Supporting Information: Hybrid Lipid Membrane Coating "Shape-Lock" Silver Nanoparticles to Prevent Surface Oxidation and Silver Ion Dissolution

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To approximate the number of lipids necessary to cover silver nanoparticles (AgNPs) in a given volume of stock solution the first step requires that the number of nanoparticles per mL (N) is estimated. The first step to determine the number of nanoparticles per mL is to first determine the number of Ag atoms (Q) present in 1 mL of the stock solution where the quantity of $AgNO_3$ used for synthesis is known. Assuming the reduction of Ag^+ to Ag^0 goes to 100% completion, using Eq 1, where N_a is Avogadro's number, Q is determined by

$$Q = (\text{mol Ag}^+)(N_a) \qquad \text{Eq. 1}$$

Next determine the total number of Ag^0 atoms per nanoparticle (q_i) of a given volume using Eq 2,

$$q_i = V_i * \left(\frac{\rho_{Ag}}{FW}\right)(N_a) \qquad \text{Eq. 2}$$

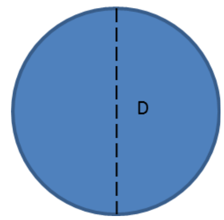
where q_i is the number of atoms contained in one nanoparticle of a given volume (i = rod, sphere, triangle), V_i is the volume of the nanoparticle shape, ρ_{Ag} is the density of Ag (g/nm^3), and F.W. is the atomic weight of Ag (g/mol). This equation operates from the known relationship between volume and density to determine mass that is converted to moles and subsequently to the number of atoms.

The volume (V_i) and surface area (SA_i) of a nanoparticle of a given shape can be derived from the following equations where,

Shape (V_i, SA_i) **Reference Graphic**

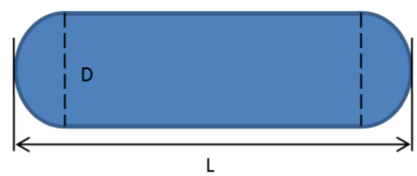
$$V_{sphere} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 \quad \text{Eq. 3}$$

$$SA_{sphere} = 4\pi\left(\frac{D}{2}\right)^2 \quad \text{Eq. 4}$$



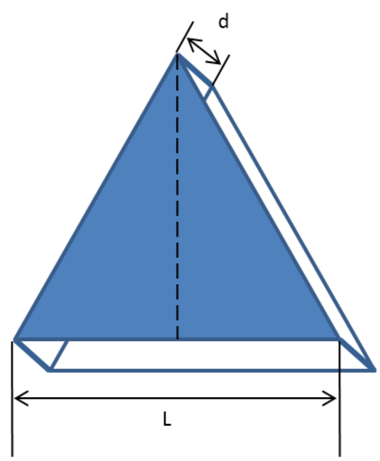
$$V_{rod} = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 + (L - D)\left(\pi\left(\frac{D}{2}\right)^2\right) \quad \text{Eq. 5}$$

$$SA_{rod} = 4\pi\left(\frac{D}{2}\right)^2 + (L - D)(\pi D) \quad \text{Eq. 6}$$



$$V_{triangle} = d\left(\frac{L}{2}(L * Sin(60))\right) \quad \text{Eq. 7}$$

$$SA_{triangle} = L\left((L * Sin(60)) + 3d\right) \quad \text{Eq. 8}$$



For a synthesis method that results in a heterogeneous mixture of AgNPs of varying shapes, the estimation of the total number of nanoparticles in 1 mL of stock must take into account the presence of other shapes. To determine the total number of nanoparticles or entities present in solution, we must determine the size and percent shape composition in each batch of AgNP synthesized by TEM analysis. If the percent shape composition of the final batch of nanoparticles (P_{sphere}, P_{rod}, and $P_{triangle}$), the quantity of Ag atoms required to form each constituent particle (q_{sphere}, q_{rod}, and $q_{triangle}$), and the total number of Ag atoms (Q) is known then the relationship between total number of nanoparticles (N_T) present and the number of constituent nanoparticles (N_{sphere}, N_{rod}, and $N_{triangle}$), is as follows,

$$N_{sphere} = N_T * P_{sphere} \quad \text{Eq. 9}$$

$$N_{rod} = N_T * P_{rod} \quad \text{Eq. 10}$$

$$N_{triangle} = N_T * P_{triangle} \quad \text{Eq. 11}$$

Therefore, the total number of atoms is,

$$Q = N_{sphere} * q_{sphere} + N_{rod} * q_{rod} + N_{triangle} * q_{triangle} \quad \text{Eq. 12}$$

Substitute of the known relations,

$$Q = P_{sphere} * N_T * q_{sphere} + P_{rod} * N_T * q_{rod} + P_{triangle} * N_T * q_{triangle} \quad \text{Eq. 13}$$

This can be rearranged to the following,

$$N_T = \frac{Q}{P_{sphere} * q_{sphere} + P_{rod} * q_{rod} + P_{triangle} * q_{triangle}} \quad \text{Eq.14}$$

After N_T is calculated, substitute that value back into Eq 9, 10, or 11 to calculate N_{sphere}, N_{rod}, $N_{triangle}$ that will be used to determine the number of lipids required to completely cover the AgNPs in a heterogeneous solution. The amount of PC required to cover an AgNP is calculated by using the SA for each shape of nanoparticle, Eq 4, 6, or 8 and dividing the surface of a sphere by the polar head group of lipid-based on a PC head group size of 69.4 Å^2 as in Eq 17.[1] Similarly, the outer leaflet (OF) is determined by using the SA of the AgNP based on the shape and an additional 4 nm in diameter as seen in Eq 18. This is an overestimate due to tessellation of the lipids around the AgNP and somewhat of an underestimate due to an anticipated 1 nm water cushion that separates the lipids from the surface, as observed with supported bilayers on glass beads.[2]

$$\mathrm{IF} = \frac{4\pi r^2}{69.4\ \mathrm{A}^{\circ 2}} \qquad \text{Eq. 17}$$

$$\mathrm{OF} = \frac{4\ \pi(\frac{D+4.}{2})^{2}}{69.4\ \mathrm{A}^{\circ 2}} \qquad \text{Eq. 18}$$

Total lipids needed per nanoparticle is IF + OF, which can be multiplied by N_{sphere}, N_{rod}, or $N_{triangle}$ to determine the number of lipids required for a 1 mL sample of stock with varying shapes and sizes.

For example, for a spherical nanoparticle of roughly 11 nm diameter, an estimated 611 molecules of PC are required for a single inner leaflet of lipids around the AgNP core and an additional ~1124 lipids are required to create an outer leaflet of lipids. Similarly, calculations for rods of length 20 nm and width 6 nm and triangles with a face width 32 nm and 18 nm thickness, yields an inner leaflet PC of ~580 and ~5417, for rods and triangles respectively, and outer counts of ~967 and ~7142 molecules, for rods and triangles respectively.

For a 1 mL solution of blue AgNPs, with shape distributions of spheres (35%), rods (1%), and triangles (64%), a total of 1.46 nmol of lipids are required for complete coverage. To account for this, any inefficiency in the transfer of liposomes to the silver surface and differences due to shape we used a total of 3.36 nmol and found that this provided complete coverage as demonstrated by cyanide stability (*vide infra*).

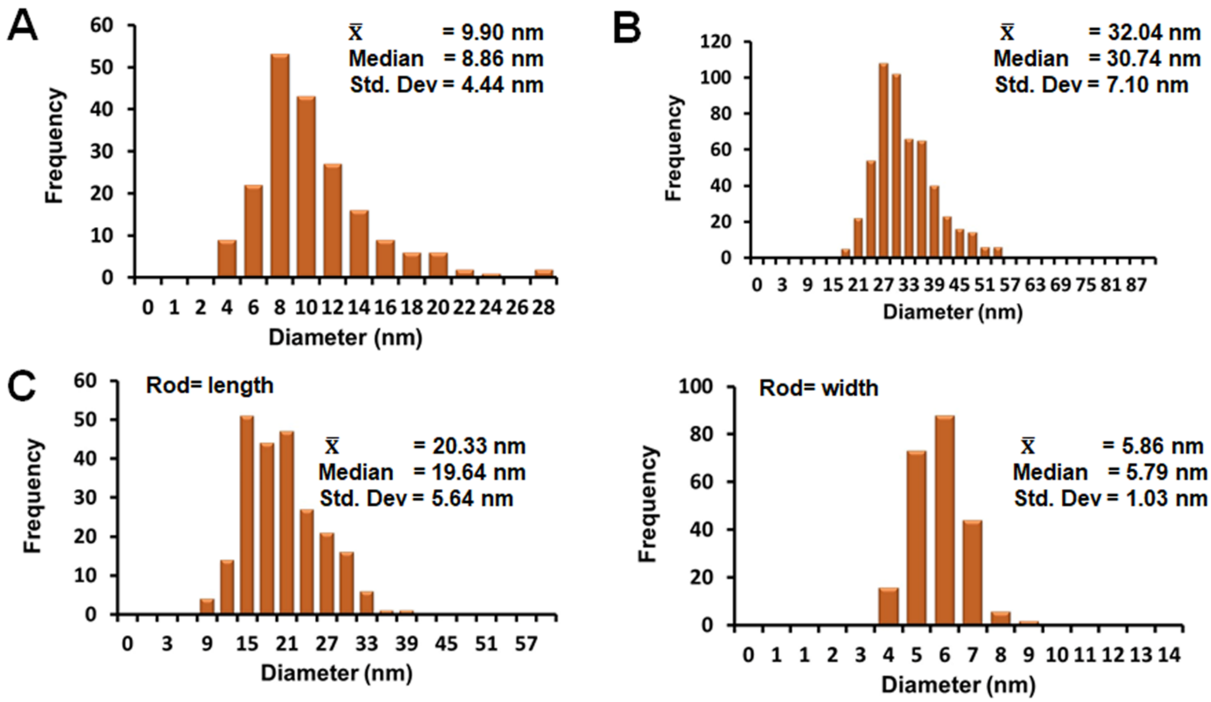


Figure S1. Representative distribution histogram analysis of A) spherical, B) triangular and C) rod-shaped (length and width) citrate-capped AgNPs nanoparticles

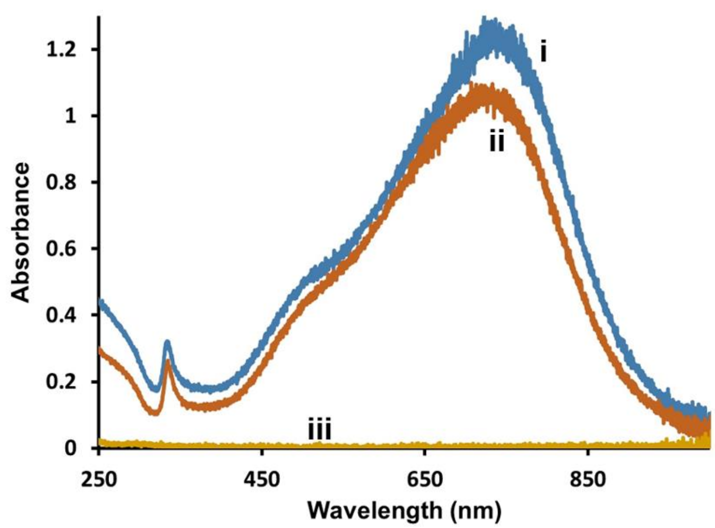


Figure S2. Representative UV-vis spectra of triangular-shaped Ag-SOA-HT (OD =1.2) i) before and ii) after the addition of KCN, and iii) Ag-SOA after KCN in 10 mM sodium phosphate buffer pH 8

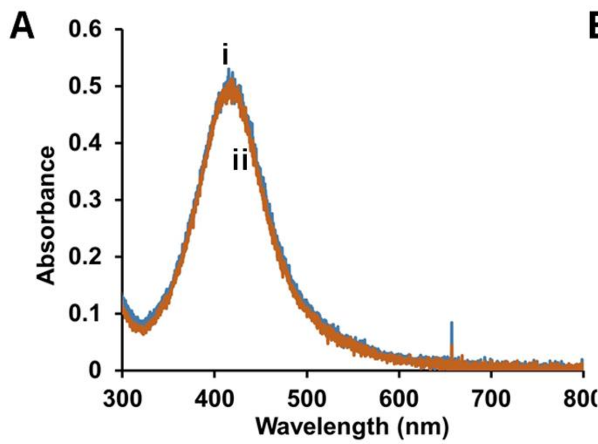


Figure S3. Representative UV-vis spectra of A) spherical and B) rod-shaped Ag-SOA-HT i) before and ii) after the addition of KCN in 10 mM sodium phosphate buffer pH 8.

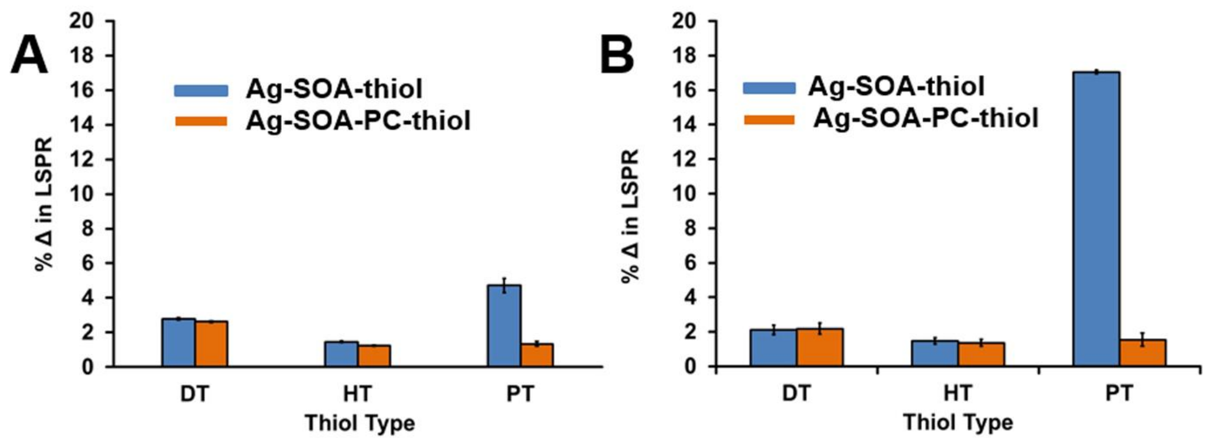


Figure S4. Percent change in the LSPR band of the triangular-shaped Ag-SOA-thiol (blue) and Ag-SOA-PC-thiol (orange) nanoparticles after A) 1 day and B) 21 days after preparation in H_2O at 25 ºC in the dark.

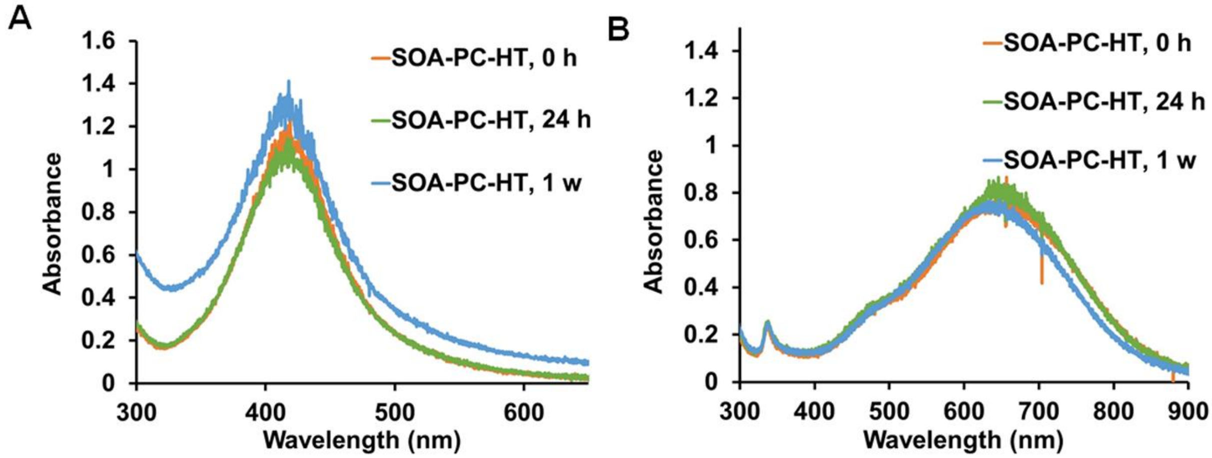


Figure S5. Representative UV-vis spectra of A) spherical and B) triangular-shaped Ag-SOA-PC-HT compositions in H_2O at 25 ºC after initial synthesis, 24 h, and 1 week.

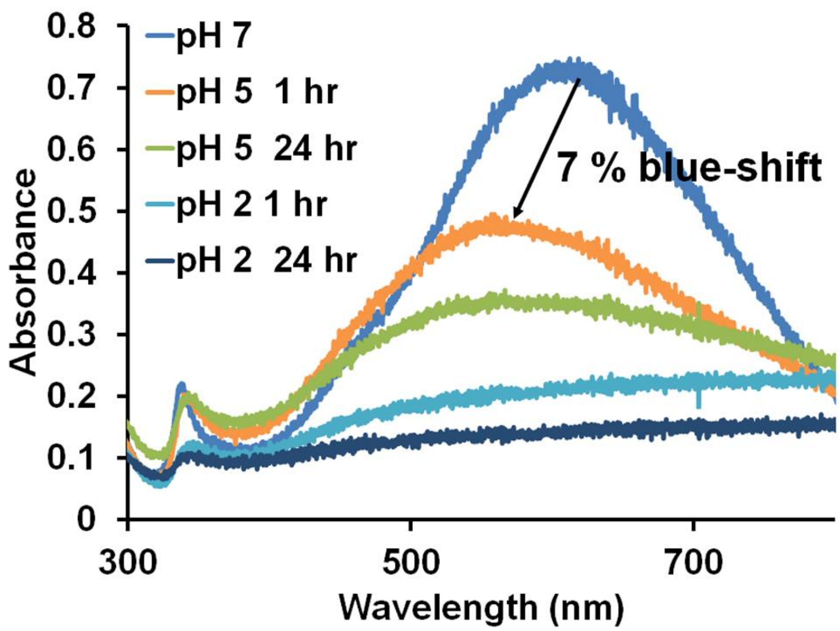


Figure S6. Representative UV-vis spectra of triangular-shaped Ag-SOA-PC-HT nanoparticles at pH 7, pH 5, and pH 2 after 1 hour in H_2O at 25 ºC.

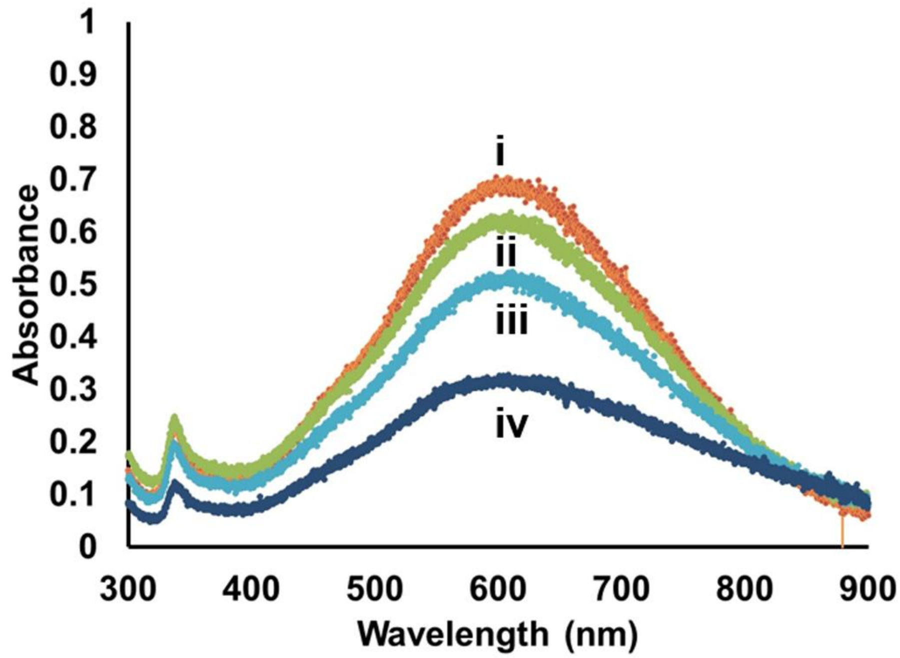


Figure S7. Representative UV-vis spectra of triangular-shaped Ag-SOA-PC-HT nanoparticles in the presence of varying concentrations of NaCl from i) 0 mM, ii) 50 mM, iii) 100, and iv) 150 mM in H_2O at 25 ºC.

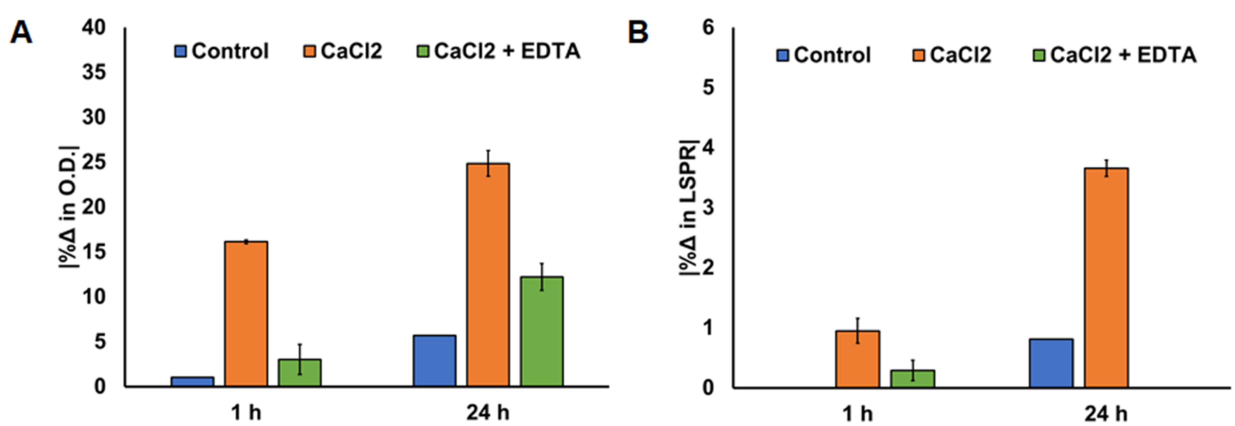


Figure S8. Percent change in the A) O.D. and B) LSPR band of the triangular-shaped Ag-SOA-PC-HT before and after exposure to 50 mM $CaCl_2$ and 100 µL of 500 mM EDTA in H_2O at 25 ºC.

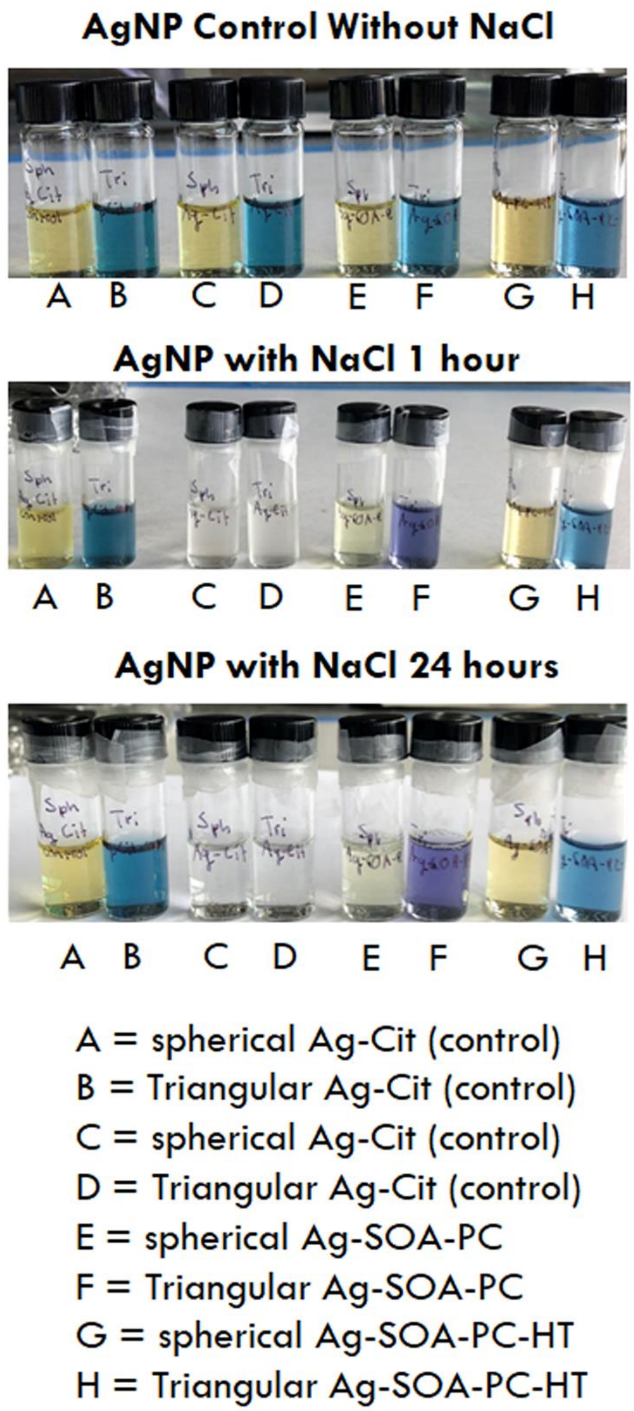


Figure S9. Images of spherical and triangular-shaped Ag-Cit, Ag-SOA-PC, and Ag-SOA-PC-HT nanoparticles in the absence and presence of 50 mM NaCl in H_2O after 1 h and 24 h.

Table S1. Tabulated ICP-MS results from **Figure 7A**, showing Ag^+ ion release from differentially coated spherical AgNPs.

Surface Coating	Concentration of Ag^+ (μg/L)		
	Initial	24 hours	1 week
Cit	56.11 ± 10.89	140.37 ± 7.57	92.92 ± 8.67
SOA-PC	395.96 ± 32.47	783.56 ± 37.79	1228.27 ± 87.75
SOA-PC-PT	4.08 ± 2.66	0.11 ± 0.04	0.11 ± 0.02
SOA-PC-HT	1.01 ± 0.42	0.11 ± 0.05	0.10 ± 0.01

Table S2. Tabulated ICP-MS results from **Figure 7B**, showing Ag^+ ion release from differentially coated triangular AgNPs.

Surface Coating	Concentration of Ag^+ (μg/L)		
	Initial	24 hours	1 week
Cit	37.41 ± 0.22	98.80 ± 1.85	112.44 ± 2.84
SOA-PC	452.83 ± 19.58	425.85 ± 28.76	434.26 ± 43.23
SOA-PC-PT	0.98 ± 0.94	0.06 ± 0.02	0.97 ± 0.19
SOA-PC-HT	13.03 ± 7.84	1.20 ± 0.94	0.02 ± 0.00

REFERENCES

1. Nagle, J. F.; Tristram-Nagle, S., Structure of lipid bilayers. *Biochim Biophys Acta* **2000,** *1469* (3), 159-95.

2. Bayerl, T. M.; Bloom, M., Physical properties of single phospholipid bilayers adsorbed to micro glass beads. A new vesicular model system studied by 2H-nuclear magnetic resonance. *Biophys J* **1990,** *58* (2), 357-62.