Electronic Supplementary Information (ESI) for the paper:

"Appearance of SERS activity in single silver nanoparticles by laser-induced reshaping"

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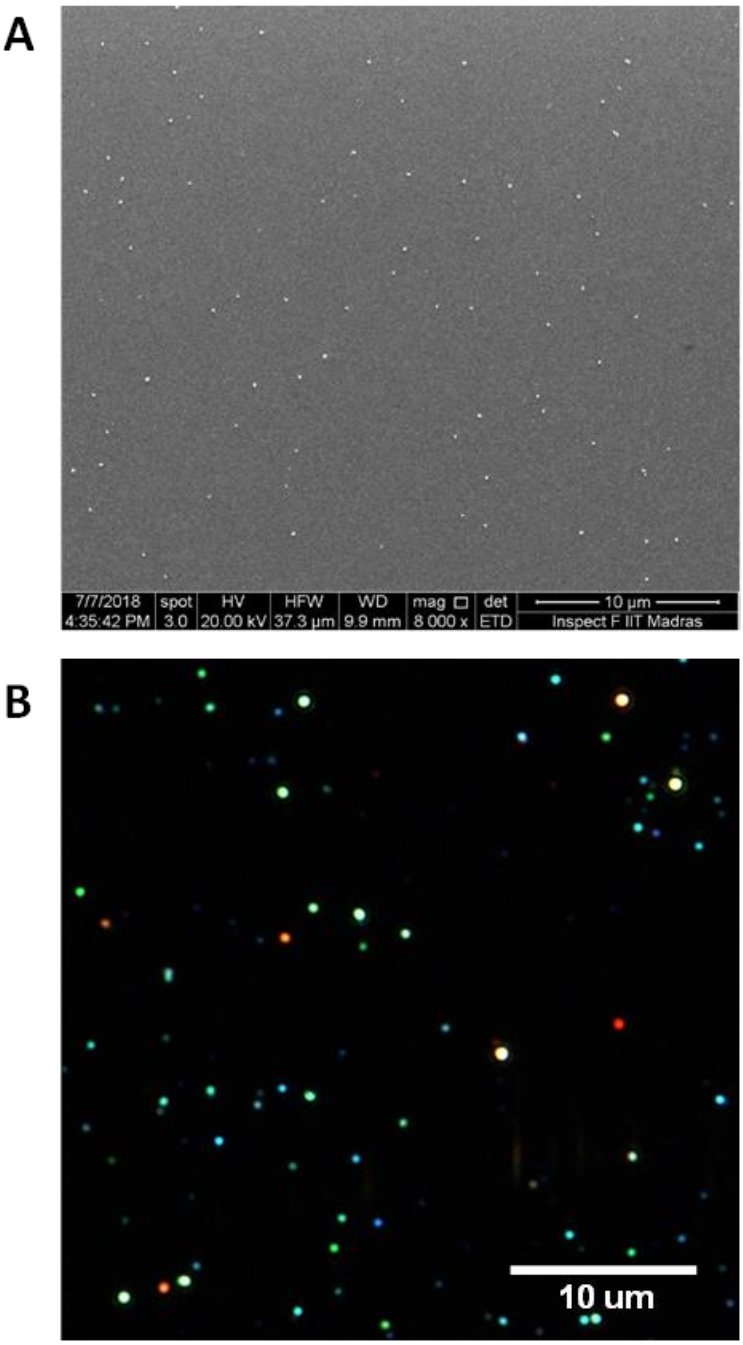

Fig. S1 Verification of AgNPs immobilization was done using FESEM imaging. It can be seen that interparticle distances are similar in FESEM and DFM images. (A) FESEM image, (B) DFM image of AgNPs immobilized in a given area of 36 x 36 μm^2.

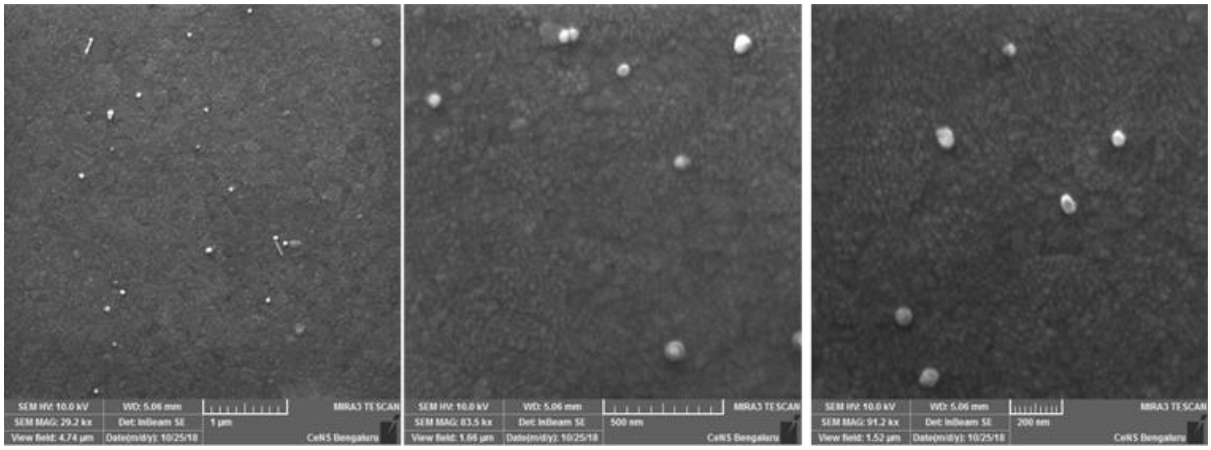

Fig. S2 High magnification FESEM images depicting different morphologies of the immobilized single AgNPs at various locations. Some aggregates were also seen.

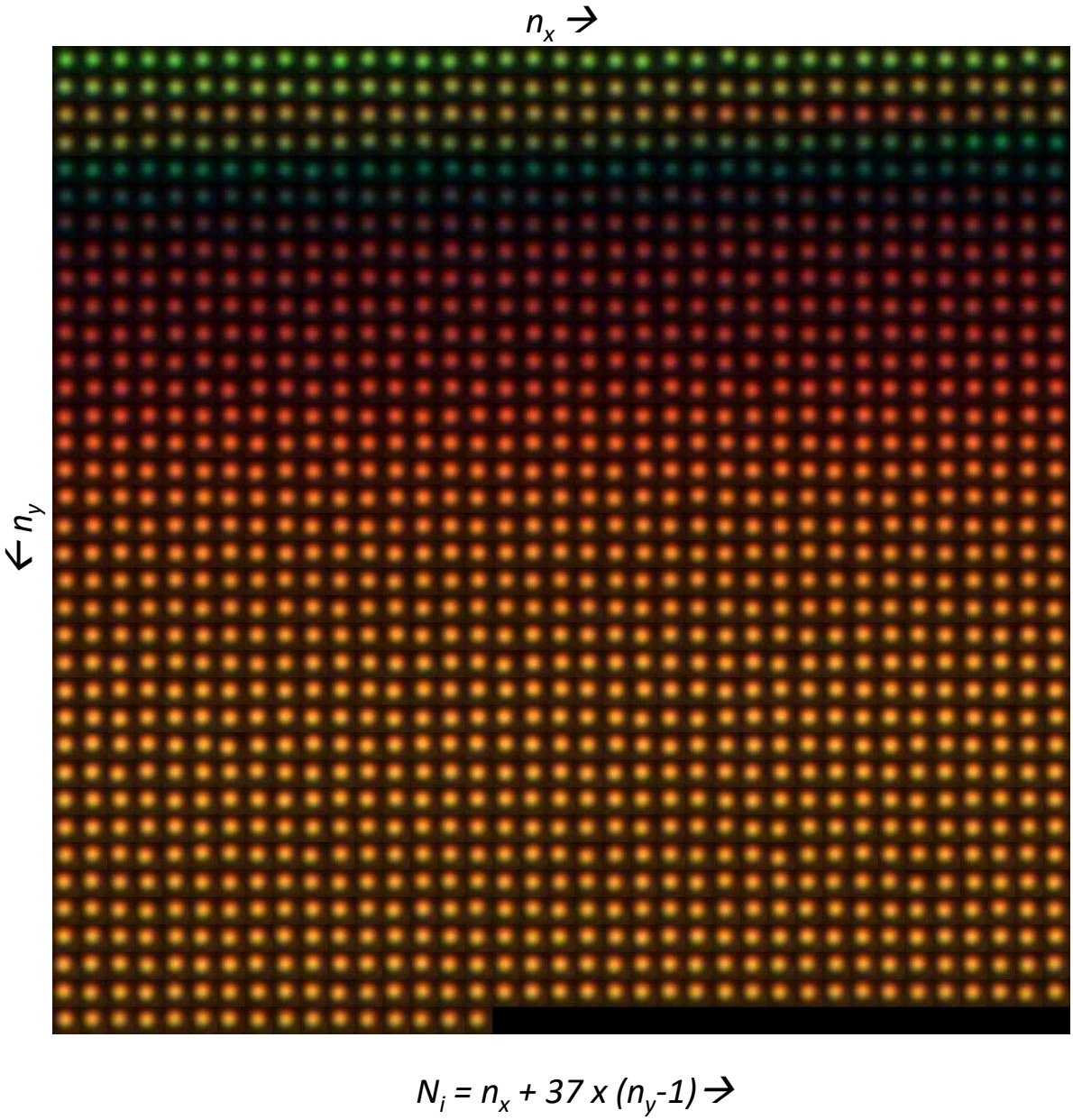

Fig. S3 Montage of the DFM images for single AgNPs for which intensity profiles are shown in Fig. 2 of the main text. Number of data point shown in Fig. 2 can be correlated to the image by position calculated using the formula given in below image. Here N_i is data point in time and n_x and n_y increase in steps of 1.

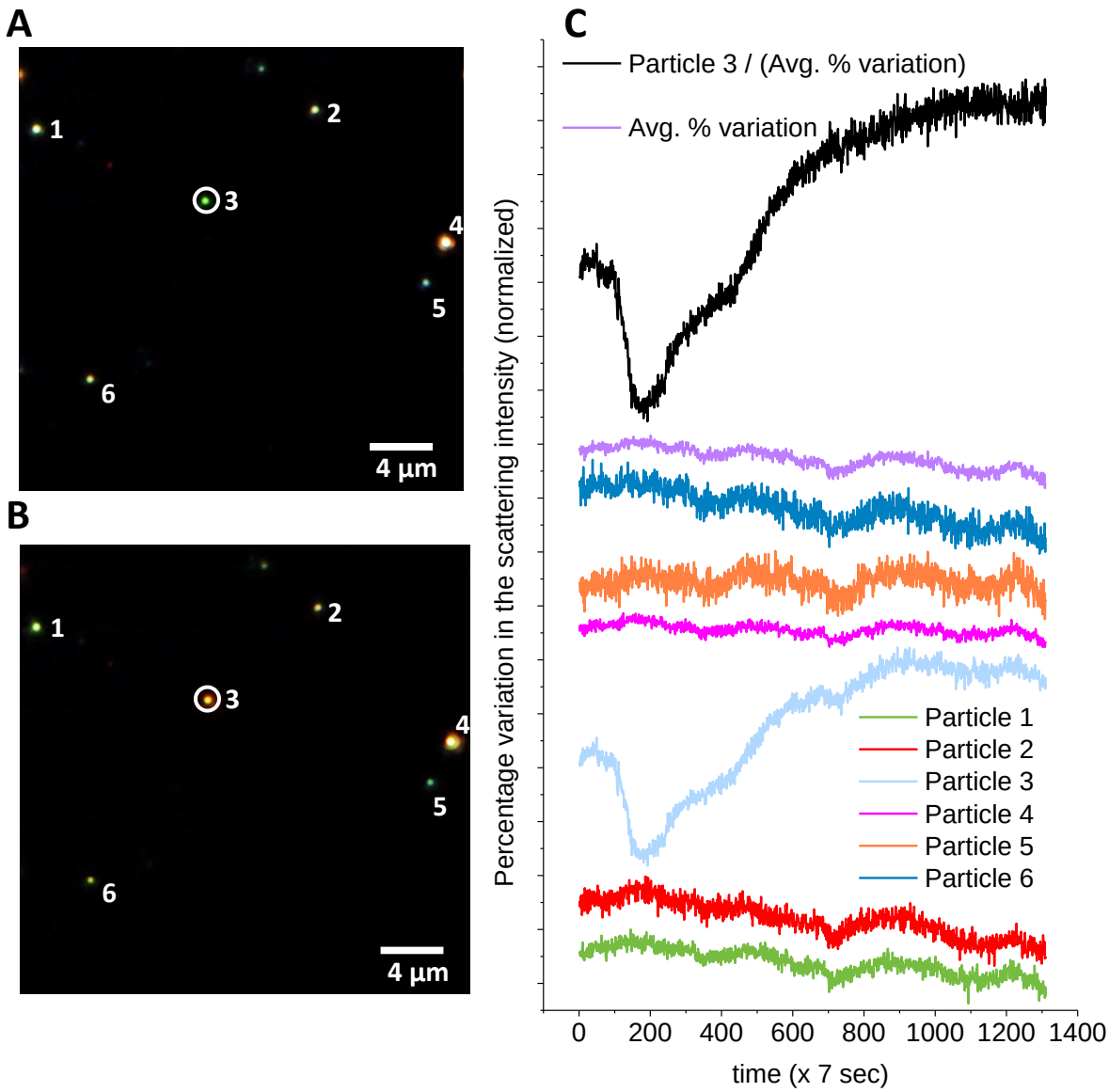

Fig. S4 Large area dark field images of the region surrounding single AgNP (particle 3) for which intensity profiles are shown in Fig. 2 of the main text. (A) At the beginning of the observation. Monitored particle inside the confocal volume is encircled. (B) At the end of the observation. (C) Graph shows percentage variations in the scattering intensity of particles (1,2,4,5,6) in the surrounding region of particle 3 which were averaged to obtain better correction spectrum (spectrum with purple color). Particle 3 spectrum was corrected by dividing the same with correction spectrum is shown on the top. It can be seen that similar kind of variations were removed after correction.

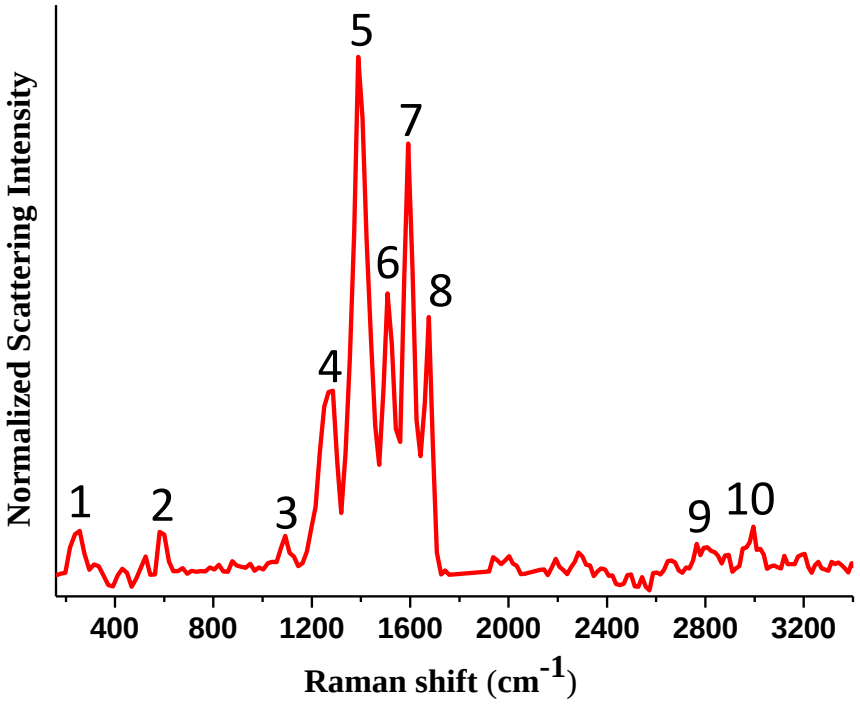

Fig. S5 SERS spectrum of citrate ligand on the AgNP for which intensity profiles are shown in Fig. 2 of main text. Corresponding Raman band assignments are provided in Table S1 given below.

Table S1 Citrate SERS band assignments

S.No.	Wavenumber(cm-1)	Band assignments[1-4]
1	246.6	ν(Ag-O)
2	582	δ(COO)
3	1092.2	δ(C-O ter. alc)
4	1285.2	$\delta(CH_2)+\omega(CH_2)$
5	1388	ν_{sy} (COO-)
6	1508.1	ν_{as}(COO-)
7	1592.3	ν_{as}(COO-)
8	1675.7	ν_{as}(COO-) + δ(OH)
9	2795.9	ν_{sy} (CH)
10	3000.1	ν_{as}(CH)

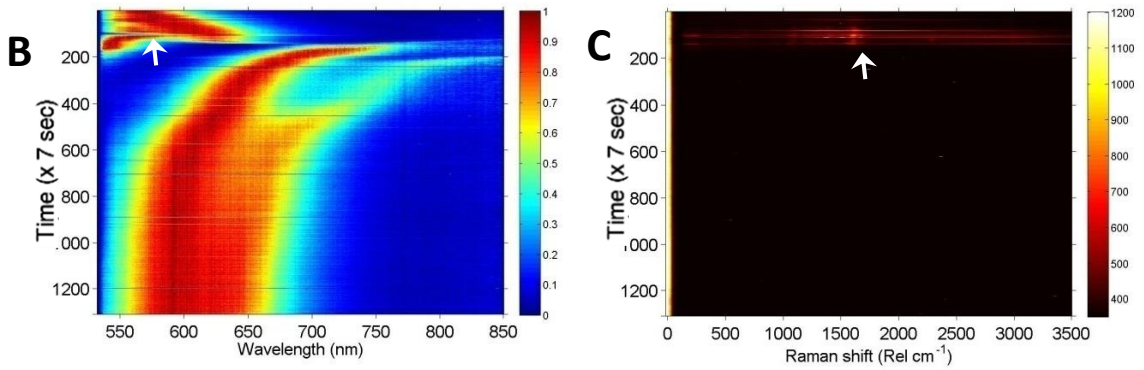

Fig. S6 Temporal plasmonic colormap and Raman intensity map of changes in the plasmonic and Raman scattering of AgNP for which intensity profiles are shown in the Fig. 3A of the main text.

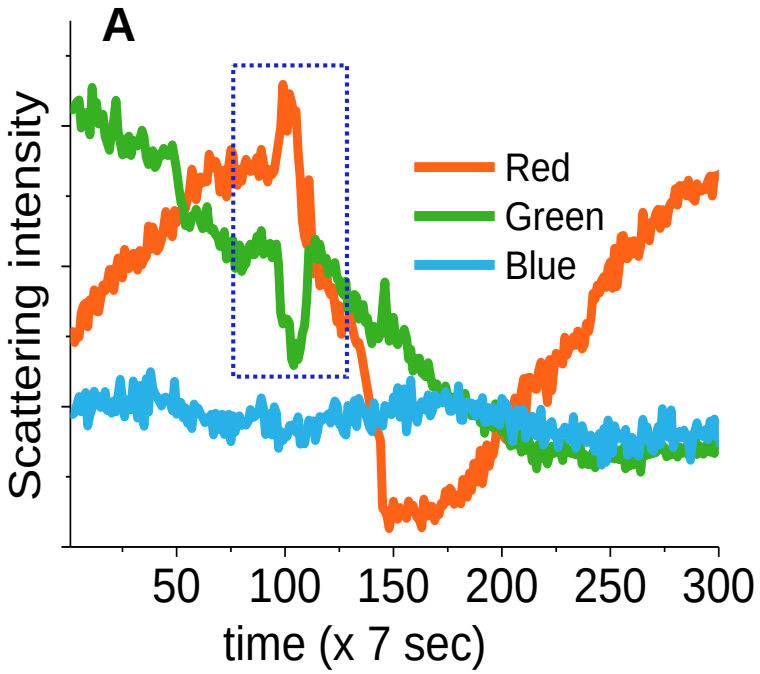

Fig S7. RGB profile for the particle calculated from the time-dependent DFM images. Blue color box indicating the time position when SERS activity was observed in the nanoparticle.

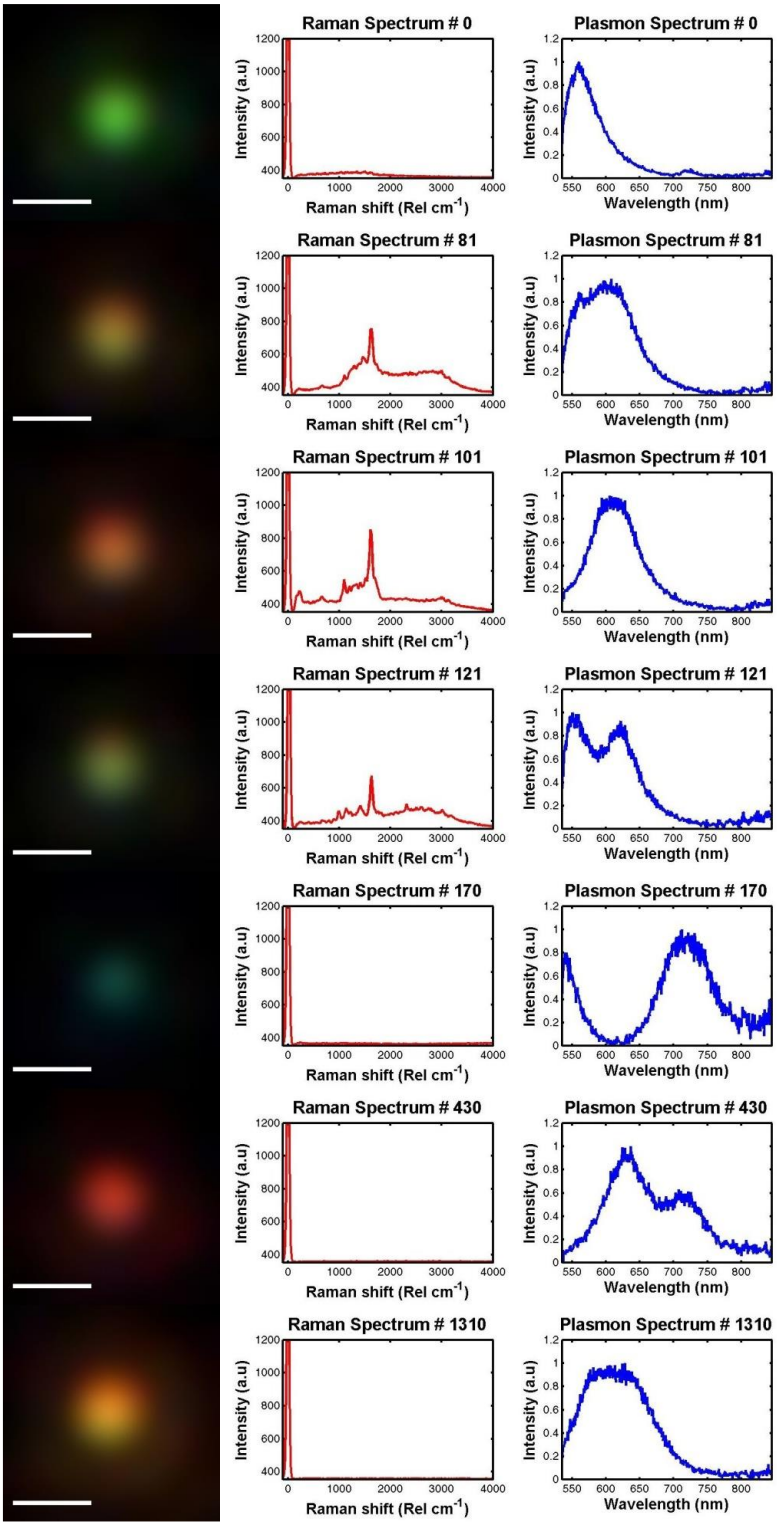

Fig. S8 Plasmonic and Raman scattering spectra corresponding to the time points of interest of AgNP for which intensity profiles are shown in Fig. 2 of the main text.

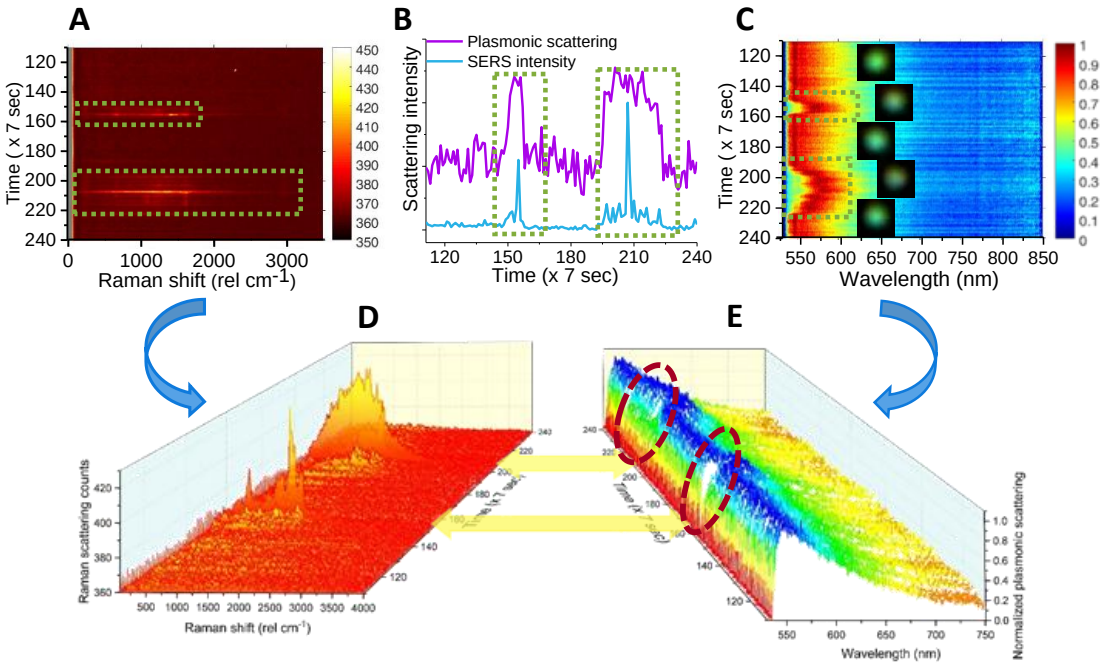

Fig. S9 (A) Raman intensity map, (B) Correlating integrated intensity profiles for Raman and plasmonic spectral match and (C) Plasmonic scattering colormap and their corresponding time-lapse Raman and plasmonic scattering spectra (D&E) for isolated AgNP. All the figures show that abrupt changes occurred during time 145-160 and 190-220 (x 7 sec) shown with wine colored dotted circles, the whole spectra are presented in D & E.

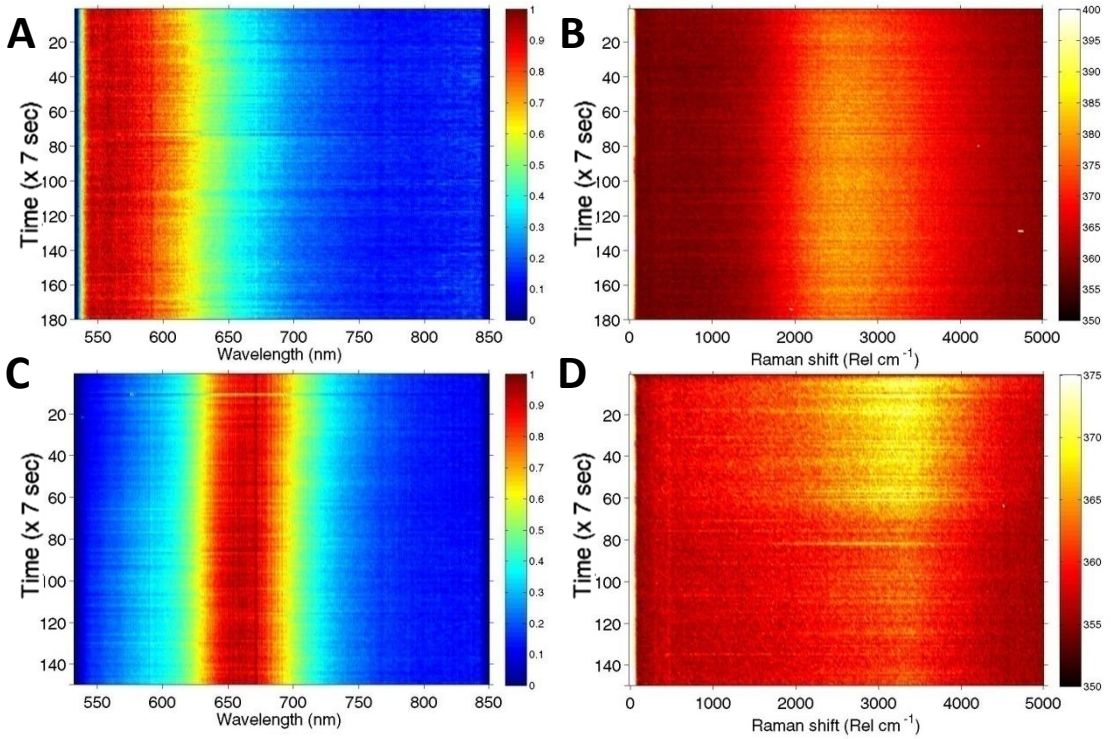

Fig. S10 A plasmonic scattering colormap (left) and Raman intensity map (right) of two AuNPs.

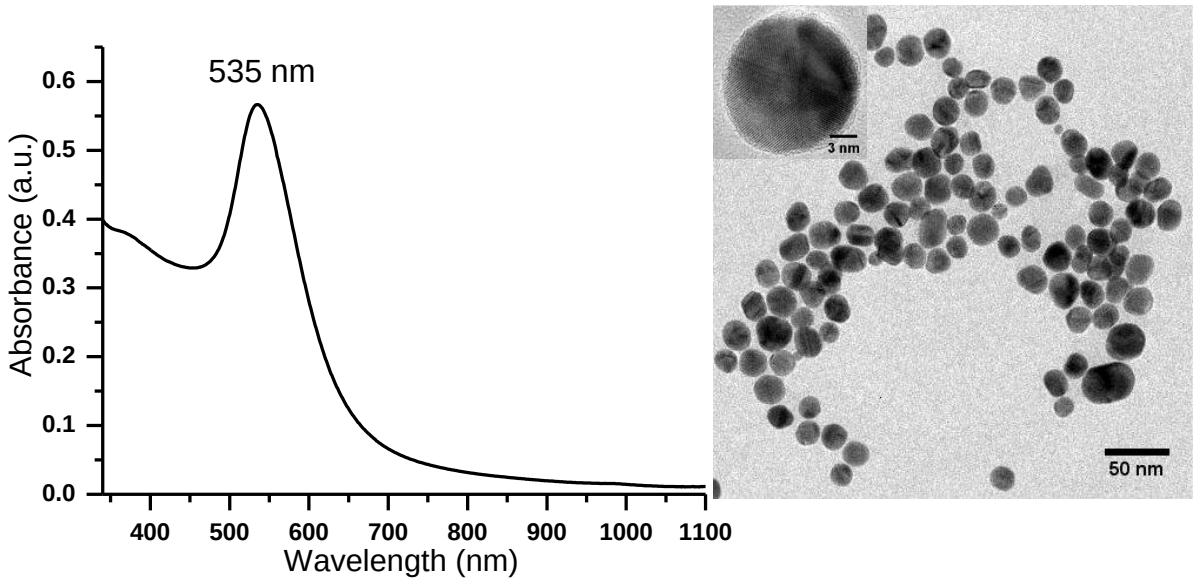

Fig. S11 (A) UV-Vis spectrum of the AuNPs used in this study. (B) TEM (scale bar – 50 nm) image of AuNPs. HRTEM (scale bar – 3 nm) of one particle is shown in the inset.

Table S2 Changes in the Silver content in water collected after washing out immobilized AgNPs in the area of 22 x 22 mm

S. No.	Washing time (hours)	Ag in ppb
1	0	7.14
2	6	3.47
3	12	0.79
4	18	0.32
5	24	0.28

Calculations of the number of atoms and nanoparticles formed by Ag ions release and their effect on the increment of the volume of nanoparticles

Silver ion release by ICP-MS (6 h) = 3.47 ppb (3.47 ug/L or 3.47 ng/mL)

For ICP-MS measurements, volume of DI water used for washing immobilized sample = 500 uL, hence, silver ion release = 1.74 ng/500 uL.

Molarity of the silver ions solution with 1.74 ng in 500 uL = 32.3 nM

Applying dilution correction, number of atoms in the 32.3 nM = $32.3 \times 10^{-9} \times 50 \times 6.02 \times 10^{23}$ = 0.97×10^{18} atoms (Note: 10 uL AgNP volume used for immobilization was washed with 500 uL milliQ water)

No. of atoms present in 50 nm diameter AgNP = 3.9×10^{6}

∴ Total no. of NPs which could be formed = $0.97 \times 10^{18} / 3.9 \times 10^{6} = 2.5 \times 10^{11}$ AgNPs of 50 nm diameter

For 50 nm nanoparticles which could be changed to 70 nm particles = 1.4×10^{11} NPs.

Calculations of the percentage change in RGB intensity:

For particle images before and after (I_b and I_a, respectively) with RGB intensities I_{bR}, I_{bG}, I_{bB} and I_{aR}, I_{aG}, I_{aB} following formulae were used to calculate R/G% and B/G% change as given below,

$$\frac{R}{G}\%\ change = \frac{(I_{aR}/I_{aG}) - (I_{bR}/I_{bG})}{(I_{bR}/I_{bG})}$$

$$\frac{B}{G}\%\ change = \frac{(I_{aB}/I_{aG}) - (I_{bB}/I_{bG})}{(I_{bB}/I_{bG})}$$

References

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