

Supporting Information

LSPR-dependent SERS performance of silver nanoplates with highly stability and broad tunable LSPR prepared through a improved seeds-mediated strategy

*Taixing Tan, Chungui Tian, * Zhiyu Ren, Jun Yang, Yajie Chen, Li Sun, Zhongtao Li, Aiping Wu,*

*Jie Yin, Honggang Fu**

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the

People's Republic of China; School of Chemistry and Materials Science, Heilongjiang

University, No.74 Xuefu Road, Nangang District, Harbin 150080, People's Republic of China.

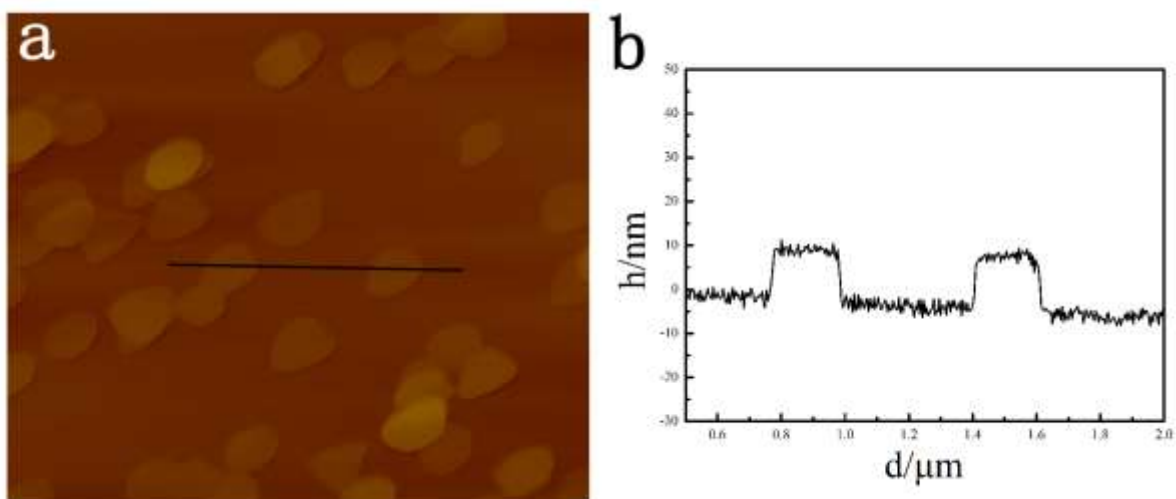


Figure S1. a) is the AFM image of silver nanoplates corresponding to the sample Ag-210.

The thickness profile of the silver nanoplates indicating the thickness is ~ 12 nm.

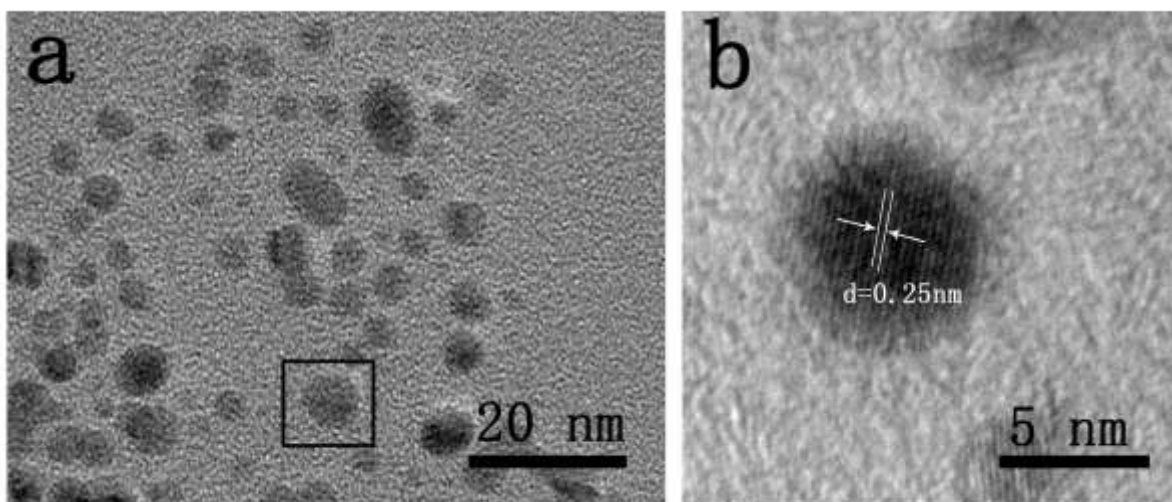


Figure S2. TEM images of silver seeds. a) is the image of silver nanoparticles with a size of 5 ± 2 nm. b) is the high resolution TEM image of silver seeds with a 0.25 nm lattice fringes corresponding to the forbidden $1/3$ (422) reflection.

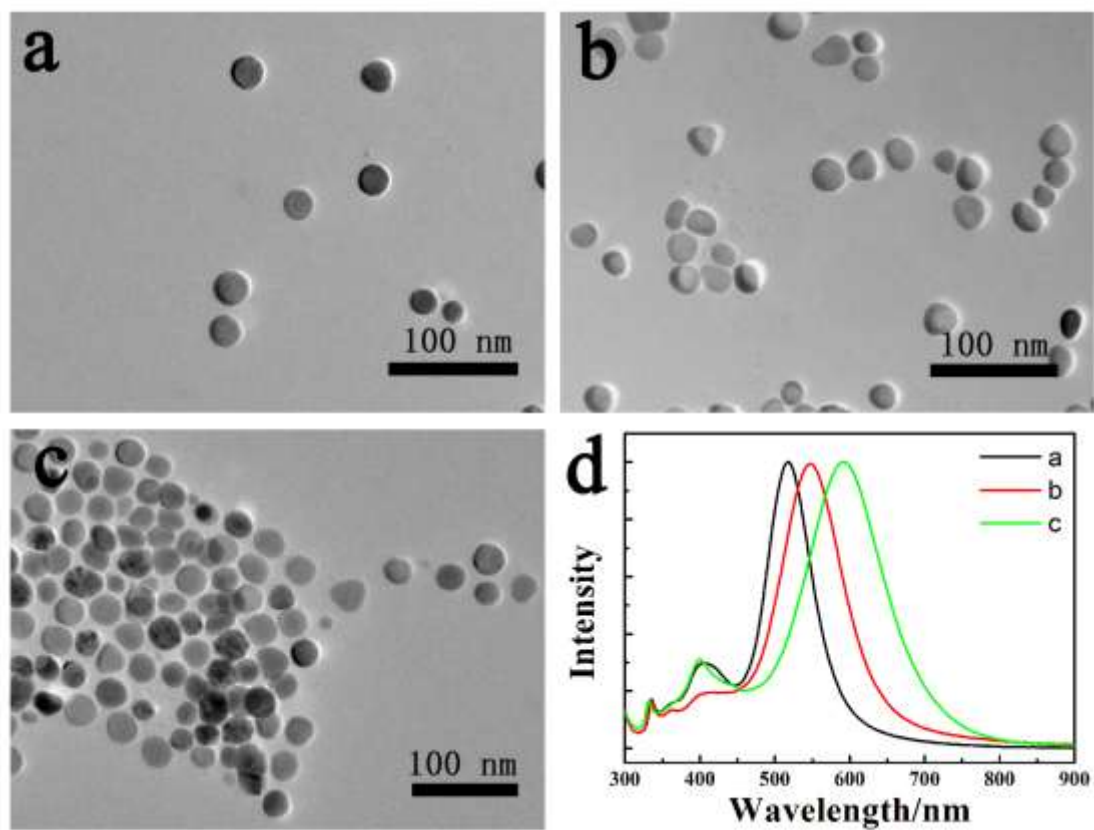


Figure S3. TEM images of silver nanoplates prepared under the conditions with different concentration of citrate when seeds grow and the corresponding extinction spectra. a) no citrate was added to the growth solution. b) Concentration of citrate is 0.1 mM. c) Citrate concentration is 5 mM.

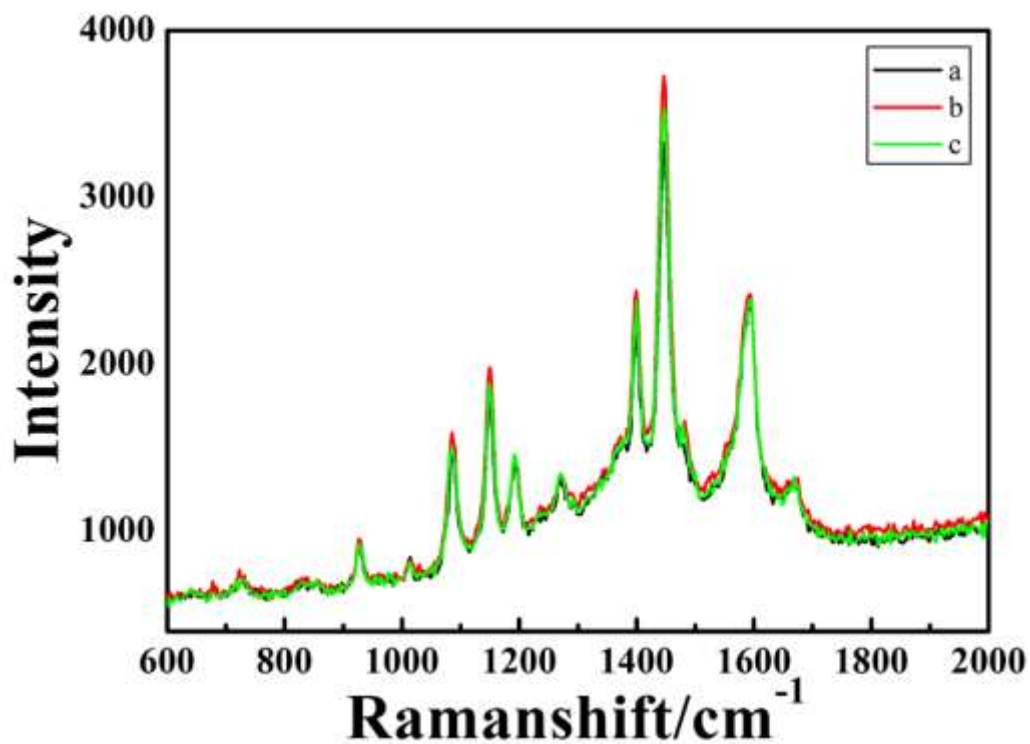


Figure S4. SERS signals collected based on the solution measurement with high reproducibility. Ag nanoplate's dispersion absorbed with 4-ATP as enhancement substrate.

SERS spectra (a, b, c) collected at three different positions of the same sample.

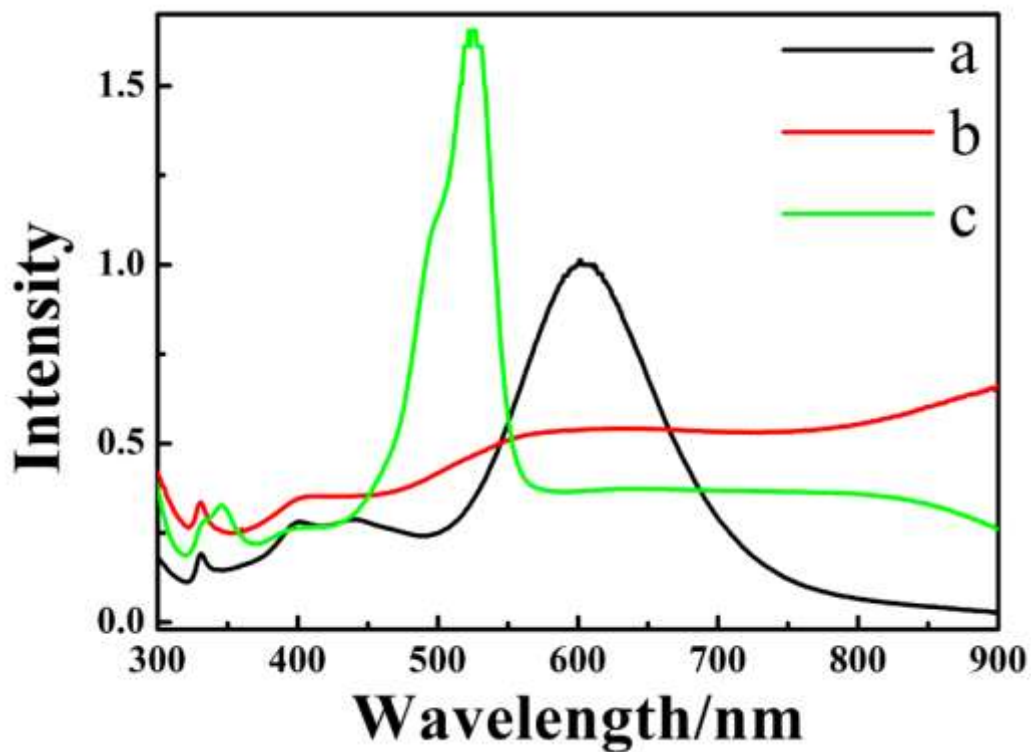


Figure S5. Extinction spectra of silver nanoplates and after the absorption of probe molecules when SDS is not used to protect the dispersion. The extinction spectra of silver nanoplates of Ag-614 (a). The extinction spectra of Ag-614 after the absorption of 4-ATP (b). The extinction spectra of Ag-614 after the absorption of R-6G (c).

The calculation of enhancement factors

In order to evaluate the enhancement factors, we need to figure out how much probe molecules were absorbed on the silver nanoplates. The total amount of probe molecules that were added to the silver nanoplates dispersion was known. And after the absorption of probe molecules on the silver nanoplates, the remaining probe molecules were still in the solution. Centrifugation was used to eliminate the silver nanoplates in the solution, at the same time the probe molecules absorbed on the silver nanoplates was removed, only left the unabsorbed molecules in the solution. As the concentration of probe molecules (both 4-ATP and R-6G) have linear relationship with the absorbency at the character absorption peak. As to the respect, the extinction spectra were used to detect the concentration of the residual probe molecules. In this way, the amount of probe molecules that absorbed on the silver nanoplates can be obtained by subtract the residual probe molecules from the original ones.

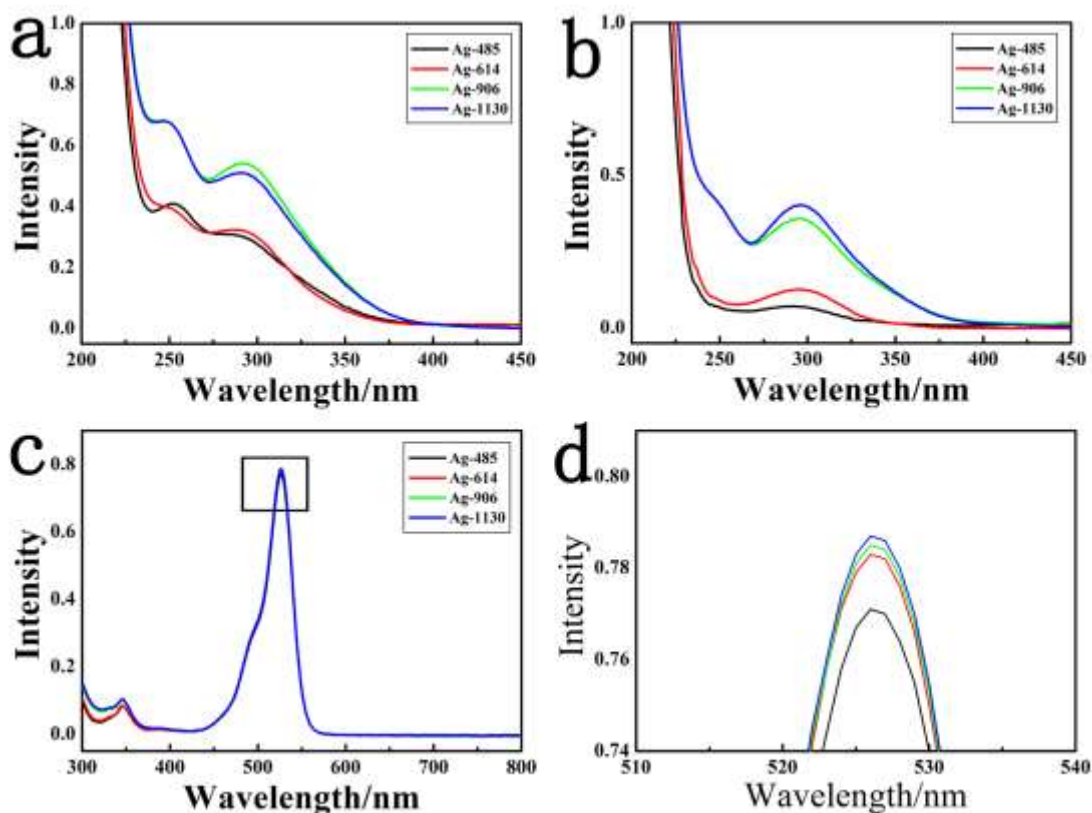


Figure S6. the extinction spectra of probe molecule (4-ATP and R-6G) that were remaining in the solution after eliminating the ones that absorbed on the silver nanoplates for all the four samples. The absorption peak (a) of 4-ATP is located at 250 nm. As the background (b) of the solution at the 250 nm has some extent absorption, the actual remaining probe molecules is obtained by subtract the background. As to R-6G, the concentration remaining in the solution was still very high. The diluted solution by 5 times was used to detect the extinction spectra in (c). The magnified spectra were given in (d).

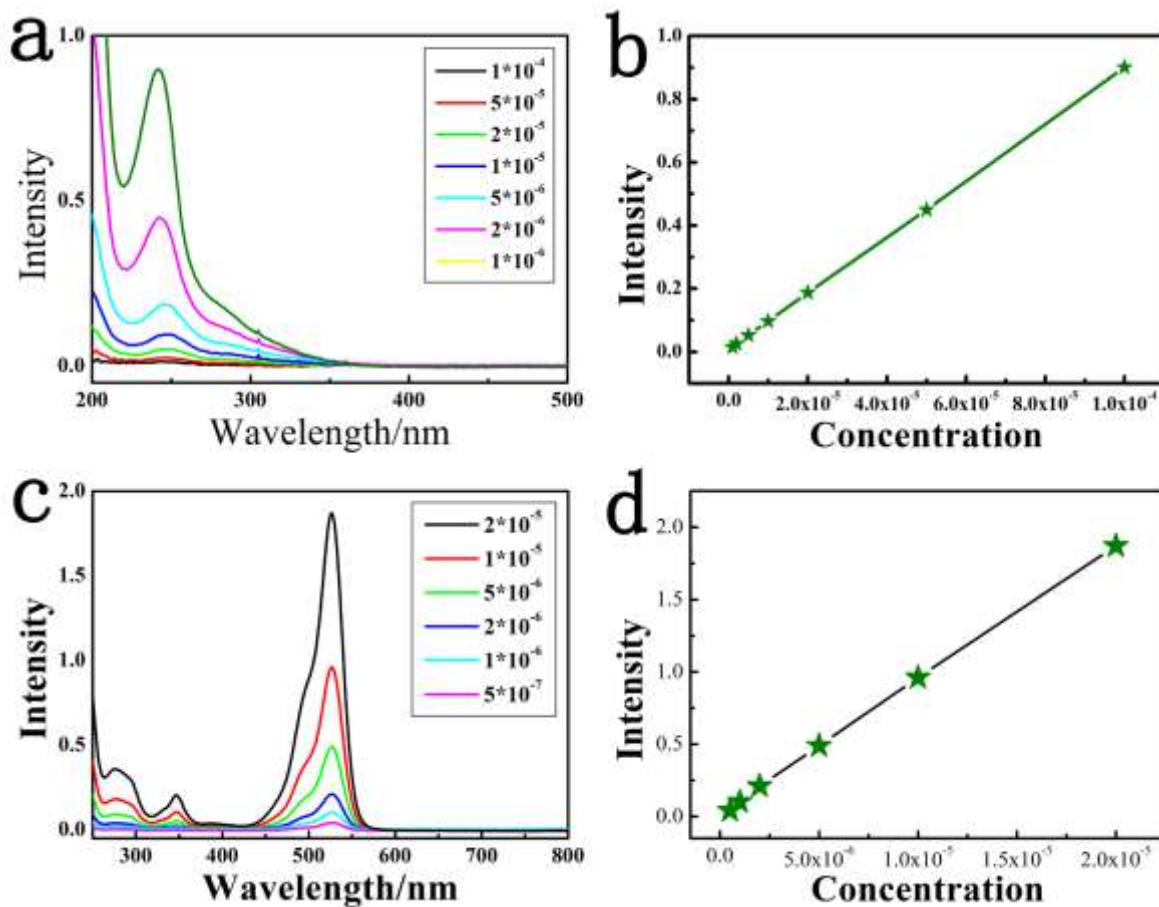


Figure S7. The linear relationship between the UV-Vis absorption spectra and the concentration of the probe molecules of 4-ATP (a, b) and R-6G (c, d)

The comparison of SERS performance between Ag-485 and silver nanosphere:

To investigate the effect of shape that would have on SERS activity, experiments were carried out by comparing SERS properties on silver nanoplate (Ag-485) and silver nanosphere (Ag-NS). The size of Ag-NS is about 40nm according to the TEM images (Figure S8 in revised ESI). Ag-NS with a LSPR at 438nm was synthesized by a classical method in which citrate serve as reduction under reflux.^[1] In Figure S9 (Figure S9 in revised ESI), the SERS spectra are presented based on those two shapes. When at the laser excitation of 458nm, the SERS intensity base on Ag-485 is stronger than that on Ag-NS. However, at excitation line of 633nm, the SERS intensity base on Ag-485 is much weaker than that on Ag-NS. The comparison between Ag-NS and Ag-485 shows that the variation of SERS intensity on Ag-485 is larger than that on Ag-NS. Based on silver nanosphere (Figure S8 in revised ESI), the Enhanced Factors (EF) of R-6G is $1.60\text{E}+04$ at 458nm laser excitation, which is 2.4 times larger than that ($6.60\text{E}+03$) at 633nm laser excitation line. As a comparison on silver nanoplate (Ag-485), the Enhanced Factors (EF) of R-6G is $2.10\text{E}+04$ at 458nm laser excitation line, which is 11.6 times larger than that ($1.80\text{E}+03$) at 633nm laser excitation line. The variation of EF on silver nanosphere is much less than that on silver nanoplate, indicating the study on nanoplates can get a stronger dependence on SPR. The different variations of SERS performance are attributed to the difference of LSPR bands of the two samples. The LSPR band of NS is much broad than that of Ag-485. The width at half-peak of the LSPR band is only 90nm for Ag-485nm, comparing with 155nm for Ag-NS. More important, the LSPR band of Ag-NS significantly extends to the long wavelength region. As a consequence, the LSPR band of both Ag-485 and Ag-NS can overlap the 458nm laser excitation line, but only the LSPR band of Ag-NS can couple with 633nm laser excitation line to some extent. In the SERS measurement, the LSPR can be excited at 458 nm laser excitation for both Ag-NS and Ag-485, but only for Ag-NS at 633

laser excitation. Therefore, broadening of SPR band would weaken the evaluation of the dependence of SERS on SPR. Moreover, the narrow SPR band of Ag-485 indicate it is the perfect material for the LSPR-dependent SERS study.

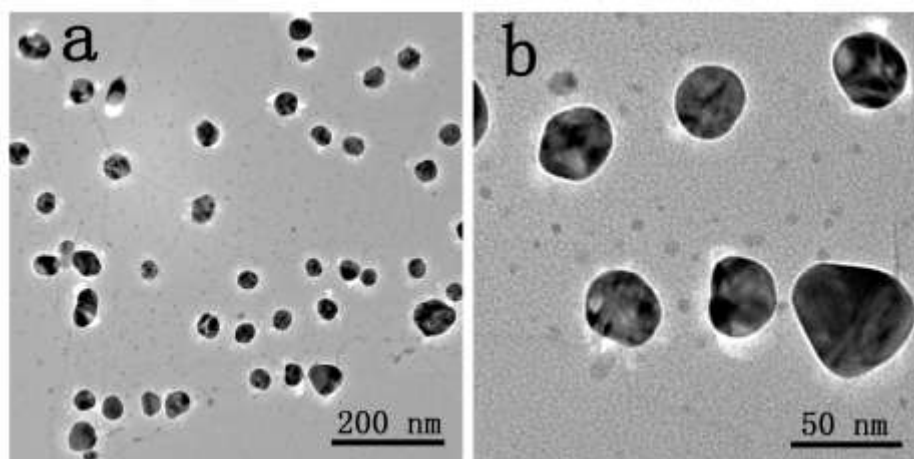


Figure S8: The TEM images of silver nanosphere. b) is a magnified area of a).

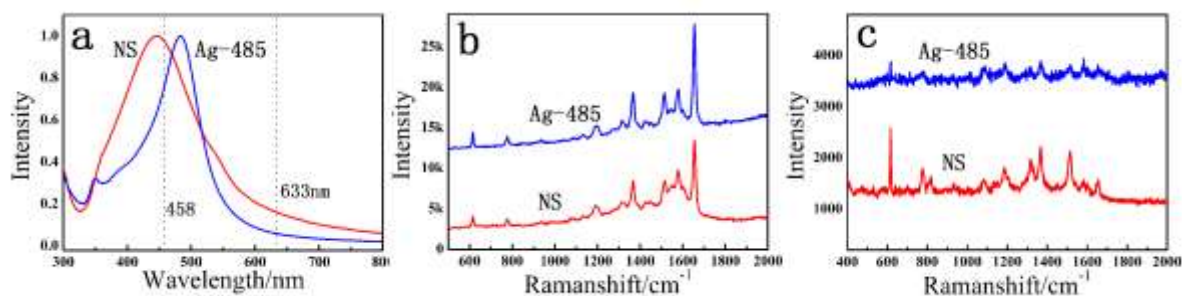


Figure S9: The extinction spectra (a) of and the SERS spectra of R-6G (b—at 458nm excitation; c—at 633nm excitation) on silver nanoplates (Ag-485) and silver nanosphere (Ag-NS). The blue line and red line represents those properties on the 485 and the NS, respectively.

References

- [1] P. C. Lee and D. Meisel, J. Phys. Chem., 1982, 86, 3391.