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Fractal-geometry microelectrodes improves silver dendritic-based Surface Enhanced Raman Scattering.

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Abstract

Raman spectroscopy is a widely employed light-scattering-based method used for analyte identification and quantification. Despite the inherent benefits of this analytical technique, including being nondestructive and water-compatible, it faces important challenges related to the low intensities of the generated signals, as only one in 10^{10} incident photons is scattered. Surface Enhanced Raman Scattering (SERS) is a powerful technique that significantly boosts the Raman signals of molecules through enhancement of the electromagnetic (EM) field via metallic nanostructured surfaces, such as nanoparticles, dendrites and metasurfaces. The proximity between features in the metallic nanostructures, known as hot spots, offer additional enhancement in the Raman signals. Ag nanodendritic structures grown at the edges of metallic microelectrodes are SERS-active and provide an important enhancement in Raman signal amplitudes, and have found important applications in the detection and quantification of adulterated food and pharmaceuticals products. However, the prediction of the formation of hot spots in nanodendritic structures, including density, location and controlled formation of nanogaps within the nanostructures, remains a challenge. Our theoretical and experimental work provide with insights on the dynamics of dendritic growth based on local oscillatory electroosmotic flow between microelectrodes with variable axial shape. Our models also indicate that a local induced pressure field ceases the nanodendritic growth, resulting in nanogaps between nanostructures and a consequent extra boost in the EM enhancement. Here, we present an extended theoretical model that predicts the controlled nanodendritic growth to promote localized hot spots based on geometric parameters, and experimental validation using a Raman reporter. The model is used to guide the design and fabrication of microelectrodes of different shapes, including fractal and round shapes. The microelectrodes are fabricated on silicon via maskless photolithography and electron beam metal film evaporation. We demonstrate the SERS signal enhancement obtained from the fractal shape microelectrodes compared to previously established geometries by comparing the analytic enhancement factor (EF). Our approach shows the potential of fractal shapes for monitoring and risk analysis in the pharmaceutical and food industry settings, improving the performance of well-established SERS substrates with no changes in the cost of the fabrication process.

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