Supplementary information (ESI) for Nanoscale
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Electronic Supplementary Information

Graphene oxide and shape-controlled silver nanoparticle hybrid for ultrasensitive single-particle surface-enhanced Raman scattering (SERS) sensing †

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Detailed calculation of enhancement factor

Enhancement factors (EF) for these particles were estimated using the expression EF = $(I_{sers}/I_{ref}) \times (N_{ref}/N_{sers})$, where I_{sers} is the intensity of the specific Raman band from the analyte adsorbed on a SRES active substrate, and N_{sers} is the number of molecules contributing to I_{sers}. Similarly, I_{ref} is the intensity of the same Raman band from the bulk analyte, normalized with the laser power and acquisition time, and N_{ref} is the number of molecules that yield I_{ref}. Here, 1083 cm^{-1} Raman band of 4-MBT is selected for EF calculation. For a more comprehensive estimate of EF, we utilize the average intensity from 20 sample points of the substrate. The diameter of the laser beam is measured at ~520 nm, which is larger than a single Ag nanoparticle. So N_{sers} is determined by the surface area of a single Ag nanoparticle. For Ag octahedron, the surface area is calculated to be 3.42×10^5. Taking 4.5×10^{14} molecules/cm^2 for a monolayer of 4-MBT on silver (assume the binding of 4-MBT on silver is similar to that of gold), the number of molecules excited under the laser spot is approximated at 1.54×10^6 molecules.

N_{ref} was calculated from the probe volume of a MBT solution in a 100 μm thick glass cell assuming a diffraction limited spot. The measured laser diameter and the focal depth (h) are 910 nm and 4320 nm, respectively. The effective excitation volume (V) is $V = A \times h = 2.81 \times 10^9$ nm^3. The larger confocal volume in ethanol solution than that in ideal dry condition is caused by the distortion of laser spot in solution. The number of 4-MBT molecules in ethanol (1 mol L^{-1}) excited by the laser beam is therefore $N_{ref} = 1.69 \times 10^9$ molecules. The average enhancement factor, based on mean intensity from 20 sample points, is estimated to be $\sim 9.2 \times 10^5$.

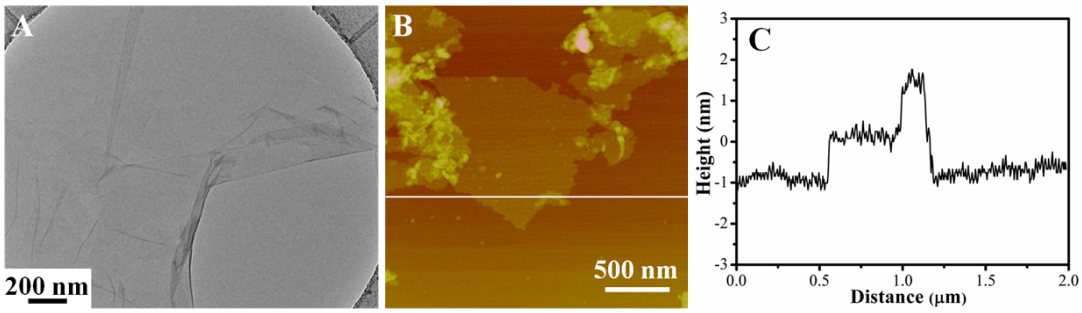

Fig. S1. (A) TEM image of GO, (B) AFM images and (C) corresponding height profiles of GO on silicon substrates.

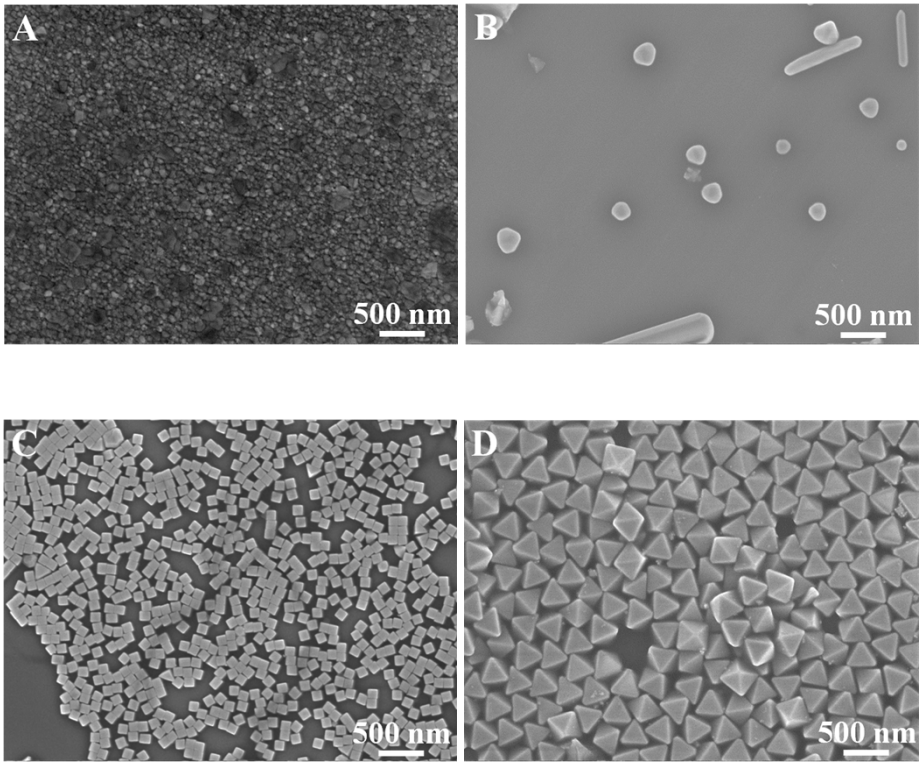

Fig. S2. SEM images of (A) Ag film fabricated by vacuum thermal evaporation, (B) Ag nanospheres, (C) Ag nanocubes, and (D) Ag octahedra.

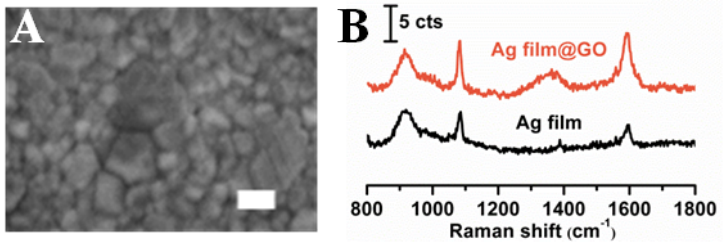

Fig. S3. (A) SEM images of Ag film. The scale bar is 100 nm. (B) The corresponding SERS spectra of 4-MBT adsorbed on Ag film (black line) and Ag film@GO (orange line).

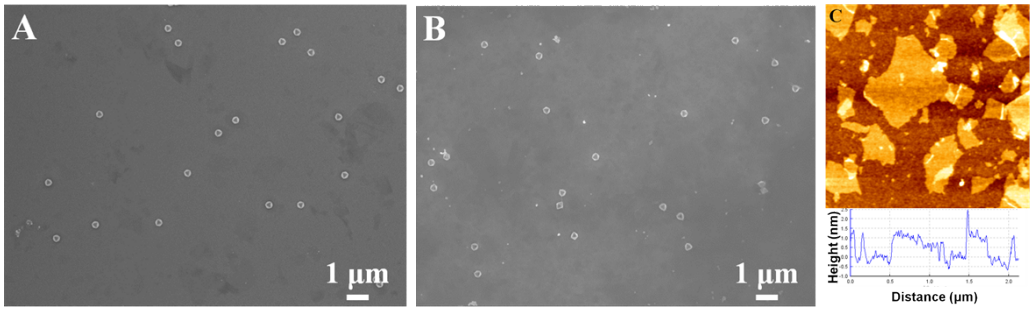

Fig. S4. SEM images of (A) GO@Ag octahedra and (B) Ag octahedra@GO hybrid on Si substrates. (C) AFM image and corresponding height profile of GO@Ag octahedra. The areas of Ag octahedra are carefully avoided due to the great disparity in the cross-sectional profiles of Ag octahedra and GO.

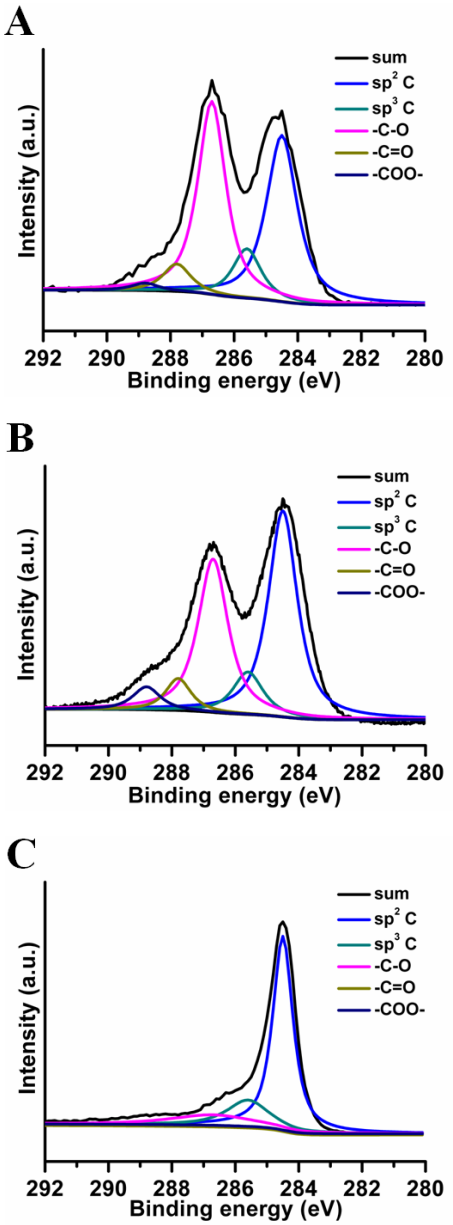

Fig. S5 Fig. S5. Curve fit of C1s spectra of (A) GO, (B) $RGO_{7/3}$, and (C) $RGO_{9/1}$.

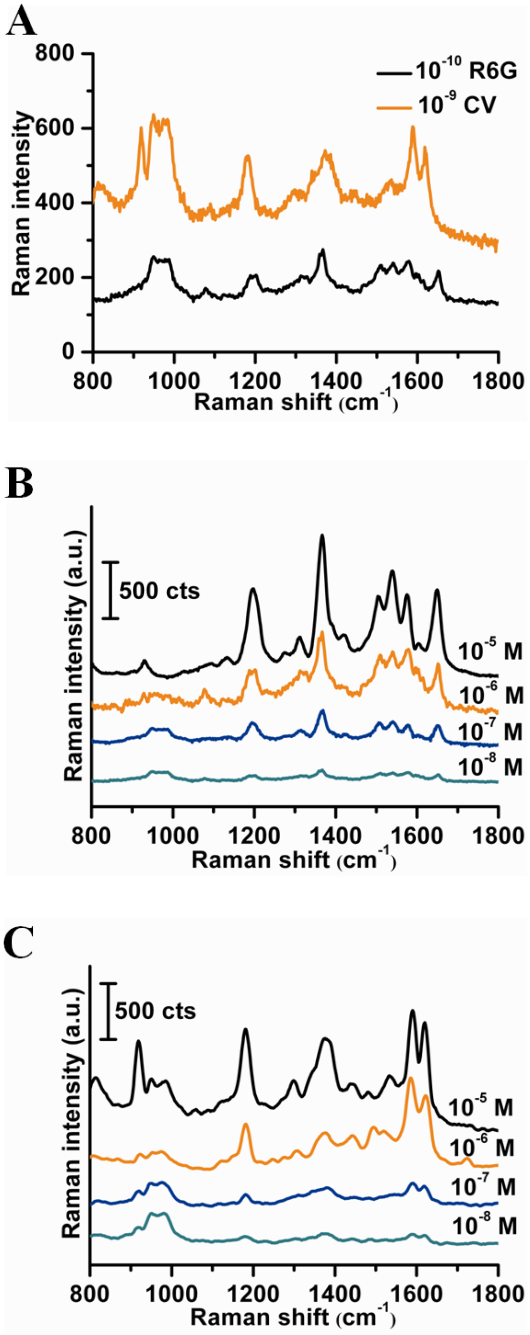

Fig. S6. (A) SERS spectra of 10^{-10} M R6G and 10^{-9} M CV deposited on Ag octahedron@GO. SERS spectra of R6G (B) and CV (C) on deposited Ag octahedron by soaking in the solution with different concentrations. For both R6G and CV, the concentrations from top to bottom are 10^{-5}, 10^{-6}, 10^{-7} and 10^{-8} M.