Supporting Information

Nanocrystalline Ag microflowers as versatile SERS platform

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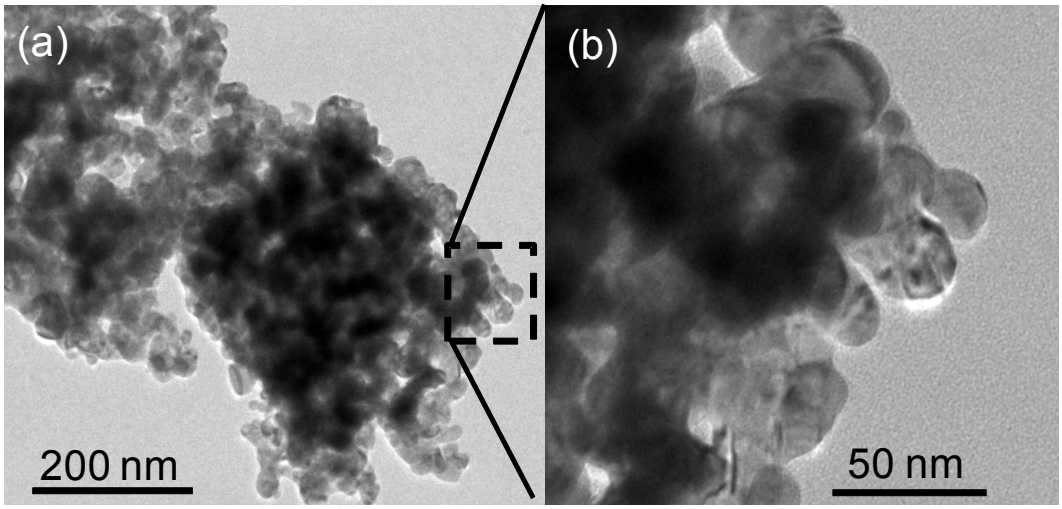

Figure S1. (a) TEM image of the arm-tip of a Ag microflower. (b) Magnified image shows the presence of nanoparticles of ~ 25 - 40 nm.

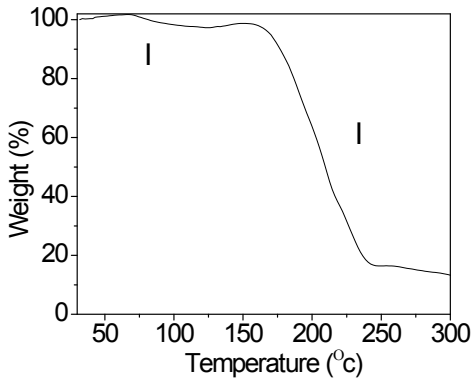

Figure S2. TGA of AgToABr showing various stages (I-II) of decomposition.

Composition of AgBr complex

As shown in thermo gravimetric analysis (TGA) plot, the decomposition of AgToABr starts at ~ 165 °C) and completes at 230 °C. Weight loss occurs in two steps - region I (~3%) corresponding to solvent evaporation and regions II (~81.35%) corresponding to decomposition, and desorption of ToABr, ToA, chlorine, bromine. The AgBr residue is ~15.65 wt%.

Molecular weight of ToABr = 546.79 g/mol

Molecular weight of AgBr = 187.77 g/mol

AgCl molecular weight = 143.32 g/mol

15.65 wt% = AgBr = 187.77 g/mol

100 wt% = x = 1199.8 (~1200) g/mol

$(AgCl_2)^-$ + ToA^+ + ToABr = 178.92+466+546.79 = 1192≈1200

Hence, the empirically derived formula is $(AgCl_2)^-$ToA. ToABr, which in a simplified way, is written as AgToABr.

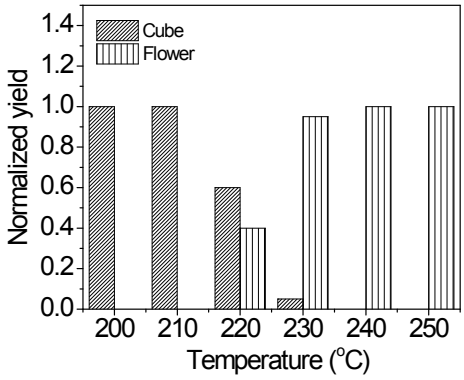

Figure S3. (a) Histogram showing the normalized yield of AgBr microcubes and microflowers at different thermolysis temperatures.

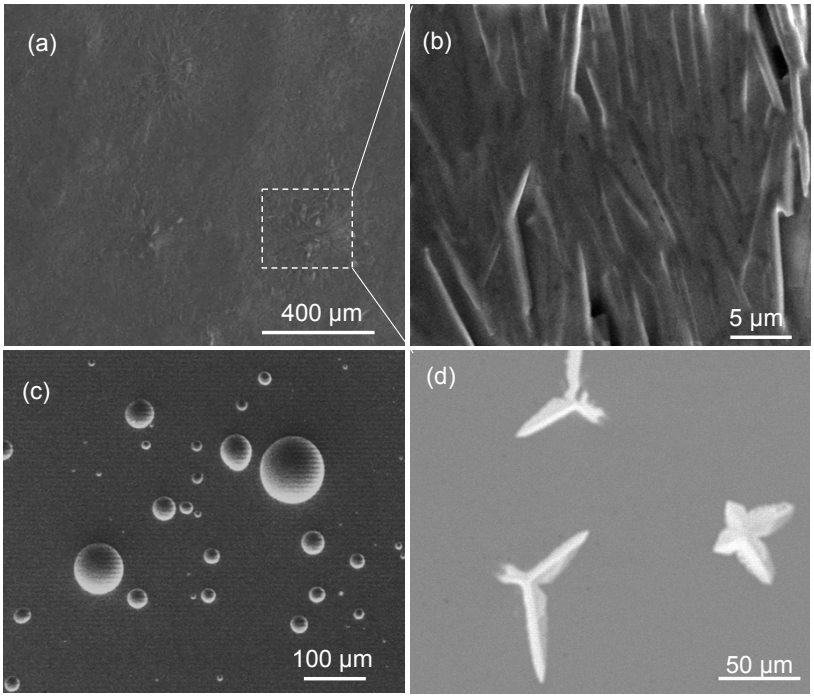

Figure S4. SEM images of (a-b) AgToABr film at different magnifications, (c) dewetting of AgToABr film on heating to 240 °C. (d) After 240 °C treatment for ~20 minutes, the Si substrate is covered with a large number of AgBr microcrytsals. In d, microflowers were surrounded by molten precursor. Hence, the image is not sharp.

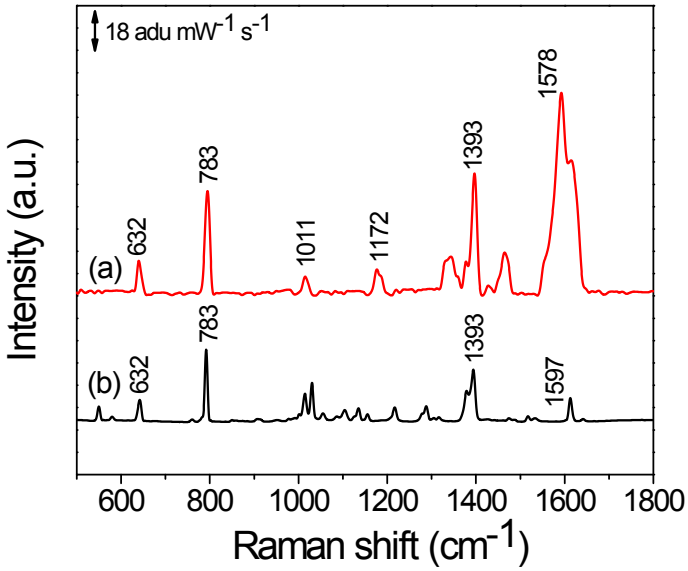

Figure S5. (a) SERS (1 μM) and (b) normal Raman spectra (bulk) of 1,2,3- benzotriazole.

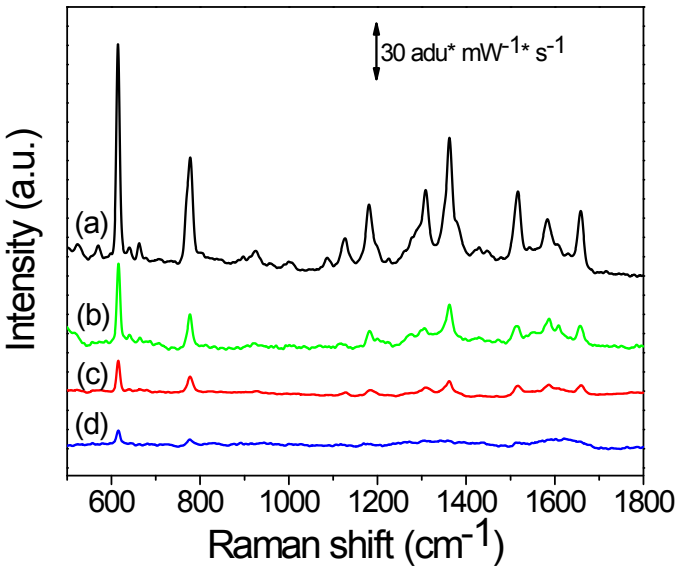

Figure S6. SERS of R6G solution of (a) 10^{-9}, (b) 10^{-12}, (c) 10^{-15} and 10^{-18} M concentrations. In each experiment, 200 nL of the solution was used.

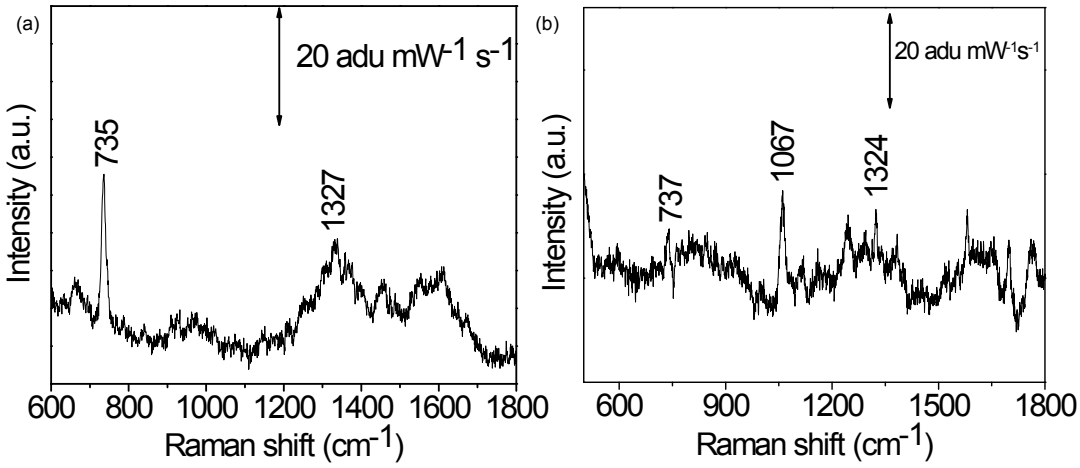

Figure S7. SERS of (a) salmon sperm DNA adsorbed from a solution of concentration, 0.75 nM. (b) single stranded oligonucleotide (oligo A). Solution of concentration, 67 nM.

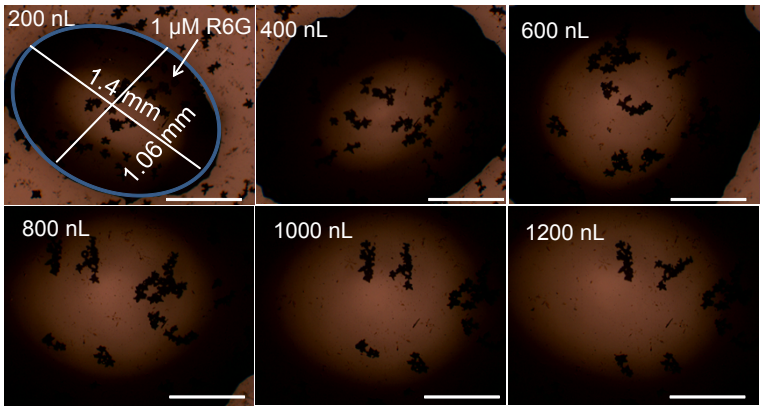

Figure S8. Optical microscopy images showing different volumes of R6G solution dropped on the Ag microflowers containing a glass substrate. Scale bar, 500 µm.

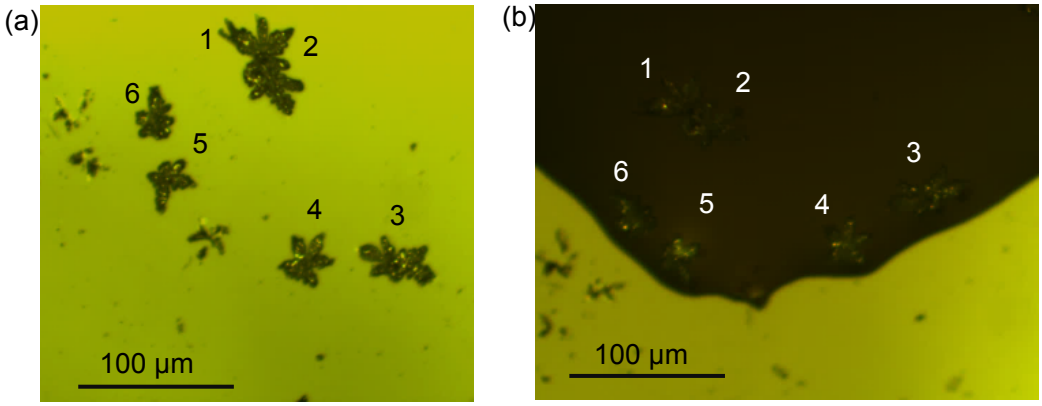

Figure S9. Optical microscope images of Ag microflowers before (a) and after (b) addition of R6G solution. No agglomeration was observed upon adding the solution.

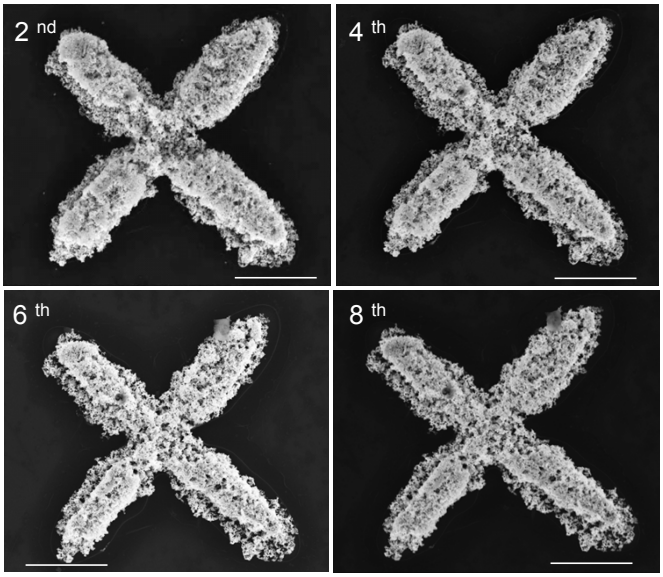

Figure S10. SEM images of the Ag microflower shown in Figure 6 at intermediate cycles. Scale bar, 10 μm.

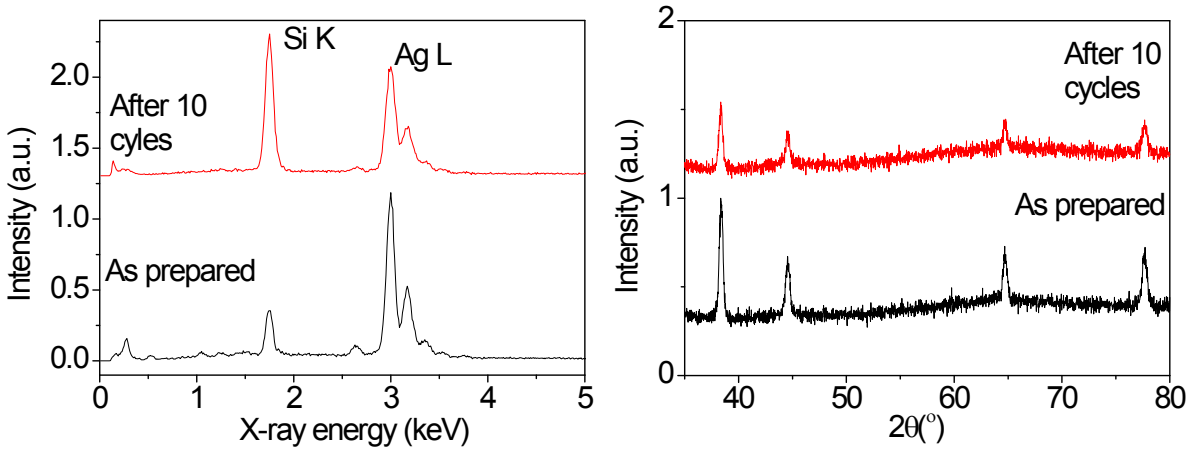

Figure S11. (a) EDS and (b) XRD of as-prepared Ag microflowers and after 10 cycles of washing.

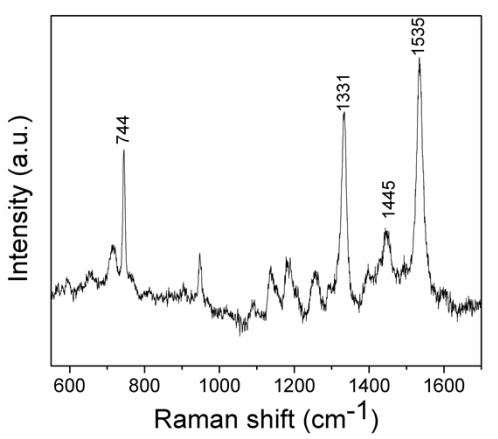

Figure S12. Raman spectrum of bulk OPD using 632 nm laser source and accumulation time of 30 s.

[1] H.-Z. Yu, J. Zhang, H.-L. Zhang, Z.-F. Liu, *Langmuir* 1998, **15**, 16.
[2] A. D. McFarland, M. A. Young, J. A. Dieringer, R. P.Van Duyne, *J. Phys. Chem. B* 2005, **109**, 11279.

Note S1

Calculation of enhancement factor:

The enhancement factor was calculated by incubating the silver microflower in 1 mM thiophenol solution and collecting the SERS spectra from four different places (tip, center, arm centre and arm edge) of a single microflower. The enhancement factor, G was calculated by the method of Yu et. al.[1]

$G = (I_{SERS}/ I_{NORM}) \times (N_{BULK}/N_{SURF})$

where I_{SERS} and I_{NORM} are the intensities of a band in SERS and normal Raman of the thiophenol molecule, respectively. The number of probe molecules which are illuminated under the laser beam in bulk and SERS experiments are termed as N_{BULK} and N_{SURF} respectively. N_{SURF} is the product of C, the surface density of thiophenol (6.8×10^{14} molecules cm^{-2})[2] and A, the laser spot area respectively. N_{BULK} is given by the formula Ahρ/

m, where h, ρ, and m are the penetration depth (100 μm), the density (1.079 g cm^{-3}), and the molecular weight (110.18 g mol^{-1}) of thiophenol, respectively. The enhancement factor of the microflower structure is of the order of 10^7.