



Silver coated gold nanocolloids entrapped in organized Langmuir–Blodgett Film of stearic acid: Potential evidence of a new SERS active substrate



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ABSTRACT

SERS active substrate containing silver coated gold (Au@Ag) nanocolloids entrapped in the Langmuir–Blodgett (LB) film matrix of stearic acid (SA) has been reported. The SERS efficacy of the *as prepared* substrate has been tested with trace concentrations of Rhodamine 6G (R6G) molecules. Enhancement factors ranging from 10^4 – 10^{13} orders of magnitude have been estimated for the characteristic vibrational signatures of R6G molecule. The colossal enhancement factors also signify the superiority of the *as prepared* substrate in comparison to Au@Ag nanocolloids. The optical responses and the morphological features of the substrates are estimated with aid of UV–vis absorption spectra and FESEM, AFM images respectively. Correlations between the surface morphologies, fractal dimensions and roughness features of the *as prepared* substrates are also drawn. The electric field distributions around the aggregated nanocolloids entrapped in the SA matrix have been envisaged with the aid of three dimensional finite difference time domain (3D-FDTD) simulations. Tuning the interparticle localized surface plasmon (LSP) coupling between the aggregated nanocolloids may be achieved by lifting the LB film of SA at different surface pressures.

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1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy has been established as a powerful technique which allows enormous enhancements of Raman signals from probe molecules upon their adsorption on the nano structured surfaces [1–4]. It is successfully applied to understand the orientations and trace identifications of molecules or ions down to single molecule detection limit [5–8]. The genesis behind the huge enhancements of SERS signals is still not clear. However, the general consensus is that, both the electromagnetic (EM) and the chemical enhancement (CHEM) mechanisms are simultaneously operative [9–12]. The EM effect is considered to be more dominant and results from the generation of localized surface plasmons (LSPs) of the metallic nanostructures [13]. The CHEM mechanism owes to the transfer of an electron from the Fermi level (E_F) of the nanostructured substrate to the

HOMO or LUMO of the adsorbed analyte or vice versa [14–16]. Size, shape and morphology of the surfaces synergistically play an important role toward the enhancements of SERS signals [17–22]. Aroca et al. [23–30] reported a series of pioneering works where Langmuir–Blodgett (LB) technique had been successfully utilized to record the SERS of monolayer and multilayered organic molecules. In those reports, LB films of organic molecules had been used as integral part of molecular architectures for the SERS active substrates. However, the recent trends of research in this area, albeit scarce, are focused toward the fabrication of new SERS sensitive substrates using LB technique, which are reproducible, facile to prepare and favor interparticle LSP couplings [31–33].

With these things in mind, here we report the fabrication of a novel SERS active substrate of silver coated gold (Au@Ag) nanocolloids (NCs) self assembled in the bilayer Langmuir–Blodgett (LB) film matrix of stearic acid (SA). The efficacy of the SERS activity has been tested with Rhodamine 6G (R6G) molecule. Enhancements of the Raman bands have been discussed in the light of EM mechanism. The spatial distribution of electric fields around the self assembled Au@Ag nanoparticles are also estimated with the

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aid of three dimensional finite difference time domain (3D-FDTD) simulation studies.

2. Experimental procedure

2.1. Materials and methods

R6G molecule; ~95% dye content, SA; >99% purity and chloroauric acid (HAuCl_4) of spectroscopic grades were purchased from Sigma–Aldrich and were used as received. Silver nitrate (AgNO_3), tri-sodium citrate, ascorbic acid (AS), ethanol and acetone were purchased from E-Merck (Germany) and were used without further purification. Spectral grade chloroform was purchased from SRL India and was used as received. All the glasswares used in the synthesis were cleaned with freshly prepared aqua-regia and were thoroughly rinsed with distilled water prior to use. The required solutions were prepared using triple distilled water subsequently deionized (18.2 M Ω cm resistivity and pH ~6.8) through Milli-Q-plus system of Millipore Corporation, USA.

Spherical gold nanocolloids (AuNCs) of average particle diameter ~25 nm were synthesized by citrate reduction method as reported by Frens [34]. The AuNC, thus prepared, was used as core for the synthesis of Au@Ag nanocolloid according to the recipe described by Jana et al. [35]. Briefly, 10 ml of the AuNC aqueous solution was prepared with suitable dilution. To it, 50 μL 0.1 M aqueous solution of AS was added and then 250 μL of 0.01 M aqueous solution of AgNO_3 was subsequently added drop wise with continuous stirring. The color of the colloidal solution turns from red to greenish yellow, indicating the formation of Au@Ag nanocolloid having ~25 nm core diameter and ~13 nm shell thickness. The HRTEM image and EDX spectra of the *as synthesized* Au@AgNC are shown in the inset of Fig. 1 and Fig. S1 (Supplementary Material) respectively. The EDX spectrum confirms the existence of silver and gold in Au@Ag nanocolloidal solution.

The quartz glass slides were cleaned vigorously with ethanol, deionized water and acetone. The bilayer LB films of SA were lifted on the quartz substrates by Y-type deposition technique using computer controlled LB trough (Model No. D2007, Apex Instruments). Chloroform was used as solvent in the spreading solution of SA. Triple distilled deionized water was used as sub phase. The pressure–area (π -A) isotherm of SA was estimated with a film balance and the surface pressure was measured by the Wilhelmy

method using a filter paper. SA solution in chloroform solvent was spread drop wise by a syringe on the water subphase. After a delay of 20 min, allowing the solvent to evaporate, the film was compressed by moving the barrier at a constant speed of 2 mm/min. The pressure area (π -A) isotherm was recorded throughout the compression steps.

The first layer of the SA was lifted by upstroke and the subsequent second layer was deposited by down stroke so that the hydrophilic part of the SA molecule can point outwards. The bilayer LB films of SA were dipped in the Au@Ag nanocolloids (Au@AgNCs) for 24 h. The films were then removed from the colloid, washed thoroughly with deionized water and dried in hot air oven to remove excess silver ions from the film surface. To verify the elemental identity of the *as prepared* substrates, were identified with the aid of EDX analysis and is shown in Fig. S2 (Supplementary Material). The *as prepared* substrates were then incubated in 1.0×10^{-6} M, 1.0×10^{-8} M, 1.0×10^{-12} M and 1.0×10^{-14} M aqueous solution of R6G for 1 h.

2.2. Instrumentation

The absorption spectra were recorded using Jasco UV-vis Absorption Spectrometer (Model No: V-630). The surface enhanced resonance Raman scattering [SER(R)S] spectra were recorded by J–Y Horiba Confocal Triple Raman Spectrometer (Model: T 64000) fitted with gratings of 1800 groove/mm and a TE cooled synapse CCD detector from J–Y Horiba. The samples were excited using 514.5 nm green line of Ar+ laser manufactured by Spectra Physics, USA (Model.Stabilite2017) with spot size 1 μm in diameter at a laser power ~50 μW incident on the sample. The acquisition times for recording the SER(R)S spectra were fixed at 20 s. The scattered signals were collected at 180° scattering angle to the excitations from an Olympus open stage microscope of 10x objective. The detector and the data acquisition were controlled by Lab Spec 5 software as provided by Horiba. HRTEM and EDX analysis were carried out with Tecnai TF20 ST Transmission Electron Microscope with 200 KV accelerating voltage and EDAX make Si (Li) type EDX detector respectively. The surface morphology of the LB films was observed by Field Emission Scanning Electron Microscope (FESEM) (QUANTA FEG 250) at excitation energy of 10 kV. The EDX analyses of the *as prepared* substrates were performed by Quanta 200 equipped with EDAX made Si (Li) type EDX detector. The surface roughnesses of the *as prepared* samples were imaged by Atomic Force Microscope (AFM) (Veeco dilnnova) operated in the tapping mode. Antimony doped silicon tip with typical resonant frequency of 300 kHz and force constant 40 N/m were used.

2.3. Theoretical calculations

The spatial distributions of electric fields around the plasmonic nanomaterials were estimated from 3D-FDTD simulations. The simulations were performed using 3D-FDTD Lumerical Solutions, Inc. [36]. The dimension of the Yell cell, used in the calculations, was fixed at 1 nm \times 1 nm \times 1 nm. The Johnson–Christy dielectric data for silver and gold were imported and water with real refractive index 1.33 was chosen for the back ground medium. All the models were excited with plane polarized light wave whose electric field amplitude is 1.0 V/m. Perfectly matched layer (PML) boundary condition was introduced to avoid reflection and back scattering of electric field from the pre-selected boundary. Incident light of 514.5 nm wavelength was used for the excitations and the duration of all the simulations was fixed at 500 fs to ensure full convergence of the electric field. The fractal dimensions were estimated using “Image J” [37] software considering around 300/350 nanoparticles.

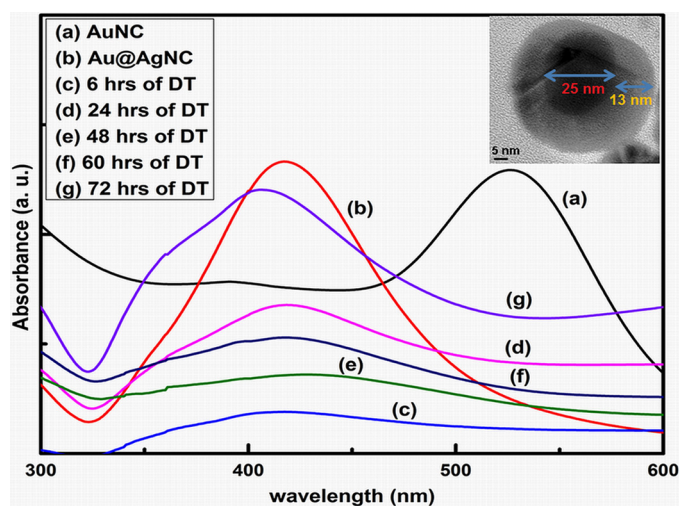


Fig. 1. Room temperature UV–vis electronic absorption spectra of (a) AuNC, (b) Au@AgNC and ((c)–(g)) Au@AgNC self-assembled in the bilayer LB film of SA at various DTs. Inset shows the HRTEM image of the *as synthesized* Au@AgNC.

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