Towards Label-Free SERS Detection: Universal Fabrication of Highly Efficient Plasmonic Platforms

Sara Gullace
Verónica Montes-García, Victor Martín, David Larios, Valentina Girelli Consolaro, Fernando Obelleiro, Giuseppe Calogero, Stefano Casalini, and Paolo Samorì

Université de Strasbourg, 8 Allée Gaspard Monge, Strasbourg 67000, France
University of Messina, V.le F. Stagno d'Alcontres 31, Messina 98166, Italy

gullace@unistra.fr

Being characterized by high sensitiveness, surface-enhanced Raman scattering (SERS) spectroscopy currently represents one of the most promising analytical techniques in the field of sensors development. [1] Generally, identification of the analytes relies on the enhancement of the Raman active modes of target species or their Raman reporters when in close proximity to plasmonic substrates. High sensitivity can be ensured by the accurate design and engineering of the hot-spot size and density, i.e. the optimization of the interparticle distance. Herein, we report the fabrication of highly efficient plasmonic sensing platforms by electrostatic layer-by-layer deposition of metal nanoparticles (NPs). In order to optimize the response, we investigated the role of the NPs size and composition, as well as the hot-spot size and density. The analysis of the SERS performance of all the different platforms revealed that 89 nm Au@Ag core@shell NPs ensured the best SERS efficiency when electrostatically assembled using GO@PDDA (viz. poly(diallyldimethylammonium chloride) - functionalized graphene oxide) as interlayer. (Figure 1)
The high performance of this plasmonic platform as a label-free SERS substrate has been successfully tested by comparing the SERS and Raman spectra of methylene blue, methyl orange, and dopamine in Milli-Q water. Furthermore, we challenged our sensing platform to detect tamoxifen (TAM), a well-known anticancer cytotoxic drug, which has been found as contaminant in hospital effluents. We were able to observe a linear variation of the signals of TAM as a function of its concentration (0.09 – 0.9 mg mL^{-1}) achieving a limit-of-detection of 3 × 10^{-2} mg mL^{-1}, outperforming the previously reported SERS sensors (3.7 × 10^{-1} mg mL^{-1}). [2] In addition, TAM detection was successfully achieved even in a complex matrix such as tap water. (Figure 2) [3]

References

[1] Langer, et al., ACS Nano, 14 (2020), 28
[2] Sakir, et al., Microchem. J. (2020), 154, 104628
[3] Gullace, et al., Small, 33 (2021), 2100755

Figures

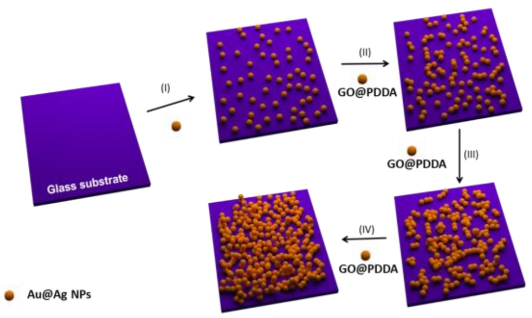

Figure 1: Schematic representation of assemblies of Au@Ag NPs fabricated by electrostatic LbL deposition using GO@PDDA as interlayer.

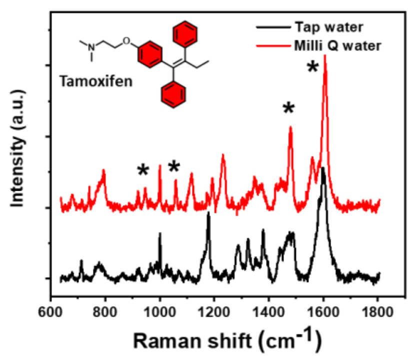

Figure 2: Representative SERS spectra of 0.9 mg mL^{-1} TAM in Milli Q and tap water.