ESI† Supporting Information

Nanoporous Silver Microstructure for a Single Particle Surface-Enhanced Raman Scattering Spectroscopy

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**Fig. S1** SEM images with low and high magnification including the pore size distribution of of nanoporous Ag microstructure (np-AgMs) by galvanic replacement using Zn plate and NaCl solution at various concentrations: (A1) 0 M, (A2) 0.01 M, (A3) 0.1 M, (A4) 0.5 M and (A5) 1 M.
**Fig. S2** (A) EDS spectra of hexapods AgCl microstructure (6pAgCl) and (B) EDS spectra of nanoporous Ag microstructure (np-AgMs) galvanized by using Zn plate and 1 M of NaCl solution
Fig. S3 Optical microscopic images of np-AgMs using low magnification (A) with pipette tip, (B) with solution, (C) using high magnification and (D) solution surround the isolated particles. No aggregation and agglomeration were observed upon adding the solution.
Fig S4. The possible patterns of the particles isolated from the hexapod np-AgMs found under the optical microscope.
Fig. S5  (Top) Designed particle including the determined plane waves used in FDTD calculations. (Bottom) Excited near-field images of an electromagnetic field on the Hexapods silver microstructure by FDTD calculations. The color scales cover the range: 4.57 (red) to 0.001 (blue) V/m.

Near field images of the electromagnetic field using a software PLANC-FDTD (Information and Mathematical Science Laboratory Inc., Ver. 6.2) were calculated. In FDTD calculation, the designed particle was generated with the dimension length and shape similar to the particles observed from SEM images. The mesh sizes were set to 50 nm inside and outside a silver microstructure. According to the particle size in micrometers, three plane waves were used in the calculations to observe the phenomenon of surrounding electric fields. The calculated electric fields generated surround the particle supports the conclusion that the SERS enhancement is high at the junction and the center of a square planar particle (brown arrow), while a lower SERS enhancement is observed on the tips. These calculations are in good agreement with the SERS signal observed in the experiment shown in Fig 3 of the manuscript.