Supporting Information

Flexible Nanoimprinted Substrate Integrating Piezoelectric Potential and Photonic-Plasmonic Resonances

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Methodology

Fabrication of Piezoelectric Thin Films

In the process of fabricating the piezoelectric thin film for Atomic Force Microscopy (AFM) analysis, nanocomposites incorporating Polyvinylidene Fluoride (PVDF) were synthesized using a solvent-based nanoimprinting technique. Initially, a solution containing 20% PVDF in Dimethylformamide (DMF) solvent was prepared and stirred thoroughly in a hot bath at 60°C for one hour to ensure uniformity. The PVDF solution was then spin-coated onto a Linear Silicon Nanostamp substrate at 1 V for 20 seconds to achieve an even coating. Subsequently, the coated substrate was transferred carefully to a hot plate and annealed at 70°C. Finally, the PVDF polymer film was peeled off meticulously from the stamp.

Preparation of prob molecule solution:

The probe molecules (4-aminobenzenethiol) (4-ABT) was prepared by dissolving the powder in distilled water at an initial concentration of 10^{-1} M. Then, Deionized water was used to further dilute the solution, resulting in a final concentration of 10^{-5} M. Then drop cast on the PVDF and PVDF HFP nanoimprinted samples.

Surface Enhanced Raman Spectroscopy (SERS):

Raman data were obtained using a Raman system consisting of a spectrograph (SP2300i, Princeton Instruments), a CCD camera (iDus 401, Andor), and a monochromatic green laser power supply (wavelength 532 nm, power 5mW, model: MGL-III-532) with a beam splitter and long pass filter (RazorEdge, Semrock). For the imprinted samples, an average of approximately 30 measurements is presented.

Atomic Force Microscopy(AFM):

AFM images were captured using an MFP-3D instrument from Asylum Research in Amplitude Modulation Mode (AC mode). The imaging was performed using monolithic silicon probes (Tap300Al-G) with an aluminum reflective coating (Budget Sensors). The probe tips had the following specifications: a force constant ranging from 20 to 75 N/m (nominal 40 N/m), a resonance frequency range of 200 to 400 kHz (nominal 300 kHz), and a length ranging from 115 to 135 μm (nominal 125 μm).

UV-vis reflection spectroscopy:

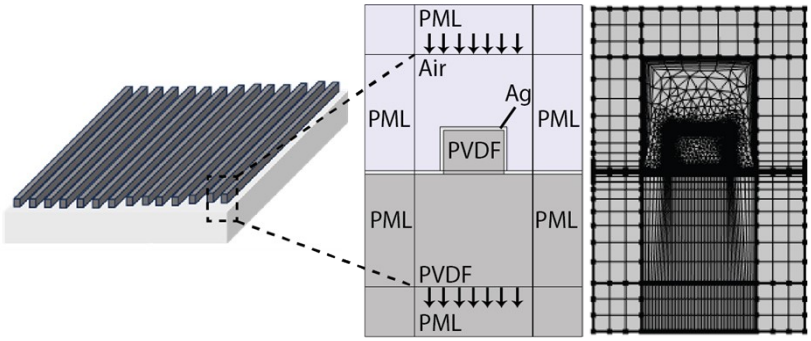
The specular reflectance of the substrates was measured using a LAMBDA™ 750 UV/Vis/NIR spectrophotometer from PerkinElmer. An aluminum mirror served as a reference standard (Rbackground) for calculating relative changes in reflectance ($\Delta R/R = (R_{sample} - R_{background}) / R_{background}$). The spectral data were acquired over a wavelength range of 250 to 1000 nm with a step size of 1 nm.

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR measurements were performed using a NICOLET iS50 FT-IR spectrometer, providing detailed spectral analysis for the samples under investigation.

Finite Element Simulations

The model uses the Electromagnetic Waves module in COMSOL® Multiphysics. An incident wave propagating perpendicular to the nanoimprinted surface with electric polarization in the x-axis is considered. The surface is modelled as a 2D geometry, consisting of the PVDF trenches covered with 10 nm thick silver coating. The refractive indices are taken as 1 for air, 1.4 + i0.02 for PVDF while the refractive indices of silver are taken from Johnson and Christy.[1] The structures are periodic in the x-axis, as such a single unit cell is modelled, and the structure's periodicity is accounted for using Floquet periodicity. The physical domains are surrounded by Perfectly Matched Layers (PML) to prevent back-reflected waves.



The model first solves for the background electric field solution in the absence of the nanoscale feature, then this background electric field is utilized in a scattered field formulation with the nanoimprinted feature present. The Raman enhancement factor can then be calculated from the line integrals of the background electric field and of the scattered field on the nanoimprinted surface:[2]

$$EF = \frac{1}{A_0}\int \frac{|E_{scattered}|^4}{|E_0|^4} dA$$

where A_0 is the area of the unstructured surface, $E_{scattered}$ is the electric fields that are locally enhanced on the metallic surfaces, and E_0 is the background electric field.

The influence of the applied load on the Raman Enhancement factor is modelled by applying a uniform surface current density to the silver layer. There are no alterations made to the incoming electromagnetic beam, nor to the geometry of the model, therefore, any changes to the enhancement factor are due to the surface current density. The magnitude of the surface current density is approximated using a separate finite element model, where a load is applied on macro-scale block of PVDF. The strain generates a piezoelectric potential which drops along the thin film towards the ground. This drop of the piezoelectric potential is used in a simple electric circuit model of the 10 nm thick silver coating to obtain a surface current density. The obtained surface current density is then transferred to the Raman Enhancement Factor model to obtain the expected EF in the presence of a load.

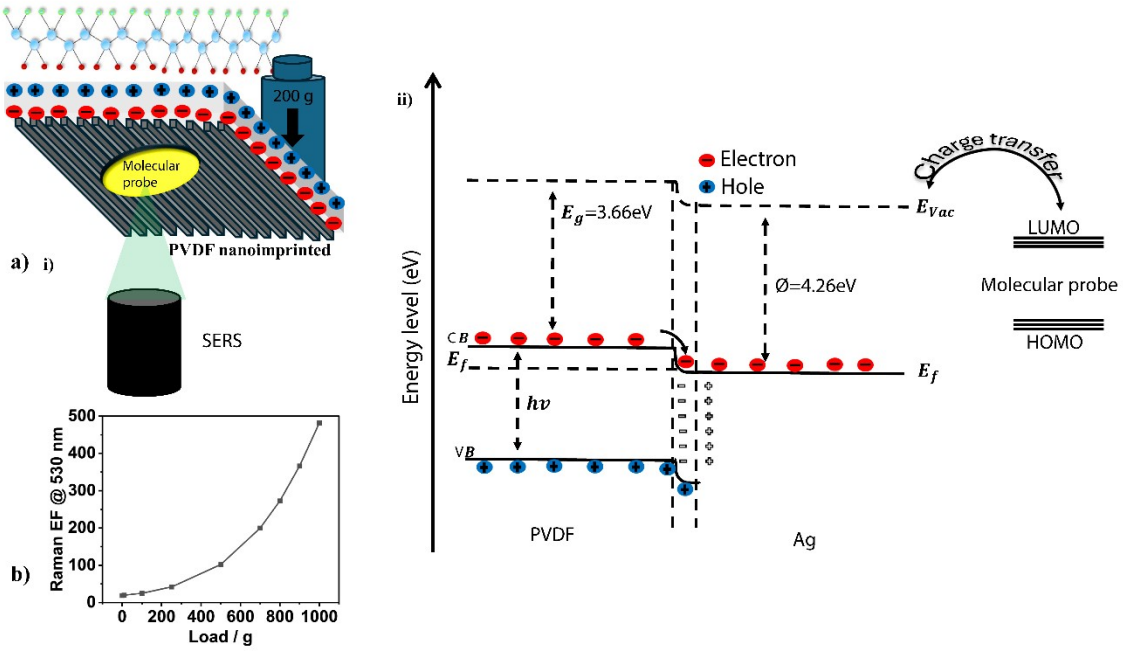


Fig S1. (a) Mechanism of SERS enhancement in a PVDF/Ag nanostructure system under applied pressure, demonstrating how PVDF's piezoelectric effect generates an electric field that amplifies charge transfer and the local electromagnetic field for improved SERS performance with 4-ABT as the probe molecule. (b) A plot of COMSOL generated Enhancement factor with applied weight, at 530 nm, a wavelength that corresponds closely to the Raman excitation wavelength of 532 nm.

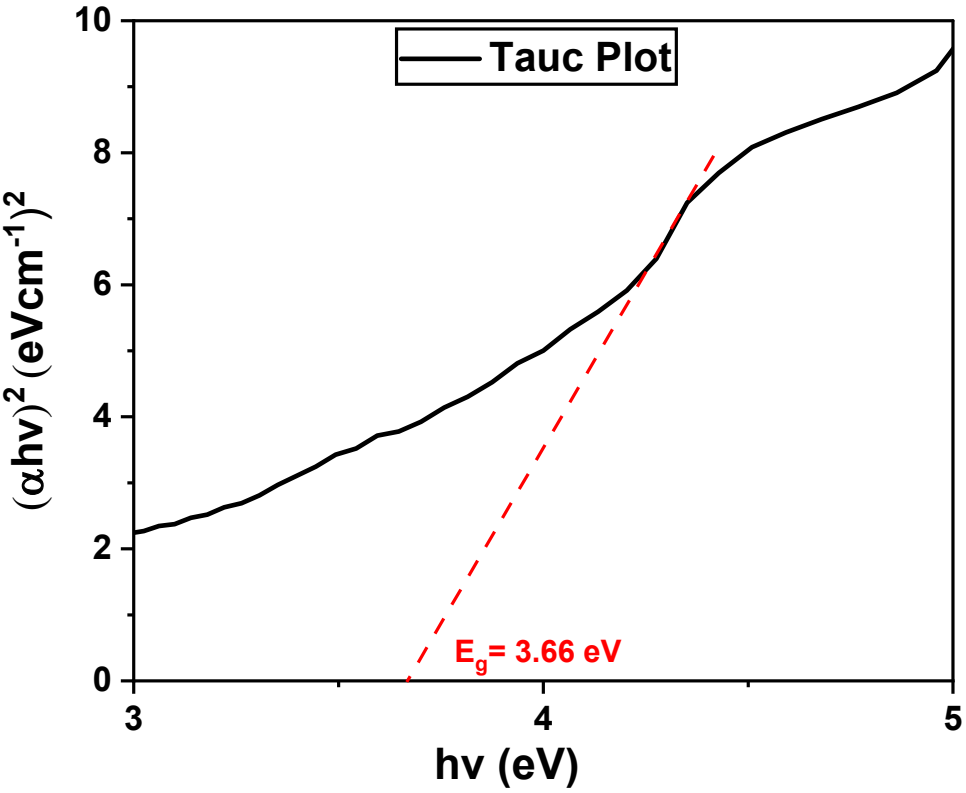


Figure S 2: Tauc Plot of imprinted PVDF

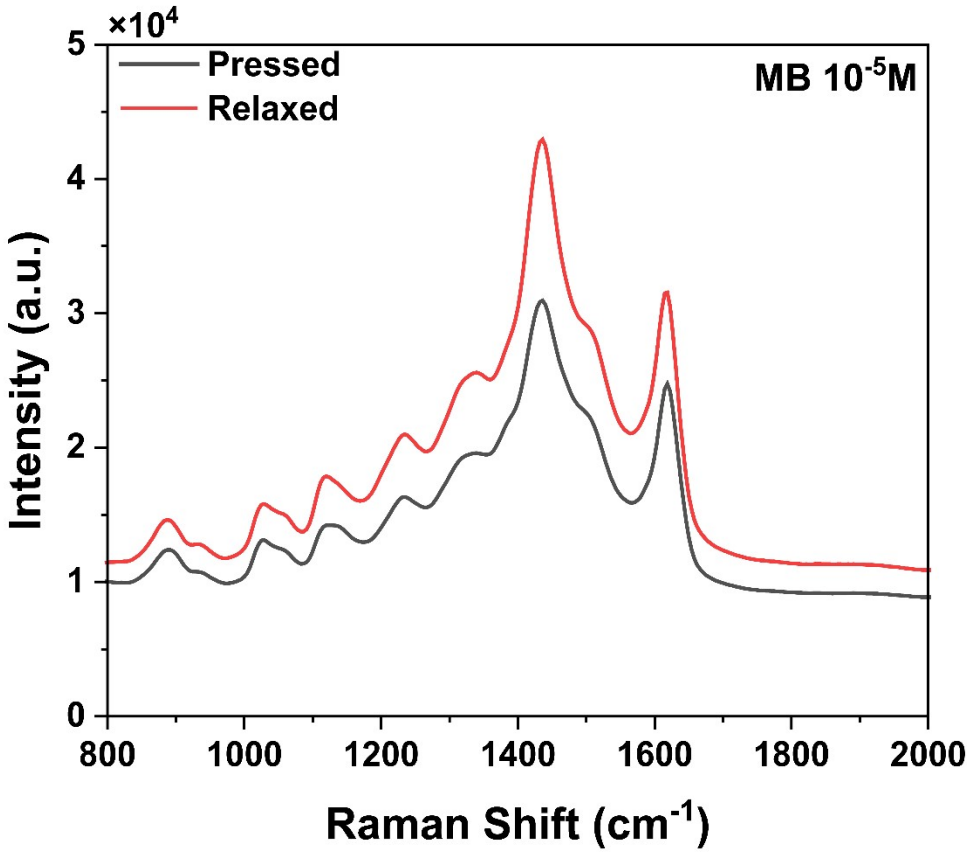


Figure S 3: MB SERS intensity in imprinted PDMS/Ag (non-piezoelectric) under applied pressure

References

[1] P. B. Johnson, R. W. Christy, *Physical Review. B, Solid State* **1972**, *6*, 4370–4379.

[2] I. Knorr, K. Christou, J. Meinertz, A. Selle, J. Ihlemann, G. Marowsky, **2008**.