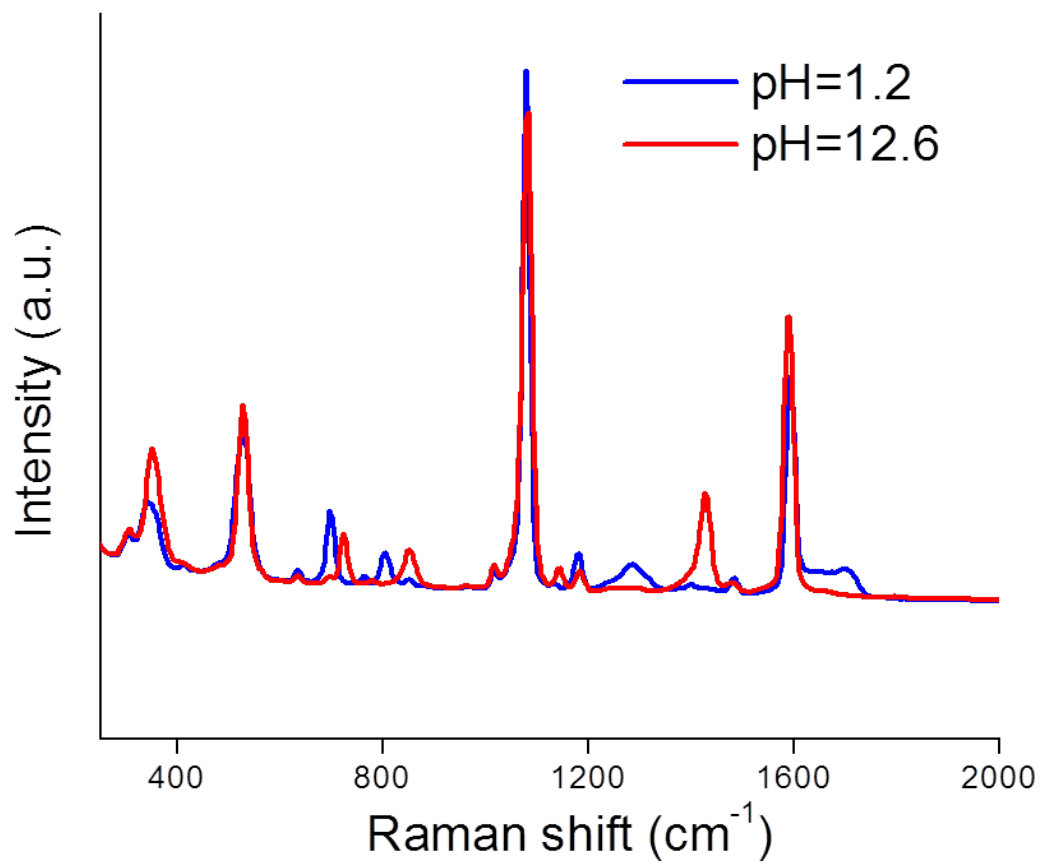


Figure S8 SERS spectra of probe at pH=1.2 and 12.6.

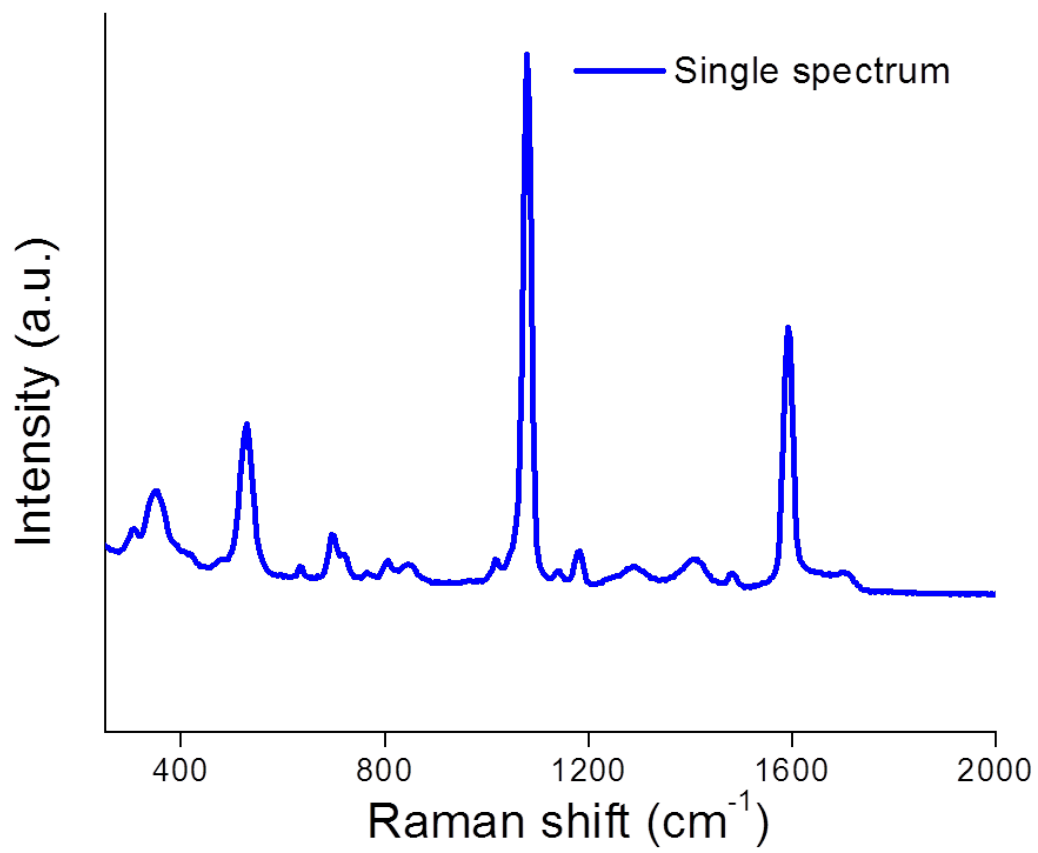


Figure S9 Single Raman spectrum from a random selected pixel in the Raman map.

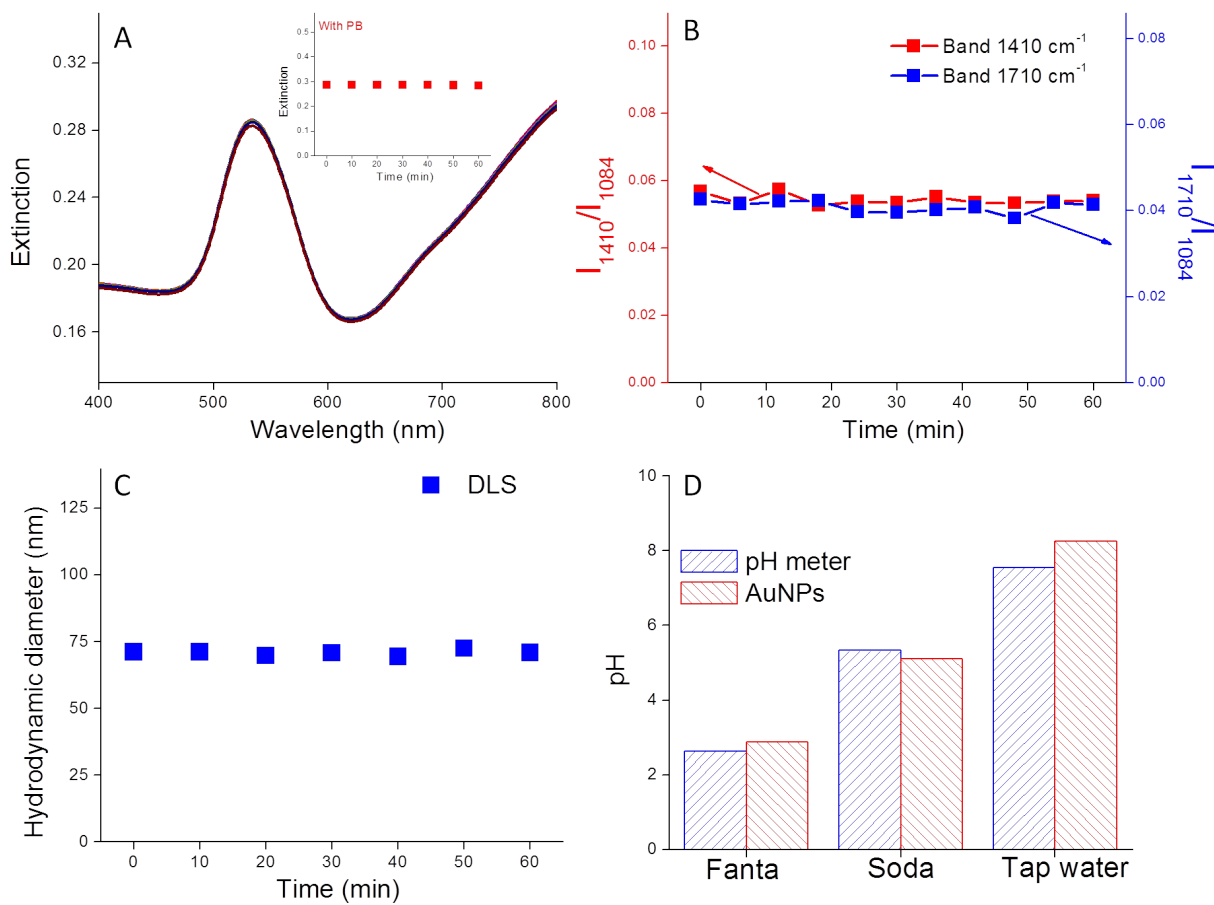


Figure S10 A) Variations of the UV-VIS extinction spectra, B) pH indicator values, and C) hydrodynamic diameter of the pH probe in 0.01 M PB solution as a function of time; D) pH values of three real water samples measured by our pH probe and a commercial pH meter in our lab.

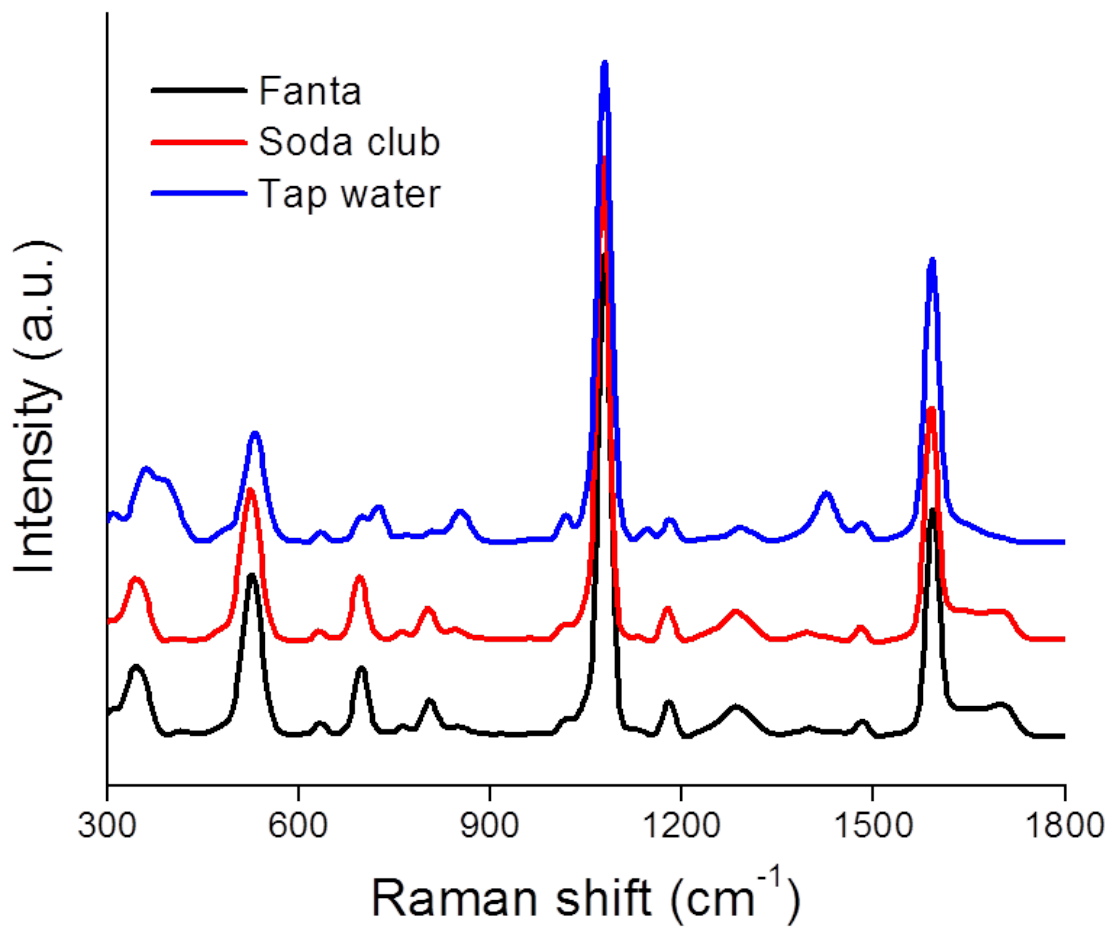


Figure S11 SERS spectra of our pH probe suspended in Fanta, club soda, and tap water.

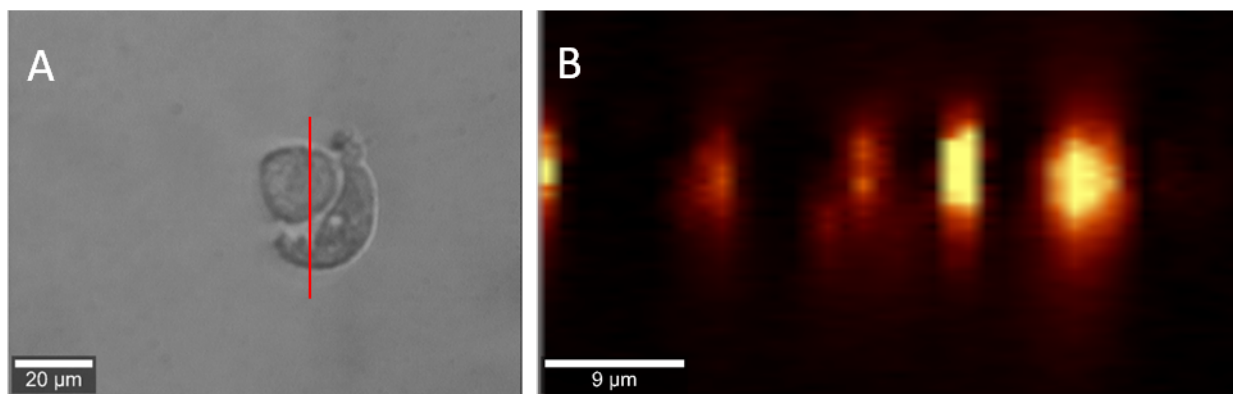


Figure S12 A) Optical image of prostate cancer cell and B) Y-Z cross section Raman scan (marked by the red line) of the cancer cell.

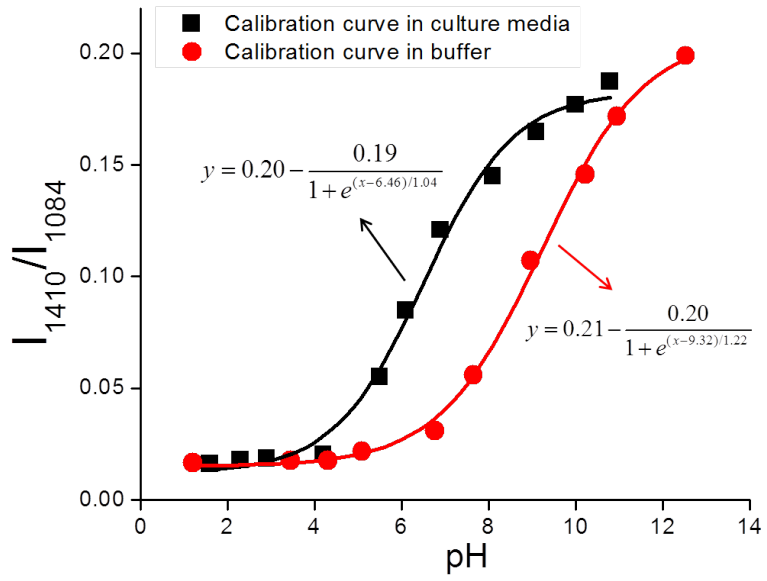


Figure S-13 pH calibration curves for pH probes in cell media (black squares) and in buffer (red circles)

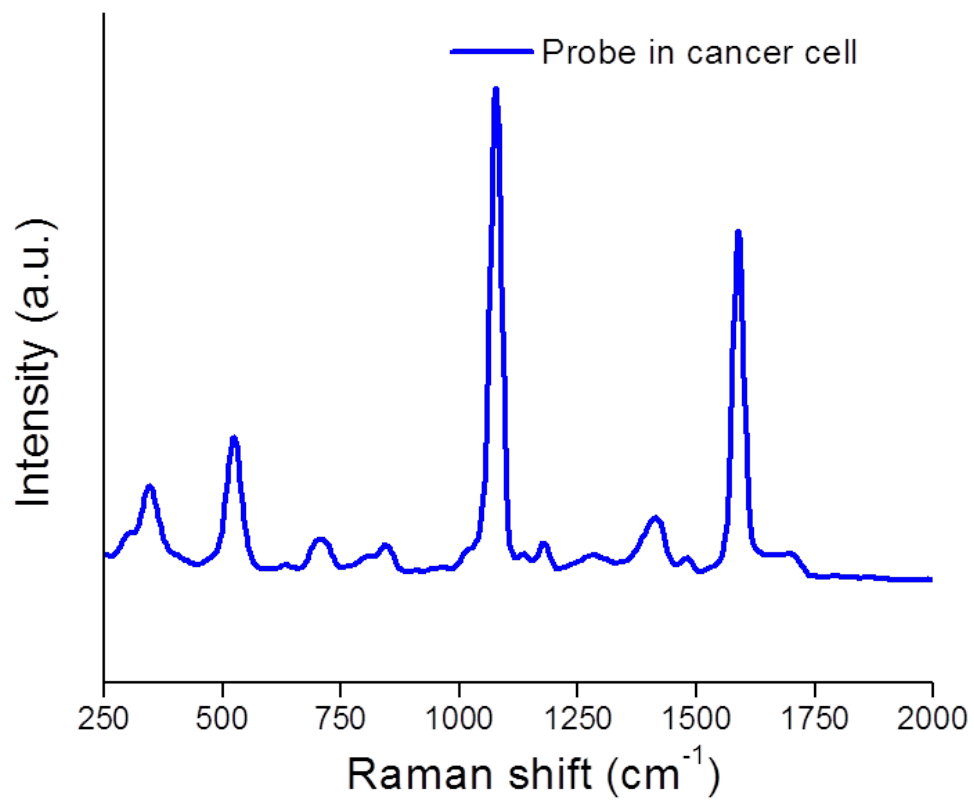


Figure S-14 SERS spectrum of the pH probe inside the cancer cell

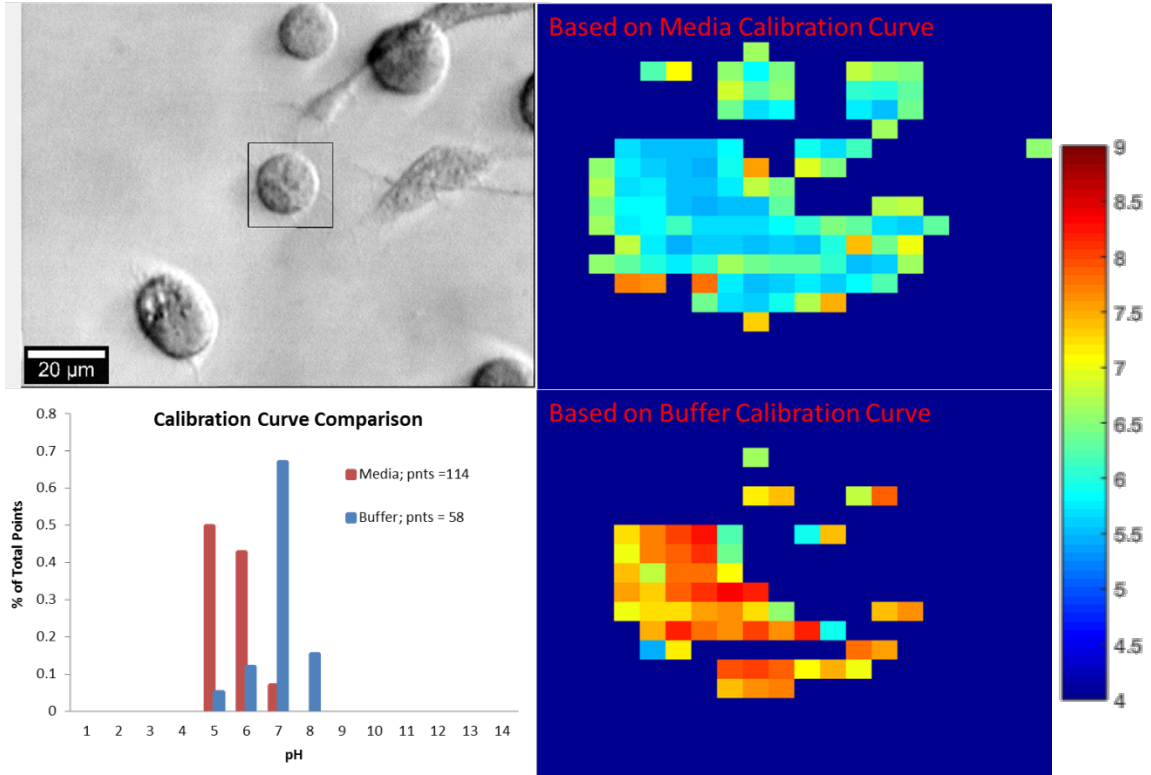


Figure S15 Comparison of the pH calculated for a given cell with the two different calibration curves.

