Supporting Information

Ag nanosheet-assembled micro-hemispheres as effective SERS substrates

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The Supporting Information includes:

Part S1 Experimental section

For the synthesis of Ag micro-hemisphere arrays, 2 g L^{-1} $AgNO_3$ and 18 g L^{-1} citric acid were added to 50 mL deionized (DI) water, followed by stirring until complete dissolution of the solute. Such an aqueous solution was used as the electrolyte in the electrodeposition. A rectangular graphite sheet was used as anode and a piece of ITO substrate (2 cm × 0.5 cm) was used as cathode (Fig. S1, schematic of the fabrication set-up). The electrodeposition of the Ag micro-hemispheres was carried out under a constant current density of 170 μA cm^{-2} for 60 min at room temperature. The ITO substrate with the electrodeposited products was then taken out, cleaned with DI water several times and dried with high-purity flowing nitrogen.

The resultant products were characterized by using X-ray diffraction (XRD) (Philips X'pert-PRO), scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscope (TEM, JEOL 2010) and Ultraviolet-Visible-Near-Infrared spectrophotometer (Hitachi, U-4100). The Ag micro-hemispheres were cleaned by using a plasma cleaner (PDC-32G, high power) for 10 min, and then used as SERS substrates. SERS measurement was conducted on a confocal microprobe Raman system (Renishaw, inVia) with the excitation wavelength of 514.5 nm in consideration of the UV–vis spectrum of the micro-hemispheres. During SERS measurement, the laser light was vertically projected onto the samples with a resultant beam diameter of ~ 5 μm.

To ensure good molecule adsorption, the Ag micro-hemispheres on ITO substrates were immersed in 1.5 mL R6G solutions (10^{-6} and 10^{-15} M aqueous solution) for 2 h, taken out and then dried with high-purity flowing nitrogen. For the estimation of enhancement factor for R6G, 10 μL of 10^{-11} M R6G solution was dispersed to 15 mm^2 Ag micro-hemisphere substrate and dried in high-purity argon. For PCB-77 detection, 1.5 μL 10^{-4}, 3×10^{-5}, 10^{-5}, 3×10^{-6}, and 10^{-6} M PCB-77 n-hexane solutions were dispersed to five Ag micro-hemisphere substrates (6 mm^2) and dried in the fuming cupboard. All the spectra were acquired with the acquisition time of 10 s.

Part S2 Estimation of enhancement factor

For estimation of the enhancement factor of the Ag micro-hemispheres, 10 μL of 3×10^{-3} M R6G ethanol solution was dispersed on a silicon wafer, and formed a spreading area of 10 mm in diameter. The enhancement factor is calculated by comparing the ratios of the peak intensities of R6G molecules on a single Ag micro-hemisphere (Curve b in Fig. 2) to the corresponding un-enhanced signals from a pure R6G film (reference sample, Curve a in Fig. 2):

$$EF = \frac{I_{SERS} N_{\mathrm{Re}f}}{I_{\mathrm{Re}f} N_{SERS}} \tag{1}$$

where I_{SERS} and I_{Ref} are the Raman intensities of the spectra, N_{SERS} and N_{Ref} are the number of R6G molecules illuminated by the laser absorbed on the micro-hemisphere and in the reference sample, respectively. For the pure R6G film with a area of 10 mm^2, considering the laser spot is a circle with a diameter of 5 μm, the number of the R6G molecules illuminated by the laser (N_{Ref}) is $3\times10^{-3}\times10^{-5}\times6.02\times10^{23}\times\pi(5\mu m/2)^2/10mm^2 = 3.5\times10^{10}$. For estimation of N_{SERS} and I_{SERS}, 10 μL of 10^{-11} M R6G aqueous solution was dispersed to 15 mm^2 ITO substrate with ~ 7.5×10^5 Ag micro-hemispheres (supposing micro-hemispheres cover about half of the ITO substrate surface). Supposing all R6G molecules absorbed on Ag micro-hemispheres, N_{SERS} was estimated to be 80. For the band at 612 cm^{-1}, $I_{\mathrm{SERS}}/I_{\mathrm{Ref}}$ was 0.25. For a single micro-hemisphere with an average size of 3.99 μm while the laser spot is a circle with a diameter of 5 μm, it needs revised version (multiplying $(3.99/5)^2$). Therefore average enhancement factor for the band at 612 cm^{-1} is calculated to be 7×10^7. In the same way, the average enhancement factor for PCB-77 is calculated to be 3×10^3.

Fig. S1 to S6

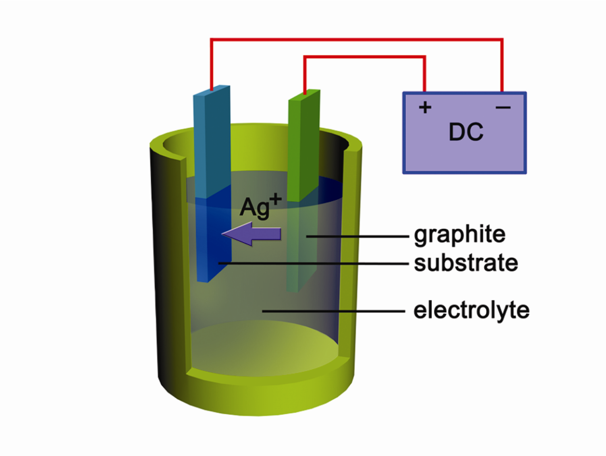

Fig. S1. Schematic set-up for the electrodeposition of Ag micro-hemispheres on ITO substrate.

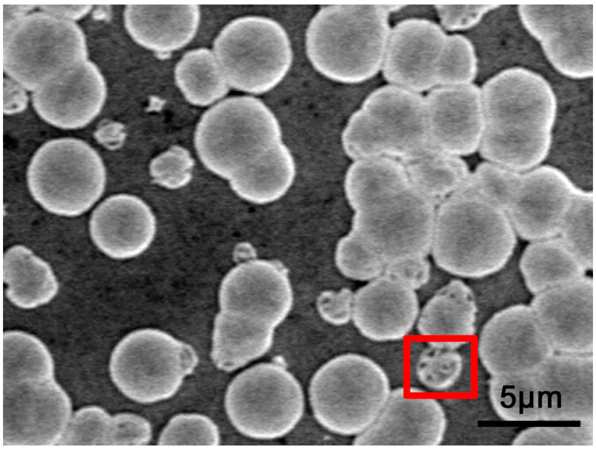

Fig. S2. SEM image of Ag micro-hemispheres with some imperfect ones (marked with red rectangular frame for attention).

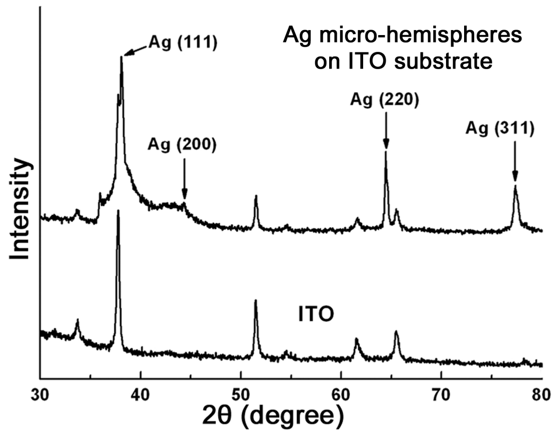

Fig. S3. XRD spectra taken from the ITO substrate with (top) and without (bottom) the Ag micro-hemispheres.

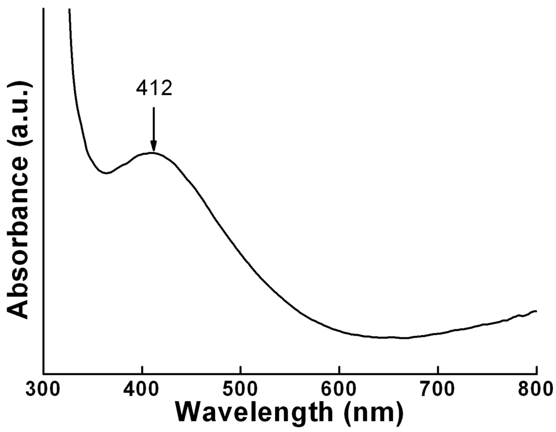

Fig. S4. The UV–vis spectrum of micro-hemispheres.

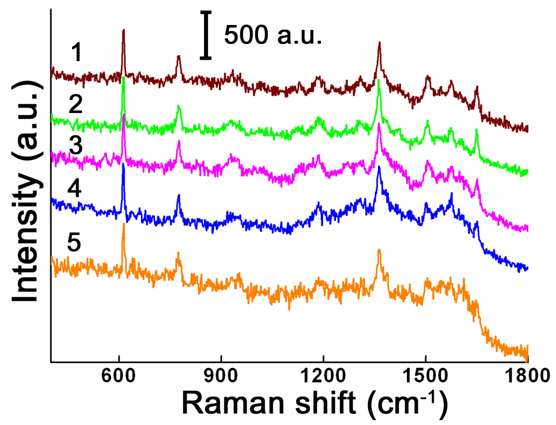

Fig. S5. SERS spectra of 10^{-11} M R6G from five randomly chosen individual micro-hemispheres. Each spectrum has been divided by the surface area of the corresponding micro-hemisphere.

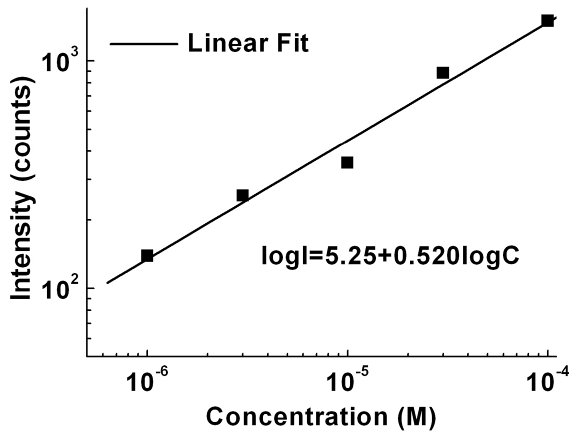

Fig. S6. The linear relationship between the logarithmic intensities (1596 cm^{-1}) and the concentrations of PCB-77.