proceedings

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Abstract

Plasmonic Nanopores as Tunable Optical Platforms for Single-Molecule Detection †

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† Presented at the XXXV EUROSENSORS Conference, Lecce, Italy, 10–13 September 2023.

Abstract: Tunable plasmonic nanostructures are of the utmost importance in sensing applications due to their ability to precisely manipulate and control light–matter interactions at the nanoscale. The easy control of geometrical features enables the optimization of their optical properties, such as the resonance frequency, intensity, and spectral width, to match the specific requirements of the sensing system. Enhanced sensing performances are thus achieved in terms of the sensitivity and selectivity towards target analytes, leading to improved detection limits and accuracy. Additionally, tunable plasmonic nanostructures offer the flexibility to adapt to different sensing conditions and analytes, making them versatile platforms for a wide range of sensing applications. In this work, a low-cost and optimized fabrication protocol was developed to realize highly ordered nanopores in thin gold films with tunable plasmonic features. Performances of the realized nanostructures were tested by different metal-enhanced spectroscopies, in particular Surface-Enhanced Raman Spectroscopies.

Keywords: plasmonics; nanopores; metal nanostructures arrays; surface-enhanced spectroscopies; nanosphere lithography

Citation: Colombelli, A.; Lospinoso, D.; Manera, M.G. Plasmonic Nanopores as Tunable Optical Platforms for Single-Molecule Detection. *Proceedings* **2024**, *97*, 154. https://doi.org/10.3390/proceedings2024097154

Academic Editors: Pietro Siciliano and Luca Francioso

Published: 7 April 2024

1. Introduction

Plasmonic nanostructures with tunable optical properties can be used for the sensitive optical detection of biological and chemical compounds [1–3], with many applications in medical research, environmental studies, and spectroscopy [4]. The realization of optimized sensing platforms depends strongly on the ability to finely control the optical features of nanostructures, which are, in turn, intimately linked to their geometrical and compositional properties. For this purpose, Surface-Enhanced Raman Scattering (SERS) transducers have been realized, based on the efficient excitation of surface plasmons (SP), which determine the increase in and the concentration of the near optical field with respect to the exciting one, especially localized in small geometric features ("hot spot"). The ability to create nanomaterials on solid support that can be easily integrated with microfluidics, capable of simultaneously guaranteeing a high amplification of the Raman signal, together with their reproducibility over a large area by means of hot spots uniformly distributed on the substrate, is needed. For this purpose, a very interesting potentiality is offered by the suitable preparation of ordered arrays of nanopores in thin metal films. These structures, in fact, allow obtaining a uniform distribution of the amplified electric fields due to the interaction between localized surface plasmons resonances (LSPR) and propagating surface resonances (SPPR), as well as the possibility of modulating the intensity and the spectral position of these modes by acting on the periodicity, the size of the pores, or the composition of the metal film, making them the proper choice both for refractive index sensing and surface-enhanced spectroscopy applications [5].

2. Materials and Methods

In this work, an efficient and reproducible fabrication protocol is presented, based on a modified nanosphere lithography (NSL) [6] method to realize highly ordered nanopores in thin gold films with tuning plasmonic features [7]. Based on the self-assembly of close-packed polystyrene particles at the air/water interface, this approach enables the fabrication of a large-area colloidal mask with a high-quality crystal-like structure and hexagonal symmetry, easily transferrable onto solid supports. The subsequent controlled reduction in the particle size allows obtaining a non-close-packed monolayer, which is used as a sacrificial mask to realize the nanopore array by metal evaporation. The relationships between the geometric characteristics of different types of nanostructures and optical phenomena such as enhanced absorption or extraordinary transmission were investigated in detail. Theoretical and experimental studies were conducted, as well as a comparison of the optical characteristics of four types of structures, with two different diameters and thickness, evidencing their hybrid nature as a result of an interplay between localized and propagating plasmon modes (Figure 1). Great electric field enhancement and local confinement onto the surface of the transducer were found due to the interaction with light, with the potential modulation of their optical properties according to their geometric characteristics.

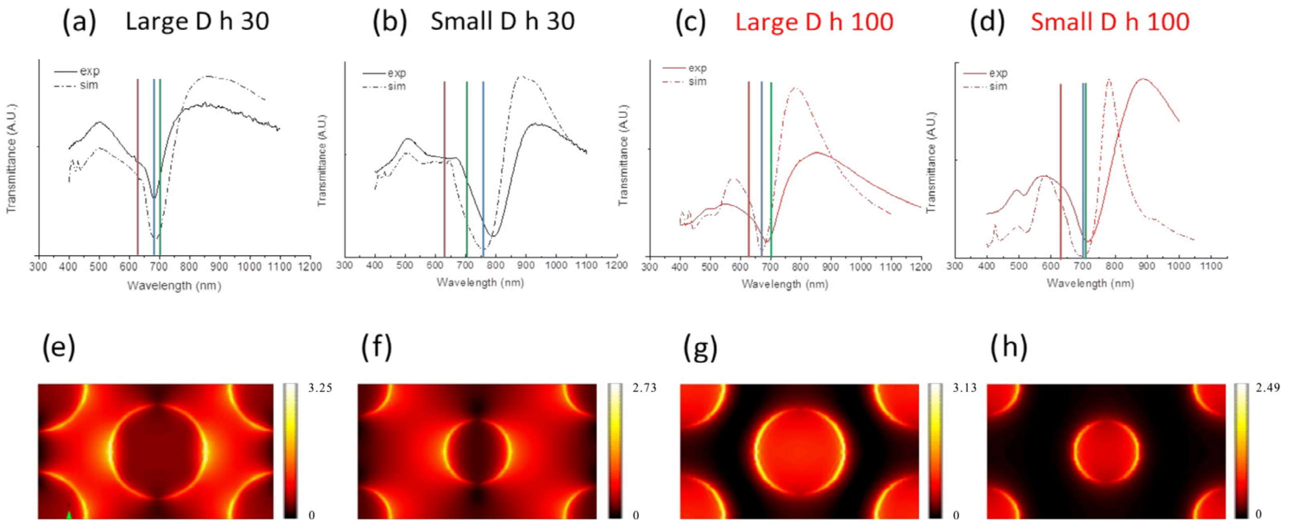

Figure 1. (**a**–**d**) Simulated (dashed lines) and experimental transmittance spectra shown together for comparison. Vertical lines indicate the position of the excitation wavelength (red), the strongest minimum wavelength λ3 (blue), and the Raman band position of the selected Raman probe (green). (**e**–**h**) Horizontal cross sections of the local field distribution at the strong minimum position λ3.

3. Discussion

The performances of the nanostructures thus realized were tested as SERS substrates. Higher performances (enhancement factor EF up to 107) than similar nanostructures reported in the literature [8,9], close to single molecule detection, were obtained. These results were achieved also due to the possibility of exploiting the most effective resonances for the enhancement mechanism as well as their spectral position relative to the excitation wavelength and the investigated Raman band.

Author Contributions: Conceptualization, M.G.M. and D.L.; methodology, A.C.; software, A.C.; validation, D.L.; formal analysis, M.G.M. and D.L.; investigation, A.C. and D.L.; writing—original draft preparation A.C. and D.L.; writing—review and editing and supervision, M.G.M.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors are grateful to Enrico Melissano, Pasquale Cretì, and Adriana Campa for metal deposition and oxygen plasma etching routines in the clean room facilities.

Conflicts of Interest: The authors declare no conflicts of interest.

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