

Gold Nanostar Substrates for SERS-based Chemical Sensing in the Femtomolar Regime

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Supporting Information

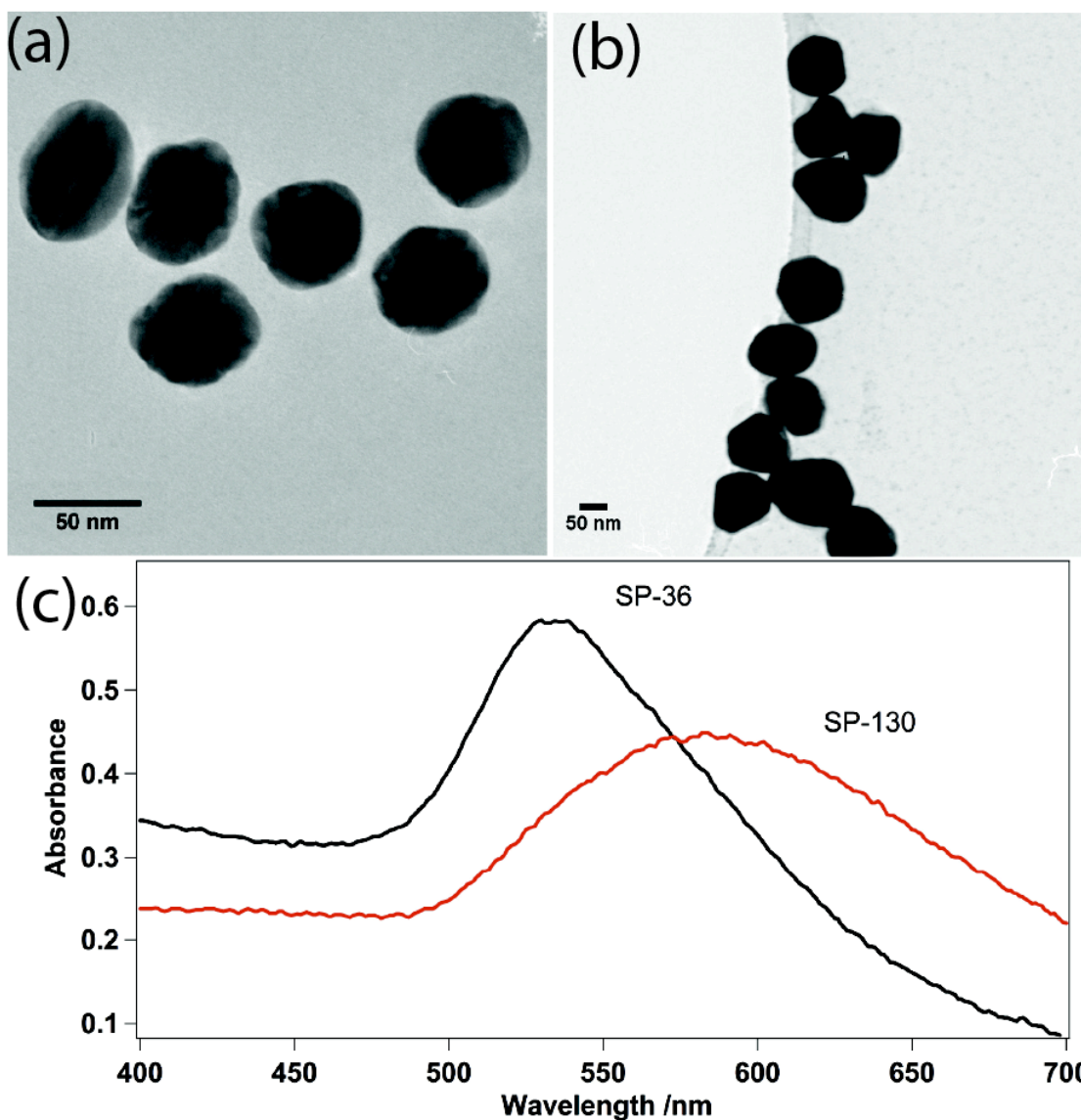


Fig. S1 Gold nanospheres of 36 nm (SP-36) and 130 nm (SP-130) in diameter, values equivalent to the inner (i.e. core) and outer (i.e. the imaginary sphere traced by the outermost atoms on the tips) diameter of nanostars, were synthesized and analyzed for SERS. Transmission electron micrographs of (a) SP-36, (b) SP-130, and (c) their UV-visible spectra.

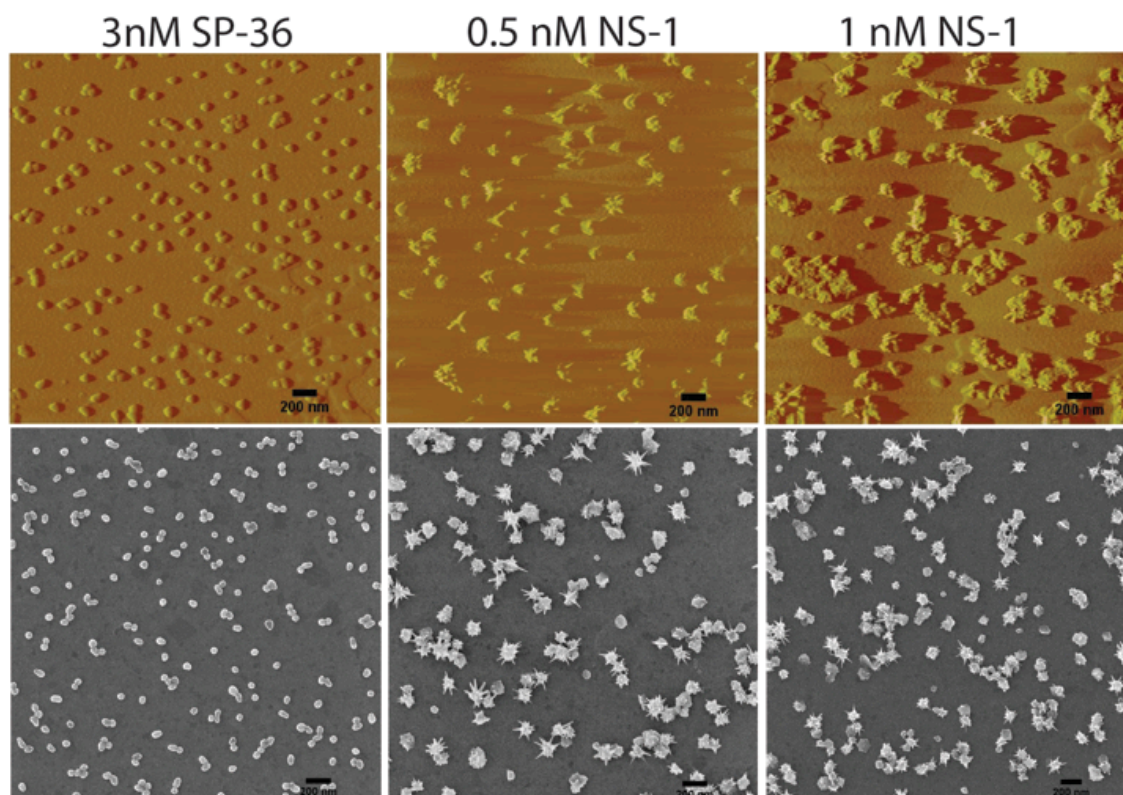


Fig. S2 Atomic force micrographs of SP-36 and NS-1SERS substrates at different densities. Surface roughness factor, $RMS_{[Rq]}$ value for 3 nM SP-36, 0.5 nM NS-1 and 1nM NS-1 are 12.66 nm, 27.67 nm and 34.11 nm respectively.

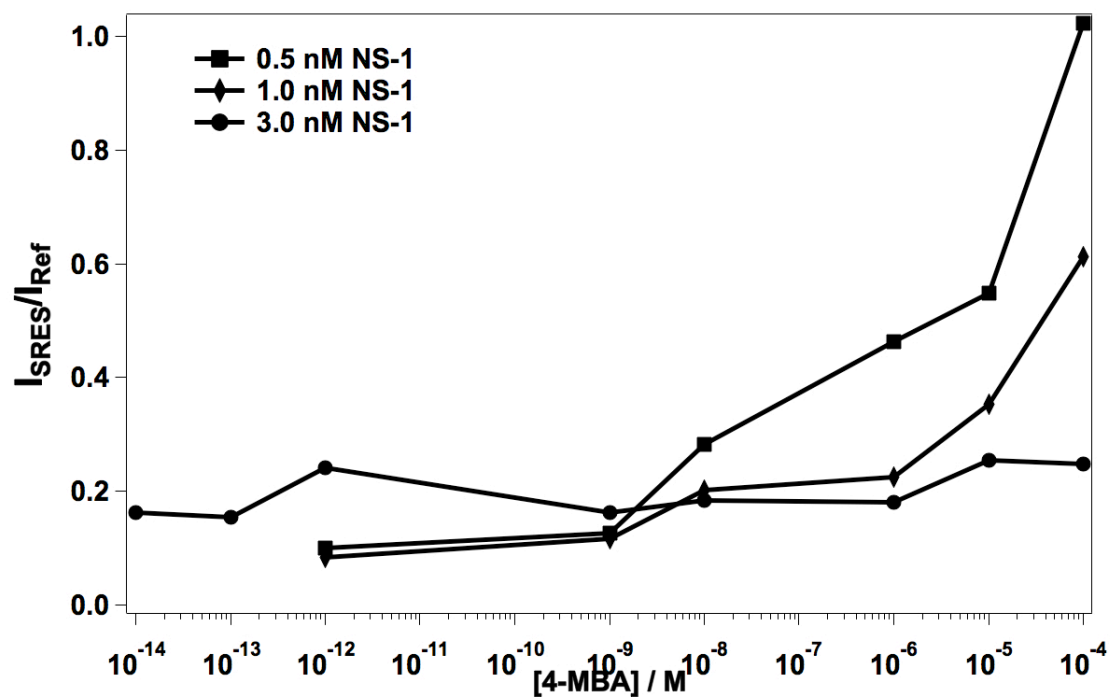


Fig. S3 SERS response for MBA slightly varies as a function of the NS-1 density on the SERS substrate. The plotted SERS responses were collected under 785 nm laser (166 μ W).

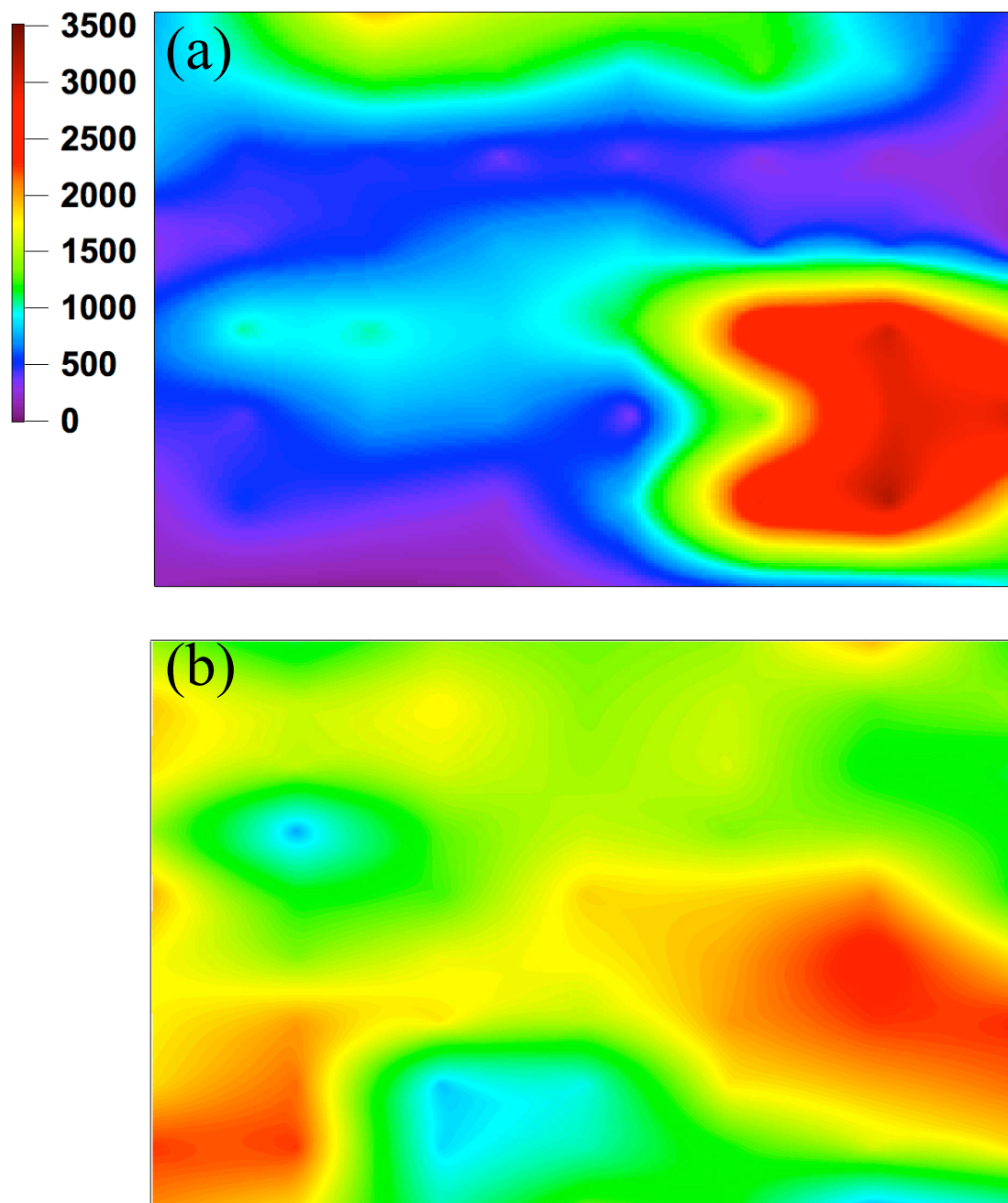


Fig. S4 SERS maps for (a) 1 pM MBA on NS-1 substrate, and (b) 10 nM MBA on SP-130 substrate. The spatial variation of the SERS intensity of the peak at 1077 cm^{-1} was used to construct the map. Map size $20 \times 20\ \mu\text{m}^2$, step increment $2\ \mu\text{m}$, data acquisition time 10 s, single accumulation, laser power $166\ \mu\text{W}$ of 785nm diode laser and $492\ \mu\text{W}$ of 633 nm He Ne laser.

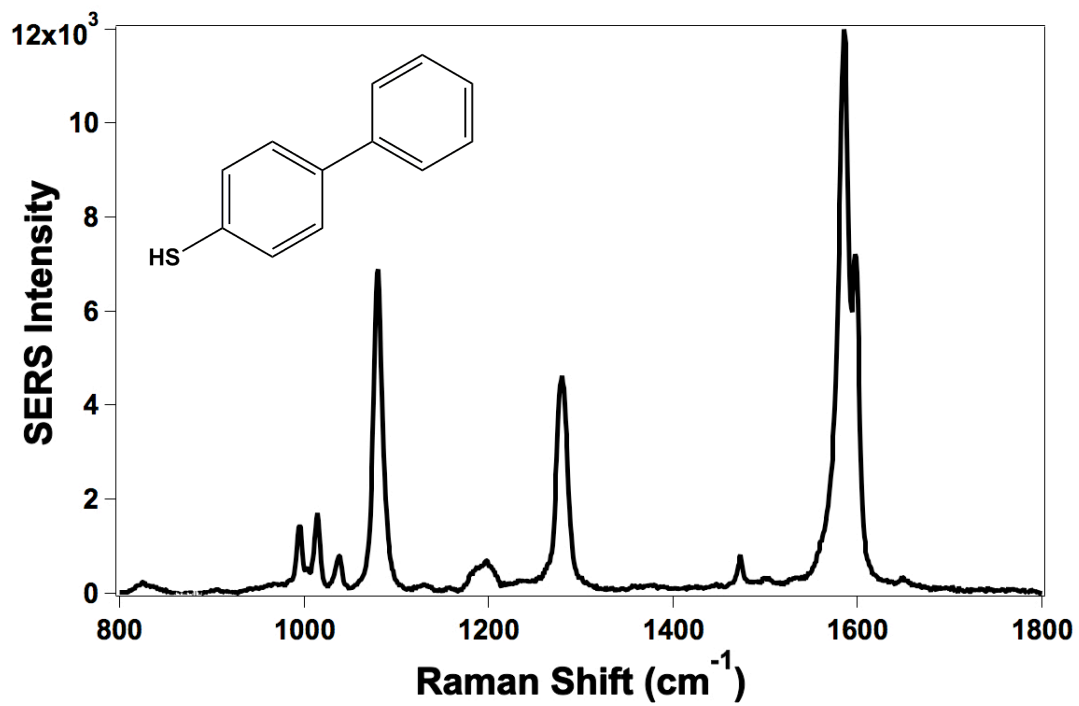


Fig. S5 Raman spectrum of solid DBT under 785 nm laser (166 μW).

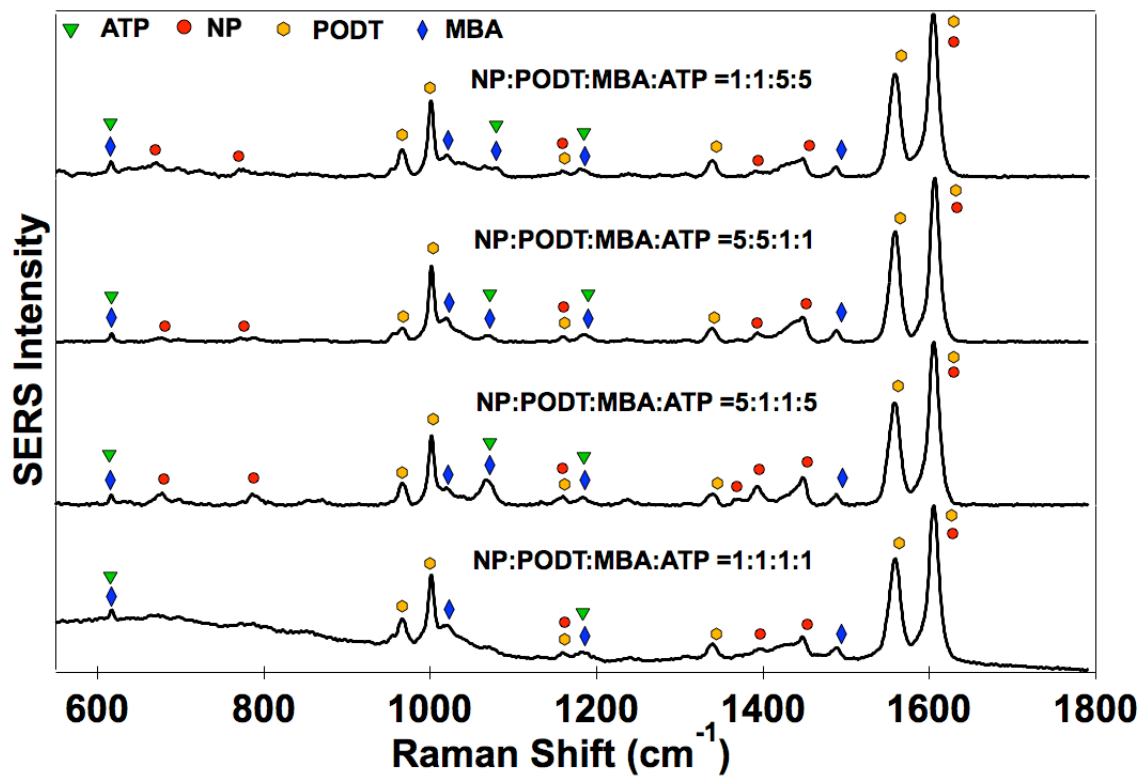


Fig. S6 SERS spectra show the characteristic peaks for analytes in 4-plex chemical sensing experiments for 10^{-6} M analytes on 3 nM NS-1 substrate. SERS spectra were collected under 785 nm laser excitation (1 accumulation, 10 s exposure).

Table S1: Characteristic SERS peaks of the analyte molecules used in multiplexing sensing study.

MBA	Raman Shift (cm ⁻¹)	Peak assignment
	718	Out-of-plane CCC vibration of the aromatic ring; MBA is oriented parallel (stay flat) to the surface ¹
	1020	Due to the decarboxylation of MBA during its adsorption to a rough gold surface ¹
	1077	Aromatic ring vibration ¹
	1124	In-phase vibrations of phenyl ring enhanced by pi conjugations; appear when molecule is in parallel (flat) to the gold surface ²
	1421	Symmetric stretching vibration of dissociated carboxylate group (COO ⁻) ¹
	1588	Aromatic ring vibration ¹
ATP	921	π CH ³
	1089	NH ₂ rock ⁴
	1180	CN stretching in aromatic amines ⁵
	1589	CC stretching in phenyl ring and NH ₂ bend ⁴
Nap	787	Ring deformation ^{6,7}
	1143	CH bend ⁶
	1166	CC stretching, CC bending ⁸
	1375	CC stretching, ring deformation and stretching ⁸
	1450	Ring stretching ⁶
	1567, 1580, 1612	Ring stretching ⁶
PODT	957,993	Phenyl ring deformation ⁹
	1280 to 1350 and 1450 to 1530	N=N-O symmetric stretching ⁵
	1410 to 1440	N=N aromatic stretching ⁵
	1528, 1549	Oxadiazole ring trans and cis vibrations ⁹
	1609	Phenyl ring vibration ⁹

References

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