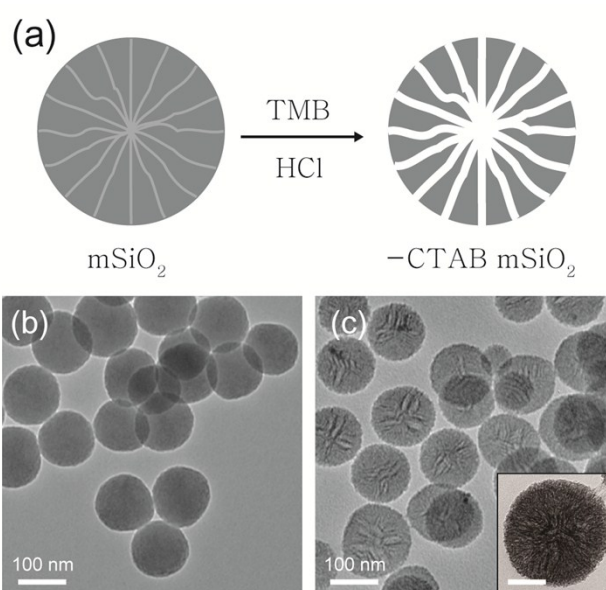# Supporting Information

Hollow and inward-bumpy gold nanoshells fabricated using expanded silica mesopores as templates

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Fig. S1 (a) Schematic illustration for the fabrication of pore-expanded mSiO$_2$ NPs. (b,c) TEM images of (b) mSiO$_2$ NPs and (c) pore-expanded mSiO$_2$ NPs. The scale bar in the inset of Fig. S1c indicates 50 nm.
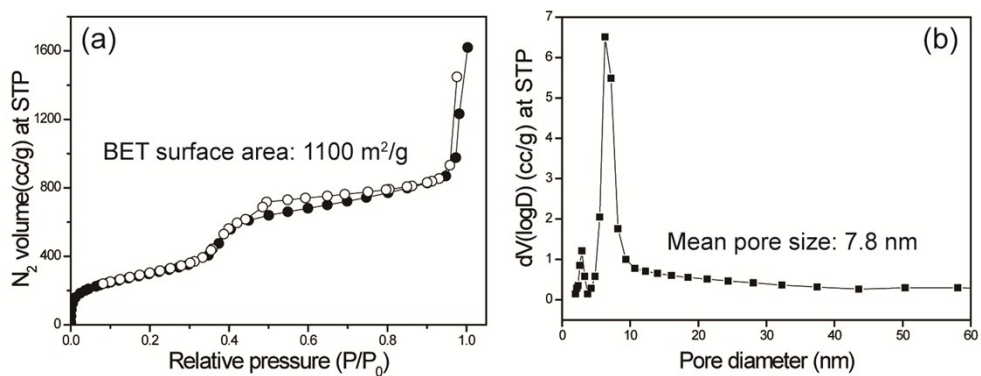
Fig. S2 (a) N_2 adsorption/desorption isotherms of pore-expanded $mSiO_2$ NPs, where closed and open circles correspond to adsorption and desorption points, respectively. (b) Pore-size distribution plot corresponding to the N_2 adsorption/desorption isotherm of pore-expanded $mSiO_2$ NPs.
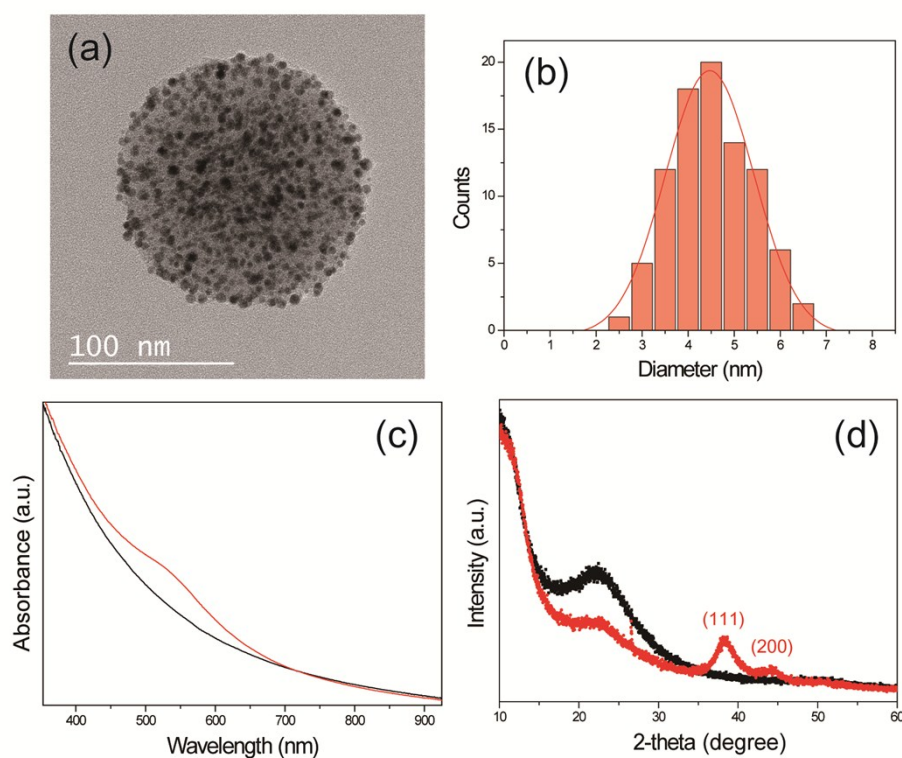

Fig. S3 (a) HRTEM image of Au-$mSiO_2$ NPs. (b) Size-histogram of Au seed in Au-mSiO2 NPs. (c) UV-vis absorption and (d) XRD data of (black) $mSiO_2$ NPs and (red) Au-$mSiO_2$ NPs.
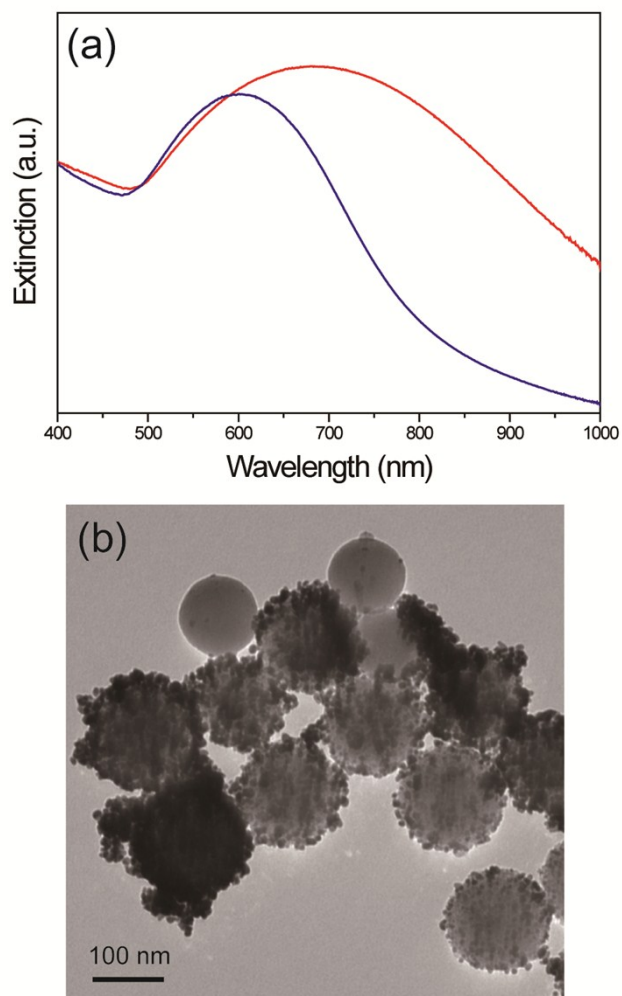
Fig. S4 (a) UV-vis extinction spectra of Au NPs synthesized by (blue) the conventional method and (red) our sequential reduction method. (b) TEM image of irregular Au NPs synthesized by the conventional method.
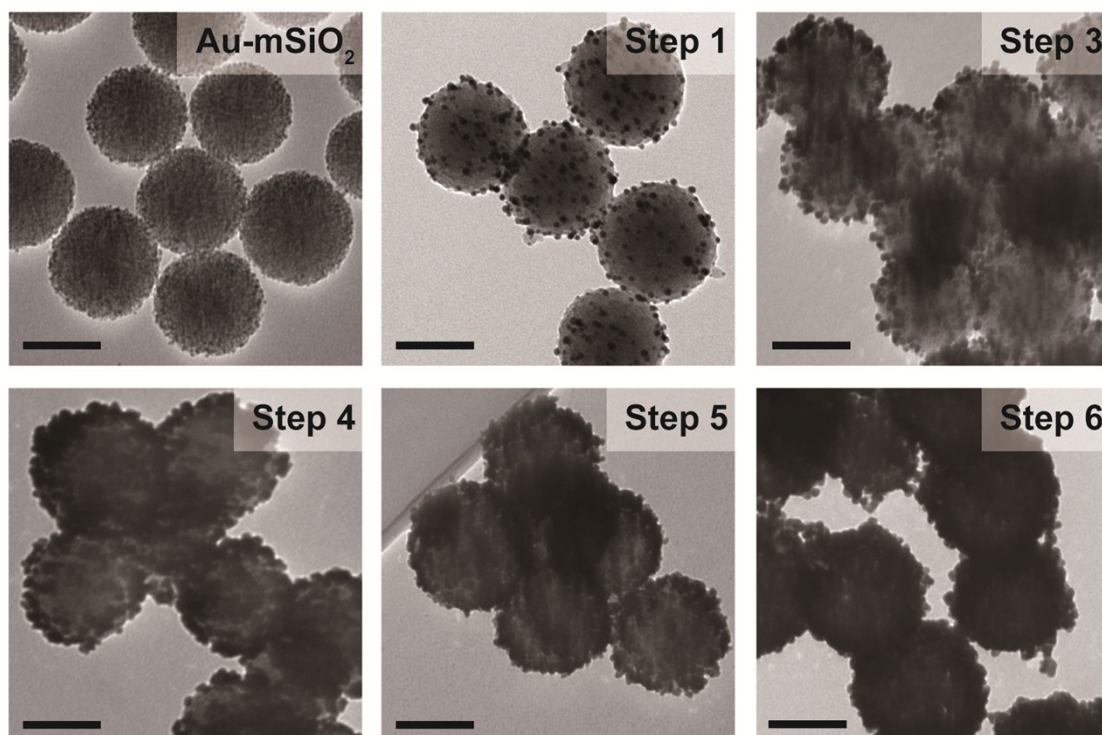
Fig. S5 TEM images of progressively growing Au NSs. Each scale bar indicates 100 nm.
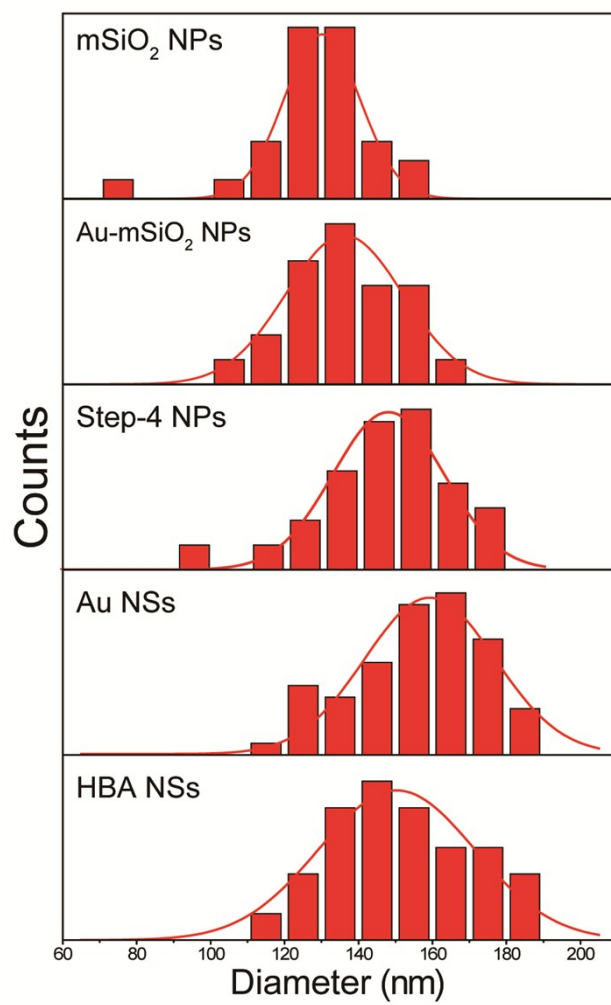
Fig. S6 Particle size-distribution histograms of respectively indicated samples.
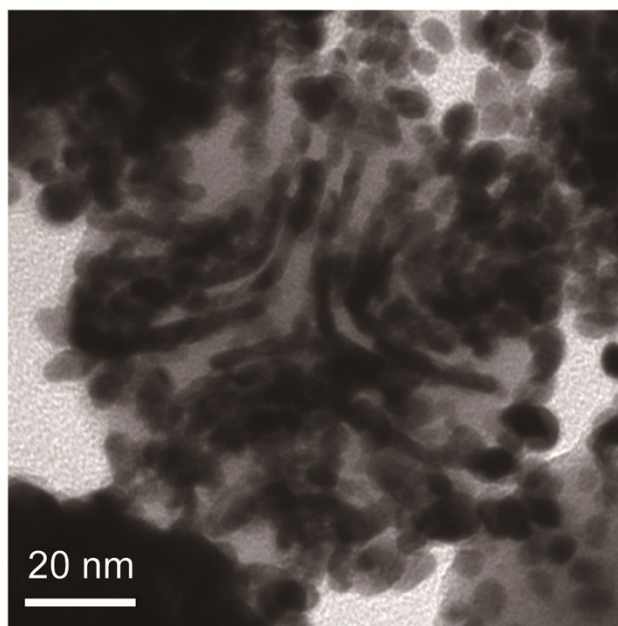
Fig. S7 TEM image of inward grown Au nanotips in mesoporous silica NPs.
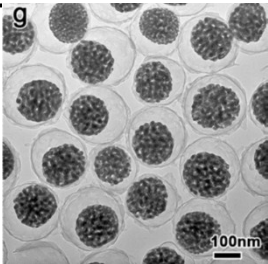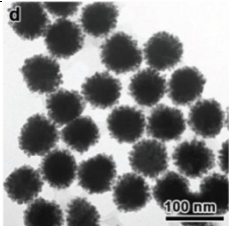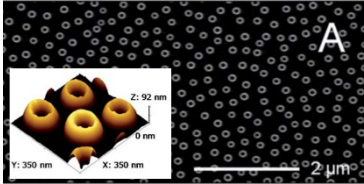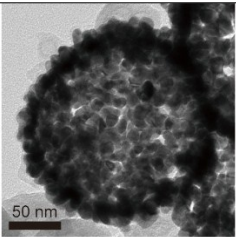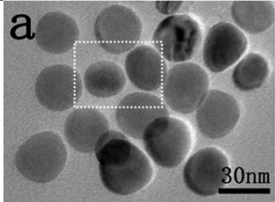
- Calculations of Raman enhancement factors.

The SERS enhancement factor (EF) has been calculated following the reported method:[30] $EF = (I_{SERS} \times N_{Raman}) / (I_{Raman} \times N_{SERS})$, where I_{SERS} and I_{Raman} are the SERS intensity and the normal Raman intensity, respectively. N_{SERS} and N_{Raman} are the numbers of probed molecules in the measurements of SERS and normal Raman, respectively. For SERS measurements, a V_{SERS} volume of a R6G ethanol solution with a concentration of C_{SERS} was dropped to an area of S_{SERS} on the substrate of HBA NSs supported on a Si wafer. For normal Raman measurements, a V_{Raman} volume of a R6G ethanol solution with a concentration of C_{Raman} was dropped to an area of S_{Raman} on a Si wafer. Ethanol on both wafers was dried in ambient conditions, and the spot sizes of the laser were the same throughout measurements. Thus,
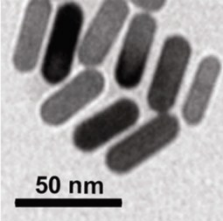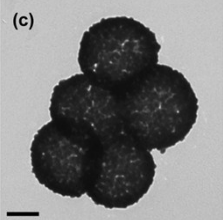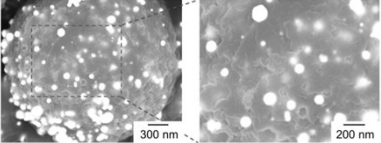
$$EF = \frac{I_{SERS}}{I_{Raman}} \cdot \frac{C_{Raman}V_{Raman}}{C_{SERS}V_{SERS}} \cdot \frac{S_{SERS}}{S_{Raman}}$$

In SERS measurements, 10 µL of a 10 µM R6G ethanol solution was spread over a circular area of 13 mm^2 on the substrate of HBA NSs. However, in normal Raman measurements, 10 µL of a 0.10 M R6G ethanol solution was spread over a circular area 13 mm^2 on a Si wafer. I_{SERS} / I_{Raman} was 1000 / 55 for the band at 1382 cm^{-1}. Therefore, EF was calculated as 1.8×10^5.

Table S1. SERS EFs of various plasmonic nanoparticles.

Entry	EF	Excitation wavelength, Raman probe	Reference
Porous Au-Ag nanospheres	1.3×10^7	633 nm, crystal violet	ref. 24
Island-on-Au NSs	5.0×10^6	633 nm, crystal violet	ref. 11
Au nanorings array	5.0×10^5	532 nm, 4-aminothiophenol	ref. 41
HBA NSs	1.8×10^5	532 nm, R6G	this work
Ag nanoplates	1.7×10^5	633 nm, R6G	ref 42

Au nanorods	1.7×10^5	785 nm, rose bengal	ref. 40
Hollow and porous Au NSs	1.0×10^5	532 nm, methylene blue	ref. 17
Au-mSiO$_2$ hybrid microspheres	3.2×10^3	633 nm, crystal violet	ref. 22
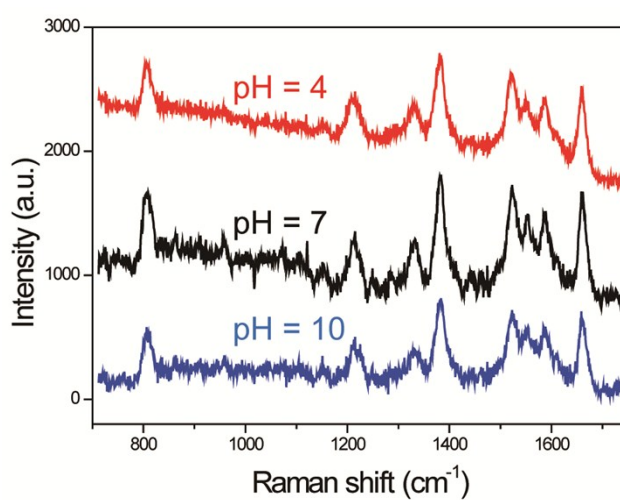
Fig. S8 SERS spectra of 10 μM R6G(ethanol) adosrbed on HBA NSs at different pH values.
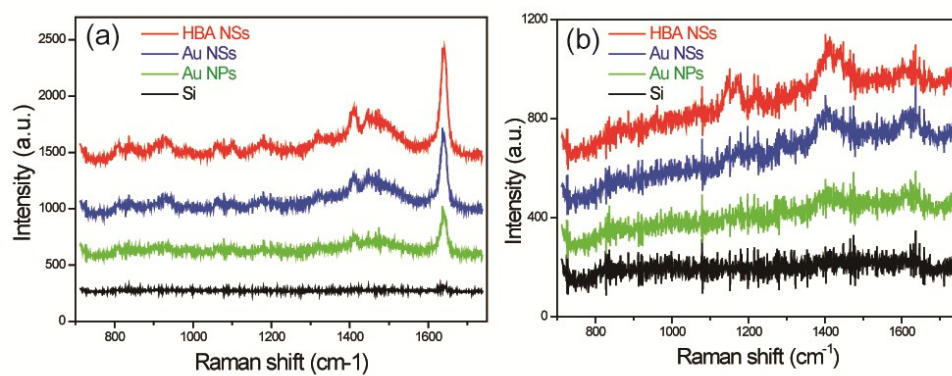
Fig. S9 SERS spectra of (a) 10 μM MB(ethanol) and (b) 10 μM MO(*aq*) adsorbed on HBA NSs, Au NSs, Au NPs, and Si. Note that 0.10 M MB(ethanol) and 0.10 M MO(*aq*) were used to record the Raman signals of the Si substrate.