

Surface-Enhanced Raman Spectroscopy (SERS) Study on Polyoxometalate-Functionalized Gold-Silver Nanocomposites

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Biographical Information

Kang Xia's research focuses on the controlled design of hybrid materials consisting of polyoxometalates and metal nanoparticles as well as their applications. To date, he has developed a series of efficient catalytic materials based on polyoxometalate-modified gold nanoparticles and further diverse materials and applications are in exploration.

Dong Junyu's research focuses on the design and fabrication of substrate for surface-enhanced Raman spectroscopy and the vibrational strong coupling effect between the confined light field and molecules. He mainly specializes in bottom-up self-assembly of nanometallic structures in experiment, and electromagnetic field analysis based on surface plasmonics in simulation.

I. Introduction

Metal nanoparticles are attracting materials across research fields spanning from catalysis, biochemistry to energy conversion, owing to their unique physical and chemical properties. Understanding and further manipulating the structure-activity relationship holds core interest, and magnificent efforts have been made in recent years, yet it is still an on-going task.¹ Both of us are conducting metal nanoparticle-related research and are dedicated to working it out.

Based on experiences on constructing robust electronic interaction between gold nanoparticles and polyoxometalate ligands,^{2,3} Kang makes it that gold-silver nanocomposites can be prepared with controlled structures (i.e., alloy/core-shell). Considering that gold/silver as plasmonic metals have optical activity, it is expected that polyoxometalate-modified metal surface can lead to some interesting properties in practical fields such as surface-enhanced Raman spectroscopy (SERS), which has proven to be a powerful spectroscopic tool by virtue of its ability to enhance the intensities of Raman scattering signals by multiple orders of magnitude compared to traditional spontaneous Raman spectroscopy. As this significant signal enhancement can be achieved through the interaction of a target molecule with an excited localized surface plasmon resonance (LSPR) on a noble metal substrate, the gold-silver nanostructures have the potential to provide a practical scenario to design novel SERS substrates by the controllable LSPR properties.

With high sensitivity (down to the single-molecule level), robust multiplexing capabilities, and low background noise, SERS has shown great potential in molecular identification, with promising applications in diverse fields.⁴ As one of the cooperators, Junyu has acquired experience in SERS research from construction, characterization, and analysis, especially in the utilization of plasmonic nanomaterials including gold nanoparticles. Meanwhile, despite some reports of polyoxometalate-modified metal nanoparticles in SERS,⁵ systematic and thorough studies are still greatly lacking. Herein, employing currently developed gold-silver nanocomposite into SERS is believed to be an interesting topic from perspectives of both fundamental science and practical application.

II. Experimental methods

Method of sample preparation

Kang provided all the colloidal solutions of noble metal nanoparticles. As the target molecule for Raman

measurements, Rhodamine 6G (R6G) was chosen to characterize the SERS intensity of the sample. A NaCl aqueous solution (100 to 12.5 mM, depending on samples), an R6G aqueous solution (20 μ M, prepared from the stock 10 mM solution in water), and the metal nanoparticle colloid were mixed at the volume ratio of 1:1:2, which is used to promote aggregation between nanoparticles to enhance the SERS effect as well as to prevent an overly strong coffee-ring effect in the sample. Then, a 20 μ L sample solution was applied dropwise to the silicon substrate with a hydrophilic surface. Finally, the samples were dried in the vacuum chamber at room temperature for the Raman measurements.

Raman measurements

Raman spectroscopy data are collected using a confocal Raman microscope (Renishaw inVia), employing a 532 nm excitation wavelength and an 1800 lines/mm diffraction grating. The photon collection for all Raman measurements is conducted using a 50x objective lens, focusing a laser spot of 1 μ m diameter on the samples. The excitation power is carefully adjusted to 0.48 mW with the exposure duration varied to prevent spectrometer saturation. Before recording the spectrum of each sample, the spectrometer was calibrated using the characteristic line of silicon (520 cm^{-1}) as a reference. All Raman spectra undergo baseline correction using Windows®-based Raman Environment (WiRE), a software program integrated with the spectrometer, which is to ensure accurate spectral analysis and interpretation of the SERS effects.

Scanning electron microscope imaging

For morphological characterizations, SEM images are obtained using a scanning electron microscope equipped with a cold-field-emission gun (Model Regulus 8230, Hitachi). This microscope boasts a resolution as fine as 0.7 nm and offers magnification capabilities of up to 2,000,000x. The electron acceleration voltage for capturing SEM images is adjusted to 5 kV tailored to avoid sample damage due to the thermal effects of noble metal nanoparticles.

III. Result and discussion

Noble metal nanoparticles and their aggregates have superior localized surface plasmonic resonance (LSPR) properties. When the wavelength of the incident light matches the LSPR peak position, a strong resonance will occur between the nanoparticles, which can enhance the electric field strength by more than five orders of magnitude as known as the hot-spot effect. In the hotspot area, as the molecules are affected by the strong electric field, their weak Raman spectral signals will be enhanced, which is known as surface-enhanced Raman spectroscopy (SERS). Therefore, the position of the LSPR peak largely determines the SERS properties of nanoparticles. Hence, we measured the UV-vis spectra of all the noble metal nanoparticles including gold nanoparticle (AuNP), silver nanoparticle (AgNP), novel gold-silver hybrid nanostructure No. 1 (Au-AgNS#1) and novel gold-silver hybrid nanostructure No. 2 (Au-AgNS#2, Fig. 1). According to the UV-vis spectrum, the LSPR peaks of AuNP and AgNP are at 550 and 400 nm, respectively, while the LSPR peak of Au-AgNS#1 is at 530 nm, which is closer to the wavelength of pump laser 532 nm. In contrast, Au-AgNS#2, which is the control group, has no obvious LSPR peak. Accordingly, we predict that under 532 nm laser pumping, AgNP, AuNP, and Au-AgNS#1 will sequentially acquire stronger SERS properties, while Au-AgNS#2 will not have obvious SERS properties.

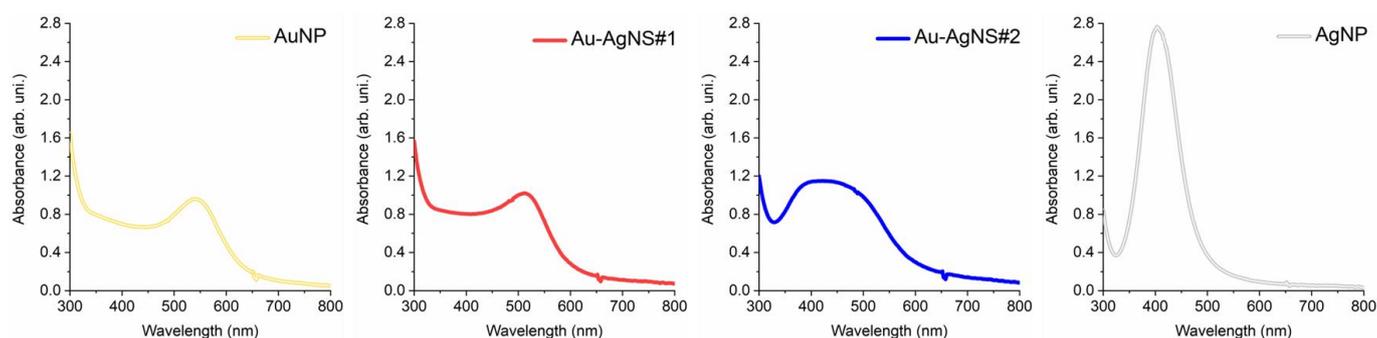


Figure 1. UV-vis spectra of different noble metal nanoparticles.

Due to the small size of our nanoparticles (2-5 nm) and their small scattering efficiency, the inter-particle hot spot effect is not strong enough to enhance Raman signals. Thus, we tried to assemble the nanoparticles into clusters to obtain a notable SERS enhancement effect. In this regard, adding electrolyte solution into the colloid can disturb the Coulombic equilibrium between nanoparticles and thus promote the bottom-up self-assembly process. Specifically, a gradient concentration of NaCl solution was added to the sample solution to detect the SERS intensity of AuNP, by which a positive correlation between the SERS intensity of nanoparticles and the concentration of NaCl was observed (Fig. 2). Whereas, when the concentration of NaCl solution was further increased to 200 mM, significant agglomeration and precipitation of nanoparticles was observed leading to the loss of SERS activity (Fig. 3). Therefore, we confirmed that addition of 100 mM can be the appropriate condition for enhancing SERS activity.

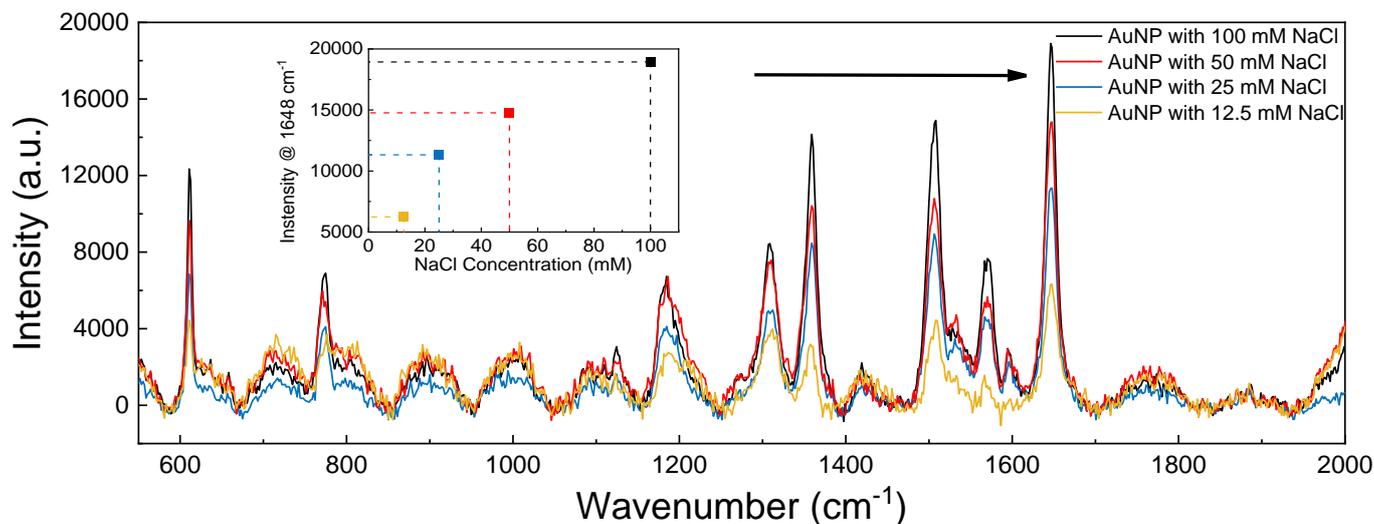


Figure 2. The Raman spectra of the AuNP samples with a gradient concentration of NaCl. A positive correlation between the SERS intensity of nanoparticles and the concentration of NaCl is shown in the top-left panel.

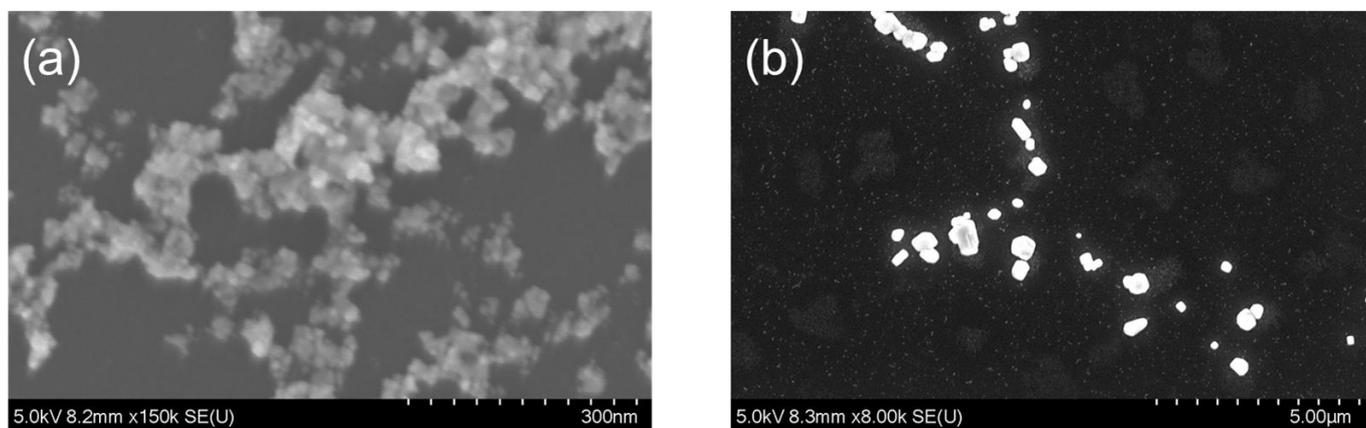


Figure 3. The SEM images of the AuNP samples with a different concentration of NaCl. (a) AuNP with 100 mM NaCl. (b) AuNP with 200 mM. When an excessively high concentration of NaCl solution is added during sample preparation, excessive aggregation of AuNP occurs, and bulk gold nuggets form. At this condition, a few precipitates can be observed in the sample with the naked eye, and the SERS activity of the sample is completely absent.

Subsequently, we performed Raman measurements for each sample respectively. AuNP exhibited better SERS performance than AgNP while Au-AgNS#2 had no Raman features at all, which consisted well with our prediction based on the LSPR peak position (Fig. 4). However, we did not get the expected SERS signal in Au-AgNS#1 either. By comparing the morphologic characterization of AuNP and Au-AgNS#1 under confocal optical microscopy, there existed significant difference in general structures between the two samples (Fig. 5). Therefore, we suspected that this special surface state of Au-AgNS#1 can make it difficult for R6G molecules to attach, thus leading no SERS signal. In addition, Au-AgNS#1 may have undergone rapid aggregation and formed a bulk structure during the drying process, which also leads to the absence of SERS signal.

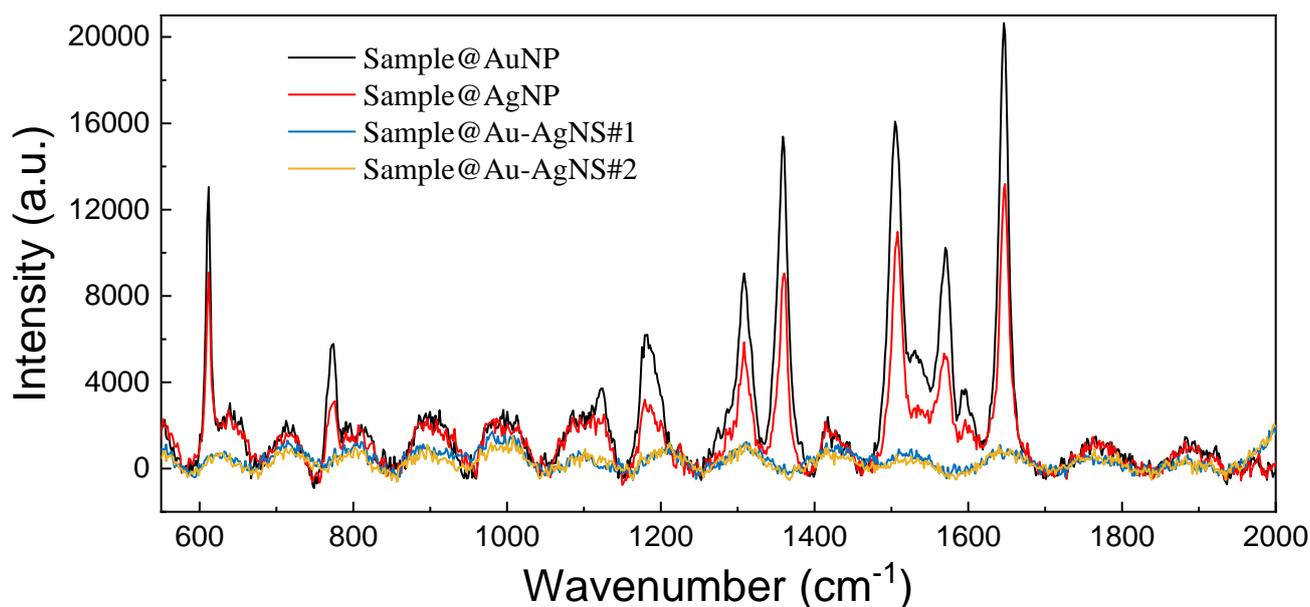


Figure 4. The Raman spectra of samples with different nanoparticles (AuNP, AgNP, Au-AgNS#1 and Au-AgNS#2).

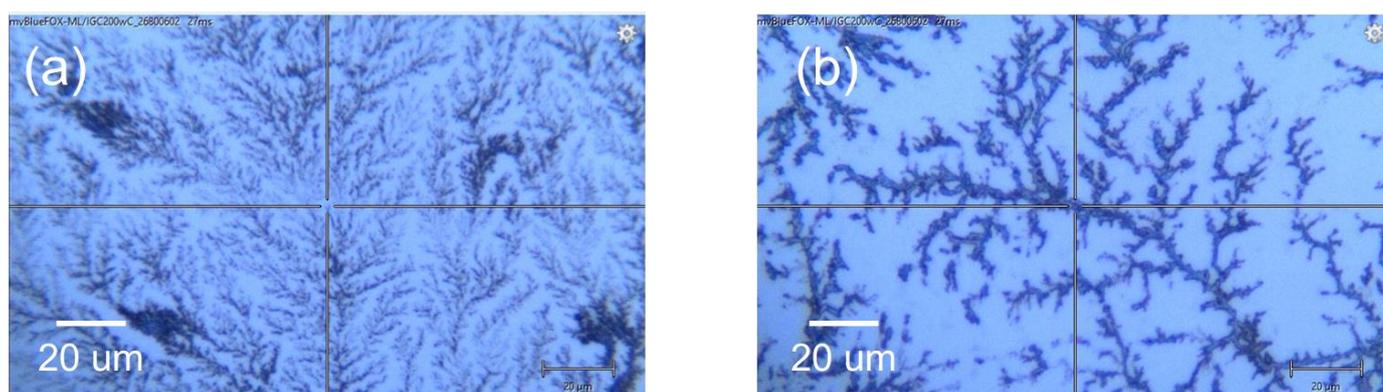


Figure 5. The optical microscope images of the samples with (a) AuNP and (b) Au-AgNS#1. More severe aggregation occurred in the Au-AgNS#1 sample in comparison to the AuNP sample. This may be explained by that Au-AgNS#1 had a different microstructure, resulting in a greater susceptibility to bulking and thus loss of SERS activity.

IV. Conclusion

Based on the above analysis, we conclude that SERS can be a feasible tool for distinguishing AuNP and AgNP effectively, yet for Au-Ag hybrid materials, further exploration is still needed. Hence, we plan to combine the nanovial technology developed in Goda laboratory, with the metal nanoparticles encapsulated in the nanovial to complete the assembly in the next experiment and test it in liquid form.⁶ We expect that technique will not only increase the probability

of pigment molecules adsorbing on as-tested nanostructure, but also avoid the damage during drying process. Further collaborations are still underway and ongoing progress is anticipated.

V. Acknowledgements

We would like to express the greatest gratitude to our supervising professor, Prof. Kazuya Yamaguchi and Prof. Keisuke Goda, and our assistant supervising professor, Prof. Kazuhiro Takanabe and Prof. Hidefumi Akiyama for their support and approval of this joint research, as well as the MERIT-WINGS program for providing us with this valuable opportunity for the joint research.

VI. References

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