

Dense 2D Arrays of Au@Ag and Au@Ag@Au as Efficient SERS Substrates

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1. Introduction

Surface enhanced Raman scattering (SERS) is recognized as an extremely powerful technique for highly sensitive and spatially resolved detection. This technique takes advantage of the strong near-field light induced by metallic nanostructures to enhance the weak Raman signal of the analyte up to 14 orders of magnitude. Up to now, research on SERS substrates focused on two different approaches, the first relies on top-down techniques, such as lithography, and allows good control of optical properties of the device but has huge limits concerning the scalability of the substrate, which is usually limited a sub millimeters in size; the second relies on bottom-up techniques and usually cannot guarantee high enhancement factor (due to low density of metallic nanostructures) and good reproducibility and is limited to small-size (diameter < 20 nm) nanoparticles. In order to overcome the main issues of the common SERS substrates, we developed a SERS substrate which shows both good control of optical properties and good reproducibility.

2. Experimental Details

Gold nanoparticles (AuNPs), core-shell Ag-coated Au nanoparticles (Au@AgNPs) [1] and double shell Au-coated core-shell nanoparticles (Au@Ag@AuNPs) are synthesized by seed-growth method to obtain various final sizes. Those NPs are deposited by our hybrid method [2], which combines electrophoresis, solvent evaporation and self-assembly. These samples are then characterized by UV-visible spectroscopy to verify their localized surface plasmon resonance (LSPR). Afterwards, Rhodamine 6G is deposited on the substrate to serve as a probe for SERS testing of our 2D arrays.

3. Results

As shown in Fig. 1b, large (diameter > 50 nm) uniform-size Au@AgNPs can be arrayed on a substrate with a dense coverage. The size of AuNPs, Au@AgNPs and Au@Ag@AuNPs can be controlled in a wide range allowing the design of SERS substrates whose LSPR spans from green ($\lambda_{\text{LSPR}} = 500$ nm) to NIR ($\lambda_{\text{LSPR}} = 800$ nm). LSPR of each NP can be controlled by varying Au:Ag molar ratio composition, size and interparticle distance as shown in Fig 1a. These optical and morphological properties could be tuned to match the target probe material (vibrational frequency of the molecule) and the laser excitation wavelength to obtain a higher enhancement. The highest average (from large sample area) enhancement factor ($\text{EF} \approx 10^6$)

now is obtained from Au@AgNPs.

4. Conclusions

The 2D array of metallic nanoparticles developed in our group was recognized as a good candidate for a SERS based sensor because of its very high coverage of metallic nanoparticles on large scale substrates, high tunability of its optical response and good SERS enhancement. We determined that Au@AgNPs and Au@Ag@AuNPs act as efficient SERS-active nanomaterials able to overcome difficulties related to AgNPs synthesis and low SERS activity of AuNPs.

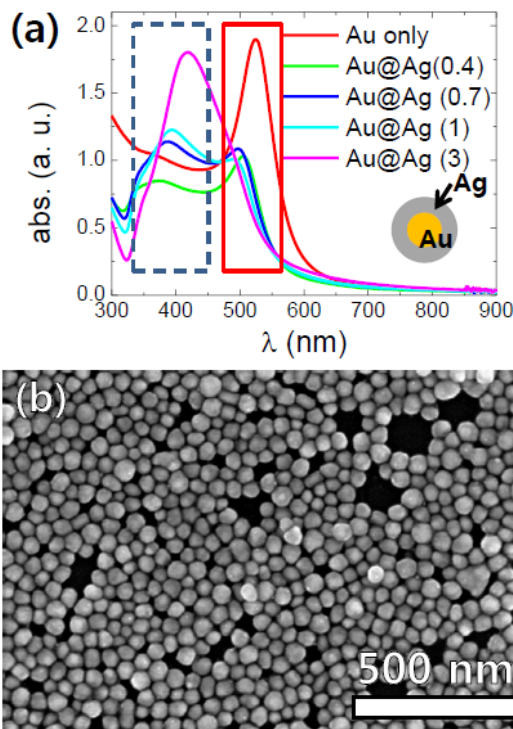


Fig 1. (a) Extinction spectra of Au@AgNPs with various Au:Ag molar ratio. (b) SEM image of Au₁@Ag₃NPs on ITO/quartz.

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References

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