Supporting Information

Electrochemically Engineered Hierarchical Flower-like Ag Nanostructures within Al_2O_3 Honeycomb Microchannel Periodic Arrays for Ultra-Sensitive SERS Detection

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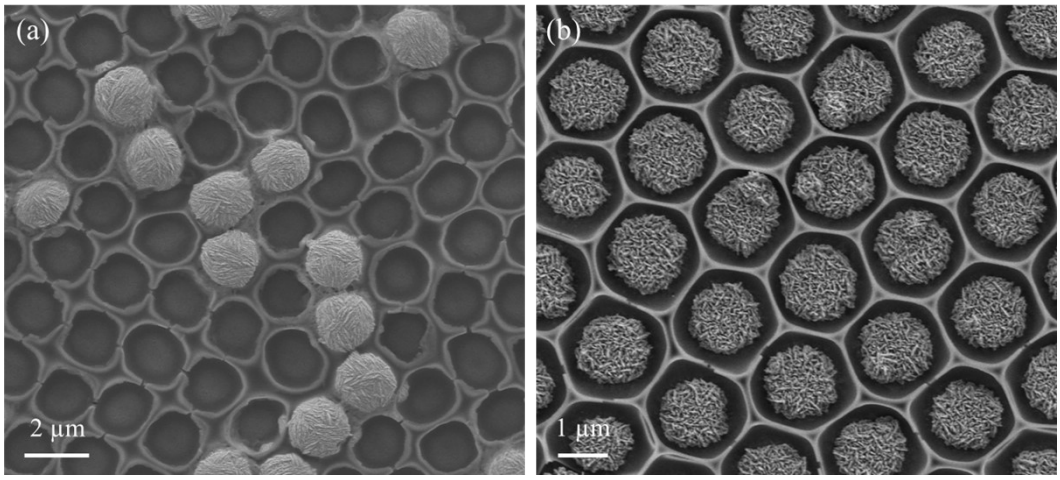

Fig. S1 SEM images of Ag nanostructures grown inside of Al_2O_3 HMPAs on ITO surface (a) without Au sputtering and (b) with Au sputtering.

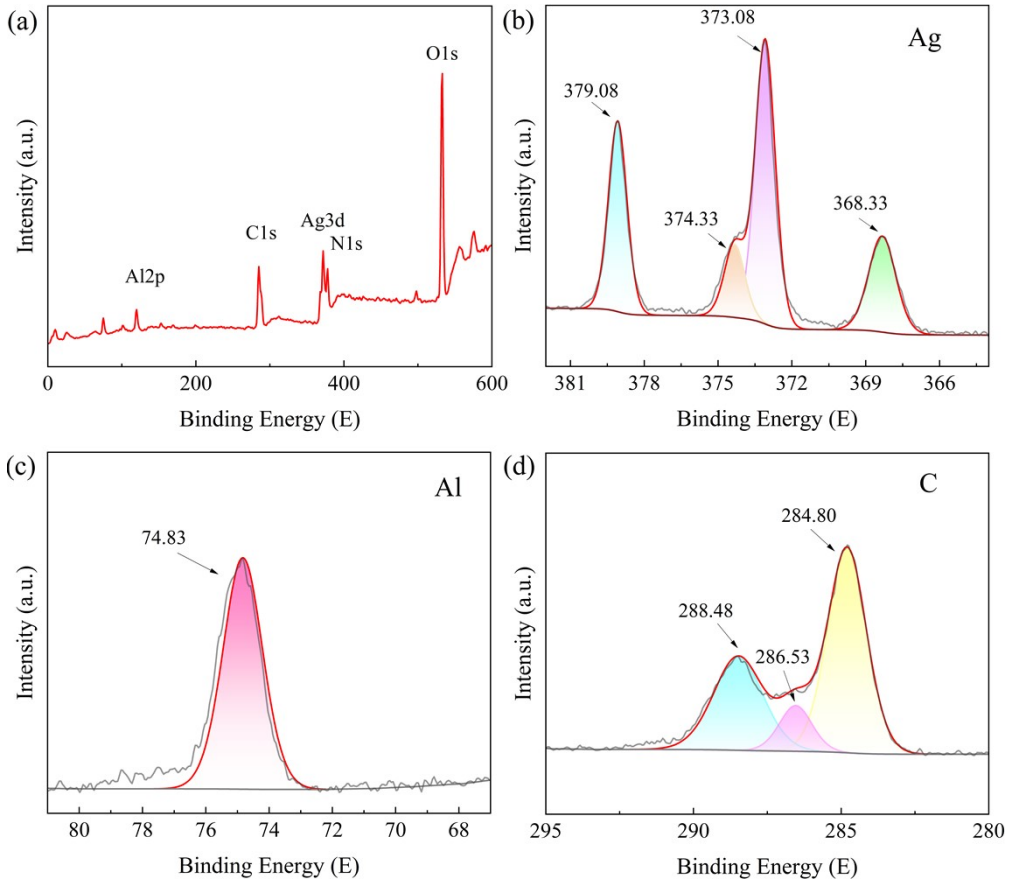

Fig. S2 XPS spectra of flower-like Ag nanostructures synthesized within Al_2O_3 HMPAs: (a) Survey scan of as-prepared sample confirming the presence Ag and Al_2O_3, (b) high resolution XPS spectrum of indicating metallic Ag, (c) high resolution XPS spectrum corresponding to Al_2O_3, and (d) high resolution C1s spectrum showing adventitious carbon and oxidized species.

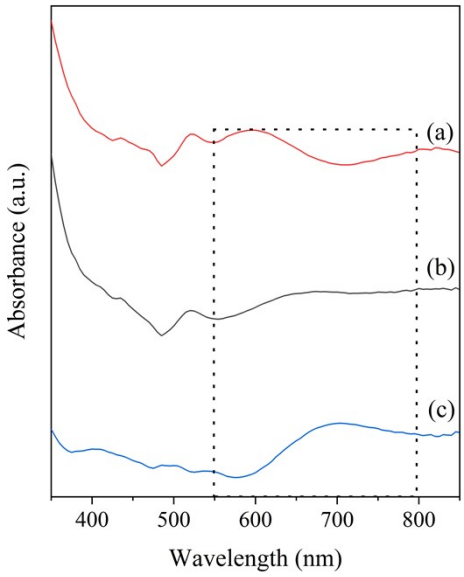

Fig. S3 UV-vis absorption spectra of Al_2O_3 HMPAs on ITO glass slide (a) before and (b) after electrodeposition of hierarchical flower-like Ag nanostructures, and (c) the difference of spectra before and after growing the hierarchical flower-like Ag nanostructures int the HMPAs that was obtained by directly subtracting the curve a from curve b.

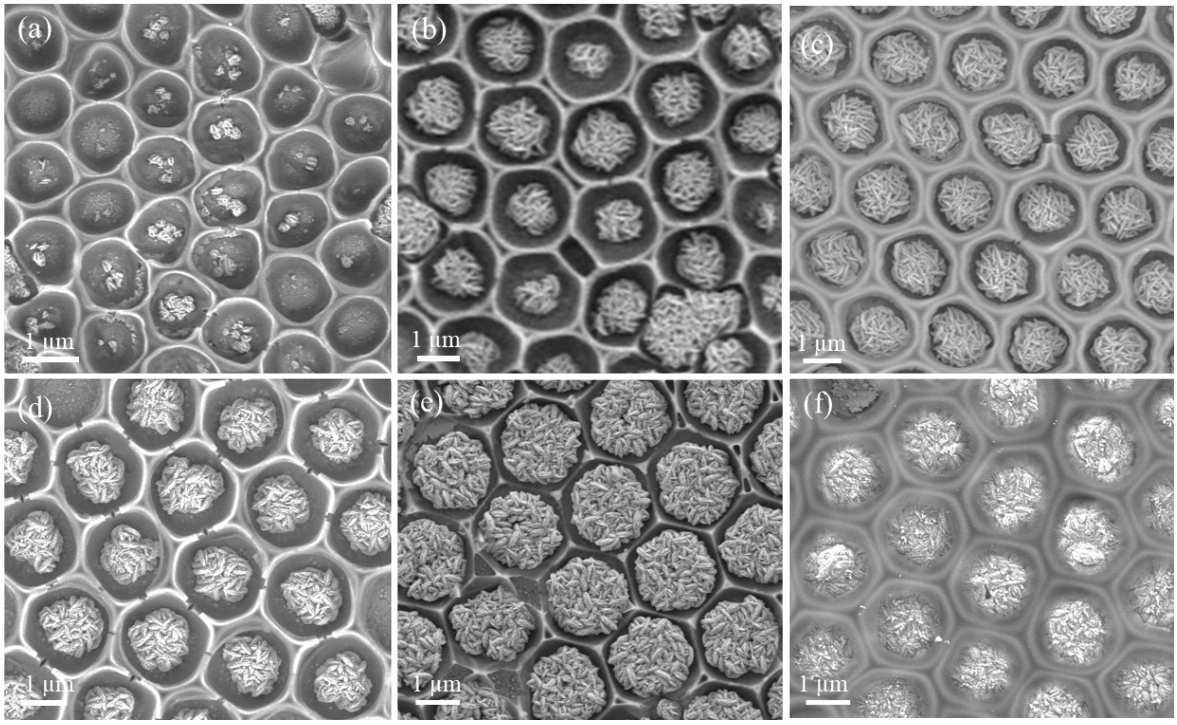

Fig. S4 SEM images of Ag nanostructures grown inside the Al_2O_3 HPMAs under different concentrations of $AgNO_3$: (a) 1 mM, (b) 5 mM, (c) 10 mM, (d) 15 mM, (e) 20 mM, and (f) 30 mM.

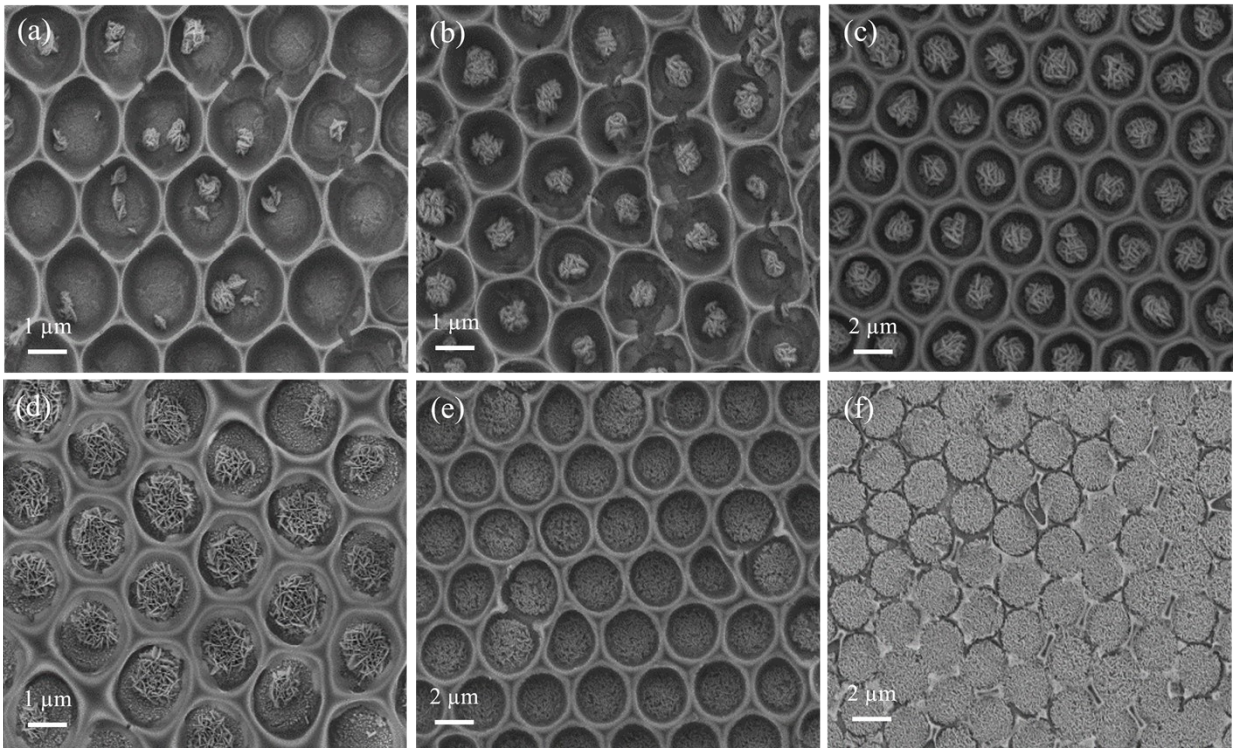

Fig. S5 SEM images of Ag nanostructures grown inside the Al_2O_3 bowls by varying the current density from (a) 25 µA/cm^2, (b) 50 µA/cm^2, (c) 100 µA/cm^2, (d) 150 µA/cm^2, (e) 200 µA/cm^2 and (f) 250 µA/cm^2.

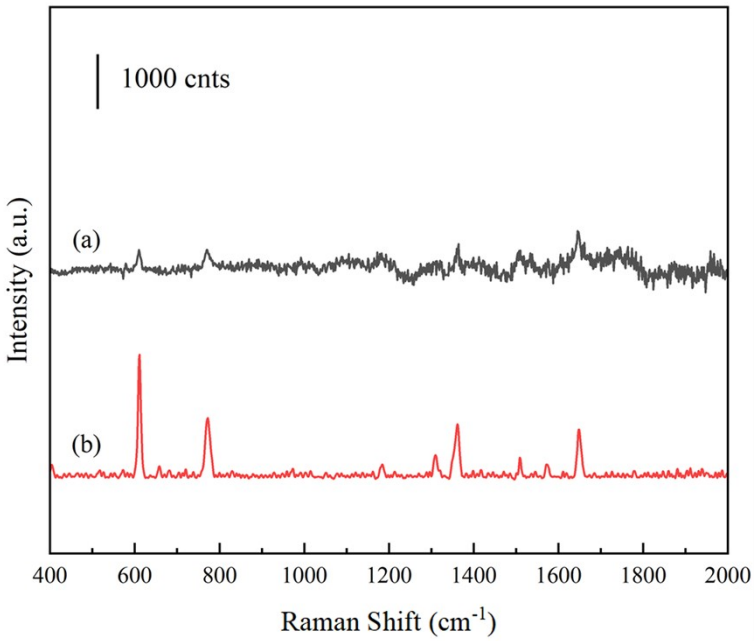

Fig. S6 The comparison between the Raman signal of R-6G (10^{-3} M) on a glass slide (spectrum a) and the SERS signal of R-6G (10^{-10} M) utilizing the hierarchical flower-like Ag nanostructures (spectrum b).

The SERS enhancement factor calculated for the fabricated hierarchical flower-like Ag nanostructures was 6.99×10^7. The EF was determined using the standard equation:

$$EF = \frac{I_{SERS} \times C_0}{I_0 \times C_{SERS}}$$

where C_0 and I_0 represents the concentration and intensity of the normal Raman signal, while C_{SERS} and I_{SERS} corresponds to the concentration and intensity for the SERS signal, respectively.

Table S1

The comparison of present study of hierarchical flowerlike Ag nanostructures with previous studies reported in the literature.

Sample	Detected Analyte	Enhancement Factor/LOD	Value of R^2	Reference
Ag NPs	R-6G	6.7×10^6 Not reported	0.977	[1]
2D $Cs_2AgBiBr_6$ nanoflakes	R-6G	1.37×10^7 1×10^{-10} M	0.97	[2]
MoS_2 nanobelts	R-6G	1.1×10^4 10^{-7} M	Not reported	[3]
WO_3-x nanoplatelets	R-6G	5.5×10^7 Not reported	Not reported	[4]
$W_{18}O_{49}$/monolayer MoS_2	R-6G	3.45×10^7 1×10^{-10} M	0.9915	[5]
Ag nanoflowers	R-6G	6.99×10^7 9.3×10^{-11} M	0.997	*This work*

References:

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