Porous plasmonic nanostructures for Surface Enhanced Raman Scattering: development of biosensing platforms

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The assembly of Surface Enhanced Raman Scattering (SERS) active plasmonic nanostructures in meso/macroporous spongiform matrixes yields functional hybrid nanosystems. Indeed, the combination of metals and dielectrics, the huge surface area and an improved stability of the particles embedded in the porous structure provide benefits in terms of SERS enhancement and bioanalyte pre-concentration or separation [1].

In this work, we present three plasmonic nanostructures that take advantage from peculiar features related to their porosity: mesoporous silicon (pSi) decorated with Ag nanoparticles (NPs), graphene-metal based aerogels and flower-like Ag nanostructures. Densely packed and uniformly distributed silver NPs were synthesized *in situ* from $AgNO_3$ solutions on pSi-PDMS membranes (Fig.1a), either by immersion plating or in a controlled microfluidic environment [2]. Such nanostructures are featured by Localized Surface Plasmon Resonances in the whole Vis-NIR range, thanks to the high refractive index substrate, and present an optimal stability due to the direct growth of the NPs from the silicon pores. Aerogels based on reduced Graphene Oxide (rGO) decorated with Ag NPs (Fig. 1b) were obtained by exploiting a one-pot hydrothermal process followed by a freeze-drying step [3], by starting from an aqueous dispersion of commercial GO single-layer flakes and adding $AgNO_3$ with different reducing agents, such as trisodium citrate [4]. Their SERS application takes advantage from the synergic plasmonic and charge transfer enhancements obtained by coupling Ag NPs to rGO and from the high surface area of the 3D sponge-like nanostructured network, able to concentrate and adsorb biomolecules from highly diluted solutions. Flower-like porous nanostructured Ag NPs forming a nano-net architecture (Fig. 1c) were produced by using L-cysteine as reducing/stabilizing agent under mild condition, by following a modified procedure discussed in the recent literature [5]. These last structures can be easily immobilized on PDMS or on filter paper, and the presence of a multitude of sharp edges forming nanogaps, which act as Raman hot-spots, can be fruitfully exploited for SERS.

After the morphological and compositional characterization of the synthesized NPs, their SERS response was tested by using organic chromophores. A critical comparison concerning the Raman enhancements obtained for the three SERS-active substrates was performed, approaching single molecule detection regime. Finally, different surface grafting strategies for oligo-probes immobilization were developed and compared, exploiting the different surface chemistry of the metal NPs and rGO. The plasmonic nanostructures were then tested for the detection of miRNAs, a class of useful cancer biomarkers, through the application of an innovative two-step hybridization assay [6].

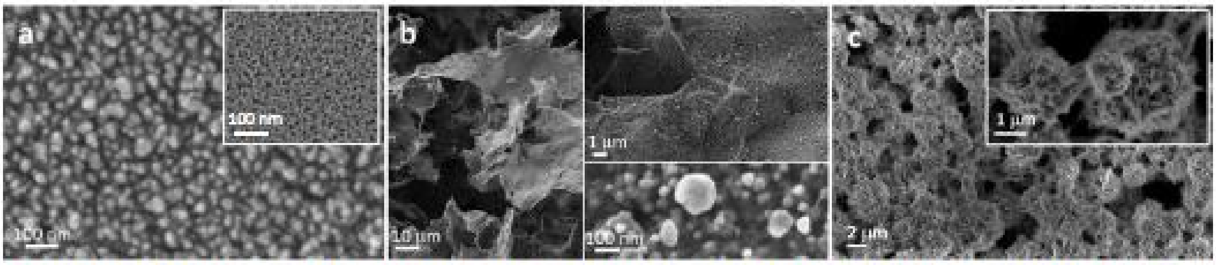

Figure 1: FESEM images of the porous plasmonic nanostructures: a) Ag NPs on pSi. The inset shows the porous matrix under the dense NP coverage; b) Ag NPs coated rGO aerogel at different magnification levels; c) flower-like Ag nanonet. A detail of the porous nanostructures is provided in the inset.

References

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