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# Single-Particle SERS Enhancement with Optimized Gold-Nanostar Morphologies

by Thomas Li, Yusong Choi, and Mark H Griep

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# **Single-Particle SERS Enhancement with Optimized Gold-Nanostar Morphologies**

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| 14. ABSTRACT<br><p>The field of plasmonic nano-additives is expanding beyond the targeted synthesis of energy-tuned absorption materials toward the development of additive structures that efficiently translate the absorbed energy into a material response. In this work, the methodology to create gold nanostars with tailored extrusion features is optimized through a detailed investigation on the impact of each reaction chemical on the resulting structure morphology. Key elements including silver nitrate, ascorbic acid, and chloroauric acid concentrations are isolated to control nanostar tip length, symmetry, and quantity. Utilizing the optimized gold-nanostar structure, a Raman tag sensitive to the plasmon field is integrated into nanostar structure at defined locations to isolate the regions of maximal plasmon intensity. The reporter molecule demonstrated an 18-fold enhancement in Raman signal intensity when adhered to the nanostar protrusions over other locations on the particle, isolating the area of highest plasmon intensity at the nanostar tips.</p> |                             |                                    |                                      |                                                             |                                                           |
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## 1. Introduction

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Plasmonic nanomaterials have been the focus of intense study in recent years, with widespread, realized application areas including sensing,<sup>1</sup> photothermal therapy,<sup>2</sup> bioimaging,<sup>3</sup> photocatalysts,<sup>4</sup> optical lenses,<sup>5,6</sup> thermal history measurements,<sup>7</sup> and polymer nanocomposites.<sup>8,9</sup> The extensive application potential results from the unique light–matter interactions with tailored plasmonic particles and structures. At a size scale smaller than the wavelength of light, metal nanoparticles generate a localized surface plasmon resonance (SPR) upon electromagnetic (EM) irradiation, where the oscillating electric field of the incident light is in resonance with collective oscillation of the nanoparticle’s electron cloud. The large oscillations of the electron cloud enhance the nanoparticle’s effective absorption cross-sectional area, resulting in a photon-trapping area up to an order of magnitude larger than the base-particle dimensions.

Apart from an amplified optical-extinction coefficient, synthesis methodologies are available to tune the resonance peak across the ultraviolet (UV), visible (Vis), and near-infrared spectrum to tailor the materials’ use in select energy regions. By inducing asymmetry in the nanomaterials’ structure, the resonance band can be shifted to the desired location in the EM spectrum. Multiple asymmetric morphologies have been optimized to exploit this tunability including silver nanoplates (AgNPs),<sup>10</sup> gold nanorods,<sup>11–13</sup> gold nanostars (AuNSs),<sup>8</sup> hollow gold nanoshells,<sup>14</sup> and core-shell designs.<sup>15,16</sup> In the case of silver nanoplates, for example, the aspect ratio is based upon the ratio of plate thickness to plate diameter, with a high aspect ratio leading to a red-shifted resonance. For gold-based materials, such as nanorods, the asymmetric morphology results in two separate resonance peaks corresponding to the transverse and longitudinal SPR. The multiple resonance modes highlight the ability to manipulate the plasmonic field based on the particle structure, providing the opportunity to focus the intensity of the plasmon in select regions of the particle. Recent efforts have demonstrated the ability to utilize high-intensity plasmon fields to manipulate the local environment and transfer energy to adjacent molecules.

In this work, methods to precisely tailor the morphology of AuNSs and locate/optimize the maximal plasmonic energy-transfer regions are reported. The sharp protrusions on AuNSs have been shown to serve as focusing points for plasmon energy<sup>17</sup>; thus, optimization of the synthesis protocol will allow for tailoring of the plasmon-focusing effects through design of the protruding spikes. With the creation of the focused-plasmon points, the energy can be utilized to enhance the Raman signature of attached molecules without the need of a precise

nanogap between adjacent plasmonic structures as used in traditional surface enhanced Raman spectroscopy (SERS) approaches.<sup>18,19</sup>

## **2. Experimental Procedure**

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### **2.1 Materials**

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Unless specified, all chemicals were purchased from Sigma-Aldrich (St Louis, Missouri) and used without further purification. Primary chemicals include silver nitrate ( $\text{AgNO}_3$ ), trisodium citrate (Na-Cit), sodium borohydride ( $\text{NaBH}_4$ ), hydrochloric acid (HCl), chloroauric acid ( $\text{HAuCl}_4$ ), ascorbic acid (AA), poly(ethylene glycol) methyl ether thiol (mPEG-SH), copper (II) chloride, sodium dodecyl sulfate, sodium hydroxide, and hydroxylamine hydrochloride. All solutions were prepared in Milli-Q water.

### **2.2 Citrate-Stabilized Ag-Nanoseed Synthesis**

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Citrate-stabilized silver nanoseeds were synthesized following the previously reported method.<sup>20</sup> In a large beaker, a 200-mL solution of  $\text{AgNO}_3$  (0.25 mM) and Na-Cit (0.25 mM) was prepared. This solution was stirred for 30 min following the addition of 6 mL of  $\text{NaBH}_4$  (10 mM). The solution was left undisturbed overnight and stored at room temperature until use.

### **2.3 Ag-Core AuNS Synthesis**

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AuNSs with silver cores were synthesized following the previously reported method.<sup>21</sup> The previously synthesized Ag nanoseeds (0.75 mL) was added to 9 mL of distilled deionized (DDI) water and stirred for 1 min. Next, 7.5  $\mu\text{L}$  of 100-mM HCl was added followed by 1 mL of 2.5-mM  $\text{HAuCl}_4$ . Afterward, 60  $\mu\text{L}$  of 10-mM  $\text{AgNO}_3$  and 50  $\mu\text{L}$  of 100-mM AA were added simultaneously under vigorous stirring. After 1 min, 20  $\mu\text{L}$  of 2-mM mPEG-SH was added and the solution was stirred for 30 min. The nanostars were then collected via centrifugation at 8,500  $\times g$ , washed thrice in water, and resuspended in 10 mL of DDI water.

Modifications of this procedure were made to create 10 variations of nanostars toward optimizing the morphology for enhance protrusions. These modifications were halving or doubling the amounts of the following: Ag nanoseeds, HCl,  $\text{HAuCl}_4$ ,  $\text{AgNO}_3$ , and AA. Each modification was made noncongruent with other modifications, with Table 1 outlining the chemicals utilized for each sample.

## 2.4 Transmission Electron Microscopy (TEM) Grid Preparation

Transmission electron microscopy (TEM) was used to analyze the structural properties of the nanostars. TEM grids were prepared with copper oxide (CuO<sub>2</sub>)–Au–Ag nanostars and Au–Ag nanostars. A 3-μL drop of the Au–Ag nanostars solution was placed on the TEM grid. The water was allowed to slowly evaporate at room temperature. A drop of the CuO<sub>2</sub>–Au–Ag-nanostars solution was placed on the TEM grid. The ethanol was allowed to slowly evaporate at room temperature. Structural characterization was obtained by TEM on a Jeol 2100 (Peabody, Massachusetts) at 200 KeV.

## 2.5 Single Particles SERS Synthesis

Two sets of AuNSs were synthesized with rhodamine 6g (Rh6G) for Raman analysis. A total of 50μl of 0.1-mM Rh6G was added to the samples at select points in the synthesis procedure to isolate the Raman tag into specified locations within the particle.

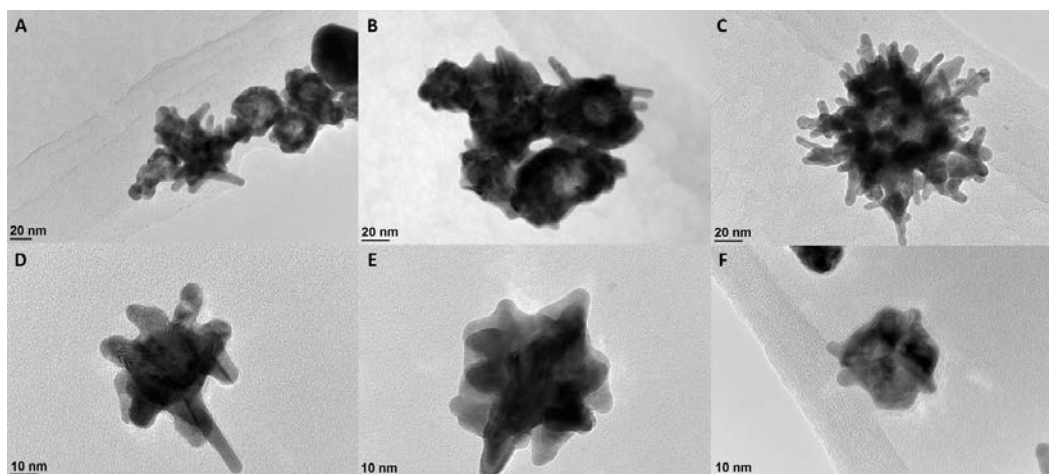
## 3. Results

### 3.1 Morphology Optimization

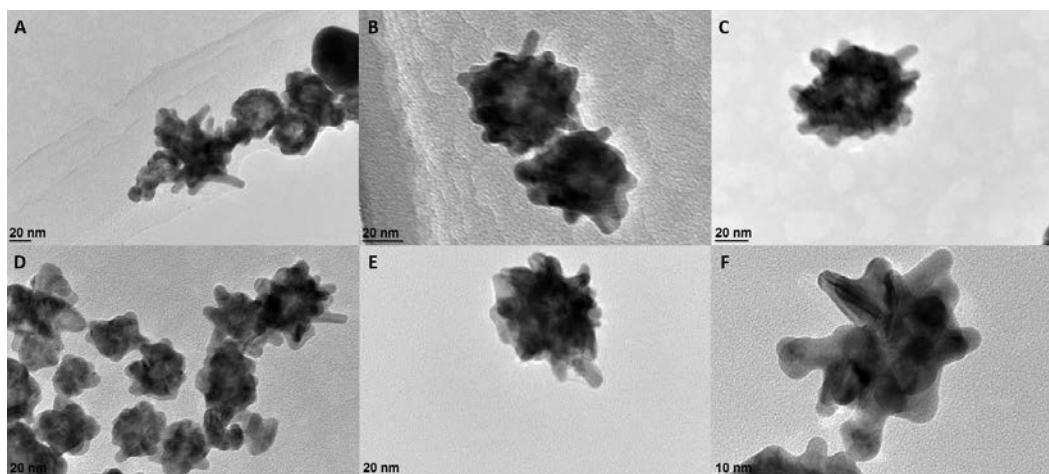
Alterations to the selected parameters described in Table 1 produced the AuNSs shown in the TEM images of Figs. 1 and 2. Initial image analysis demonstrates an enhancement of the star tips' density when the HCl concentration was doubled versus control. Additionally, an increased symmetric formation correlates with an increase in HAuCl<sub>4</sub> concentration. The same symmetric formation was also noted when the ascorbic-acid concentration was halved. Furthermore, halving the concentration of AgNO<sub>3</sub> produced a higher degree of star tips but not to the degree as seen when the HCl was doubled.

**Table 1 Reactants used for the preparation of sample variants, with yellow-highlighted regions corresponding to key alteration from control**

|                           | Control | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 |
|---------------------------|---------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| Ag NPs                    | 0.75 mL | 0.375 mL | 1.5 mL   | 0.75 mL  | 0.75 mL  | 0.75 mL  | 0.75 mL  | 0.75 mL  | 0.75 mL  | 0.75 mL  | 0.75 mL   |
| DDI                       | 9 mL    | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL     | 9 mL      |
| 0.1 M HCl                 | 7.5 μL  | 7.5 μL   | 7.5 μL   | 3.75 μL  | 15 μL    | 7.5 μL   | 7.5 μL   | 7.5 μL   | 7.5 μL   | 7.5 μL   | 7.5 μL    |
| 2.5 mM HAuCl <sub>4</sub> | 1 mL    | 1 mL     | 1 mL     | 1 mL     | 1 mL     | 0.5 mL   | 2 mL     | 1 mL     | 1 mL     | 1 mL     | 1 mL      |
| 100 mM AA                 | 50 μL   | 50 μL    | 50 μL    | 50 μL    | 50 μL    | 50 μL    | 50 μL    | 25 μL    | 100 μL   | 50 μL    | 50 μL     |
| 10 mM AgNO <sub>3</sub>   | 60 μL   | 60 μL    | 60 μL    | 60 μL    | 60 μL    | 60 μL    | 60 μL    | 60 μL    | 60 μL    | 30 μL    | 120 μL    |
| 2 mM mPEG-SH              | 20 μL   | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL    | 20 μL     |

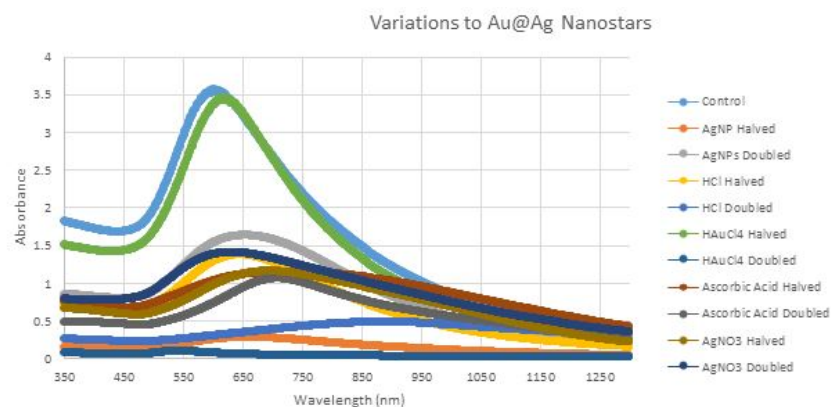


**Fig. 1** With A) as unaltered control, TEM images of synthesized AuNS resulting from test-reaction conditions focused on *doubled* concentrations of B) Ag nanoparticles, C) 0.1-M HCl, D) 2.5-mM HAuCL4, E) 100-mM ascorbic acid, and F) 10-mM AgNO3

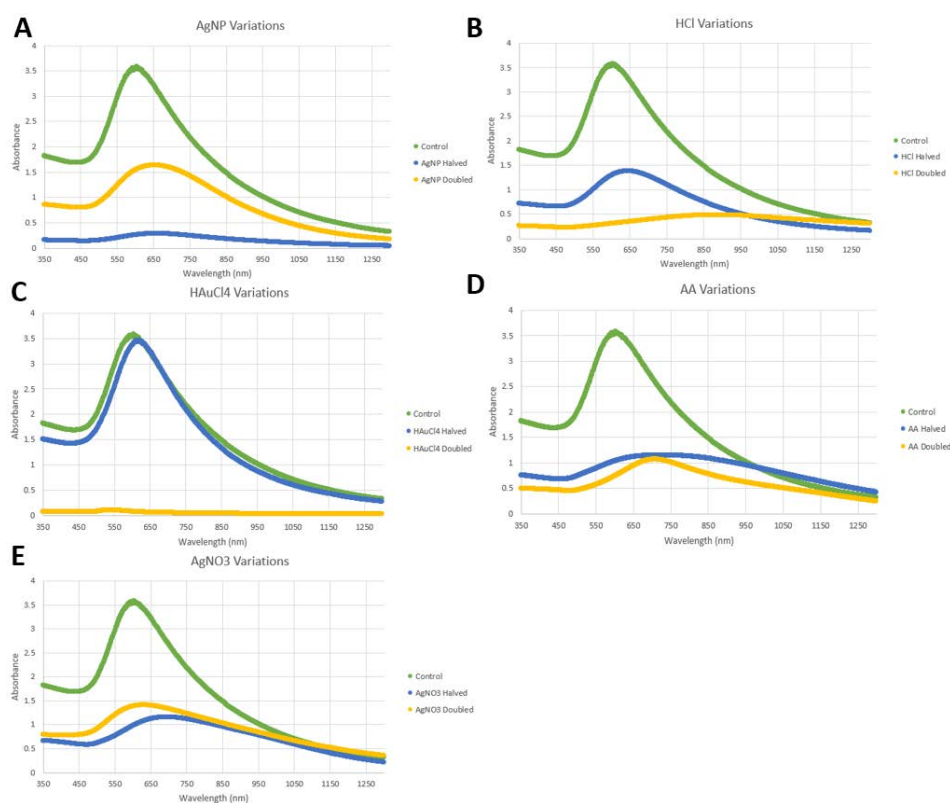


**Fig. 2** With A) as unaltered control, TEM images of synthesized AuNS resulting from test-reaction conditions focused on *halved* concentrations of B) Ag nanoparticles, C) 0.1-M HCl, D) 2.5-mM HAuCL4, E) 100-mM ascorbic acid, and F) 10-mM AgNO3

To analyze the impact of morphology on the resulting plasmonic absorption properties, UV–Vis spectroscopy was measured from 350 nm to 1300 nm as shown in Fig. 3. Figure 4 isolates the absorbance properties of each altered chemical species with respect to the control. The control sample shows a saturation peak of 604 nm and a normalized range from 534 nm to 705 nm.



**Fig. 3 Overall UV-Vis absorption spectra of prepared AuNS samples**



**Fig. 4 Isolated UV-Vis absorption with targeted synthesis-parameter adjustments of A) AgNP, B) 0.1-M HCl, C), 2.5-mM HAuCl<sub>4</sub>, D) 100-mM AA, and E) 10-mM AgNO<sub>3</sub>; halved parameters are blue, doubled parameters are yellow, and green is control**

The normalized ranges are provided in Table 2 with the samples' names matching those in Table 1. It was noted the majority of the samples had the same wavelength range as those of the control yet the absorbance levels were reduced, correlating to a lower concentration of plasmonic materials. A comparison with the TEM images in Figs. 1 and 2 shows a greater dispersity of nanostars with defined tips than those

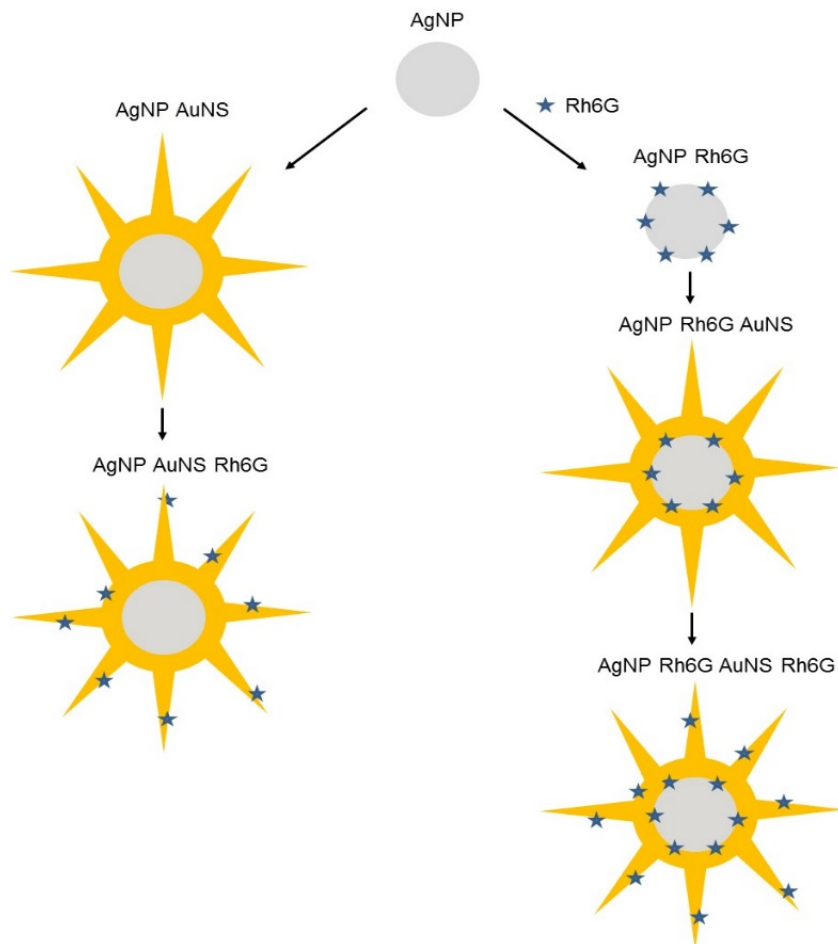
of the control. In conjunction with the visual analysis from the TEM, it can be concluded the number of tips shifts the absorbance range with the enhanced star-tip density.

**Table 2 Normalized resonance peaks and absorption range of prepared samples; sample (S) names correspond with the solution variation in Table 1**

| Sample  | Lower Wavelegth (nm) | Saturation Peak (nm) | Upper Wavelength (nm) | Wavelength Range (nm) |
|---------|----------------------|----------------------|-----------------------|-----------------------|
| Control | 534                  | 604                  | 705                   | 171                   |
| S1      | 552                  | 658                  | 797                   | 245                   |
| S2      | 547                  | 653                  | 801                   | 254                   |
| S3      | 552                  | 644                  | 772                   | 220                   |
| S4      | 647                  | 881                  | 1187                  | 540                   |
| S5      | 545                  | 611                  | 719                   | 174                   |
| S6      | 509                  | 540                  | 566                   | 57                    |
| S7      | 558                  | 728                  | 970                   | 412                   |
| S8      | 604                  | 707                  | 860                   | 256                   |
| S9      | 573                  | 694                  | 899                   | 326                   |
| S10     | 530                  | 633                  | 820                   | 290                   |

### 3.2 Single-Particle SERS

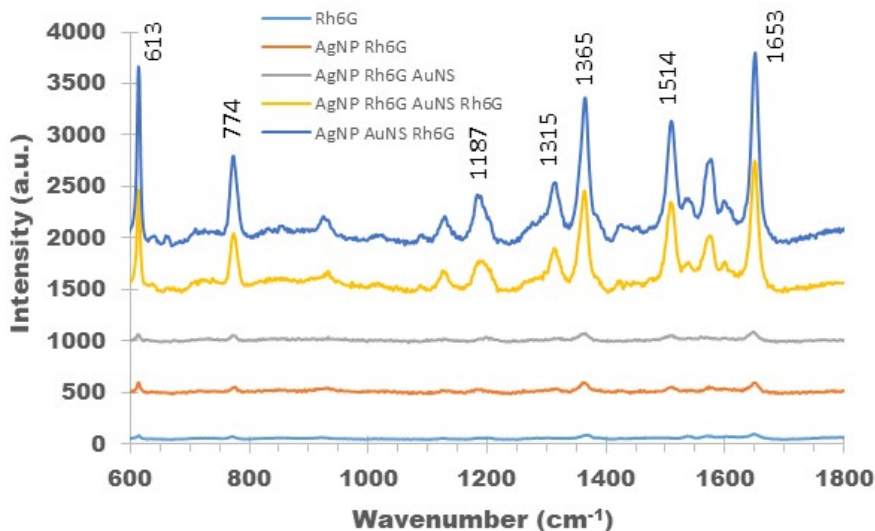
To localize the regions of maximal plasmonic field strength within the multilayered nanostar structure, a plasmonically enhanced sensitizer was integrated at specific stages of the material synthesis. An Rh6G was used as the sensitizer due to its previously demonstrated utility as a SERS probe. As shown in Fig. 5, the Rh6G molecule was adsorbed with four distinct configurations to isolate plasmonic strength at the AgNP surface, AgNP–AuNS interface, AuNS protrusions, and combined interface/protrusions. With these configurations the Raman enhancement can be isolated to specific regions within the hybrid particle to determine if the AgNP core, Ag–Au interface, or AuNS protrusions yield the strongest plasmon field intensities.



**Fig. 5 Schematic of synthesis steps to create single-particle SERS enhancement**

With the hybridized particles prepared as described in Fig. 5, Raman analysis was performed to analyze the Rh6G SERS signal on each construct. As shown in Fig. 6, a marked difference in signal intensities is evident. With the Rh6G control, this Raman signal is from a concentrated deposition of the reporter molecule whereas the presence of Rh6G hybridized onto the nanoparticle hybrids will be of substantially lower concentration. All hybridized nanoparticles were prepared to the same concentration for Raman analysis. Although the Rh6G control is measured from a higher concentration of reporters, the signal enhancement resulting from the AuNS is clear. Compared to the Rh6G control, AuNS structures with Rh6G absorbed to the protrusions resulted in an 18-fold signal enhancement. The samples attaching Rh6G at the AgNP surface and AgNP–AuNS interface demonstrated no clear enhancement above control, although SERS activity cannot be ruled out since the Rh6G concentration is lower in the hybridized samples. Comparing the two samples, which adhered Rh6G at the nanostar protrusions, it is interesting to note the addition of Rh6G at the AuNP–AuNS interface reduced the subsequent SERS performance, reducing the signal enhancement to 12-fold over control. It is likely

the presence of Rh6G on the AgNP surface prior to AuNS growth hindered subsequent star formation, limiting subsequent SERS activity. This likelihood notwithstanding, the results demonstrate the primary region on the AuNS construct for enhanced plasmon field strength is associated with the gold protrusions from the particle core.



**Fig. 6** Raman signal generated from Rh6G in control state and when attached in specified regions of AgNP–AuNS core-shell particle

## 4. Conclusions

In this work we analyzed the impact of each chemical component involved in AuNS synthesis on the particles' final morphology. By isolating the individual reactants and varying their respective concentrations to 0.5 and 2 times the molar concentrations utilized in standard protocols, key synthesis variables were identified. In particular, it was found the morphology of the nanostars can be directly altered with slight variations in the amount of AgNO<sub>3</sub> and HCl used. An increase to the number of tips was achieved by either reducing the AgNO<sub>3</sub> or providing an excess of HCl in the reaction. It was also found that amount of HAuCl<sub>4</sub> could hinder nanostar formation when applied in excess of the noted standard conditions. Utilizing the produced AuNS particles, identification of the particle regions associated with maximal plasmonic activity was achieved. Incorporating the Rh6G Raman tag on the AuNS protrusions yielded an 18-fold increase in Raman signal intensity over control and when Rh6G was on the AgNP core and Ag–Au interface. Therefore, optimizing the synthesis procedure to allow precise control over the AuNS-protrusion features is a critical step toward optimizing AuNS particles toward select plasmonic applications.

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## List of Symbols, Acronyms, and Abbreviations

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|                    |                                          |
|--------------------|------------------------------------------|
| AA                 | ascorbic acid                            |
| Ag                 | silver                                   |
| AgNO <sub>3</sub>  | silver nitrate                           |
| AgNP               | silver nanoplate                         |
| Au                 | gold                                     |
| AuNS               | gold nanostar                            |
| CuO <sub>2</sub>   | copper oxide                             |
| DDI                | distilled deionized                      |
| EM                 | electromagnetic                          |
| HAuCl <sub>4</sub> | chloroauric acid                         |
| HCl                | hydrochloric acid                        |
| mPEG-SH            | poly(ethylene glycol) methyl ether thiol |
| Na-Cit             | sodium citrate                           |
| NaBH <sub>4</sub>  | sodium borohydride                       |
| Rh6G               | rhodamine 6G                             |
| S                  | sample                                   |
| SERS               | surface enhanced Raman spectroscopy      |
| SPR                | surface plasmon resonance                |
| TEM                | transmission electron microscope         |
| UV                 | ultraviolet                              |
| Vis                | visible                                  |

1 DEFENSE TECHNICAL  
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2 DIR ARL  
(PDF) IMAL HRA  
RECORDS MGMT  
RDRL DCL  
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1 GOVT PRINTG OFC  
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4 ARL  
(PDF) RDRL WMM A  
J SANDS  
RDRL WMM G  
M GRIEP  
J LENHART  
T LI