Supporting Information

Au@Ag Core-Shell Nanocubes: Epitaxial Growth Synthesis and Surface-Enhanced Raman Scattering Performance

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Size and occupancy of Au@Ag core-shell NCs

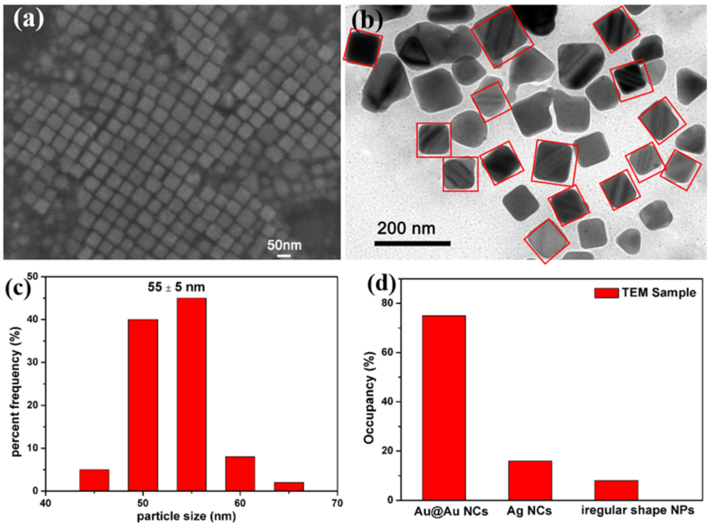

Fig. S1 SEM image (a), TEM image (b), the size distribution histograms (c) and the occupancy (d) of the Au@Ag core-shell NCs

Synthesis of Pure Ag NCs

The synthesis procedure of pure Ag NCs is described as follows. Typically, KBr (100 μL, 10 mM) was mixed with CTAC (5 mL, 20 mM) solution. Successively, the mixture was heated at 60°C for 10 min, then quickly added $AgNO_3$ (100μL, 10 mM) and AA (300 μL, 100 mM) all in once with pipette, then left undisturbed at 60 °C for 6 h to obtain Ag NCs and the color of solution changed into yellow. Finally, the as-prepared pure Ag NCs solution was centrifuged (11000 rpm, 30 min) and re-dispersed in deionized water for later characterization.

Comparing with the synthesis process of Au@Ag core-shell NCs, under same reaction conditions but absence of the Au seed, the as-prepared pure Ag NCs have the morphology of well-defined cubic shape. As shown in Fig. S2, the mean size of pure Ag NCs (52 ± 5 nm) is slight smaller compared with the Au@Ag core-shell NCs (55 ± 5 nm). These nanocubes both exhibited a truncated cubic morphology in the SEM images.

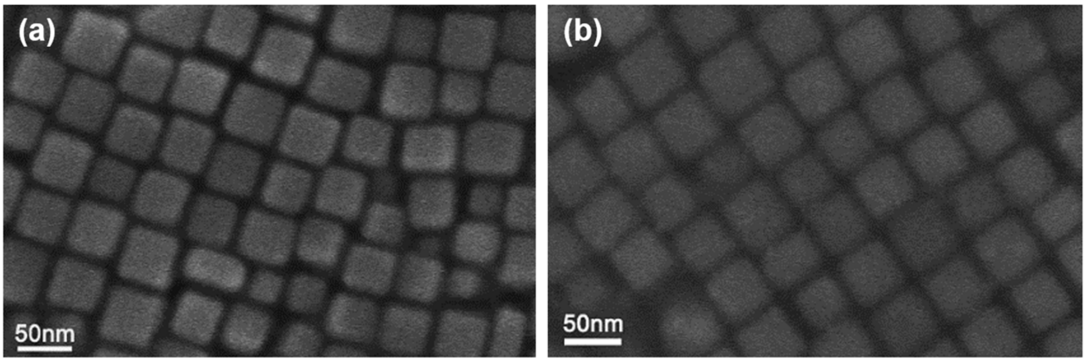

Fig. S2 SEM images of (a) pure Ag NCs and (b) Au@Ag core-shell NCs.

Absorption Spectra of Nanocubes

The absorption spectra of the Au@Ag core-shell NCs and the pure Ag NCs have been experimentally measured and theoretically calculated for comparing their optical properties. As shown in Fig. S3(a), there are a main peak at 465 nm and two notable peaks at 387 nm and 351 nm, respectively, which are very resemble to those of Au@Ag core-shell NCs excepting a weak shoulder near 550nm and a little blue shift.

The FEM-calculated absorption spectra of pure Ag NC and Au@Ag core-shell NCs with same edge length of 55 nm are shown in Fig.S3 (b). It exhibits an excellent agreement with those experimental results shown in Fig S2 (a), for example, the distinct red shift of main peak of Au@Ag core-shell NCs, and the peak positions and spectral line shapes. According to the plasmon hybridization described below, as shown in Fig.S3(b), the calculated absorption peaks of pure Ag NC and Au@Ag core-shell NCs can be assigned to the plasmon resonant coupling of dipole, quadrupole, and arguably multipole modes, respectively, in the order from longer to shorter wavelengths.[31] It should be noticed that the calculated absorption spectra were obtained for the isolated nanocubes, but the experimental absorption spectra were measured for the solutions with the pure Ag NCs or Au@Ag core-shell NCs.

Fig.S3 (a) experimental absorption spectra and (b) calculated absorption spectra of Au@Ag core-shell NCs (black curve) and pure Ag NCs (red curve)

The wavelength-dependent electric field enhancement

The wavelength-dependent enhancement spectra are shown in Fig. S4, which are theoretically simulated for the same positions located on the edges of both Au@Ag core-shell nanocubes and pure Ag nanocubes. The wavelengths corresponding to the electric field enhancement peaks are generally consisted with that of plasmonic resonance peaks of the absorption spectra in Fig. S3. And, by comparing the values of the electric field enhancements at the wavelength of 785 nm, it is clear that the Au@Ag core-shell NCs have superior enhancement than that of pure Ag NC, which is correspondent match the results in the SERS experiments.

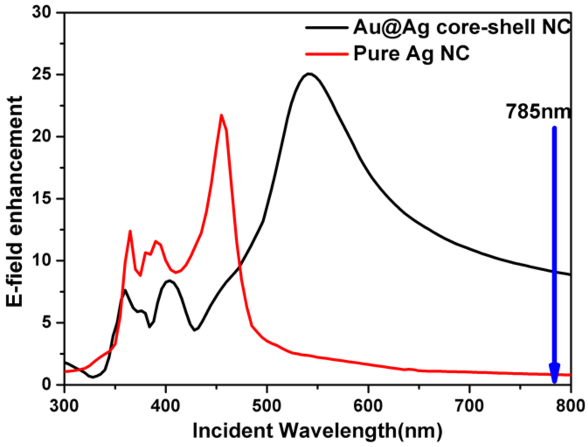

Fig. S4 The wavelength-dependent electric field enhancements of Au@Ag core-shell NC and pure Ag NC

Plasmon Hybridization

The schematic diagram of plasmon hybridization of the Au@Ag core-shell NC is plotted in Fig. S5. In fact, the LSPR effect of the bimetallic nanocube is raised not only from the plasmonic interaction of corners and edges but also from those of the core and the shell in the nanostructure. As shown in Fig. S5, in the heterogeneous nanostructure, the plasmonic effect of Ag shell can be thought as the hybridization of two simple plasmonic systems representing a solid Ag cube and an Ag cavity with an ellipsoidal shape, which results in a strong induced dipole moment with symmetric charge distribution and a weak induced dipole moment with anti-symmetric charge distribution, corresponding to the bonding mode with lower energy and the anti-bonding mode with higher energy, respectively. Similarly, the plasmons effect of the bimetallic cube comes from the plasmons hybridization between the Au ellipsoidal core and the Ag shell, which results in electric mutipole moments that correspond to various bonding and anti-bonding modes. As shown in Fig. S3(b), the calculated absorption spectra provide the LSPR characteristics of the Au@Ag core-shell cube and the pure Ag cube, such as the dipole plasmon resonances at 510 and 468 nm, which are quire consistent with our experimental results (Fig. S3 (a)). Clearly, the plasmon coupling between the core and the shell has strong dependence on the thickness of Ag shell and the shape of Au ellipsoidal core. It is the plasmon hybridization in the bimetallic nanostructure that further explains the physical origin of the plasmon response and the electric field enhancement of the reported Au@Ag core-shell NC.

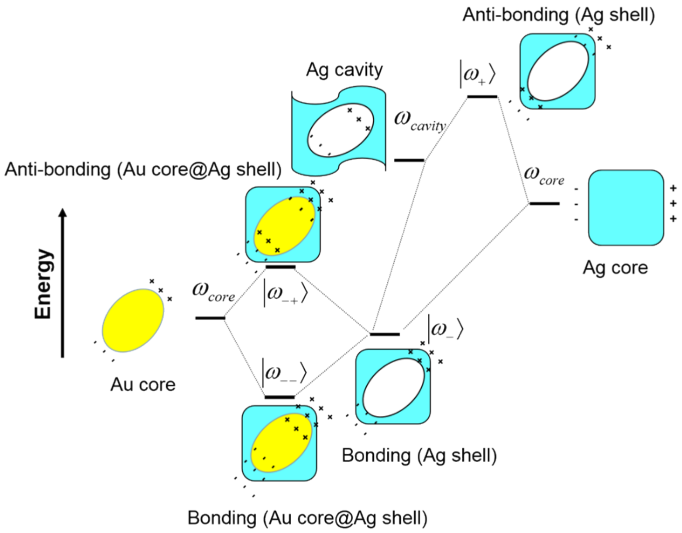

Fig. S5 Plasmon hybridization diagram of Au@Ag core-shell NC structure

Stability of SERS solution

To evaluate the stability of the SERS solution, the Raman spectra of the 4MBA labeled Au@Ag core-shell NCs were measured for different time intervals and shown in Fig. S6. It clearly displays the nice time stability of the SERS solution.

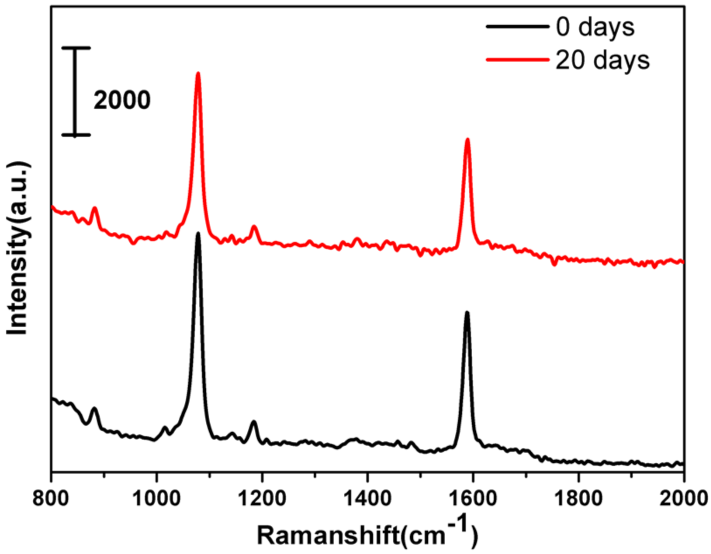

Fig. S6 Raman spectra of 4-MBA labeled Au@Ag core-shell NCs solution at different days