## SUPPORTING INFORMATION

Focusing Ion Funnel-assisted Ambient Electrospray enables High-Density and Uniform Deposition of Non-spherical Gold Nanoparticles for Highly Sensitive Surface-enhanced Raman Scattering

Baris Akbali,<sup>a,b</sup> Cedric Boisdon,<sup>a</sup> Barry L. Smith,<sup>a</sup> Boonphop Chaisrikhwun,<sup>c</sup> Kanet Wongravee,<sup>d</sup> Tirayut Vilaivan,<sup>d</sup> Cassio Lima,<sup>e</sup> Chen-Han Huang,<sup>f</sup> Tsan-Yao Chen,<sup>b</sup> Royston Goodacre,<sup>e</sup> Simon Maher <sup>a,\*</sup>

<sup>a</sup>Department of Electrical Engineering and Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, UK. E-mail: s.maher@liverpool.ac.uk

<sup>b</sup>Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan.

<sup>c</sup>Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

<sup>d</sup>Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

<sup>e</sup>Centre for Metabolomics Research, Department of Biochemistry, Cell and Systems Biology, Institute of Systems, Molecular and Integrative Biology, University of Liverpool, Biosciences Building, Crown Street, Liverpool, L69 7ZB, UK.

<sup>f</sup>Department of Biomedical Engineering, National Central University, Zhongli 10608, Taiwan.

\* For correspondence, e-mail: <a>s.maher@liverpool.ac.uk</a>

## Supporting Information Contents

Item	Details
Table S1	Calculated resistor values to generate each exponential voltage gradient.
Figure S1	Schematic illustration of the ESI needle and focusing ion funnel using 1.6 mm wide electrodes and an electrode gap of 1.0 mm showing applied voltage at each electrode for each exponential gradient tested.
Figure S2	Experimental setup for ESD of AuNPs on a SERS substrate using a focusing ion funnel.
Figure S3	Electric field maps for the various ion funnel gradients simulated.
Figure S4	Simulated hit maps of ions arriving at the SERS substrate and ion density (lons/mm <sup>2</sup> ) for each C (gradient) value.
Figure S5	SERS intensity variations over 10 random locations when the IR lamp is ON and OFF. (All the parameters kept constant).
Figure S6	SERS intensity variation bar charts A) with and B) without nebuliser. SEM images after ESD- FIF deposition C) with and D) without nebulising gas. <i>Scale bars are 500 nm</i> .
Figure S7	Electric field intensity enhancement contours for transverse plasmon excitation; A) Single Au Nanorod B) Single AuNS, C) AuNSs triplet, AuNRs triplet D) perpendicular and E) parallel to the excitation source, F) AuNR-AuNS system.
Figure S8	SERS intensities of dropcasted AuNSs and AuNRs in sequence in comparison with the other results. Inset presents SERS intensities of the sample; dropcasting AuNRs-AuNSs (first AuNRs dropcasted, waited until completely evaporates then AuNSs dropcasted) and AuNSs-AuNRs (vice versa dropcasting sequence) For all the experiments 4-ATP concentration kept at 10 <sup>-5</sup> M. All data points are means with error bars showing standard deviations from 10 replicate measurements.
Figure S9	UV-VIS absorption spectra of AuNSs (black line), AuNRs (red line), and 1:1 mixture of AuNSs and AuNRs (blue line).
Figure S10	SEM images of dropcasted A) Nanorods, B) Nanospheres, C) Nanorods/Nanospheres mixture; D)-F) ESD by focusing ion funnel of the mixture. All scale bars are 200 nm.

Gradient (C)	R1 (Ω)	R2 (Ω)	R3 (Ω)	R4 (Ω)	R5 (Ω)	R6 (Ω)	R7 (Ω)	R8 (Ω)	R9 (Ω)
10	20000	40000	79000	158000	315000	629000	1256000	2505000	4998000
50	67000	112000	187000	312000	521000	870000	1453000	2426000	4052000
100	110000	170000	263000	406000	629000	974000	1507000	2332000	3610000
400	268000	358000	478000	639000	853000	1139000	1521000	2031000	2712000
1000	441000	538000	656000	801000	977000	1192000	1455000	1775000	2166000
Linear	1111000	1111000	1111000	1111000	1111000	1111000	1111000	1111000	1111000

Table S1 Calculated resistor values to generate each exponential voltage gradient.



**Fig. S1** A) Schematic illustration of the ESI needle and focusing ion funnel using 1.6 mm wide electrodes and an electrode gap of 1.0 mm. B) Applied voltage at each electrode for each exponential gradient tested.



**Fig. S2** Experimental setup for ESD of AuNPs on a SERS substrate using a focusing ion funnel. (1) PCB standoffs. (2) Resistor network. (3) PCB. (4) Spring Loaded Pins. (5) Banana Plugs. (6) ESI emitter. (7) Illustrative deposition region. (8) Stainless-steel sheet. (9) PCB-based electrodes.



Fig. S3 Electric field maps for the various ion funnel gradients simulated.



**Fig. S4** A) (left panel) Simulated hit maps of ions arriving at the SERS substrate. (right panel) lon density (lons/mm<sup>2</sup>) for each C (gradient) value. *Total number ions kept constant for all calculations*. B) SERS intensity variation over a SERS line scan for linear and C=50 (inset photographs show the surfaces after AuNP deposition in each case; orange and green lines in the photographs indicate the location of the SERS line scans. *All scale bars are 2 mm*.



**Fig. S5** A) SERS intensity variations over 10 random locations when the IR lamp is ON and OFF, B) and C) are the corresponding SEM images. *Scale bars are 500 nm* (All the other parameters kept constant)





**Fig. S6** SERS intensity variation bar charts A) with and B) without nebuliser. Representative SEM images after FIF-ESD C) with and D) without nebulising gas. *Scale bars are 500 nm*.



**Fig. S7** Electric field intensity enhancement contours for transverse plasmon excitation; A) Single Au Nanorod B) Single AuNS, C) AuNSs triplet, AuNRs triplet D) perpendicular and E) parallel to the excitation source, F) AuNR-AuNS system. The enhancements are drawn according to a linear scale. *All scale bars are 50 nm*.



**Fig. S8** SERS intensities of dropcasted AuNSs and AuNRs in sequence in comparison with the other results. Inset shows SERS intensities for the following preparation procedures: dropcasting AuNRs-AuNSs (first AuNRs dropcasted, waited until completely evaporates then AuNSs dropcasted) and AuNSs-AuNRs (*vice versa* dropcasting sequence). For all the experiments the concentration of 4-ATP was kept constant, at 10<sup>-5</sup> M. All data points are means with error bars showing standard deviations from 10 replicate measurements.





Fig. S9 UV-VIS absorption spectra of AuNSs (black line), AuNRs (red line), and 1:1 mixture of AuNSs and AuNRs (blue line).



**Fig. S10** SEM images of dropcasted A) Nanorods, B) Nanospheres, C) Nanorods/Nanospheres mixture, D)-F) ESD by focusing ion funnel of the mixture. *All scale bars are 200 nm.*