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Surface-Sensitive and Bulk-Suppressed Raman Scattering by Transferable Nanoporous Plasmonic membranes

Raman spectroscopy is a powerful technique to characterize materials. It probes non-destructively chemical composition, crystallinity, defects, strain and coupling phenomena. However, the Raman response of surfaces or thin films is often weak and obscured by dominant bulk signals. Here we overcome this limitation by placing a transferable porous Au membrane (PAuM) on top of the surface of interest. Slot-like nanopores in the membrane act as plasmonic slot antennas and enhance the Raman response of the surface or thin film underneath. Simultaneously, the PAuM suppresses the penetration of the excitation laser into the bulk, efficiently blocking the bulk Raman signal. Using graphene as a model surface, we show that these two simultaneous effects increase the surface-to-bulk Raman signal ratio by three orders of magnitude. We find that 90% of the Raman enhancement occurs within the top 2.5 nm of the material, demonstrating truly surface-sensitive Raman scattering. To validate our approach, we analyze the surface of a $LaNiO_3$ thin film. We observe a Raman mode splitting for the $LaNiO_3$ surface-layer, which is evidence that the surface structure differs from bulk. This shows that PAuM give direct access to Raman signals of surfaces and their structural properties.

References

Roman M. Wyss, Günter Kewes, Martin Frimmer, Karl-Philipp Schlichting, Markus Parzefall, Eric Bonvin, Martin F. Sarott, Morgan Trassin, Lala Habibova, Giorgia Marcelli, Jan Vermant, Lukas Novotny, Mads C. Weber, Sebastian Heeg, https://arxiv.org/pdf/2301.04054v1.pdf *under review* (2023)

Figures

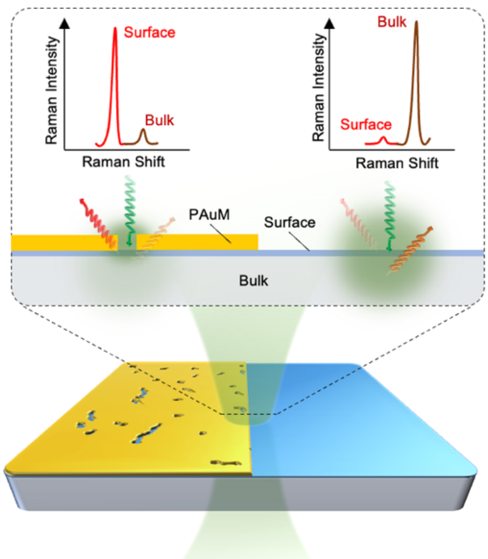

Figure 1: Nanoporous Au membranes enhance the surface Raman signal and suppress the bulk Raman signal