

In Situ Detection of Droplet pH Using Surface-Enhanced Raman Spectroscopy

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Micrometer-sized aqueous droplets (microdroplets) are ubiquitously present in the atmosphere and act as suspended reactors for numerous atmospheric reactions. pH is arguably the most important parameter dictating water chemistry of microdroplets. However, direct measurement of droplet pH is

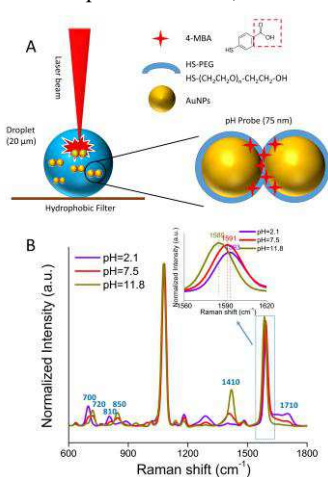


Figure 1. A) Schematics illustrating SERS interrogation of aerosol droplets collected on a superhydrophobic polyvinylidene difluoride filter and of SERS pH nanoprobes; B) SERS spectra of pH nanoprobes in bulk phosphate buffer (PB) solutions (0.6 M) that were adjusted to different pH values.

still challenging. In this study, we developed a nanoscale pH meter (pH nanoprobes) based on surface-enhanced Raman spectroscopy (SERS). As shown in Fig. 1A, the nanoprobe consists of 1) gold nanoparticle as optical antenna; 2) pH reporter that exhibits changing Raman spectra corresponding to changing solution pH; and 3) a poly(ethylene) glycol layer to endow the probes colloidal stability.

By combining the single-molecular sensitivity of SERS and high spatial resolution of confocal Raman microscopy, pH-responsive information of 4-MBA were reliably retrieved from the microdroplet three-dimensionally. In a phosphate-buffered droplet, pH at the core is 3.6 pH unit higher than the bulk solution where they are generated. This was further corroborated by the fact that two amine groups of 4-aminothiophenol coupling into one azo group, which can be significantly accelerated at basic pH, only occurred in the droplet but not in the bulk solution.