

Supporting information for the paper:

Atomically Precise Silver Clusters as New SERS Substrates

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Materials and methods:

1. Chemicals

Silver nitrate (AgNO_3 , 99% Aldrich), sodium borohydride (NaBH_4 , 99.9%, Aldrich); 2-phenylethanethiol (PETH, 98%, Aldrich); crystal violet, R6G (S. D. Fine Chem. Ltd, India), adenine (99%, Aldrich); ethanol (Changshu Yangyuan Chemical, China, AR grade), tetrahydrofuran (THF) (MERCK, HPLC grade) and toluene (Rankem, AR grade) were used in this synthesis. All the chemicals were commercially available and were used without further purification. Locally available cotton and paper were used as a substrate.

2. Synthesis of $\text{Ag}_{152}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$

The synthesis of Ag_{152} cluster protected by PET (2-phenylethanethiol, in the thiolate form) involves the following steps. Initially, 23 mg of AgNO_3 and 100 μL of PET were ground well in a clean agate mortar using a pestle. The color of the mixture changes to pale orange showing the formation of silver thiolate. To this mixture, 25 mg of solid NaBH_4 were added and the content was mixed well. 3 mL of ethanol was added to the mixture and mixed well after which 2 mL of ethanol was added for the washing the mixture. The mixture was kept for 15-30 sec till there is a color change from pale orange to deep grey. The contents were then taken into a centrifuge tube and centrifuged at 1600 rpm. The centrifugate was removed and the residue was dissolved in 5 mL toluene/THF. The Ag_{152} clusters were obtained from the toluene extract, which was dark brown in color.

3. Synthesis of $\text{Ag}_{55}(\text{SCH}_2\text{CH}_2\text{Ph})_{31}$

Similar to the above experiment only the silver and thiol ratio was taken as 1:4 and the cluster was again washed with heptanes after ethanol wash followed by the extraction in toluene.

4. Synthesis of Ag@PET nanoparticle

Similar to above experiment; here silver nitrate and thiol ratio is 1:1

5. Drop casting method

5 μ L of cluster solution was taken and drop casted on a glass slide to make a thin film and kept under ambient condition for drying. The analyte solutions were then drop casted on the film of the cluster and dried. The dried films were inserted into Raman spectrometer for the SERS measurements. For solution phase experiments, the analyte (in methanol) was mixed with cluster solution and a drop of the mixture was examined by the microRaman set-up.

6. Instrumentation

UV-Vis spectra were measured with a PerkinElmer Lambda 25 instrument in the range of 200-1100 nm. High resolution transmission electron microscopy (TEM) of clusters was carried out with a JEOL 3010 instrument. The TEM samples were drop casted on carbon-coated copper grids and allowed to dry under ambient conditions. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Biospectrometry Workstation from Applied Biosystems. The matrix used was DCTB (at 1:100 ratio of sample to matrix). A pulsed nitrogen laser of 337 nm was used for the MALDI MS studies. Mass spectra were collected in positive ion mode and were averaged for 200 shots. Scanning electron microscopic (SEM) was performed with a FEI QUANTA-200 SEM. For measurements, samples were drop casted on an indium tin oxide (ITO) coated glass and dried in vacuum. Raman spectra and images were done with a WITec GmbH, Alpha-SNOM alpha300 S confocal Raman microscope having a 532 nm and 633 nm laser as the excitation source. Background correction was done with the help of the software equipped with the Raman instrument. Initially, the spectrum is fitted with a proper polynomial which was subtracted from the original spectrum.

7. EF calculation

The enhancement factor¹ (EF) was calculated using the standard formula

$$EF = I_{\text{SERS}} * C_{\text{NR}} / I_{\text{NR}} * C_{\text{SERS}}$$

where I_{SERS} and I_{NR} are the integral intensity obtained by SERS and normal Raman scattering measurements, respectively. C_{SERS} and C_{NR} are the concentration of molecules used for SERS and

normal Raman scattering measurements, respectively. Maximum intense peak was considered for EF calculation.

Table 1. EF calculation

Substrate	Molecule	C_{SERS}	I_{SERS}	C_{NR}/I_{NR}	EF
Ag ₅₅ cluster	CV	5×10^{-5} M	210	6.6×10^{-2}	2.70×10^5
Ag@PET NP	CV	5×10^{-5} M	570	6.6×10^{-2}	7.52×10^5
Ag@Citrate	CV	5×10^{-5} M	1500	6.6×10^{-2}	1.98×10^6
Ag ₁₅₂ cluster	CV	5×10^{-9} M	120	6.6×10^{-2}	1.58×10^9
	R6G	1×10^{-7} M	180	6.0×10^{-2}	1.08×10^8
	Adenine	1×10^{-6} M	200	6.5×10^{-1}	1.30×10^8

Another way² of EF calculation is

$$EF = (I_{SERS}/I_{norm})(N_{bulk}/N_{surf})$$

Where I_{SERS} , I_{norm} , N_{bulk} , and $N_{surface}$ are the measured SERS intensities for a monolayer of probe molecules (CV) on the Ag₁₅₂ film, the measured intensity of non-enhanced or normal Raman scattering from a bulk sample, the number of the probe molecules under laser illumination for the bulk sample, and the number of the probe molecules on Ag₁₅₂ cluster, respectively. N_{bulk} and N_{surf} values were calculated on the basis of the estimated density of the surface species or bulk sample and the corresponding sampling areas. N_{bulk} and N_{surf} can be calculated from the following equation,

$$N_{surf} = 4\pi r^2 C A N$$

$$N_{bulk} = A h \rho / M$$

where r (1 nm), C ($10^6/\mu\text{M}^3$), A ($3.14 \times 1\mu\text{M}^2$), and N ($4250/\mu\text{M}^2$) are the average radius of the particles in the Ag_{152} cluster, surface density of the CV monolayer, the area of the laser spot, and the surface coverage of the particles (particles/ μm^2) in the Ag_{152} cluster, respectively. Parameters A , h (10 μM), ρ (0.83 g/cm^3), and M (407.99 g) are the area of the laser spot, the penetration depth, the density of solid CV ($\sim 0.83 \text{ gcm}^{-3}$), and the molecular weight of CV, respectively. The EF is calculated to be 1.96×10^9 for Ag_{152} with CV as the analyte.

Table 2. Frequencies and intensities of the most intense bands of Figures 2 & 3.

Figure No.	Substrate	Molecule	Frequency (cm^{-1})	I_{max}
2	Ag_{55} cluster	CV	1614	210
	Ag_{152} cluster	CV	1614	16110
	AgNPs	CV	1614	570
3	Ag_{152} cluster	CV	1614	500
		R6G	1360	180
		Adenine	730	200

Supporting information 1

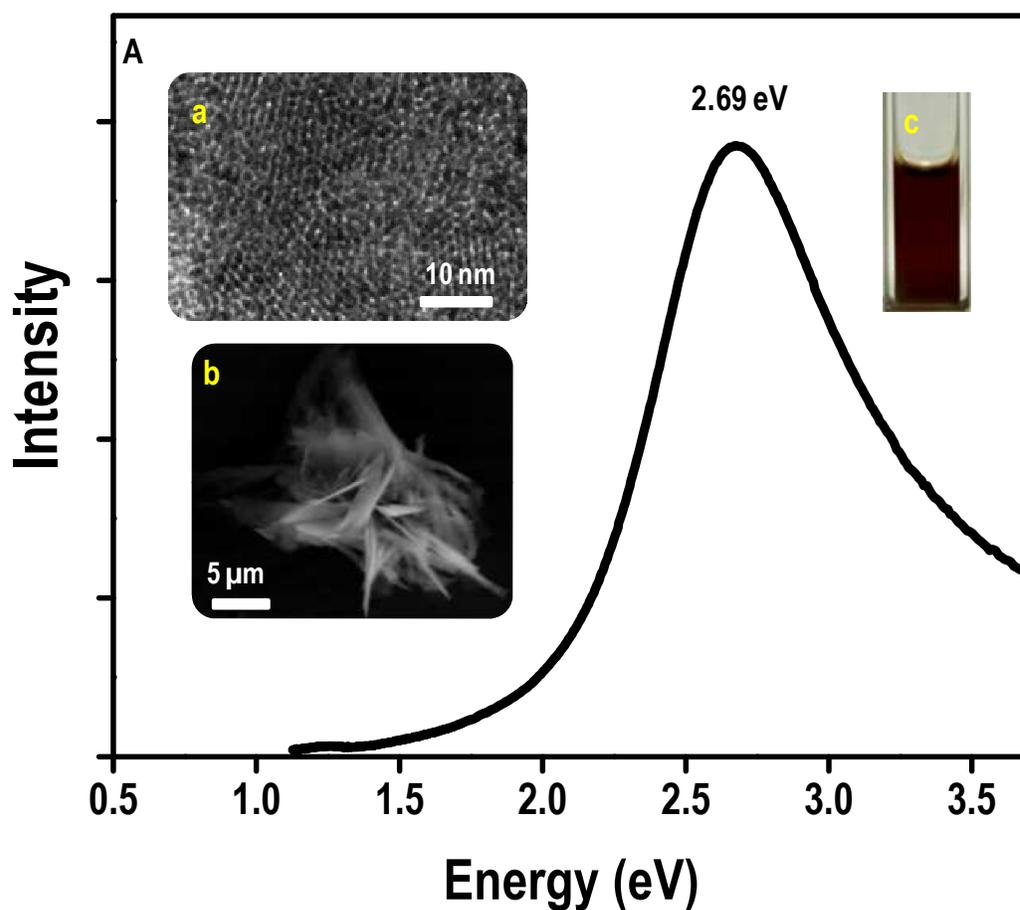


Figure S1. The optical absorption spectra of purified Ag_{152} clusters plotted in terms of energy (A), it shows the plasmonic band at 2.69 eV (460 nm). Inset: a) TEM image of the cluster which shows periodic arrangement of clusters and mono dispersity, b) SEM image of microcrystals of the cluster, and c) photograph of Ag_{152} cluster solution in toluene, taken in a cuvette.

Supporting information 2

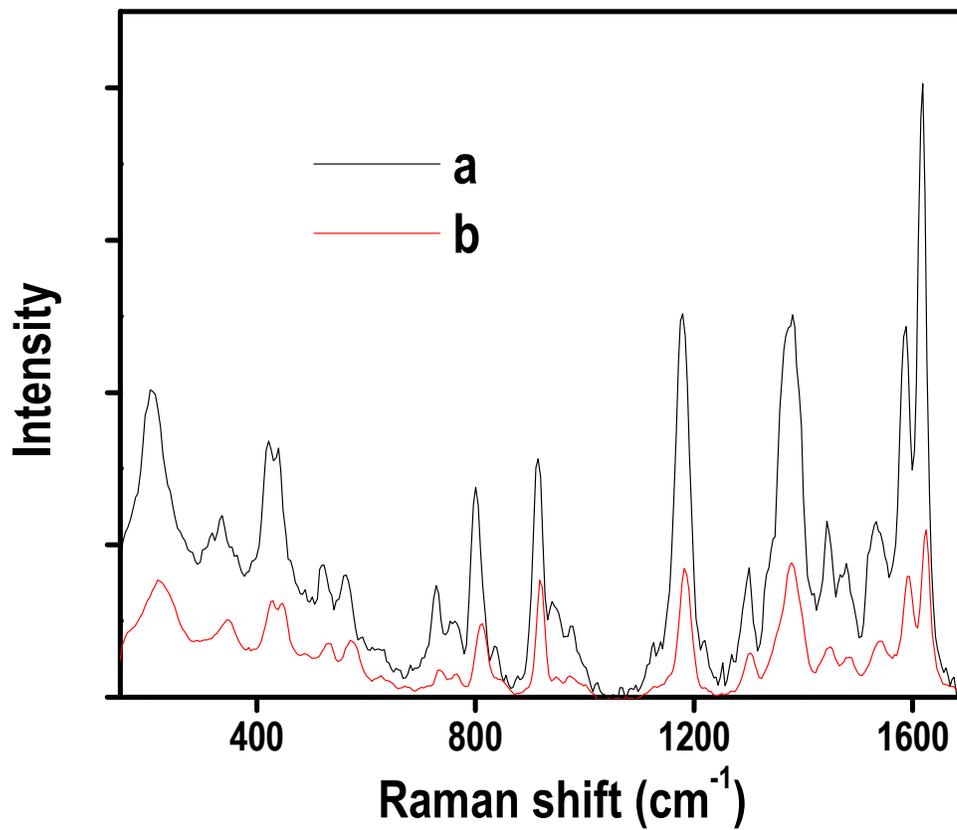


Figure S2. The SERS spectrum of CV ($5 \mu\text{M}$) taken from (a) drop casted film of Ag_{152} cluster and (b) Raman spectrum of bulk CV.

Supporting information 3

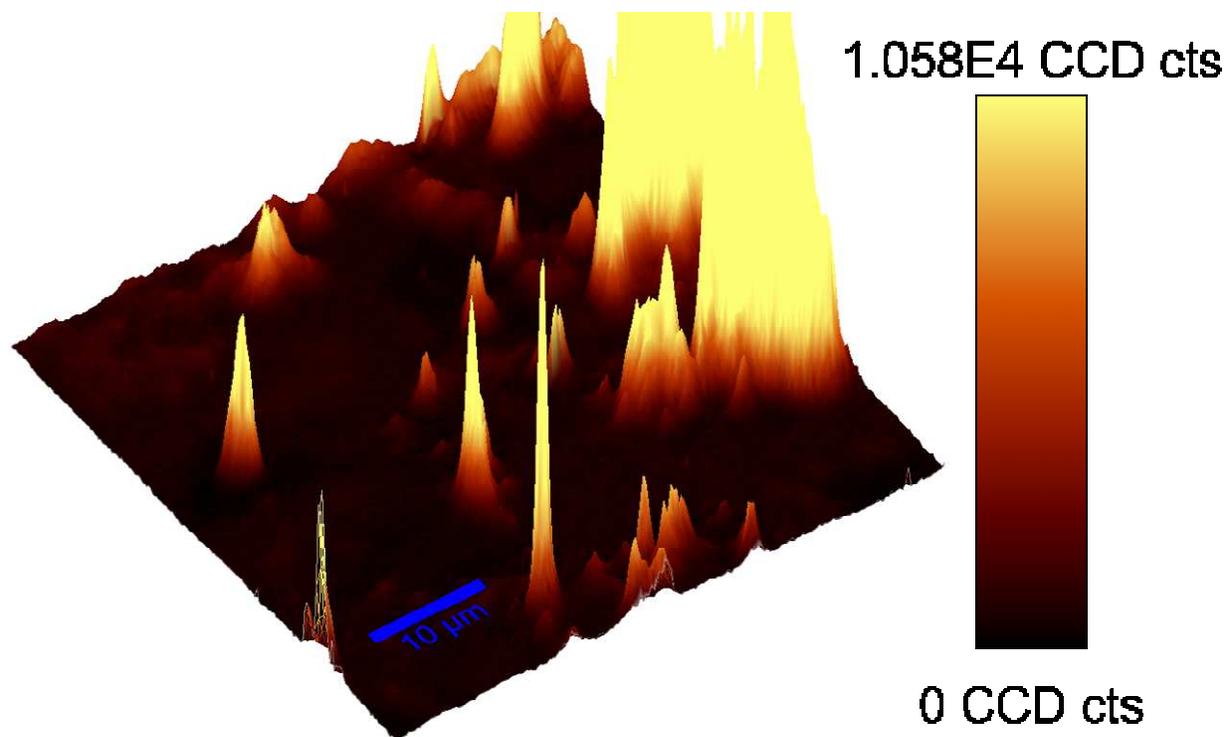


Figure S3. The Raman image of a selected area collected in a wider (150 cm^{-1} to 1700 cm^{-1}) window.

Supporting information 4

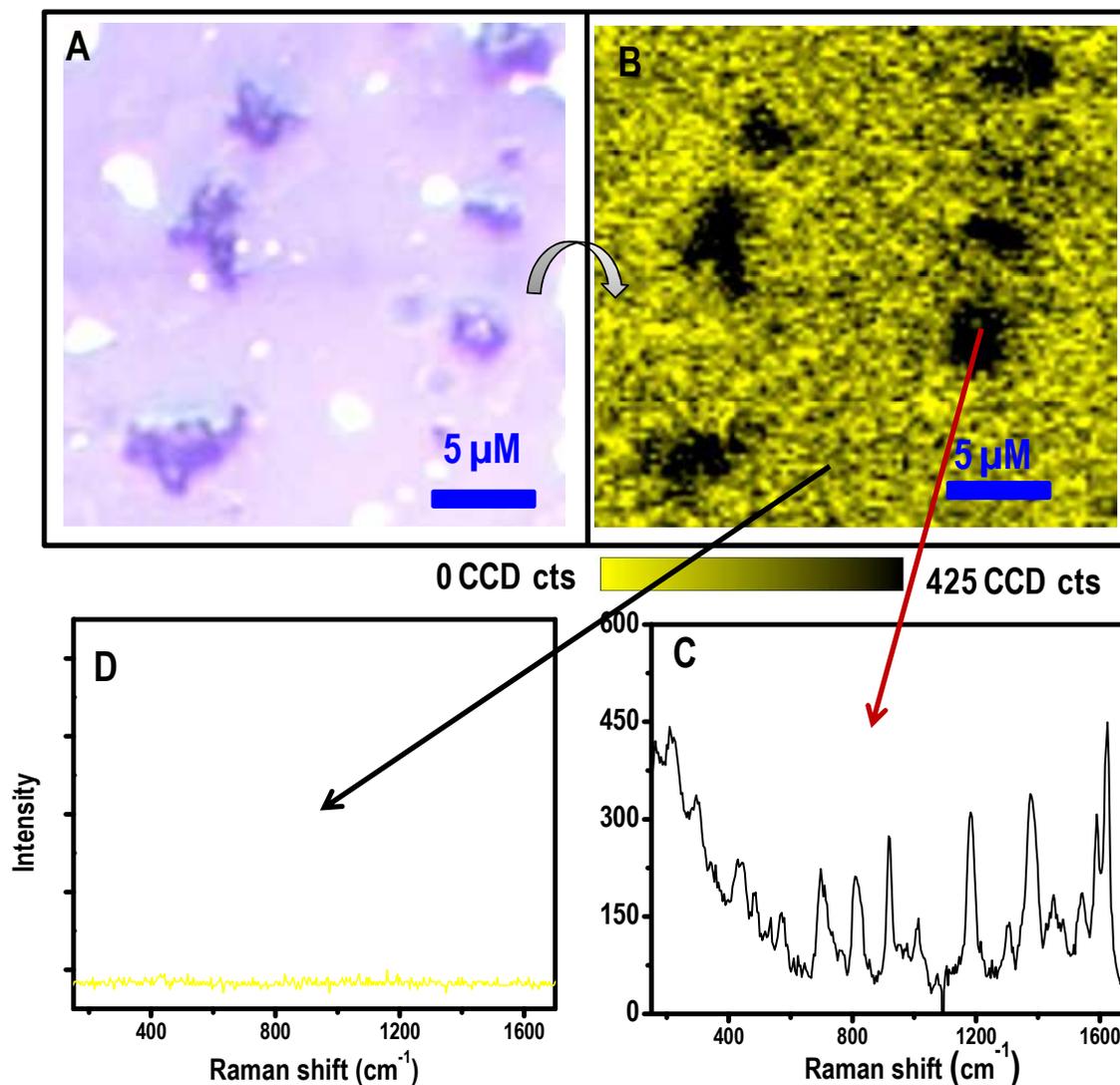


Figure S4. A: the optical image of a selected part of the sample. B: Corresponding Raman image, which shows that the “hot spot” are on the cluster surface and intensity comes spontaneously from all the area of each microcrystal. C and D: SERS spectra from the dark green and light yellow zone, respectively.

Supporting information 5

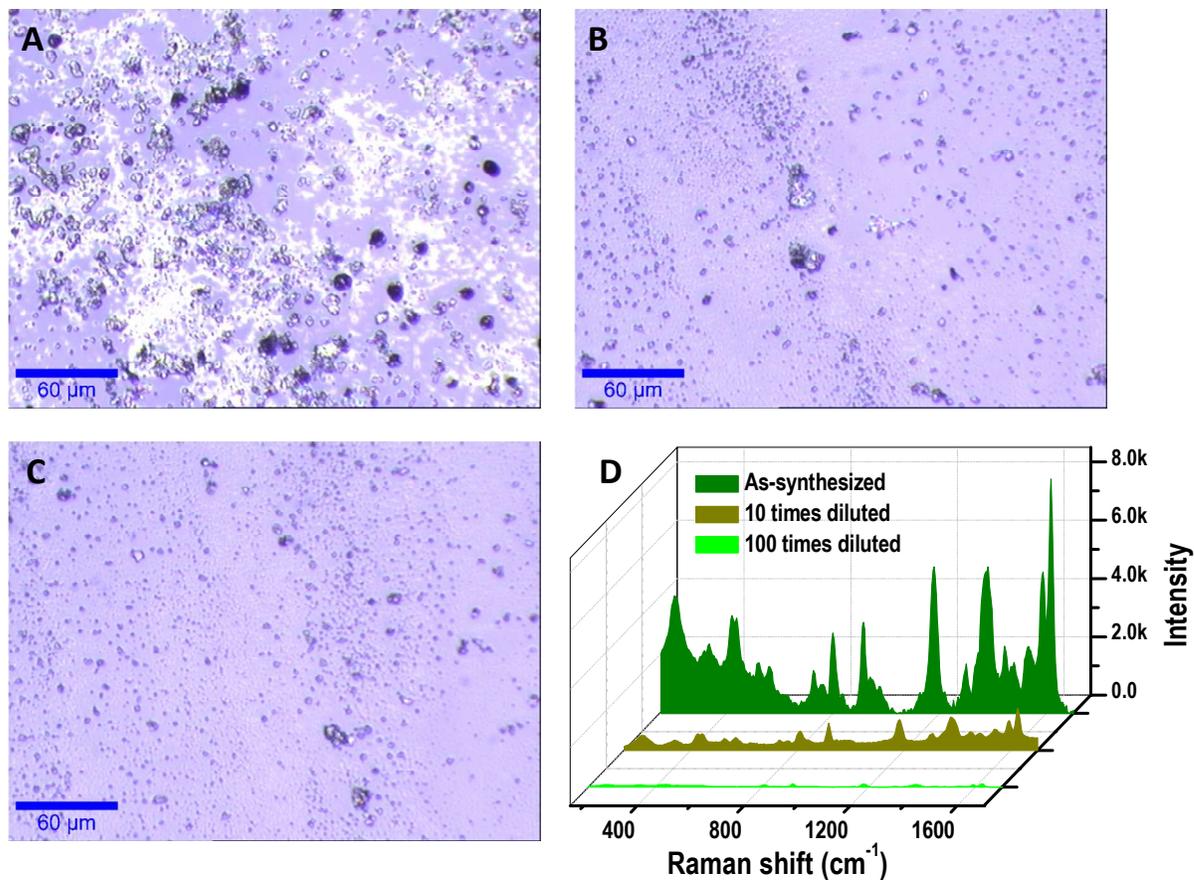


Figure S5. Morphological change on dilution of the cluster solution; A: drop casted as-synthesized clusters, B: 10 times diluted; and C: 100 times diluted. D: SERS spectra for different cluster concentrations among which as-synthesized cluster showing maximum SERS intensity. For all the cases, same concentration (5 μM) of CV was added.

Supporting information 6

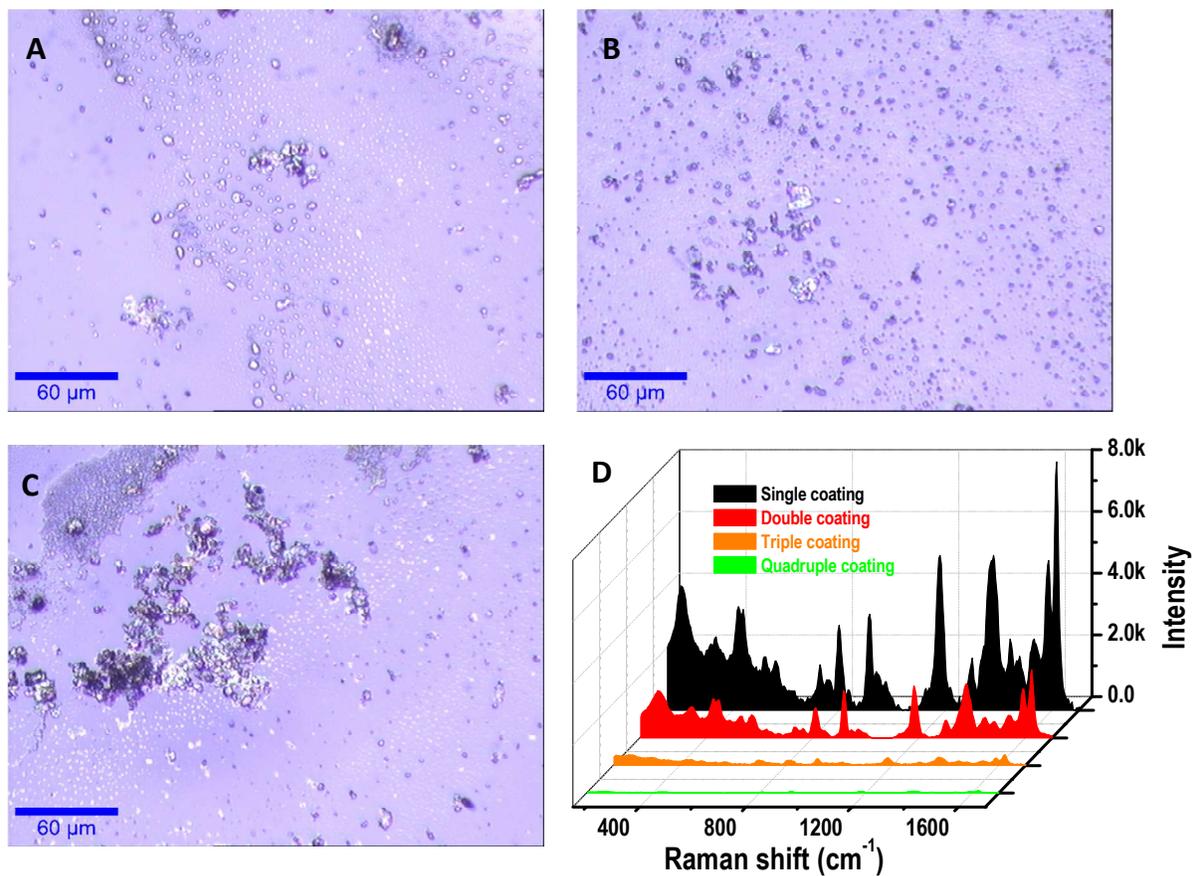


Figure S6. Morphological change in coating variation; A: single coating, B: double coating; C: triple coating. D: SERS spectra for different number of coatings. Single coating shows the maximum intensity. For all the cases, same concentration (5 μM) of CV was used.

Supporting information 7

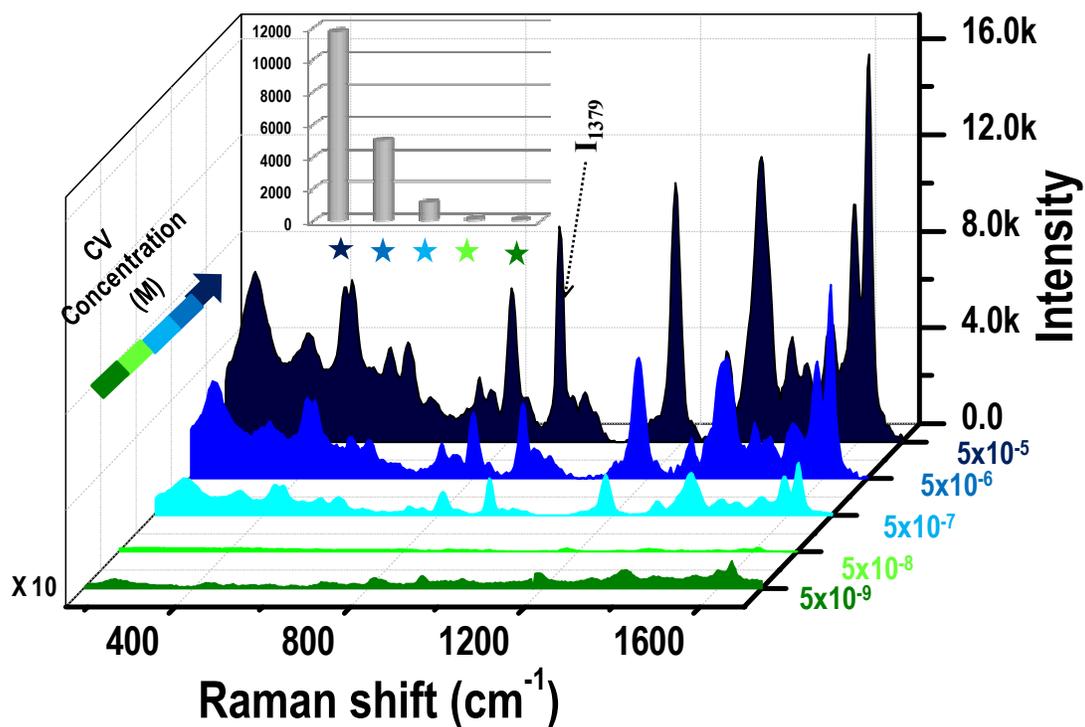


Figure S7. The SERS spectra of crystal violet with different concentrations. The lower detection limit is 5×10^{-9} M. The spectrum is expanded 10 times in the Figure. Inset shows the intensity of the 1379 cm^{-1} peak for all the CV concentrations.

Supporting information 8

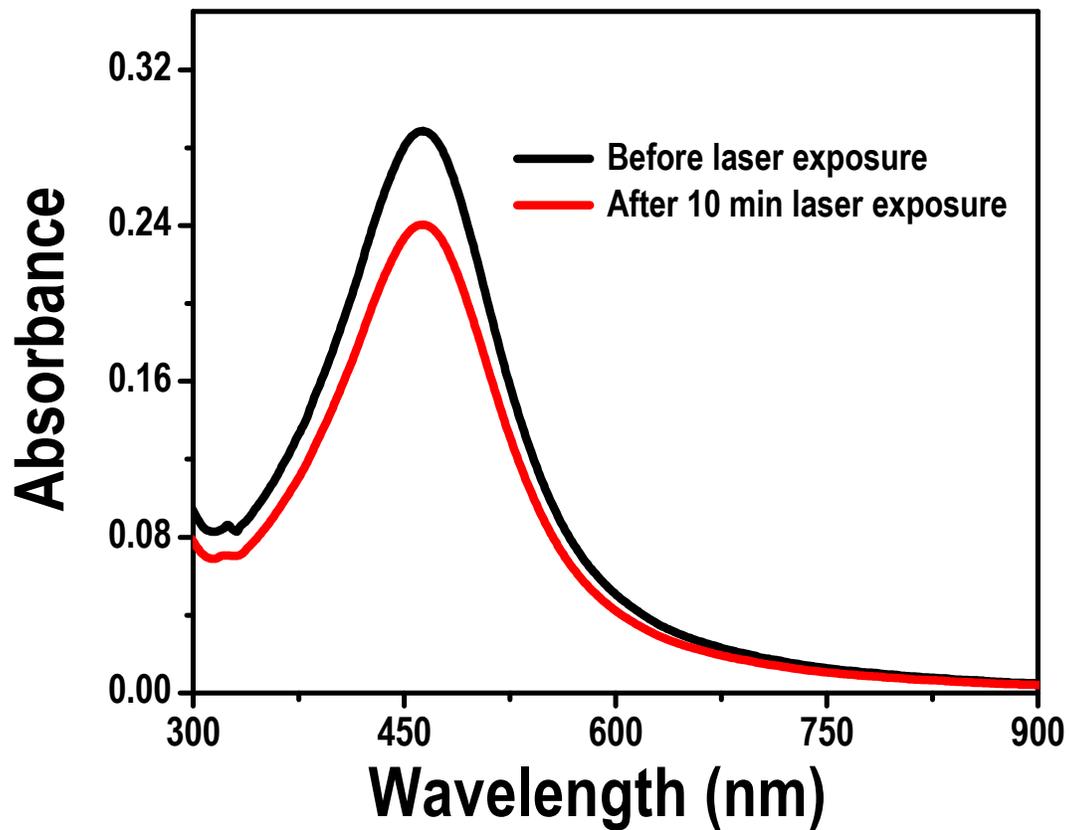


Figure S8. UV/Vis of cluster solution taken before and after the laser exposure. There as some laser induced damage to the cluster. For this experiment, the selected area was exposed for 10 minutes and redispersed in toluene to check the UV/Vis.

Supporting information 9

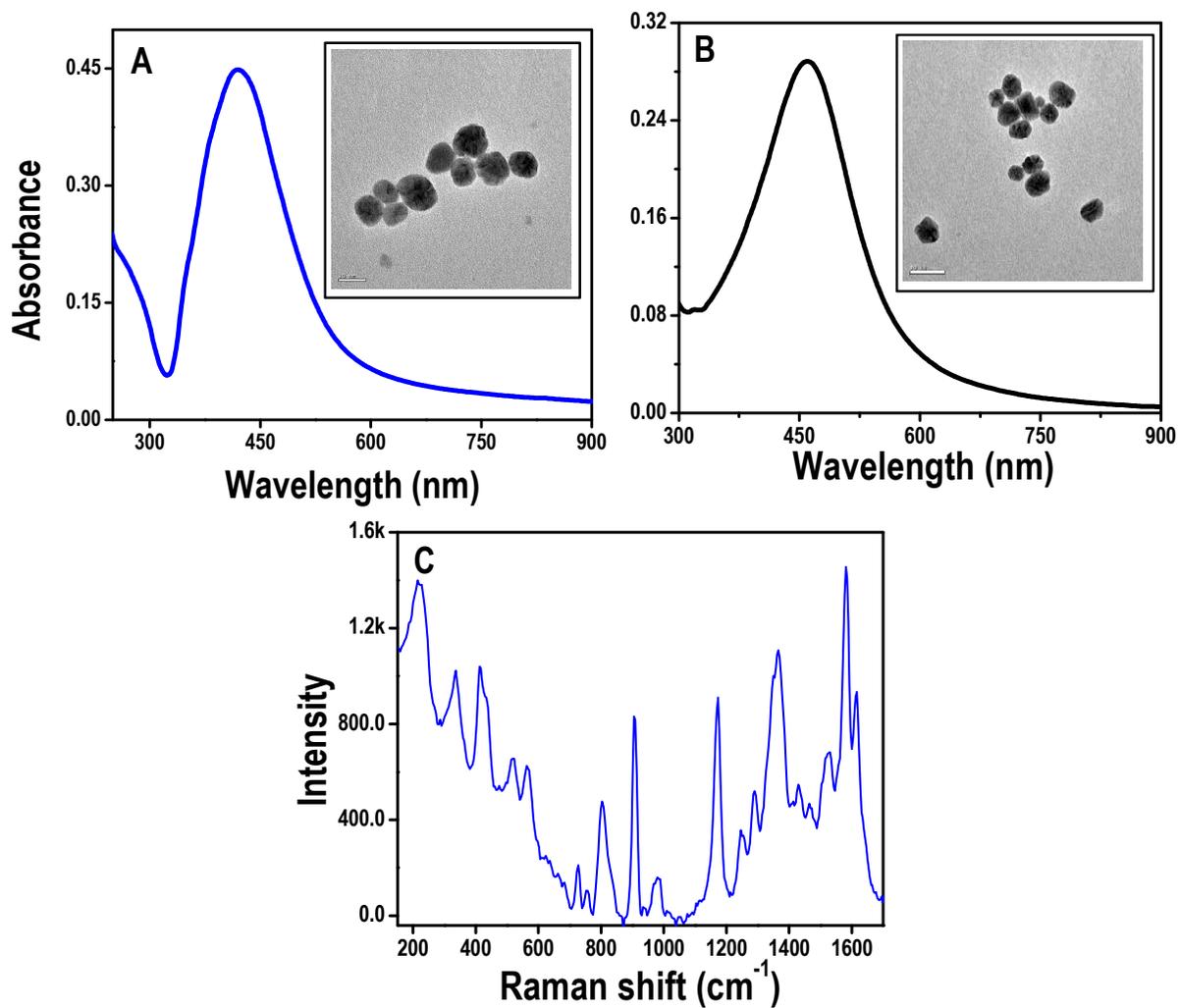


Figure S9. UV/Vis spectra of Ag@citrate (A) and Ag@PET (B) nanoparticles which show the characteristic SPR at 400 nm and 460 nm, respectively. Insets show the corresponding TEM images. C: Raman spectrum of CV taken from a drop casted film of Ag@citrate nanoparticle.

Supporting information 10

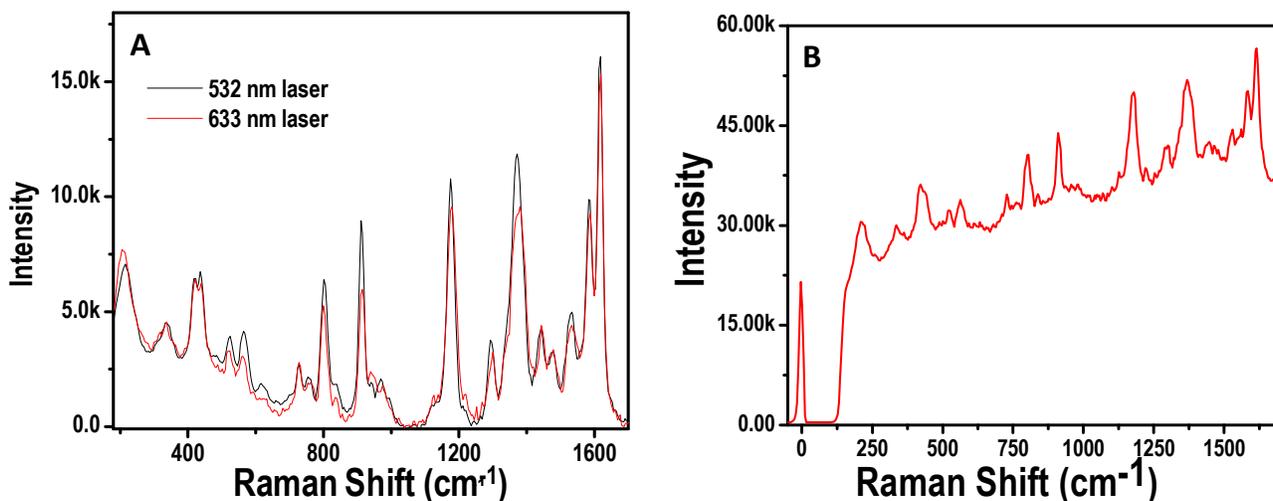


Figure S10. SERS spectra of 50 μM CV with 532 (black trace) and 633 nm (red trace) excitation (A). The corresponding data without background correction is given in Figure B (for 532 nm excitation).

1. Kumar, G. V. P.; Shruthi, S.; Vibha, B.; Reddy, B. A. A.; Kundu, T. K.; Narayana, C. Hot Spots in Ag Core–Au Shell Nanoparticles Potent for Surface-Enhanced Raman Scattering Studies of Biomolecules. *The Journal of Physical Chemistry C* **2007**, *111* (11), 4388-4392.
2. Shibu, E. S.; Kimura, K.; Pradeep, T. Gold Nanoparticle Superlattices: Novel Surface Enhanced Raman Scattering Active Substrates. *Chemistry of Materials* **2009**, *21* (16), 3773-3781.