Tuning Plasmon Resonance of Gold Nanostars for Enhancements of Nonlinear Optical Response and Raman Scattering

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ABSTRACT: Localized surface plasmon resonances (LSPRs) of metal nanostructures are highly related to the shape, which could greatly enhance the light–matter interaction at nanoscale. Here, we investigate the LSPRs of gold nanostars corresponding to the unique morphology and demonstrate surface-enhanced Raman scattering (SERS) activities and nonlinear refraction properties of two typical structures. By adjusting the synthesis condition, the main plasmon resonance could be tuned from 557 to 760 nm. The plasmon modes and intense field enhancement near the sharp tips are revealed by finite-difference timed-domain (FDTD) simulations. The nonlinear refractive index |γ| reaches to the maximum value when the excitation wavelength is resonant to the LSPRs wavelength. The maximum value of |γ| for long-branched nanostars (λSP = 706 nm) is 5.843 × 10−14 cm2/GW, which is about 1.5 times larger than that of spherical-like nanostars with λSP = 563 nm. The SERS activity of long-branched nanostars is about 15 times larger than that of spherical-like gold nanostars.

1. INTRODUCTION

Seeking architectural building blocks with controlled morphology and property is a significant challenge for future nanodevices and applications. Metal nanostructures have attracted intense attention because of their exceptional physical and chemical properties. The localized surface plasmon resonances (LSPRs) of noble metal nanoparticles, originated from the collective oscillations of conduction electrons, are strongly determined by the size, shape, composition, and the surrounding environment. More than spherical nanoparticles, anisotropic and complex metal nanostructures, such as nanorods, multipods, multibranched nanostars, and dendritic structures, are of special interest on account of their more tunable and versatile properties.

The multibranched gold nanostars possess complex shapes as well as unique optical plasmon properties and show great potential applications including sensing, surface-enhanced Raman scattering (SERS), catalysis, and photothermal therapy. The LSPRs in gold nanostars could introduce tunable plasmon peaks from visible to near-infrared region by tuning the shape and branch length. Gold nanostars are considered as a solid core with protruding prolate tips and exhibit multiple plasmon resonances originating from the hybridization of plasmons associated with the core and the individual tips of the star. The multiple plasmon resonances exhibit high polarization dependence, large extinctive cross section, and intense local field enhancement, which make gold nanostars highly sensitive for optical sensing application. The rough surface with edge, corner, gap, and tip on gold nanostars could concentrate intense local field without aggregation or particle–particle gap, which afford hotspots for SERS, especially producing multiple hotspots in one nanostar for single particle SERS or single molecule SERS. The large field enhancement confined at surface vicinity also makes nanostars suitable for the amplification of optical signals like fluorescence and nonlinear optical responses. Moreover, gold nanostars with complex shape produce large surface area and high index facets with high surface energy, which increase the SERS activity as well as catalytic activity.

Normally, by bottom-up wet-chemical synthesis methods, thermodynamically preferred shapes for face-centered cubic gold nanocrystals possess high degrees of symmetry like nanospheres or polyhedrons. For synthesis of multibranched gold nanostars with anisotropic and complex morphology, a kinetically controlled growth method should be applied. The seed-mediated growth using cetyltrimethylammonium bromide (CTAB), poly(vinylpyrrolidone) (PVP), and other molecules as surfactant could provide precise shape and size control to synthesize gold nanostars. The seedless synthesis strategy with high facility was also shown to synthesize gold nanostars by exerting an efficient factor for kinetically controlled growth, such as molecular adsorption on specific facet, pH value, and trigger ions. Other methods like galvanic replacement have also been reported to synthesize gold nanostars.
In this paper, we investigated the LSPRs of gold nanostars corresponding to the unique morphology. The gold nanostars were synthesized by one-pot seedless method in the presence of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), which act as both reducing and capping agents. The size and shape of gold nanostars were controlled by the reaction condition (gold precursor concentration, HEPES concentration, temperature, etc.). Finite-difference timed-domain (FDTD) simulations were performed to reveal the morphology induced plasmon modes. LSPRs can induce intense field enhancement located near the surface of nanostars, especially around the sharp tips to produce hotspots. The large local field account for many plasmon-enhanced optical responses. We demonstrated the enhanced nonlinear refraction property and the use of gold nanostars as ultrasensitive SERS sensors.

2. EXPERIMENTAL SECTION

The gold nanostars were synthesized by the following process. A solution of HEPES with concentration of 100 mM was prepared with ultrapure water, and the pH value was adjusted to 7.4 ± 0.1 at room temperature by adding an appropriate amount of 1 M NaOH solution. In a typical experiment, different volumes (from 0.5 to 10 mL) of 100 mM HEPES (pH 7.4) were mixed with 3 mL of ultrapure water followed by the adding 150 μL of 10 mM HAuCl₄ solution. Without shaking, the color of solution changed from light yellow to slightly purple and finally to greenish blue at 10 and 30 °C. The tips of the gold nanostars would be longer and sharper at 10 °C compared with that of the nanostars synthesized at 30 °C.

Gold content of all samples was kept with the same concentration about 1.67 nM preparing for SERS measurements. As-synthesized gold nanostars (5 mL) were mixed with the diethylthiodicarbocyanine iodide (DTDCI, 1 mM, 5 μL) uniformly by gentle inversion for 10 s. The concentration of the DTDCI was 1 μM in the final solution. The mixed solution was placed undisturbed about 48 h for the adsorption of DTDCI molecules onto the nanostars. We got rid of the supernatant solution by centrifugation and then dropped the precipitate on the slide. The precipitate would be a round film with the diameter about 3 mm.

Transmission electron microscope (TEM) observations were performed with a JEOL 2010 HT TEM operated at 200 kV. The extinction spectra of the samples were measured using a TU-1810 UV−vis spectrophotometer (Purkinje General Instrument Co. Ltd.). All SERS measurements were performed using a HORIBA Jobin Yvon Lab RAM HR. A typical 785 nm wavelength diode laser coupled to a holographic notch filter was used to excite the samples. Scans were taken on an extended range (450−1700 cm⁻¹) with the excitation power of 100 mW and the acquisition time of 1 s. The nonlinear refraction responses of the gold nanostars solution with optical length of 1 mm were measured by closed-aperture Z-scanning.

The ultrafast laser pulses were generated using a Ti:sapphire laser (Mira 900, Coherent) with a pulse width of 2.5 ps and a repetition rate of 76 MHz.

The FDTD simulations were performed using FDTD Solutions 6.5 (Lumerical Solutions, Inc.). The dielectric constants of gold were taken from the Handbook of Optical Constants of Solids edited by Palik. In the calculations, the mesh around the Au nanostructure was 0.5 nm × 0.5 nm × 0.5 nm. The refractive index of the environment medium was taken to be 1.333.

3. RESULTS AND DISCUSSION

We use a one-pot seedless method to synthesize gold nanostars by directly reacting gold precursor with HEPES solution. The HEPES is a well-known zwitterionic molecule for preparing pH
buffer solution and widely used in chemistry and biology. Here, the HEPES acts as both reducing and capping agent. Gold ions are reduced by the HEPES, and the growth of gold nanocrystal is guided by the adsorption of HEPES on specific crystal plane of gold. It has been reported that the piperazine in HEPES can bind on the different gold facets with the weakest binding on the \{111\} planes, which results in the growth of three-dimensional multibranched gold with tips grow along \langle111\rangle direction.\textsuperscript{34} Figures 1a−c show the TEM images of gold nanostars synthesized assisted by the HEPES at 30 °C. The products are high yield (>90%) gold nanostars with several branches.

Gold nanostars show different optical properties than spherical gold nanocrystals. Figure 1d shows the gold nanocrystals synthesized by adding different volume of HEPES. As the volume of HEPES (100 mM) increases from 1 to 6 mL, the main extinction peak red-shifts from 557 to 704 nm. The initial extinction peak at 557 nm originates from nearly spherical nanoparticles with small surface roughness. The subsequent extinction band with red-shifting, being attributed to the longitudinal plasmon resonances along the branches, indicates the appearance and growth of the branches. The length growth of branches can be seen in the Figures 1a−c, where the average branch length changes from about 0 to 20 nm. As the HEPES molecules act as reducing agents, the high amount of adding HEPES means the high reducing ability in the reaction solution and then leads to the length growth of branches. The transversal plasmon resonances also appear on the spectra around 500 nm with weak intensity. We also note the full width at half-maximum (FWHM) increases from 144 to 212 nm along the red-shift of extinction band. The broadening of band should results from the new band arising at around 900 nm.

We perform the similar reactions by changing the amount of HEPES at relative lower temperature. The reaction kinetics influenced by the temperature as well as the reducing ability. Figures 2a−c show the TEM images of gold nanostars synthesized at 10 °C. The average branch lengths are about 15, 25, and 42 nm for the HEPES volume of 3, 6, and 8 mL, respectively. At this temperature, the growth of gold is slower than that at 30 °C, which is confirmed by the reaction fact that the solution color changes slowly. However, the branches can grow longer at low temperature and the length difference of branches is larger. As the branch length increases, the main extinction peak red-shifts from 572 to 760 nm in Figure 2d. The extinction at around 900 nm increases more obviously than that in Figure 1d. We plot the intensity ratio of 900 nm to the main peak (peak 1) in Figure 2e. The ratio increases from 0.02 to 0.82, and the ratio calculated from Figure 1d gives the maximum value only about 0.26.

The extinction properties of gold nanostars and the origination of peak at around 900 nm are calculated and revealed by the FDTD simulation. According to the TEM images, we design a four-branched 3-D structure composed of an 8 nm spherical core with a long branch and three short branches (see Figure 3a). The long branch with the length of 17 nm and short branch with the length of 7 nm have an angle about 109°, and the angle between three short branches is 120°. Figure 3b shows the extinction spectrum with an excitation light normal to the plane determined by a long branch and a short branch. The angle between the polarization direction and the long branch is 74.2° to make the electric field projection ratio to the long branch and to the short branch be 1:3. The structure exhibits an extinction peak at 735 and 915 nm in the range from 500 to 1000 nm. From the field distribution in the inset, we attribute the 735 nm peak to the longitudinal plasmon resonance of three short branches. The peak at 915 nm is
attributed to the longitudinal plasmon resonance of the long branch. For this complex nanostructure, there exist coupling and hybridization of plasmon modes associated with the core and different branches, which can be observed at the field distribution (see Figure 3b). Now we go to understand the spectral broadening and the arising band near 900 nm in Figures 1d and 2d. As the gold nanostars in experiments usually have multiple branches with different lengths, the extinction spectra measured in solution are broadened because they are the overlap of many plasmon modes from nanostars with different length and random orientation. At relatively lower temperature, some branches could grow very long in the slow growth condition and the length difference of branches is large. The plasmon modes corresponding to the branches with different lengths have different plasmon resonance peaks, and the mode overlap broadens the spectral width. Then, the products grown at low temperature have large plasmon extinction intensity at around 900 nm.

As shown in Figure 3b, LSPRs concentrate large electric field near the surface of gold nanostars, especially near the sharp tips. The large local field enhancement can effectively amplify a variety of optical signals. Here, we use nonlinear optical responses (nonlinear refraction) to reveal the local field enhancement of gold nanostars. Two types of samples with LSPR of 563 and 706 nm are measured by the closed-aperture Z-scan method. The sample with LSPR at 563 nm is spherical-like shape, while the sample with LSPR peak at 706 nm is star shape with sharp branches. The closed-aperture transmittance normalized by the open-aperture transmittance (\(T_{CL}/T_{OP}\)) as a function of Z-position is shown in Figure 4a. The peak-to-valley configuration indicates that the sign of the nonlinear refractive index \(\gamma\) is negative, corresponding to self-defocusing effect. The nonlinear refraction signal of spherical-like nanostars (\(\lambda_{SP} = 563 \text{ nm}\)) is stronger than that of the long-branched nanostars (\(\lambda_{SP} = 706 \text{ nm}\)) with the excitation wavelength at 563 nm. But the results are opposite when the excitation wavelength is 706 nm. These two structures are incubated with 1 mM DTDCI overnight for the adsorption of Raman tag on the gold surface. Without gold nanostructures, the Raman signals of pure DTDCI molecules are hard to detect. Both the two DTDCI-coupled nanostructures exhibit obviously Raman signals, and the SERS activity of long-branched gold nanostars is about 15 times larger than that of spherical-like gold nanostars. There are two reasons for the great SERS activities of gold nanostars in our experiments. The excitation wavelength is 785 nm for the Raman measurement, which is closer to the plasmon resonance of long-branched nanostars than that of spherical-like nanostars. Most important, the sharp tip on the nanostars with great field enhancement plays the major role for the large SERS signals.

Figure 4a. Normalized closed-aperture Z-scan transmittance divided by the open-aperture one. The blue and red curves represent two different gold nanostructures with the LSPR at 563 and 706 nm, respectively. The scatter dots are the experimental data while the solid curves are theoretically fitting curves by employing the standard Z-scan theory. The excitation wavelengths for the upper, middle, and bottom curves are 563, 706, and 795 nm, respectively. The Z-scan curves are shifted vertically for clarity. (b) Excitation wavelength dependence of the nonlinear refraction index \(\gamma\) of two different gold nanostructures. The inset shows the linear extinction spectra of the two samples with the same peak intensity.
Figure 5. Raman spectra ($\lambda_{\text{exc}} = 785$ nm) of pure DTDCI (black line) and two DTDCI-coupled gold nanostructures with different shapes. All the samples were dispersed on the slide with the same DTDCI concentration of 1 $\mu$M. The SERS curves are shifted vertically for clarity. The inset shows the extinction spectra of the two samples with the same content of gold.

4. CONCLUSIONS

In conclusion, we synthesis gold nanostars with sharp branches by directly reacting gold precursor with HEPES. The plasmon optical properties of gold nanostars can be tuned by reaction condition of HEPES concentration and temperature. The extinction band position is tuned from 557 to 760 nm in the visible range, and the FWHM is also tuned due to the arising plasmon mode around 900 nm in the near-infrared region. Through FDTD simulations, the plasmon modes and intense field enhancement near the sharp tips are revealed. We compare the nonlinear optical responses and SERS activities of spherical-like and long-branched gold nanostars. The nonlinear refractive index at the resonant wavelength of LSPR for long branched gold nanostars is 1.5 times larger than that of spherical-like gold nanostars. The long branched nanostars ($\lambda_{\text{SP}} = 706$ nm) show 1 order of magnitude higher SERS signals than that of the spherical-like nanostars. The outstanding plasmon-enhanced optical effects of gold nanostars are attributed to the large field enhancement of the sharp tips and the unique plasmon resonances of the complex geometry.

ASSOCIATED CONTENT

Supporting Information

Figures of the 3-D gold nanostructure of spherical-like gold nanostar for FDTD simulation and the simulated extinction spectrum; inset: the local electric field enhancement near the sharp tips are revealed. We compare the nonlinear optical responses and SERS activities of spherical-like and long-branched gold nanostars. The nonlinear refractive index at the resonant wavelength of LSPR for long branched gold nanostars is 1.5 times larger than that of spherical-like gold nanostars. The long branched nanostars ($\lambda_{\text{SP}} = 706$ nm) show 1 order of magnitude higher SERS signals than that of the spherical-like nanostars. The outstanding plasmon-enhanced optical effects of gold nanostars are attributed to the large field enhancement of the sharp tips and the unique plasmon resonances of the complex geometry.

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Notes

The authors declare no competing financial interest.

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