Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Tunable Au-Ag Nanobowl Arrays For Size-Selective Plasmonic Biosensing

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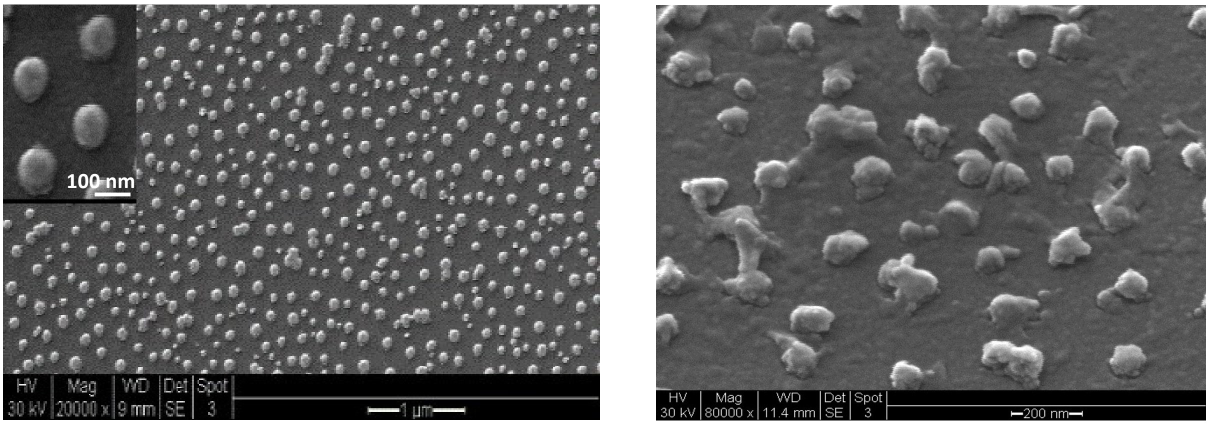


Figure S1. SEM image of original 80 nm Ag nanoparticle arrays, left, and 80 nm Ag nanoparticle arrays which were sonicated in acetone for longer periods of time, (ca. 10-20 minutes) and subjected to 0.1 M $HAuCl_4$ solution, right. Although these particles most likely also contain a mixture of gold and silver, the bowl-like shape is not apparent. The more effective mask lift-off, particularly from the sides of the particles, could allow for less differentiation in gold deposition yielding a ‘rounder’ structure.

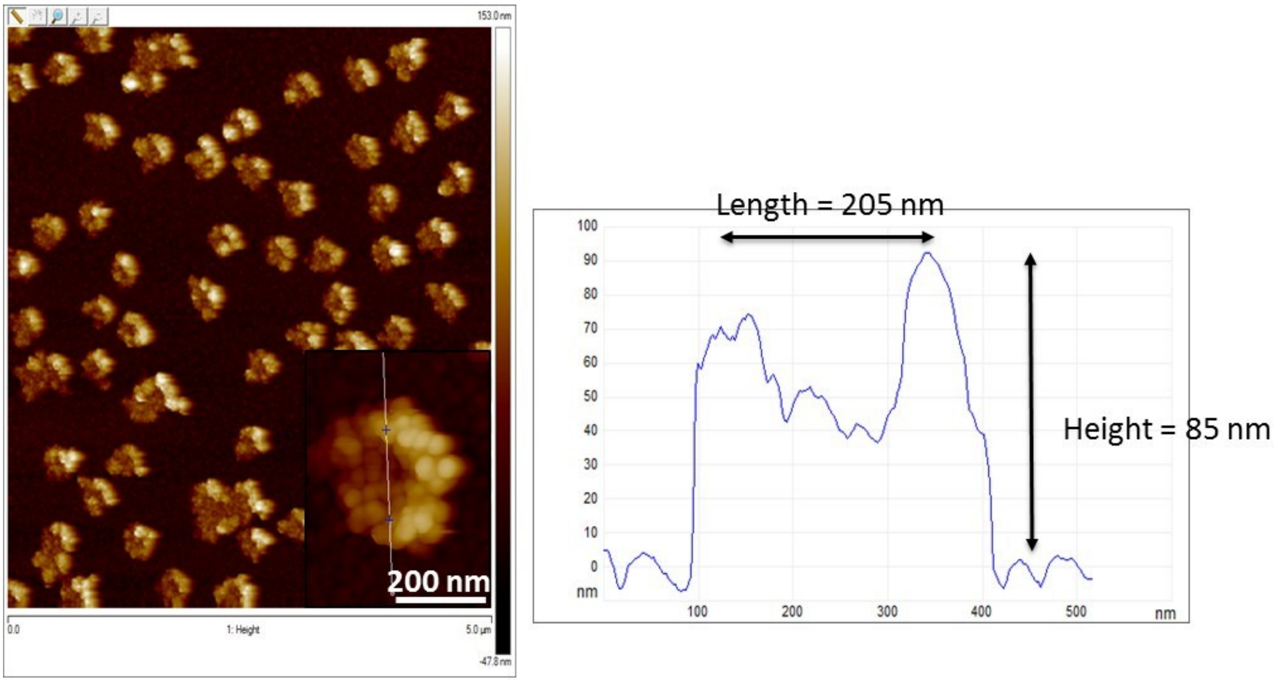
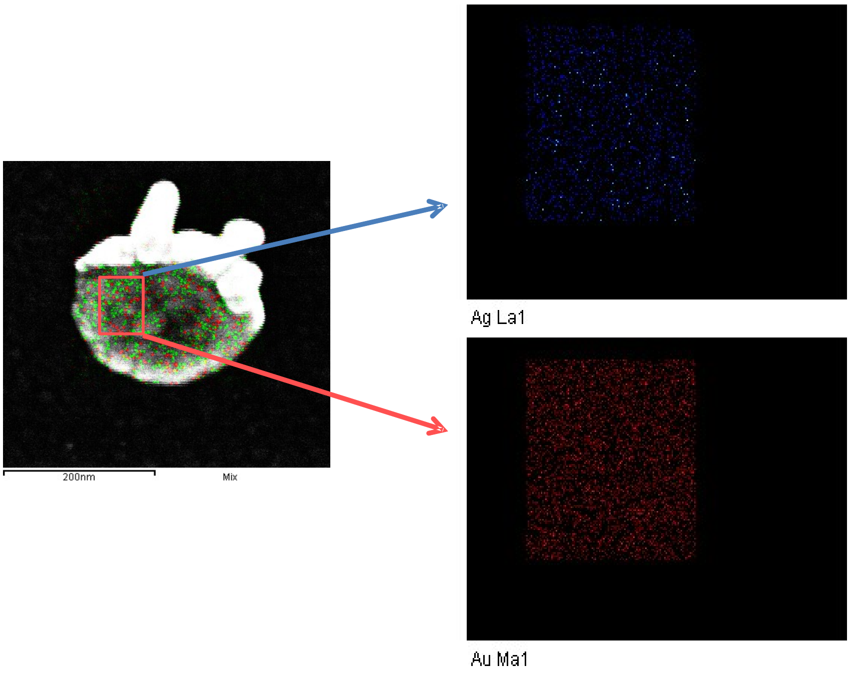
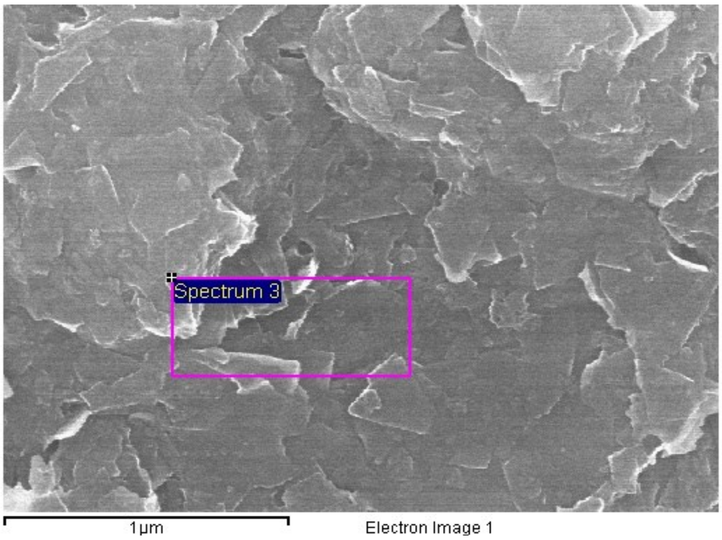


Figure S2. AFM image of 210 nm Au-Ag nanobowls show a fairly dense uniform array. The plot to the right is a cross sectional analysis of an individual nanobowl selected in the insert. In most cases, a clear bowl-like shape is observed, with lower intensities in the middle of the structures. For these 210 nm arrays, lengths ranged from 200 to 220 nm and heights ranged from 65 to 85 nm.



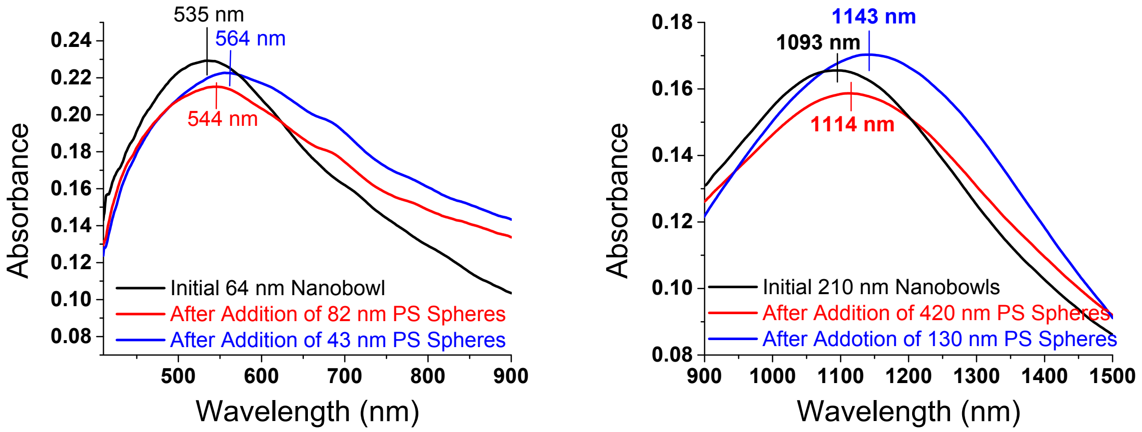
Element	Weight%	Atomic%
O K	37.4	58.0
Na K	4.2	4.5
Al K	3.1	2.9
Si K	31.0	27.4
K K	5.5	3.5
Ti K	2.6	1.3
Ag L	3.6	0.8
Au M	12.7	1.6
Totals	100.00	

Figure S3. A combination of SEM and EDX show the nanobowls are a well-dispersed combination of both gold and silver, with approximately 4x more gold than silver. All of the elements listed in the table other than gold and silver are shown in the scan of just the glass substrate, see **Figure S4** below. The glass contains O, Na, Si, and K, and the samples were taken using Al posts. The small amount of Ti appears to either be a contaminant in the chamber or in the glass substrate. A total of 5 different nanobowl substrates were measured and in all samples the ratio of concentrations of gold to silver ranged from 4-5.8 times.



Element	Weight%	Atomic%
O K	19.1	30.3
Na K	5.8	6.4
Al K	2.1	1.9
Si K	57.4	51.7
K K	11.6	7.5
Ti K	4.1	2.2
Totals	100.00	

Figure S4. A combination of SEM and EDX carried out on a clean glass slide which was sonicated in ethanol for 5 minutes and coated with PELCO conductive graphite, whose carbon signal was subtracted. This ‘background’ scan reveals that the glass substrate contains all of the elements found in the table above except for those in the nanobowls, mainly silver and gold.



Nanobowl size	**Plasmon shift**	
	43 nm PS sphere	82 nm PS sphere
64 nm	29	9
	130 nm PS sphere	420 nm PS sphere
210 nm	50	21

Figure S5. A control experiment in which polystyrene spheres of different size were added to 64 nm and 210 nm Au-Ag nanobowls. Similar to the trends observed with different sized gold colloids, where the larger shift is observed for the smaller polystyrene spheres that are able to fit inside the nanobowls. In addition, the shifts observed overall with the 210 nm nanobowls are larger than those observed with the 64 nm nanobowls due to the increased refractive index sensitivity of the 210 nm nanobowls.

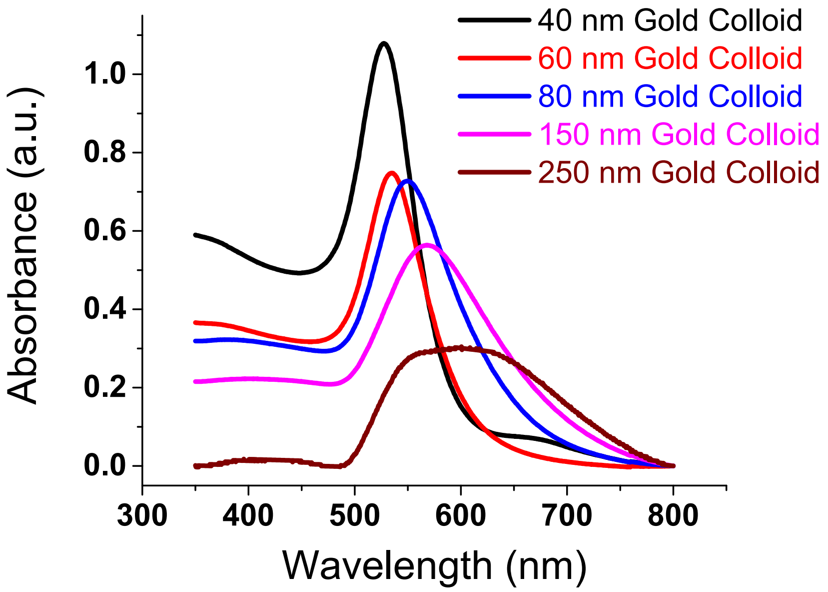
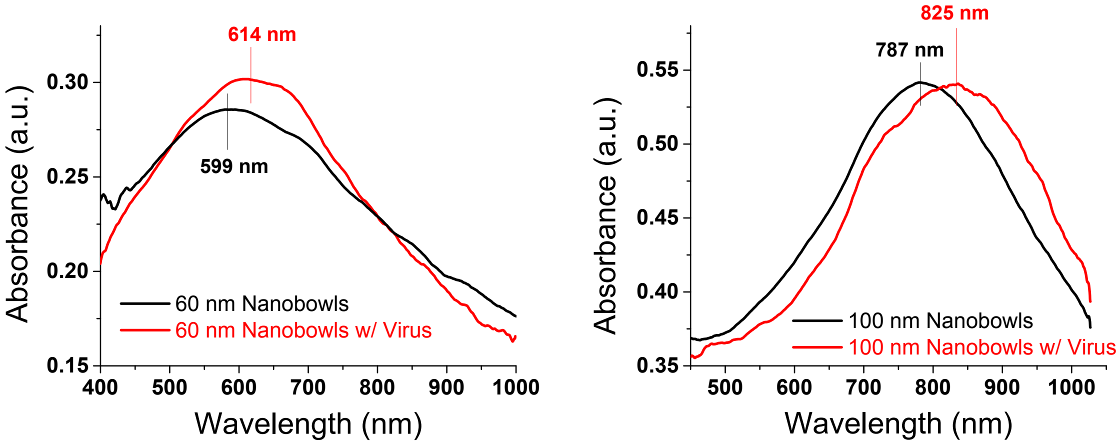


Figure S6. Absorption spectra of the different sized gold colloids used to bind to the nanobowl arrays. LSPR and SERS data is shown in Figure 5 and tabulated in Table 2 of the main text.



Nanobowl size	Plasmon shift
64 nm	15
130 nm	38

Figure S7. Additional data obtained to investigate nonspecific binding of components of the virus solution to the nanobowl arrays. Instead of a self-assembled monolayer of 1:3 MUA/OT, a 1:3 mixture of MUA/PEG(5000)thiol was added to the nanobowls, followed by addition of the virus solution. The shifts observed were significantly lower than those observed with the MUA/OT mixture, and similar to those observed with the addition of polystyrene spheres. Thus, the PEG mixture appears to be more effective at repelling nonspecific binding in these particular virus solutions.

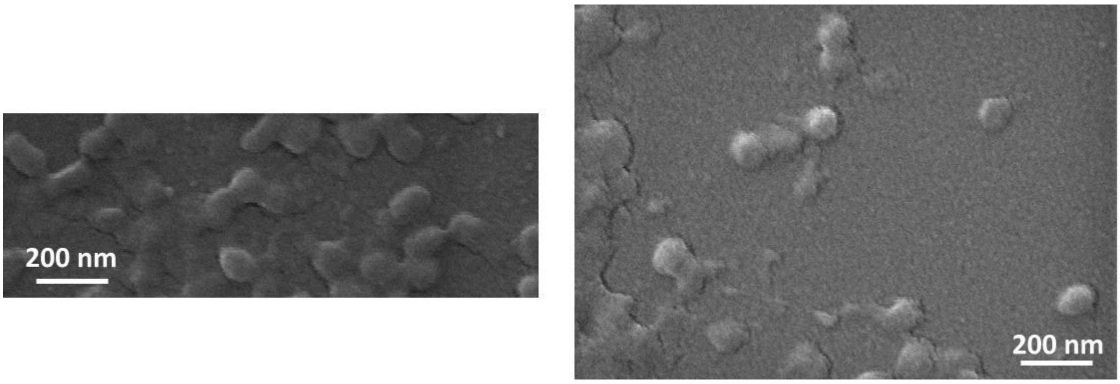


Figure S8. SEM images of virus particles on glass. Samples were coated with 10 nm of gold prior to SEM measurements to avoid charging.