ABSTRACT

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Title: Fabrication and characterization of SERS active substrates using self-assembly and Langmuir-Blodgett deposition technique.

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This thesis embodies the results of investigations which were carried out at the Department of Physics, Jadavpur University under the supervision of Prof. (Dr.) Joydeep Chowdhury. The thesis comprises of eight chapters.

Chapter 1 contains general introduction with a brief review of the existing experimental and theoretical knowledge relevant to the present work and the outline of the purpose and problems studied in the present investigation.

Chapter 2 describes the materials used in the experimental work, sample preparations, synthesis of silver, gold, silver coated gold nanocolloids and discusses various experimental procedures such as Langmuir-Blodgett (LB) deposition technique, Raman, UV-Vis absorption, Field Emission Scanning Electron Microscope (FESEM), High Resolution Tunnelling Electron Microscope (HRTEM), Energy Dispersive X-Ray Analysis (EDX), Atomic Force Microscope (AFM), X-Ray Photoelectron Spectroscopy (XPS) study.

Chapter 3 explains the electrodynamical and quantum chemical calculations and computational details that have been employed in this thesis work.

Chapter 4 deals with the fabrication of a highly sensitive SERS active substrate by self-assembly of silver nanocolloids (Ag NCs) in the bilayer Langmuir- Blodgett (LB) film of stearic acid (SA). Rhodamine 6G (R6G) has been used as the probe molecule to test the efficacy of the as prepared substrate. Gigantic enhancement factors $\sim 10^{12}$ orders of magnitude have been estimated from the surface enhanced resonance Raman scattering [SER(R)S] spectrum of R6G. The optical properties of the as prepared substrates have been envisaged by UV- Vis absorption spectra, while their morphological features are mapped through FESEM and AFM images. A correlation has been drawn between the SER(R)S efficacy and the corresponding FESEM and AFM images of the as prepared substrates. Electric field distributions around the aggregated AgNCs have been estimated with the aid of 3D- FDTD simulation studies.

Chapter 5 discusses the fabrication of SERS active substrate containing silver coated gold (Au@Ag) nanocolloids entrapped in the LB film matrix of SA. The SERS efficacy of the as prepared substrate has been tested with trace concentrations of R6G molecules. Enhancement factors ranging from $\sim 10^4 - 10^{13}$ orders of magnitude have been estimated for the characteristic vibrational signatures of R6G molecule. The optical responses and the morphological features of the substrates are estimated with the 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 3D-FDTD simulations.

Chapter 6 depicts a facile procedure towards the fabrication of highly reproducible, large area SERS active substrates through integration of LB and self-assembly technique. Gold nanoparticles with average particle diameter of ~ 55 nm have been self-assembled on the monolayer LB film matrix of poly (methyl methacrylate). The plasmonic architectures of the substrates have been tuned by lifting the LB film at different surface pressures. The as prepared substrates show their respective efficacies as efficient SERS sensing scaffolds for detecting 4-Mercaptopyridine (4-MPy) molecule at ultrasensitive concentrations. The optical responses and morphological features of the substrates have been envisaged with various characterization techniques. 3D-FDTD simulation studies have been employed to estimate the electric field distributions around the aggregated gold nanoparticles.

Chapter 7 is focused to explore in details the topographical features of SERS active substrates, fabricated through LB and self-assembly techniques, in presence of the probe 4-Mpy molecule. The statistical parameters (ca. lateral correlation length, Hurst exponent, interface width and fractal dimensions) associated with the topographical features of the bare SERS active substrate are also compared with the same substrate in presence of 4-Mpy.

Chapter 8 reports the adsorptive behaviour of probe 4MPy molecule with gold nanoparticles (AuNPs) embedded in the bilayer LB film matrix of SA. The as fabricated AuNps entrapped within the LB film template of SA proved to be a good SERS sensing platform that can sense the analyte 4MPy molecules at trace concentrations ~ 1.0×10^{-9} M. X-ray photoelectron spectroscopy together with SERS spectral analysis signify the adsorption of the analyte 4MPy with AuNPs via sulfur atom. The experimental observations are supported by Born-Oppenheimer on the fly Molecular Dynamics (BO-OF-MD), time resolved wavelet transform theory (WT) and DFT calculations based on adcluster models. The time resolved vibrational frequency estimations as obtained from WT theory further corroborates experimentally recorded down shifts of the enhanced Raman bands at 711 and 1092 cm^{-1} in comparison to their normal Raman counterparts at 723 and 1114 cm^{-1} respectively. The molecule → metal charge transfer (CT) contribution to the overall enhancement of the SERS spectra of 4MPy molecule has been suggested from electron density difference calculations.

All the results incorporated in the thesis have been published in different journals of international repute. List of publications along with the available reprints are included in the APPENDIX.

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