

Supplementary Information

Gold nanostars as a colloidal substrate for in-solution SERS measurements using a handheld Raman spectrometer

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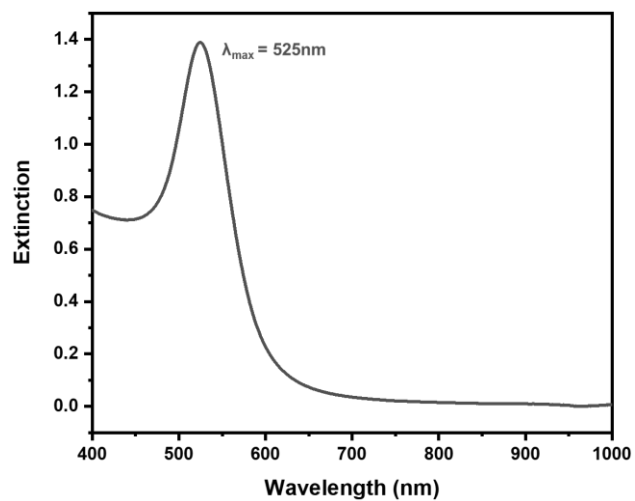


Figure SI1. UV-Vis spectrum of citrate capped gold nanoparticles (30 nm).

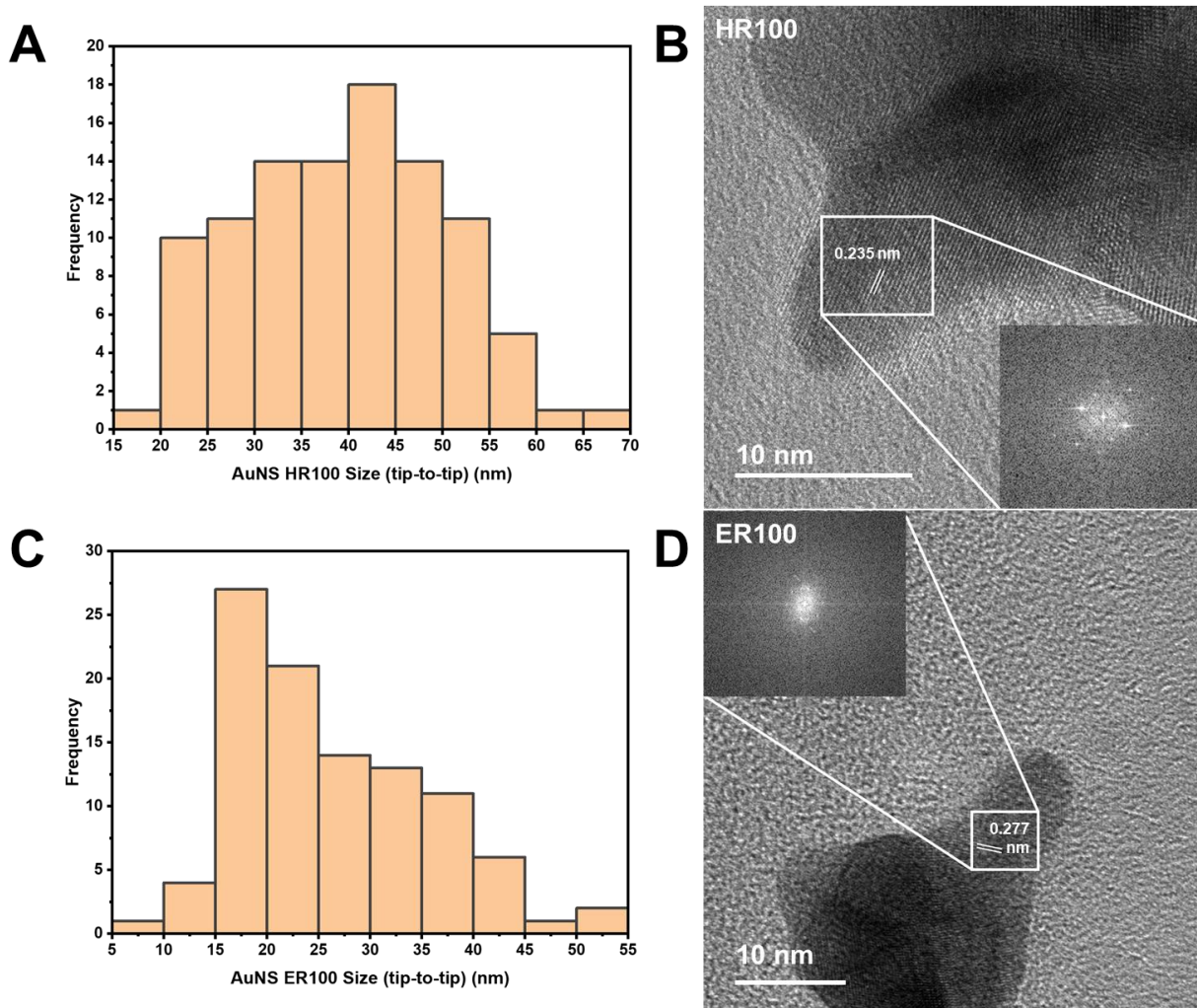


Figure S12. Histograms and TEM images of AuNS using HEPES (A and B) and EPPS (C and D) at R 100. The white boxes represent the area where FFT analysis was performed.

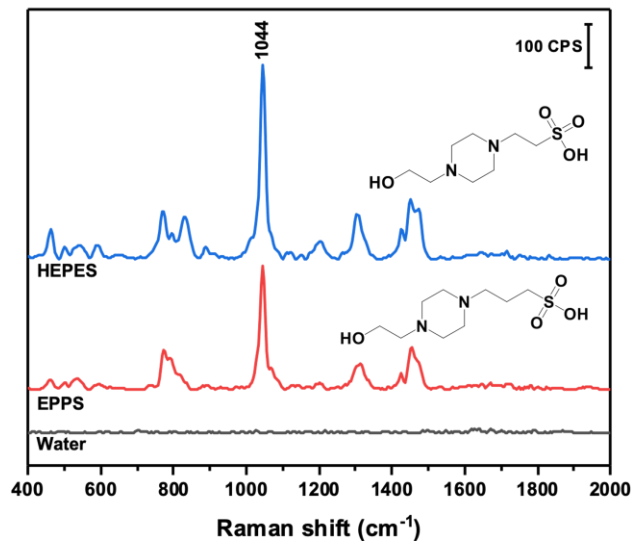


Figure SI3. Solution Raman spectra of water, EPPS and HEPES buffer.

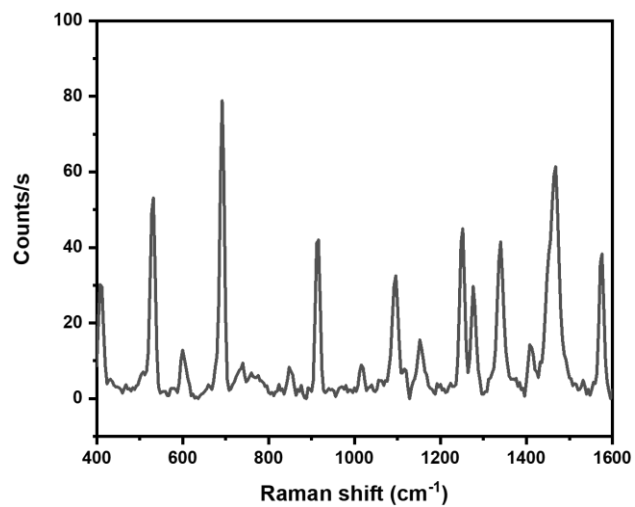


Figure SI4. Raman spectrum of solid methimazole.

Table S11. Major bands assignments listed for the SERS spectrum of 4-mercaptobenzonitrile on AuNS.

Band position (cm⁻¹)	Assignment¹⁻³
1075	C-S and C-C stretching
1178	C-H bending and C-C stretch
1204	C-H bending and C-C≡N stretching modes
1586	C-C stretch
2233	C≡N stretch

Table S12. Major bands assignments listed for the SERS spectrum of thiabendazole on AuNS.

Band position (cm⁻¹)	Assignment⁴
788	C-H out-of-plane bending
1012	C-H out-of-plane bending
1276	ring stretching
1580	ring stretching and C=N stretching

Table SI3. Major bands assignments listed for the SERS spectrum of methimazole on AuNS.

Band position (cm⁻¹)	Assignment⁵⁻¹⁰
500	S-C-N in plane bending
616	ring out-of-plane bending, ring C-H and N-H out-of-plane bending
1037	ring bending, ring C-H bending and C-S-H bending
1086	ring C-N stretching and ring C-H bending
1145	C-S stretching, ring C-H bending and C-N stretching
1320	ring C-N stretching, ring bending and ring C-H bending
1364	C-N stretching, ring bending and ring C-H bending

Table S14. Major bands assignments listed for the SERS spectrum of malachite green on AuNS.

Band position (cm⁻¹)	Assignment¹¹
1172	in-plane C-H ring vibration
1220	C-H rocking
1368	N-phenyl stretching vibration
1592	C-C stretching
1616	C-C stretching

Table S15. Major bands assignments listed for the SERS spectrum of ciprofloxacin on AuNS.

Band position (cm⁻¹)	Assignment^{12, 13}
1392	symmetric O-C-O stretching
1496	Asymmetric O-C-O stretching
1544	quinolone ring stretching
1636	Asymmetric aromatic ring stretching

Analyte descriptions

Thiabendazole (TBZ) is a common fungicide applied after harvest to prevent mold and rot on fruit and vegetables.¹⁴ The use of TBZ has been classified as likely to be carcinogenic at high concentrations and poses thyroid hormone production imbalance risks.^{15, 16} Since TBZ is widely used in fruits and vegetables ranging from applesauce to sweet potatoes, the maximum residue limit (MRL) will differ per commodity. For example, the United States Environmental Protection Agency (US EPA) has set a tolerance limit of 5 ppm and 10 ppm for applesauce and sweet potatoes, respectively ($\sim 25\text{-}50\ \mu\text{M}$).¹⁷ Figure 6A shows the SERS spectrum of $5\ \mu\text{M}$ TBZ adsorbed on AuNS before and after the addition of NaCl (200 mM). The major bands are summarized in Table SI2 according to a previously published paper.⁴

Malachite green (MG) is a highly effective fungicide used to mitigate fungi and parasite growth in the aquaculture industry.¹⁸ In Canada, MG is approved for use on aquarium fish only, and is not permitted for use on food-producing animals/fish.¹⁹ MG and its metabolite, leucomalachite green, are known to reside in fish tissue and are known to have mutagenic and teratogenic effects on humans.^{18, 19} While its use on aquarium fish is approved, improper disposal or careless treatment of aquarium fish could lead to accidental contamination of surrounding bodies of water and fish. Figure 6C shows the in-solution SERS spectrum of $0.5\ \mu\text{M}$ MG adsorbed on colloidal AuNS before and after the addition of NaCl. These bands are summarized in Table SI4 according to a previously published paper.¹¹ MG was used as an example of a fluorescent dye to show the capability of AuNS to detect such a molecule.

Ciprofloxacin (Cipro) is a fluoroquinolone antibiotic used to treat bacterial infections relating to the urinary tract, prostatitis, sinusitis, bones and joints.²⁰ Figure 6D shows the SERS spectrum of Cipro adsorbed on AuNS before and after the addition of NaCl at a concentration of 5 μ M. These bands are summarized in Table SI5 according to previously published papers.^{12, 13}

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