

L.7: Densely packed Ag-Au alloy nano-particle films as efficient SERS substrates

Noble metal nanoparticles exhibit strong optical response due to collective oscillations of free electrons, known as localized surface plasmon resonance (LSPR). LSPR can be tuned by morphology and composition of the nanoparticles. In Ag-Au alloy nanoparticles, LSPR in dipolar mode can be tuned in the entire visible region by varying the alloy composition. Densely packed alloy nanoparticle films are particularly important for trace molecular detection through surface enhanced Raman scattering (SERS) technique. SERS mainly depends on the enhanced near fields in between the nanoparticle, known as hot spots. For synthesis of alloy nanoparticle films, pulsed laser deposition (PLD) is an attractive method due to sub-monolayer film growth with precise control on its composition through sequential ablation of separate pure metal targets. PLD-grown densely packed Ag-Au alloy nanoparticle films have been shown to be efficient SERS substrates for easy detection of trace dye molecules (at about 500 nanomolar concentration).

Ag-Au alloy nanoparticle films of varying compositions were produced through sequential laser ablation process using a KrF excimer laser (248 nm wavelength, 20 ns pulse duration and 10 Hz repetition rate). Figure L.7.1 presents transmission spectra of the alloy films of different compositions.

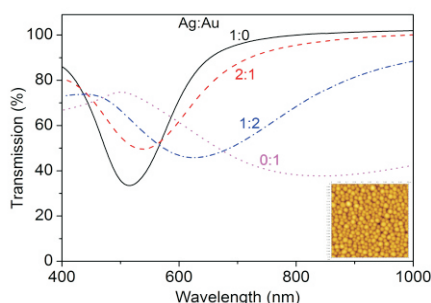


Fig. L.7.1: Transmission spectra of Ag-Au alloy nanoparticle films grown with varying ratio of no. of ablation pulses of Ag and Au; Inset: AFM image (500 nm X 500 nm) of pure Ag film.

With increase in Au concentration in the films, the LSPR wavelength corresponding to minimum transmission undergoes a systematic red-shift from ~ 450 to 800 nm. The LSPR band-width also increased with an increase in Au concentration which is attributed to corresponding increase in both homogeneous and inhomogeneous broadening. The inset AFM image in Fig. L.7.1 shows densely packed nanoparticles with number density of ~ 8×10^{10} particles/cm². The alloy formation was further confirmed through X-ray photoelectron spectroscopy and Energy dispersive spectroscopy. Figure L.7.2 presents real and imaginary parts

of the dielectric function, as determined by spectroscopic ellipsometry. The ellipsometry data (Ψ, Δ) was simulated using four Gaussian oscillators, two for interband transitions and two for the plasmon resonance. Figure L.7.2(a) shows modification of free electron relaxator behavior (in terms of negative real part of ϵ) into oscillatory behavior in the nanoparticle films, supporting the resonance phenomenon. The oscillator wavelength systematically red shifted with an increase in Au concentration in Ag-Au films.

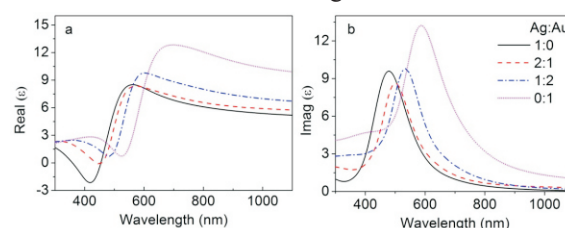


Fig. L.7.2: Real (a) and imaginary (b) parts of dielectric response (ϵ) of Ag-Au nanoparticle films.

SERS response of Rh6G dye was studied (excitation wavelength: 633 nm and integration time: 10 s) by dipping Ag-Au film substrates in 500 nM dye aqueous solution, followed by rinsing with de-ionized water. Figure L.7.3 presents SERS spectra obtained from these films showing different intensities of Raman vibration modes of the dye for different alloy compositions.

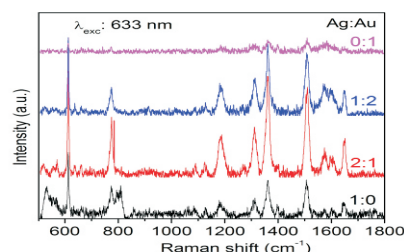


Fig. L.7.3: SERS spectra of Rh6G dye in presence of Ag-Au nanoparticle films of different compositions.

The Raman peaks of dye were not observed in the event of (i) absence of nanoparticle films and (ii) presence of continuous metal films of different compositions. With respect to pure metal films, alloy nanoparticle films were relatively more efficient SERS substrates for the used excitation wavelength. The SERS intensity is influenced by various parameters e.g. excitation wavelength, nanoparticle size, inter-particle spacing, hot spot density etc. The observed strong SERS intensity is caused by electromagnetic field enhancement from the LSPR excitation generating hotspots at the gaps between the nanoparticles. The strong LSPR response of Ag-Au alloy nanoparticle films of controlled morphology shows promise towards its application for trace analyte detection.

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