

Electronic Supplementary Information

**Synthesis of micro-sized shell-isolated 3D plasmonic
superstructures for *in situ* single-particle SERS
monitoring**

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Experimental section

Chemicals and Materials: Tetrachloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), silver nitrate (AgNO_3), ammonium hydroxide and 4-nitrothiophenol (4-NTP) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride (NaBH_4) and succinic acid were purchased from Aladdin Reagent (Shanghai, China). Ascorbic acid was purchased from SangonBiotech (Shanghai, China). (3-aminopropyl)trimethoxysilane (APTMS), 3-mercaptopropyltrimethoxysilane (MPTMS) and sodium silicate solution were obtained from Sigma-Aldrich. All chemicals were of analytical grade or better and used as received. All solutions were prepared with ultrapure Milli-Q water (18.2 $\text{M}\Omega \text{ cm}$).

Synthesis of Ag@SiO₂ microspheres: Hierarchical Ag microspheres were firstly prepared by a modified acid-directed self-assembly synthesis.¹ In this synthesis, succinic acid was not only employed as the reducing agent, but also used to induce the assembly of Ag nanoparticles into well-defined structures. 5 mL AgNO_3 (1 M) aqueous solution and 0.8 mL succinic acid (0.25 M) were added to 65 mL deionized water in an ice-water bath under magnetic stirring. 5 mL aqueous solution of ascorbic acid (1 M) was then quickly injected into the mixture, leading to an immediate change of the solution color from colorless to dark gray. The reaction mixture was stirred vigorously for 20 min to ensure complete reduction. The resultant Ag microspheres were washed twice with water to remove excess reagents, and the pellet was resuspended in a flask containing 30 mL deionized water. These microparticles were

then encapsulated with a thin silica shell following the method developed by Tian and co-workers.² In a typical procedure, 20 mL APTMS (1mM) was added into the flask and stirred at room temperature for 20 min. Afterward, 160 mL sodium silicate solution (diluted to 0.54% (wt/wt) with deionized water and adjusted to pH ~10.2 with hydrochloric acid) was added and the mixture was stirred for 3 min. The reaction mixture was then placed in a 90 °C oil bath and stirred for another 30 min, followed by quickly transferring into an ice bath to stop the reaction. After collected by centrifugation and washed with water for three times, the Ag@SiO₂ microspheres were resuspended in 80 mL deionized water and used as the stock solution.

Synthesis of Ag/Au core/satellite Superstructures: Au nanoparticles (Au NPs) were synthesized according to the Frens' method, that is, reduction of HAuCl₄ by sodium citrate.³ The Ag/Au 3D superstructures were fabricated through the strong and stable thiol-Au interaction. 50 μL MPTMS ethanol solution (10%) and 250 μL of an aqueous ammonium hydroxide solution (25%) were added into 4 mL Ag@SiO₂ suspension followed by incubation at room temperature for 40 min. The resultant products were purified by centrifugation, and then resuspended in 3 mL ethanol. Finally, 7 mL 20-nm Au NP colloid was added to the Ag@SiO₂ suspension and reacted overnight under magnetic stirring. The suspension was washed 3 times with water to remove the free Au NPs and then redispersed in 1 mL water.

To perform the *in situ* SERS study, 200 μL of 4-NTP (1 mM) ethanol solution was added to 1 mL suspension of the Ag/Au 3D superstructures and incubated overnight to form a 4-NTP molecular SAM on the small satellite Au NPs surface. Then the

Ag/Au 3D superstructures were successively collected by centrifugation, washed three times with ethanol and resuspended in 1 mL water.

Characterization: UV-vis spectra were recorded using an Agilent HP8453 spectrophotometer. Transmission electron microscopy (TEM) images and energy dispersive spectroscopy (EDS) spectrum were measured with a JEOL JEM-2011 electron microscope at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were measured using Nova NanoSEM NPE207 operating at the voltage of 3 kV. For TEM and SEM imaging, the samples were deposited onto Cu grids followed by drying in air. SERS spectra were recorded with a Horiba XploRA confocal Raman microspectrometer with a 638 nm excitation laser. Samples were excited with the laser power of 0.24 mW and the acquisition time of 10 s.

References

1. L. L. Kang, P. Xu, B. Zhang, H. H. Tsai, X. J. Han and H. L. Wang, *Chem. Commun.*, 2013, **49**, 3389.
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3. G., Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.

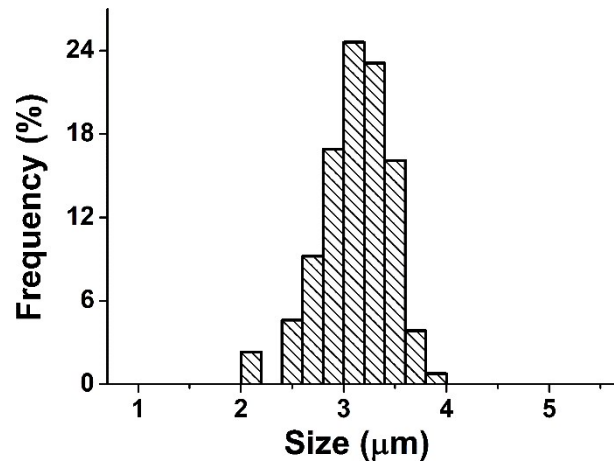


Fig. S1 Size-histogram of Ag microspheres based on TEM measurement. 100 randomly chosen particles were analyzed. The diameter of each particle was estimated by determining the longest distance between two points at the edge. The resulting average size is about 3.1 μm , the standard deviation is 0.3 μm .

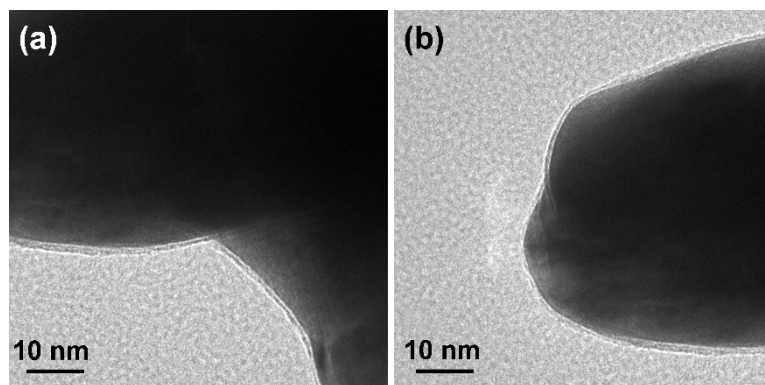


Fig. S2 (a and b) TEM images showing ultrathin silica shells covering the surface of Ag cores.

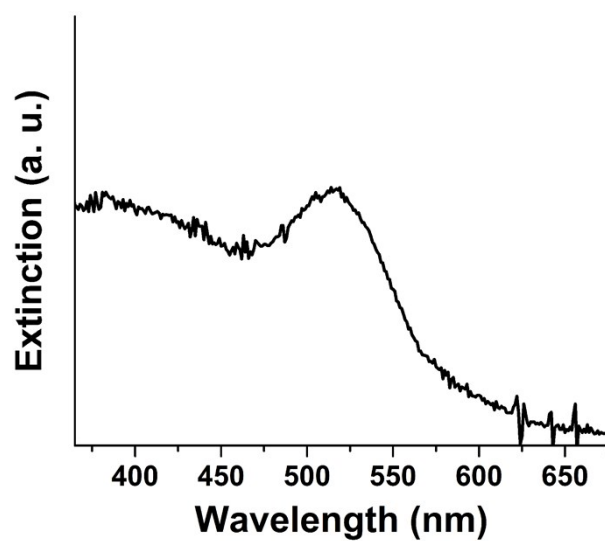


Fig. S3 UV/vis extinction spectrum of the Ag/Au core/satellite superstructures. The characteristic SPR peak of gold nanoparticles is clearly seen at about 520 nm. The peak feature of the silver core is different from the nano-sized silver particles with a wide peak centered at about 430 nm. The broad half-peak width is mainly because the average size of Ag@SiO₂@Au core/satellite particles is much larger than the nanoscale.

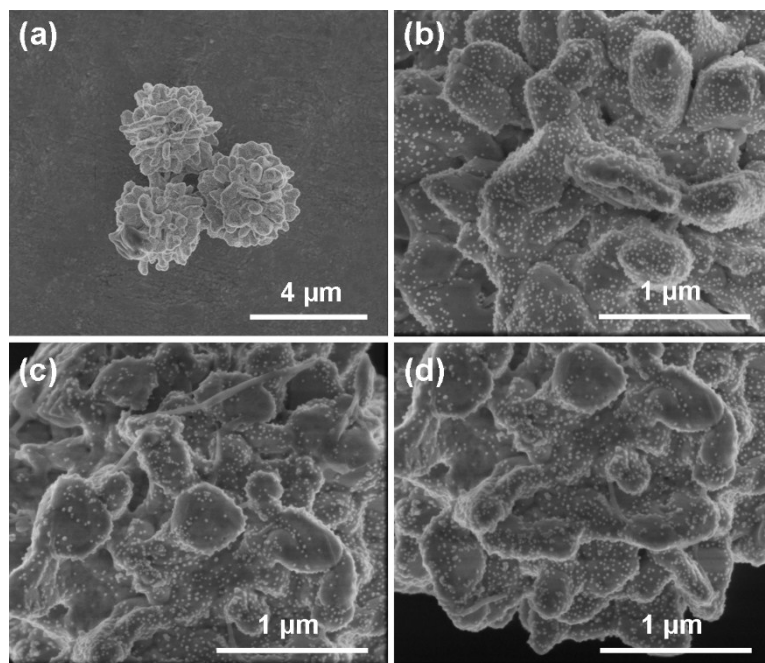


Fig. S4 (a) SEM image of three Ag/Au core/satellite superstructures. (b-d) Magnified SEM images of local areas of different Ag/Au superstructures.

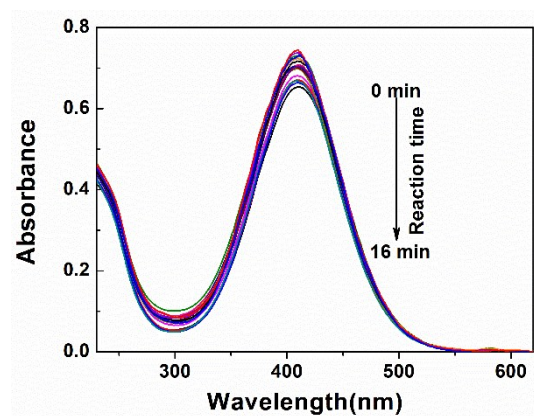


Fig. S5 Absorption spectra of 4-NTP aqueous solution in the presence of NaBH₄ as a function of reaction time.

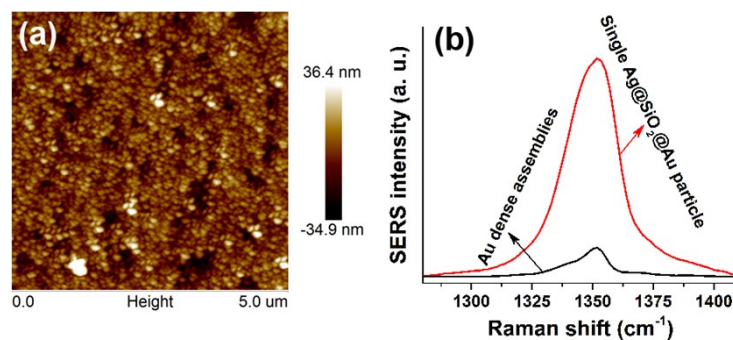


Fig. S6 (a) Atom force microscope image of the closely-packed assembly of gold nanoparticles on a thiol-functionalized glass slide. (b) SERS spectra of 4-NTP measured from the surfaces of gold assembly and a single Ag/Au 3D superstructure. After forming a molecular monolayer of 4-NTP, SERS spectra from multiple points of the gold assembly were measured. It is found that the average spectral intensity was ten times less than that recorded from the Ag/Au core/satellite superstructures. It should be mentioned that the gold self-assembly stated above presents a quasi-two-dimensional distribution which means more 4-NTP molecules would be located at the focal plane of the radiation laser, thus acquiring more efficient SERS excitation compared to the three dimensional structure of Ag/Au core/satellite superstructures.. That is to say, the signal enhancement contributed from the small gold catalysts should be subtle in the case of single-particle SERS. Therefore, we can conclude that it is the flower-like silver core that plays a decisive role for the Raman amplification in the study.

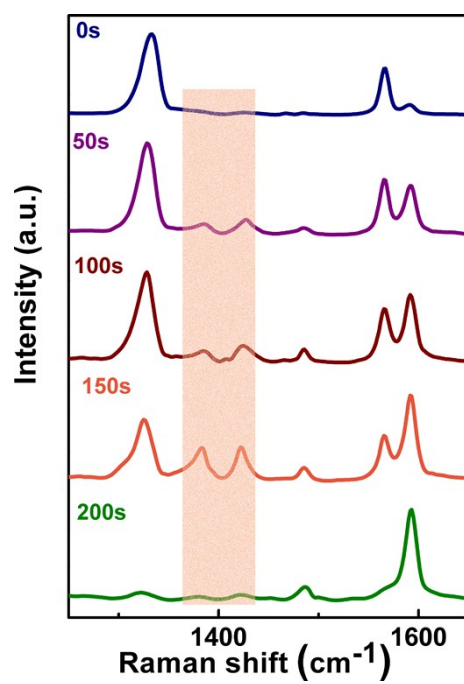


Fig. S7 Time-dependent SERS spectra acquired from the surface of Ag/Au core/satellite superstructures without the thin silica shell. The bands ascribed to 4,4'-DMAB could be clearly observed as labeled by the orange-colored bar.