Supporting information

Correlative SEM SERS for quantitative analysis of dimer nanoparticles

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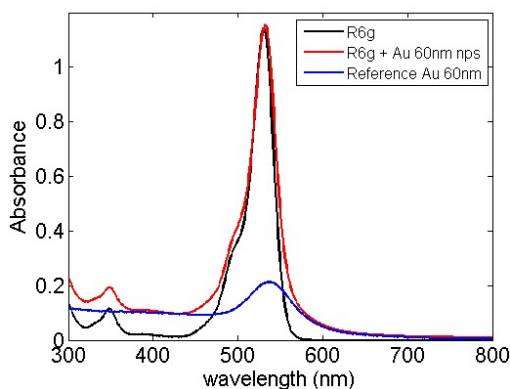* Corresponding Author: E-mail: f.j.timmermans@utwente.nl

Figure S1. UV-Vis Absorption spectroscopy of Rhodamine 6g in ethanol solution (black), 60 nm gold nps added to the R6g solution (red) this sample is used for SEM-SERS experiments, and pure 60nm gold nps at the same concentration as reference (blue).
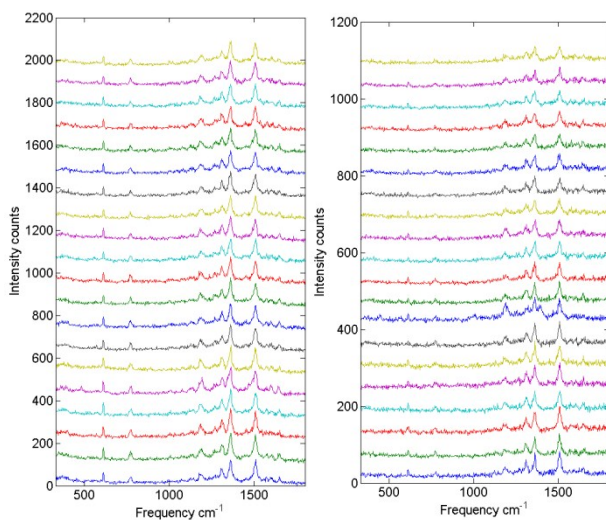

Figure S2. Verification of the sample stability under laser illumination with a measurement of 20 SERS spectra recorded on two different sample locations at 800 µW excitation power recorded with 1 second integration time, for 20 seconds per location.
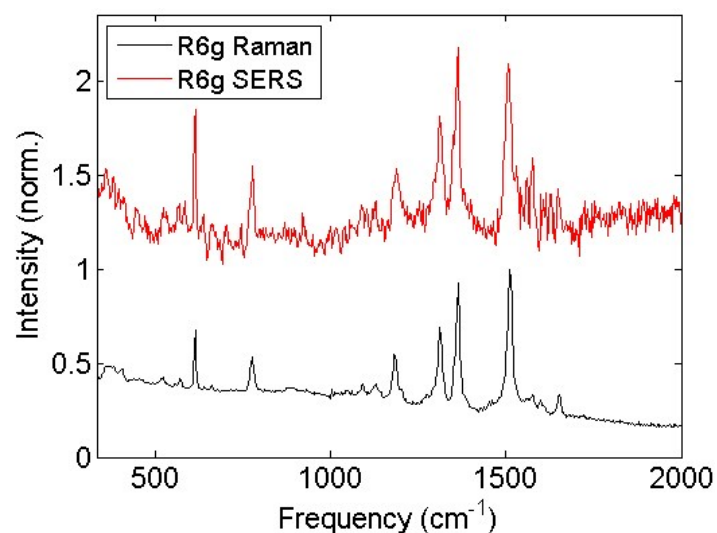
Figure S3. Comparison of the R6g SERS spectrum (red) and the spontaneous R6g Raman spectrum (black). The spectra are normalized and the R6g SERS spectrum is offset to +1 for clarity. The R6g Raman spectrum is measured in an ethanol solution and the ethanol spectrum is subtracted from the measured spectrum, the R6g fluorescence is observed as the low-frequency background component.
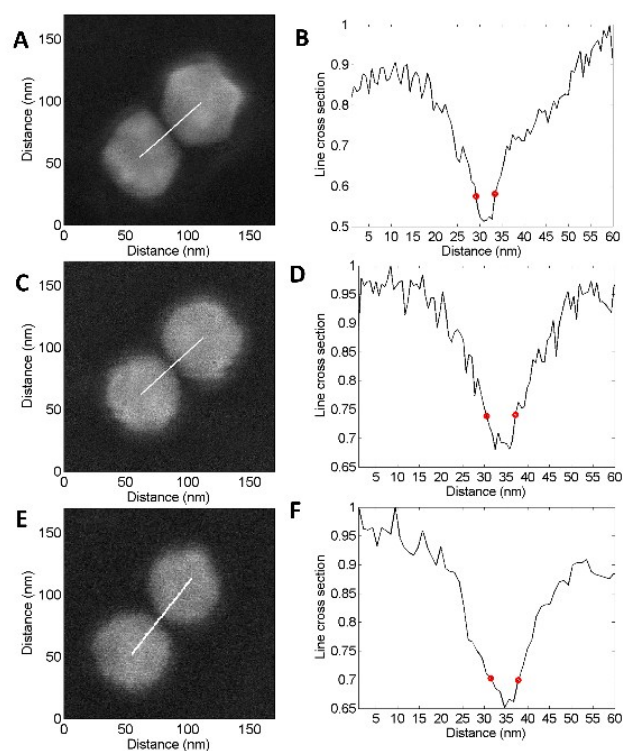

Figure S4. Measurement of the gapsize for observed structures. (A, C, E) SEM images with a line inset indicating the cross section through the nanoparticles for analysis of the secondary electron signal. (B, D, F) Electron scattered signal strength across the line cross section indicated in the SEM images, the red dots indicate the measured edges of the gap between the nanoparticles.

Raman bands	Raman band frequency (cm^{-1})	Scatter Cross Section (m^2·sr^{-1})
C-C-C ring in-plane bending	610	1.70 E-33
C-H out-of-plane bending	774	1.88 E-33
Aromatic C-C stretching	1308	5.39 E-33
Aromatic C-C stretching	1360	6.94 E-33
Aromatic C-C stretching	1509	8.34 E-33
Aromatic C-C stretching	1650	1.08 E-33

Table S1. Measured R6g Raman scattering cross section for multiple prominent R6g bands. The measurement is performed in solution with ethanol, with a small amount of toluene added as internal reference standard.

The presented cross section values have been corrected for the internal field factor term, which influences the Raman scattering cross section based on the solvent medium. The differential Raman cross section is proportional to the internal field factor term "L", as shown in eq. 1. L depends on the refractive index of the medium at the Stokes shifted (n_R) and excitation (n_0) wavelength as indicated in eq. 2. Since the scatter cross section of R6g is measured in an ethanol solution an appropriate correction is made to obtain the vacuum cross section of R6g using eq. 3.

$$\left(\frac{d\sigma}{d\Omega}\right)_{k\perp}^{-} = \frac{h}{2^3 \cdot c \cdot \epsilon_0^2} \cdot \frac{b_k^2 \cdot (\nu_0 - \nu_k)^4}{1 - e^{-h \cdot c \cdot \nu_k / k_b \cdot T}} \cdot g_j \cdot \left(\alpha_k'^2 + \frac{7}{45}\gamma_k'^2\right) \cdot L \tag{1}$$

$$L = \frac{n_R}{n_0} \cdot \frac{(n_R^2 + 2)^2}{3^2} \cdot \frac{(n_o^2 + 2)^2}{3^2} \tag{2}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{vacuum} = \frac{1}{L}\left(\frac{d\sigma}{d\Omega}\right)_{solution} \tag{3}$$

Gap (nm)	Pol (º)	D (nm)	EF	Gap (nm)	Pol (º)	D (nm)	EF	Gap (nm)	Pol (º)	D (nm)	EF
2.4	24	58 ; 66	932	3.9	50	60 ; 62	778	5.5	72	58 ; 59	448
2.5	19	60 ; 59	1156	4.0	23	70 ; 56	504	5.6	39	60 ; 60	1062
2.5	38	54 ; 58	5718	4.0	75	55 ; 58	797	5.6	62	57 ; 59	629
2.7	35	60 ; 60	3537	4.3	33	56 ; 60	638	6.0	45	60 ; 60	2096
2.9	62	60 ; 61	880	4.4	18	62 ; 59	3648	6.0	60	60 ; 58	881
2.9	80	60 ; 55	658	4.5	1	58 ; 58	1695	6.0	60	60 ; 50	516
3.0	7	57 ; 60	1483	4.5	41	60 ; 60	372	6.1	22	58 ; 59	1159
3.0	65	65 ; 58	796	4.6	72	62 ; 59	239	6.4	31	60 ; 59	2442
3.1	29	60 ; 60	1190	5.0	33	60 ; 60	684	6.5	38	60 ; 62	823
3.1	32	68 ; 66	1768	5.0	40	63 ; 58	476	6.7	41	60 ; 57	3935
3.1	88	60 ; 62	349	5.0	57	60 ; 60	4826	6.9	37	60 ; 58	697
3.2	2	60 ; 62	15848	5.1	39	60 ; 50	1692	7.0	44	60 ; 60	1182
3.2	49	59 ; 59	440	5.3	20	60 ; 60	473	7.8	46	62 ; 57	1233
3.5	15	58 ; 60	590	5.3	35	60 ; 60	798	8.0	7	54 ; 55	517
3.6	35	59 ; 57	10313	5.3	34	58 ; 62	901	8.5	60	60 ; 59	666

Table S2. Data table showing the structure averaged enhancement factor (EF) recorded from dimers of for varying gap sized (Gap), orientations (Pol), and diameters (D). The enhancement factor is calculated based on the SERS signal strength of the Raman bands presented in table S1.