

Electronic Supplementary Information for

**Assembling Substrate-less Plasmonic Metacrystals at the Oil/Water Interface
for Multiplex Ultratrace Analyte Detection**

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Methods

Chemicals. Silver nitrate ($\geq 99\%$), 1,5-pentanediol (PD, $\geq 97.0\%$), poly(vinyl pyrrolidone) (PVP, average $M_w = 55,000$), n-decane, 1H,1H,2H,2H-perfluorodecanethiol (PFDT, 97%), and 1-hexadecanethiol (C16SH, $\geq 95\%$) were purchased from Sigma Aldrich; copper(II) chloride ($\geq 98\%$) was purchased from Alfa Aesar; silicone elastomer curing agent and silicone elastomer base (Sylgard 184) were purchased from Dow Corning. Gellan Gum (KELKOGEL®) was kindly sponsored by CP Kelco (USA). All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

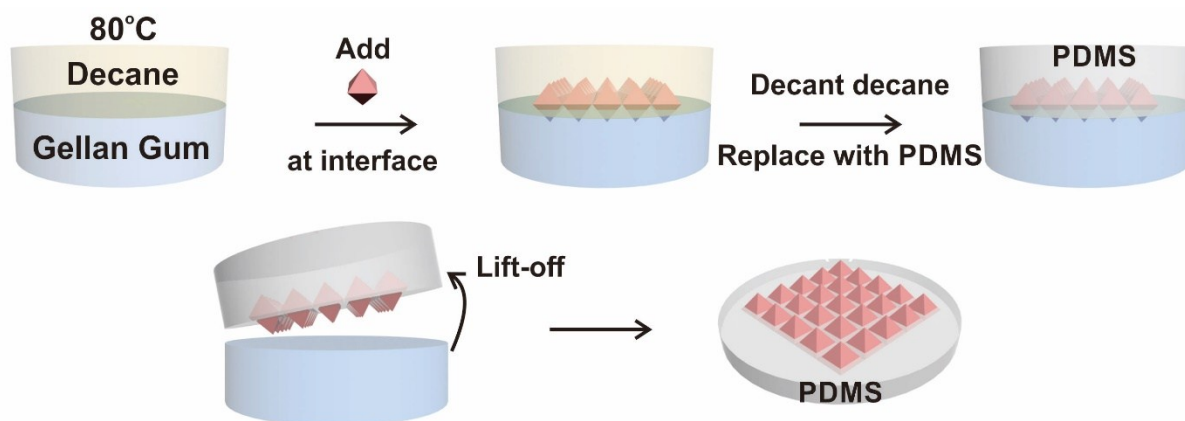
Synthesis & purification of Ag octahedra. The preparation of Ag octahedra was carried out following the methods described in literature,¹ starting first with the synthesis of Ag nanocubes. In a typical nanocube synthesis, 10 mL of CuCl_2 (8 mg/mL), PVP (20 mg/mL) and, AgNO_3 (20 mg/mL) were separately dissolved in PD. 35 μL CuCl_2 solution was added to the AgNO_3 solution. 20 mL PD was then heated to $190\text{ }^\circ\text{C}$ for 10 min. 250 μL PVP precursor was added to a round-bottom flask dropwise every 30 s while 500 μL AgNO_3 precursor was injected into the flask every minute in one go. The reaction was allowed to proceed for approximately 20 min. After the synthesis of nanocubes is completed, the injection was continued using more concentrated precursor solutions. 10 mL of CuCl_2 (8 mg/mL), 30 mL of PVP (20 mg/mL) and AgNO_3 (40 mg/mL) were separately prepared in PD. After fully dissolving the AgNO_3 precursors, 120 μL CuCl_2 solution was added into the Ag precursor solution. The nanocube solution in PD was heated to $190\text{ }^\circ\text{C}$ and the PVP and Ag precursors were alternately injected into the flask following the same procedure as described earlier. The reaction was allowed to proceed until the precursors were used up. The Ag octahedra solution was re-dispersed in 20 mL ethanol after removing the PD via multiple centrifugation rounds, and diluted to approximately 200 mL using an aqueous PVP solution (0.2 g/L). This solution was then vacuum filtered multiple times using PVDF filter membranes (Durapore®) with pore sizes ranging from 5000 nm, 650 nm, 450 nm and 220 nm to remove impurities before finally dispersing in ethanol.

Ligand exchange reactions. The purified Ag octahedra dispersion was generally allowed to sediment overnight. 0.5 μL of the sediment was dispersed in ethanol and centrifuged once more before dispersing in 1.5 mL of ethanol/isopropyl alcohol (1:1). 100 μL of 10 mM thiol solution (PFDT or C16SH) was then added dropwise to this dispersion under stirring. Ligand exchange was allowed to take place for 4 hrs, followed by 2 rounds of centrifugation, re-dispersal in 1.5 mL of ethanol/isopropyl alcohol (1:1), and addition of fresh thiol solution under stirring. This step was allowed to continue for another 3 hrs, followed by 3 rounds of centrifugation and washing with isopropyl alcohol/water (1:1). For ligand exchange with thermally evaporated Ag film, the substrate was immersed in a 10 mM thiol solution for at least 12 hrs to allow the self-assembled monolayers to form before rinsing with ethanol to remove the excess unbound thiols.

Interfacial self-assembly and gel-trapping experiments. The oil/water interface was used for the self-assembly of Ag octahedra, using decane as the oil phase. Ag octahedra was typically dispersed in a isopropyl alcohol/water (1:1) mix and added dropwise to the interface. For the gel-trapping experiments, 2 wt% gellan gum aqueous solution was used as the water phase instead. The gel trapping experiments were slightly modified from the procedure reported by Paunov and coworkers.^{2, 3} The gellan gum solution was first heated to approximately 80°C in an oil bath to ensure that the gel was fully hydrated. Subsequently, pre-heated n-decane was added to the top of the gellan gum solution to create the oil phase. Ag octahedra were then added to the oil/water interface and the entire mixture was left at 80°C for approximately 15 min before being allowed to cool slowly to room temperature. Once the gel had set in the aqueous phase, the oil phase was then decanted gently. In place of n-decane, a layer of premixed PDMS precursor mixture (5:1 elastomer:curing agent) was poured over the nanoparticle monolayer and the container was left at room temperature for the PDMS to cure. After the PDMS had hardened, it was lifted off from the gel and washed in hot water. Scanning electron microscopy characterization was performed using JEOL-JSM-7600F at an accelerating voltage of 5 kV. Extinction measurements were carried out using Cary 60 Spectrophotometer.

Surface-enhanced Raman scattering measurements. SERS measurements were carried out using both x-z and x-y imaging modes of the RAMANtouch microspectrometer (Nanophoton Inc, Osaka, Japan) with an excitation wavelength of 532 nm (power = 64.8 μ W). A 20 \times (N.A. 0.45) objective lens with 1 s accumulation time (unless otherwise stated) was used for data collection between 300 cm^{-1} to 1800 cm^{-1} . At least three x-z SERS imaging experiments (each x-z SERS image is 400 $\mu\text{m} \times 200 \mu\text{m}$) were carried out on different areas of the plasmonic metacrystals to ensure the reproducibility of the SERS intensities. All SERS spectra were obtained by averaging at least 3 individual spectra where 20 individual pixels were chosen from each spectra from various nanoarrays. Methylene blue (3.20 mg/mL, 10^{-2} M) and coumarin 30 (34.7 $\mu\text{g/mL}$, 10^{-4} M) were prepared in solution using ultrapure water and 10 % toluene/decane mixture respectively. Serial dilutions were performed to give a series of concentrations, ranging from 10^{-4} M to 10^{-9} M and 10^{-5} M to 10^{-9} M for methylene blue and coumarin 30 respectively.

Contact angle measurements of Ag films functionalized with self-assembled monolayer of thiols. Contact angles of the functionalized 114-nm thick Ag films were measured on a Theta Lite tensiometer equipped with a Firewire digital camera. Static contact angle was measured with a 4- μL ultrapure sessile water droplet. A total of five readings were taken at different spots on the same substrate for each of the thiol-functionalized Ag film and averaged to obtain the bulk contact angles.



Scheme S1. Schematic depicting the process of Ag octahedra self-assembly at the oil/water interface, followed by transferring to a solid surface using the gel-trapping technique.

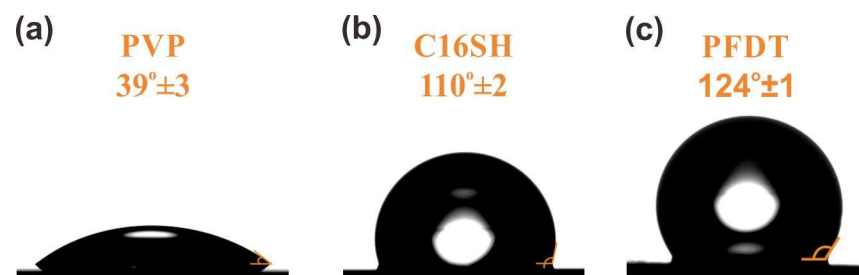


Figure S1. Bulk contact angle measurements of Ag film functionalized with (a) PVP, (b) C16SH, and (c) PFDT.

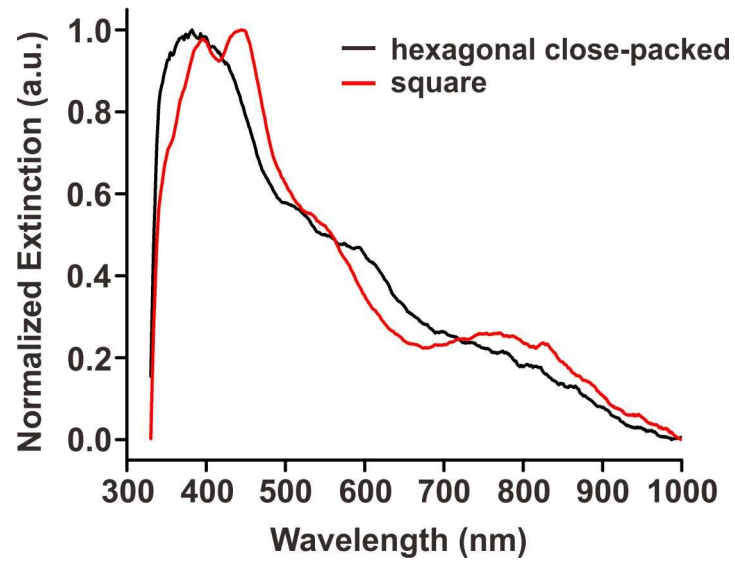


Figure S2. Extinction spectra of the two metacrystals.

Table S1. SERS vibrational modes of methylene blue and their vibrational band assignments.⁴

| Methylene Blue peaks (cm⁻¹) | Band assignment^[47] |
|---|---------------------------------------|
| 457 | C-N-C skeletal deformation |
| 507 | C-N-C skeletal deformation |
| 683 | C-H out-of-plane bending |
| 1191 | C-N stretching |
| 1406 | C-H in-plane ring deformation |
| 1451 | Asymmetry C-N stretching |
| 1637 | C-C ring stretching |

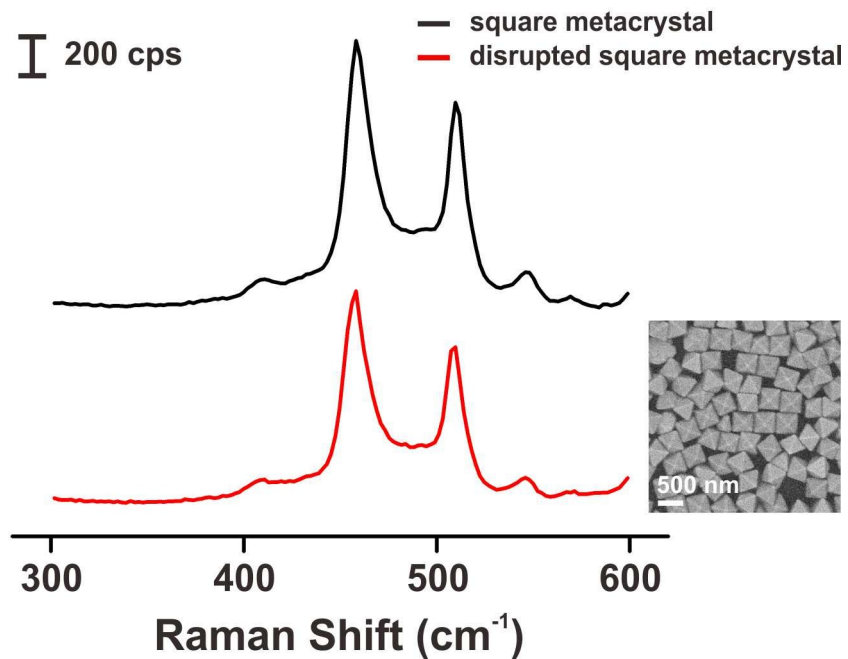


Figure S3. Comparison of the SERS signals between the square metacryystal and disrupted square metacrystal assembled using PFDT-functionalized Ag octahedra. SEM image on the right shows the disrupted metacrystal.

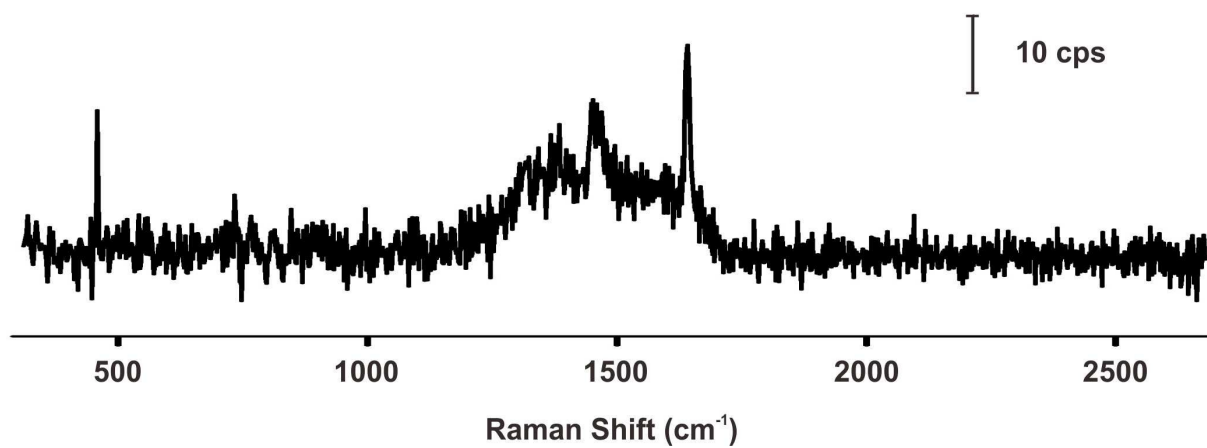


Figure S4. Full SERS spectrum of 1 nM methylene blue measured using the square metacrystal.

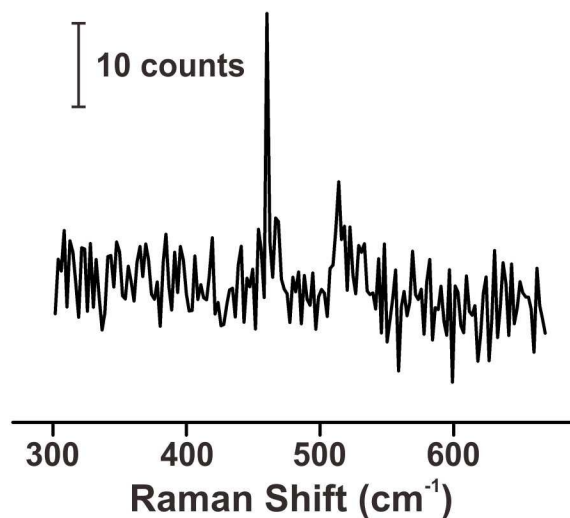


Figure S5. Normal Raman spectrum of 1 mM methylene blue at an acquisition time of 200 s.

$$\begin{aligned}
 \text{Analytical EF of methylene blue} &= [(I_{\text{SERS}}) / (I_{\text{Raman}})] \times [(C_{\text{Raman}}) / (C_{\text{SERS}})] \\
 &= [20 / (40 / 200)] \times (10^{-3} / 10^{-9}) \\
 &= 1 \times 10^8
 \end{aligned}$$

Where C_{SERS} and C_{Raman} are the corresponding concentration measured using self-assembled monolayers at liquid/liquid interface (10^{-9} M for methylene) and normal Raman (10^{-3} M for methylene blue), respectively. I_{SERS} and I_{Raman} are the signals recorded on SERS and normal Raman at their respective concentration per unit time.

Table S2. SERS vibrational modes of coumarin 30 and their vibrational band assignments.⁵

| Coumarin 30 peaks (cm⁻¹) | Band assignment^[51,52] |
|--|--|
| 620 | out of plane ring deformation |
| 654 | C-H wag |
| 746 | ring stretching |
| 779 | ring stretching |
| 1503 | asymmetric C=C stretching |
| 1598 | asymmetric C=C stretching |
| 1638 | asymmetric C=C stretching |

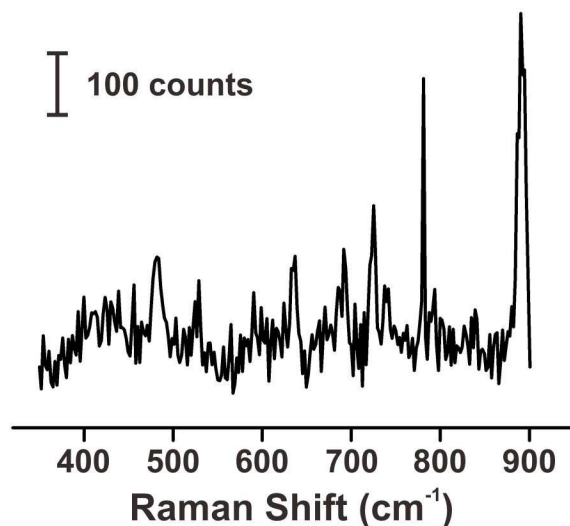


Figure S6. Normal Raman spectrum of 1 mM coumarin 30 in ethanol at an acquisition time of 200 s.

$$\begin{aligned}
 \text{Analytical EF of coumarin 30} &= [(I_{\text{SERS}}) / (I_{\text{Raman}})] \times [(C_{\text{Raman}}) / (C_{\text{SERS}})] \\
 &= [36 / (50 / 200)] \times (10^{-3} / 10^{-9}) \\
 &= 1 \times 10^8
 \end{aligned}$$

Where C_{SERS} and C_{Raman} are the corresponding concentration measured using self-assembled monolayers at liquid/liquid interface (10^{-9} M for coumarin 30) and normal Raman (10^{-3} M for coumarin 30), respectively. I_{SERS} and I_{Raman} are the signals recorded on SERS and normal Raman at their respective concentration per unit time.

References

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