

Supporting Information for:

Shaping the Synthesis and Assembly of Symmetrically Stellated Au/Pd Nanocrystals with Aromatic Additives

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Chemicals. L-ascorbic acid (L-AA, $C_6H_8O_6$, 99%), palladium(II) chloride ($PdCl_2$, 99.98%), chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.9%), sodium borohydride ($NaBH_4$, 98.5%), cetyltrimethylammonium bromide (CTAB, 98%, lot # SLBD0174 V), and sodium salicylate ($NaC_6H_5O_3$, 99.5 %) were used as purchased from Sigma Aldrich. 3-Methyl salicylic acid ($C_8H_8O_3$, 98%), 2, 6-dihydroxybenzoic acid ($C_7H_6O_4$, 98%), 5-bromosalicylic acid ($C_7H_5BrO_3$, 99%), and 5-aminosalicylic acid ($C_7H_7NO_3$, 98%). Concentrated hydrochloric acid (HCl, 12.1 M) was purchased from Mallinckrodt. Nanopure water ($18.2\text{ M}\Omega \cdot \text{cm}$) was used in all experiments. An aqueous 10 mM H_2PdCl_4 solution was prepared by stirring dissolved $PdCl_2$ (44.6 mg) in 25 mL of HCl (pH 1.69) for 1 h while heating and stirring at 70 °C.

Synthesis Details. Au-Pd octopods are prepared by a double seeded method in which gold nanoparticle seeds are prepared first. These seeds are then used to make gold nanoparticle cores, which are then used to synthesize Au-Pd octopods via seed-mediated co-reduction. Each step is described below.

Gold Nanoparticle Seeds. To make the initial Au seeds, 1 mL of $HAuCl_4$ (2.5 mM), 5 mL of CTAB (150 mM), and 4 mL water were combined. While this solution was stirring vigorously (~800 RPM) 0.6 mL of a freshly-prepared ice-cold solution of $NaBH_4$ (10 mM) was rapidly injected via pipette, turning the solution from yellow-orange to brown. This solution was left stirring at 800 RPM at room temperature for 3 hours to ensure the full decomposition of $NaBH_4$. A 0.2 mL aliquot was then diluted with 19.8 mL of

water. The seeds were aged at room temperature for 3 days to prepare Au cores for Au-Pd nanocrystal formation.

Gold Nanoparticle Cores. To synthesize Au cores, 0.1 mL of HAuCl_4 (10 mM) solution was added to 2 mL of CTAB (0.2 M) solution followed immediately by 1.5 mL of L-AA (0.1) solution, which when added turned the mixture from yellow-orange to clear. This solution was immediately diluted to 25 mL with water followed promptly by adding 1.0 seed solution. This reaction vial was capped and allowed to sit undisturbed in a 25°C oil bath for 24 h. During the 24 h, the solution turned from clear to lavender.

Gold-Palladium Octopods. To prepare Au/Pd octopods, 2 mL of water or a solution containing an aromatic additive (3-methylsalicylic acid (20 mM), sodium salicylate (40 mM), 2, 6-dihydroxybenzoic acid (16 mM), 5-bromosalicylic acid (8 mM), or 5-aminosalicylic acid (6 mM)) was added to the entire Au core solution. This procedure was followed by the simultaneous addition via separate pipettes of 2 mL H_2PdCl_4 (1 mM) and HAuCl_4 (200 mM). The vial was gently mixed by inversion followed promptly by the addition of 0.5 mL of L-AA (0.1 M) solution. This vial was then capped and allowed to sit, without stirring, in a 25 °C oil bath for 24 h.

Characterization. Images of the nanoparticles were taken via a FEI Quanta 600F Environmental scanning electron microscope operated at 30 kV and a spot size of 3. STEM/TEM images were taken on a JEOL JEM 3200FS transmission electron microscope at 300 kV and a spot size of 1 with a Gatan 4k x 4k Ultrascan 4000. Energy dispersive X-ray spectra were obtained with an Oxford INCA dispersive X-ray system interfaced to the JEM 3200FS TEM, operating at 300 kV. Samples for TEM analysis were prepared by washing a carbon-coated copper grid with chloroform to remove Formvar, then drop-casting a dispersed particle solution onto the grid. Samples for SEM and EDX analysis were prepared by drop-casting a dispersed particle solution onto a silicon wafer and then washing the wafer twice with methanol after initial solvent evaporation. Raman measurements were measured using a Renishaw InVia microscope using WiRE software. Zeta potentials of prepared solutions were performed on a Malvern Zetasizer Nano Zs instrument at 25 °C with a 633 nm laser. To prepare the zeta potential measurements, concentrated samples were diluted 20:1 in water resulting in an attenuator of 9 and a UV/vis peak absorbance of 0.222. FT-IR was performed on a Vertex 70v. For FT-IR experiments, 0.1 mL of each unwashed sample was individually dropcasted onto a clean silicon wafer and vacuum dried for at least 3 hours.

XPS experiments were performed using PHI *VersaProbe* II instrument equipped with monochromatic Al $K\alpha$ source. Instrument base pressure was ca. 4.8×10^{-10} torr. An X-ray power of 25 W at 15 kV was used for all experiments with a 100 μm beam size. The instrument work function was calibrated to give a binding energy (BE) of 84.0 eV for Au $4f_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a BEs of 932.7 eV and 368.3 eV for Cu $2p_{3/2}$ and Ag $3d_{5/2}$ photoemission lines, respectively. The ultimate *VersaProbe* II instrumental resolution was determined to be 0.12 eV using the Fermi edge of the valence band for metallic silver for UPS (HeII line). Dual charge compensation was used on all samples. High-resolution Au 4f, Pd 3p and C 1s spectra were taken with a minimum of 10 - 60s scans using a 0.1 eV step and pass energies 23.5 eV, 93.9 eV, and 11.75 eV, respectively, using PHI software *SmartSoft -XPS* v2.0 and processed using PHI *MultiPack* v9.0 and CasaXPS v.2.3.14. The carbon 1s peak was fitted using a combination of Gaussians and Lorentzians with 30-50% of Lorentzian contents. Shirley background was used for curve-fitting.

For XPS experiments, the samples were drop casted onto native surface of silicon wafer (see Figure S9E), dried, and then washed at least three times with methanol until no excess surfactant was observable. With the $1.3 \times 1.3 \text{ mm}^2$ field of view in secondary electron x-ray imaging (SXI) mode the samples were examined in order to select the region with the best uniformity and was representative of the sample (see Figure S9B-D). To confirm reproducibility of XPS measurements, spectra was collected from three spots per sample labelled B-1, B-2, B-3; C-1, C-2, C-3 and D-1, D-2, D-3 (Figure S9 A-D) for samples prepared with 2 mL of 0.04 M sodium salicylate, 2 mL 0.006 M 5-aminosalicylic acid, and without additives, respectively. The resulting spectra showed a good consistency even for the spots separated as far as $\sim 1000 \mu\text{m}$ as seen from the Figure S9A for Pd $3p_{1/2}$ transition, the weakest feature among selected regions of study.

The Au 4f and Pd 3p levels binding energies reported here were measured in relation to adventitious (aliphatic) carbon (deconvoluted C 1s component of at 284.8 eV, see Fig. S8C). The convoluted carbon 1s suggests the presence of sp^2 (at the same as adventitious component binding energy of 284.8 eV) and sp^3 ($\sim 286 \text{ eV}$) C species and consistent with the literature reports.¹

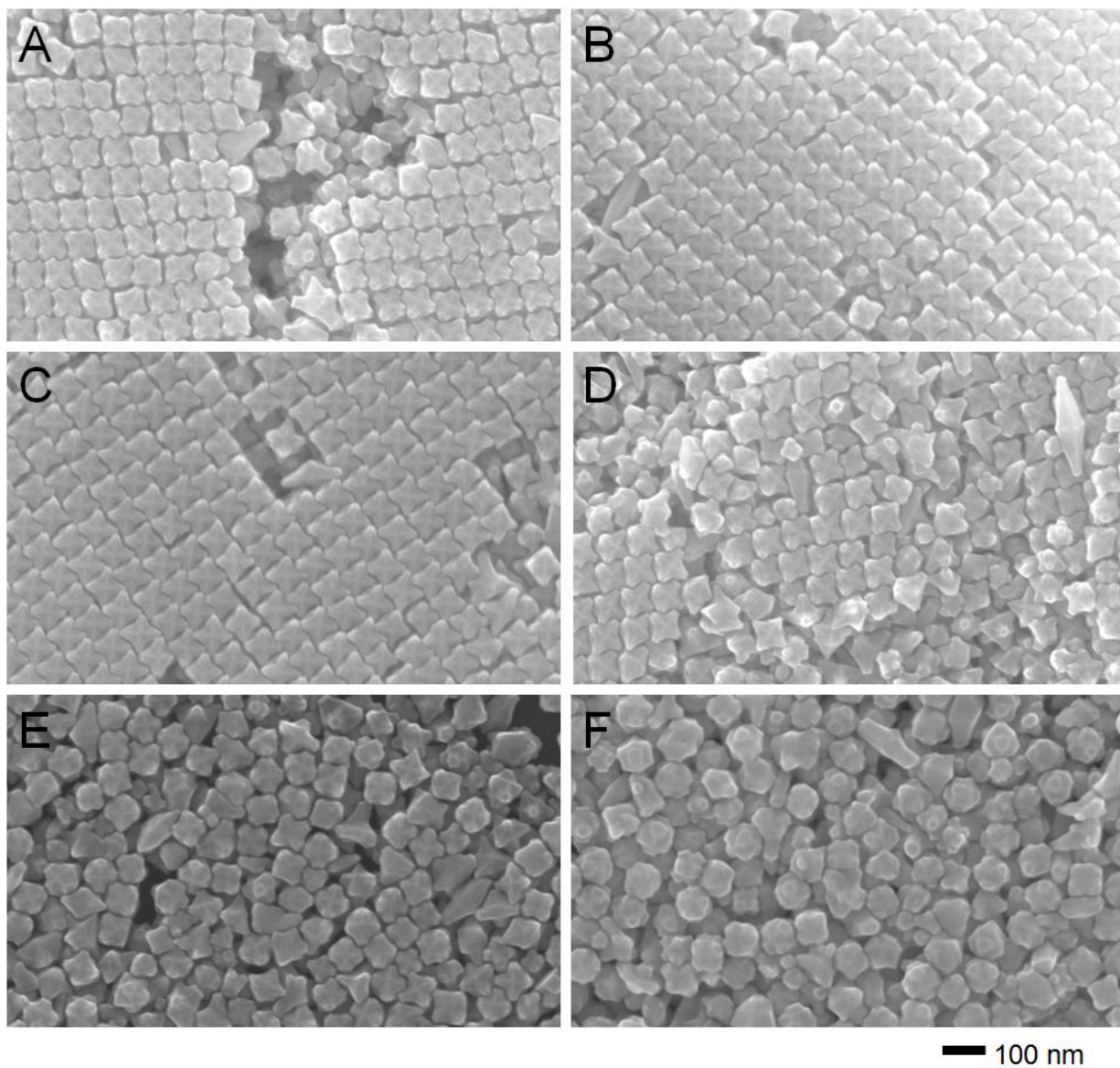


Figure S1. SEM images of Au/Pd octopods prepared with 2.0 mL of 3-methylsalicylic acid at the following concentrations: (A) 0 mM, (B) 2 mM, (C) 4 mM, (D) 6 mM, (E) 8 mM, and (F) 10 mM.

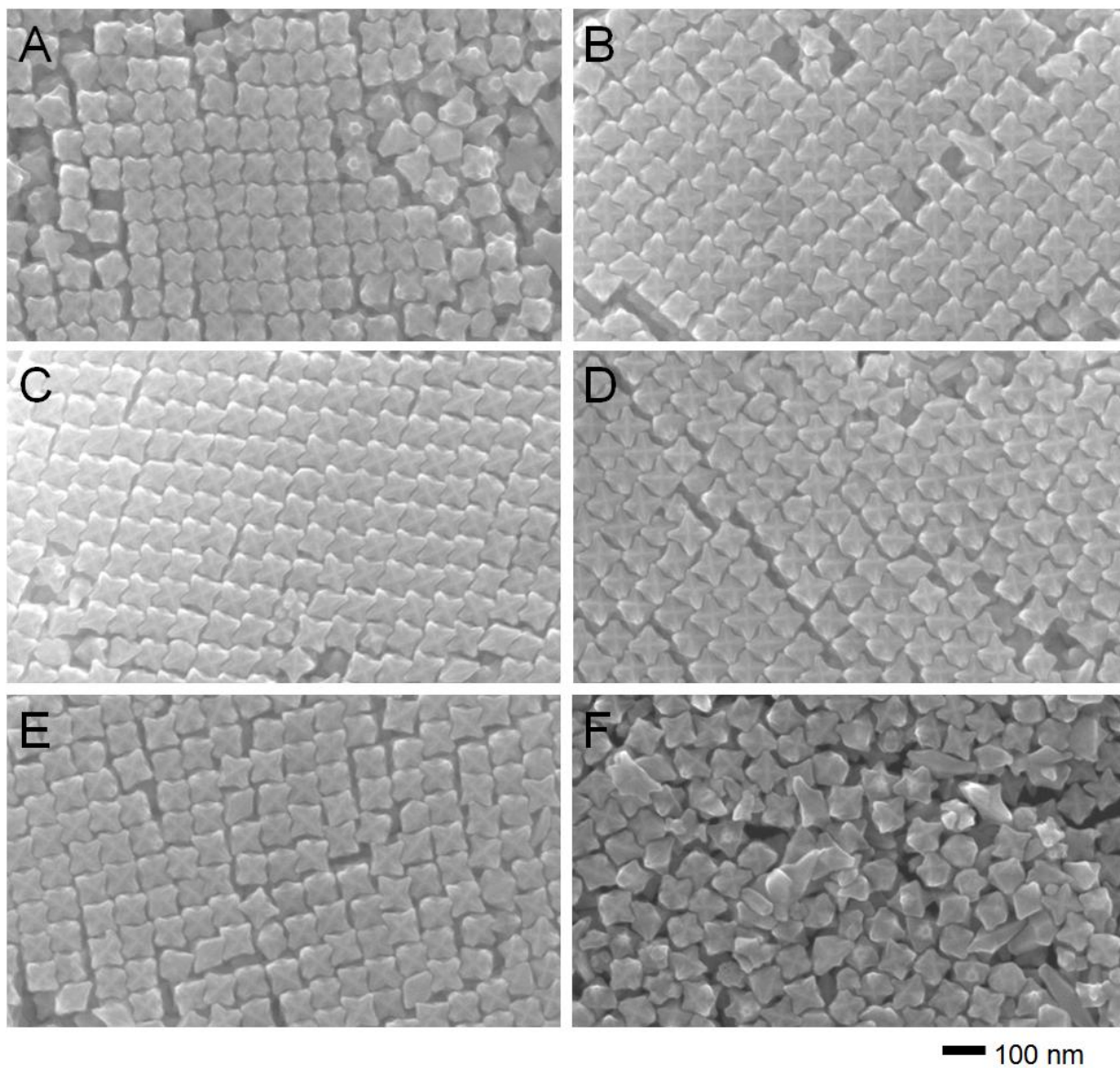


Figure S2. SEM images of Au/Pd octopods prepared with 2.0 mL of sodium salicylate at the following concentrations: (A) 0 M, (B) 0.02 M, (C) 0.04 M, (D) 0.06 M, (E) 0.08 M, and (F) 0.1 M.

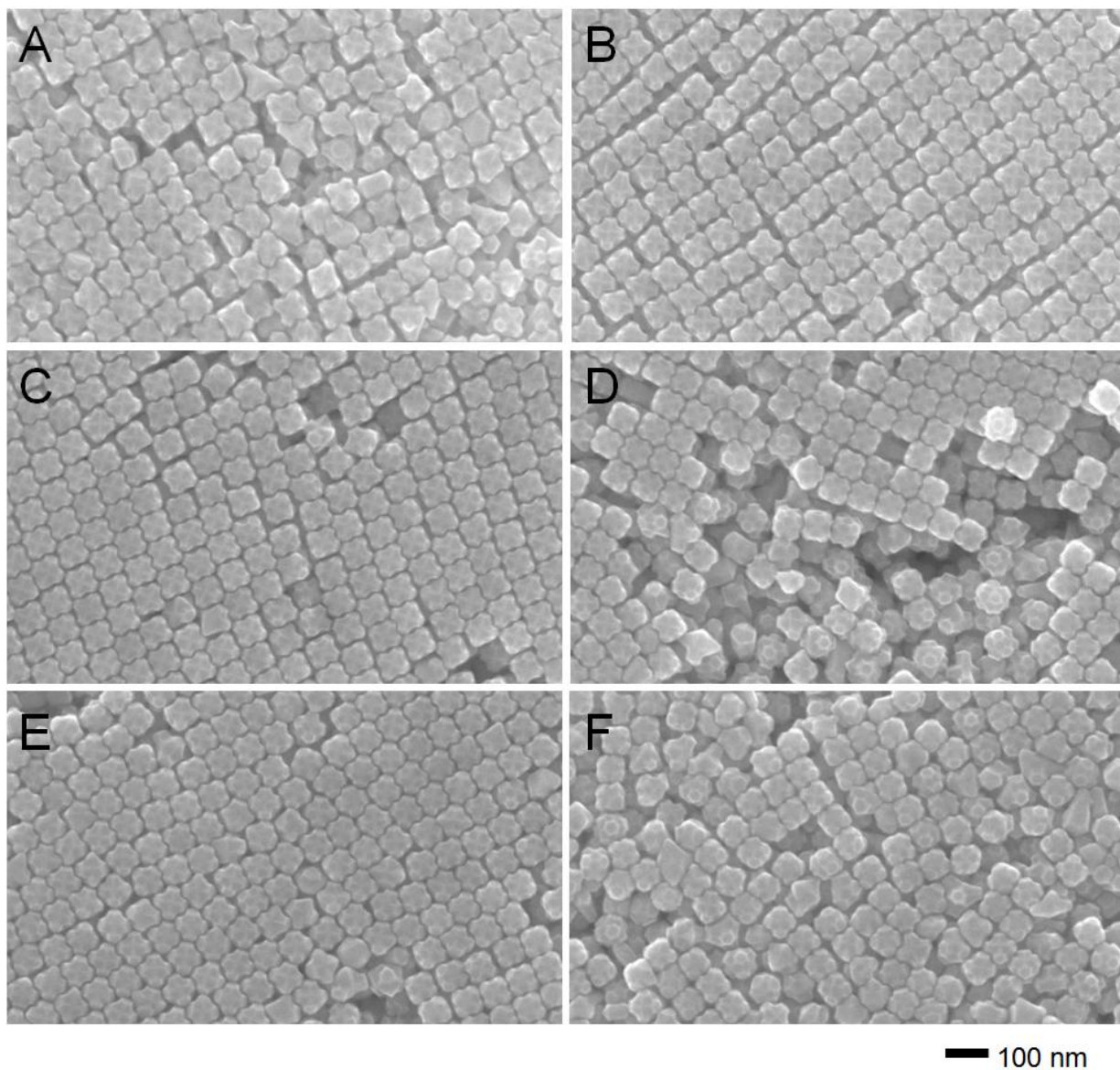


Figure S3. SEM images of Au/Pd octopods prepared with 2.0 mL of 6-dihydroxybenzoic acid at the following concentrations: (A) 0 mM, (B) 4 mM, (C) 8 mM, (D) 12 mM, (E) 16 mM, and (F) 20 mM.

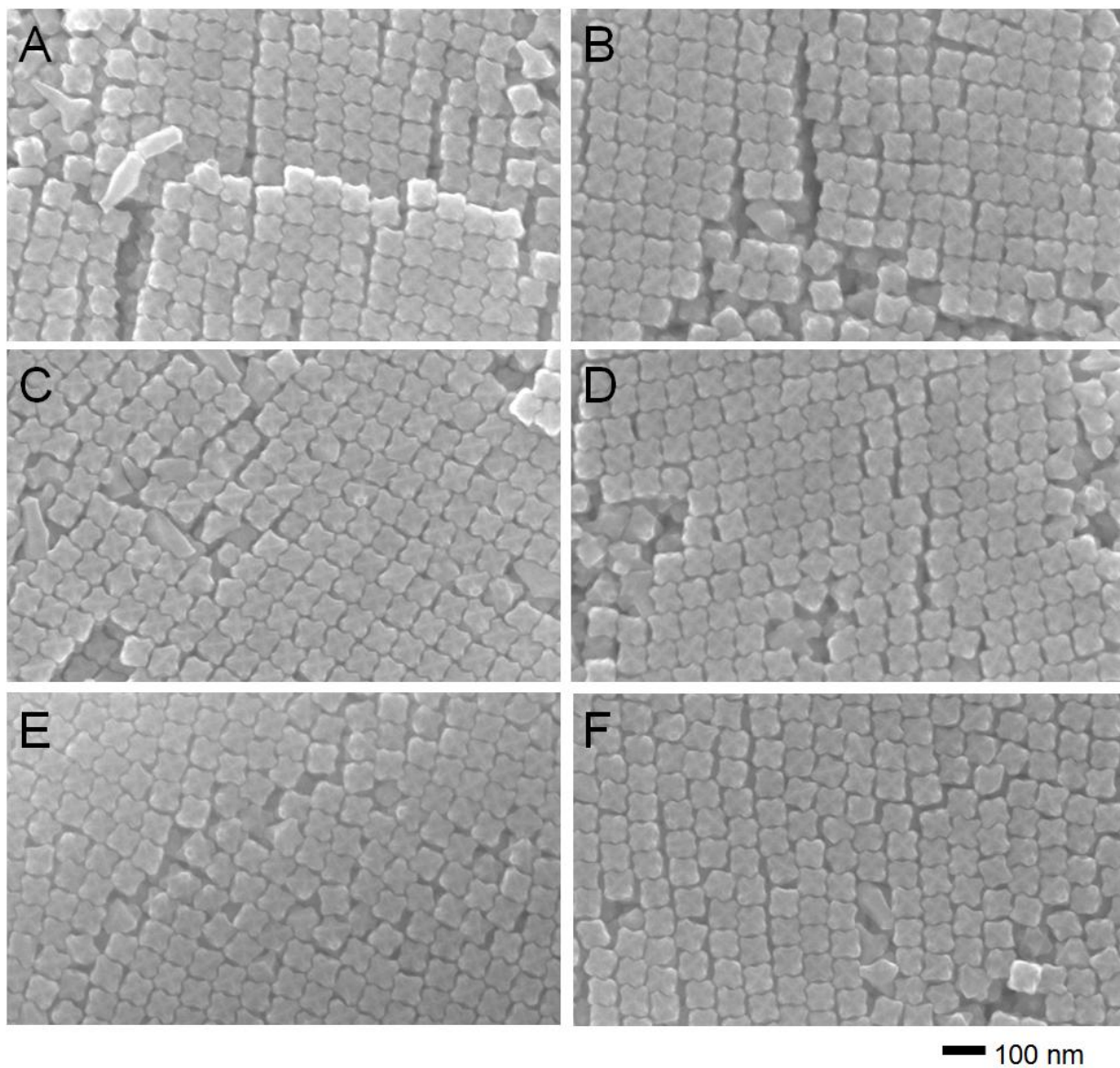


Figure S4. SEM images of Au/Pd octopods prepared with 2.0 mL of 5-bromosalicylic acid at the following concentrations: (A) 0 mM, (B) 2 mM, (C) 4 mM, (D) 6 mM, (E) 8 mM, and (F) 10 mM.

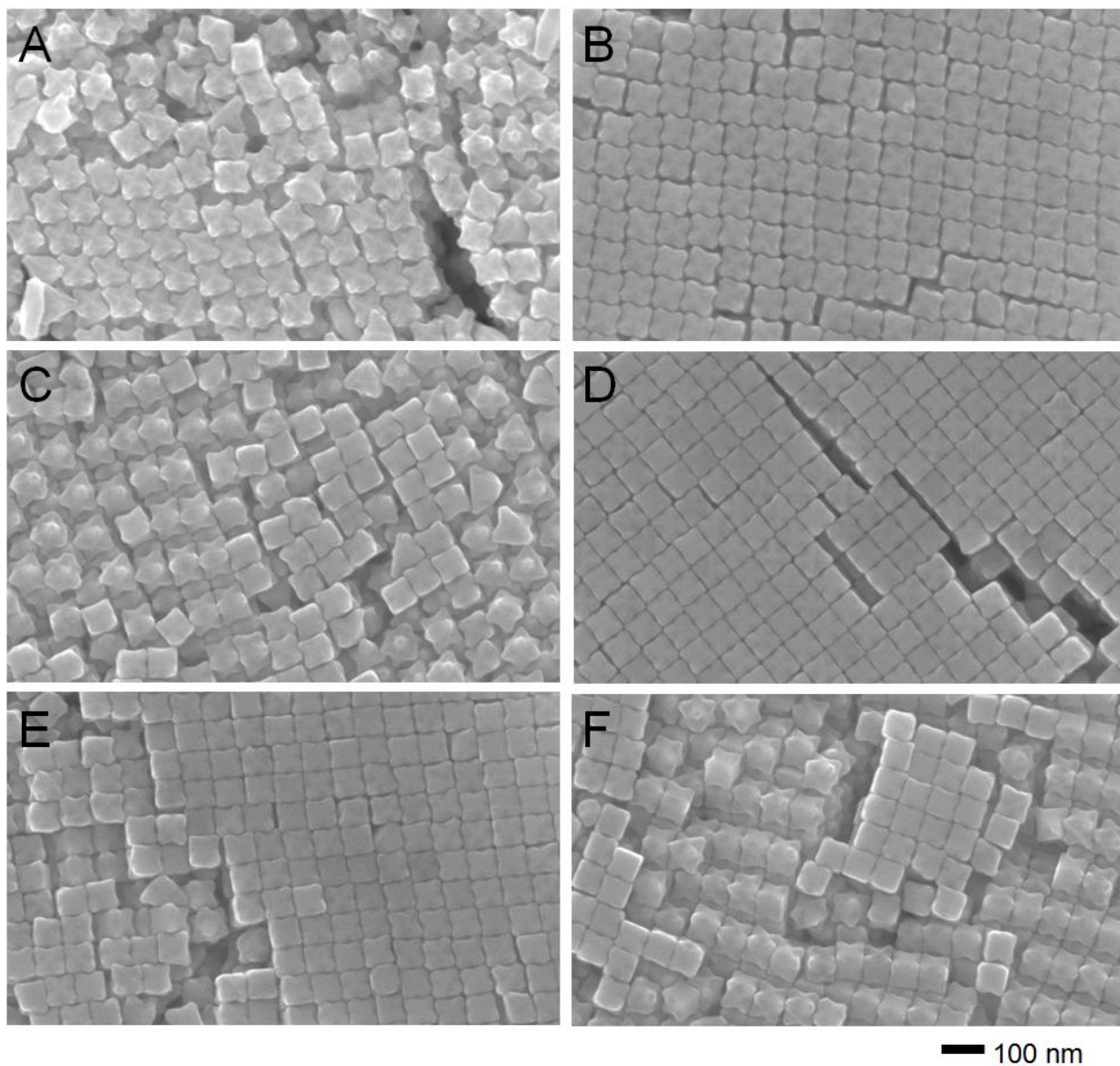


Figure S5. SEM images of Au/Pd octopods prepared with 2.0 mL of 5-aminosalicylic acid at the following concentrations: (A) 0 mM, (B) 2 mM, (C) 4 mM, (D) 6 mM, (E) 8 mM, and (F) 10 mM.

Sample	pK _a	Measurement	A	B	C	D	E	F
3-Methyl salicylic acid	3.06	Conc. (M)	0	0.02	0.04	0.06	0.08	0.1
		pH	2.48	2.46	2.48	2.50	2.54	2.58
Sodium salicylate	2.97	Conc. (M)	0	0.02	0.04	0.06	0.08	0.1
		pH	2.49	2.49	2.50	2.52	2.60	2.68
2, 6-Dihydroxybenzioc acid	1.23	Conc. (M)	0	0.004	0.008	0.012	0.016	0.02
		pH	2.43	2.36	2.34	2.29	2.27	2.25
5-Bromosalicylic acid	2.78	Conc. (M)	0	0.002	0.004	0.006	0.008	0.01
		pH	2.36	2.34	2.32	2.33	2.34	2.31
5-Aminosalicylic acid	2.41	Conc. (M)	0	0.002	0.004	0.006	0.008	0.01
		pH	2.55	2.54	2.55	2.56	2.58	2.55

Table S1. pH measurements of the growth solution that forms Au/Pd octopods during synthesis for each aromatic additive.

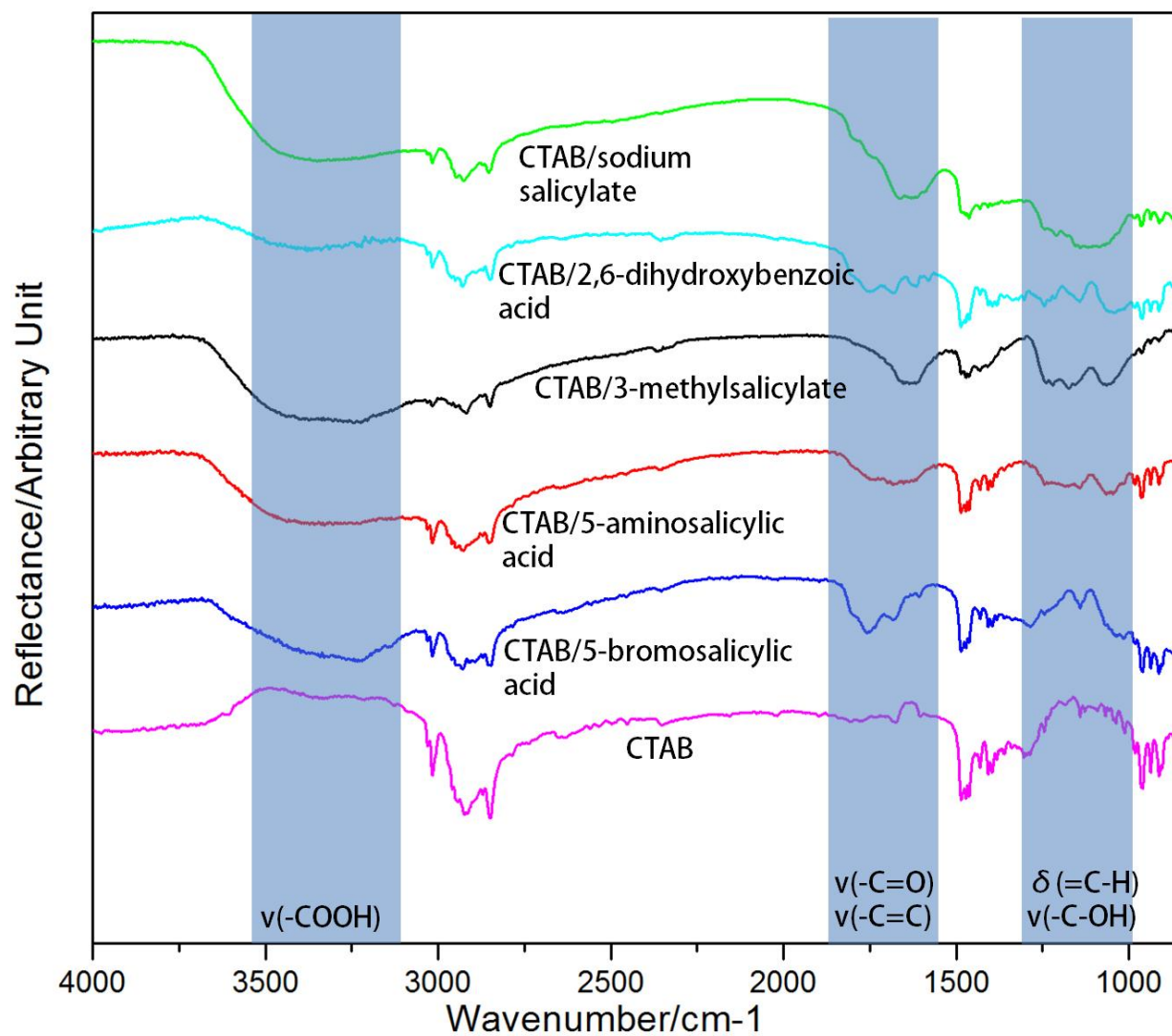


Figure S6. IR spectra of dried samples of Au/Pd octopods mixed with CTAB and an aromatic additive as well as a spectrum of Au/Pd octopods with only CTAB.

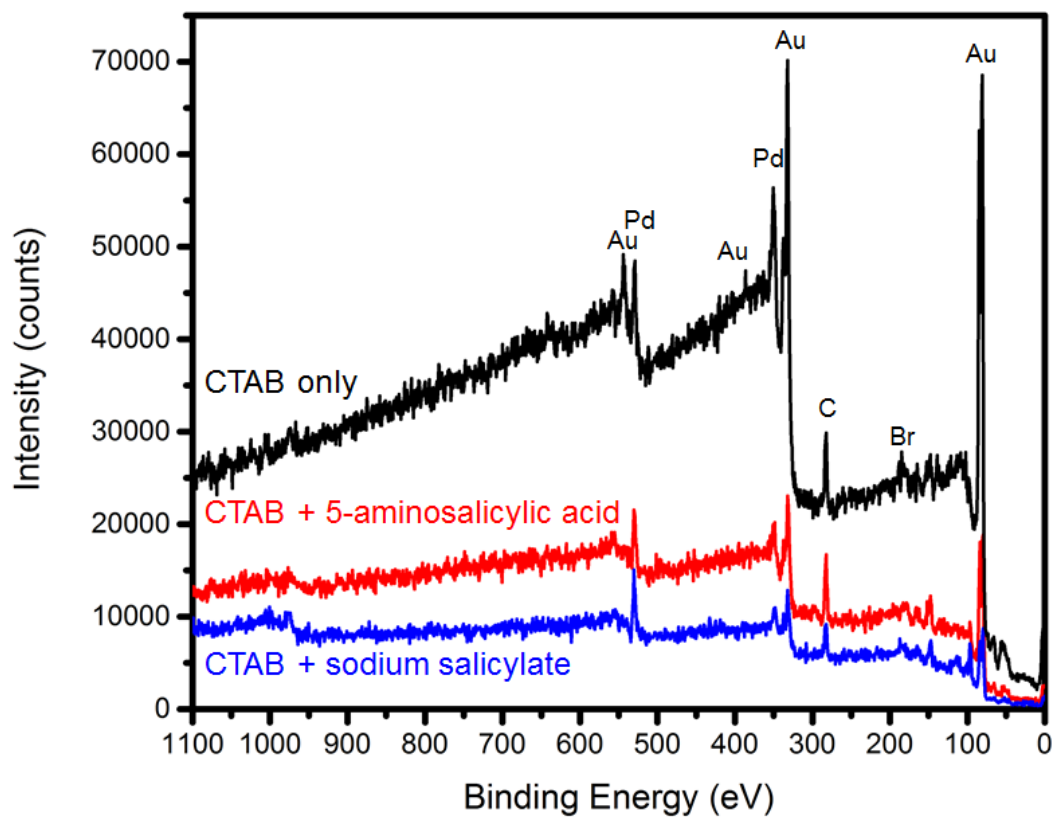


Figure S7. XPS long-range spectra for octopods prepared without additives (black), with 5-aminosalicylic acid (red), and with sodium salicylate (blue).

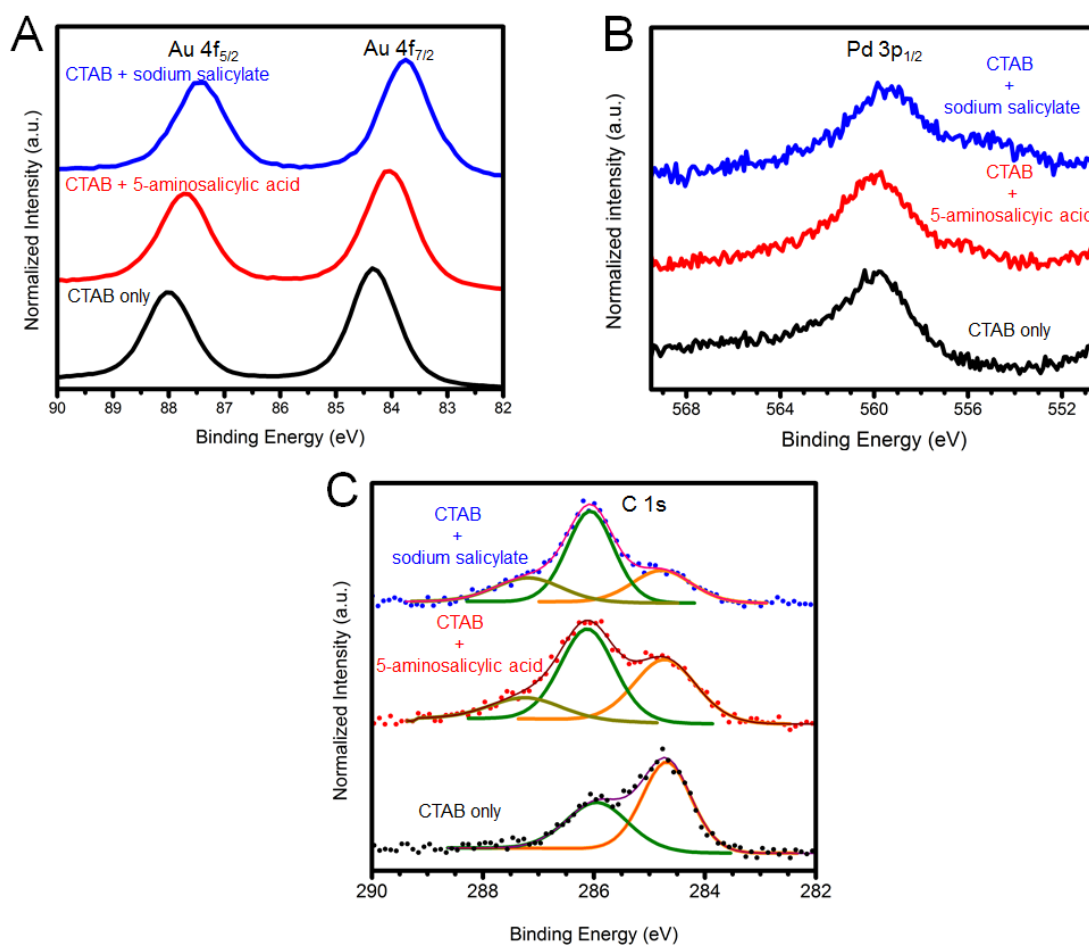


Figure S8. XPS spectra of octopods without aromatic additives (black), with 2 mL 0.006 M 5-aminosalicylic acid (red), and with 2 mL 0.04 M sodium salicylate (blue). In A) the Au 4f_{5/2} and Au 4f_{7/2} region, in B) the Pd p_{1/2} region, and in C) the C 1s region, where the solid lines underneath spectra correspond to deconvoluted peaks. For C) the orange peaks correspond to the adventitious hydrocarbon peak which was used for spectral calibrations, while assignments of the green and olive peaks cannot be made with certainty.

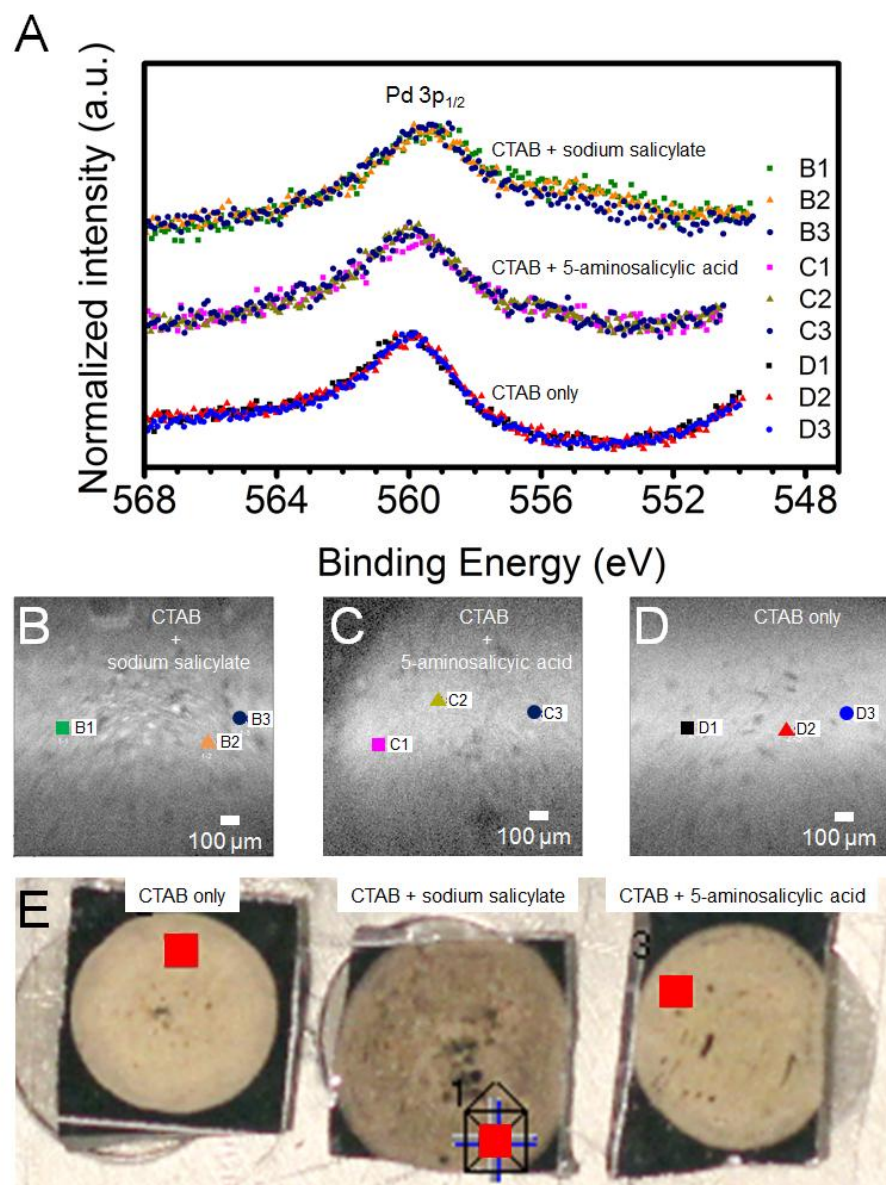


Figure S9. A) XPS spectra in the Pd $3p_{1/2}$ region of three separate scans of samples prepared with 2 mL 0.04 M sodium salicylate (top three), 2 mL 0.006 M 5-aminosalicylic acid (middle three), and without aromatic additives (bottom three). B-D) Corresponding SXI images indicating where on each sample spectra was acquired. E) Image of the samples dropcasted onto Si wafers indicating by the red squares where XPS was acquired.

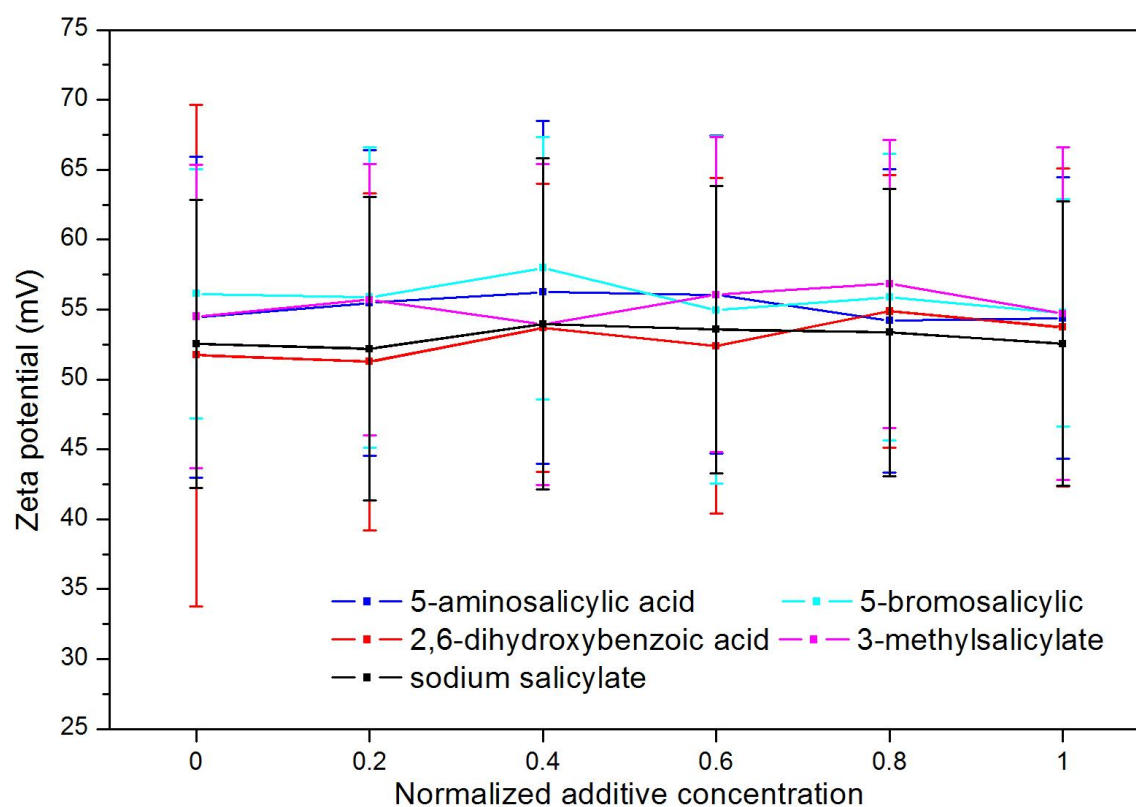


Figure S10. Plot of normalized additive concentration versus zeta potential. Normalization was done by taking the concentration of the additive divided by the maximum concentration of that additive in the study. Error bars represent standard deviation.

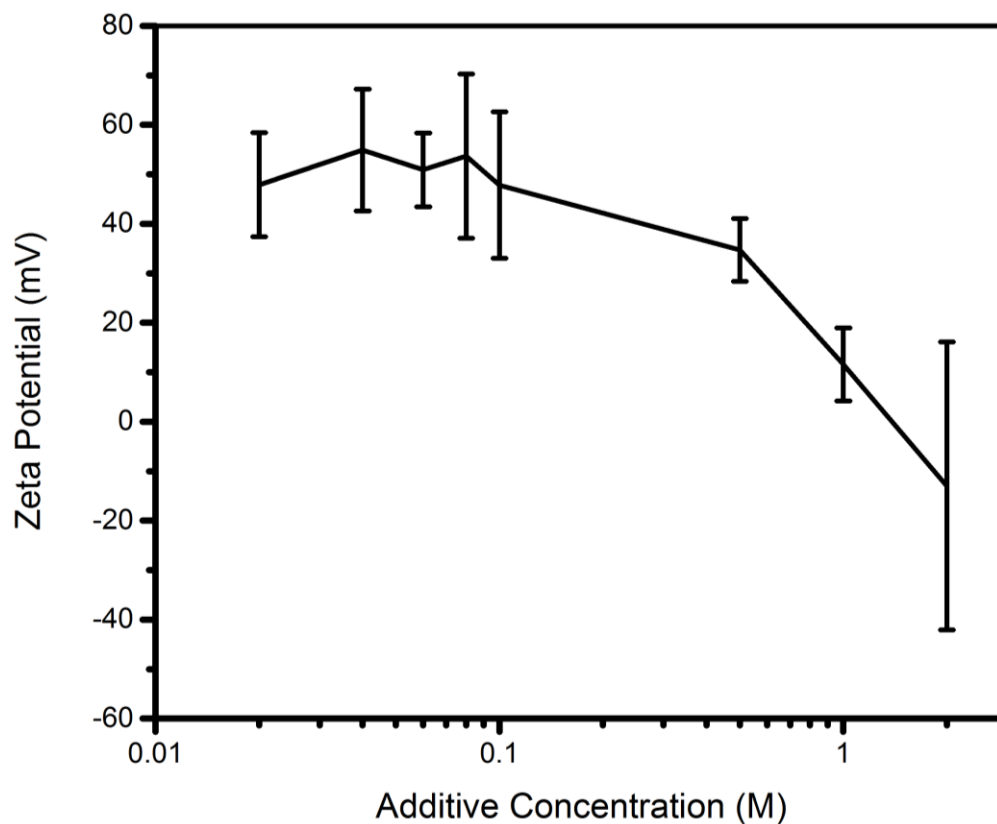


Figure S11. Plot of zeta potential measurements for nanoparticle solutions with varying concentrations of sodium salicylate. A difference in zeta potential can be observed, but only after adding considerably more organic additives than used in the study to generate homogeneous octopod samples.

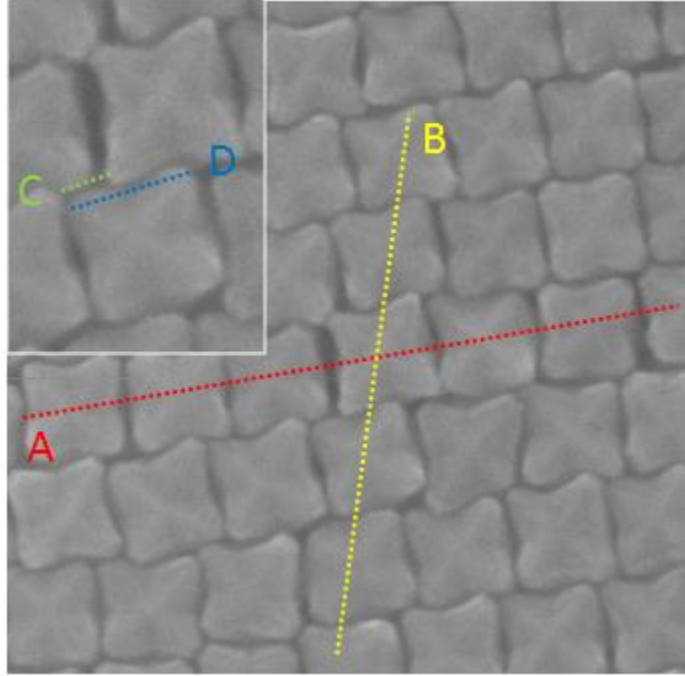


Figure S12. SEM image of assembled octopods with labels showing how % offset was measured. Line A shows the direction where octopods pack tip-to-tip with little offset. Line B shows the direction where the octopods pack tip-to-tip with some offset. Direction B is used for the offset measurements. Line C (top left inset) shows the distance between tips of two neighbor octopods along the direction indicated in Line B. Line D (top left inset) shows the tip-to-tip measurement of one octopod. The % offset is therefore calculated through the use of the following equation: $\% \text{ lattice offset} = \frac{C}{D} \times 100$.

Octopod Volume Proof

The volume of eight-pointed structures has been calculated before; however, no equation has been derived to take into account the unique structural features of octopods that include their hexagonal tips and tapered branches. Here, an equation is derived to account for these structural features and provide information about the octopod.

In deriving a method for calculating the volume of an octopod from scanning electron microscopy (SEM) images, the three-dimensional configuration of an octopod and its connection to the two-dimensional measurements that can be obtained from SEM imaging must be considered. For convenience and ease, the fewest parameters possible should be used and all parameters should be able to be measured facily, with little to no ambiguity from the measurement of one particle to another.

Octopods are eight-branched nanostructures with O_h symmetry. They can be thought of as structures with one branch protruding from each of the eight vertices of a cube. As shown in Figure S13, particles typically lay with four branches toward and four away from the substrate.

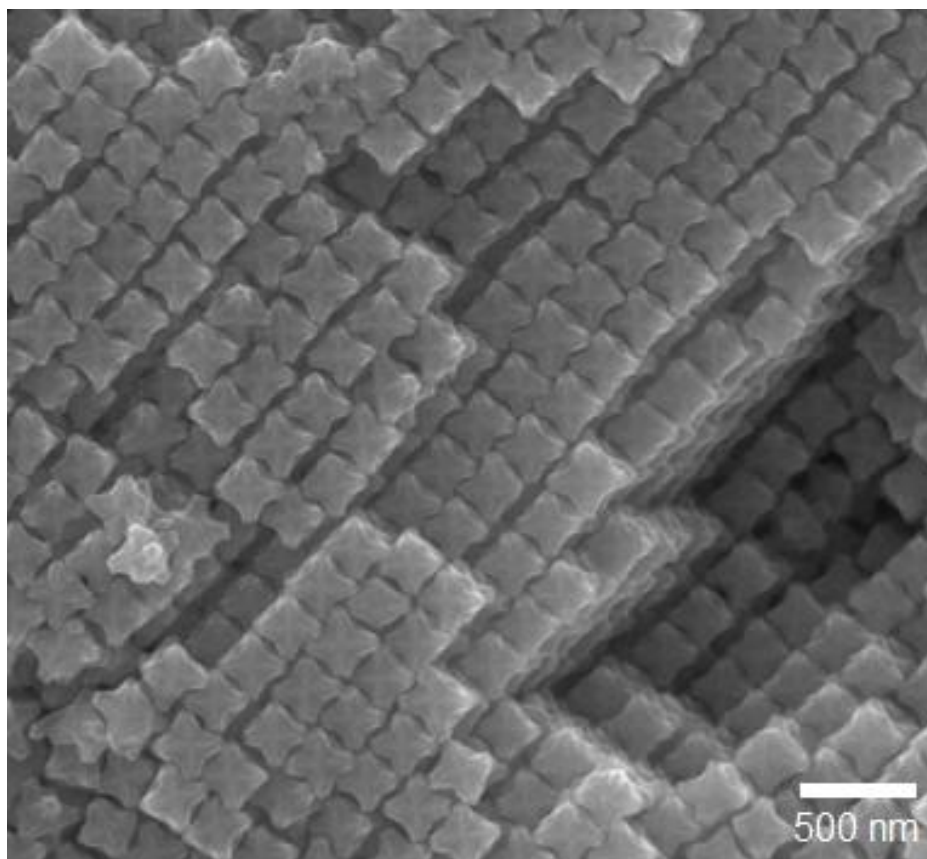


Figure S13

From SEM images of particles with this orientation, three parameters are easily measurable: tip-to-tip branch length (hereby denoted as x), tip thickness (hereby denoted as y), and branch base thickness (hereby denoted as q). These parameters are shown in Figure S14.

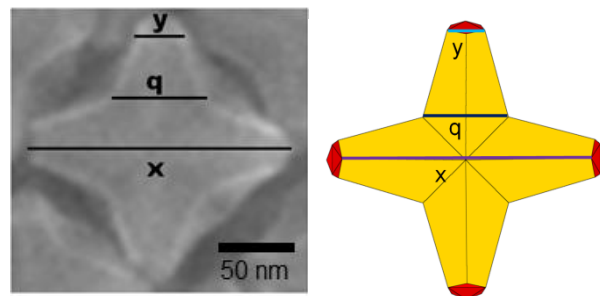


Figure S14

It should be noted that, while parameters y and q are directly relatable to the structure from measurements of two-dimensional SEM images, x is not. As indicated in Figure S15, parameter x shows the true tip-to-tip distance between two branches but does not account for the ascending and descending slope of the branches. So, for this proof, volume and surface area formulae will be derived in terms of z , which is the true length of a branch that accounts for its change in slope in all three dimensions. Afterward, z will be substituted for x , which is the measurable parameter.

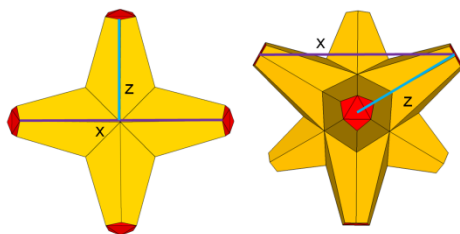


Figure S15

For the following proof, each branch will be approximated as a truncated hexagonal pyramid. This approximation simplifies the model so that the slopes of each of the edges of the hexagonal pyramid are the same. The truncated hexagonal pyramid design is based upon Figure S16, which shows an SEM image of an octopod so that one tip is facing away from the substrate. In this image, the tip is truncated so that a hexagon forms (outlined in red for clarity). Each edge along the hexagonal pyramid is tapered (shown in yellow dashes for clarity).

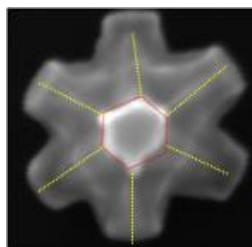


Figure S16

To mitigate the overlap of one branch with its neighbor, the truncated hexagonal pyramid will be separated into an additional section, as shown in Figure S17. For clarity, a is denoted as the center point of the base of the hexagonal pyramid that has overlap with its neighbors, b is denoted as the center point

of the base of the hexagonal pyramid that has no overlap with its neighbors, and c is the center point of the truncated tip of the hexagonal pyramid.

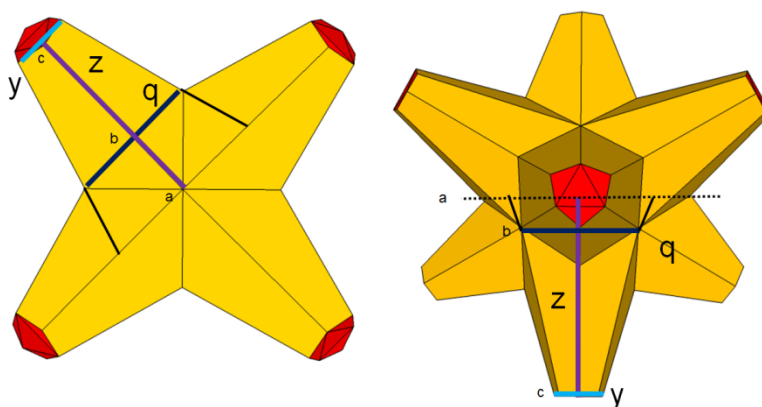


Figure S17

Truncating the branch at point b creates the surface shown in Figure S18.

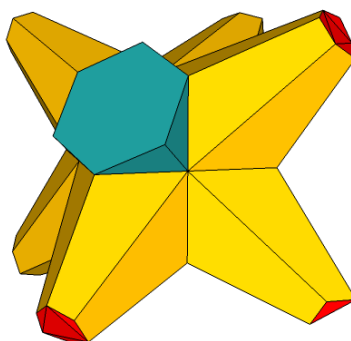


Figure S18

Figure S19 shows the abstracted portion of this interior region of the branch that does not overlap with its neighbors. It is an irregular polyhedron.

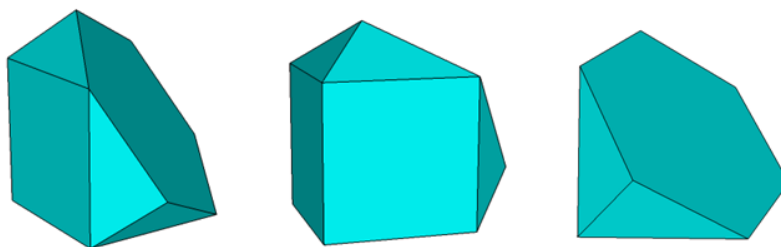


Figure S19

Therefore, we can generalize an equation that takes into account the two pieces that make up each branch: the truncated hexagonal pyramid and the irregular polyhedron.

$$Volume = 8(V_{irregular\ polyhedron} + V_{hexagonal\ pyramid})$$

For the irregular polyhedron portion, the square top could be completed by adding a triangular pyramid to the base of the hexagon, as shown in Figure S20. In doing so, the shape can now be thought of as three irregular tetrahedra attached to a cube.

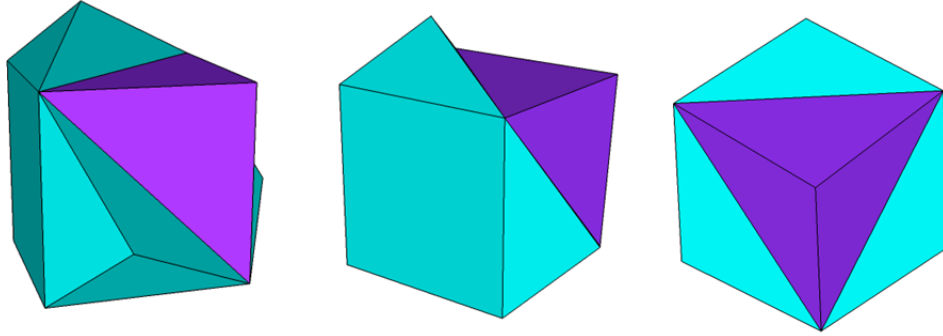


Figure S20

In Figure S21, the triangular pyramid is cut into one third. This irregular tetrahedron can be compared with one of the irregular tetrahedra on the exterior of the cube, painted green. Here, line *e* bisects the parallelogram formed from one third of the hexagon face of the irregular polyhedron. Thus, the interior angles of the tetrahedra must match. In addition, lines *f* and *g* intersect, thereby showing that the internal angles θ_1 and θ_2 are the same. Therefore, these two tetrahedra are the same size and volume. The irregular polyhedron portion can be modeled as the volume of a cube of size s_a , where s_a is the side of one of the vertices of the cube.

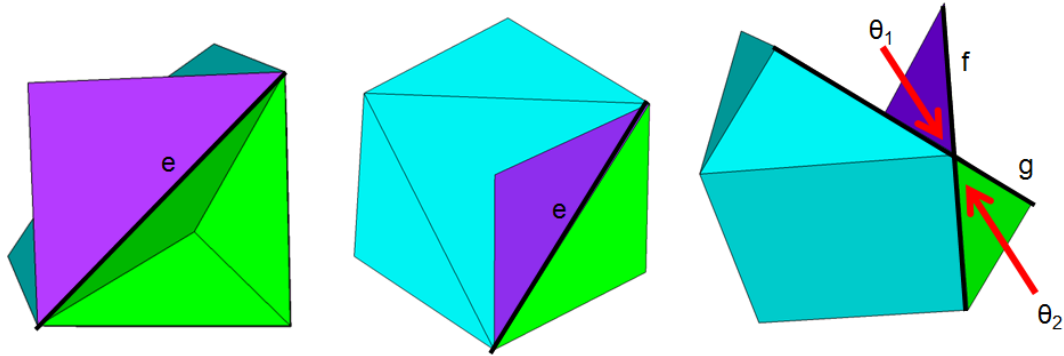


Figure S21

As shown in Figure S22 there is a relationship between s_a and q . Looking in the direction where four branches face away from the substrate, a right triangle forms where s_a forms both bases and q forms the hypotenuse. Therefore, $s_a = \frac{q}{\sqrt{2}}$.

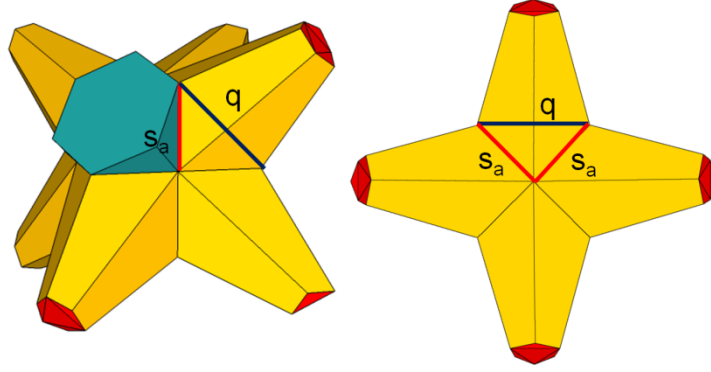


Figure S22

The volume of the irregular polyhedron can now be given in terms of q .

$$V_{\text{irregular polyhedron}} = \frac{\sqrt{2}q^3}{4}$$

The total volume of the octopod can be expressed with this defined term. In addition, the truncated hexagonal pyramid can be broken down into the two terms: one with a base at point b and one with a base at point c.

$$\text{Volume} = 8 \left(V_b - V_c + \frac{\sqrt{2}q^3}{4} \right)$$

The volume of a hexagonal pyramid can be derived from the following equation where n is the number of sides of the regular polyhedron, h is the height of the polyhedron, and s is one side of the polyhedron:

$$V_{\text{Pyramid}} = \frac{n}{12} h s^2 \cot \frac{\pi}{n}$$

Therefore, for a hexagonal pyramid (HP), where $n = 6$:

$$V_{HP} = \frac{\sqrt{3}}{2} h s^2$$

The entire volume can then be rewritten in terms of h and s at points b and c.

$$\text{Volume} = 4\sqrt{3}(h_b s_b^2 - h_c s_c^2) + 2\sqrt{2}q^3$$

For clarity, Figure S23 shows the volume of an octopod with the branches not truncated. The length from the truncated base c to the nontruncated tip will be defined as z_0 .

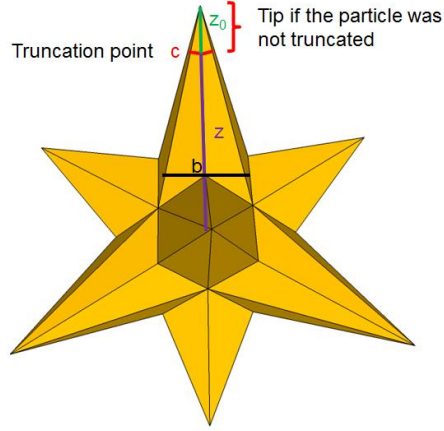


Figure S23

From this figure, it can be determined that $h_b = z + z_0 - \frac{q}{\sqrt{2}}$, $s_b = \frac{q}{2}$, $h_c = z_0$, and $s_c = \frac{y}{2}$. The entire volume can now be expressed in terms of z , z_0 , q , and y .

$$Volume = 4\sqrt{3} \left(\left(z + z_0 - \frac{q}{\sqrt{2}} \right) \frac{q^2}{4} - \frac{z_0 y^2}{4} \right) + 2\sqrt{2}q^3$$

This equation can be simplified and re-arranged.

$$Volume = \sqrt{3} \left(z_0(q^2 - y^2) + zq^2 - \frac{\sqrt{2}q^3}{2} \right) + 2\sqrt{2}q^3$$

However, z_0 is not a measurable parameter. Fortunately, it can be substituted with already defined variables.

Cutting the branch in half from the perspective shown in Proof Figure 11 in half results in a right triangle with angle $\frac{\theta}{2}$, which is opposite to bases $\frac{y}{2}$ and $\frac{q}{2}$. The height of the right triangle is $z + z_0$. See Figure S24 for details.

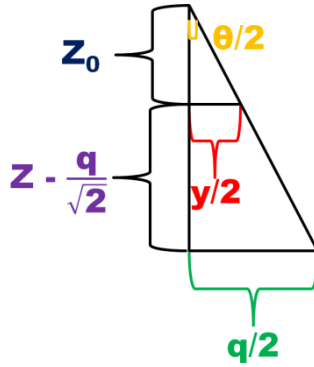


Figure S24

From this right triangle:

$$\tan \frac{\theta}{2} = \frac{\frac{q}{2}}{z + z_0 - \frac{q}{\sqrt{2}}} = \frac{\frac{y}{2}}{z_0}$$

This equation can then be solved for z_0 .

$$z_0 = \frac{yz - \frac{\sqrt{2}yq}{2}}{q - y}$$

Therefore, the equation for the volume of an octopod can be rewritten in terms of q , y , and z .

$$Volume = \sqrt{3} \left(\left(\frac{yz - \frac{\sqrt{2}yq}{2}}{q - y} \right) (q^2 - y^2) + zq^2 - \frac{\sqrt{2}q^3}{2} \right) + 2\sqrt{2}q^3$$

This equation can be simplified.

$$Volume = \sqrt{3} \left(\left(yz - \frac{\sqrt{2}yq}{2} \right) (q + y) + zq^2 - \frac{\sqrt{2}q^3}{2} \right) + 2\sqrt{2}q^3$$

Finally, z needs to be transformed into an expression in terms of x , y , and q . First, considering the octahedral symmetry of the branches, if the planar distance measured between two branches is x then the distance between each branch is $\frac{x}{\sqrt{2}}$. This proof is summarized in Figure S25.

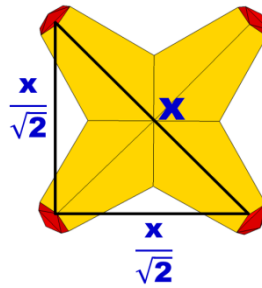


Figure S25

The relationship between x and z can be simplified to the shape of a cube where each vertex of a cube represents the tip of one of the branches of an octopod. In this model, x is a diagonal of one side of the cube, equivalent to the branch tip-to-tip measurement shown in Figure S25. As already noted, the side of

the cube would be $\frac{x}{\sqrt{2}}$. Parameter z would be the measurement from the interior of the particle to one branch tip. A summary of this model is shown in Figure S26.

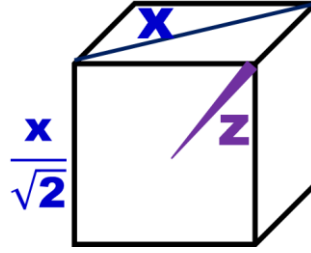


Figure S26

Therefore, it is possible to set z in terms of x and using the Pythagorean theorem.

$$z = \frac{\sqrt{6}}{4} x$$

Finally, this expression for z can be substituted into the main equation for volume to yield the master equation for the volume of an octopod.

$$Volume = \sqrt{3} \left(\left(\frac{\sqrt{6}}{4} xy - \frac{\sqrt{2} y q}{2} \right) (q + y) + \frac{\sqrt{6}}{4} x q^2 - \frac{\sqrt{2} q^3}{2} \right) + 2\sqrt{2} q^3$$

Octopod Surface Area Estimation Proof

The surface of an octopod is composed of 6 hexagonal faces located where the hexagonal pyramid is truncated and 48 quadrilateral faces along the sides of the branches. Like in the volume proof, for the surface area approximation will assume that the branches are truncated hexagonal pyramids. Figure S27 shows one face of a branch normal to the viewer. The blue dashed line cuts the face into two pieces: a trapezoid and a right triangle with hypotenuse $\frac{q}{\sqrt{2}}$. The sides of that right triangle would be approximately equal to $\frac{q}{2}$ (the parameter q would go “through” the branch and therefore the on-face edge would be a close approximation).

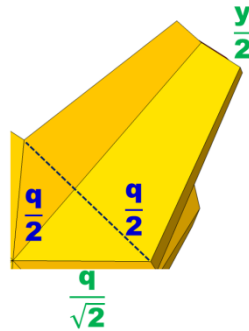


Figure S27

Recalling Proof Figure 13, it is possible to define one of the sides of the branch in terms of x and q . Figure S28 shows that this side is equal to $\frac{1}{2}\sqrt{x^2 - xq + 2q^2}$.

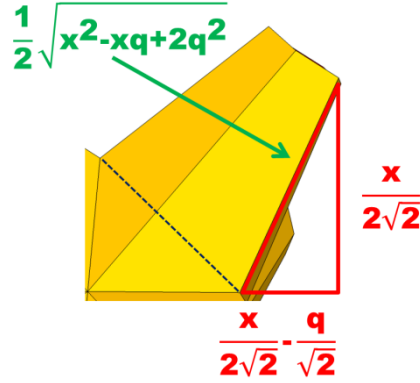


Figure S28

For the surface area approximation, both long sides of the trapezoid will be assumed to be equivalent. Figure S29 summarizes the calculated and estimated values for each of the sides of the quadrilateral.

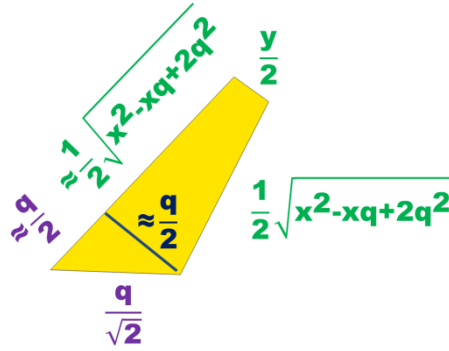


Figure S29

The area of the quadrilateral is the sum of the right triangle and the trapezoid with height $\frac{1}{2}\sqrt{x^2 - xq + 2q^2}$.

$$\text{Area of quadrilateral} \approx \frac{1}{8}q^2 + \frac{1}{8}qy\sqrt{x^2 - xq + 2q^2}$$

The area of the hexagon region can be expressed in terms of y , where y is the diameter of the hexagon.

$$\text{Area of hexagon} = \frac{3\sqrt{3}}{8}y^2$$

Adding together the 48 quadrilateral faces and 8 hexagons gives the master equation that approximates the surface area of an octopod.

$$\text{Surface area} \approx 6q^2 + 6qy\sqrt{x^2 - xq + 2q^2} + 3\sqrt{3}y^2$$

Reference

(1) Osswald, S.; Yushin, G.; Mochalin, V.; Kucheyev, S. O.; Gogotsi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 11635.