

Electronic Supplementary Information

Revealing Synergistic Effect of Capillary Force and Electrostatic

Attraction towards D-SERS Sensitivity

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EXPERIMENTAL SECTION

Material and reagents. Silver nitrate, ascorbic acid, sodium hydroxide, hydrochloric acid, cyclohexane and sodium carbonate were provided by Sinopharm Chemical Reagent Co., Ltd. Sodium citrate was provided by Xilong Chemical Co., Ltd. Spermine hydrochloride was from Shanghaiyuanye Bio-Technology Co., Ltd. Sodium chloride and isopropanol (98%) were from Saan Chemical Technology (Shanghai) Co., Ltd. Crystal ponceau 6r was from Sangon Biotech (Shanghai) Co., Ltd. Malachite green was from Shanghai Macklin Biochemical Co., Ltd. Benzopyrene was from Beijing Shenzhou Kechuang Biotechnology Co., Ltd. Ammonium hydroxide solution (25%-28% solution in water) was from Shanghai Titan Scientific Co., Ltd. All chemicals were used without further purification, and Milli-Q water was utilized in all experiments. The pH of malachite green solution was adjusted to 4~5 by hydrochloric acid.

Preparation of 77±5 nm Cit-Ag NPs. Cit-Ag NPs was synthesized as follows¹. An 80 µL ascorbic acid (0.1 M) was added into a 47.5 mL of boiling water, and then a mixture containing 1 mL sodium citrate (1 wt%), 0.25 mL AgNO₃ (1 wt%) and 0.2 mL NaCl (20 mM) was quickly added. The Cit-Ag NPs seed colloid was obtained after vigorously stirring for 1 h. Then, a 2 mL of Cit-Ag seeds was mixed with a 5 mL of ascorbic acid (20 mM) in a 47.5 mL water, and the 77±5 nm Cit-Ag NPs colloid was obtained by adding a 0.18 mL solution of silver-ammonia complex (2 mL AgNO₃ (1 wt %) mixed with 0.8 mL of ammonia (25-28%)) and stirring for 1 hour.

Preparation of 78±6 nm Spe-Ag NPs. Spe-Ag NPs was synthesized using a modified method and will be discussed elsewhere². Briefly, 0.24 mL ascorbic acid (0.1 M), 0.24 mL spermine hydrochloride (0.1 M) and 0.18 mL NaOH (0.1 M) were successively added into a 50 mL of water, and then a 0.4 mL of AgNO₃ (0.1 M) was added with vigorous stirring for 30 min to obtain Spe-Ag seeds colloid. Then, the 78±6 nm Spe-Ag NPs colloid was obtained by adding a 5 mL of AgNO₃ (0.01 M) at the rate of 80 µL/min into a 30 mL aqueous solution containing 10 mL Spe-Ag seeds and ascorbic acid (1.63 mM).

The surface potentials of Cit-Ag NPs and Spe-Ag NPs were evaluated by Zeta potential as 32 mV and -35 mV, respectively (Figure S1A). The corresponding extinction spectra (Figure S1B) show the LSPR peaks of Spe-Ag and Cit-Ag NPs were located at 462 nm and 460 nm, respectively. The very close peak position and similar shape of the LSPR for these two NPs indicate the similar morphologies and size distributions, which was further confirmed by SEM images in Figure S1C-D (large scale ones are in Figure S2) with a diameter at ~77 nm and ~78 nm for Cit-Ag NPs and Spe-Ag NPs, respectively. It should be noted that a few triangular and rod-like NPs were observed in the Spe-Ag NPs case, which may be responsible for the stronger extinction than that of Cit-Ag NPs in the range of 600-800 nm in Figure S1B.

Pretreatment of hydrophilic silicon wafer. The silicon wafer was twice cleaned sequentially with detergent, ethanol and water, and soaked in aqua regia solution for 1 hour, and then thoroughly washed by water before being soaked in piranha solution for 3 hours, and neutralized with NaCO₃ solution, and finally stored in ethanol for further using.

Self-assembly of Cit-/Spe-Ag NPs at the liquid interface. Before self-assembly at the liquid interface, the Spe-Ag NPs was transferred from water into isopropanol solution by centrifugating a 1.5 mL of Spe-Ag NPs at 3800 rpm for 10 minutes to remove the supernatant and then redistribute in a 1.5 mL of isopropanol. When it came to the Cit-Ag NPs case, the centrifuge rate was increased to 5000 rpm and the concentrated Cit-Ag NPs colloid was washed by 1 mM sodium chloride before being

redistributed in a 1.5 mL of isopropanol. In a polyethylene box containing 2 mL cyclohexane and 2 mL water, the Cit-/Spe-Ag NPs isopropanol solution was added slowly. A highly close-packed film of Ag NPs was formed at the cyclohexane/water liquid interface and then carefully transferred to the silicon wafer surface. The obtained Cit-/Spe-Ag NPs films before drying were named as negative/positive D-SERS substrates, and the dried ones were negative/positive solid SERS substrates.

SERS measurements. For the D-SERS substrates or solid SERS substrates, a 10 μL of target solution was dripped onto the surface and the SERS spectra were continuously collected until the Ag NPs film was dried. For the droplet D-SERS measurement, a 1 μL of target solution was mixed with a 1 μL of 100 times concentrated Spe-/Cit-Ag NPs on the silicon wafer, and the SERS spectra were continuously collected until solution was dried.

All SERS measurements were performed on an optical fiber micro-Raman spectrometer (B&W TekInc., i-Raman Plus) with an excitation wavelength of 785 nm, and an integration time of 12 s.

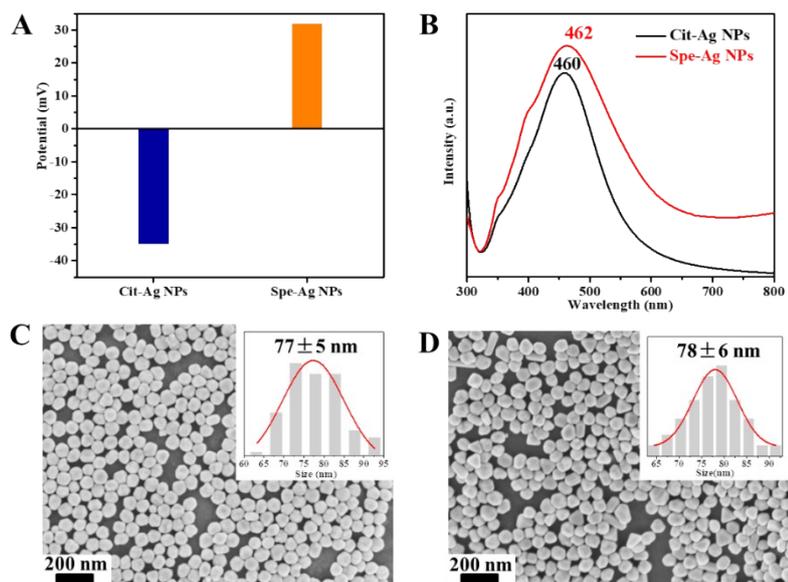


Figure S1. Zeta potential (A) of Cit-Ag NPs and Spe-Ag NPs colloid, and their extinction spectra (B). SEM images of Cit-Ag NPs (C) and Spe-Ag NPs (D), and insets being the corresponding size distributions.

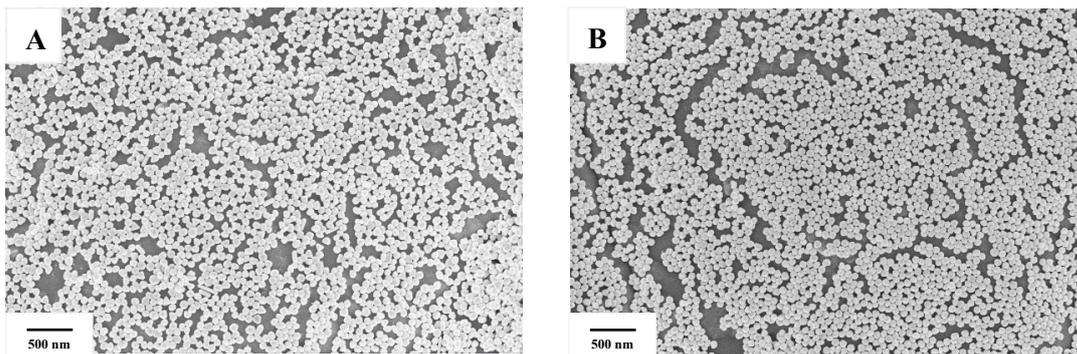


Figure S2. SEM images of one monolayer of 78 ± 6 nm Cit-Ag NPs (A) and 77 ± 5 nm Spe-Ag NPs (B) on the hydrophobic Si surface by liquid-liquid interface assembly.

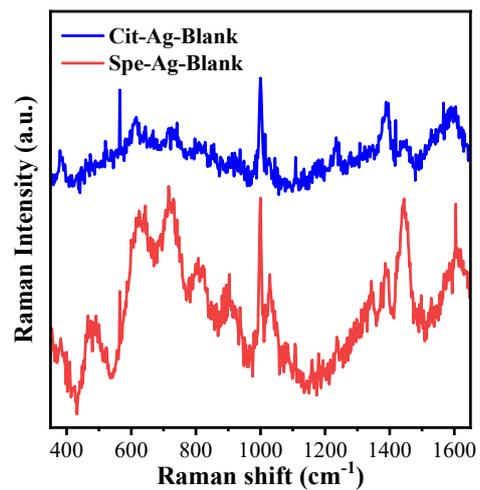


Figure S3. SERS spectra of positive/negative D-SERS substrates free of target molecules.

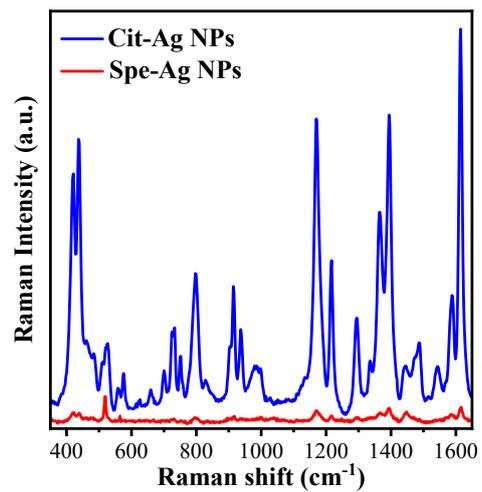


Figure S4. SERS spectra of 1 mg/L malachite green obtained on the negative (blue) and positive (red) D-SERS substrate.

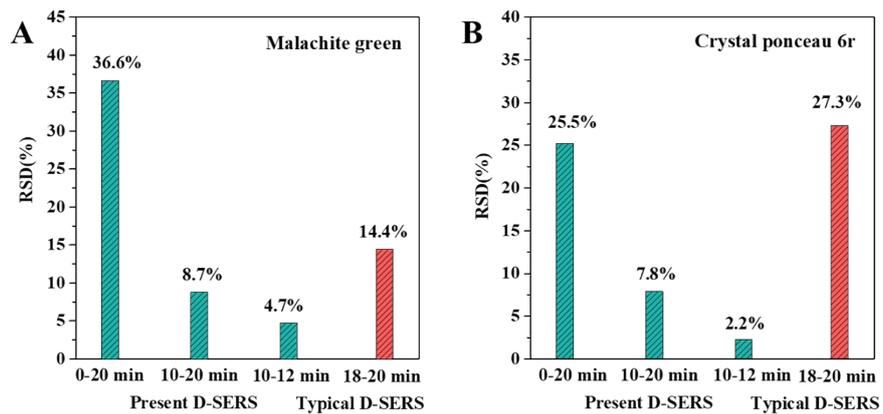


Figure S5. Time interval dependent RSD of the SERS signal of the 1614 cm^{-1} peak of 1 mg/L malachite green (A) and that of the 1570 cm^{-1} peak of 1 mg/L crystal ponceau 6r (B) on the present (green column) and typical (red column) D-SERS substrates.

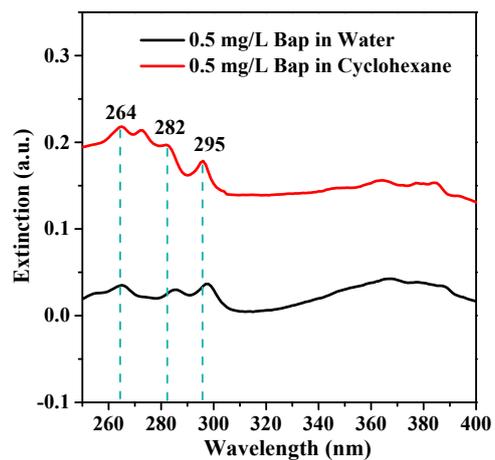


Figure S6. Extinction spectra of 0.5 mg/L BaP in water (black line) and cyclohexane (red line).

As shown in Figure S6, the characteristic extinction spectra peaks located at 264, 282 and 295 nm of BaP dissolved in no matter water or cyclohexane could be all observed. The 282 and 295 nm peaks of BaP were blue shift from polar solvent (water) to non-polar solvent (cyclohexane), owing to solvent effect³.

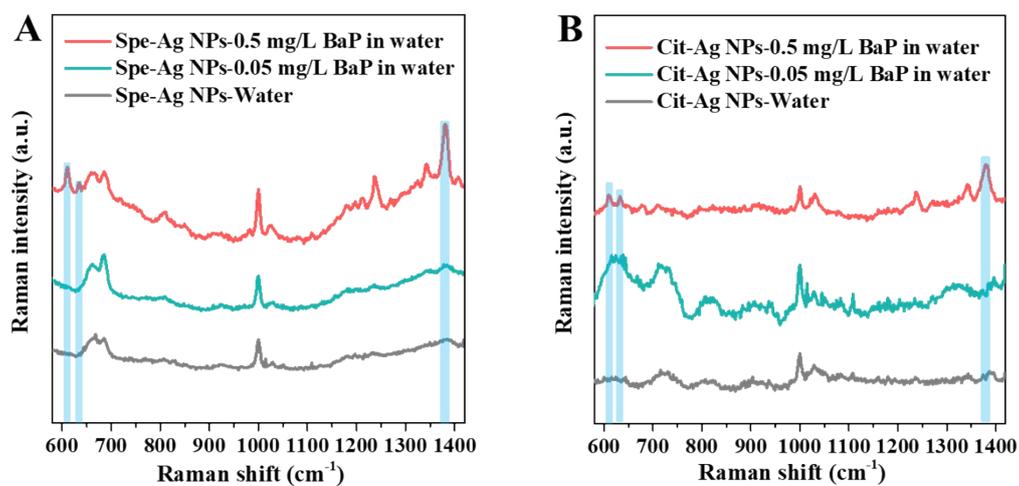


Figure S7. Concentration-dependent SERS spectra of BaP on positive (A) and negative (B) D-SERS substrates.

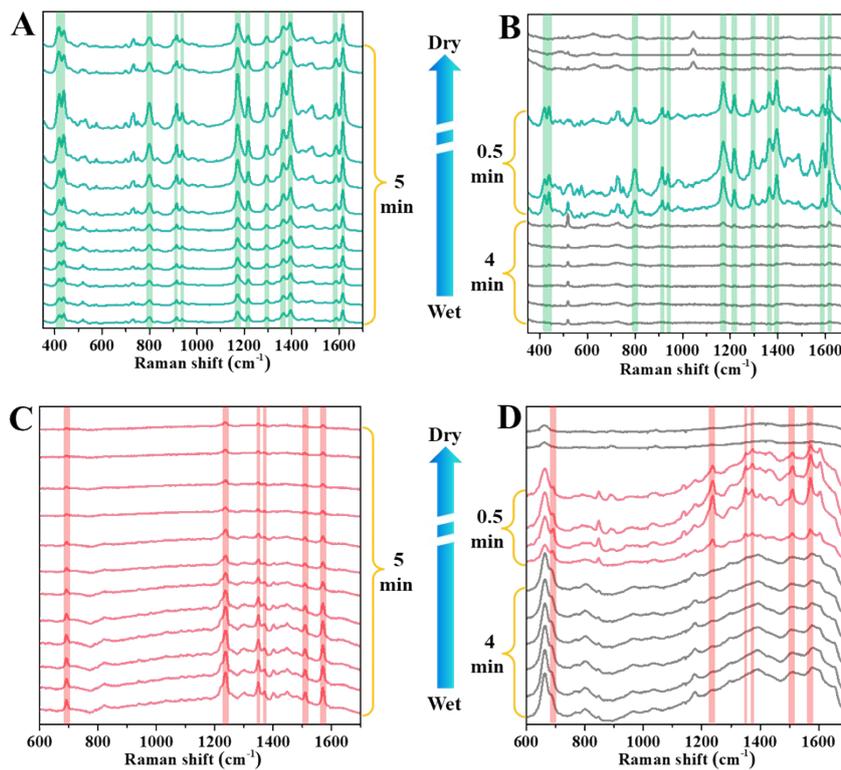


Figure S8. Time-dependent SERS spectra of 10 mg/L malachite green on the negative (A) and positive (B) droplet D-SERS substrates. Time-dependent SERS spectra of 1 mg/L crystal ponceau 6r on the positive (C) and negative (D) droplet D-SERS substrates.

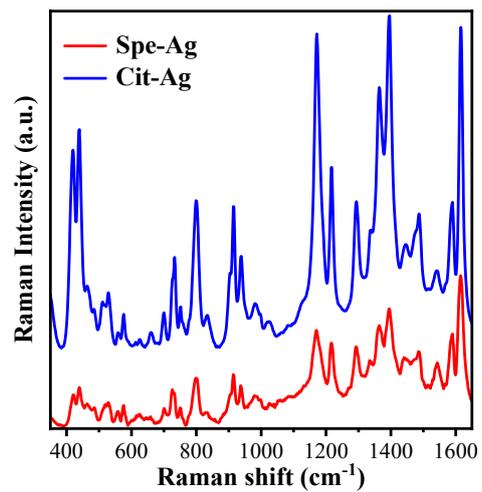


Figure S9. SERS spectra of 10 mg/L malachite green obtained on negative (blue) and (red) positive droplet D-SERS substrate.

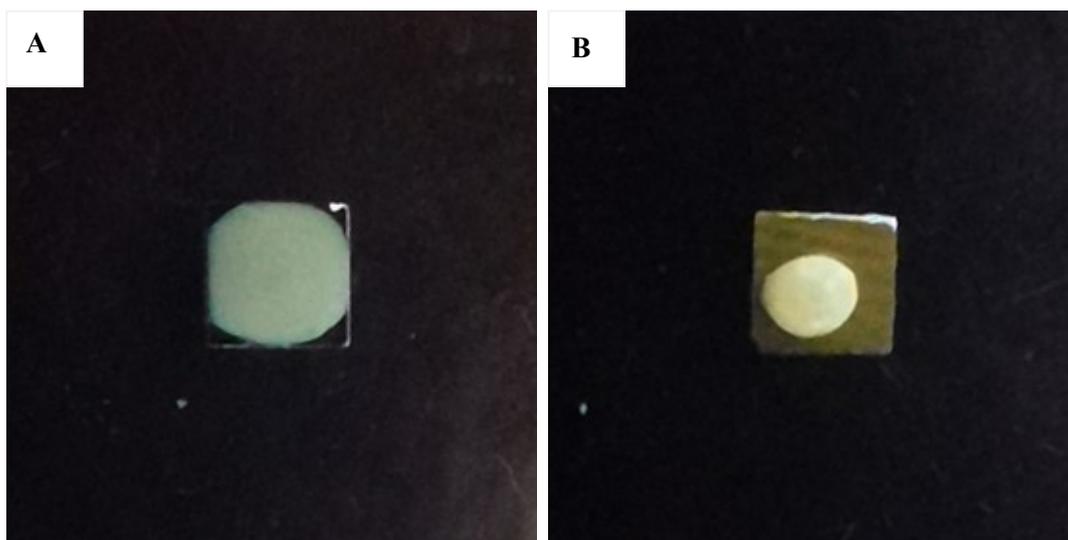


Figure S10. Optical images of droplet D-SERS measurement on the hydrophilic Si (A) and hydrophobic gold coating Si surface (B).

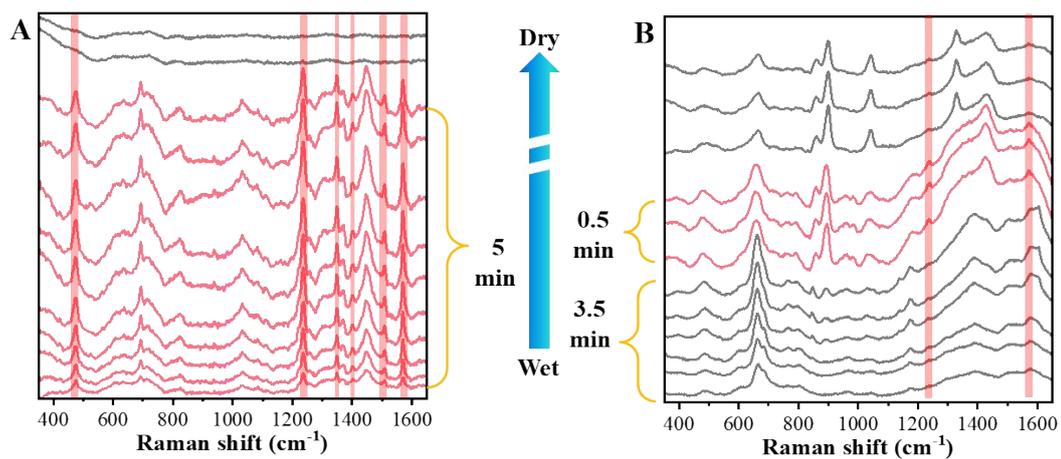


Figure S11. Time dependent SERS spectra of 1 mg/L crystal ponceau 6r obtained on positive (A) and negative (B) the hydrophobic droplet D-SERS substrates.

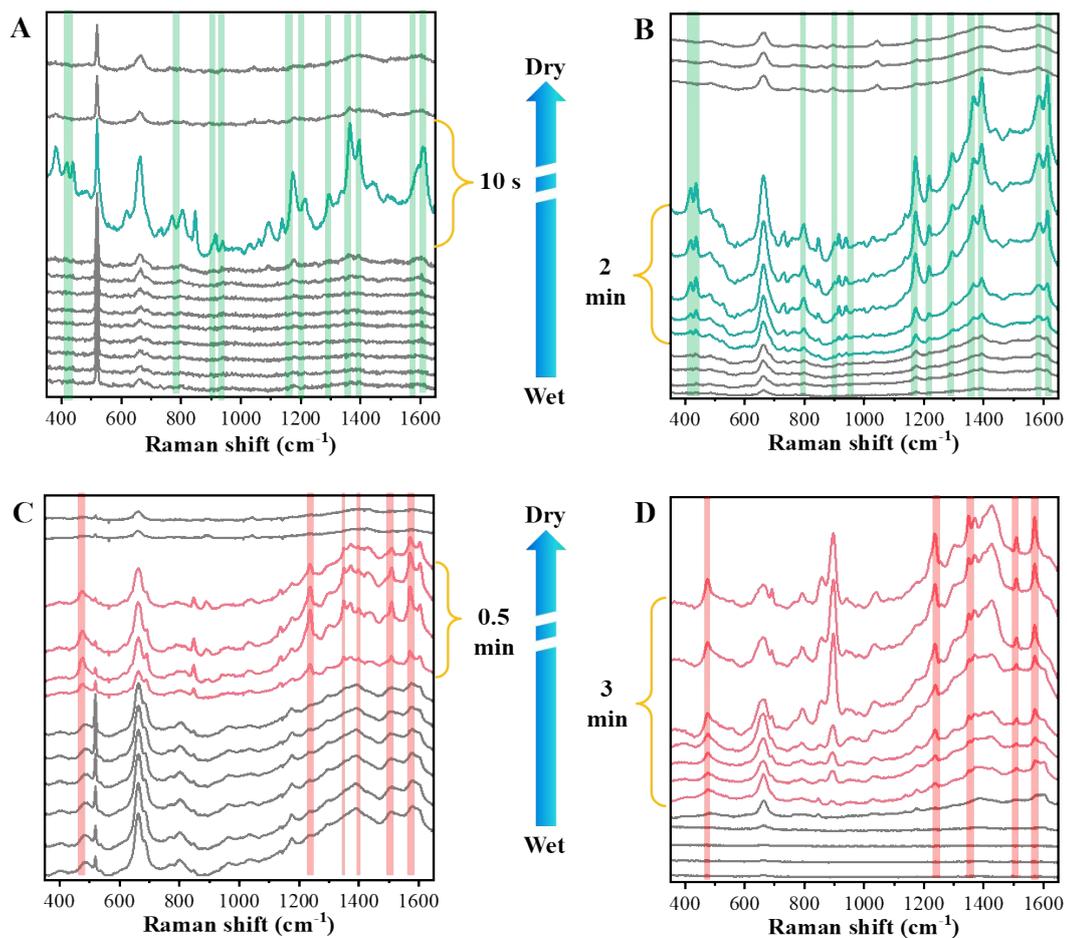


Figure S12. Time-dependent SERS spectra of 1 mg/L malachite green on the hydrophilic (A) and hydrophobic (B) droplet D-SERS substrates. Time-dependent SERS spectra of 10 mg/L crystal ponceau 6r on the hydrophilic (C) and hydrophobic (D) droplet D-SERS substrates.

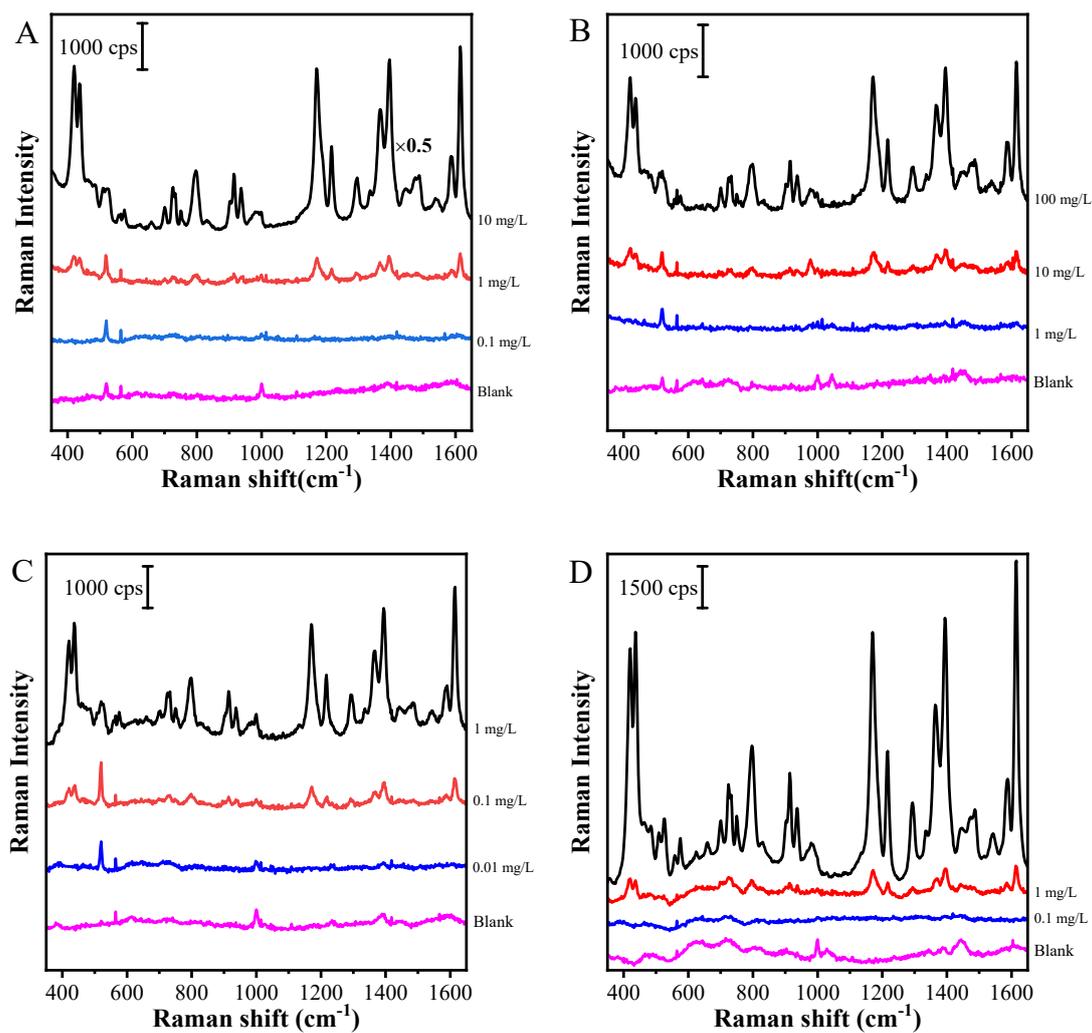


Figure S13. Concentration-dependent SERS spectra of malachite green on negative (A) and positive (B) solid substrates, and negative (C) and positive (D) D-SERS substrates.

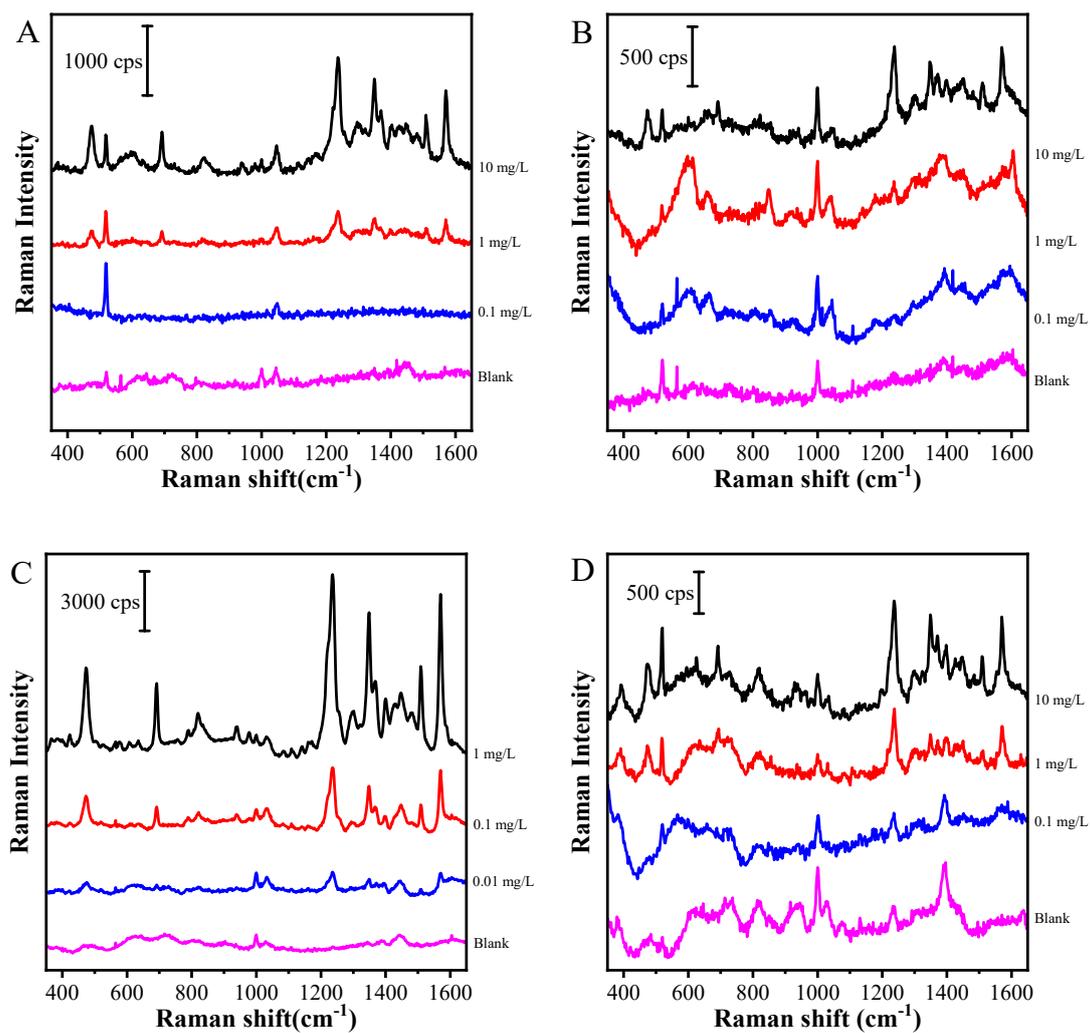


Figure S14. Concentration-dependent SERS spectra of crystal ponceau 6r on positive (A) and negative (B) solid substrates, and positive (C) and negative (D) D-SERS substrates.

REFERENCES

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