Supplementary Figures

Realizing Nano Electrospray Ionization with Disposable Pipette Tips under Super Atmospheric Pressure

Md. Matiur Rahman¹, Kenzo Hiraoka¹ and Lee Chuin Chen²*

¹Clean Energy Research Center, University of Yamanashi, 4-3-11, Takeda, Kofu, Yamanashi, 400-8511 Japan
²Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-3-11, Takeda, Kofu, Yamanashi, 400-8511 Japan

*Corresponding author:
L.C. Chen, Tel: +8155-220-8072
Email: leechuin@yamanashi.ac.jp

Keywords: High pressure electrospray, Nano electrospray, Disposable pipette tips, Gel loading tip, Corona discharge, Aqueous solution.
Supplementary Figure S1. Photograph showing the appearance of corona discharge during an attempt to electrospray the aqueous solution from the gel loading tip under atmospheric pressure. During the experiment, the high voltage (H.V.) applied to the emitter was gradually increased, but the electrospray was not observed over the H.V. range up to the appearance electrical discharge (as indicated by the dim blue-purple light at the tip).
Supplementary Figure S2. Microscopic inspection on the electrospray of aqueous solution (cytochrome c in 100 mM ammonium acetate) from the gel loading tip under super-atmospheric pressure. A metal wire (titanium, dia.: 50 μm) was inserted into the gel loading tip. The applied voltages to the metal wire are a) 0 kV, b) 3.2 kV, and c) 4.2 kV. Stable cone jet mode could be sustained with minimum solution flow rate at 3.2 kV. The pressure of the ion source was 4 atm.
Supplementary Figure S3. Determination of solution flow rate for the nanoESI from gel loading tip.

a) The position of the liquid-air meniscus at different time. b) The plot of liquid volume against time.

c) Solution flow rate estimated from (b). d) The recorded total ion current and the averaged mass spectrum. The initial loaded volume was 600 nL. The dashed line in c indicates the average solution flow rate of 12 nL/min. The air pressure in the ion source was 3 atm. The fast-forwarded video for this measurement is included in the supplementary video.
Supplementary Figure S4. Positive and negative ion mass spectra of a) & b) lysozyme, c) & d) myoglobin, e) & f) albumin, and g) & h) concanavalin A, each of $10^{-6}$ M in 100 mM ammonium acetate aqueous solution acquired under 3 atm ion source pressure. The double dots in g and h indicate the peaks from the dimer of concanavalin A.
Supplementary Figure S5. Rapid mass spectrometric analysis of raw sample using gel loading tip as nanoESI emitter. The metallic wire (in this case a silver coated copper wire) was used to pierce a few mm into the sample to collect the bio-fluid. After dried, the wire was inserted to the gel loading tip preloaded with 5 µL aqueous solution. The ESI was conducted under 3 atm. All biological sample (potato, lemon, grape, radish root and tomato) were purchased from the local market of Yamanashi city, Japan and analyzed without any sample preparation.
**Supplementary Figure S6.** Rapid detection of proteins from viscous bio-fluid of a) raw chicken egg white, b) human saliva from one of the author, c) and d) human serum (Sigma Aldrich), using solid wire sampling technique and gel loading tip as nanoESI emitter. The metallic wire was dipped a few mm into the viscous fluid. The bio-fluid adhered to the wire surface was dried and was inserted into the gel loading tip preloaded with 5 μL aqueous solution. The ESI was conducted under 3 atm.