

Sensitive and specific detection of explosives in solution and vapour by Surface-Enhanced Raman Spectroscopy on silver nanocubes

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SUPPORTING INFORMATION

Calculation of enhancement factor EF

SERS enhancement factors for analytes were calculated using formula (1) and (2):

$$EF = \frac{I_{SERS} \times N_{bulk}}{I_{RS} \times N_{SERS}} \quad (1)$$

Where I_{SERS} and I_{RS} are the intensity of the band in SERS and Raman spectra respectively, N_{bulk} is an estimation of the number of molecules that probed the Raman measurement sample, whereas N_{SERS} is the number of molecules probed in SERS. For all spectra, base line were corrected to get peak intensity. The number of analyte molecules were estimated using the following equation assuming that molecules were uniformly distributed on the substrate for N_{SERS} , whereas in N_{bulk} , powder of the analyte sample was used[1, 2].

$$N_{SERS} = CVN_A S_{scan}/S_{sub} \quad (2)$$

$$N_{Bulk} = M\rho hN_A A_{Raman} \quad (3)$$

C: molar concentration for analyte solution; V is the volume of the droplet =100 μ L in SERS, S_{scan} is the area of Raman scanning, S_{scan} = 4.4 μ m², and S_{sub} is the area of the substrate; S_{sub} =64 mm². N_A : Avogadro constant= 6.02 \times 10²³ mol⁻¹.

A_{Raman} is the laser spot diameter, was calculated for 633nm using the formula (Laser spot diameter = 1.22 λ / NA) [3], NA= 0.75, So A_{Raman} = 1.03 μ m. M is the molecular weight, ρ is the analyte molecule density, and h is the confocal depth.

For 10⁻⁷M of Rh-6G,

$$N_{SERS} = 10^{-7} \times 10^{-4} \times 6.02 \times 10^{23} \times (4.4 \times 10^{-12}) / (6.4 \times 10^{-5}) = 4.14 \times 10^5 \text{ molecules}$$

$$N_{bulk} = 479.02 \times 1.25 \times (2.1 \times 10^{-6}) \times (6.02 \times 10^{23}) \times (1.03 \times 10^{-7}) = 7.79 \times 10^{14} \text{ molecules}$$

$$EF = \frac{27510 \times 7.79 \times 10^{14}}{594 \times 4.14 \times 10^5} = 8.71 \times 10^{10}$$

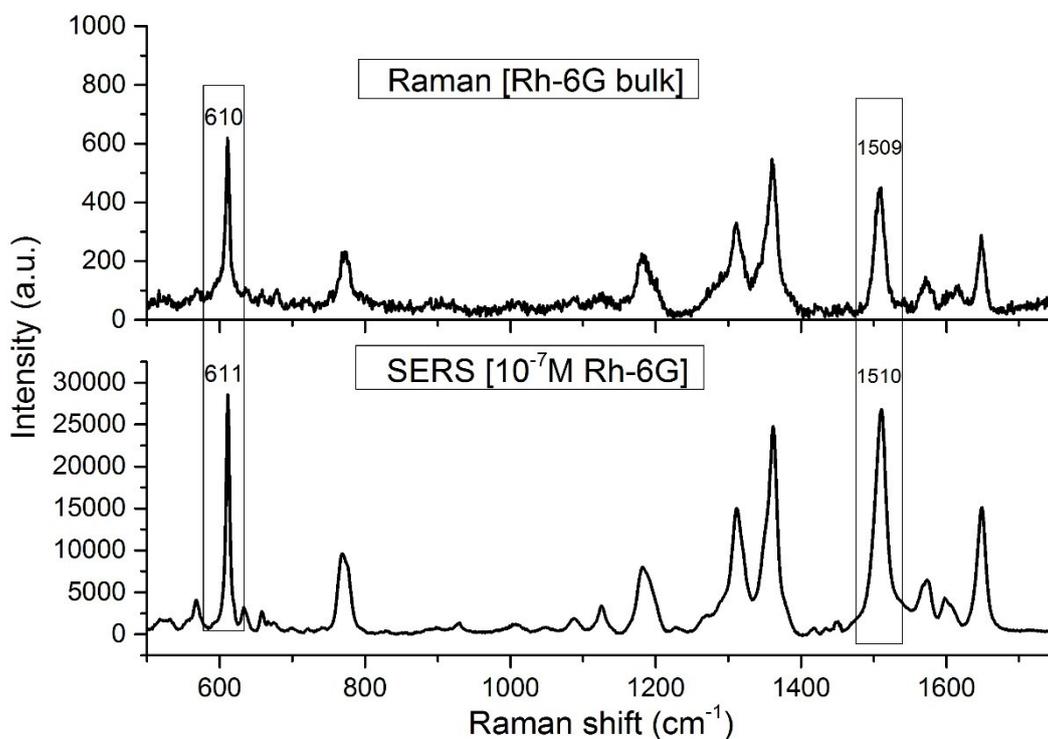


Figure S1. Raman [top] and SERS [bottom] spectra of bulk and 10⁻⁷ M of Rh-6G with selected bands for SERS enhancement factor calculation.

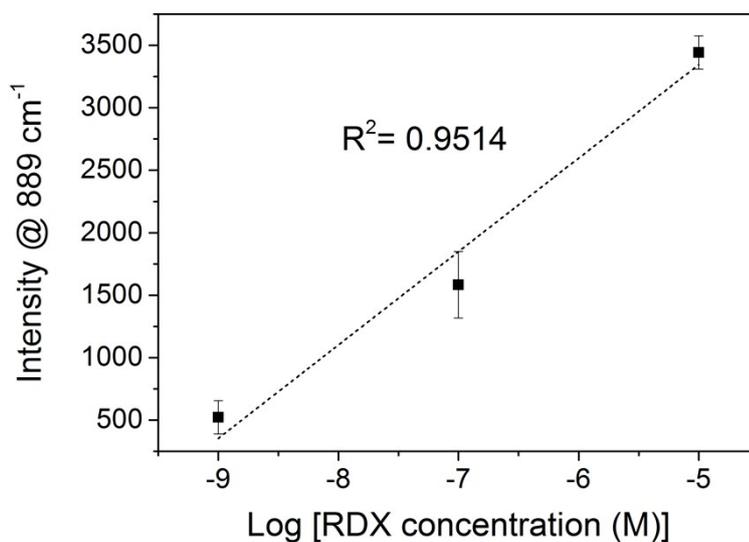


Figure S2: The linear relation between SERS intensity of the band 889 cm⁻¹ of RDX and samples concentration.

Table S1. Raman active modes and measured SERS signals of Rh-6G, DNT and RDX.

Analyte	$\tilde{\nu}_i$ (Raman) (cm ⁻¹)	$\tilde{\nu}_i$ (SERS) (cm ⁻¹)
Rh-6G (10 ⁻⁷ M)	610	611
	773	769
	1184	1183
	1310	1311
	1360	1361
	1509	1511
	1647	1649
DNT (10 ⁻⁵ M)	791	813
	834	858
	1071	1073
	1134	1160
	1206	1217
	1354	1366
	1543	1564
	1614	1608
	2936	2969
RDX (10 ⁻⁵ M)	881	890
	939	944
	1215	1234
	1272	1285
	1647	1649

Table S2. Estimated enhancement factor main bands of Rhodamine 6G, DNT and RDX.

Sample	Signals	Bands intensities		Enhancement factor EF
		Raman	SERS	
Rh-6G, 10 ⁻⁷ M	611 cm ⁻¹	594	27510	8.71 × 10 ¹⁰
	1511 cm ⁻¹	421	26756	1.19 × 10 ¹¹
DNT, 10 ⁻⁵ M	1366 cm ⁻¹	697.35	19764	2.46 × 10 ⁸
DNT, 10 ⁻⁹ M	1369 cm ⁻¹	697.35	1027	1.28 × 10 ¹⁰
RDX, 10 ⁻⁵ M	890 cm ⁻¹	765.62	3838.1	6.07 × 10 ⁷
RDX, 10 ⁻⁹ M	890 cm ⁻¹	765.62	584.52	9.26 × 10 ¹⁰

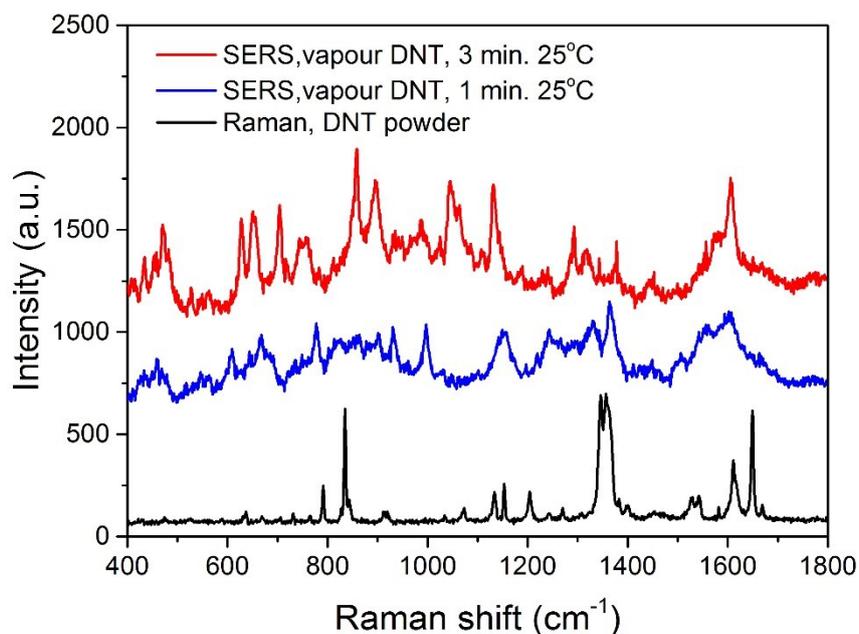


Figure S3: Raman spectrum of powder DNT, and SERS of vapour DNT 1, and 3 minutes exposure time at room temperature 25 °C.

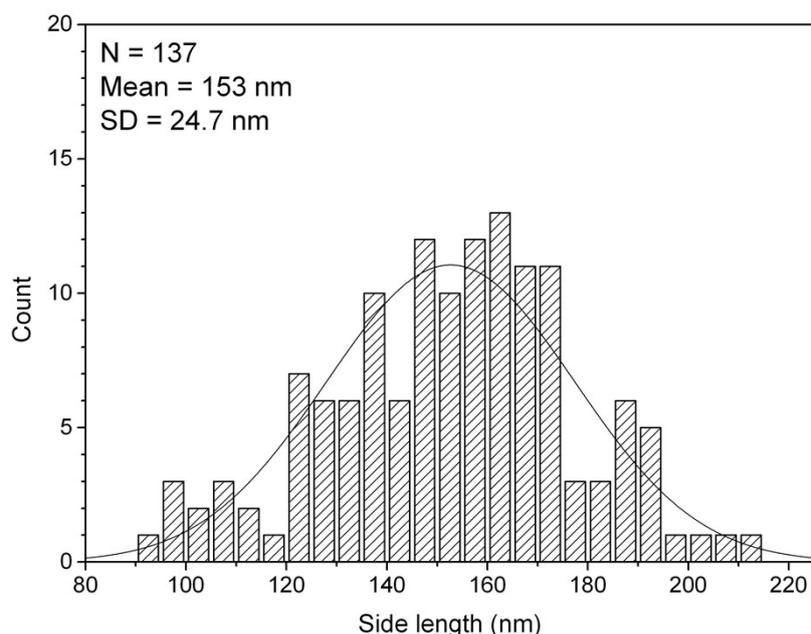


Figure S4 Size distribution histogram of AgNCs, side lengths of 137 cubes were measured with average of 153 nm \pm S.D. of 25 nm.

Synthesis of silver nanospheres:

Silver nanoparticles were synthesised by dissolving 3.6 mg of AgNO_3 in 20 mL of deionized water and brought to boiling. A solution of 1% of sodium citrate was prepared by dissolving of 20 mg in 2 mL water, and then it was added to the AgNO_3 solution. The solution was left boiling for 1 hour. The silver nanoparticles product was brownish and had an absorption peak at 460 nm corresponding to AgNSs plasmonic resonance (Fig. S5).

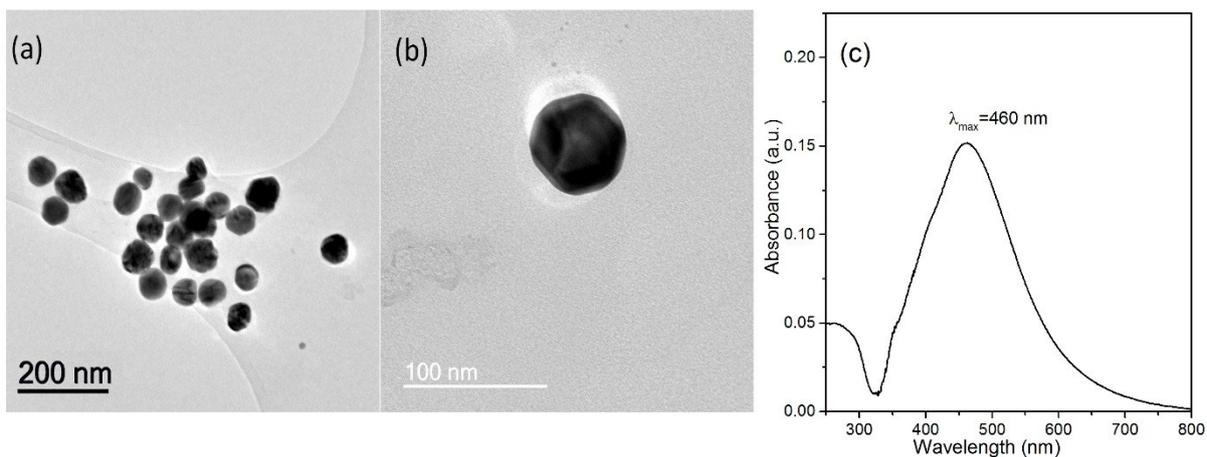


Figure S5: Transmission electron microscope images of silver nanoparticles AgNPs (a), (b) and UV-Vis absorption spectra of silver nanoparticles AgNSs, where the surface plasmon resonances (SPR) absorption peak is 460 nm.

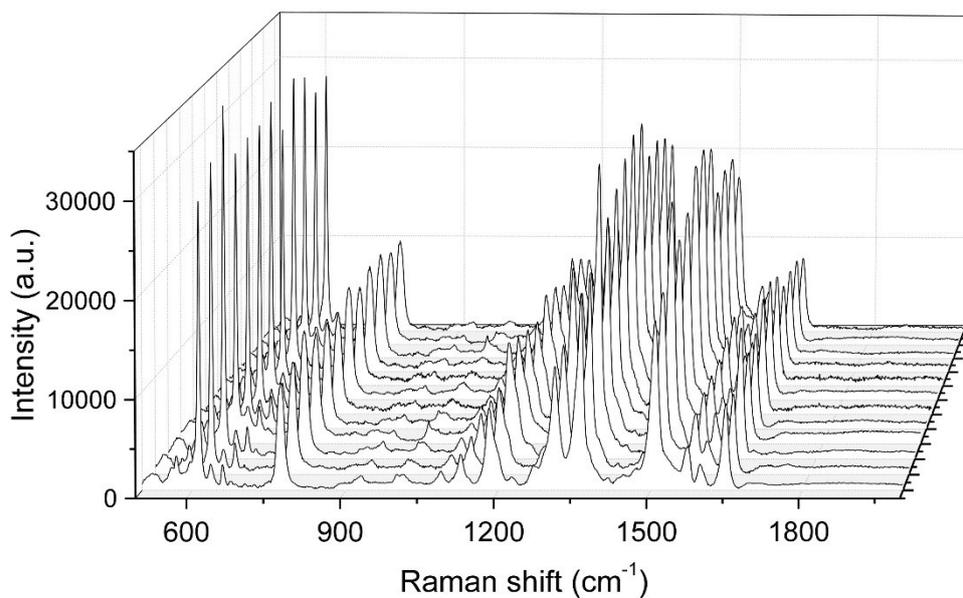


Figure S6: Mapping of SERS spectra of Rh-6G from a 10^{-7} M solution across a AgNCs substrate, showing high SERS reproducibility.

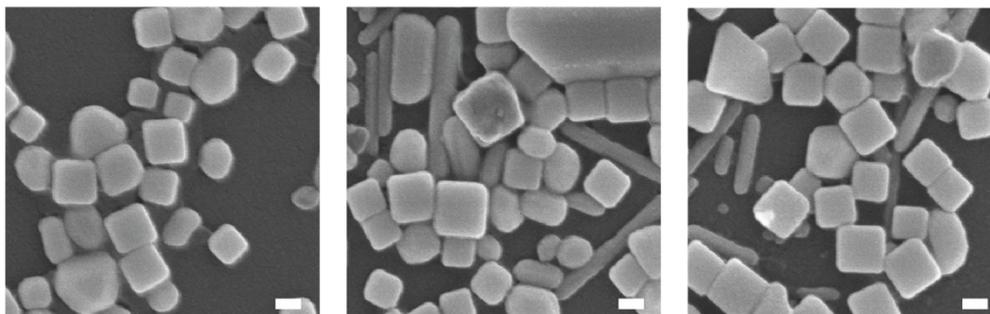


Figure S7: Additional SEM imagery of the as deposited AgNC substrates showing typical particle densities and size distributions. All scale bars 100 nm.

Electric field calculation (simulation):

A commercial-grade simulator based on the finite-difference time-domain method (*Lumerical-FDTD*) was used for the electric field calculations. The simulations were performed in 3D with data recorded at 633 nm to match the experimental laser excitation wavelength. Convergence testing was performed by increasing mesh resolution until the maximum of the electric field remained constant. Optical constants for the medium were set to that of air ($n = 1$; $k = 0$) and the particles had a 2 nm thick dielectric layer surrounding them ($n = 1.5$; $k = 0$), whilst optical constants for silver were taken from reference [4]. The refractive index of the substrate was set to represent glass ($n = 1.5$; $k = 0$).

References:

1. Qi, D., et al., *Improved SERS sensitivity on plasmon-free TiO₂ photonic microarray by enhancing light-matter coupling*. Journal of the American Chemical Society, 2014. **136**(28): p. 9886-9889.
2. Cong, S., et al., *Noble metal-comparable SERS enhancement from semiconducting metal oxides by making oxygen vacancies*. Nature communications, 2015. **6**.
3. Horiba, *What analysis spot size is used for a Raman microscope?* <http://www.horiba.com/scientific/products/raman-spectroscopy/raman-academy/raman-faqs/what-analysis-spot-or-laser-spot-size-is-used-for-a-raman-microscope/>. 2017.
4. Johnson, P.B. and R.-W. Christy, *Optical constants of the noble metals*. Physical review B, 1972. **6**(12): p. 4370.