Optical properties of segmented Ag–Au wire at single particle level studied with a home-built micro-spectrometer

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Abstract
Nanomaterials having hetero-metallic junctions are being explored for sensing, catalytic, and biomedical applications. Insight into the bimetallic junction at nanoscale is important from both fundamental and application perspectives. In this study, we synthesized segmented Au–Ag wire by sequentially electroplating Au and Ag in cylindrical pores in anodic alumina membrane filters. We probed the one photon, two photon, and second harmonic signal in Au–Ag wire at single particle level by focusing laser beam to a diffraction limited spot using a home-built sample scanning type micro-spectrometer. When exciting the Au–Ag junctions into the mid-UV range using two-photon excitation, we observed two luminescence peaks at 455 and 520 nm, respectively, possibly because of the surface plasmon resonances supported by the sharp boundary and granular nanostructures on the Au–Ag interface. Interestingly, we also observed intense second harmonic generation (SHG) signal from the junction with a yield more than two orders of magnitude higher than that from the Au tips. The SHG intensity as a function of excitation wavelength showed a similar trend to the two-photon excited luminescence emission spectrum, indicating that the SHG signal was enhanced in the presence of optical resonances. The observation of enhanced radiative properties of the bimetallic junction in the suggested that the Au–Ag wire may serve as an excellent imaging probe or single particle sensors.

KEYWORDS
hetero-metallic nanowires, second harmonic generation, surface plasmon resonance, two-photon excitation luminescence, up-conversion luminescence

1 | INTRODUCTION

Noble metal nanoparticles are gaining great interests in technological applications because of their unique opto-electronic properties. As compared to bulk counterparts, noble metallic nanoparticles and their assemblies support surface plasmon resonances (SPR) that incite unusual linear and non-linear optical properties. In addition, these noble metal nanoparticles have excellent photo-stability, low cytotoxicity, and can be readily modified with biomolecules to achieve molecular
specificity. For these reasons, they are developed into a variety of optical imaging labels and used as single particle probes in sensing,1–3 understanding biological processes cellular and sub-cellular levels,4–7 and in targeted drug delivery.8,9

The SPR in noble metal nanoparticle is dependent on the particle size, shape, and chemical composition. More importantly, the SPR wavelength and spectral feature are sensitive to local environments.10 Because of these unique properties, metallic nanoparticles and their assemblies are being used in micro-environmental sensing.11–13 For example, by monitoring linear Rayleigh scattering, the small changes of the refractive index of the surrounding medium caused by biomolecules binding can be detected around individual or coupled plasmonic structures.14–16 Xiong et al.,17 demonstrated that using Au–Ag core–shell nanoparticles as probes, they can map the concentration of a signaling agent, H₂S, in living cells based on Ag₂S formation-induced spectral shifts of the nanoprobe. In other examples, Rayleigh scattering circular dichroism enhanced by Au nanoparticle SPR was used to probe chiral biomolecules or chiral structures in local environment.18–20

It has been shown that second harmonic generation (SHG) based sensing can be more sensitive to environments than sensing in the linear optical regime for spherical Au nanoparticles.21,22 SHG is a non-linear process where two photons of fundamental frequency ω are converted to one photon at the second harmonic frequency 2ω.23 Studies show that SHG can be generated from a variety of individual metallic nanoparticles and their assemblies including nanospheres and nanorods,21,24,25 silica-coated Au nanoparticles,26,27 nanotips,28 Au–Ag clusters,29 Au–Ag core–shell30 and alloyed particles,31 nanocups,32 nanotriangles,33 curved nanowires,34 and so forth. From these studies, it is demonstrated that SHG intensity profile when excited at different wavelengths closely resembles the corresponding SPR extinction spectra of the nanostructures, suggesting that SHG is enhanced when SPR is resonantly excited.25,28 The search for nano-scaled materials, for example, pure or hybrid small particles, particle assemblies or composites that give strong non-linear responses is an active area of research.14,35–37

The optical properties of pure Au or Ag nanowires have been studied extensively.38–41 Individual nanowires showed multipolar transverse and longitudinal SPR modes, which are sensitive to the diameter and the aspect ratio of the nanowire. For capacitively or conductively coupled nanowire dimers, it was found that the longitudinal multipole modes of coupled homodimers split into bonding and anti-bonding modes.42–45 However, there is little study on optical properties in segmented bimetallic nanowires. Especilly, there is yet no consensus on how bimetallic interfaces contribute to surface plasmon generation or propagation in bimetallic nanoparticles or nanowires. For example, for Au–Ag core–shell type of bimetallic nanoparticles, two collective electron oscillations were observed: one at ~400 nm and the other at ~520 nm, similar to the characteristic Ag and Au nanosphere SPRs, respectively.46–49 Increasing the Ag wall thickness damps the characteristic Au SPR, possibly indicating that the SPRs in a core–shell particle are originated from collective electron oscillations between outer surface of the shell metal, and between core–shell metallic interfaces, respectively.

It was reported that in interfaced hetero Au–Ag dimers, an unusually enhanced SPR mode in the spectral region of the characteristic Au SPR, as well as a charge transfer (CT) SPR between Au and Ag domains, can be observed.50 On the other hand, it was suggested that electron scattering between the Au–Ag interface is negligible in core–shell type of particles.51 A study on barcoded AgAuAg nanorod showed that the longitudinal SPR is insensitive to the relative composition of Ag and Au, which indicates that the collective electron oscillations are not significantly influenced by the Ag–Au interface.52 To our knowledge, a systematic study on the optical properties of Ag–Au nanowire at single particle level is not reported.

In this study, we synthesized Au–Ag nanowire (~200 nm × 11 μm) consisting of 11 Au and Ag segments. The nanowires were imaged by optical and electron microscopic techniques and their polarized single particle scattering spectra were collected. We also probed the one photon, two photon, and second harmonic signal at the various locations along the length of wire by focusing the laser beam to a diffraction limited spot using a home-built sample-scanning micro-spectrometer. Finally, the spectra collected at different locations were compared.

2 | MATERIALS AND METHODS

2.1 | Synthesis of segmented nanowires

Au–Ag striped nanowires were synthesized by sequential electro-deposition of Au and Ag into a mesoporous aluminum membrane according to the published procedures.53,54 The metal to be deposited was selected using different metal plating solutions and the length of the metal stripe was controlled by the total number of electrons passing through the electrode. Nanowires ending with Ag were capped with a Au cap to prevent acid etching of Ag during particle release in the next step. After electro-deposition of desired nanowires, the nanowires were released from the template membrane by first etching
with 33% HNO$_3$ for 1 min to remove Ag backing electrode, followed by immersing in 3 M NaOH for at least 30 min to dissolve the alumina membrane. For later use, the suspended nanowires were rinsed with ethanol three times, degassed and stored in ethanol in an air tight vial.

The scanning electron microscopic (SEM) and energy dispersive X-ray (EDX) images were measured by using a field emission SEM (JEOL JSM-6400F). A JEOL JEM-100 CXII transmission electron microscope (TEM) was used to measure the TEM images of the synthesized nanowires in which the samples were prepared by dropping 10 µL of particle solution onto carbon-coated copper grids and drying overnight.

### 2.2 Optical measurements

Single nanowires were deposited on Corning cover glasses and exposed to aqueous solution when their spectra measured. The luminescence spectra of individual nanowires were acquired using our home-built micro-spectroscopic and imaging system as described previously. A schematic of the optical setup and data collection scheme is provided in Figure 1(A), (B), respectively. The optical excitation wavelength required for this study was obtained from an air-cooled, continuous wave (CW) Ar ion laser (35-LAP-431, CVI/Melles Griot), a CW 592 nm fiber laser (VFLP-1000-592-OEM1, MPB Communications), a pulsed Ti-sapphire oscillator (80 MHz, 140 fs, 680–1050 nm, Coherent, Chameleon Ultra II), or a Ti-sapphire pumped OPO (80 MHZ, 140 fs, 550–650 nm, Mira PP automatic, Coherent). All laser beams were first expanded and then focused to a diffraction limited spot using a high numerical aperture objective (NA 1.4, oil). The laser power is specified in figure captions. The signal of interest was filtered using proper combinations of dichroic mirrors and band-pass/short-pass/long-pass filters (Figure 1(A)). The detection was from a micro-spectroscopic system that consists of a transmission grating (70 grooves/mm, Edmund Optics) and a CMOS camera (Hamamatsu ORCA 2.8). The spectrometer was calibrated using three different laser lines and the spectral resolution was estimated to be $\sim$ 5 nm. The acquired luminescence spectra were corrected for transmission grating and detector profiles using manufacturer reported data. The micro-spectral system can be operated simultaneously under the bright-field mode to find the particles and the laser beam in the field of view. The sample was mounted on a 3D piezo-stage (PI Nano, Physik Instrumente).

The scattering spectra were collected by toggling the micro-spectral system to the dark-field mode. The sample was illuminated with a white light lamp and the signal was collected with a dark field objective (NA = 0.7–1.25). The scattering spectra were corrected for lamp, grating, and the detector profiles using 100 nm silica particles.

![Experimental Scheme](image-url)

**FIGURE 1** Experimental Scheme. (A) Schematic of the optical setup. L = lens, DC-LP/SP = Dichroic-long-pass/short-pass filter, NF = Notch filter, LP/SP = long-pass/short-pass filter, TG = transmission grating, CCD = charge coupled device (camera). (B) Data collection scheme used in this study. A simple cartoon of nanowire with gold and silver segments coded yellow and gray is also shown.
3 | RESULTS AND DISCUSSION

3.1 | Electron and optical microscopic imaging

The SEM–EDX elemental images of the hetero-metallic nanowires are provided in Figure 2(A), (B). In the images, the gold and silver segments are clearly visible. As expected from the sequential electro-deposition experiment, the nanowire has a size of \( \sim 200 \text{nm} \times 11 \mu\text{m} \) and consisted of 11 Au and Ag segments, each with \( \sim 1.0 \mu\text{m} \) in length. We also measured the TEM images of Au–Ag junction and a Au tip of a nanowire (Figure 2(C), (D)). We found that the Au tip is generally flat, with visible nanostructures up to \( \sim 5 \text{nm} \) (Figure 2(D)). Note that under a TEM, Au and Ag were not readily distinguishable because of their high electron densities. We were unable to determine the smoothness of the junctions. However, it is reasonable to assume that the junctions have smoothness similar to that of the tips.

The Ag and Au segments can be identified in dark-field images under 460 nm light illumination. Figure 2(E) shows the dark-field image of nanowires coded as 0111010111, where 1 represents Ag and 0 represents Au segment with 1\( \mu \text{m} \) in length, respectively. In the images, the bright and dark regions along the length of the wire represent Ag and Au segments, respectively. The observed contrast is due to the difference in scattering efficiency of Au and Ag; that is scattering of silver being higher than that of gold. For completeness, the bright-field images of the nanowire are also reported in Figure 2(F). Here, the gold and silver segments are distinguished as darker and brighter regions, respectively. Again, the contrast arises due to scattering of silver being higher than that of gold.

![Figure 2](image_url)
3.2 | Scattering and one photon luminescence spectra

Figure 3(A) shows the UV–VIS spectrum of the nanowire solution in methanol. The overall extinction spectra showed a broad and structureless peak extending from visible to near IR region and no individual SPR band can be identified in the visible range. In small Au or Ag nanowires with a diameter of a few 10s of nanometers and a length of several times of the illumination wavelength, their extinction spectra are dominated by the transverse mode SPR and a sum of multipole resonances in the longitudinal direction. As the diameter of the nanowire increases and approaches the excitation wavelength, the transverse SP resonance shifts to the longer wavelength and broadens because of inhomogeneous polarization in a larger volume. Meanwhile, a series of multipoles along the transverse direction are excited. Similar phenomena can be observed in segmented nanowire suspensions resulting in a broad and structureless peak.

Similarly, light scattering from different metallic segments in individual Au–Ag nanowires also showed structureless spectra using white light illumination (Figure 3(B)). For Au segments, when the illumination was polarized parallel (P) to the nanowire, the scattering was completely structureless, with scattering efficiency increasing as the illumination wavelength increases. When the illumination was polarized vertical (V) to the nanowire, the scattering intensity became more intense. A large hump can be identified extending from 500 nm to beyond 700 nm. The broad, strong absorption is consistent with the SPRs from large spherical Au nanoparticles and should be originated from the transverse SPRs of the Au segment with a diameter of ∼200 nm. The Ag segments showed similar patterns for illuminations polarized parallel and vertical to the nanowire. The difference is that for the vertically polarized illumination, the absorption band of Ag
started from \(\sim 420\) nm and extended beyond \(700\) nm, which also should originate from the transverse mode Ag SPRs. For both polarized illuminations, Ag segments always showed higher scattering efficiency in the blue region (\(420–550\) nm). This is why Ag segments have higher intensity in the dark-field images when illuminated using blue light (\(460\) nm).

In the junction area, if diffuse light source is used, the scattering spectra can have contributions from neighboring Au and Ag segments, and the scattering from the neighboring Au and Ag segments could overwhelm subtle differences that may be present at the junction. A systematic study on the scattering spectra of junction region using nanowire of variable size, segment number and order remains to be explored.

Using a laser beam focused to the diffraction limited spot, we were able to measure the optical response at different locations on the segmented nanowire. When excited at \(488\) nm with a focused CW laser beam, Au and Ag segments showed different luminescence spectra. Figure 3(C) shows the single-photon luminescence spectra obtained by selectively exciting a Ag segment, a Au segment, a junction, and a Au tip of a segmented nanowire. The laser beam was polarized vertical to the nanowire. The luminescence of Au segments shows an emission peak at \(\sim 520\) nm irrespective of the excitation location within the Au segment, or different segments in the nanowire. The junction spectra showed slightly different contribution in the \(550–650\) nm range. When the laser beam was polarized vertical to the nanowire, the junction region shows a nearly identical emission spectrum with half of the intensity when the laser beam is polarized parallel (Figure 3(D)). This observation shows that the single-photon luminescence can have contribution from metallic nanostructures and has electric dipole origin.

Single-photon luminescence of bulk Au and Au nanoparticles has been extensively studied.\(^{56–59}\) In bulk Au, a weak emission peak at \(\sim 520\) nm can be observed when excited at \(488\) nm and it is attributed to the inter-band transitions of electrons from d orbital to sp orbitals. In spherical Au nanoparticles, the \(520\) nm luminescence is greatly enhanced. The enhanced luminescence in Au nanoparticles could be SPR emission\(^{57,59–61}\) or the inter-band transitions enhanced by the local electric field.\(^{62–65}\) Here, in the Au segments in the nanowire, the luminescence intensity was larger than that from bulk Au. The luminescence may also involve both mechanisms as that from gold nanoparticles.

Compared to the Au segments, Au tips showed a similar emission maximum at \(520\) nm, with more emission from \(550\) to \(600\) nm region. The total emission intensity was enhanced, possibly because of the SP resonances supported by the sharp corner and/or granular structures at the tips.

The luminescence of Ag segments showed a tail-like emission peak since the excitation wavelength (\(488\) nm) was longer than the inter-band transition or the characteristic Ag SPR.\(^{63,66}\) Similarly, the Ag segment luminescence may involve both mechanisms as that from gold segments. Most interesting were the Au–Ag junctions, which showed an emission maximum at \(520\) nm, resembling the Au segment luminescence (Figure 3(C)). Ag may also contribute to the total luminescence in the junction. However, the total luminescence intensity from the junction was more intense than that from either Au or Ag segments by a factor of \(\sim 2\), which showed the special property of the bimetallic junctions.

### 3.3 Up-conversion luminescence

To further investigate the luminescence properties of the hetero-metallic junctions in the blue region, we excited the nanowires into the mid-UV using two-photon excitation with a pulsed \(592\) nm femtosecond laser. To better understand the special property of the junctions, the laser beam was polarized parallel to the nanowire to minimize the effect of the transverse mode SPR. The two-photon excitation luminescence (TPEL) spectra for different regions of the segmented nanowires are in Figure 4(A). All Au and Ag segments and Au tips showed similar front tail-like peaks, as frequently reported in the literature for multi-photon excitation luminescence of Au or Ag nanostructures.\(^{51,63,65,67}\)

We showed that this front slope is also visible in up-conversion luminescence of Au nanoparticles when excited by a CW laser.\(^{55}\) The up-converted luminescence is associated with a phonon-assisted up-conversion process, possibly enhanced by SPR of gold nanoparticles. It has a second order dependence on laser power, so one cannot distinguish this phonon-assisted luminescence from two-photon excitation luminescence just judging from the laser power dependence. Here, in the Au and Ag segments and Au tips, the same up-conversion process may explain part of this front tail-like slope.

To confirm this, we focused a CW \(592\) nm laser beam onto different regions of the nanowires. The laser beam was polarized parallel to the nanowire. The luminescence spectra are shown in Figure 4(B). All Au and Ag, Au tips, and Au–Ag junctions showed this similar front-tailing spectrum. The quantum yield at the junctions was again enhanced by a factor of \(\sim 2\) as compared to segments. These observations possibly suggest that in TPEL, phonon-assisted up-conversion luminescence may contribute to the front tail-like slope in the TPEL emission significantly, especially at an emission wavelength close to the excitation wavelength.
Interestingly, the junctions showed a completely different TPEL spectrum: two weak emission peaks, at ~455 nm and 520 nm, respectively, can be identified on top of the front tail-like slope (Figure 4(A)). As compared to that of Au segments, the integrated luminescence intensity of Au–Ag junctions was ~3 times higher. The origin of the 455 nm and 520 nm peaks in the junctions in the TPEL spectra must be related to this unique Au–Ag interface. Although as aforementioned, we were unable to collect junction-specific, white light scattering profiles due to instrument limitation, the observed TPEL peaks appeared to be consistent with the expected SPR bands of Ag and Au nano-features. For small pure Au and Ag spherical nanoparticles, they show characteristic SPR peaks at 520 and 400 nm, respectively.68,69 Composite Au–Ag nanoparticles show much more complicated optical properties. For spherical Au–Ag alloy nanoparticles, for example, one sees a continuous shift of the SPR peak from Ag-SPR to Au-SPR as the fraction of Au increases.31 For Au–Ag core–shell spherical nanoparticles, there are two SPR bands: one resembles Au- and the other resembles Ag-nanosphere SP resonances.30 Here, for the Au–Ag interface in our segmented nanowires, the 520 nm and 455 nm peaks can be ascribed to the SP resonances from Au and Ag nanostructures on the interface, respectively. Indeed, the sharp boundary between Au and Ag, as well as the intercalated granule nanostructures on the interface, can support localized SPR modes. The 455 nm peak was red-shifted with respect to the characteristic Ag SPR and why this happens is still under investigation. A plausible reason is that Au atoms may mix into Ag lattice, causing the red shift of Ag SPR.31

To the best of our knowledge, this is the first time the unique local optical responses of a hetero-metallic interface within a long nanowire (aspect ratio ~55) to be reported: when using a monochromatic laser beam focused down to a diffraction limited spot on the junctions, two emission peaks can be observed, possibly representing SP resonances supported by the Au and Ag nanostructures on the interface. The SP resonances lead to the enhanced up- and down-conversion photoluminescence.

### 3.4 Second harmonic generation

When we shifted the femtosecond laser excitation wavelength from 592 nm to the near IR range, we can observe strong second harmonic signals in addition to TPEL in the visible wavelength range from the Au–Ag junctions. Figure 5(A) shows selected two-photon excitation spectra of Au–Ag junctions in a segmented nanowire using different near IR excitation wavelengths (850–970 nm). The laser beam was polarized parallel to the nanowire (or vertical to the interface). The sharp peaks in all spectra (curves a–e) were the SHG signals and the broad front tail-like peaks were from the two-photon excitation luminescence. The two emission bands at 455 and 520 nm, as observed with 592 nm pulsed excitation, are not...
FIGURE 5  Two-photon excitation luminescence and second harmonic generation spectra of a Au–Ag junction in a segmented nanowire. (A) TPEL and SHG spectra of a junction excited at 890, 910, 930, 950, and 970 nm, respectively (curves a–e). The spectrum for a Au tip excited at 890 nm is also shown (curve f). Laser power, pulse width and collection time were \( \sim 5 \text{ mW} \), 200 fs, and 0.2 s, respectively. All spectra are normalized according to the same square of laser power. (B) SHG intensity as a function of the fundamental (excitation) wavelength.

FIGURE 6  Second harmonic (SHG) and two-photon excitation luminescence intensities as a function of the laser power for a Au–Ag junction in a segmented Au–Ag nanowire. The inset shows the ratio of SHG/TPEL intensities. Fundamental wavelength of 910 nm (pulsed, \( \sim 200 \text{ fs} \)) was used for excitation.

visible. However, an enhanced signal in the range of \( \sim 420–600 \text{ nm} \) is observed. This could suggest that the two photon luminescence at the junction is SPR enhanced. To show that the emissions were from two-photon processes, we measured the TPEL and SHG spectra at a fixed fundamental wavelength of 910 nm but with variable laser power. Both SHG and TPEL signal intensities scale non-linearly with an order of 2 with respect to the laser intensity (Figure 6). The ratio of SHG to TPEL, as shown in the inset, was found to be nearly constant over a large excitation power range.

SHG is a non-linear process that involves non-centrosymmetric centers.\(^{22}\) It is frequently generated at interfaces where the inversion symmetry is broken. For this reason, SHG is widely used to probe interfacial structures and interfacial processes such as adsorption on solid–liquid or liquid–liquid interfaces. In recent years, it has been demonstrated that SHG can be generated from noble metal nanoparticles and their assemblies. It is important to note that under dipole approximation, SHG is forbidden for spherical metal nanoparticles with centrosymmetric lattices. However, because of imperfection of the nanoparticles and multipolar plasmons, SHG can be detected even in spherical metal nanoparticles.\(^{70}\)
Here, we showed that the SHG is clearly generated on the Au–Ag interface in segmented nanowires. Parallel experiments on Au tips of the nanowires did not show any detectable SH signal under the same experimental conditions. The SHG signal was not detectable in the TPEL background noise (curve f in Figure 5(A)). Assuming the SHG signal was the same level of the background noise from a Au tip, the SH signal from junctions was at least ~100 times more intense.

Further, in above experiments, the excitation laser beam was linearly polarized and perpendicular to the interface (i.e., parallel along the nanowire). To better characterize the SH signals, we rotated the nanowires by 90° in the focal plane. We found that the SHG signal is reduced significantly when the polarization of the excitation laser beam was parallel to the Au–Ag interface. An average drop of 40% ± 5% of the SHG signal intensity was measured from multiple junctions when the laser beam is polarized normal to the interface. Together, our experimental data unambiguously show that the observed SHG signal is generated by the Au and Ag atoms on the interface and has an electric dipole origin.

More interestingly, it was noticed from Figure 5(A) that the intensity of SHG signal varies with the excitation wavelength. Shown in Figure 5(A),(B), starting from 890 nm excitation, the SHG signal increased to reach a maximum at 910 nm as the excitation wavelength increased. The corresponding SHG wavelength was 455 nm, consistent with the TPEL peak at 455 nm. The SHG signal then dropped and increased again as the excitation wavelength increased further to 970 nm. We were not able to measure the full excitation spectrum. However, it can be projected that the SH signal increases and approaches a second maximum as the fundamental wavelength goes toward 1040 nm; double of the other TPEL peak wavelength at 520 nm where Au SPR resides. The SHG intensity showed the same trend as the TPEL emission spectrum, indicating that the SHG signal is greatly enhanced in the presence of optical resonances. It has been shown that the local field generated by SPR enhances SHG in metal layers and nanoparticles. In segmented nanowire, it is possible that the SHG from junction is enhanced by SPR for the same mechanism.

The strong SHG on the junction suggests that nanostructures containing one or multiple hetero-metal junctions, for example, metallic Janus or segmented nanoparticles, may serve as excellent imaging labels or single particle sensors.

### 4 CONCLUSIONS

Using a laser scanning micro-spectrometer, we studied the local optical responses at different locations on segmented Au–Ag nanowires. We found that Au–Ag junctions show different optical properties from the Au and Ag segments and Au tips. The single-photon and multi-photon excitation luminescence intensity at the junctions were enhanced. Especially, when the junctions were excited in the mid-UV range using two-photon excitation, two emission peaks can be observed at 455 and 520 nm, possibly due to the SPR resonances supported by the sharp boundary and intercalated Au and Ag nanogranules in the junction area.

We also found that Au–Ag junctions in the segmented nanowires showed strong SHG signals. The SHG signal was more than 2 orders of magnitude intense than those generated on Au tips under the same experimental conditions. Further, the SH showed dipole-like characteristic in response to excitation laser beam polarization. These suggest that the bimetallic Au–Ag interface was responsible for the generation of the intense SHG signal. The SHG intensity showed similar trend to the TPEL emission spectrum, indicating that the SHG signal was enhanced in the presence of optical resonances. The SPR resonances of the nanostructured on the interfaces possibly contributed to the enhanced luminescence, as well as the SHG signals. These observations suggest that nanostructures containing hetero-metal junctions, for example, metallic Janus particles or segmented nanoparticles, may serve as excellent imaging labels or single particle sensors.

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### CONFLICT OF INTEREST

Authors have no conflict of interest relevant to this article.

### AUTHOR CONTRIBUTIONS

Bhanu Bhakta Neupane: Conceptualization, formal analysis, writing original draft, writing review and editing; Thomas E. Chase: Investigation and methodology; Luyang Zhao: Investigation and methodology; Gufeng Wang:
Conceptualization, funding acquisition, supervision, writing review and editing: Lin He: Conceptualization, funding acquisition, methodology, and supervision.

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DATA AVAILABILITY
The raw data required to reproduce these findings are not shared at this time as the data also form part of an ongoing study.

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