

Name: Peer Review Information for "Abnormally Weak Surface-Enhanced Raman Scattering Activity of Tip-Rich Au Nanostars: The Role of Interfacial Defects"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The authors have successfully demonstrated the low SERS activity of defect-rich Au nanostars. If this is the case, there is no doubt that it states something very physicochemically important. Indeed, TEM measurements and electromagnetic simulations show crystal defects and the resulting changes in near-field intensities, respectively. However, the reviewer considers that it should be a little more careful in drawing conclusions from these experimental results. First, it is necessary to align the plasmon resonance wavelengths of the gold nanoparticles and the nanostars. As the authors also know, the complex permittivity of gold is highly dependent on wavelength. 1) The authors must show the readers a matched spectrum of their resonant wavelengths, then measure the SERS and compare the two conditions. 2) Subsequently, ultrafast spectroscopy should be used to measure the plasmon phase relaxation dynamics to show that the T_2 of the nanostar structure is actually shorter than the T_2 of the gold nanoparticles. 2)' If the measurement of 2) is difficult, it is necessary to measure each near-field spectrum, have the same resonance wavelength, and estimate and compare T_2 from the width of the near-field spectrum.

Reviewer: 2

Comments to the Author

The manuscript by Yujing et al describes the synthesis of Au nanostars with defects and show how the presence of crystallographic defect influences the plasmonics and SERS properties of the nanostructure.

I find that the topic of the manuscript fairly unique because the manuscript describes the "negative result" providing new physical insight into the problem, rather than show-casing the high enhancement factors and practical applications of metallic nanostructures. Although the plasmon damping by surface roughness or by adsorbates (chemical interface damping) have been extensively studied, the role of

interfacial defect (twin boundaries and others) has not been studied. I think that this point alone deserves scientific attention, although I do find several weak points of the manuscript (see below).

I thus recommend the manuscript to be published to JPCL, provided the authors could revise or improve the following aspects of the work:

1. page 3, lines 14-17: "photo-electron resonance-amplified local electromagnetic fields" I don't understand what this terminology is actually referring to. This term needs clarification.
2. The authors claim that the enhanced SERS activity of nanostars upon thermal annealing is caused by the removal of defects (Fig. 5). If this were true, the authors should be able to recover sharp LSP-resonance as well (approaching the simulated spectra shown Fig. 4a, (I)). Could the authors measure the extinction spectra of the annealed nanostars?
3. The structureless extinction spectrum (II in Fig 4a) may appear from the heavily damped nanostars, but it could also arise from the large dispersity of the nanostars. Could the authors measure the dark-field scattering spectra of individual nanostars to confirm their claim?
4. As far as the presented data is concerned, it appears that chemical-interface damping (CID) by ligands, not by the defect-induced damping may also offer an alternative explanation. In other words, if the chemical ligands on original nanostars were causing significant damping, and the annealing removes most of the ligands, it may explain what is observed. Could the authors provide the counter-argument on this possibility?

Author's Response to Peer Review Comments:

Dear Prof. Editor,

Thank you for promoting the improvement of our work. We have done additional experiments and made the corresponding revisions of our manuscript (Manuscript ID: jz-2021-040887), according to your and the two reviewer's comments and requirements. The corrections are marked in red in the new version. Please find the attached revised manuscript together with two "Replies to Reviewers" (in the next pages)

Thank you for your attention!

With best regards!

Yours sincerely,

Haoming Bao

Replies to Reviewer #1

Dear Referee,

Thank you for your reviewing our manuscript and comments. We have done additional experiments and made the corresponding revisions, according to your and another referee's suggestions, as well as the editorial requirements. The corrections are marked in red color in the revised version. Here there are some replies as follows.

Comment 1: The authors must show the readers a matched spectrum of their resonant wavelengths, then measure the SERS and compare the two conditions.

Response: Thank you! We have made some relevant attempts via adjusting the size and other structural parameters of the NPs and NSs. It is difficult to align the plasmon resonance wavelengths of the Au nanoparticles (NPs) and the nanostars (NSs) to the same position. Of course, if extremely decrease the NS tip length to a very small value, the two wavelengths are expected to be very close. However, the defect in the Au NSs is also greatly reduced, and NSs evolve to NPs in structure, losing the significance of the comparison. Accordingly, the performance comparison of the NSs and NPs at various measurement conditions (including different excitation wavelengths) could be an alternative method to prove the weak SERS activity of these NSs. The data show the NSs achieve much weaker signals than the NPs under all the conditions, as shown in Fig.2b. However, the LSPR peak of the NSs covers the wavelength of 785 nm while the NPs do not, and this suggests that the NSs should be more suitable for being excited at 785 nm than the NPs. Therefore, it is reasonable to believe that the NSs have weak SERS activity even though at relatively matched excitation wavelengths.

We also preformed some experiments for confirming this. We have tried to obtain the Au NSs with shorter tips by changing the addition amount of the induced ions during preparation. Fig.R1a shows the morphology of the Au NSs with much shorter tips. The corresponding SPR peak was adjusted to 790 nm (this is almost the smallest SPR peak of NSs we can achieve), while the 120 nm spherical Au NPs show the much higher SPR around 580 nm (Fig.R1 b). Both colloidal solutions of Au NSs and Au NPs are the same in particle number and mass.

For estimating their SERS activity, we dropped their colloidal solutions separately on a Si wafer to form ~5 μm thick NPs-built film and NSs-built film. The Raman spectra were measured after dropping 10 μL of 10-5M 4-nitrobenzenethiol (4-NTP) solution on these two films and drying under 785 nm excitations. Fig.R1c shows the corresponding Raman spectra. The Raman signals from the newly-prepared Au NSs with shorter tips are still

much weaker than those from the Au NPs even at the optimal excitation wavelength.

All of these data indicate the abnormally weak SERS activity of the Au NSs.

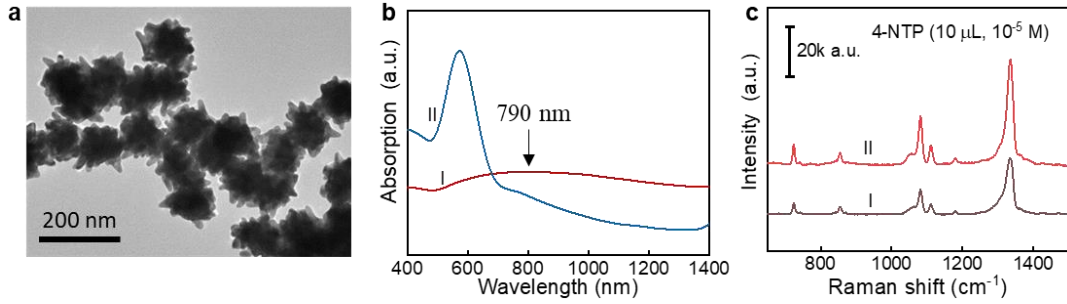


Fig.R1 (a): TEM image of the newly-prepared NSs. (b): The extinction spectra of the colloidal solutions for the newly-prepared NSs (I) and the 120 nm spherical Au NPs (II). Both colloidal solutions are the same in particle number and mass. (c): The Raman spectra measured of the NSs-built film (I) and NPs-built film (II) after dropping 10 μL of 10^{-5}M 4-NTP solution on them and drying, under 785 nm excitations.

To better demonstrate these, we have made corresponding rearrangements and additional discussion in the revised version (see the last paragraph in page 6, Fig.3a, and Fig.S4).

Comment 2: Subsequently, ultrafast spectroscopy should be used to measure the plasmon phase relaxation dynamics to show that the T2 of the nanostar structure is actually shorter than the T2 of the gold nanoparticles. 2)’ If the measurement of 2) is difficult, it is necessary to measure each near-field spectrum, have the same resonance wavelength, and estimate and compare T2 from the width of the near-field spectrum.

Response: Thank you for this suggestion! It is not convenient for us to perform the ultrafast spectroscopy and the near-field spectrum measurement. Here, we have performed alternative dark-field scattering spectra measurements. The data show that the NS has a wide transverse mode centered at about 600 nm and a longitudinal mode centered at about 1000 nm, and the NP only has one sharp transverse mode peak at 620 nm, as shown by Fig. R2a. Because the width of this mode can reflect the dephasing time and damping (Sönnichsen, C. et al. *Phys. Rev. Lett.* 2002, 88, 077402), we compared their widths of the transverse modes, and the data show the Au NS has a much wider transverse mode peak than the Au NP (Fig.R2b). This indicates the heavy damping of these Au NSs.

According to the equation of $T2=2\hbar/D$ (Sönnichsen, C. et al. *Phys. Rev. Lett.* 2002, 88, 077402), where $T2$ is the dephasing time, $\hbar$ is the reduced Planck constant, and D is the width of the resonance peak in energy (full width at half maximum or FWHM), the $T2$ values of the NP and NS are estimated as about 3.2 and 1.2 fs, respectively. Considering

the rich defects in the Au NSs, we think this improved total damping should be mainly attributed to the increase of bulk damping. Because the original bulk damping usually has a very limited contribution to the total damping, reasonably, the bulk damping has been improved by dozens of times.

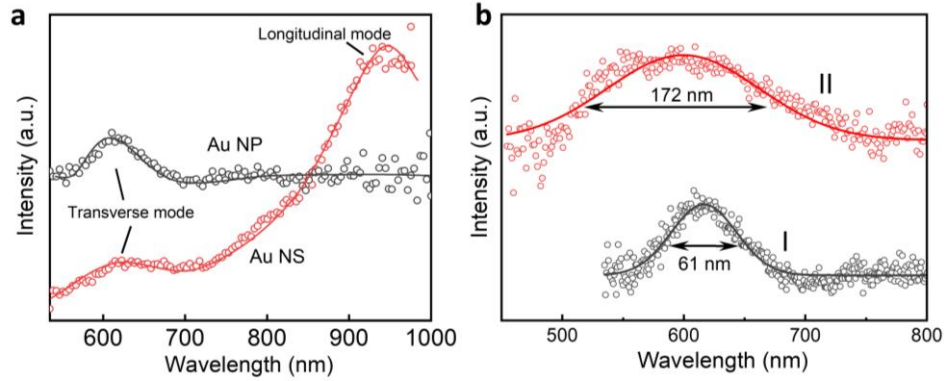


Fig.R2 (a) Typical dark-field scattering spectra of the individual Au NS and NP at a wide range from 520 to 1000 nm. (b) Dark-field scattering spectra (around the transverse mode) of the individual Au NP (I) and the individual Au NS (II).

The corresponding additions have been made in the revised version (see the second paragraph in page 7, Fig.3b, and Fig.S5).

Finally, the authors sincerely thank you and appreciate you for your very helpful comments and suggestions. It is your comments and suggestions that our manuscript has been much improved.

Best regards

Haoming Bao

Replies to Reviewer #2

Dear Referee,

Thank you for your reviewing our manuscript and comments. We have done additional experiments and made the corresponding revisions, according to your and another referee's suggestions, as well as the editorial requirements. The corrections are marked in red color in the revised version. Here there are some replies as follows.

Comment 1: page 3, lines 14-17:"photo-electron resonance-amplified local electromagnetic fields" I don't understand what this terminology is actually referring to. This term needs clarification.

Response: Thank you! We have noticed that we had used a vague expression here. What we wanted to express was: light-excited localized plasmon resonance (LSPR), which amplifies the electric fields near the metal surfaces.

The corresponding clarification has been made in the new version (see the first paragraph in Page 3).

Comment 2: The authors claim that the enhanced SERS activity of nanostars upon thermal annealing is caused by the removal of defects (Fig.5). If this were true, the authors should be able to recover sharp LSP-resonance as well (approaching the simulated spectra shown Fig. 4a, (I)). Could the authors measure the extinction spectra of the annealed nanostars?

Response: Thank you! Since annealing can induce morphological change and agglomeration of Au NSs especially at high temperature, the extinction spectra of the annealed NSs can't be recovered to the sharp LSP-resonance.

Nonetheless, we have tried to measure the extinction spectra of our originally-prepared NSs annealed at the relatively low temperature at which annealing would remove partial point defects but not induce significant morphologic change. The NSs-build film, which was prepared by dropping the colloidal solution on a Si wafer and drying, was firstly annealed at a relatively low temperature for 4 h and then ultrasonically vibrated in water to form a NSs' colloidal solution. The absorbance spectra were measured for the obtained NSs' colloidal solutions as shown in Fig.R1. The increase of the annealing temperature indeed leads to the more obvious LSPR of the NSs, mainly due to the reduction of the point defects. These data greatly support the thermal-induced defect removal, which explains the improvement of NSs' SERS activity.

The corresponding additions and discussion have been made in the new version (see

the last paragraph in Page 10 and Fig.S9).

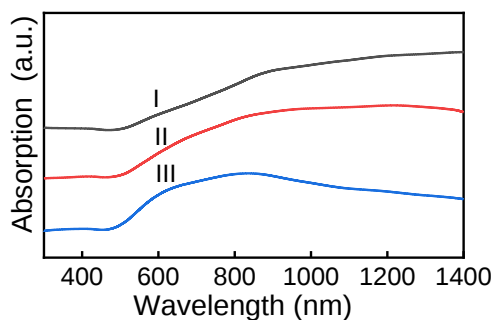


Fig.R1 Extinction spectra of our originally-prepared NSs after annealing at (I) 100 °C, (II) 200 °C and (III) 300 °C for 4h.

Comment 3: The structureless extinction spectrum (II in Fig.4a) may appear from the heavily damped nanostars, but it could also arise from the large dispersity of the nanostars. Could the authors measure the dark-field scattering spectra of individual nanostars to confirm their claim?

Response: Thank you for this good suggestion! We have measured the dark-field scattering spectra of an individual NS as well as an individual NP for comparison. The data show the NS has a wide transverse mode centered at about 620 nm and a longitudinal mode centered at about 1000 nm, and the NP only has one sharp transverse mode peak at 620 nm, as shown by Fig.R2a. Because the width of the mode can reflect the damping (Sönnichsen, C. et al. *Physical Review Letters* 2002, 88, 077402.), we compared their widths of the transverse modes, and the data show the Au NS has a much wider transverse mode peak than the Au NP, (about 172 nm versus 61 nm), as shown in Fig.R2b. These indicate the very heavy damping of our Au NSs, and we think it should be the main reason for the broad extinction peak.

Considering the homogenous structure, size, and morphology of these NSs, we think that the dispersity of the NSs could be partly responsible for the broad extinction peak in the spectrum, but could have very limited contributions. Although we cannot give the contribution proportions from these two aspects, it is reasonable to claim that the broad extinction peak could suggest the heavy damping of the NSs.

The corresponding additions have been made in the revised version (see the second paragraph in page 7, Fig.3b, and Fig.S5).

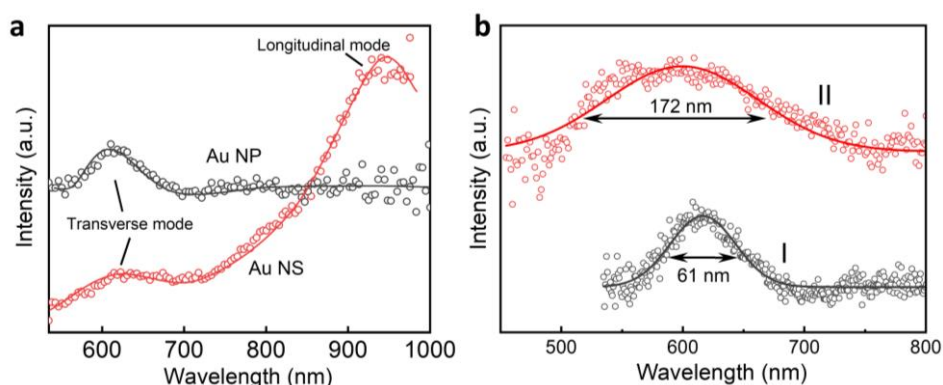


Fig.R2 (a) Typical dark-field scattering spectra of the individual Au NS and NP at a wide range from 520 to 1000 nm. (b) Dark-field scattering spectra (around the transverse mode) of the individual Au NP (I) and the individual Au NS (II).

Comment 4: As far as the presented data is concerned, it appears that chemical-interface damping (CID) by ligands, not by the defect-induced damping may also offer an alternative explanation. In other words, if the chemical ligands on original nanostars were causing significant damping, and the annealing removes most of the ligands, it may explain what is observed. Could the authors provide the counter-argument on this possibility?

Response: Thank you! We have performed additional experiments and eliminated this possibility of chemical-interface damping (CID). The main experimental evidence is as follows:

Direct Raman spectra. The tris (hydroxymethyl) aminomethane molecules were the mainly used organic ligands in the Au NS fabrication. They can be easily removed via the subsequent centrifugations due to their weak combination with Au (electrostatic interactions between N and Au atoms). More importantly, the Raman spectrum of the NSs-film shows no obvious peaks (Fig.R3a), indicating the absence or very low content of any surface ligands.

Oxygen plasma cleaning. Further, we used the oxygen plasma to clean a dry NSs film which has been dropped with 10 uL of Tris solutions (0.1 M) and dried naturally. The Raman spectra suggest that the tris molecules can be removed with a cleaning duration of about 90 min (Fig.R3b). On this basis, we cleaned the originally-prepared NSs-film with oxygen plasma for different durations and then estimated the Raman activities via measuring the SERS spectra after dropping of 4-NTP solution (10 μ L, 10^{-5} M) and drying. The data show that these films achieve similar signal intensities, even though they have experienced different cleaning durations (Fig.R3c), suggesting the originally-prepared NSs have no or ignorable CID.

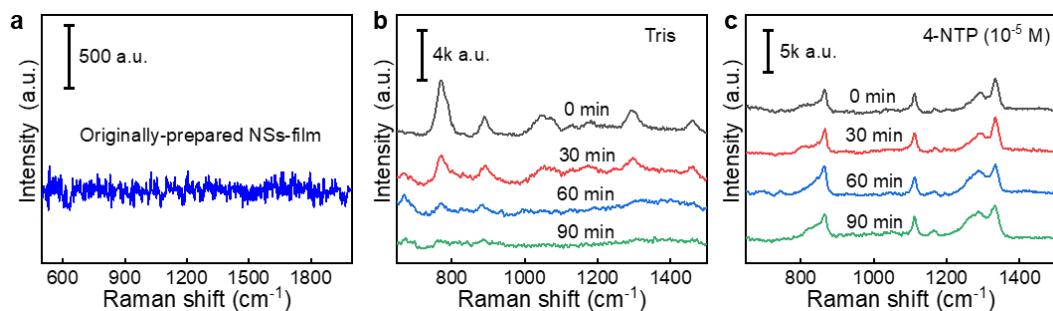


Fig.R3 (a) Raman spectrum of the originally-prepared NSs-film. (b) Raman spectra of the tris-dropped Au NSs film after experienced oxygen plasma cleaning for different durations. (c) The Raman spectra of the originally-prepared NSs-film after experienced different plasma cleaning for durations and then dropping 10 μL of 10^{-5} M 4-NTP solution and drying. All these measurements were performed under the excitation of 785 nm.

The corresponding discussion and revisions have been made in the new version (see the last paragraph in Page 7, Fig.S6, and section 3 in Supporting Information).

Finally, the authors sincerely thank you and appreciate you for your very helpful comments and suggestions. It is your comments and suggestions that our manuscript has been much improved.

Best regards

Haoming Bao
