Supplementary Information

Size Tunable Au@Ag Core-Shell Nanoparticles: Synthesis and SERS Properties

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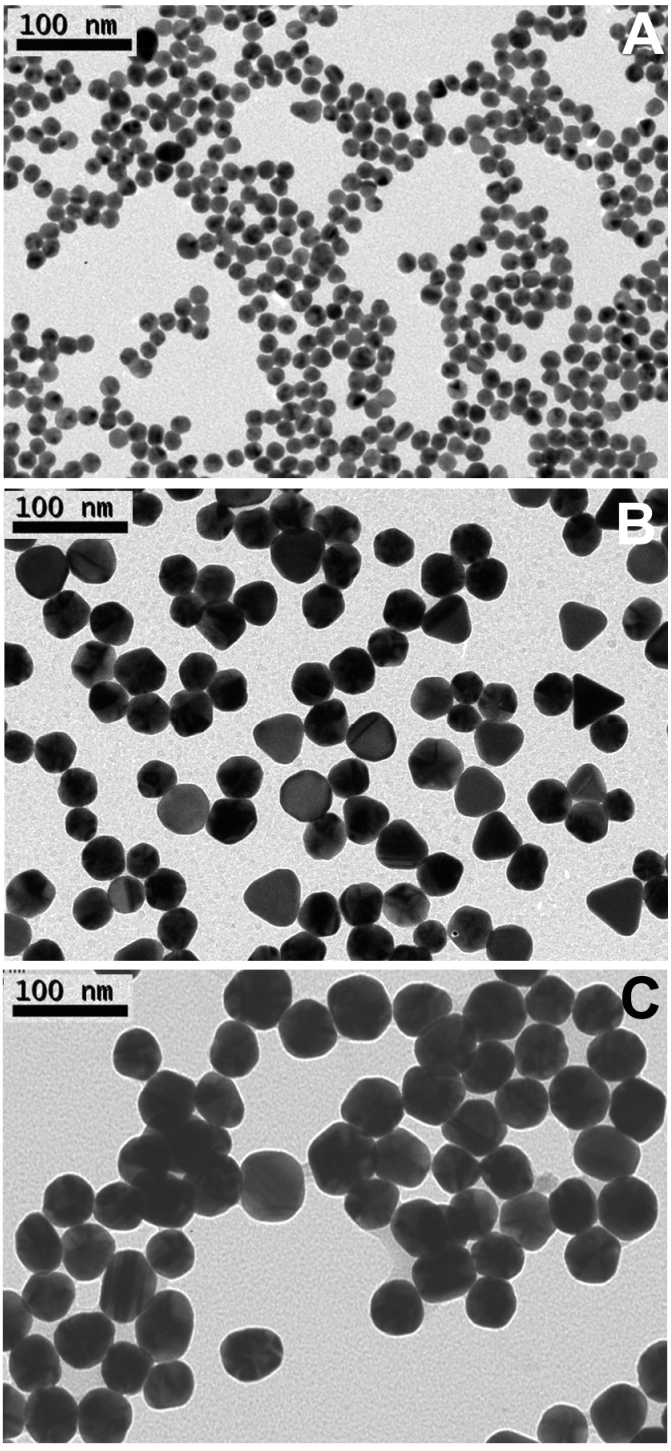


Figure S1. TEM images of citrate-stabilized Au NPs used as seeds. The particles sizes are: 15.4 ± 1.3, 32.4 ± 3.4 and 54.5 ± 4.9 nm.

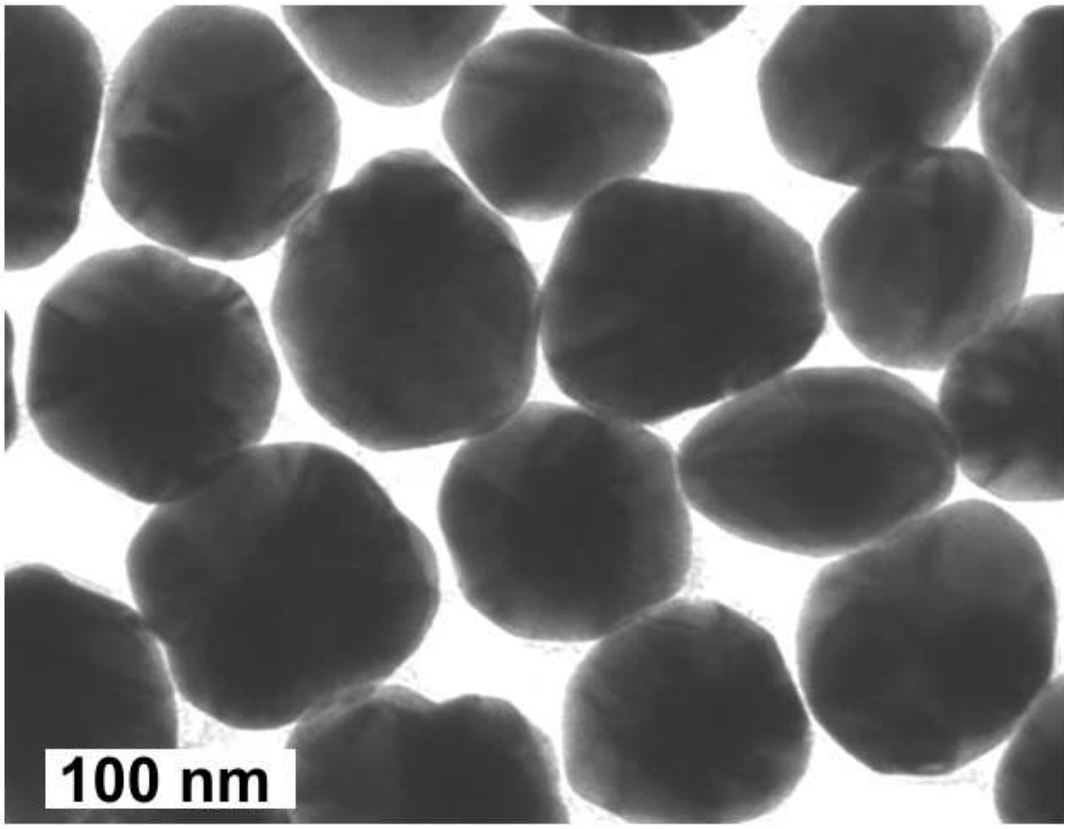


Figure S2. TEM images of Au@Ag core-shell nanoparticles of ca. 100 nm. Due to the large size of the particles the Au core cannot always be distinguished from the Ag shell.

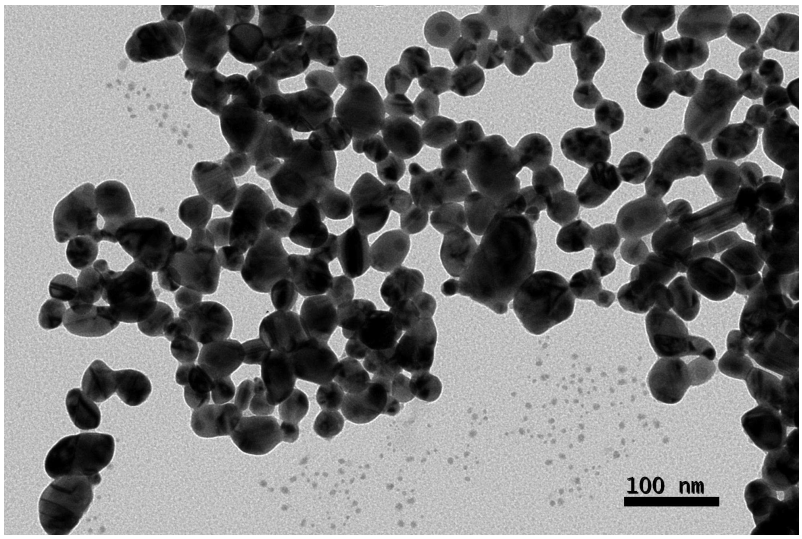
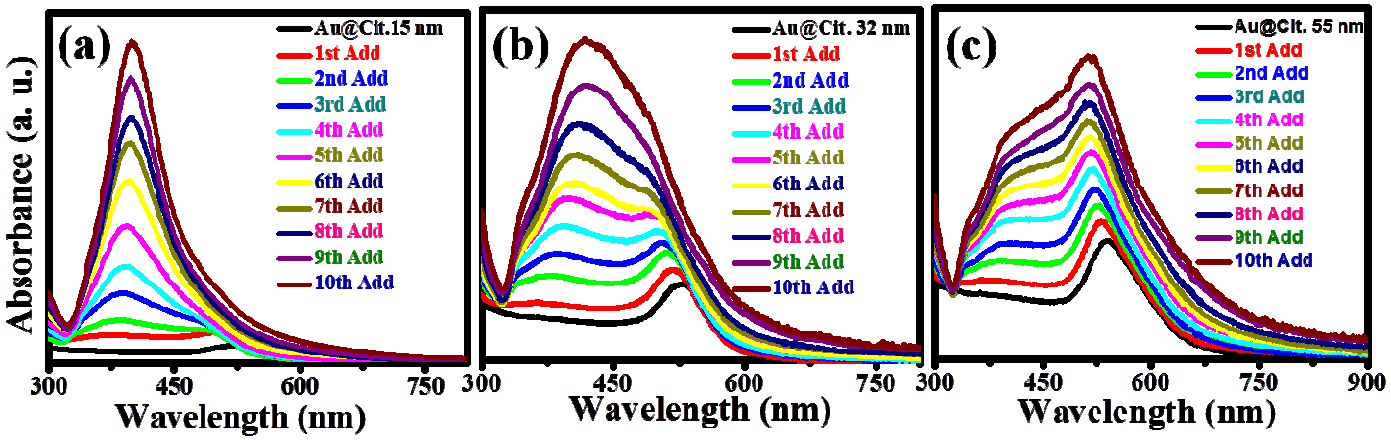


Figure S3. TEM images of Au@Ag nanoparticles obtained with high $AgNO_3$ concentration.



FigureS4. Evolution of extinction spectra of Au colloids of~15 nm (a), ~32 nm (b) and ~ 55 nm (c) during the deposition of Ag shell via step wise addition of Ag^{+} ions.

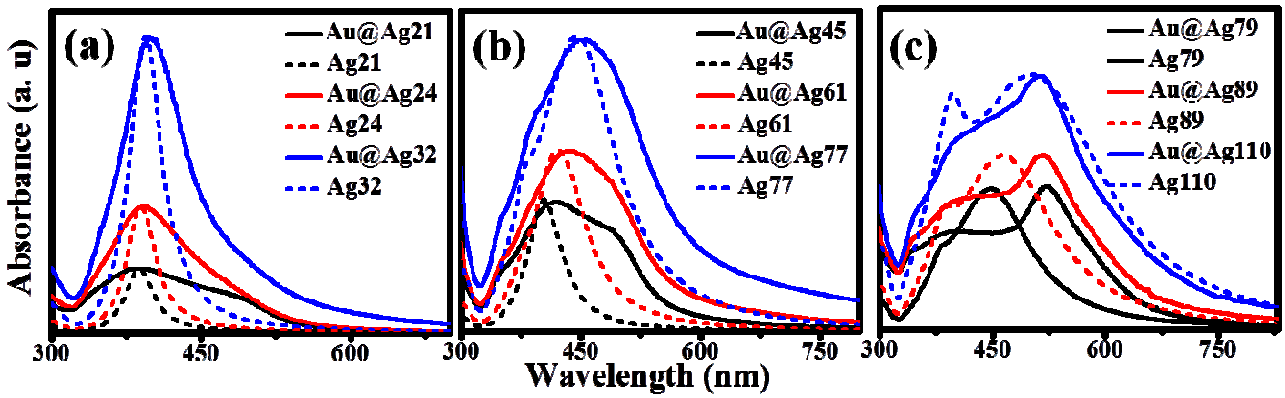


Figure S5. Measured extinction spectra of Au@Ag core-shell colloids obtained after 3, 5 and 10 additions of Ag^{+} ions to different size Au NPs cores: (a) ~15 nm, (b) ~ 32nm, (c) ~55 nm (solid lines). Calculated extinction spectra of pure Ag NPs with the same diameter as the core-shell NPs (dotted lines).

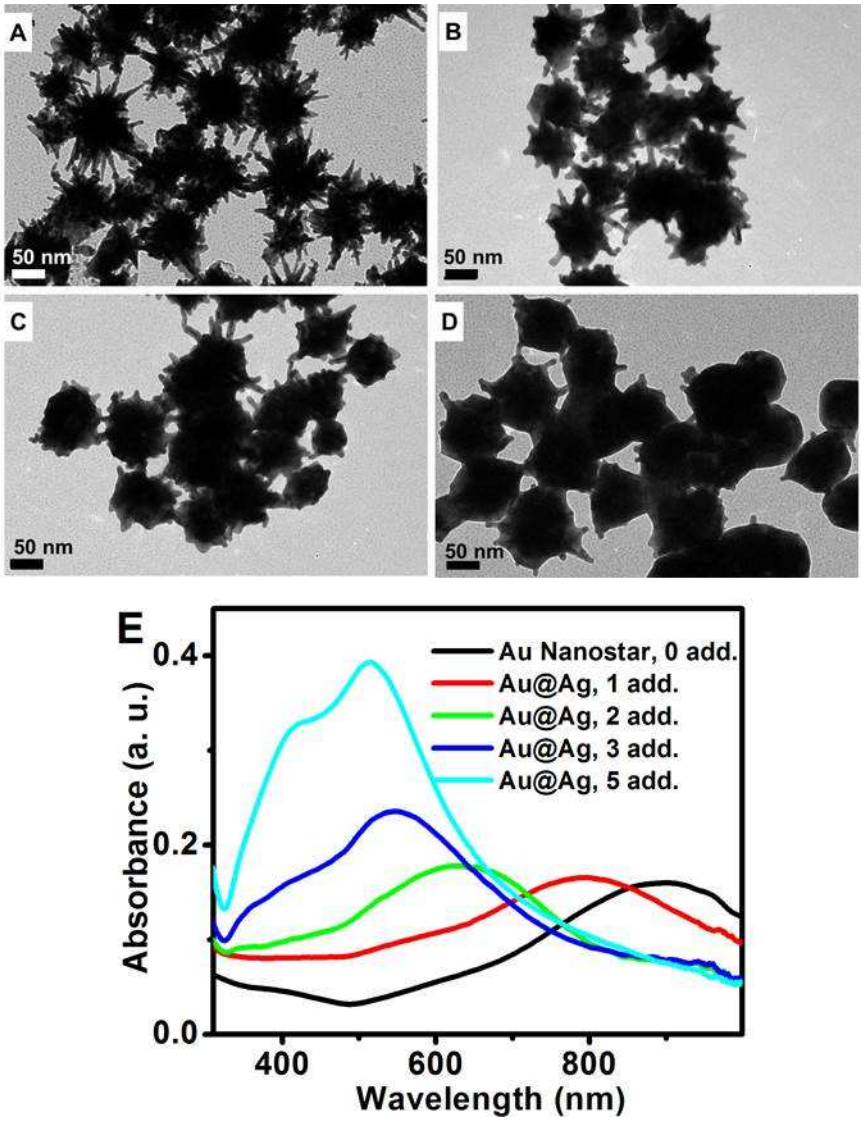


Figure S6. TEM images of Au nanostars (A), and Au@Ag core-shell nanostars (B-D) after different additions of Ag^{+} ions (2 add. (B), 3 add (C), and 5 add. (D)). (E) Evolution of extinction spectra of Au@Ag nanostars after the deposition of Ag shell via step wise addition.

Synthesis of Au nanostars: Au nanostar was synthesized as described by Vo-Dinh *et al*[1] Briefly, 1 mL of 15 nm citrate-stabilized Au colloids (see experimental section) was added to 100 mL of 0.25 mM $HAuCl_4$ aqueous solution containing 100 µL of 1 M HCl. Then 50 µL of 0.01 M

$AgNO_3$ solution in water and 500 µL of 0.1 M ascorbic acid were added simultaneously. The solution was stirred for 30 seconds and used for the synthesis of Au@Ag nanostar.

Synthesis of Au@Ag core-shell nanostar: For the first cycle, 20 µL AA (100 mM), 5 µL $AgNO_3$ (100 mM) and 25 µL NaOH (100 mM) were added to a beaker containing 10 mL of as prepared Au nanostar at room temperature. The reaction was continued for 30 minutes under slow stirring before performing a new addition of 20 µL AA (100 mM), 5 µL $AgNO_3$ (100 mM) and 25 µL NaOH (100 mM). After a selected number of additions the resulting particles were centrifuged at 1800 rpm for 20 min and redispersed in 10 mL of water.

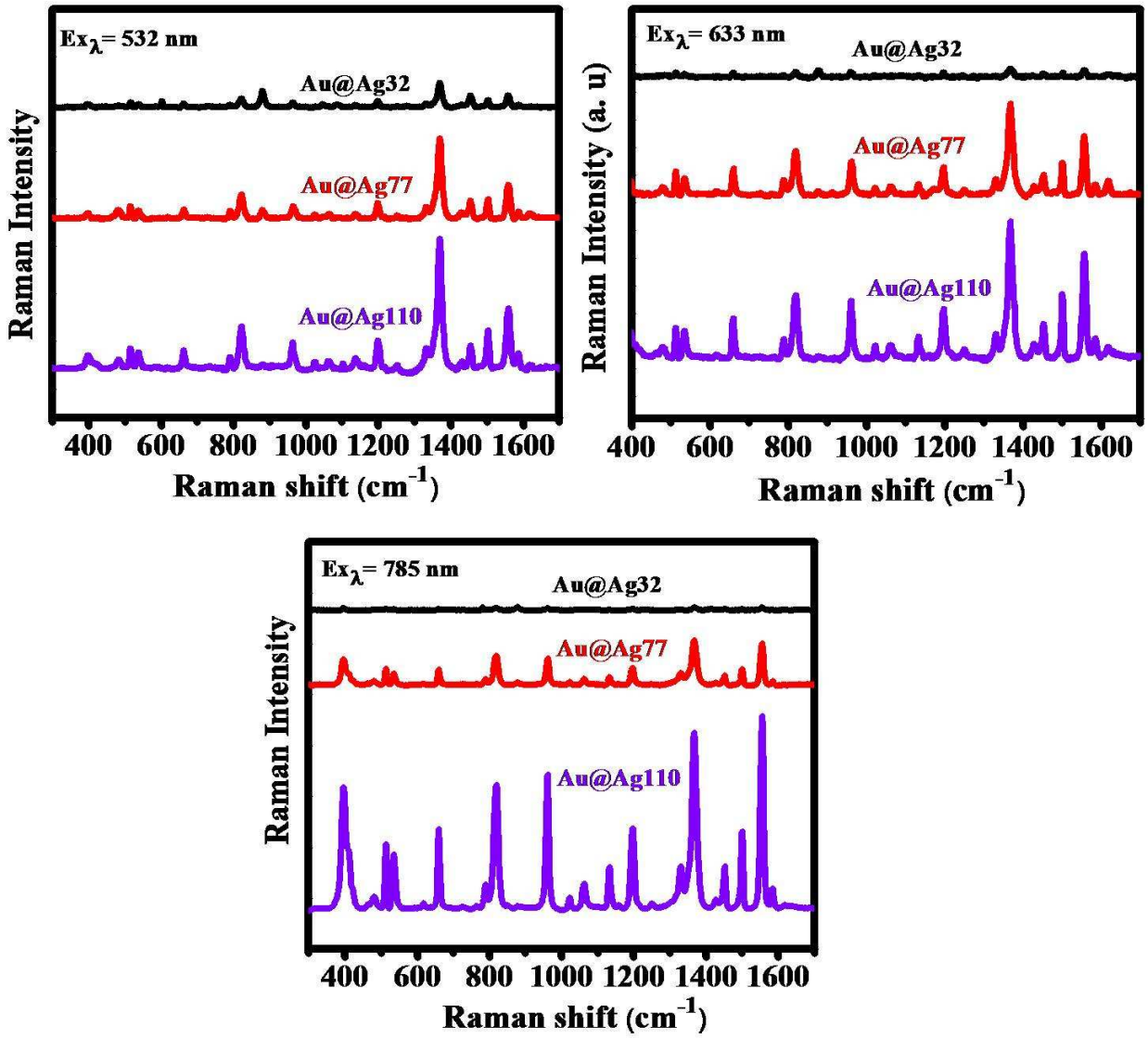


Figure S7. SERS spectra of 1-NAT on Au@Ag core-shell NPs of sizes ~ 32, 77, and 110 nm in recorded at the excitation wavelengths of 532, 633, and 785 nm.

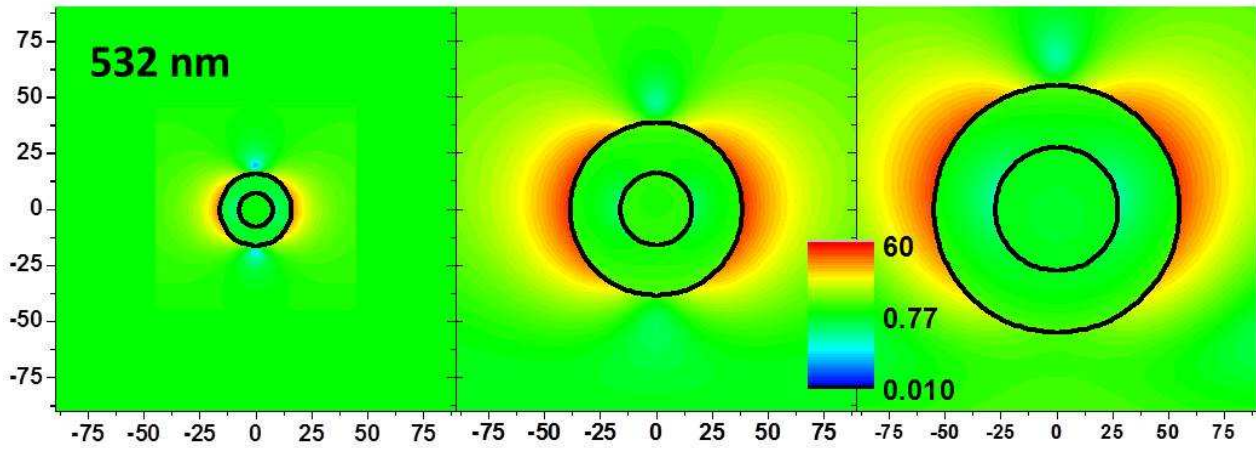


Figure S8. The plot of calculated near-field enhancement ($|E/E_{incident}|^2$) for Au@Ag core-shell NPs with different inner and outer diameters (15 and 32 nm (a), 32 and 77 nm, (b) and 55 and 110 nm (c)) Incident light is coming from below. For the calculations, the wavelength of 532 nm was used. The vertical and horizontal axes are in nanometers.

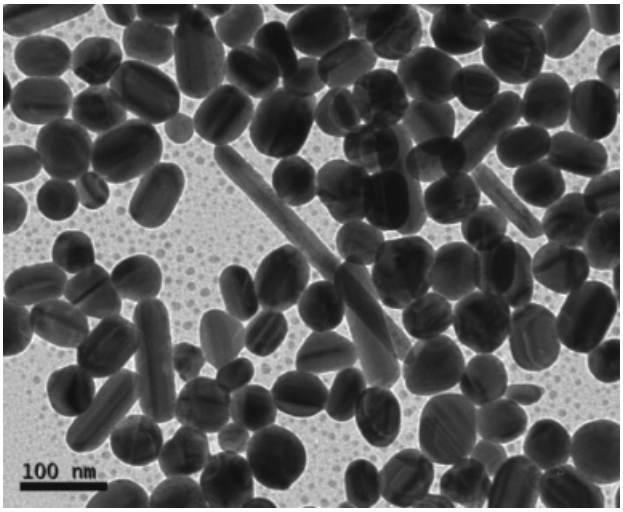


Figure S9. TEM image of the Ag NPs prepared by citrate reduction method.

Reference:

1. Yuan, H.; Khoury, C. G.; Hwang, H.; Wilson, C. M.; Grant, G. A.; Vo-Dinh, T. *Nanotechnology* **2012**, 23, 075102.