Electronic Supplementary Information for:

Hydrophobic Teflon films as concentrators for single-molecule SERS detection

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Experimental details

Materials: Silver nitrate ($AgNO_3$, 99%) and trisodium citrate dehydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Rhodamine 6G (R6G, 99%) was obtained from Sigma-Aldrich (St.Louis, USA). All chemicals were used as received without further purification. Starting with R6G aqueous solutions of 10^{-3} M, concentrations down to 10^{-15} M were prepared through successive dilution by factors of 10 or 100. The Teflon film was obtained from SHIMADZU which is an accessory of SIL-6A model sample syringes for Liquid Chromatography assay. It is a round septum with a radius of 4 mm, made from polytetrafluoroethylene (PTFE). Prior to use, Teflon film was cleaned in aqua regia and then successively sonicated in distilled water, absolute ethanol, and double-deionized water, and then dried in an oven at 60 □. Deionized water (18.2 MΩ·cm, produced by a Milli-Q system) was used throughout the whole work.

Synthesis and Characterization of Silver Nanoparticles (Ag-NPs): Silver colloids were prepared according to the description of Lee and Meisel with a little modification. A 45-mg sample of $AgNO_3$ was suspended in 250-mL of deionized water and heated to boiling. Then, 10-mL of 0.5% solution of sodium citrate was added dropwise to the boiling solution under vigorous stirring. The solution was kept boiling for about an hour. The as-prepared silver colloids were used without any purification. The UV-visible spectrum of the greenish yellow suspension, which shows a maximum absorption at 428 nm, is shown in Figure S3. According to the TEM analyses, Ag-NPs are mostly spherical with an average diameter of ~70 nm.

Preparation of the SERS sample: The procedures for preparing SERS substrate were concluded as follow (see Figure 1): 1) adhering the Teflon film to a piece of glass slide with double-sided tapes; 2) depositing 3-μL silver colloidal solution on the Teflon film and drying it in air; 3) placing 3-μL R6G aqueous solution on the top of dried Ag-NPs attached to the Teflon film and allowing it to evaporate naturally.

Characterization: The SERS spectra were measured under ambient conditions using a JY LABRAM-HR confocal micro-Raman

Spectroscopy. The 514.5 nm radiation from an Ar$^+$ ion laser was used as the excitation source. The laser beam focused by a 50 × microscpe objective (NA = 0.5) resulting in a spot size of around 10 μm in diameter with a long working distance. The laser power on the samples was ca. 1 mw and the date acquisition was 0.5 s for the collection of each spectrum. The Raman band of a silicon film at 520 cm^{-1} was used to calibrate the spectrometer. The UV-visible extinction spectrum of silver colloids was recorded using a Shimadzu UV-1601 spectrometer. Scanning electron microscopy (SEM) images were obtained with a field emission scanning microscopy (FESEM, Philips Model XL30 S FEG). Transmission electron microscopy (TEM) was performed with a JEOL JEM 2100F microscopy with an accelerating voltage of 200 kV.

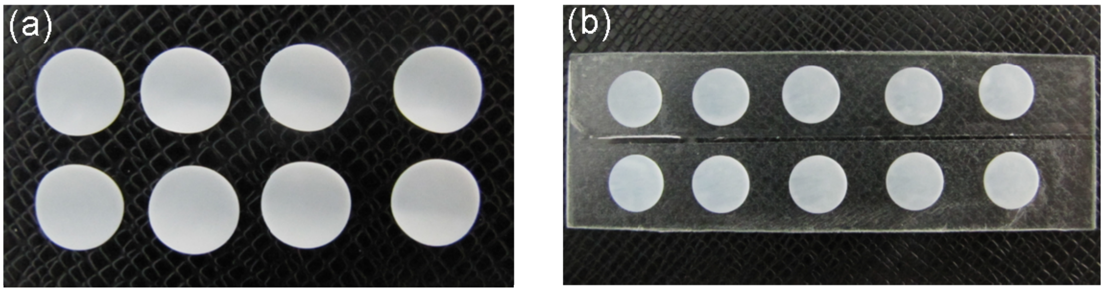

Figure S1. Photographs of the (a) Teflon films and (b) Teflon films adhered to a glass slide.

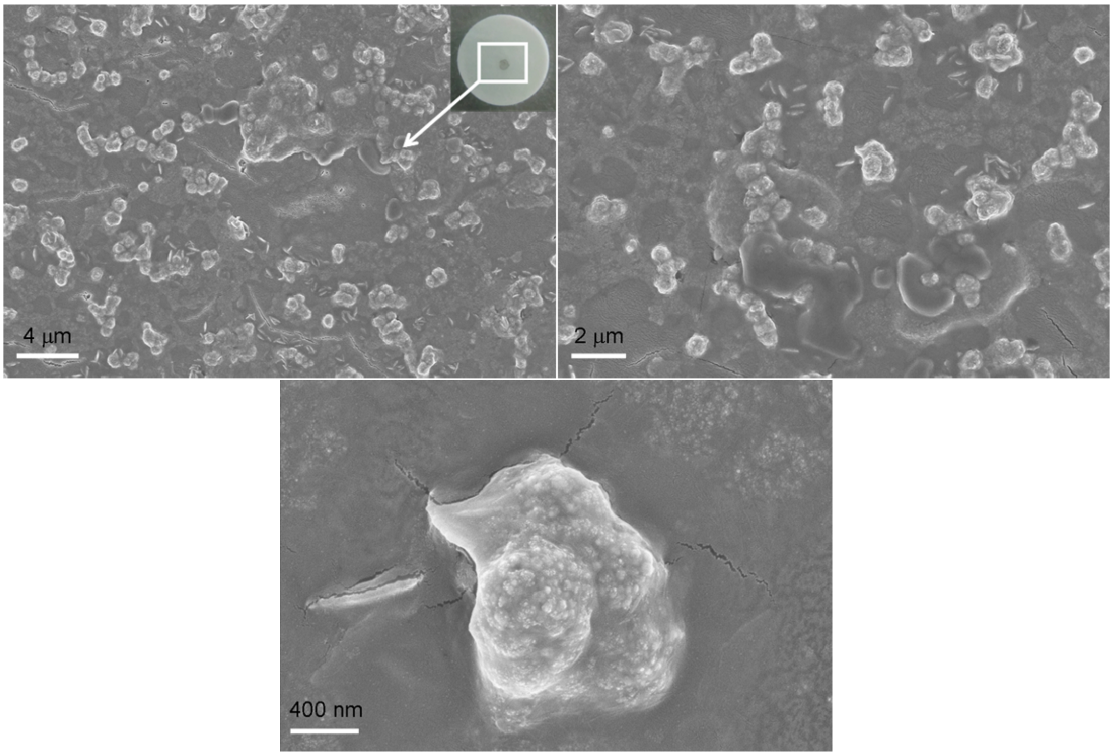

Figure S2. SEM images of silver nanoparticle aggregates on the hydrophobic Teflon film. The Inset picture is the corresponding photograph of silver nanoparticle aggregates deposited on the Teflon film.

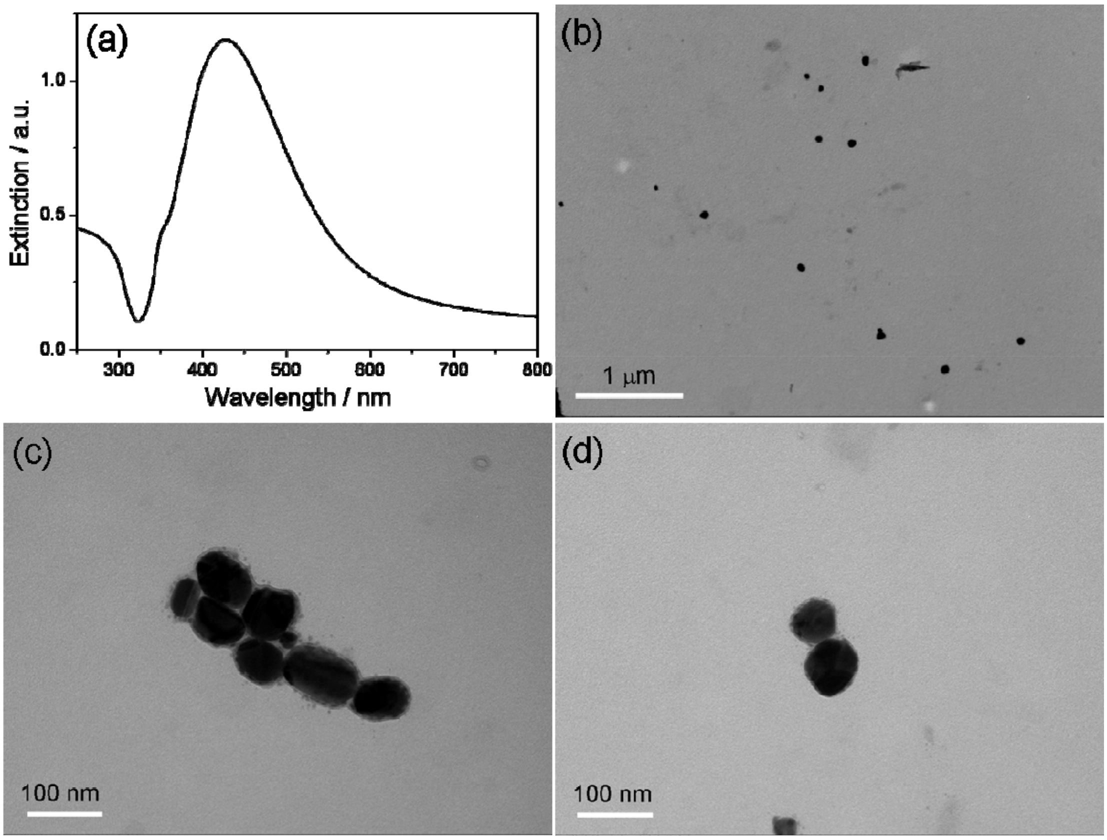

Figure S3. (a) UV-visible spectrum of silver colloids and (b, c, d) TEM images of the synthesized Ag-NPs.

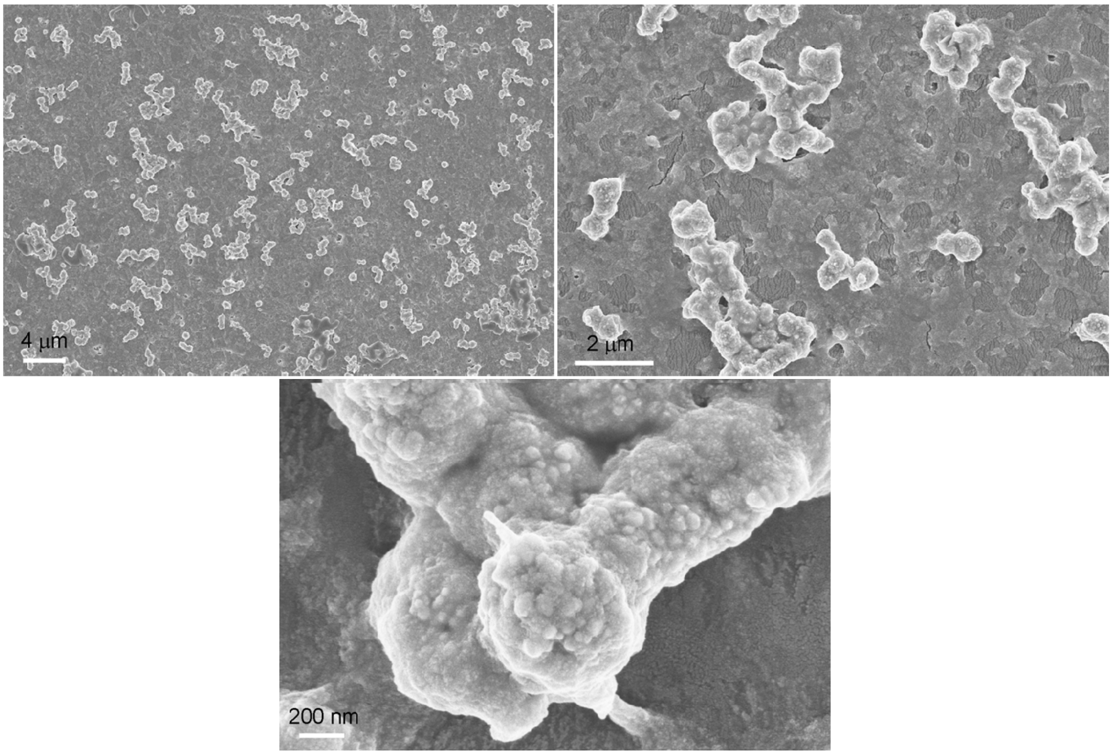

Figure S4. SEM images of dried R6G solutes attached to Ag-NPs deposited on the Teflon film.

The average enhancement factor (EF) value is calculated according to the following formula:

$$EF = (I_{SERS} / N_{SERS}) / (I_{Nor} / N_{Nor})$$

Where I_{SERS} and I_{Nor} are the signal intensities of SERS and normal Raman spectra of R6G at the same band (here, ~1650 cm^{-1}), and N_{SERS} and N_{Nor} represent the corresponding number of molecules in the focused incident laser spot. We assume the R6G molecules distributed evenly on the SERS substrates. N_{SERS} and N_{Nor} can be calculated according to surface density of R6G and the area of the laser spot. In the normal Raman characterization, 3-μL of 1.0×10^{-4} M R6G aqueous solution is dispersed to an area of 1.57 mm^2 on a piece of clean glass slide. The area of laser spot is calculated to be 78.5 μm^2 according to the diameter of laser spot (~10 μm). So, N_{Nor} is approximately equal to 9.03×10^9. In our SERS experiment, silver nanoparticle aggregates are confined to an area with a diameter of ~0.5 mm where the R6G solution is dropped on. So, 3-μL of 1.0×10^{-15} M R6G aqueous solution is dispersed to an area of about 0.196 mm^2. Calculated in a similar manner above, N_{SERS} is estimated to be 0.7224. In Figure S6, we can get that the I_{SERS} and I_{Nor} are 91 unites and 200 unites at the Raman band of ~1650 cm^{-1}, respectively. So, the EF is conservatively calculated to be 5.7×10^9.

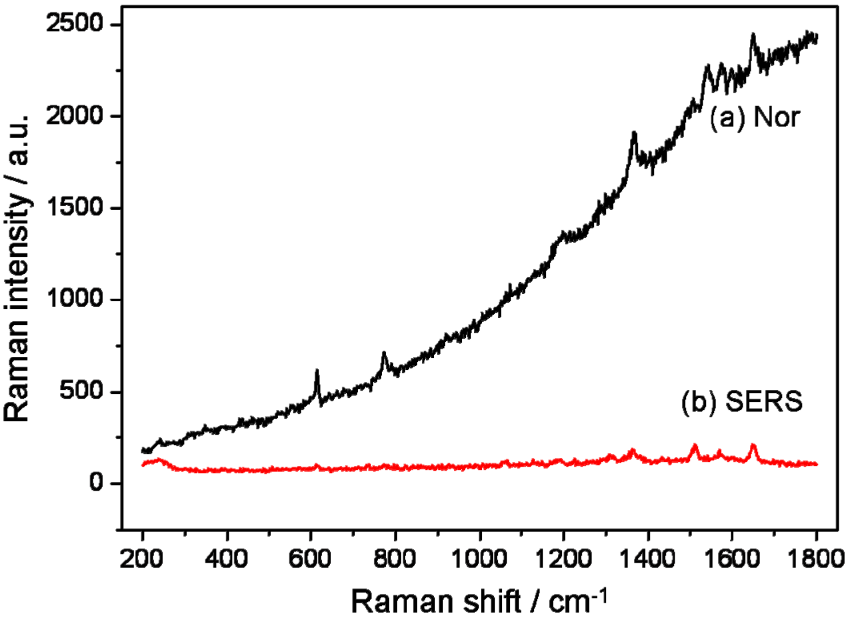

Figure S5. (a) The normal Raman spectrum of 3-μL 1.0×10^{-4} M R6G solution on the glass slide and (b) The SERS spectrum of 3-μL 1.0×10^{-15} M R6G solution adsorbed on Ag-NPs deposited on the Teflon film.[1]

Notes and references

1. H. B. Tang, G. W. Meng, Q. Huang, Z. Zhang, Z. L. Huang and C. H. Zhu, *Adv. Funct. Mater.*, 2012, **22**, 218.