

**Electronic Supplementary Information**

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**Three-dimensional hydrodynamic focusing  
microfluidic emitter: a strategy to inhibit sample  
ion expansion in nanoelectrospray ionization**

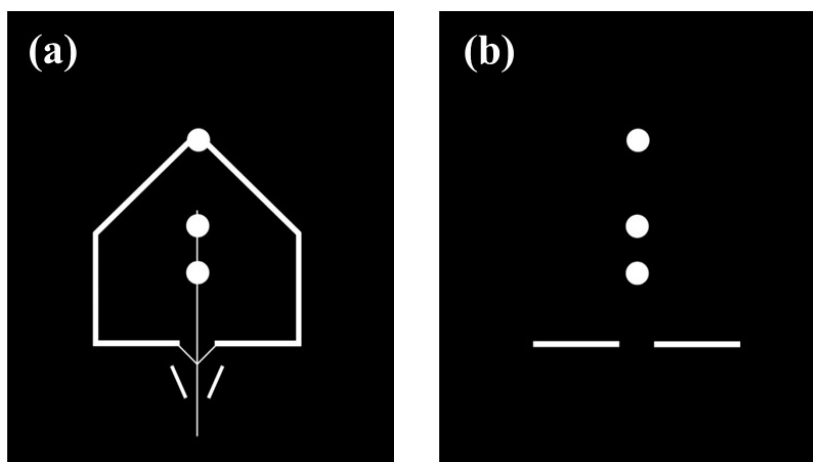
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**Fig. S1.** Designed photomasks for the first and the second layer in 3D HFNE. (a) the photomask for the second layer, (b) the photomask for the first layer.

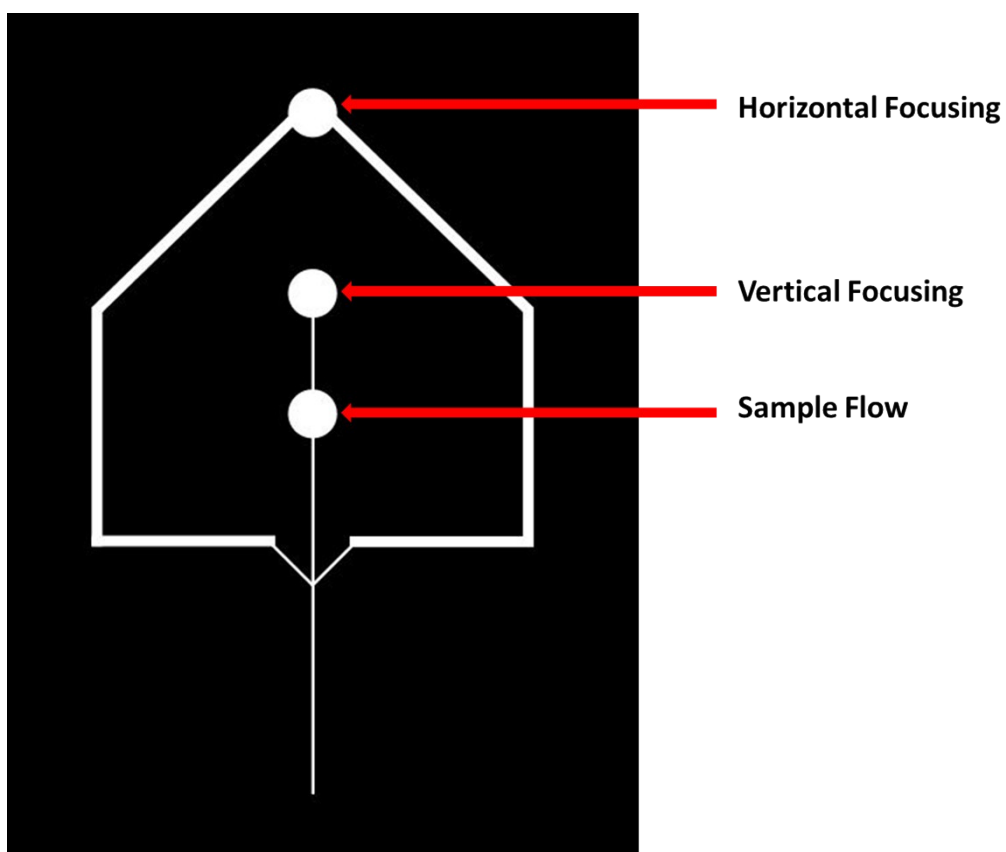
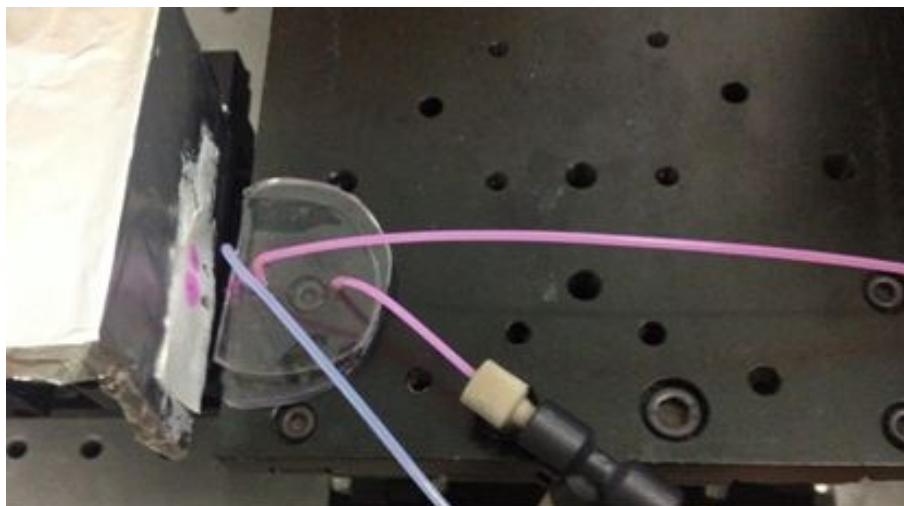


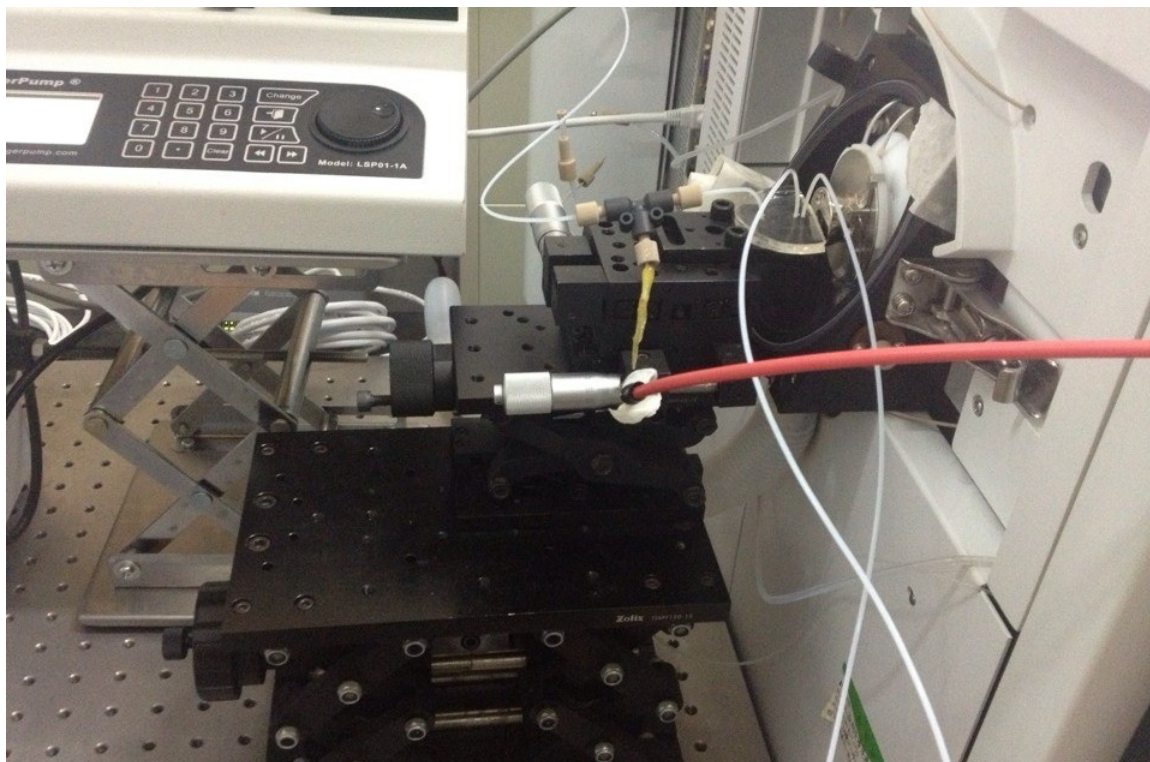
Fig. S2. Inlets assignments for the sample flow and two focusing flows.



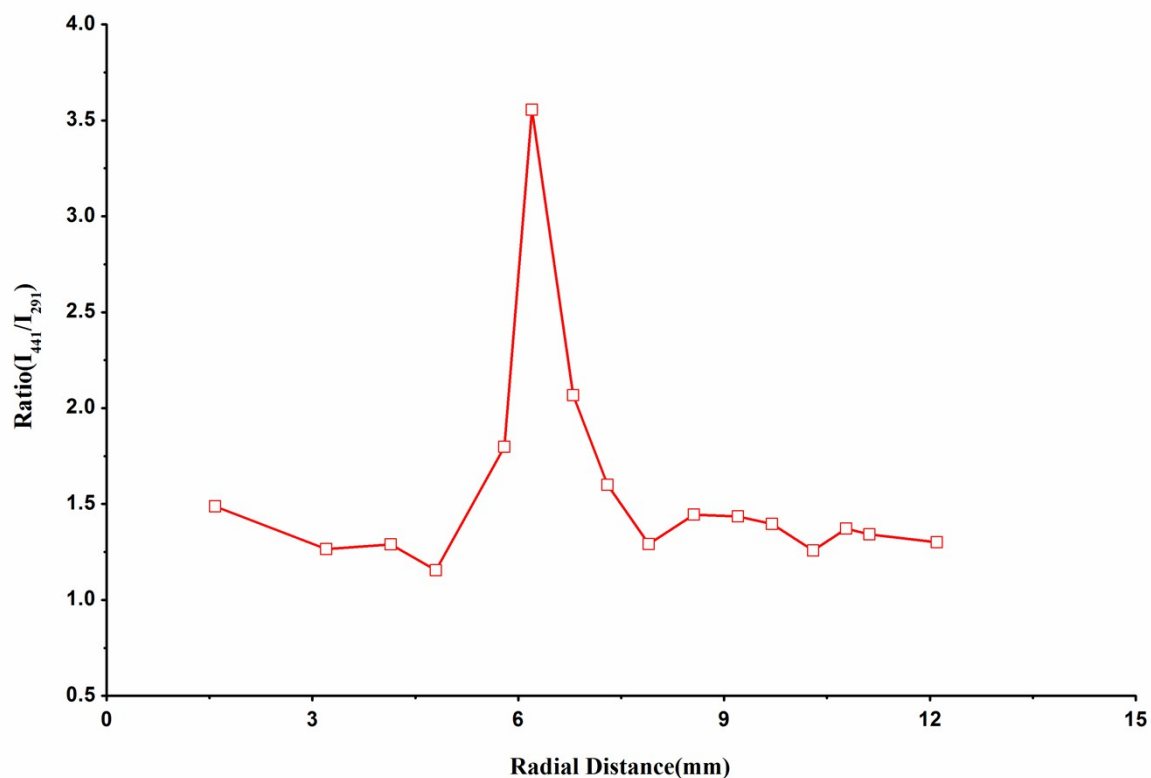
**Fig. S3.** The instrumental setup to collect ion deposition patterns for the wrapped charged aerosol plume from 3D HFNE under different flow rates.

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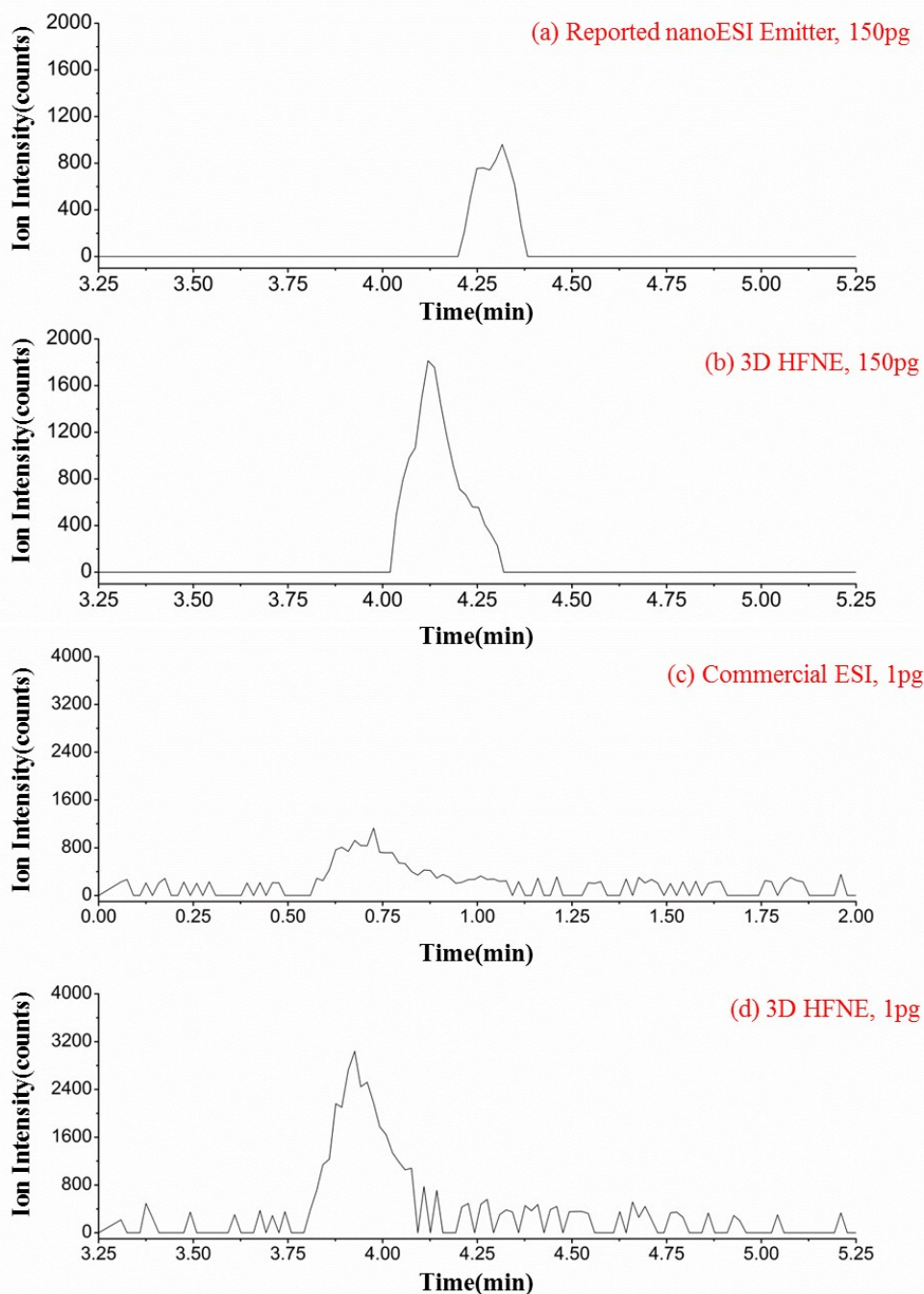


**Fig. S4.** The practical photograph for an on-line 3D HFNE coupled with TOF-MS.

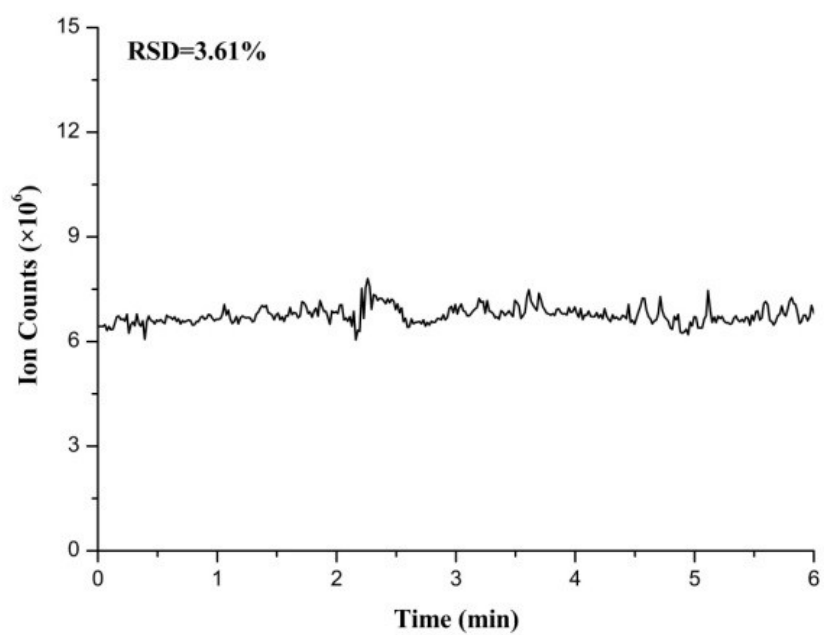


**Fig. S5.** Ratios between metamifop (sample) and isoprothiolane (background ion) collected at different radial distance. Metamifop (5ng/ $\mu$ L) was infused as the sample flow at 0.3 $\mu$ L/min, and isoprothiolane (5ng/ $\mu$ L) was injected as the horizontal focus flow and the vertical focus flow at 1 $\mu$ L/min and at 0.2 $\mu$ L/min.

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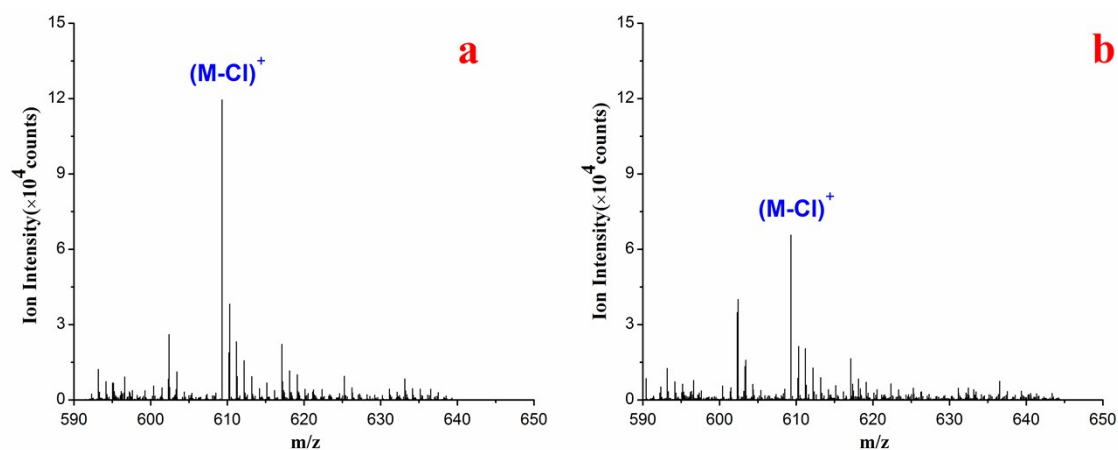
**Fig. S6.** EICs of metamifop and RhB based on commercial ESI resources and 3D HFNE. Sample solution was injected to evaluate the sensitivity as: (a) 150pg metamifop by reported nanoESI emitter, (b) 150pg metamifop by 3D HFNE, (c) 1pg RhB by commercial ESI, and (d) 1pg RhB by 3D HFNE. Infusion rates of sample flows in reported nanoESI emitter, 3D HFNE and commercial ESI were 0.3 $\mu$ L/min, 0.3 $\mu$ L/min and 200 $\mu$ L/min, and flow rates of horizontal and vertical focus flows in 3D HFNE were 1 $\mu$ L/min and 0.2 $\mu$ L/min, respectively.



**Fig. S7.** TIC of reserpine based on 3D HFNE (with 800nL/min flow rate).



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**Fig. S8.** MS spectra of reserpine based on 3D HFNE under different sample infusion rates. Reserpine solution ( $5\mu\text{g/mL}$ ) was injected at 150nL/min (a) and 30nL/min (b). Infusion rates of the horizontal focus flow in 3D HFNE were  $1.5\mu\text{L/min}$  (a) and  $0.3\mu\text{L/min}$  (b), and infusion rates of the vertical focus flow in 3D HFNE were  $0.4\mu\text{L/min}$  (a) and  $0.08\mu\text{L/min}$  (b), respectively.