Metallic Nanocrystals Near Ultra-smooth Metallic Film For SERS Application

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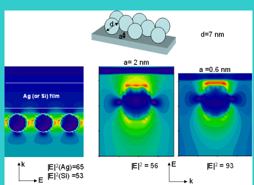
Abstract

Metallic nanocrystals, such as Ag or Au, have been extensively used to enhance Raman scattering in colloidal solutions and on rough surfaces. Few studies have examined such enhancement with nanocrystals on surfaces of well-controlled morphology and electronic properties. We report a systematic surface enhanced Raman scattering (SERS) study of metallic nanocrystals on ultra-smooth metallic films (RMS < 0.5 nm) obtained by template-stripping and also on smooth Si substrates. Significantly higher SERS signal is observed on the metallic substrate than on the Si substrate when uniform nanocrystal films form on both substrates. Theoretical modeling of the electromagnetic (EM) field is conducted by standard Finite Difference Time Domain (FDTD) methods. Our work indicates that the plasmon coupling between the metallic nanocrystals and the plasmon coupling of the metallic nanocrystals to the underlying metallic film are primarily responsible for the much higher Raman enhancement on the metallic film than on the Si substrate.

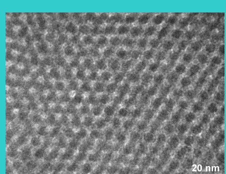
Surface Plasmon — Local Field Enhancement

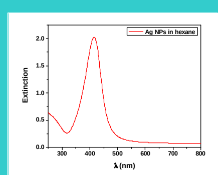


Simulations based on standard FDTD method

- Surface plasmon of metallic nanocrystals generates exceptionally high localized electromagnetic fields.
  — accounts for the EM mechanism of SERS.
- Surface plasmon resonance can be tuned by
  - Size and shape of the metallic nanocrystals
  - Dielectric medium
  - Inter-particle interaction
- EM field can be further enhanced by
  - Plasmon coupling between the metallic nanocrystals.
  - Plasmon coupling between the nanocrystals and the metallic surface.

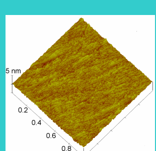
Ag Nanocrystals Synthesis



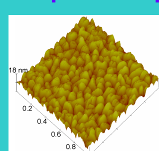


- Synthesized by thermal reduction of silver trifluoroacetate in the presence of oleic acid
  *Yang et al Langmuir **2003** 19 10081.*
- ~ 7 nm in diameter.
- Surface plasmon peak @ ~ 413 nm

Ultra-smooth Metallic Film by Template-stripping



Au film obtained by template stripping
RMS=0.26 nm

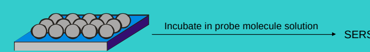


Electron beam evaporated Au film
RMS=3.5 nm

SERS Experimental

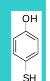
- Goal: To make direct comparison of SERS signals on different substrates.
  Key: Obtain uniform nanocrystal films on the substrates.
  Why — SERS intensity on a substrate depends on
  - The density of metallic nanocrystals
  - The density of adsorbed Raman probe molecules

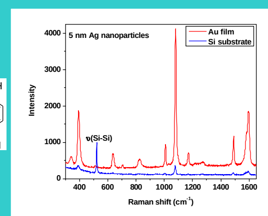
  How —
  - Drop cast
  - Spin cast
  - Langmuir-Blodgett

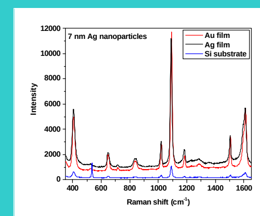


SERS Results

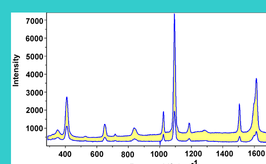
- Much higher SERS signal obtained consistently on the metallic surface than on the Si substrate with various nanocrystal film preparation methods.

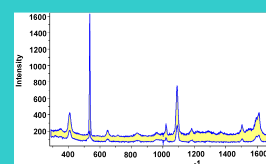


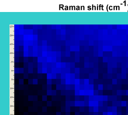


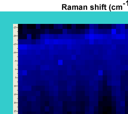


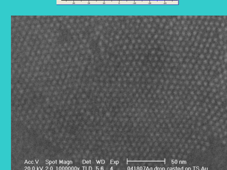
- Uniformity of SERS signal on different substrates confirmed by SERS mapping and characterization of the morphology of nanocrystal film.



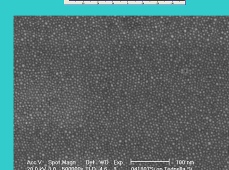








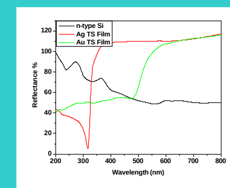
5 nm Ag nanocrystals on template-stripped Au substrate by drop casting



5 nm Ag nanocrystals on Si substrate by drop casting

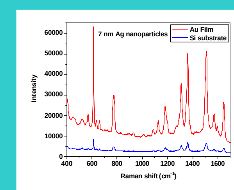
Discussions

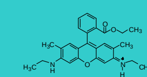
- Reflectivity difference between metallic Au/Ag film and Si substrate.



At the Raman excitation wavelength (632 nm), the reflectivity of Au/Ag film is only ~ 2 times that of the Si substrate, which will only increase the incident photons by ~ 30% at most.

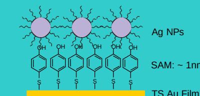
- Specific bonding between gold and sulfur.
  - Other Raman probe molecules

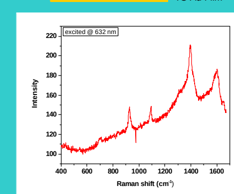




Similar results obtained with Rhodamin 6G molecule.

- Sandwich structure for detecting self-assembled monolayer (SAM) of mercaptophenol





- SERS signal is much weaker compared to the case when the substrate is incubated in mercaptophenol solution, as the number of molecules adsorbed on the metallic nanocrystals is significantly decreased.
  - Further confirms that the Au-S specific bonding does not contribute to the higher SERS signal obtained on the Au film than on the Si substrate
  - This sandwich structure can be a very useful tool to detect and characterize SAM.
    - Different vibrational modes are observed from molecules that freely adsorb onto the metal nanocrystals.
    - SAM of dithiol
      - Potentially better interaction of SAM with nanocrystals.

Conclusion

We report a systematic SERS study of Ag nanocrystals on ultra-smooth template-stripped metal film surfaces and on smooth semiconducting Si substrates. At least one order of magnitude higher SERS signal is obtained on the ultra-smooth metallic surfaces than on the Si substrates, with evidence showing that uniform nanocrystal films form on both substrates. Our results indicate that the strong Raman enhancement obtained from the metallic nanocrystals on the metallic surface originates from the plasmon coupling between the metallic nanocrystals as well as its coupling to the underlying metallic film.

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