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Bioinspired Evolutionary Algorithm-Optimized Monocrystalline Gold Double Wire Gratings as a Novel SERS Sensing Platform

Achieving reliable and quantifiable performance in large-area surface-enhanced Raman spectroscopy (SERS) substrates pose a formidable challenge, demanding substantial signal enhancement while ensuring response uniformity and reproducibility. Conventional SERS substrates are typically made of inhomogeneous materials with random resonator geometries and distributions. As a consequence, they exhibit multiple or broadened plasmonic resonances, undesired absorptive losses, and uneven field enhancement. These limitations diminish signal strength and hamper reproducibility, making it difficult to conduct comparative studies with high sensitivity. This study introduces an innovative approach that utilizes monocrystalline gold flakes to fabricate plasmonic double-wire resonators with nanometer-level precision using focused ion-beam lithography. Inspired by biological evolution strategy, the double-wire grating substrate (DWGS) geometry was evolutionary optimized to enhance both excitation and emission processes involved in generating SERS peak signature of each analyte. The use of monocrystalline material minimizes absorption losses and enhances shape fidelity during nanofabrication. DWGS demonstrates notable reproducibility (RSD=6.6%), repeatability (RSD=5.6%), and large-area homogeneity over areas $>10^4\ \mu m^2$. Moreover, it provides a SERS enhancement factor of several 10^6 and detection capability for sub-monolayer coverage. The DWGS demonstrates reusability, as well as long-term stability on the shelf. Experimental validation with various analytes, spanning from chemisorbed, physiosorbed, plant extract and even gaseous species to proteins and DNA strains, confirms the sensitive and reproducible nature of DWGSs, thereby establishing them as a promising SERS substrate for future sensing applications.

References

[1] C. V. Raman *et.al*, Nature 1928, 121, 501.
[2] M. Fleischmann *et.al*, ACS Nano 2020, 14, 28.
[3] K. Kneipp *et.al*, Chemical Reviews 2017, 117, 5002.
[4] M. G. Banaee *et.al*, ACS Nano 2011, 5, 307.
[5] J. S. Huang *et.al*, Nature Communications 2010, 1.

Figures

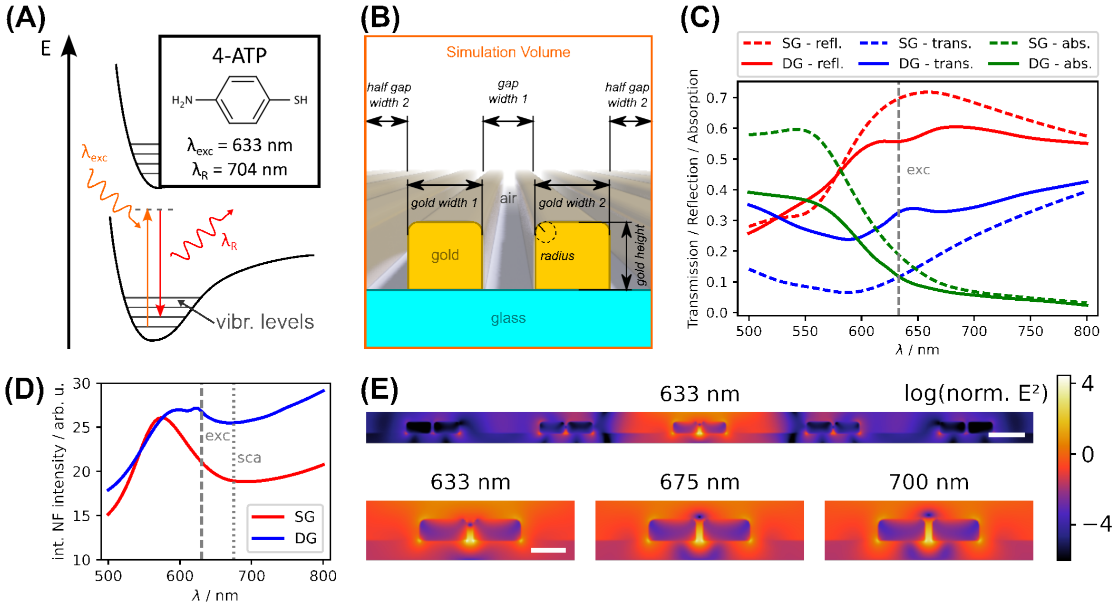

Figure 1: Numerical optimization. (A) Simplified energy level scheme of the Stokes-Raman-scattering process. The inset shows the 4-Aminothiophenol (4-ATP) molecule structure. (B) The elementary cell cross-section illustrates the potential possible free parameters for the optimization of substrates. (C) Spectra of transmission (blue), reflection (red) and absorption (green) for optimized substrates SG (dashed lines) and DG (solid lines). (D) Integrated near-field intensity enhancement for the substrates (SG, DG). (E) The optimized substrates near-fields are showcased in a vertical cross-section, illuminated from above, at three different wavelengths. Scalebar (E): top – 200 nm; bottom – 100 nm.

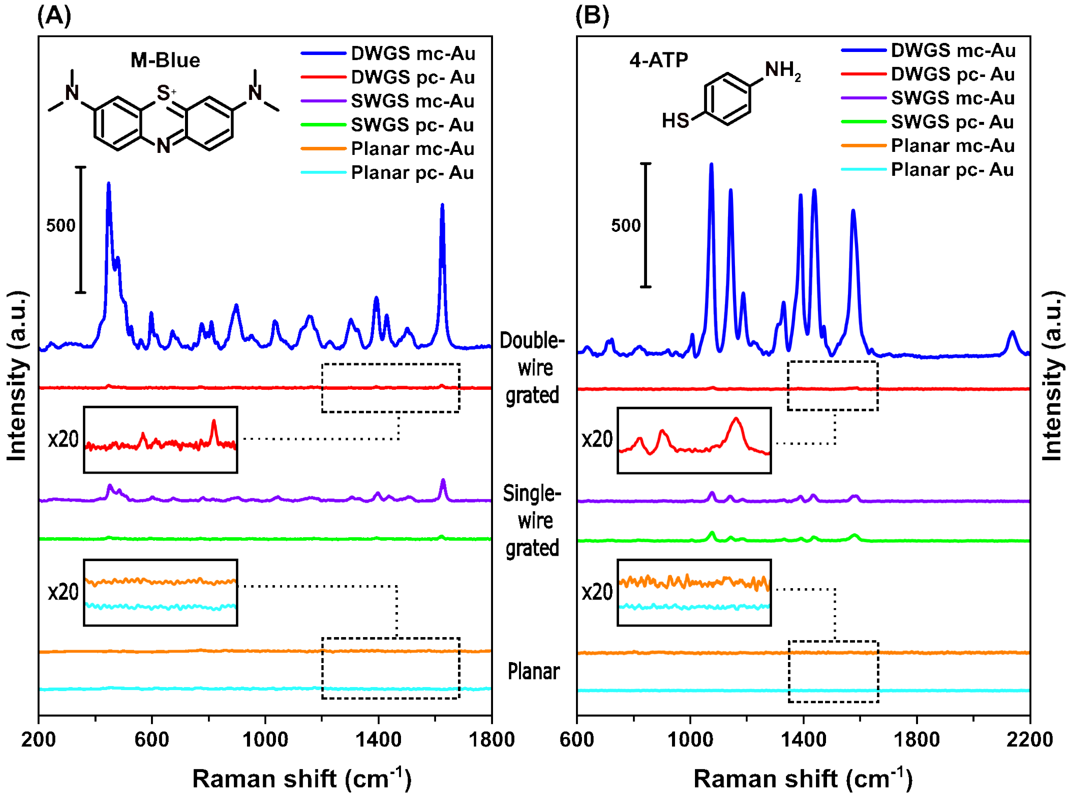

Figure 2: Panel (A) displays SERS measurements of M-Blue (1 µM) on dip-casted planar Au (non-grated), single wire grating substrate (SWGS), and double-wire grating substrate (DWGS). Both monocrystalline (mc-Au) and polycrystalline (pc-Au) gold materials were utilized for each substrate type. A zoomed-in view of the interval between 1200 cm-1 -1700 cm-1 is presented to highlight the relevant peaks. (B) Depicts SERS signals of 4-ATP SAM on the same substrates as in panel (A). Here, a zoomed-in view of the intervals between 1350 cm-1 -1650 cm-1 is provided.