Nanoscale

Supplementary Information

Anemone-like nanostructures for non-lithographic, reproducible, large-area, and ultra-sensitive SERS substrates

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Enhancement factor (EF) Calculations:

SERS spectrum of 10^{-12} M Rhodamin 6G (R6G) on nanostructured Polycarbonate (PC) film and Raman spectrum of 10^{-3} M R6G on non-structured (bare) PC film were compared. EF was calculated as 5.7×10^{11} with respect to the peak at 610 cm^{-1}.
EF is defined as

$$EF = \left(\frac{I^{SERS}/N^{SERS}}{I^{Raman}/N^{Raman}} \right)$$

Both of the substrates were coated with 40 nm silver using thermal evaporation and samples were drop casted. Droplets have a diameter about ~ 4340 μm, which is also shown in the Figure S8. N^{SERS} and N^{Raman} refer the number of probed molecules on the substrates. As seen in the Figure 8, dried droplets do not have a uniform distribution. To eliminate experimental errors, same volume (6 μL) of samples were dropped on the surface. The measurements were performed at the same regions of droplets using microscope of RAMAN module (Raman module, WITEC alpha 300S). Number of probed molecules were calculated using concentration of solutions (C), Avogadro number (N_A), molecular weight (M_w) and measurement volume (V). Data were collected by 50X objective with a 0.4 μm spot size.

I^{SERS} and I^{Raman} are the measured SERS and Raman intensities of the Rhodamin 6G (R6G) molecules on the substrates. Measured intensities were corrected based on the acquisition time (t) and power (P).

Corrected Intensity (I_{Corr}) is defined as

$$I_{Corr} = I^{Measured}/_{(tP)}$$

Samples were excited by a 532 nm laser source at 50 μW and 40 mW powers for nanostructured and non-structured substrates, respectively. For both of the substrates, signals were collected with 1s acquisition time.

Relative Standard Deviation (RSD):

RSD is defined as the ratio of standard deviation to the mean. About 10,000 individual spots were collected for the 10^{-7} M R6G concentration on nanostructured surface, which was mapped 5x5 μm^2 at different regions (Figure S7). SERS spectra are consistent for the other concentrations of R6G. RSDs for the 610, 777, 1365, 1578 and 1650 cm^{-1} peaks were determined as 8.4, 7.2, 9.6, 12.6 and 8.9%, respectively.

In addition, we imaged the sample that was used to calculate RSD values by confocal microscopy (LSM 510, Zeiss). R6G was excited by Ar laser with 488 nm wavelength and emission was collected by a high-pass filter with 505 nm cutoff wavelength. Imaged part of the droplet and fluorescence profile are given in the Figure S8, fluorescence intensity (I) was profiled using ImageJ. Droplet was examined as a function of radius $f(r)$ and we assumed fluorescence intensity is uniform through the circle ($2\pi r$). We observed a difference between the right and left side of the profile, intensities were averaged and amount of fluorescence was calculated by $\int_0^r 2\pi(rI_r)\,dr$ (Figure S8 b). In literature, it is accepted that relationship between the concentration and fluorescence intensity is linear for low concentrations of R6G.[1] Total amount of fluorescence intensity was calculated as $3.34x10^{13}$. Total amount of molecules was calculated as $3.612x10^{11}$, by volume of droplet (6 µL), concentration (10^{-7} M), and N_A. In the working region of droplet, which is also showed by red dashed circle in Figure S8, about 457 molecules were calculated per spot (0.4 µm).

[1] Hildebrandt, P.; Stockburger, M. Surface-Enhanced Resonance Raman Spectroscopy of Rhodamine 6G Adsorbed on Colloidal Silver. *J. Phys. Chem.* **1984**, 88, 5935-5944.

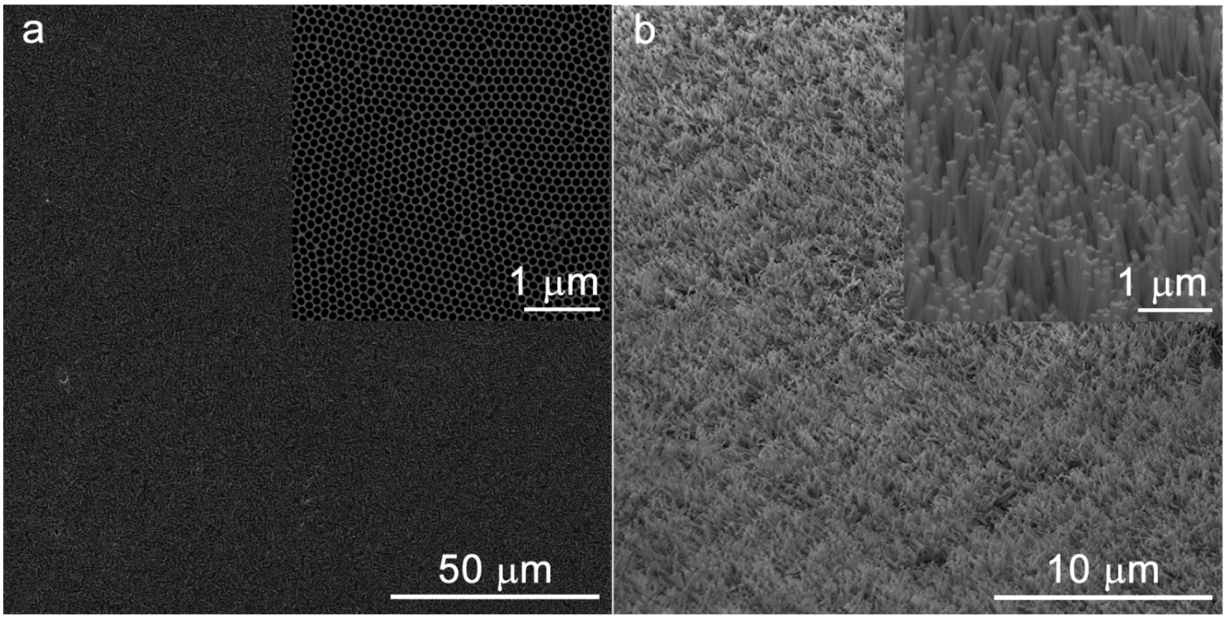

Figure S1. SEM images of AAO membrane and polymer nanopillars. SEM images of (a) AAO membrane supported on aluminium and (b) produced Polycarbonate (PC) nanopillars are given. Hexagonally packed ordered nanopores of the AAO template provide highly dense polymeric nanopillars. Area of the produced nanopilllars are directly proportional to the area of AAO membrane.

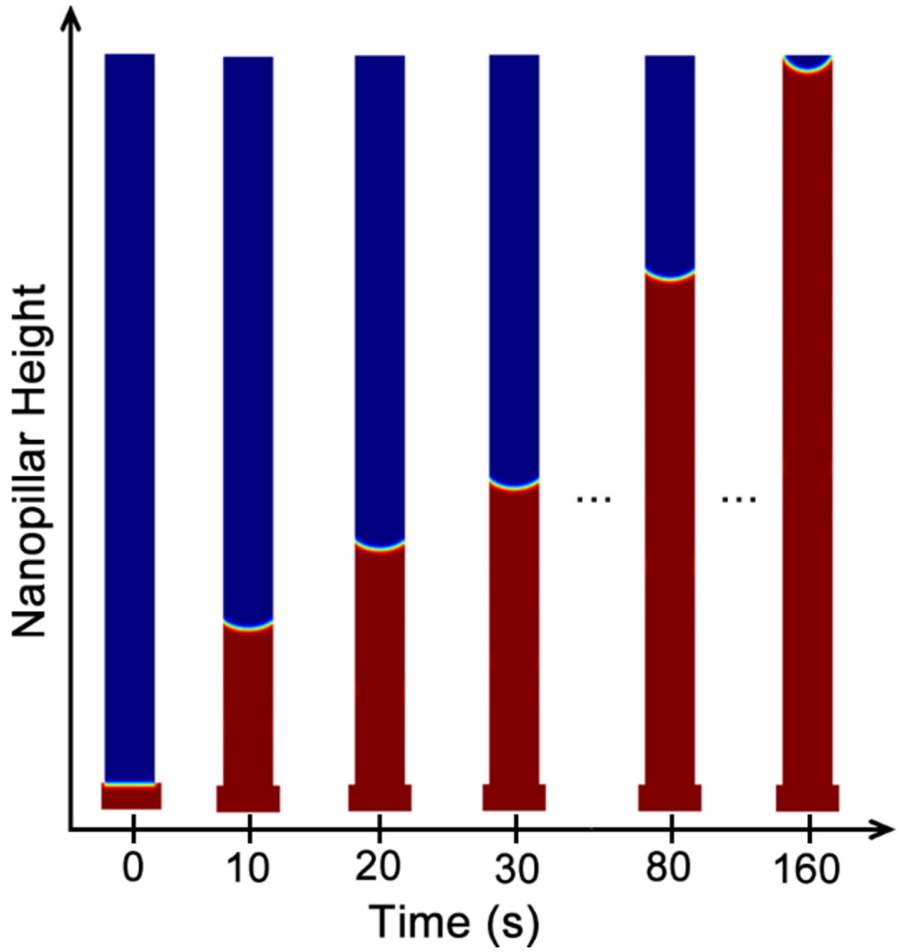

Figure S2. Snapshots of the finate element method (FEM) simulation. Polycarbonate infiltration into porous alumina membrane was simulated with pore diameter of 100 nm and pore depth of 1500 nm at 215 ^{o}C. 0.2% leakage was assumed to enable replacing air by polymer, while the driving force of polymer motion is the wetting as determined experimentally (contact angle of 50^{o}). Also, buble formation was observed at the poymer film in the experiments, which supports the leakage requirements in FEM simulations. Red and blue regions are respectively represent the polymer and air through the nanopore depth.

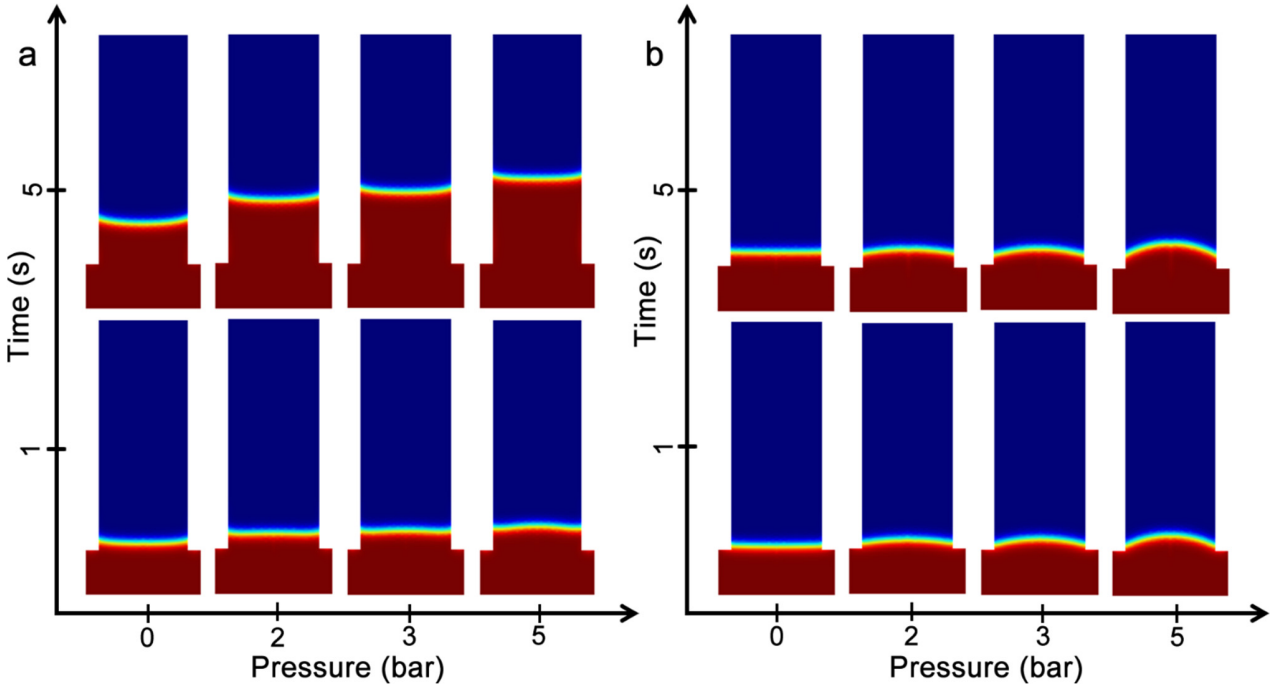

Figure S3. Pressure effect on the polymer. (a) Wetting is considered with a contact angle of = 50° and (b) no wetting is considered but instead friction is modelled at the pore wall as a no-slip boundary at 200 °C. The wetting is the origin of the experimentally observed cavity, while pressing decreases this cavity. In the case of (a) the cavity slightly return, however, in (b) when the pressure and friction dominates, the profile is also similar to the observed shape in case of pressing the polymer.

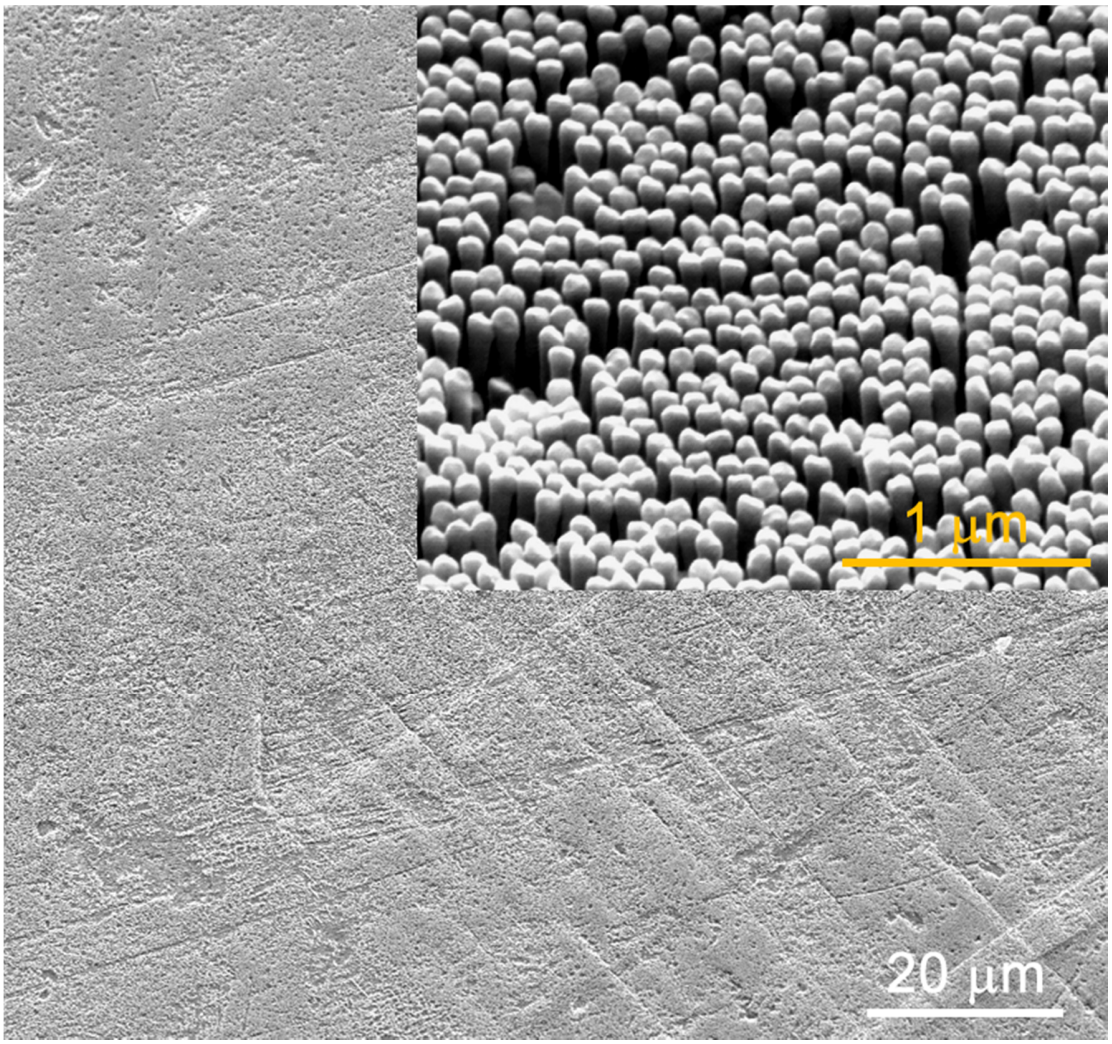

Figure S4. Wetting and pressure effect. SEM images of the nanopillars are given which were produced both under the effect of wetting and pressure. We see there is a competition between the cap shapes of the pillars, which is also showed by FEM simulations in Figure S3.

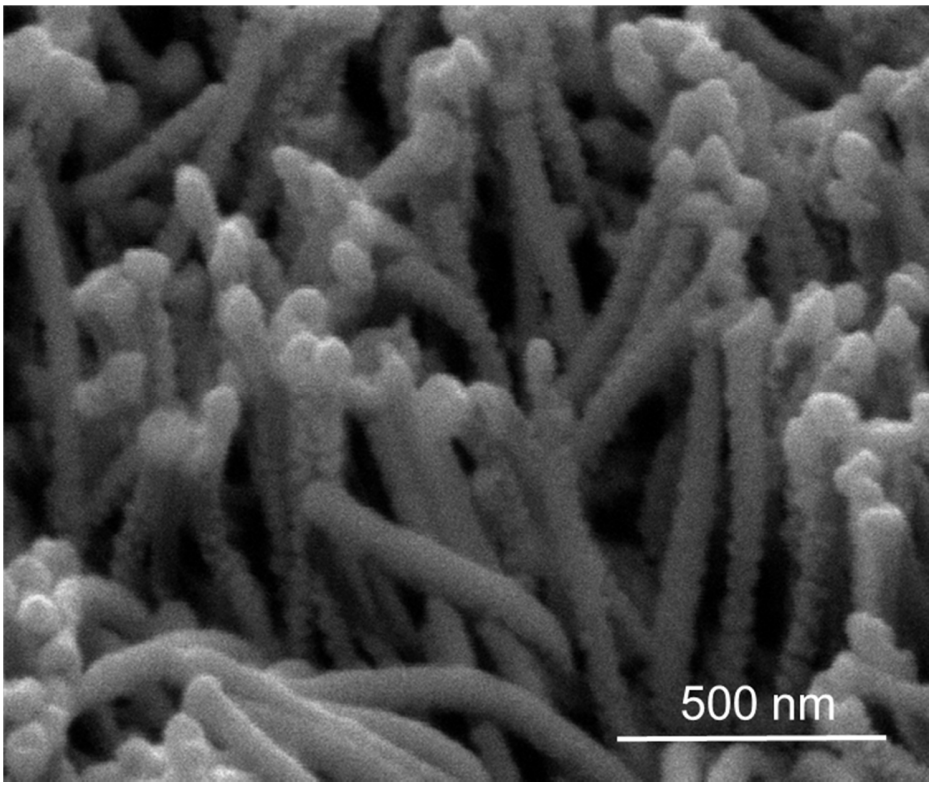

Figure S5. SEM image of the anemone-like polymeric nanopillars. Image is taken after coating with 40 nm silver using thermal evaporation. There is observed silver nanoparticle formation on the coated surface about 20 nm.

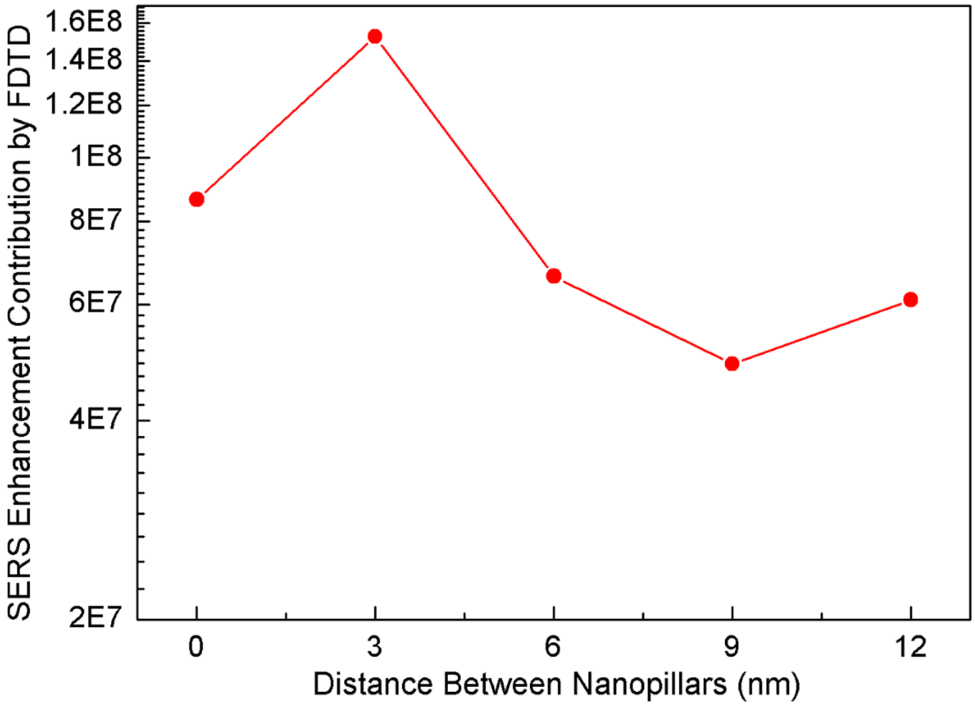

Figure S6. SERS enhancement factor by FDTD Simulations. Because produced polymeric nanopillars bend and distance between the nanopillars get narrow, we simulated nanopillars for different distances. We observed that enhancement increase up to 10^8 values when the distance between nanopillars decrease.

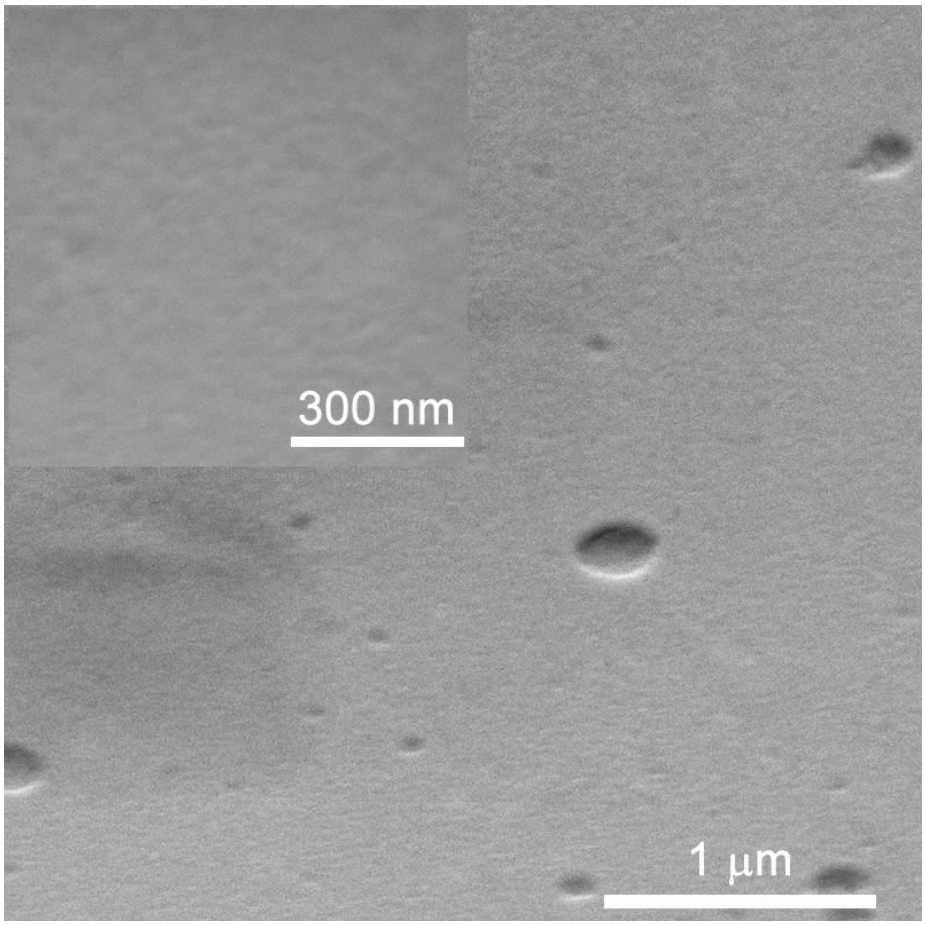

Figure S7. SEM image of the bare film. 40 nm silver coated bare polycarbonate (PC) film is given, which was produced under the same conditions of the nanostructured films. Bare film has roughness at a certain point on itself. Enhancement factor was calculated using the SERS spectrum of 10^{-12} M Rhodamin 6G (R6G) on nanostructured Polycarbonate (PC) film and Raman spectrum of 10^{-3} M R6G on this bare PC film.

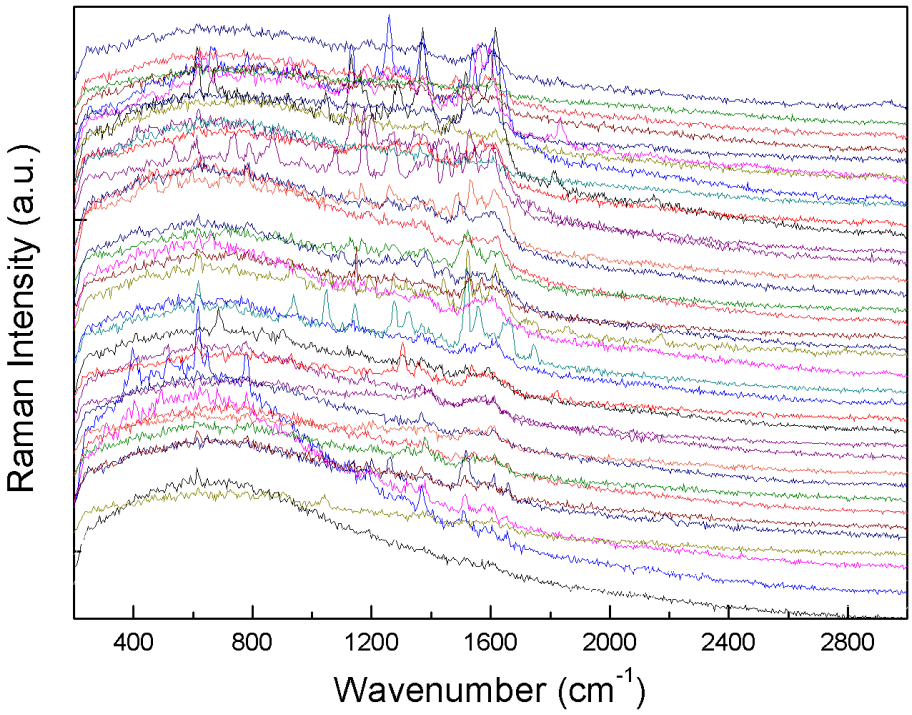

Figure S8. Reproducibility of the SERS spectra. SERS spectra of R6G on silver coated anemone-like structured substrate were collected between 350 cm^{-1} and 2900 cm^{-1} with 1 s integration time. Data was collected from 10,000 individual spots, and spectra is given for 40 spots with 250 interval, periodically.

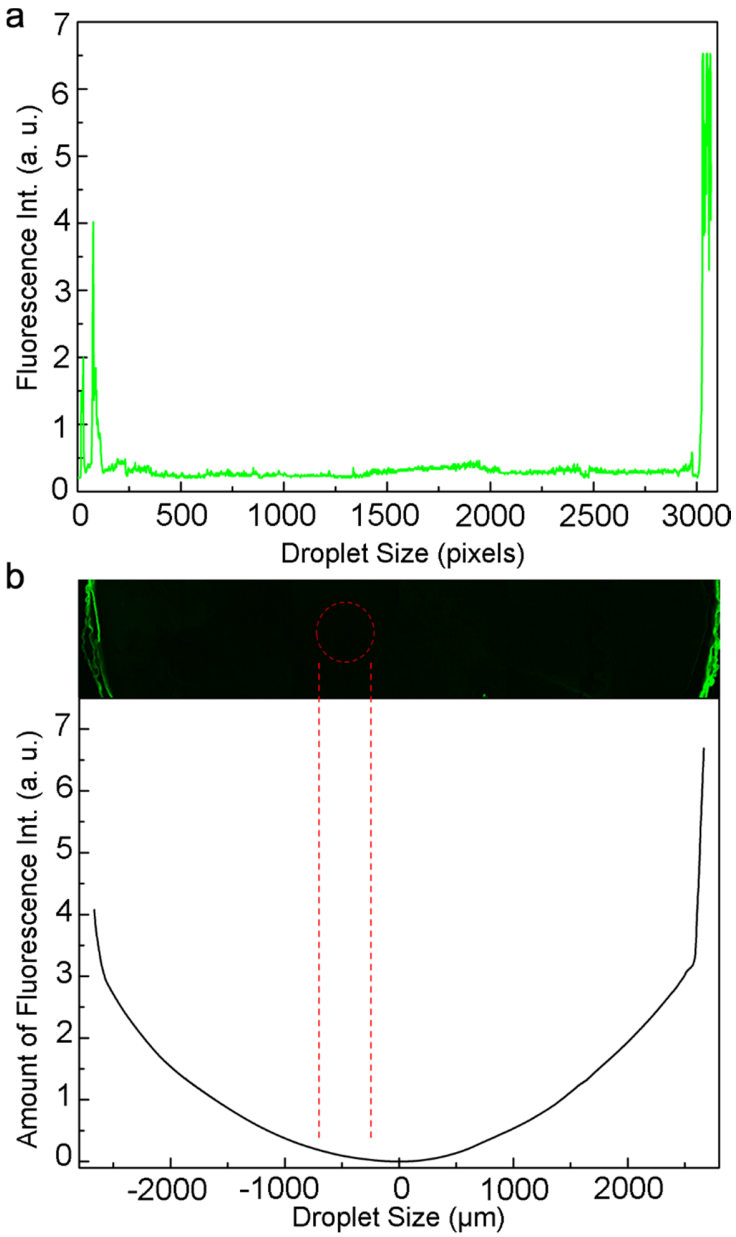

Figure S9. Confocal Microscopy image, fluorescence intensity profile, and amount of fluorescence as a function of radius (r). (a) Fluorescence intensity profile was derived from the confocal microscopy image which is given between the two graphics (a) and (b). ImageJ programme was used and observed that molecules aggregate non-uniformly at the edge region of droplet. (b) This nonuniformity is considered while calculating the amount of fluorescence for whole droplet region and it is assumed that intensity profile is consistent through the droplet radius.