Hierarchical binary structures as SERS-active substrates

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Surface-enhanced Raman spectroscopy (SERS) is a powerful analytical technique, which is capable to provide the Raman fingerprint of the biological targets nearby or in contact with the SERS active substrate. SERS substrates featuring high-density hot spots as well as good uniformity, reproducibility and high sensitivity are strongly demanded to enable the real-world application of SERS-based analytical approaches [1]. In particular, self-assembled closed packed arrays of polystyrene nanospheres covered by thin layer of gold already demonstrated to be valuable SERS substrates [2]. Herein, we propose a self-assembled hierarchical binary structure as SERS-active substrate. The substrate is composed of two layers of nanospheres featuring two different diameters: the former is a closely packed array of "large" polystyrene nanospheres, the latter is composed of "smaller" nanospheres superimposed at the interstices of the closed packed array. The whole hierarchical structure is coated with a thin layer of gold. A three-dimensional numerical analysis using the finite element method was carried out to assess the expected performances by changing the geometrical parameters. The numerical analysis has been focused to obtain information on the distribution of the electric field (i.e. hot spots) and on the enhancement factor. Once the optimal parameters combined with manufacturing constraints have been identified, we fabricated the proposed hierarchical structure using a self-assembly technique [2]. Morphological and spectral characterizations were performed demonstrating the regularity of the patterns and the repeatability of the nanostructures. The performances of the fabricated substrates have been evaluated by carrying out SERS measurements, employing the biphenyl-4-thiol (BPT) monolayer as a Raman probe molecule. The experimental results, in agreement with the numerical analysis, demonstrate that hierarchical binary structures provide a significant improvement with respect to single closed packed array SERS substrate.

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