Fabrication of a Miniaturized Flexible Metalized Micro-Rough PDMS Substrate with Dual SPR-SERS Sensing Capabilities

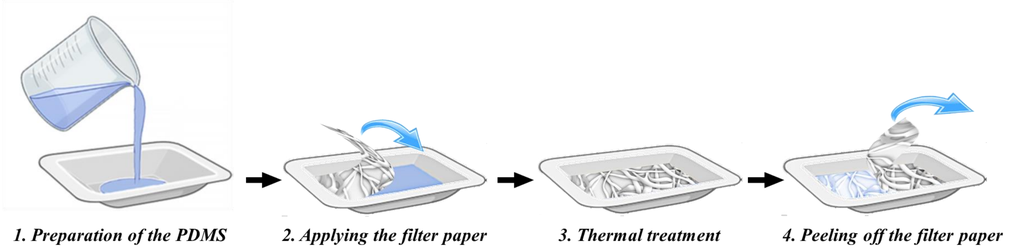
Andreea Campu [1], Mihnea Moruz [2], Monica Potara [1], Adriana Vulpoi [3], Simion Astilean [1,2], Monica Focsan [1]

[1] Nanobiophotonics and Laser Microspectroscopy Center, Interdisciplinary Research Institute in Bio-Nano-Sciences, Babes-Bolyai University, Cluj-Napoca, Romania.
[2] Biomolecular Physics Department, Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania.
[3] Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute in Bio-Nano-Sciences, Babes-Bolyai University, Cluj-Napoca, Romania.

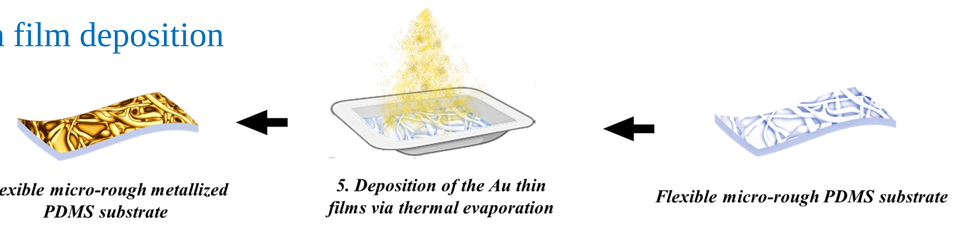
A lot of effort has been invested in the development of highly active substrates for efficient and specific biodetection of target analytes, which have a direct and significant impact on the people's lifestyle and healthcare system. In this context, our work proposes a new innovative miniaturized flexible sensing platform based on a micro-rough polydimethylsiloxane (PDMS) substrate exhibiting dual spectroscopic Surface Plasmon Resonance (SPR)-Surface Enhanced Raman Spectroscopy (SERS) detection capabilities. Specifically, a flexible PDMS substrate was prepared by imprinting the 3D micro- and nano-fiber matrix of filter paper on the substrate's surface during the thermal curing of PDMS, thus obtaining a micro- and nano-roughness of the PDMS substrate. Next, by employing a Physical Vapor Deposition (PVD) method – specifically, thermal evaporation, gold (Au) thin films of different thicknesses (e.g. 5, 10, 20 and 30 nm) were successfully deposited. The as-developed substrates were optically and morphologically characterized. 4-mercaptobenzoic acid (4-MBA), a well-known Raman reporter, was used to investigate the SPR-SERS sensing capabilities with respect to the Au thin film's thickness, thus demonstrating that the deposition of the 20 nm Au thin film exhibits the best detection performances, which was further analyzed in terms of sensitivity. Thus, a limit of detection as low as 10^{-10} M 4-MBA was determined for SPR sensing, proving its high sensitivity and supporting it further implementation as an active, fast-responsive and reliable detection platform for diagnostic and monitoring applications.

I. Fabrication of the Flexible Metalized Micro-Rough PDMS Substrate

Step 1. Fabrication of the flexible micro-rough PDMS substrate

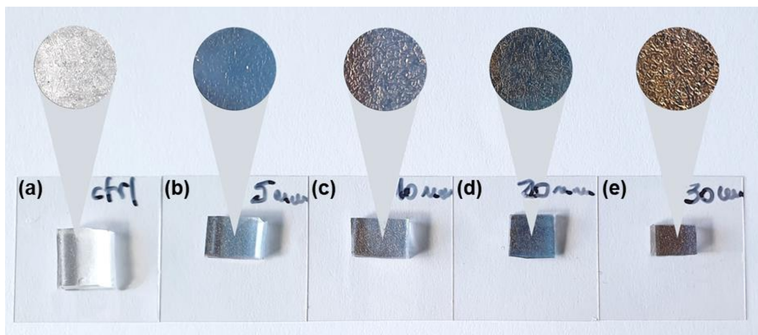


Step 2. Thin film deposition

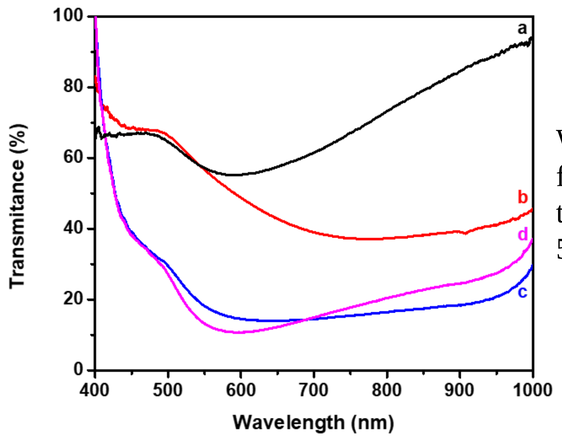


II. Optical Properties

The micro-rough surface of the flexible PDMS substrates is visible to the naked eye. The different colors after the thin film deposition suggest different Au film thicknesses.



Digital images of the flexible PDMS metallized micro-rough substrates.

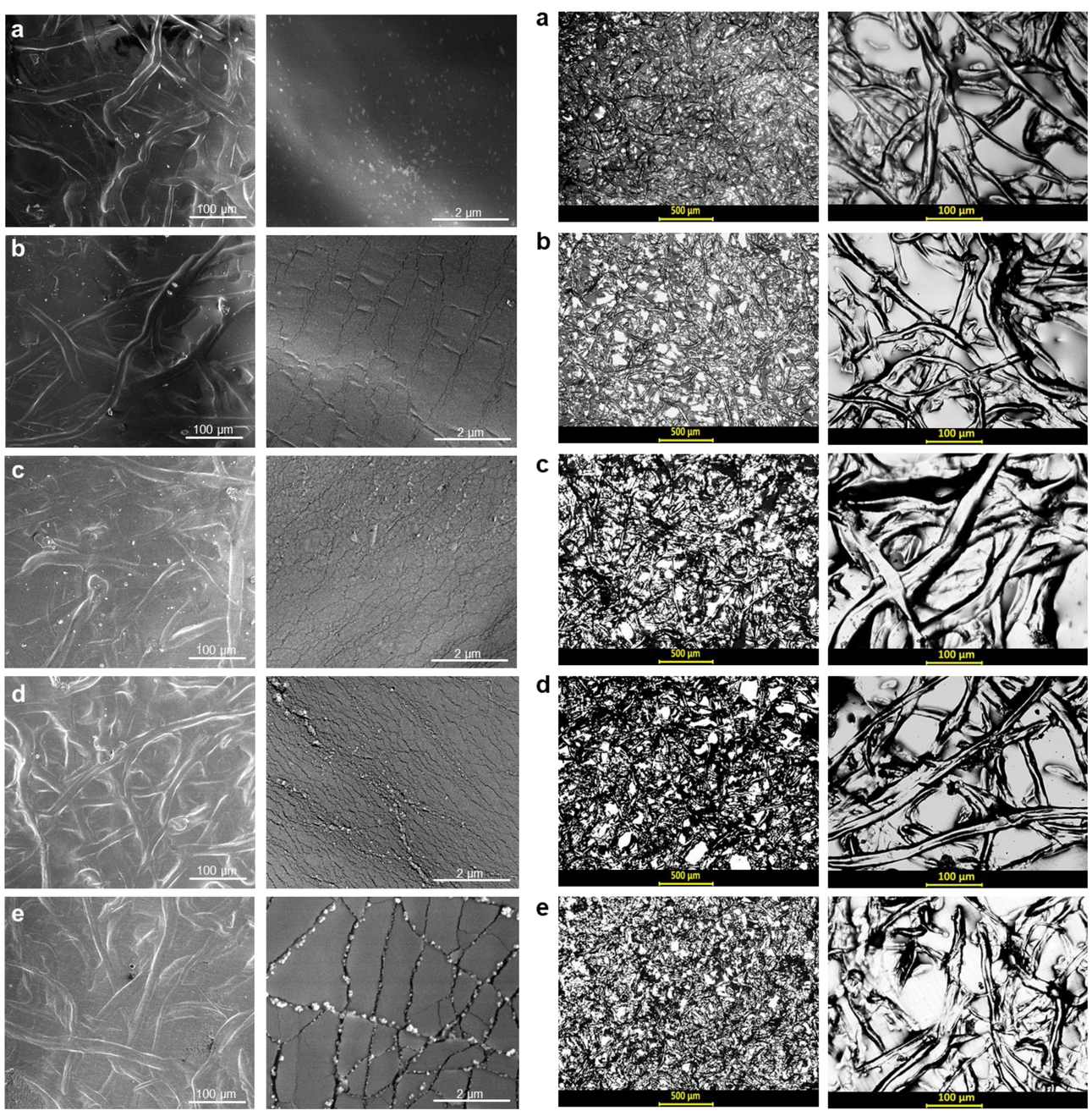


With the increase of the Au thin film thickness, the characteristic transmittance band at around 560 nm is better defined.

Thin film thickness: (a) 5 nm; (b) 10 nm; (c) 20 nm; (d) 30 nm.

III. Study of the as-developed sensing platform's morphology

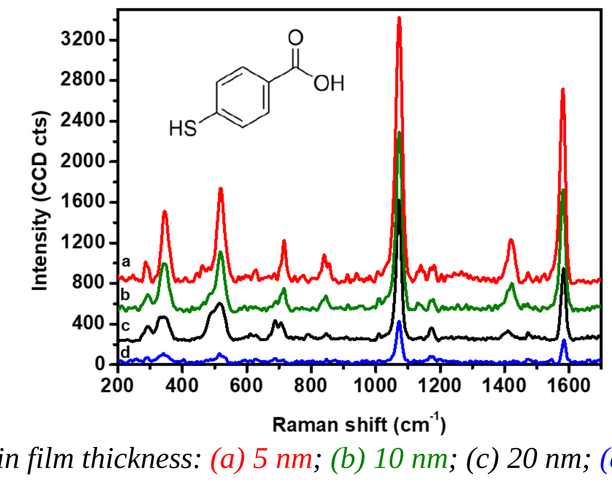
Scanning Electron Microscopy images confirm the imprinted 3D matrix of the filter paper as well as the deposition of homogeneous Au thin films. The results are confirmed also by optical microscopy images realized in reflectance.



Thin film thickness: (a) 0 nm; (b) 5 nm; (c) 10 nm; (d) 20 nm; (e) 30 nm

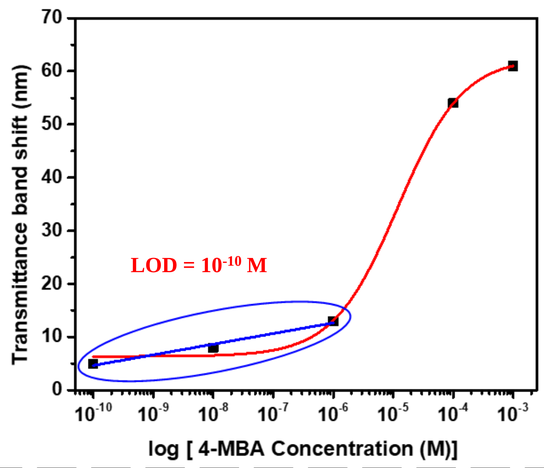
IV. Dual SERS-SPR Sensing Capabilities

The 4-MBA characteristic Raman bands were identified by all metallized PDMS substrates. However, the most intense Raman signal was obtained for the PDMS substrate with a 20 nm thick Au thin film.



Thin film thickness: (a) 5 nm; (b) 10 nm; (c) 20 nm; (d) 30 nm.

The PDMS micro-rough substrate having a 20 nm thick Au film was exposed to different 4-MBA concentrations and the transmittance band was monitored. Thus, a SPR detection limit of 10^{-10} M was determined.



V. Conclusions and Perspectives

We successfully modified the micro-roughness of the PDMS substrate by imprinting the 3D matrix of filter paper during the preparation PDMS process. Homogeneous Au thin films having different thicknesses (5, 10, 20 and 30 nm) were deposited by the PVD thermal evaporation process.

The Raman reporter 4-mercaptobenzoic acid was successfully identified *via* SERS by all developed PDMS substrates, however the best SERS performance is exhibited by the PDMS micro-rough substrate having a 20 nm thick Au film. Furthermore, the SPR sensing capabilities were demonstrated by the achieved low limit of detection (10^{-10} M 4-MBA).

The proposed sensing platform integrates advantages such as **sensitivity, low-cost, miniaturization, portability,** and **flexibility** as well as high potential to be easily adapted for personalized applications.

Acknowledgements: Funding by the CNCS-UEFISCDI Romania, under the project number PN-III-P1-1.1-PD-2021-0175 is gratefully acknowledged.