Electronic Supplementary Information

Biosynthetically grown dendritic silver nanostructures for visible Surface Enhanced Resonance Raman Spectroscopy (v-SERRS)

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1. Experimental Parameters and Details

1.1 Growth and maintenance of bacterial culture

Bacterial strain *S.aureus* was cultivated aerobically in LB media overnight (12-14 hours) at 37 ˚C and 200 rpm (Primary culture). Following incubation, 1 ml of the bacterial culture was inoculated into 30 ml of freshly autoclaved LB media (Secondary culture) and allowed to grow for another 2 hours under normal growth conditions to attain exponential growth phase for the cells. Cell growth was monitored by measuring optical density (OD) at 600 nm. For approximation, an OD value of 0.5 was equated to a cell density of ~10^8 CFU/ml. Colony culture assay of *S.aureus* with different cell population obtained by serial dilution (Fig. ES1) was also performed to testify the dilution correctness. The experimental data is summarised as Table ES1.

Fig. ES1 Colony culture of *S.aureus* with different cell population obtained by serial dilution.

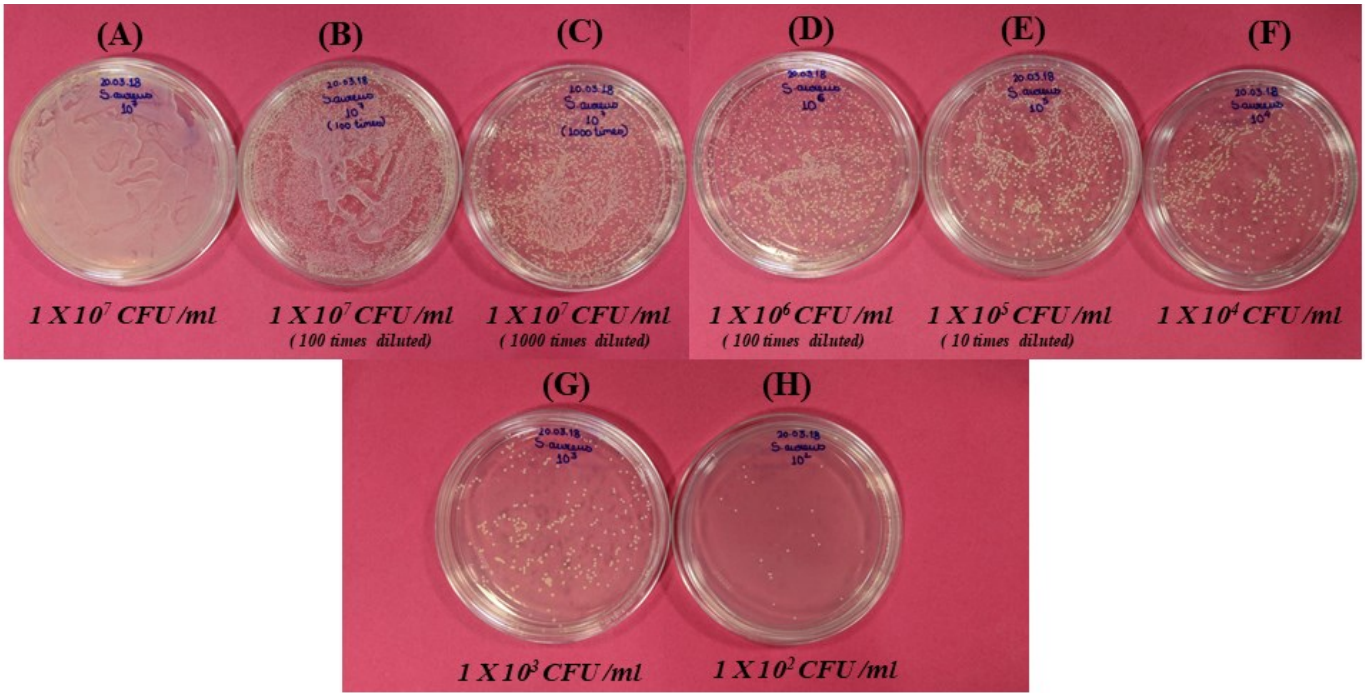


Table ES1. Comparative between the numbers of colonies expected and obtained from the serially diluted *S.aureus* samples used to acquire SERS spectrum. For each plate 200 µl of the respective cell culture was used.

S.No	CFU/ml	Dilution	Expected Colonies (100 µl)	Actual Colonies	Average	Standard Deviation
1.	10^7	1000 times	1000	995/997/983	991.66667	7.57188
2.	10^6	100 times	1000	954/892/1013	953	60.5062
3.	10^5	10 times	1000	986/990/971	982.33333	10.01665
4.	10^4	-	1000	967/877/948	930.66667	47.43768
5.	10^3	-	100	150/106/89	115	31.48015
6.	10^2	-	10	9/13/11	11.16667	1.75594

1.2 SERS measurements

All the SERS and Raman imaging experiments were conducted using WiTec Alpha 300 Combined Confocal Raman AFM system (Germany) equipped with a 532 nm laser line. Prior to every SERS experiment, the system was calibrated using a standard silicon substrate centred at 520 cm^{-1}. Laser excitation operated at 2 mW power was used for sample excitation (both R6G and *S.aureus*). The magnification was kept at 10x. SERS substrates were prepared by drop casting 5 µL colloidal dendritic silver sample onto a 1 cm x 1 cm silicon wafer followed by overnight air drying at RT. Integration time and number of accumulations per measurement was 2 sec and 50 respectively. For reproducibility data, a minimum of 10 spectra were recorded for each analyte at each concentration.

Rhodamine 6G (R6G) detection

A 10mM stock solution of R6G in water was prepared in a standard volumetric flask and labelled as stock solution. Different aqueous solutions of R6G dye with effective concentrations between $1x10^{-8}$ – $1x10^{-15}$ were prepared by serial dilution. These dilutions were designated as working solutions (WS, Table ES). Experimental readings were recorded after drop casting 5 µL of the WS

solution onto a cleaned Ag coated SERS substrate followed by exposure to the laser for acquiring Raman signals.

Table ES2. Different concentrations of R6G dye used for SERS experiments

S.No	Working Solution (WS)	Concentration (M)
1.	WS1	1×10^{-8}
2.	WS2	1×10^{-9}
3.	WS3	1×10^{-10}
4.	WS4	1×10^{-12}
5.	WS5	1×10^{-15}

4- Mercaptopyridine (4-MPy) detection

Similar to R6G, from a 1M stock solution of 4-MPy in water prepared in a standard volumetric flask, different aqueous solutions with effective concentrations between $1x10^{-3}$ – $1x10^{-8}$ were prepared by serial dilution. Experimental readings were recorded by drop casting 5 µL of dye solution onto a clean SERS substrate followed by Raman measurements.

***S.aureus* detection**

Once the OD_{600} of the *S.aureus* secondary culture reached ~ 0.5, 10 ml of the bacterial solution was transferred into autoclaved centrifuged tubes. Cell suspensions were subjected to centrifugation at 8000 rpm for 10 minutes to separate the cell mass. The cell pellet at the bottom was re-dispersed in an equal amount of water to maintain the cell density. Samples with varied cell population (10^7-10^1 CFU/ml) were prepared through serial dilution of the parent cell samples (10^8 CFU/ml). The same dilution was also verified/ visualised by colony counting method (Fig. ES1). Experimental readings were recorded in similar manner as it was done for the R6G dye detection.

2. Characterization

Morphological and chemical composition characterisations were done using Transmission Electron Microscope (JEOL 2100F) equipped with EDAX/Mapping analysis facility. The TEM was performed at an accelerating voltage of 200 kV. HRTEM and SAED acquisition was performed on the same instrument. Absorption spectra were recorded on PerkinElmer lambda-25 UV-Vis-NIR spectrophotometer. FTIR measurements were acquired on Varian 7000 FT-IR/ Raman Spectrometer with Microscope. X-ray diffraction analysis of the synthesized dendritic Ag sample was performed in the thin film mode using X'Pert PRO Analytical X-ray diffractometer using Cu Kα radiation ($\lambda = 1.54$ Å) in the range $2\theta = 20–80°$ operated at 40 keV. The obtained XRD patterns were matched with reference data from the JCPDS database. AFM micrographs were collected using the Combined Confocal Raman-AFM WiTec Alpha 300RA instrument. Laser 532 nm line was used as excitation source. All the images were recorded in the AC/tapping mode using the non-contact version while all the image processing was performed on the WiTec Project 4 software provided with the instrument.

3. Phytochemical Screening

Experimental details of the tests performed [1-5]

1. **Wagner's Test**: A few drops of the Wagner's reagent (Iodine in Potassium Iodide) were added to 1 ml of green tea extract along the sides of the glass vial. Appearance of reddish brown precipitate is a positive confirmation for the alkaloids, which was absent in our case.

2. **Benedict's test:** Green Tea extract and Benedicts' reagent* were mixed in 1:1 ratio. After addition, the mixture was heated on a water bath for 2-5 minutes. The change of colour confirms the presence of sugars in the extract. Green/Blue, orange yellow and brick red indicates traces, moderate and high levels of reducing sugars respectively.
   (Benedict's solution = 100 g of anhydrous sodium carbonate + 173 g of sodium citrate + 17.3 g of copper(II) sulfate pentahydrate in 1000 ml Milli Q)*
3. **Legal's test:** 1 ml of Green Tea Extract was mixed with Sodium Nitroprusside in Pyridine and NaOH (10%) till a 1:1 ratio was achieved. No colour change in our case indicates absence of cardiac glycosides however, in presence of glycosides; the reaction mix would change the colour to red/pink.
4. **Froth Test:** The Green Tea Extract (2ml) was diluted upto 20 ml by adding Milli Q into a 50 ml graduated cylinder. The extract carrying cylinder was shaken for 15 minutes continuously. Presence of 2 cm foam at the solution air interface confirmed saponin presence.
5. **Salkowskis' Test:** Green Tea Extract was treated with chloroform followed by addition of a few drops of Conc. Sulphuric acid. After acid addition, the reaction mix *was mixed gently and allowed to stand for 15 minutes. Appearance of golden yellow* colour confirmed triterpenes presence.
6. **Ferric Chloride Test:** 5 ml Green Tea Extract was dissolved in 5 ml of distilled water. To this, few drops of ferric chloride solution (5%) were added. Appearance of green colour confirms phenol presence in the extract.
7. **Gelatin Test:** 5 ml Green Tea extract was mixed with 2 ml of 1% Gelatin solution in 10% NaCl. Tannin presence was confirmed upon appearance of white precipitates.
8. **Alkaline Test:** Few drops of sodium hydroxide solution (10%) was added to 2 ml Green Tea Extract. Appearance of deep yellow colour that fades upon treatment with a dilute acid confirms flavaniods.
9. **Bradfords' Test:** To 200 µl Green Tea Extract, 800µl of Bradfords' reagent[§] was added. The reaction mix was gently vortexed and allowed to incubate at room temperature for the next 5 minutes. Appearance of green colour indicates presence of proteins.
   ([§]Bradford reagent: 50 mg Coomassie Brilliant Blue was mixed with 50 ml methanol followed by addition of 100 ml 85% w/v phosphoric acid. Acid solution should be added slowly into the water and not vice-versa as a safety precaution. The reagent was filtered using Whatmann filter paper #1 to remove any precipitates. The solution was stored in dark at 4ºC.)

Results

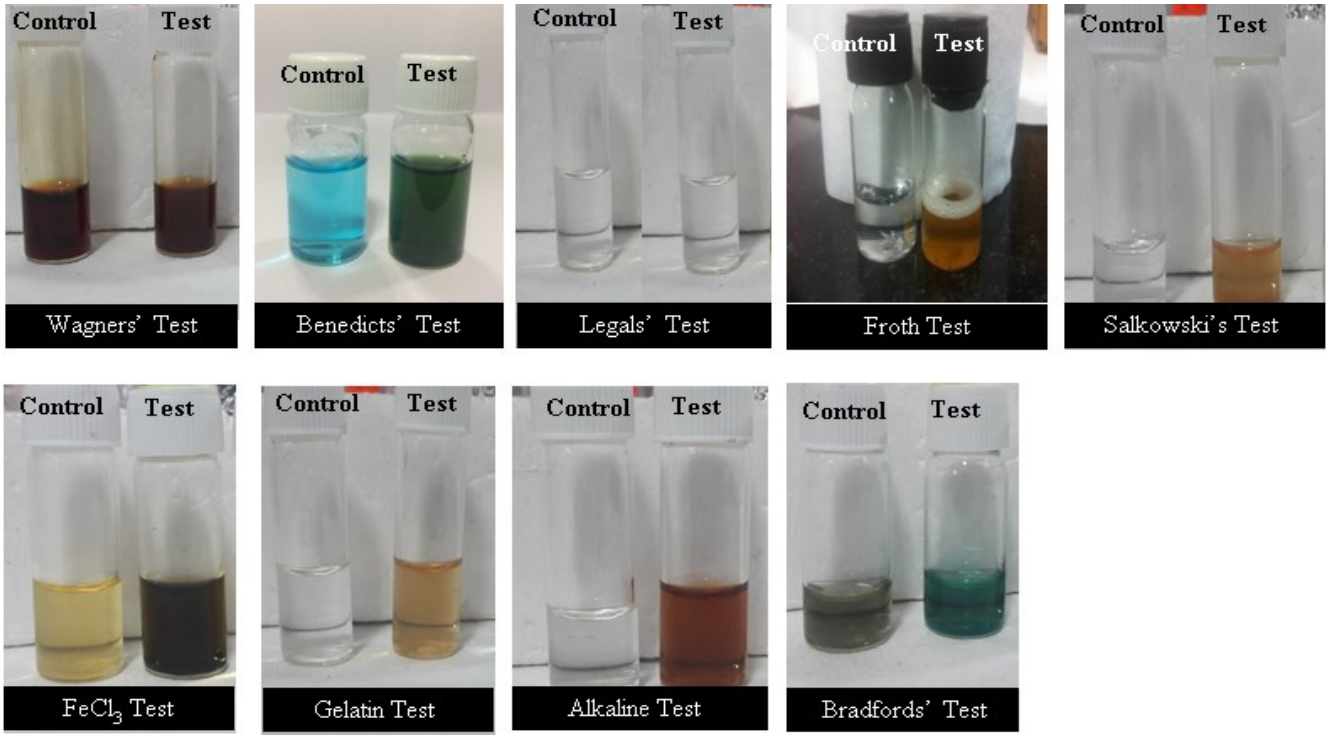


Fig. ES2. Colorometric changes observed for GTE screened for the presence of different phytochemicals. Control vial contains Milli Q while test contains GTE

S.No	Test	Phytochemical Screened	Result
1.	Wagners'	Alkaloids	Negative
2.	Benedicts'	Carbohydrates	Positive
3.	Legals'	Cardiac Glycosides	Negative
4.	Froth	Saponins	Positive
5.	Salkowski's	Phytosterols	Positive
6.	$FeCl_3$	Phenols	Positive
7.	Gelatin	Tannins	Negative
8.	Alkaline	Flavonoids	Positive
9.	Bradfords'	Proteins	Positive

4. Thin Layer Chromatography

Thin Layer Chromatography was performed for identification of metabolites in GTE. Thin layer planar chromatogram was used to separate the amino acid constituents from GTE. Conventional TLC procedure using n-butanol: acetic acid: water (12:5:3) was performed. Comprising groups were identified and mapped using standard amino acids. The experiment was run for 40 minutes to allow considerable separation. The following chemicals were used for the TLC analysis: L-amino acids (Tryptophan, Proline, Phenylalanine, Glutamine, Glycine, Leucine) standards were procured from SRL India. n-Butanol and Glacial acetic acid were obtained from Fischer Scientific. Milli Q was used as the solvent everywhere unless mentioned elsewhere.[1,2]

Table ES3. Comparative Rf values for different amino acids obtained

S.No	Amino Acid	Literature	Experimental
1.	Tryptophan	0.80	0.69
2.	Proline	0.43	0.40
3.	Phenylalanine	0.68	0.68
4.	Glutamine	0.33	0.38
5.	Glycine	0.40	0.31
6.	Leucine	0.58	0.66
7.	Alanine	0.24	
8.	Valine	0.4	
9.	Tyrosine	0.42	
10.	Lysine	0.58	
11.*	Green Tea Extract		0.65, 0.54, 0.45, 0.38

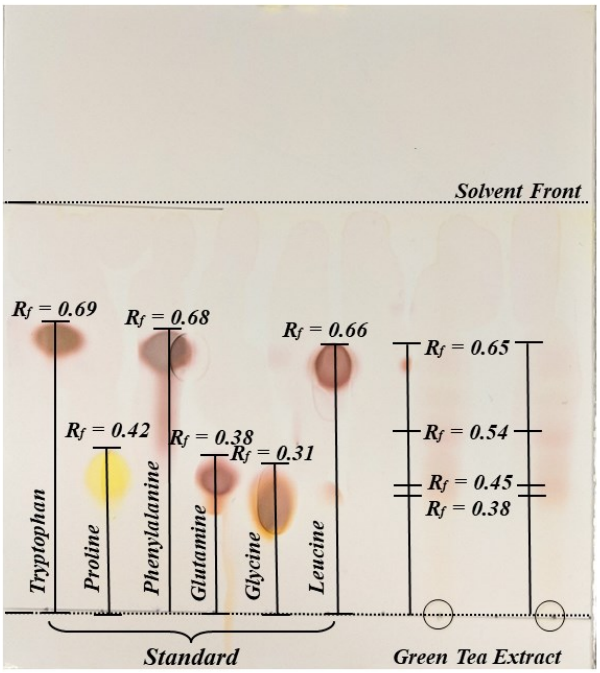


Fig. ES3. Thin Layer Chromatogram (TLC) of the used Green Tea extract indicating the different present amino acids.

5. SERS Reproducibility at 10^1 CFU/ml

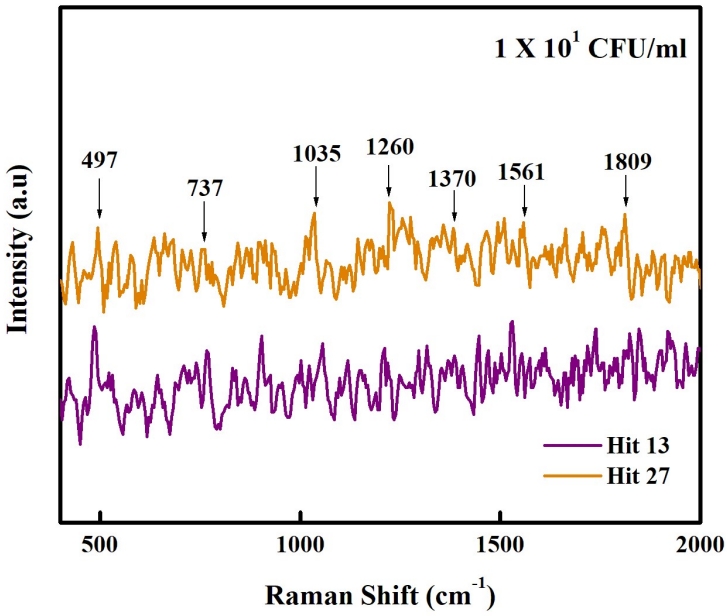


Fig. ES4. SERS spectrum for *S.aureus* (1 x 10^1 CFU/ml). The spectrum acquisition was attainable but not repetitive. This data were obtained at the 13th and the 27th hit.

Table ES4 Reader reference compilation of different biosynthetic routes adopted for synthesizing nanostructures.

S.No	Morphology	Reducing Agent	Reference
1.	Nanowire/Nanobars	*Camellia sinensis* /PVP	[6]
2.	Nanoparticles	Black Tea , Green Tea	[7]
3.	Nanoparticles	Pomegranate Peel extract	[8]
4.	Nanoparticles	Soluble Green Tea Powder	[9]
5.	Nanoparticles	Black Tea extract	[10]
6.	Nanoparticles	*Acalypha hispida* leaf extract	[11]
7.	Nanoparticles	Bauhinia tomentosa Linn. leaves extract	[12]
8.	Nanoparticles	Blackberry, Blueberry, Pomegranate and Turmeric extracts.	[13]

9.	Nanoparticles	Aqueous Sorghum Bran extract	[14]
10.	Anisotropic(urchin shaped)	*Camellia sinensis*	[15]
11.	Nanoparticles	*Camellia sinensis* leaf extract	[16]

Fig. ES5 TEM low magnification

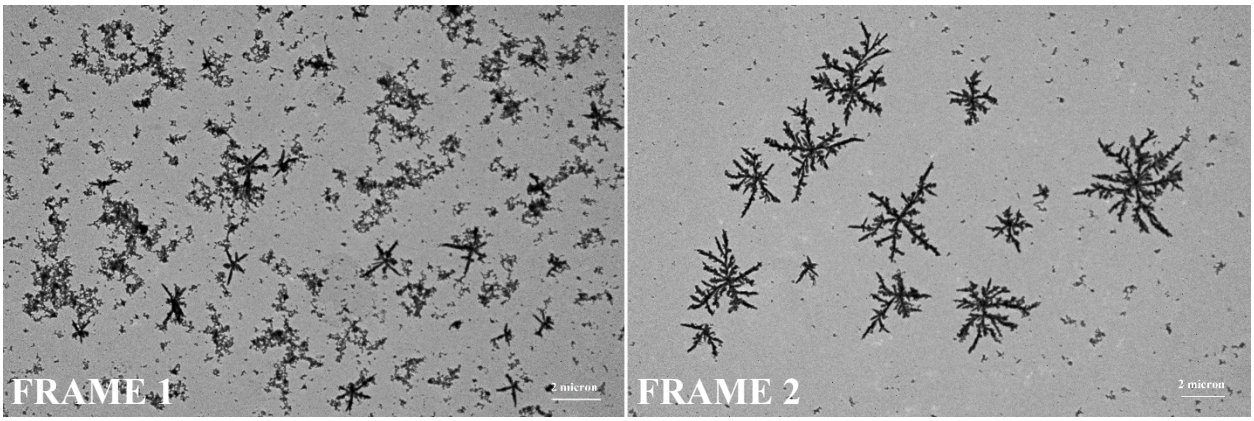
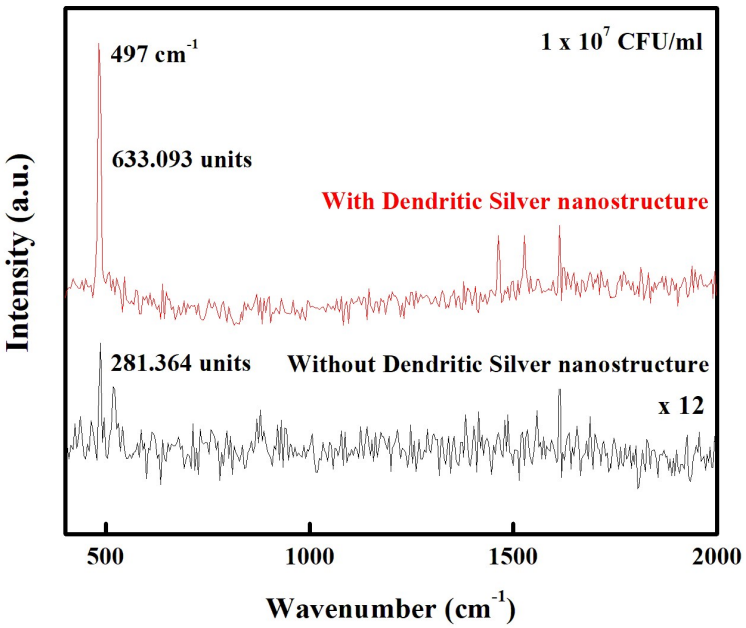


Table ES5 Reader reference compilation of different methodologies adopted for synthesizing dendritic silver nanostructures

S.No	Morphology	Synthesis Method	Templates used, if any	Reference
1.	Dendritic Silver	Electrodeposition	-	[17]
2.	Dendritic Silver	Ultrasonic Irradiation	Isopropanol , PEG 400	[18]
3.	Dendritic Silver	Photocatalytic reduction	Zinc Oxide crystals	[19]
4.	Dendritic Silver	Replacement Reaction	Zinc Plate	[20]
5.	Dendritic Silver	Wet Chemical Route	CTAB/SDBS surfactant mix	[21]
6.	Dendritic Silver	Chemical Route	p-Aminoazobenzene (PA)	[22]
7.	Dendritic Silver	Electrodeposition	Triblock copolymer P123	[23]
8.	Dendritic Silver	Sonoelectrochemistry	PVP	[24]
9.	Dendritic Silver	Chemical Reduction	TTF	[25] [30]
10.	Dendritic Silver	Electrodeposition	Au foil, KNO_3	[26]

11.	Fractal and Dendritic Ag, Au	Chemical Route	$Au(PPh_3)Cl$, $Ag(PPh_3)_4NO_3$, CTAB/TOAB, PVP	[27]
12.	Dendritic Ag	Self-Assembly	Amphiphilic calix[4]arene molecule	[28]
13.	Dendritic Ag	Electrodeposition	Surfactant	[29]
14.	Dendritic Ag	Replacement Reaction	Silicon Wafer, HF	[31]
15.	Dendritic Ag	Electroless galvanic replacement reaction	Cu substrate, Sulfate ions	[32]

Fig. ES6 Raman of *S.aureus* with and without dendritic silver.



Intensity at 497 cm^{-1}

With dendritic nanostructure = 633.093 units

Without dendritic nanostructure = 23.447 units (281.364 /12)

Estimated signal increment = 633.093:23.447 = ~ 27.009

Table ES6 Reader references for *S.aureus* detection using different nanostructure morphology and methodologies

S.No	Morphology	Analyte	LOD | EF	Reference
1.	Self-assembled Ag nanocrystals	*S.aureus*	10 CFU/ml | 2.47×10^7	[33]
2.	Au-coated magnetic nanoparticles (AuMNPs) core/shell nanocomposites	PATP	10^{-9} M	[34]
		S.aureus	10^1 cells/ml	
3.	AuNps embedded mesoporous silica	*S.aureus*	10^6 CFU/mL | 900 times	[35]
4.	Gold nanoparticles conjugated aptamer	*S.aureus*	35 CFU/ mL	[36]
		S. typhimurium	15 CFU /mL	
5.	Polyethylenimine (PEI)-modified Au coated magnetic microspheres	*S.aureus*	10^3 CFU/ml	[37]
6.	Single domain antibody coated nanoparticle labels and magnetic trapping	*S.aureus*	1 cell/ml	[38]
7.	Biosynthesized Ag nanoparticles	*S.aureus*	$3 \pm 0.20 \times 10^7$	[39]
		E.coli	$5 \pm 0.40 \times 10^7$ | 10^3 CFU/ml	
8.	Silver nanorod array	pyocyanin (*P. aeruginosa* biomarker)	5 ppb	[40]

Table ES7: Reader reference of 4MPy detection using SERS

S.No	Morphology	Analyte	LOD/EF	Reference
1.	Amorphous ZnO nanocages	4- mercaptopyridine	10^{-4} M	[41]
2.	Flower-like Fe_3O_4 nanostructured hollow microspheres	4- mercaptopyridine	10^{-5} M	[42]
3.	TiO_2 nanofibers coated with Ag nanoparticles	4-mercaptopyridine	4.9×10^5	[43]
4.	Kinked gold nanowires	4-mercaptopyridine	10^{-7} M	[44]
5.	Gold nanoparticle functionalised porous polymer monlith	4-mercaptopytidine	10^{-7} M	[45]
6.	Silver in polyelectrolyte multilayers	4-mercaptopyridine		[46]
		Rhodamine 6G (R6G)	10^9	
7.	α-Fe2O3 nanocrystals (sphere, spindle, cube)	4-mercaptopyridine	10^4	[47]
8.	Ag-NP assembled bi-nanoring arrays	Benzenethiol	10^7	[48]
		4-mercaptopyridine	10^{10}	
9.	Polydopamine assisted in situ silver nanoparticle deposition	4-mercaptopyridine	10^7	[49]
10.	Electrochemically roughened silver electrodes	4-mercaptopyridine	1mM	[50]

Table ES8: SERS activity comparative with different anisotropic structures

S.No	Morphology	Analyte	LOD/EF	Reference
1.	Gold nanostars	4- mercaptopyridine	nM	[51]
2.	Gold nanostars	five different types of breast cancer cells	-NA-	[52]
3.	Silver embedded nanostars	R6G	μM	[53]
4.	Silver coated gold tetrapod	R6G	1.73×10^6	[54]
5.	Core shell gold@silver nanorods	4-mercaptobenzoic acid (4-MBA)	$\sim 10^{10}$	[55]
6.	Ag NRs@HfO_2	Methylene Blue	10^{-6} M	[56]
		Crystal Violet	10^{-5} M	
7.	Au@Ag hexagonal nanorings	4-MBA	$\sim 10^6$	[57]
8.	Ag-NP assembled bi-nanoring arrays	R6G	$1x10^{-12}$	[58]
		Polychlorinated Bi-phenyls	$1x10^{-9}$	
9.	Ag–Au hollow nanostructures	R6G	1.73×10^6	[59]
10.	Dendritic Silver nanostructures (This study)	R6G	10^{-15} M	

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