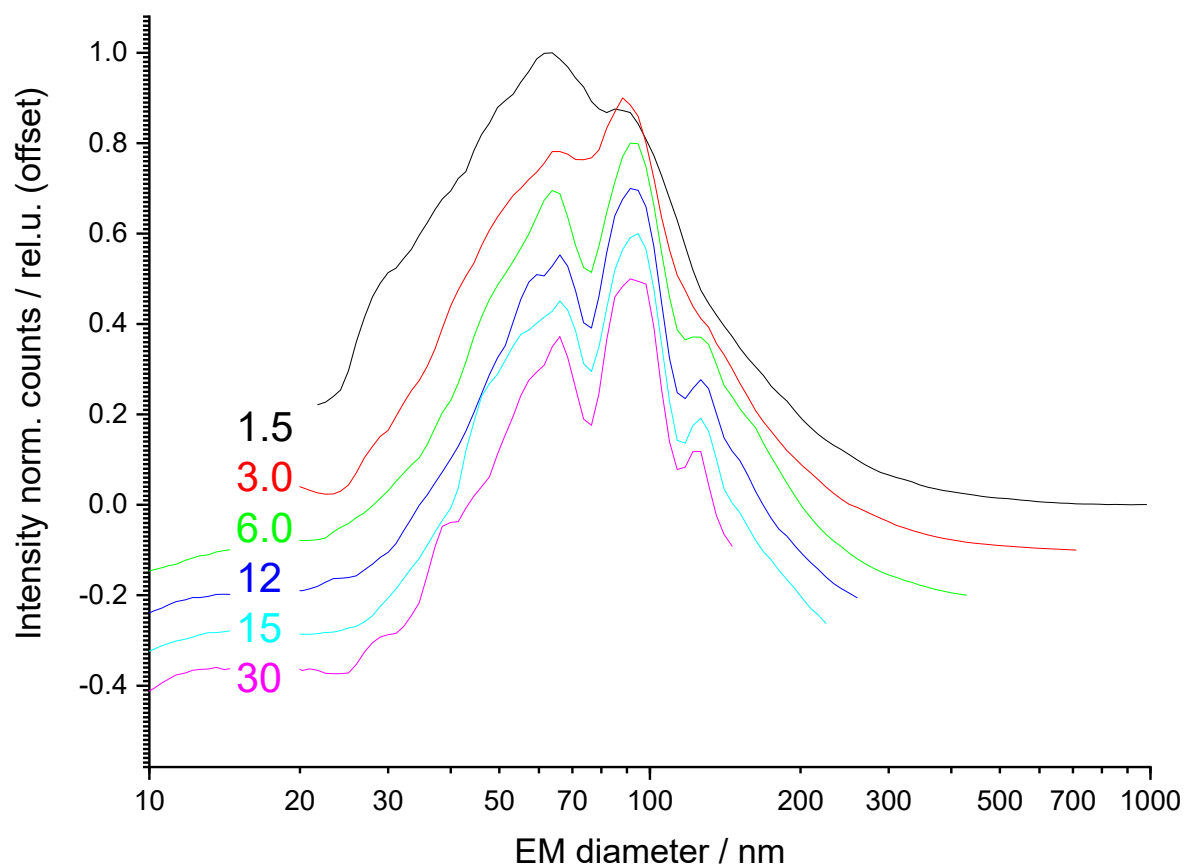


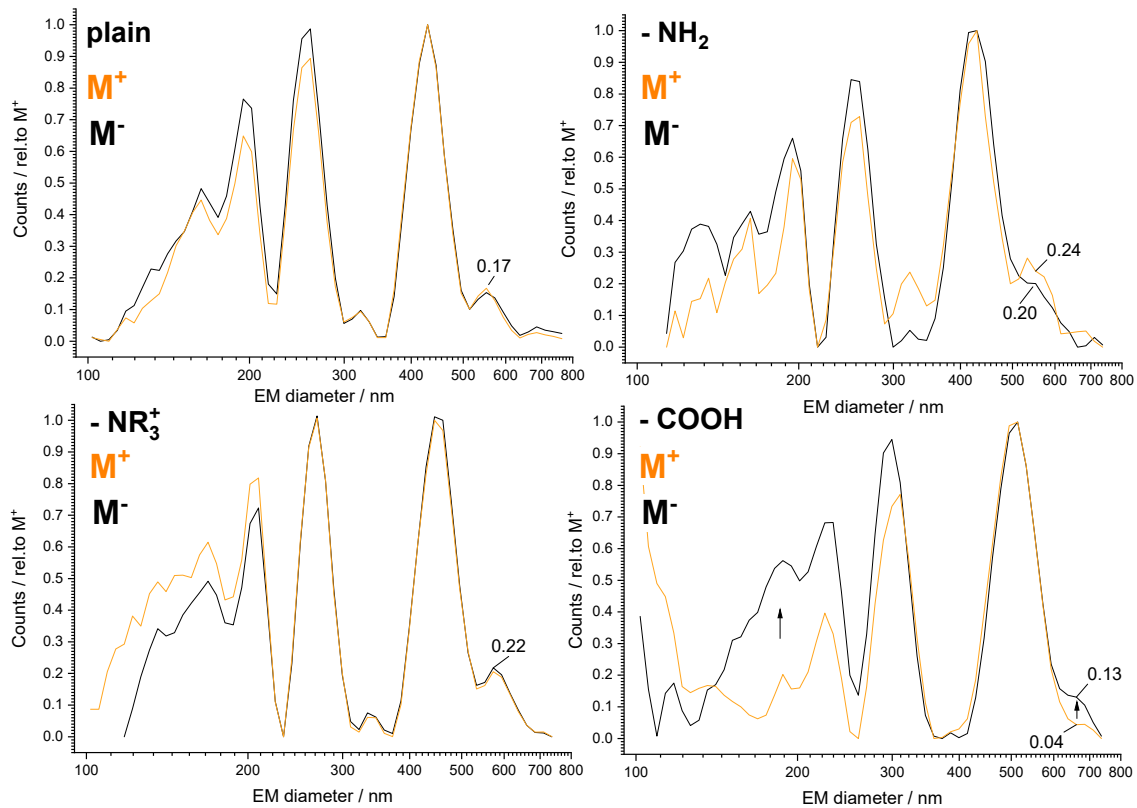
S 1- Sheath gas flow rates



S 1 IR-MALDI charged polystyrene (PS) particles of 91 nm in EM diameter measured with the long DMA (TSI 3081), at a mass concentration of 0.50 mg/mL and 0.7L/min synth. air in the ionization chamber. The aerosol gas stream was held constant at flow rate of 0.6 L/min and the sheath gas stream was varied between 2.5 and 50 times the flow rate of the aerosol gas stream.

Given a constant aerosol gas flow rate, the sheath gas flow rate is the major contributor to signal broadening in a DM analyzer setup. The sheath gas flow rate in the DM analyzer was varied from of 1.5 L/min to 30 L/min and the aerosol gas flow rate was kept constant at 0.6 L/min. Since the peak width stayed unaffected for sheath gas flow rates above 6 L/min, it can be concluded that the diffusive signal broadening is not significant at that this flow rate and beyond. This means that it is likely that the peak width is limited by the particle's size distribution and not the performance of the DM analyzer itself.

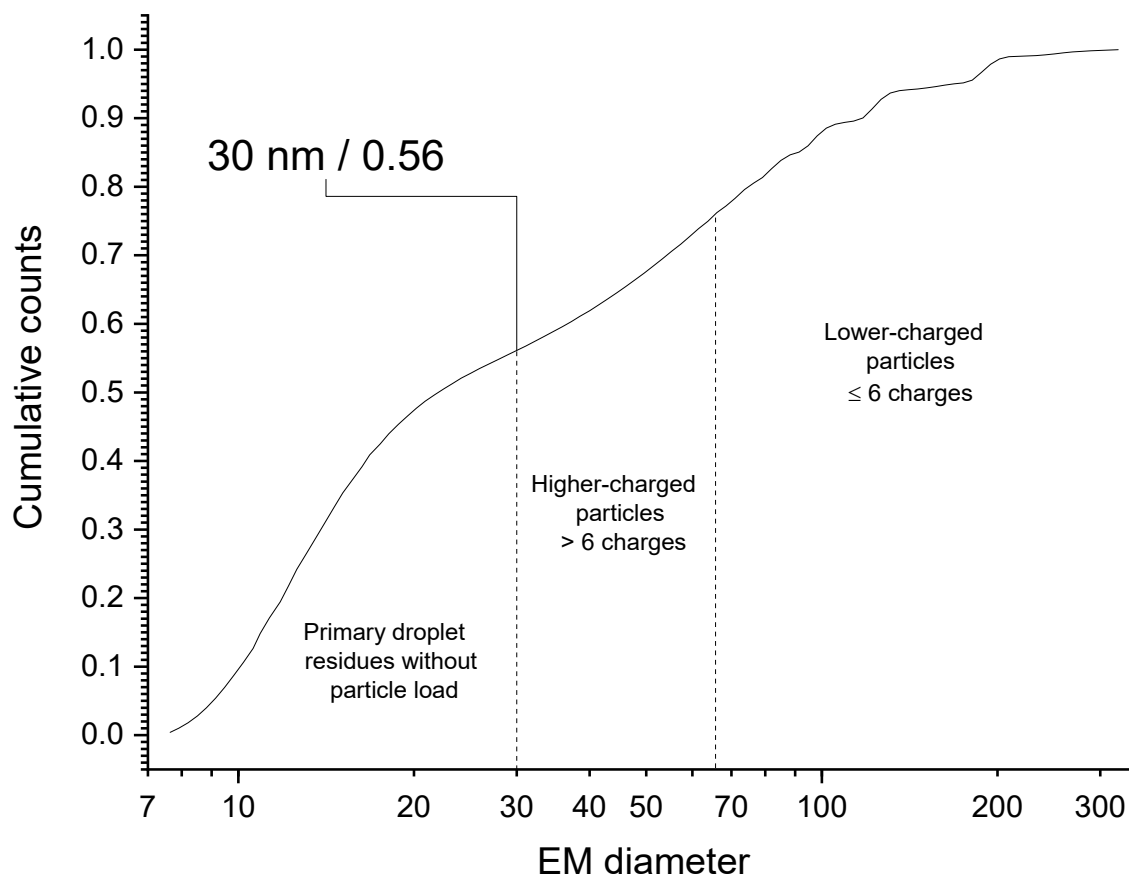
S 2 - Surface modifications



S 2 Different surface modifications of 400 - 500 nm silicate particles suspended in water and their respective spectra in the positive HV mode (negative charges, black) and negative HV mode (positive charges, orange).

As mentioned in Fig. 5 of the main text, the surface modifications may have an influence on the charge distribution and formation of dimers. The particle counts were intensity-normalized with respect to the singly charged monomer within each spectrum so that the relative influences of the four surface groups - plain, NH₂, NR₃⁺ and COOH - are shown. Here, the spectra for positive charges (black) and negative charges (orange) were compared to one another. First, the plain, NH₂- and COOH-modified particles tend to form more multiply charged particles when negatively compared to positively charged. Here, the COOH-modification represents the most extreme case. Along the same line, there is a tendency of the COOH-modified particles to form more dimers when negatively charged. The absolute counts show that there is only little difference between the surface modifications when comparing the two polarity modes, except for COOH.

S 3 - Cumulative counts



S 3 Cumulative Counts of a plain 200 nm PS particle suspended in water and charged by IR-MALDI.

The cumulative plot shows a strong and broad feature centered at 15 nm EM diameter, a less intense but still broad feature between 30 and 100 nm, and several distinct sharp features above 100 nm. Given that the particles have a nominal diameter of 200 nm and already would have more than 20 charges if they reached an EM diameter of 30 nm or less, it can be confidently concluded that the signal below 30 nm in EM diameter does not contain any particles. These are residual signals from particle debris or other impurities. From all counts, already 56% fall into that category, meaning that the probability of loading a primary droplet with at least one particle is roughly 44%.