Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Ordered mesoporous Ag superstructure synthesized via template strategy for Surface-Enhanced Raman scattering

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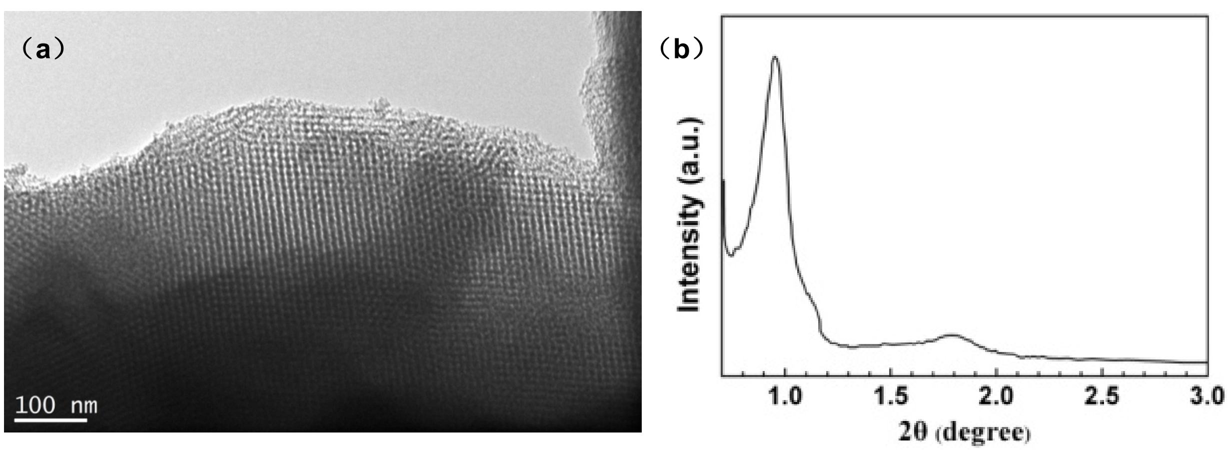


Fig.S1 TEM images of mesoporous silica KIT-6 as original hard template: a) along [531] direction and b) SAXS profile of the KIT-6 template.

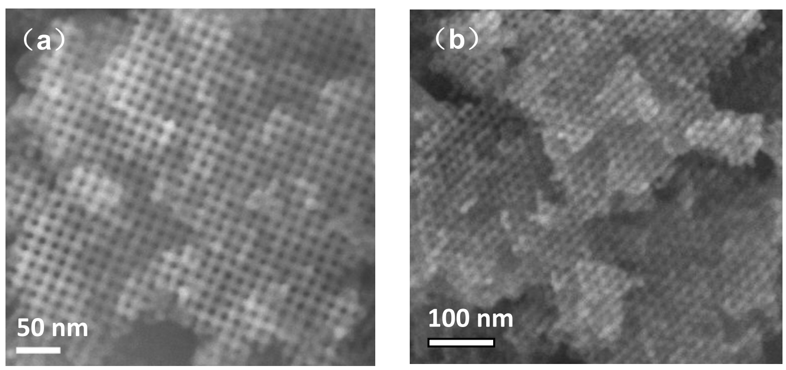


Fig.S2 (a-b) SEM images of mesoporous silver superstructure (OMAS-10) with various mesh structures.

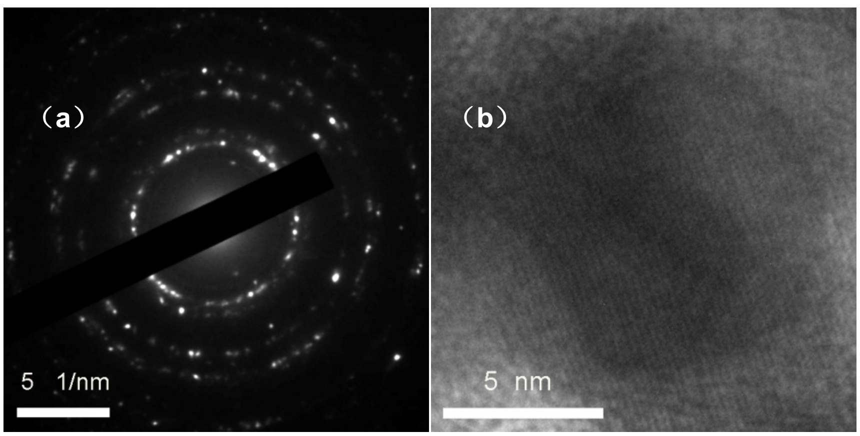


Fig.S3 (a) the SAED pattern and (b) the magnified section of the TEM image for the OMAS-10.

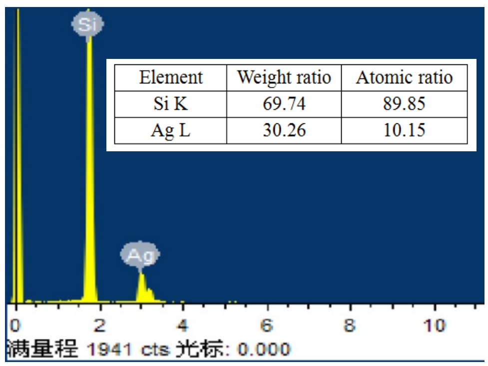


Fig.S4 The Energy Dispersive Spectrometer of mesoporous silver superstructure (OMAS-10).

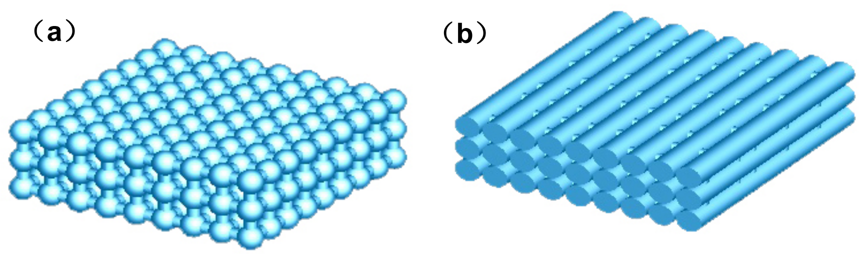


Fig.S5 The model of the ordered silver superstructure OMAS-10: D=10 nm, g=2 nm, w=5 nm: mesh topology; (b) nanowire topology.

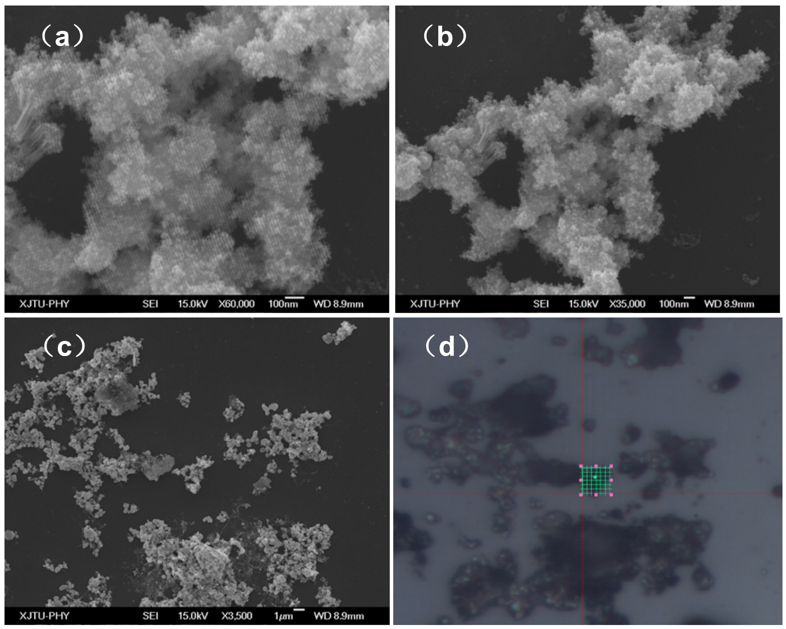
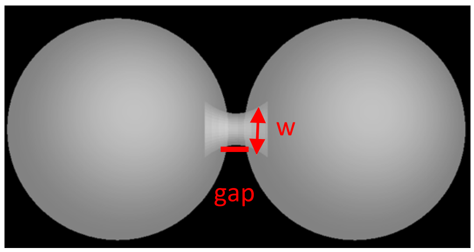


Fig.S6 (a)-(c) SEM images for large area mesoporous silver superstructure (OMAS-10) sample, (d) corresponding optical image.

Electromagnetic field calculation of OMAS
Details parameters of simulations
1. Geometry:

Mesh topology: the geometrical model is composed of individual silver sphere and the connecting rod between two silver spheres. The diameter of sphere (D) is 10 nm, the length of gap (g) is 2 nm, and the width of the connecting rod (w) is changing from 2 nm to 6 nm.



Nanowire topology: the model is made of naowire and the connecting rod between them. The parameters of connecting rod described as above.

In the simulation procedure, the center of each geometrical model is set to be the origin of a right-handed coordinate system and the mesh size is 1 nm.

2. Optical parameters:

The three-dimensional finite-difference time-domain (FDTD) simulation is used to calculate the near-field distributions at excitation wavelengths of 514 nm (in Figure 4b and Figure 4d), and 633 nm, 514nm and 785 nm for different OMAS-10 (in Figure 4a and Figure 4c). The continuous wave from 300 nm to 1800 nm was used to calculate the extinction spectra. The incident light is a plane wave propagating along the z-axis and polarized along y-axis. We assume that each geometrical model is suspended in air (n_0=1.0). The frequency (ω) dispersive and complex dielectric function for Ag, $\varepsilon_{Ag}(\omega)$, was taken the Drude-Lorentzian model.[1]

Estimation of SERS enhancement factor (EF):

The enhancement factors (EFs) of the OMAS-10 with mesh topology was estimated on the basis of

Ref [2-4]:

$$EF = \frac{I_{surface} / N_{surface}}{I_{solution} / N_{solution}} \tag{1}$$

Where $I_{surface}$ and $I_{solution}$ are the intensities of the probe molecular scattering bands in the SERS and normal Raman spectra, respectively, $N_{solution}$ and $N_{surface}$ are the probe molecular numbers in a reference solution and on the OMAS-10 substrate, respectively. According to the described in Ref [4]:

$I_{solution}$ ~1.576 and $N_{solution}$ ~ 2.5×10^7

Here, the SERS signal intensities, $I_{surface}$, were about 3200 counts for large area of OMAS-10. Considering the difference of acquisition time for CV solution (20 s) and OMAS-10 substrate (2 s), $I_{surface}$ was multiplied by 10. Then the $N_{surface}$ is estimated as:

$$N_{surface} = \frac{N_{CV-total}}{S_{total}} \times S_{eff}$$

in which, $N_{CV\text{-}total}$ is the total number of CV molecules absorbed on the OMAS-10 substrate, S_{total} is the total surface area, including bare silicon area (70%) and the surface area of OMAS-10 with less five layers. Assuming ~ 10% of the CV molecules were retained after rinsing the substrate (the same estimation as Ref.2),

$N_{CV\text{-}total} = 20\times10^{-6}\ \mathrm{L}\times10^{-7}\ \mathrm{mol/L}\times6.02\times10^{23}\times10\% = 1.2\times10^{11}$

The total surface area of the substrate can be estimated as:

$S_{total} = 70\%S_{si} + 0.5\times N_{sp}\times S_{sp} + 0.5\times N_{rod}\times S_{rod}$

The number of the Ag spheres on the substrate (N_{sp}) can be estimated as:

$$N_{sp} = \frac{30\% \times S_{Si}}{\pi(R+a)^2} \times 5 = 4.75\times10^{11}$$

where R is the average radius of the Ag sphere. a is equal to half the length of the connecting rod (g=2nm).

the number of the connecting rods between two silver spheres:

N_{rod} ~$2N_{sp}$=9.5×10^{11}

The average area of individual Ag sphere:

$S_{sp}=4\pi R^2=314$ nm^2

The area of connecting rod:

$S_{rod}=2\pi rg=62.8$ nm^2

Thus, we obtained $S_{total}=1.29\times10^{14}$nm^2

The effective of area of the OMAS-28 was estimated as follows:

$S_{eff}=0.5\times N_{0\text{-}sp}\times S_{sp}+0.5\times N_{0\text{-}rod}\times S_{rod}$

In which, $N_{0\text{-}sp}$ and $N_{0\text{-}rod}$ is the number of Ag spheres and connecting rod under one laser spot, respectively.

The area of the laser spot:

$$S_0=\pi\left(\frac{D}{2}\right)^2=\pi\left(\frac{1.22\lambda}{2\times N.A.}\right)^2=5.78\times10^5\,nm^2$$

So the number of the Ag spheres covered by the laser spot:

$$N_{0-SP}=\frac{\mathrm{S}_0}{\pi(\mathrm{R}+\mathrm{a})^2}=5112$$

The number of the connecting rod:

$N_{0\text{-}rod}$ ~$2N_{0\text{-}sp}=10224$

Therefore, the effective of area of the OMAS-28:

$S_{eff}=0.5\times N_{0\text{-}sp}\times S_{sp}+0.5\times N_{0\text{-}rod}\times S_{rod}=1.12\times10^6$nm^2

Thus, $N_{surface} = \frac{N_{CV-total}}{S_{total}} \times S_{eff}$ =1.04×10^3

Therefore, according to the equation (1), the enhancement factor of OMAS-10 with mesh topology is calculated to be about 4.85×10^8. By means of the same proceduce, we obtained the EF for OMASC-10 with nanowire topology is 1.03×10^9.

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2. Wang, Y.; Becker, M.; Wang, L.; Liu, J. Q.; Scholz, R.; Peng, J.; Gösele, U.; Christainsen, S. H.; Kim, D. H.; Steinhart, M. *Nano Lett.* **2009**, 9, 2384 - 2389.

3. Cai, W. B.; Ren, B.; Li, X. Q.; She, C. X.; Liu, F. M.; Cai, X. W.; Tian, Z. Q. *Surf. Sci.* **1998**, *406*, 9-22.

4.Tian, C. F.; Deng, Y. H.; Zhao, D. Y.; Fang, J. X. *Adv. Optical Mater.* **2015,** *3*, 404-411.