Electronic supplementary information (ESI)

A Highly-Ordered and Uniform Sunflower-like Dendritic Silver Nanocomplex Array as Reproducible SERS Substrate

Jian Chu[a], Yue Zhao[a], Shu-Hong Li[a], Wen-Wei Li[a], Xiang-Yu Chen[c], Yu-Xi Huang[a], You-Peng Chen[a], Wen-Gang Qu[b], Han-Qing Yu*[a], An-Wu Xu[b], Gang Liu[c], Yang-Chao Tian[c], Ying Xiong[c],

[a] CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry; [b] Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale; [c] National Synchrotron Radiation Laboratory, University of Science & Technology of China, Hefei, 230026, China

*** Corresponding author:**

Prof. Han-Qing Yu, Fax: +86 551 63601592; E-mail: hqyu@ustc.edu.cn

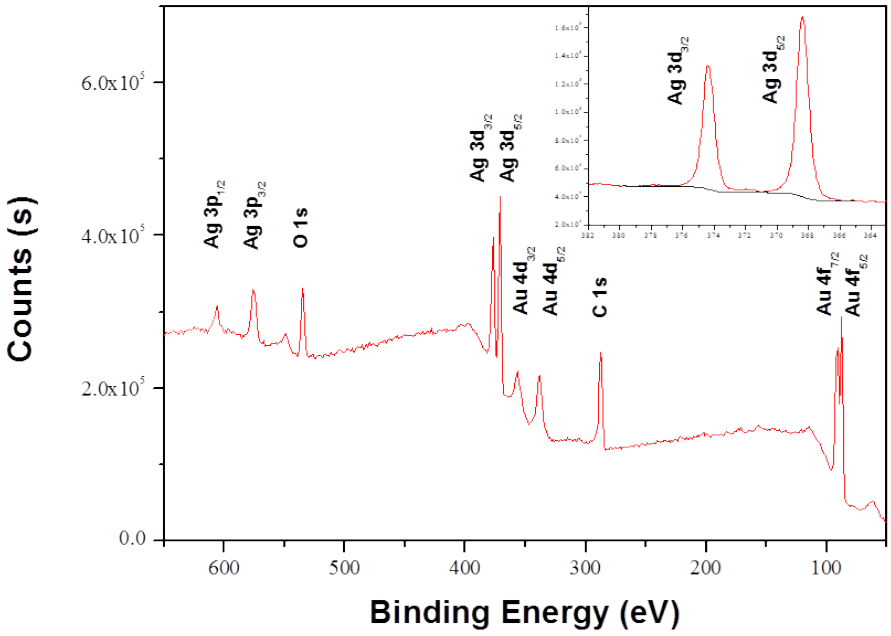

Fig. S1 XPS of the Ag nanostructure on Au film. High-resolution spectrum of the Ag (3d) region is presented in the insert

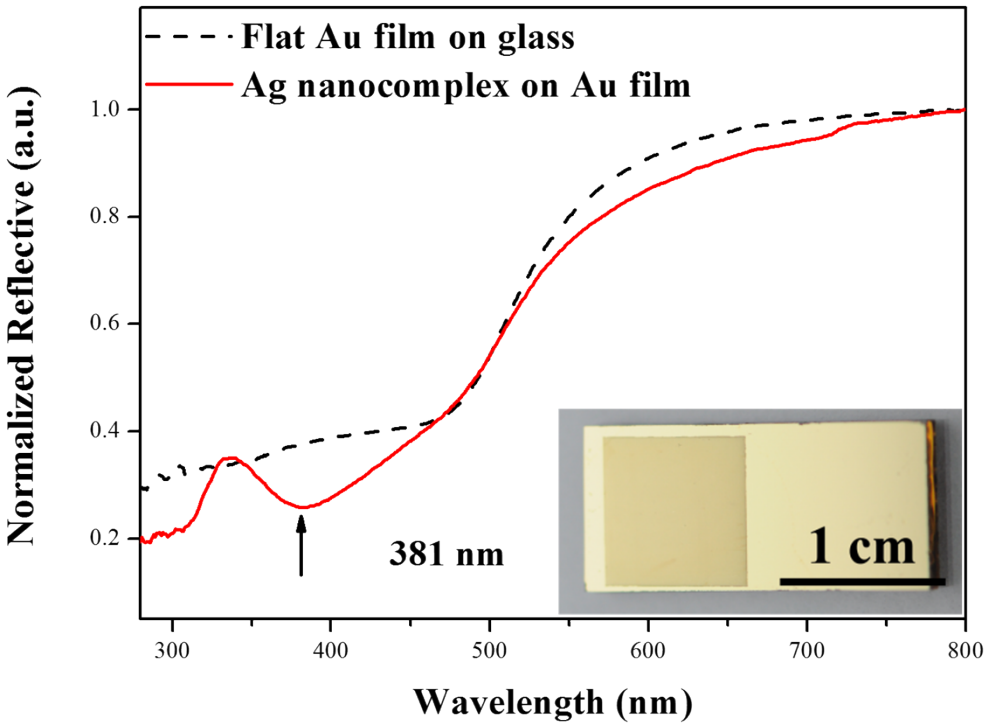

Fig. S2 Normalized UV-Vis-NIR diffuse reflectance spectrum of the Ag nanocomplex array. Insert shows the image of a fabricated Ag SERS substrate on Au film

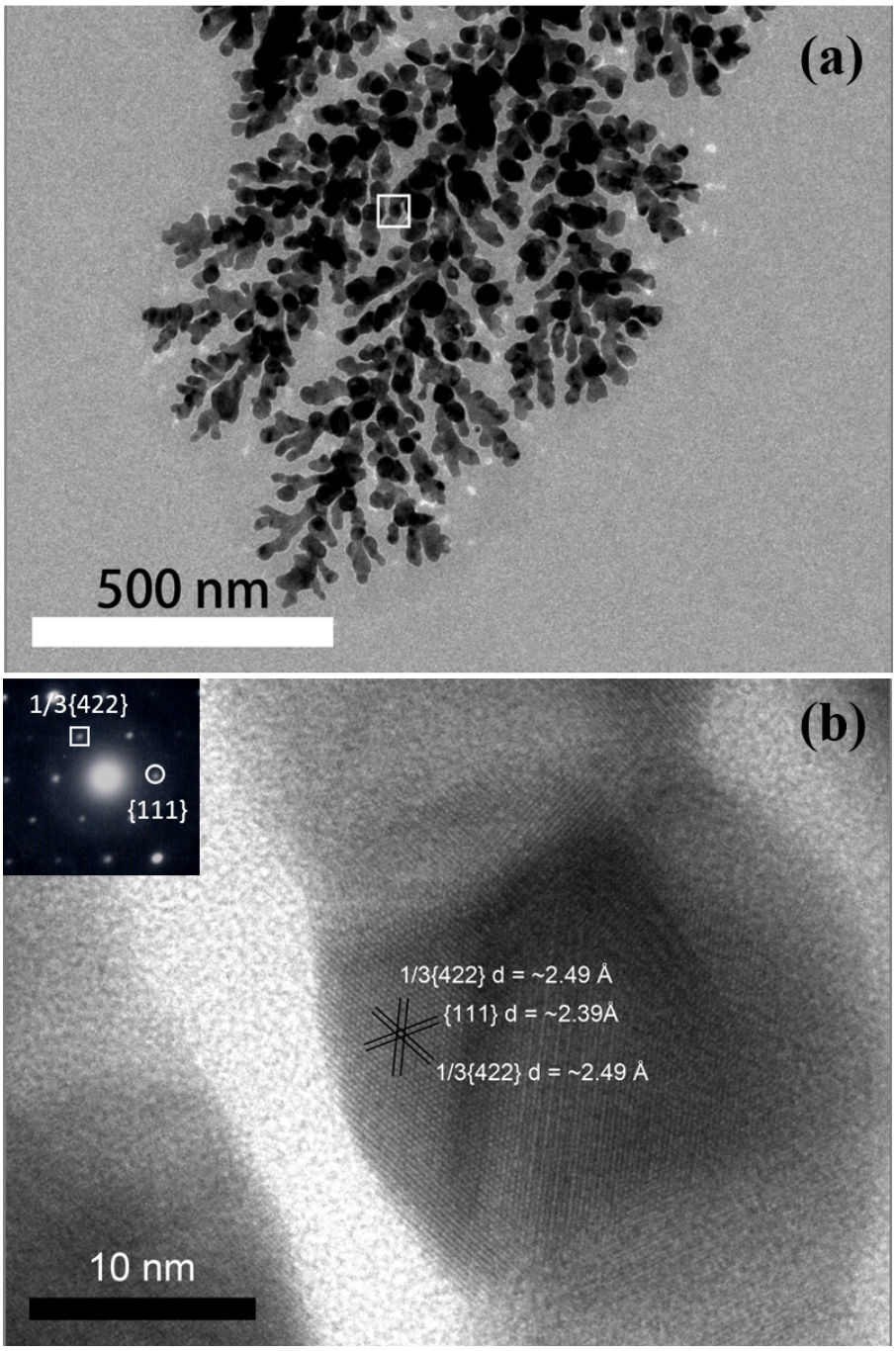

Fig. S3 (a) TEM image of the Ag dendrite nanostructure from Ag nanocomplex array; (b) HRTEM image taken from the region indicated within the box in (a). The insert shows the SAED pattern

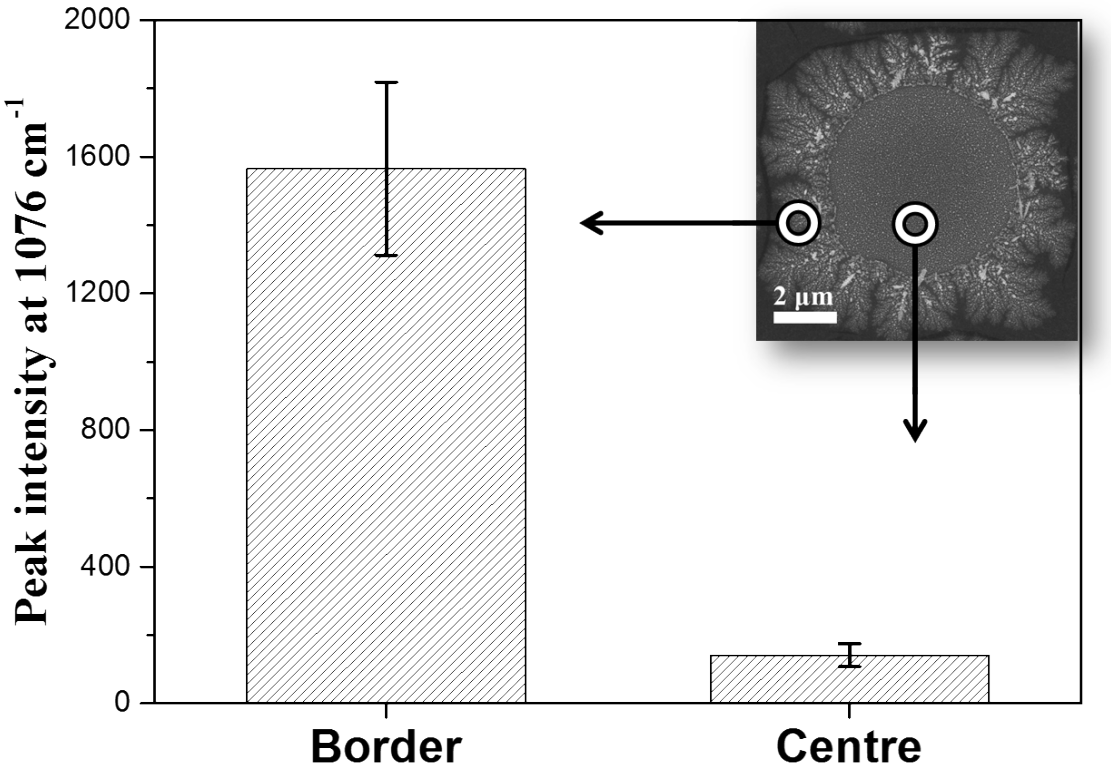

Fig. S4 Comparison between Raman peak intensities of 4-ATP recorded from the different parts of the Ag nanocomplex. The insert shows the corresponding excitation sites. Laser: 785 nm, 2 mW; Objective lens: 100× / 0.9; and integration time: 2 s; concentration of 4-ATP: 10^{-7} M.

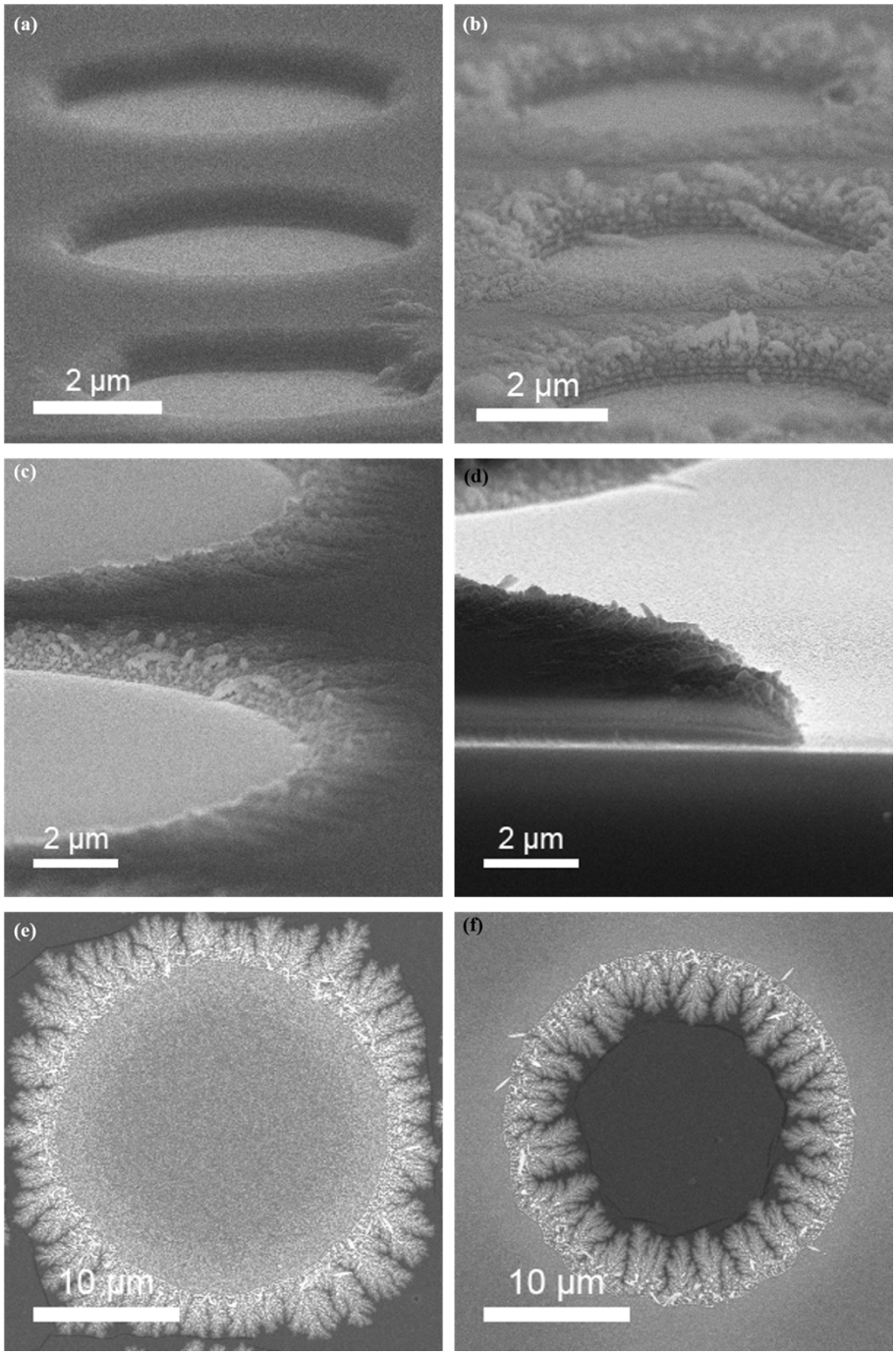

Fig. S5 SEM images of (a): the photoresist hole array on gold film (T = 10 μm, d = 6 μm; d is the hole diameter and T is period of the pattern). (b-d): side-view of Ag nanocomplex on the photoresist. The pattern of photoresist were: (b) hole array, T = 10 μm, d = 6 μm; (c) hole array, T = 30 μm, d = 26 μm; (d) dot array, T = 30 μm, d = 26 μm, respectively. (e, f): SEM images of the Ag nanocomplex in the (c, d) after the removal of photoresist.

Raman Enhancement factor of the silver nanocomplex

To evaluate the enhancement factor of the silver nanocomplex, 2 μL of 4-ATP aqueous solutions (1×10^{-5} M and 1×10^{-6} M) were dropped onto the spots with the Ag nanostructures, while 2 μL of 4-ATP aqueous solution (1×10^{-3} M) was dropped onto a bare gold-coated glass as a comparison. As shown in **Fig. 2**a, all the bands of 4-ATP exhibited an obvious enhancement on the Ag nanostructures compared with those on the bare flat Au layer on glass, indicating a significant Raman enhancement effect of the Ag nanocomplex array.

The enhancement factor (EF) is calculated with the following equation:

$$EF = (I_{SERS} / N_{SERS}) / (I_{Nor} / N_{Nor}) = (I_{SERS} / I_{Nor}) \cdot (N_{Nor} / N_{SERS})$$

where I_{SERS} and I_{Nor} are the signal intensities of SERS and normal Raman spectra of 4-ATP at the same band (~1076 cm^{-1} here), respectively, and N_{SERS} and N_{Nor} are the corresponding number of molecules in the focused incident laser spot. Assuming that the coverage area was the same of that of the liquid droplets in the enhanced and non-enhanced situations after dried in air, and the 4-ATP molecules were distributed evenly in the range of drop on substrates, so the value of N_{Nor}/N_{SERS} equaled to C_{Nor}/C_{SERS}. From the data in **Fig. 2**a, after background subtraction, $I_{Nor\ 10\text{-}3\ M} \approx 36.2$, $I_{SERS,\ 10\text{-}6\ M} \approx 4200$, $N_{Nor} / N_{SERS} = C_{Nor}/C_{SERS} = 1000$, the EF is thus calculated to be $\sim1.16\times10^{5}$.