Supporting Information

Ag@Au Hexagon Nanorings: Synthesis, Structure-dependent Optical Characteristics and Mechanism Analysis

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Size effect of gold nanosphere

In order to better understanding the physical significance of the parameters in Eq. (1), Size effect on the LSPR characteristic of Au nanosphere has been investigated. The absorption spectra of Au nanosphere with an increasing radii range from 5 to 50 nm were calculated by FEM and shown in Fig. S1(a). It presents that the LSPR peak gradually shifted from 521 nm to 556 nm as increasing of the radius of Au nanosphere, except less than 10 nm.[41] The positions of LSPR peak versus the volumes of the Au nanosphere is plotted in Fig. S1(b) and fitted into an Lorentz curve (R^2=0.98797) as followed formula:

$$P = P_0 + \frac{2A}{\pi}\frac{V_0}{4(V+V_c)^2 + V_0^2} \qquad \text{(S1)}$$

where P_0 = 567.86822 nm, A = -2.49251 nm·μl, V_0 = 32109.78971 nm^3 and V_c = -507542.40501 nm^3.

It is clear that the positions of the LSPR peaks of the Au nanospheres are not only depend on the volumes of Au nanospheres but also obey the Lorentz function due to size effect of gold nanosphere.

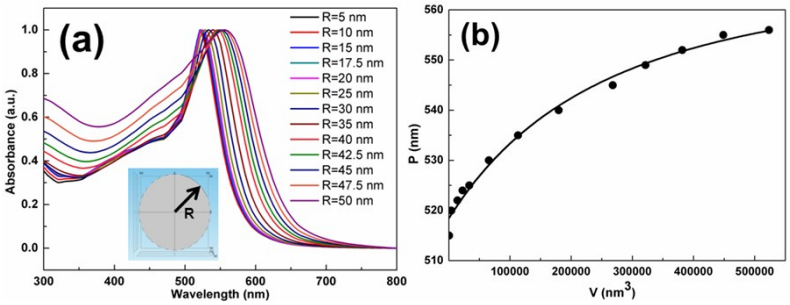

Fig. S1 (a) The calculated absorption spectra of Au nanospheres with different radii (R) and (b) positions of the LSPR peaks (P) corresponding to the volumes of Au nanospheres (V).

Relationship of the wall thickness and the dosage of $HAuCl_4$ solution

To intuitively compare the calculated results with the experimental results, it is necessary to set a relationship between the wall thickness of the Ag@Au HNR and the dosage of $HAuCl_4$ solution. Concretely, by selecting the dipole plasmon resonant peaks located at the same wavelength in Fig. 4(a) and Fig. 5(a), the wall thickness corresponding to the dosage of the $HAuCl_4$ solution are obtained and plotted in Fig. S2. As shown in Fig. S2, the fitted curve can be expressed as follow:

$$d = 13.58158\, exp(-\frac{V}{135.3859}) + 3.74884 \qquad \text{(S2)}$$

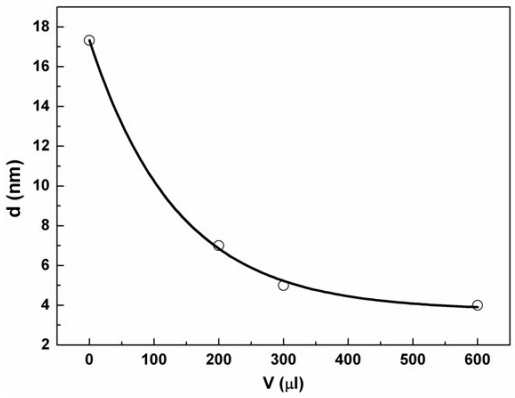

Fig. S2 Wall thickness (d) of the Ag@Au HNR dependence on the dosage of $HAuCl_4$ solution (V)

Plasmon hybridization

The schematic diagram of plasmon hybridization of the Ag@Au HNR is illustrated in Fig. S3. In fact, the LSPR effect of the bimetallic nanoring is originated not only from the plasmonic interaction of edges and corners but also from those of the gold ring and silver ring in this core-shell nanostructure. As shown in Fig. S3(a), the concentric nanostructure, the plasmonic effect of Au ring can be considered as the hybridization of two simpler plasmonic systems representing an Au hexagonal plate and an Au cavity with a hexagonal 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. Then, the plasmons effect of the hexagonal concentric ring come from the plasmons hybridization between the big Au ring and small Au ring, which results in electric multipole moments that correspond to various bonding and anti-bonding modes. Similarly, the plasmonic effect of Ag ring can also be thought as the plasmons hybridization of an Ag hexagonal plate and an Ag cavity with a hexagonal shape. As

illustrated in Fig. S3(b), the plasmonic effect of the bimetallic hexagonal ring came from the plasmons hybridization between the Au hexagonal concentric ring as shell and Ag ring as core, leading to the electric multipole moments that correspond to a various of the bonding and anti-bonding modes. It is the plasmon hybridization in the bimetallic nanostructure that explains the physical origin of the plasmon response and the electric field enhancement of the reported Ag@Au HNRs.

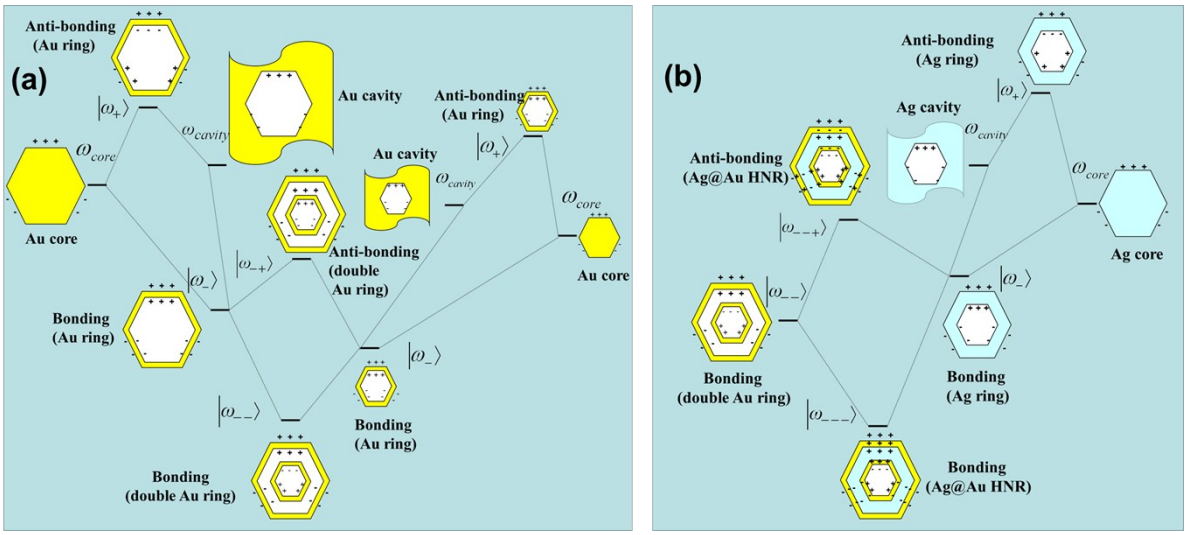

Fig. S3 Plasmon hybridization diagrams: (a) Au-Au hexagonal concentric nanostructure, and (b) Ag@Au HNR.