Supporting information

1. Experimental details

a. Silica microspheres.

The silica microspheres were prepared using a StÖber method:10 ml TEOS was added to the mixture of 150 mL ethanol, 20 mL water and 20 mL 28% NH₃·H₂O. The silica spheres were collected by centrifugation after the solution was stirred for 5h.

b. SERS test.

The ethanol solution of echinus-like $SiO_2@Ag$ particles were dropped onto clean silicon substrates and dried in an oven. Equal amount of 10^{-7} M and 10^{-2} M Rhodamine 6G (R6G) ethanol solution was dropped onto echinus-like SiO₂@Ag particles and a bare silicon substrate (as the reference), respectively.

The SERS spectra were performed on a LabRam HR (Jobin Yvon) spectrometer equipped with the 514.5 nm laser. The laser power was about 5 mW and the collection time was 1s for each sample. The laser spot had a diameter of about 1 micrometer, and the spot areas were similar in all the Raman tests. The results are shown in figure s1.



Figure s1. Raman spectra of R6G on silicon substrates and echinus-like SiO₂@Ag particles.

As shown in figure s1, several peaks during 500-1670 cm⁻¹ were typical Raman peaks of R6G. Comparing with reference sample, the Raman intensity of R6G was so greatly enhanced that the Raman peaks of R6G with 10^{-7} M solution are still detectable. The Raman enhancement factor (EF) was defined as equation 1:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{RS} / N_{RS}}$$
(1)

Where I_{SERS} is the measured Raman scattering intensity under SERS condition and I_{RS} is that for non-SERS condition. N_{SERS} and N_{RS} are the number of dye molecules radiated by the excitation laser under these two conditions, especially. It is supposed that the dye molecular distributed uniformly on the whole substrates. Comparing the intensity of peak at 1652 cm⁻¹ of 10⁻⁷ M R6G with reference (10⁻² M), the average enhancement factor is about 5*10⁴ according to equation 1.

2. HR-TEM image

The HR-TEM image of the silver nuclei which is shown fig. s2-a. The crystal spacing is 0.236 nm, which corresponds to the (111) plane of FCC silver. The HR-TEM image a part of a silver rod in the urchin-like silver structures is shown in fig. s2-b. The crystal planes have a spacing of 0.250 nm, which can be designated as (0004) planes of HCP silver.



Figure s2. HR-TEM image of the silver nuclei on silica spheres (a) and (b) a part of a silver rod in the urchin-like silver structures.

3. EDS

The EDS spectrum of the echinus-like structures is shown in figure s3 below. Only signals of Si, O and Ag elements are observed. Si and O elements come from silica spheres. No impurities are detected.



Figure s3. EDS spectrum of the echinus-like structures.

4.XPS

The XPS spectra of the urchin-like structures is shown in figure s4. From fig. s4-a, only Ag, C, O and Si elements are observed. The peaks of C 1s at 284.5 eV shown in fig. s4-b and O1s at 532.9 eV in fig. s4-c and come from the PVP molecules absorbed on the particle surface. The spectrum for C 1s can be deconvoluted into three peaks at 284.8 eV, 286.5 eV and 288.6 eV, which can be assigned to the C=O, C-N and C-C bonds, respectively. A detailed spectrum of Ag element is shown in figure s4-d. The banding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ are 367.6 eV and 373.6 eV, respectively. The value is a little smaller than pure Ag⁰ (Ag $3d_{5/2}$: 368.2 eV, Ag $3d_{3/2}$: 374.2 eV) due to the interaction of Ag particles with the O atoms in carbonyl groups of PVP molecule, which will decrease the banding energy of Ag $3d_{3/2}$ electrons. (*Miguel Jose Yacaman, et al., Chem. Mater.* 2005, 17, 6042-6052). The peak of Si 2p at 103.8 eV comes from silica spheres. From the XPS analysis, there are no impurities in the samples.



Figure s4. XPS spectra of the echinus-like silver structures. (a) the whole spectrum. (b) C 1s

spectrum. (c) O 1s spectrum. (d) Ag 3d spectrum.

5. Optical property of the echinus-like SiO₂@Ag particles



Figure s2. The UV-vis extinction spectra of silver nuclei and echinus-like SiO₂@Ag obtained with different amount of seed solution.

The extinction peak of silver nuclei decorated silica sphere locates at 475 nm, which arise from the surface plasmon resonance of silver nuclei and the plasmon coupling among these nuclei. For the samples prepared when 400 and 800 μ L seed solution was added, the extinction at long-wavelength region increases due the formation of silver shells. The peak at 375 nm maybe comes from the high-order resonance of the core-shell. Based on our characterizations, there are no impurities. The 375nm peak may come from the high-order resonance of the core-shell. Based on our characterizations, there are size of the silver shell is rather large (*N. J. Halas, et al., Appl. Phys. Lett., 1999, 75, 2897*). And it can be seen that the intensity of this peak increases with the thickness of the silver shells. As the structure of the echinus-like particles is complicated, rigorous designation of the origin of the extinction peak is difficult now.