Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Electrospray Deposition for Single Nanoparticle Studies

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Supporting Information Content

Section S1. Detailed procedure of Nanoparticles Synthesis

Chemicals. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥ 99.9% trace metals basis), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.999%), borane tert-butylamine complex (TBAB, 97%), sodium borohydride ($NaBH_4$, 99%), silver nitrate ($AgNO_3$, ≥ 99.0%), L-ascorbic acid (≥ 99.5%), hydrochloric acid (HCl, 37%, 99.999% trace metals basis, used for Au nanoparticle synthesis), hydrochloric acid (HCl, 37%, ACS reagent, used for aqua regia preparation), nitric acid (HNO_3, 70%), oleylamine (OLAM-SA, 70%), acetone (99.5%), and 2-propanol (IPA, 99.5%) were purchased from Sigma Aldrich. Hexadecyltrimethylammonium bromide (CTAB, > 98.0%), hexadecylpyridinium chloride monohydrate (CPC, > 98.0%), and oleylamine (OLAM-TCI, 50%) were purchased from TCI America. Potassium bromide (KBr, 99.999 %) was purchased from Acros Organics. All chemicals were used as received without further purification. Anhydrous toluene was obtained from a custom-built solvent purification system. Ultrapure water (18.2 MΩ·cm at 25 °C) obtained from a Barnstead® GenPure® (Thermo Scientific) water purification system was used in all experiments. All glassware was cleaned with aqua regia (a mixture of HCl and HNO_3 in 3:1 volume ratio), rinsed thoroughly with water and dried before use.

Synthesis of Au Nanorods (NRs). Au NRs were synthesized based on the seed-mediated growth method reported previously.[1] First, 125 µL of 10 mM $HAuCl_4$ solution was added to 5 mL of 100 mM CTAB solution in a 20 mL scintillation vial, to which freshly prepared 300 µL of $NaBH_4$ solution (10 mM) was rapidly injected under vigorous stirring. This seed solution was left undisturbed at 28 °C for 30 min. The growth solution was prepared by adding separately prepared solutions of 10 mL of $HAuCl_4$ (10 mM), 1.8 mL of $AgNO_3$ (10 mM) and 1.14 mL of L-ascorbic acid (100 mM) into 200 mL of CTAB solution (100 mM). Afterwards, 240 µL of seed solution was injected into the colorless growth solution. The reaction mixture was stirred for another 30 s and was left undisturbed at 30 °C for 4 h. The product was isolated via centrifugation at 8000 rpm for 10 min. After two rounds of redispersion in 50 mM CTAB followed by centrifugation, Au NRs were finally redispersed in an appropriate volume of 50 mM CTAB solution to attain an optical density (O.D.) of 2.0 at the longitudinal plasmon peak wavelength.

Synthesis of Spherical Au Seeds. Au nanospheres were synthesized by using an iterative oxidative dissolution and reductive growth method developed by the Mirkin group.[2] First, Au NRs was etched by adding 10 mM of $HAuCl_4$ into as-synthesized NR solution (O.D. = 2.0) to obtain a final concentration of 90 µM for Au^{3+}. The reaction was allowed to proceed for 4 h at 40 °C under stirring. The products were retrieved and purified by two rounds of centrifugation at 8200 rpm for

20 min followed by re-dispersion in 100 mM CPC and finally dispersed in 100 mM CPC to attain an O.D. of 1.0. Afterwards, Au concave rhombic dodecahedra (CRDs) were synthesized by using the etched NRs as seeds. In a typical reaction, 3 mL of etched NR solution in CPC (O.D. = 1.0) was added to a mixture of 10 mL of CPC (10 mM), 175 µL of $HAuCl_4$ (10 mM) and 2.25 mL of L-ascorbic acid (100 mM) and left undisturbed at 40 °C for 15 min. The reaction was stopped and purified by two rounds of centrifugation at 8000 rpm for 10 min followed by redispersion in 50 mM CTAB and finally dispersed in 50 mM CTAB solution to reach O.D. = 1.0. Subsequently, CRDs were etched by adding 10 mM $HAuCl_4$ to a final concentration of Au^{3+} equal to 60 µM. The reaction solution was kept at 40 °C for 4-6 h under stirring and the resultant nanospheres were isolated and purified by two rounds of centrifugation at 8000 rpm for 10 min and redispersion in 50 mM CTAB. The size of final spherical seed particles was controlled by monitoring the extent of etching via extinction spectroscopy at 1 h intervals. The reaction was stopped after 5 h once the plasmonic absorption peak reached 524.0 nm. The resultant nanospheres with an average diameter of ca. 19 nm were used as seeds for the preparation of Au truncated ditetragonal prisms and nano-octahedra used in this work.

Synthesis of Au Truncated Ditetragonal Prisms (TDPs). Au TDPs were synthesized by using a previously reported method with modifications.[3] Firstly, 19 nm seed particles were dispersed in 100 mM CPC solution to attain O.D. = 1.0. The growth solution was prepared by mixing 10 mL of 100 mM CPC, 0.5 mL of 1 M HCl, 0.5 mL of 10 mM $HAuCl_4$, 70 µL of 10 mL $AgNO_3$ and 70 µL of 100 mM L-ascorbic acid solutions. Afterwards, 100 µL of the above seed solution was introduced and the reaction mixture was left undisturbed at 30 °C for 3 h. Au TDPs were purified by two rounds of centrifugation at 3000 rpm for 5 min and redispersion in 50 mM CTAB solution.

Synthesis of Au Nano-Octahedra (ODs). Au ODs were synthesized according to a seed-growth method reported previously.[4] Firstly, 19 nm Au seed particles were dispersed in 100 mM CPC solution to obtain O.D.=1.0. The growth solution was prepared by mixing 10 mL of 100 mM CPC, 200 µL of 10 mM $HAuCl_4$ and 26 µL of 100 mM L-ascorbic acid solutions. Afterwards, 50 µL of the above seed solution was added and the reaction mixture was left undisturbed at 30 °C for 30 min. The Au octahedra were purified by two rounds of centrifugation at 2500 rpm for 5 min and redispersion in 50 mM CTAB solution.

Synthesis of OLAM-Capped Au Nanocrystal (NC) Seeds. Au NC seeds were synthesized according to a previously reported method.[5] OLAM-TCI was pre-dried at 100 °C under vacuum for 4 h and stored inside a N_2-filled glovebox. All syntheses were carried out under N_2 atmosphere using standard Schlenk techniques. Typically, 10 mL OLAM-TCI was loaded into a 50 mL three-neck flask. The solution was degassed under vacuum for 20 min and was refilled with N_2. Subsequently, 10 mL of anhydrous toluene was injected followed by flushing with N_2 for 20 min. Afterward, 0.25 mmol (98 mg) of $HAuCl_4 \cdot 3H_2O$ was loaded into the solution mixture followed by purging with N_2 for additional 10 min. Then a mixture of 0.25 mmol (22 mg) TBAB, 1 mL of OLAM-TCI, and 1 mL of anhydrous toluene was quickly injected into the reaction mixture, which was kept under stirring for another hour at 15 °C. Au NCs were collected via precipitation with 60 mL of acetone followed by centrifugation at 6000 rpm for 5 min. The resulting precipitates were redispersed in anhydrous toluene to reach an O.D. of 40.

Synthesis of Cu NRs. Cu NRs were synthesized according to our recently reported method.[6] In a typical reaction, 0.5 mmol (85 mg) of $CuCl_2 \cdot 2H_2O$ was mixed with 10 mL OLAM-SA in a 50 mL three-neck flask. The mixture was degassed under vacuum at 25 °C and flushed with N_2 for three times. Next, the reaction mixture was heated at 80 °C for 1 h to fully dissolve $CuCl_2$. The solution was then heated to 180 °C, forming a yellow solution. Afterward, 0.12 mL of Au NC seed solution (O.D. = 40) was injected into the mixture, which heated for another hour at 180 °C. After cooling down to room temperature, NRs were isolated by precipitation with 30 mL IPA followed by centrifugation at 3000 rpm for 3 min. The precipitates were redispersed in anhydrous toluene and stored in a N_2-filled glovebox for further use.

Section S2. Supporting Figures for Single Nanoparticle Electrospray Deposition

Figure S1. Image of pipette emitter after use

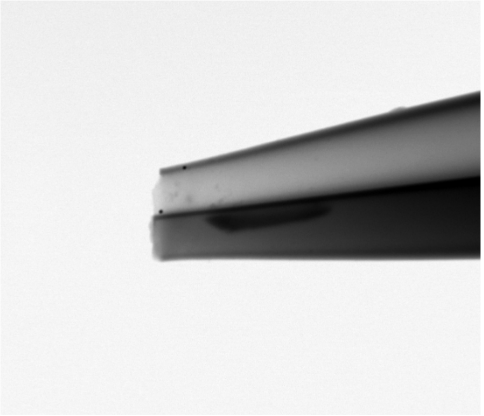

Figure S1. Electron micrograph of a 1 μm each barrel pipette emitter after electrospray deposition of Au ODs at reference condition; 2 mm spray distance, 8 nA ES current for 15 min.

Figure S2. Au ODs deposition with drop-cast method

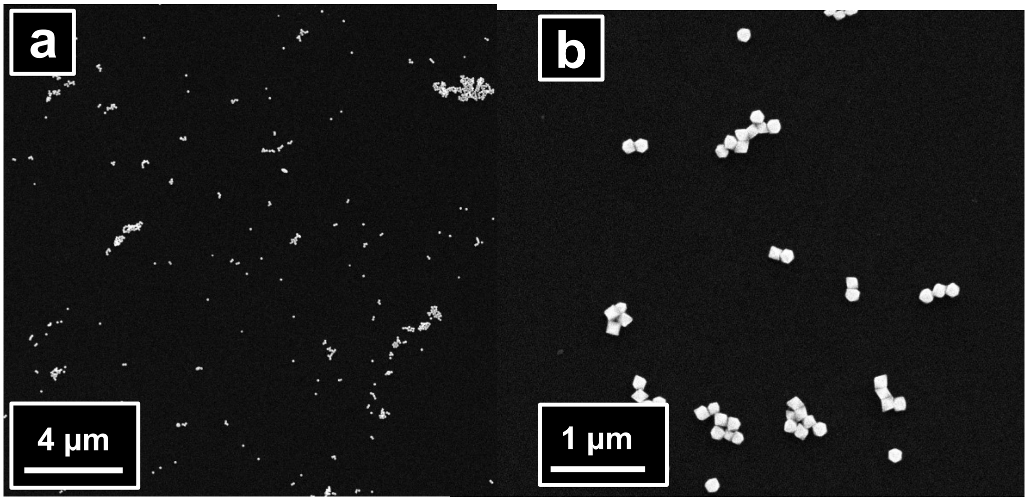

Figure S2. Electron micrographs of drop-casted sample of Au ODs (optical density in solution 0.33); **a)** 20 μm x 20 μm region of decent deposition and **b)** a 4 μm x 4 μm area shows a few single Au ODs deposited with large aggregates (more than 3 particles)

Figure S3. Cartoon demonstrating sampling areas for particle distribution study

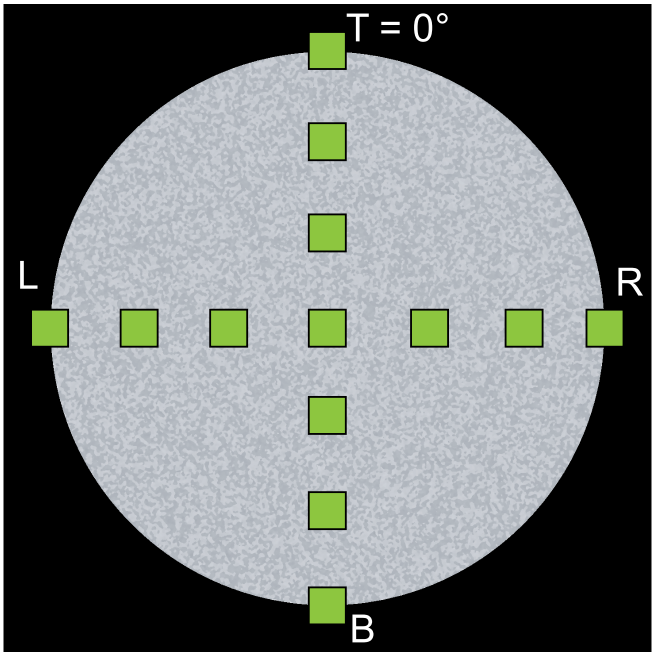

Figure S3. A cartoon demonstrating the areas imaged with electron microscopy to analyze the single Au ODs deposited across the electrospray deposited spot. L to R corresponds to the direction parallel to the theta emitter septum, and the area from L-R to T corresponds to the side of the emitter filled with Au ODs solution.

Figure S4. Particle count and surface density analysis

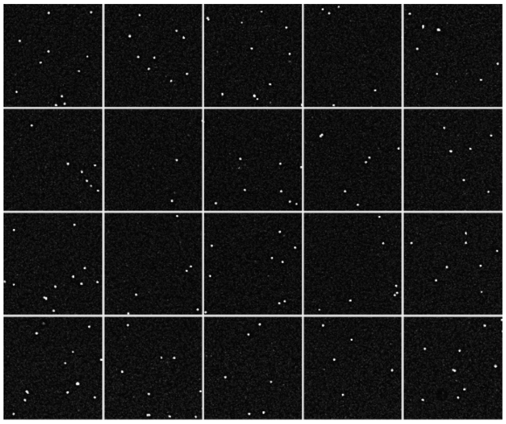

Figure S4. Demonstration for particle count per μm^2 analysis protocol. A 20 μm x 24 μm image captured at the center of an ES deposited spot is divided into smaller frames of 4 μm x 4 μm. Then #particles are counted in each frame and then divided by the area to get particles count per μm^2. Therefore 30 frames per trial are used. The deviation of particle count in these 30 frames gives the variation in the local surface density per μm^2 for the center regions of the ES deposited spots.

Figure S5. ES deposition of Au ODs at different ES current

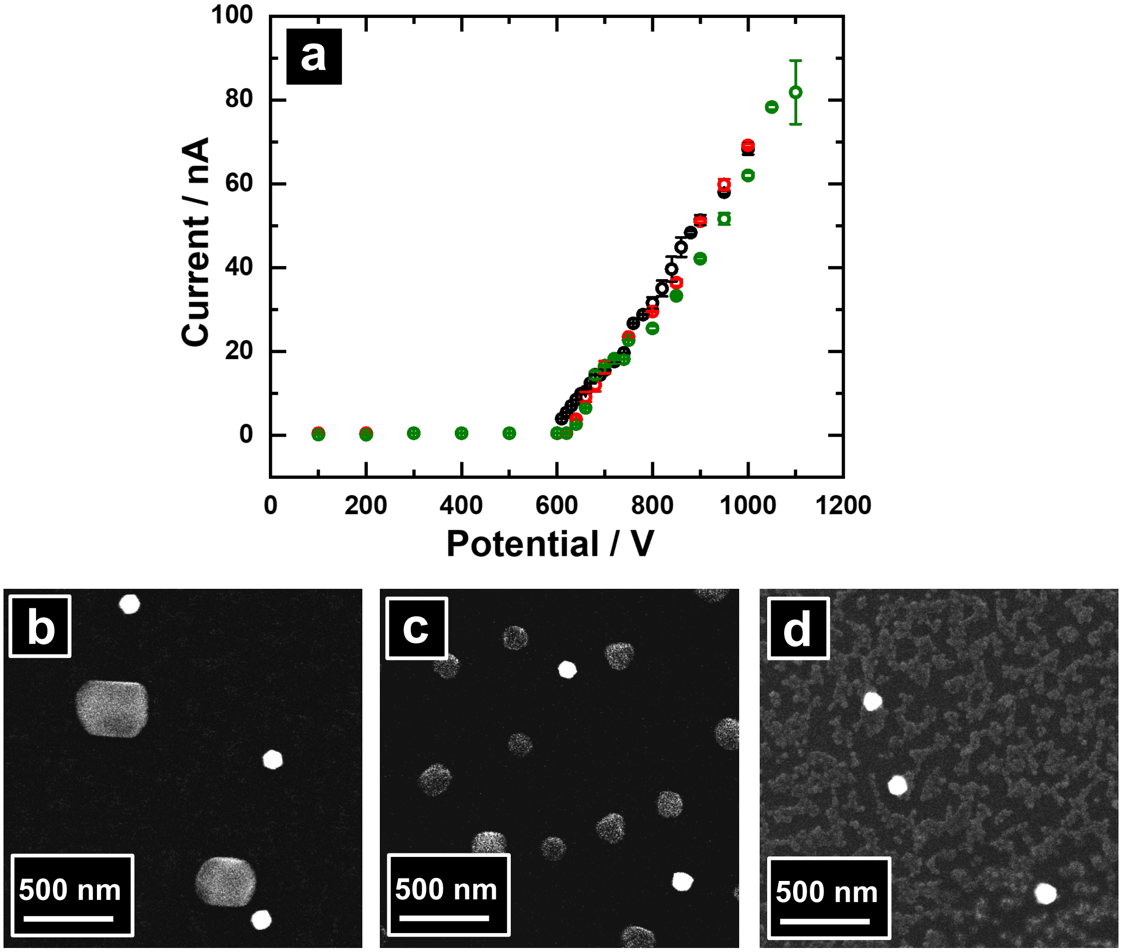

Figure S5. a) IV response recorded for 3 different theta pipette emitters; where one barrel was filled with Au OD solution and second barrel with 2.5 mM KCl solution, and 2 mm spray distance was maintained; electron micrographs of center regions from ES deposited spots at **b)** 2 nA, **c)** 4 nA and **d)** 8 nA of ES currents.

Table S1. Single particle deposition and variation in local surface density

Table S1. % Single particle and variation in local surface density for different ES operational parameters

Condition	Pipette tip size (µm)	Spray Distance (mm)	ES Current (nA)	% Single particles	% Variation in local surface density
Reference	1	2	8	96.3	8.8
Spray distance	1	0.5	8	92.8	5.6
	1	3.5	8	98.1	26.5
ES Current	1	2	2	95.8	14.4
	1	2	4	97.1	11.7
Emitter size	5	2	8	94.9	12.2
	10	2	8	57.5	15.5

Figure S6. ES deposition of Au ODs with different sizes of theta emitters

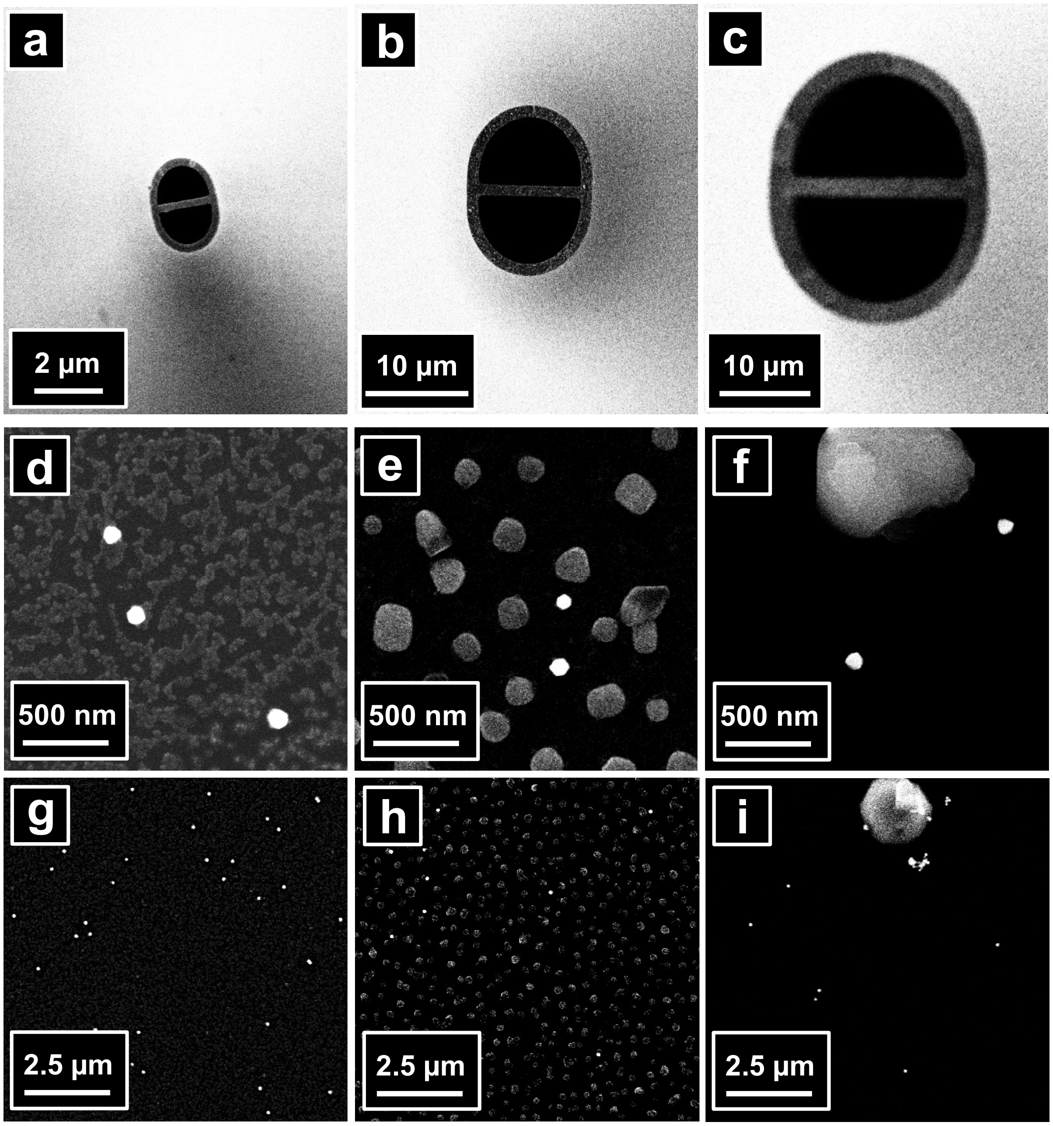

Figure S6. Electron micrographs of the theta emitter tips **a)** 1 µm, **b)** 5 µm and **c)** 10 µm each barrel; **(d-f)** corresponding central regions from the ES deposited spots with 2 mm spray distance and 8 nA ES current; **(g-h)** at a lower magnification, micrographs give better idea about the surface density and nature of single Au OD ES deposition from the three emitter sizes.

References

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