

Plasma-Fabricated Metasurfaces for SERS Detection of Warfare Chemicals

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Summary:

We report plasma grown vertical copper oxide metasurfaces decorated with silver for surface enhanced Raman detection of explosive molecules. The substrates are synthesized directly on copper in a one step oxygen plasma process and converted into broadband plasmonic sensors. The platform delivers nanomolar detection of tetryl and HMX together with good spectral reproducibility. Excitation wavelength dependent shifts in nitro vibrations reveal charge transfer contributions that matter for reliable spectral interpretation. The approach offers a scalable route toward low cost field deployable chemical sensors.

Keywords: chemical sensors, plasmonic metasurfaces, SERS, explosives detection, plasma synthesis

Background, Motivation and Objective

Surface enhanced Raman scattering is one of the most attractive routes for trace chemical sensing because it combines molecular specificity with very high sensitivity. Its practical deployment, however, is still constrained by the need for substrates that are simultaneously strong, reproducible, low cost, and scalable [1-3]. Vertically oriented nanoarchitectures are especially interesting because they expose a large active area and can host dense plasmonic hotspots at ridges, edges, and interparticle gaps. The objective of this work was to develop a simple dry process that directly converts copper into a vertical oxide metasurface and then transforms it into a high performance SERS sensor for explosive molecules.

Description of the New Method or System

Copper samples were cleaned, plasma treated in oxygen at 350 Pa, and processed for 20 min in a glow to arc transition regime at 630 V and 0.25 A while the sample temperature was maintained at about 520 °C [3]. This one step oxidation route generated densely distributed vertical CuO/Cu₂O nanosheets across the substrate. The sheets had typical widths of 5-10 μm, heights of 10-12 μm, root thickness near 1 μm, and sharpened ridges of about 50-100 nm [3]. A 100 nm Ag layer was then sputtered in two 50 nm steps, forming discontinuous nanoparticles and nanoaggregates with typical dimensions around 10-50 nm on ridges and sidewalls. The

central novelty is that plasma induced stress, fast oxidation kinetics, and structural disorder are not treated as defects to be removed, but as design variables that promote 2D sheet formation and broadband plasmonic hotspot generation.

Results

Raman spectroscopy, X ray diffraction, electron microscopy, and TEM analysis showed that the walls consist of intergrown CuO and Cu₂O domains with wedge like morphology, stacking faults, and local compositional variation [3]. Compared with classical thermal oxidation, model based analysis indicated roughly twenty times faster oxide growth under plasma exposure, consistent with enhanced adsorption and ion assisted transport [3]. After Ag deposition, the metasurface displayed strong electromagnetic confinement in nanoparticle gaps and crevices over a broad excitation range from 488 to 633 nm. Using crystal violet as a marker, the substrate showed relative standard deviation of about 9.7 percent and an analytical enhancement factor of about 6×10^6 to 9×10^6 [3]. A benchmark detection limit of about 1.5-2.0 nM was obtained for crystal violet [3].

Diffuse reflectance measurements further showed that Ag coating increased the optical response in the visible range, while simulations indicated that the strongest local fields were concentrated in the smallest nanoparticle gaps and in narrow crevices on the vertical ridges [3]. Shorter wavelength excitation preferentially

activated smaller particles and tighter gaps, whereas longer wavelengths coupled more efficiently to larger particles and wider gaps. This broadband behaviour is important because practical sensors must remain informative under different laser configurations and for analytes with different resonance conditions.

The most important application result was the detection of explosive analytes. For tetryl and HMX, clear SERS fingerprints were measured at nanomolar concentrations with estimated limits of detection of about 4-5 nM and 2-3 nM, respectively, under 488 nm excitation [3]. The tetryl spectra also revealed pronounced excitation dependent behaviour: the symmetric NO₂ stretching mode shifted from about 1376 cm⁻¹ at 633 nm to about 1334 cm⁻¹ at 535 nm and about 1327 cm⁻¹ at 488 nm [3]. This trend supports a laser dependent charge transfer contribution from Ag into the analyte LUMO, which is relevant for reference database construction and machine learning workflows that use vibrational fingerprints for hazardous chemical classification [3-5].

Discussion and Outlook

Beyond the specific explosives tested here, the results show how plasma processing can be used to tune both morphology and sensing function in a substrate integrated architecture. The oxide scaffold supplies vertical geometry, mechanical robustness, and a high density of accessible sidewalls, while the discontinuous Ag overlayer creates the local plasmonic environment required for SERS. Because the sensing surface is generated directly on copper, the route avoids lithographic alignment and multistep colloidal assembly. This is attractive for scale up, batch fabrication, and eventual integration into compact sensor heads or disposable cartridges.

The wavelength dependent red shift of tetryl also highlights an important data quality issue. Spectral position is not determined only by the analyte itself, but also by the interplay between hotspot geometry, excitation wavelength, and charge transfer at the metal molecule interface. For practical deployment, this means that reference spectra should be collected under controlled optical conditions and that spectral libraries used for automated classification should contain metadata on the excitation source and substrate type. These requirements are especially relevant for hazardous chemicals, where confident discrimination among chemically similar nitro compounds is essential.

Conclusions

The presented CuO/Cu₂O-Ag platform shows that plasma oxidation can serve as a practical fabrication route for vertical SERS metasurfaces without lithography or wet chemical multistep

growth. The combination of anisotropic oxide sheets and discontinuous Ag nanoparticles provides strong hotspot density, good reproducibility, and broadband operation. Because the process is simple and substrate integrated, it is promising for portable chemical sensors aimed at security, environmental, and field analysis applications. Future work should focus on analyte libraries, stability under real sampling conditions, and transfer of the platform into deployable sensing formats.

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