Massive Assembly of Metal Nanoparticles for Reproducible SERS Substrates

Oded Rabin[a], Xin Zhang[b], and Robert M. Briber[b]

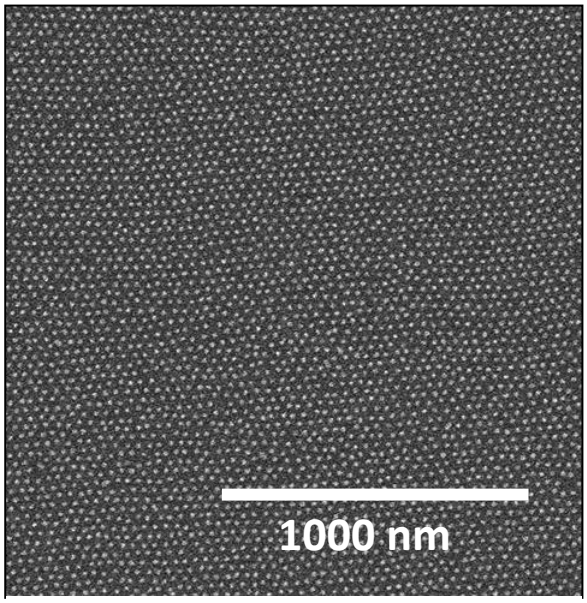
[a] *Department of Materials Science and Engineering and Institute of Research in Electronics and Applied Physics, University of Maryland – College Park, USA, oded@umd.edu,* [b] *Department of Materials Science and Engineering, University of Maryland – College Park, USA.*

Surface enhanced Raman spectroscopy (SERS), an analytical technique with high sensitivity and high chemical differentiation power, relies on the strong localization of electric fields by surface plasmons. The electric field distribution around nanostructures depends, in turn, on the nanoscale geometry of the surface and the spatial variation of the dielectric function. Small changes in this local electric field result in large changes in Raman scattering signals. Due to process variations in the mass fabrication of plasmonic nanostructures, SERS repeatability is non-trivial.

The fabrication of SERS substrates by the assembly of metal nanoparticles is an attractive approach due to its low cost and large area production. However, control over the assembly to repeatedly obtain surfaces with prescribed SERS characteristics is challenging. We demonstrate that templated assembly of metal nanoparticles on cylindrical domains of block-copolymer films results in hexagonally ordered nanoparticle arrays that have consistent optical and SERS enhancing properties across large areas and from batch-to-batch.

The fabrication of the SERS substrate consists of 3 steps: (1) The preparation of a block-copolymer film on a rigid substrate, where said film consists of an hydrophobic matrix and a hexagonal array of hydrophilic cylindrical domains. A typical diameter of the domains is 20nm, and the center-to-center distance is typically ~40 nm. The hydrophilic domains are functionalized such that they possess positive electrostatic charges in aqueous solutions. (2) The adsorption of negatively-charged, monodispersed metal nanoparticles onto the block copolymer film, selectively occurring on the hydrophilic cylindrical domains due to the electrostatic interactions. (3) The electroless deposition of metal on the adsorbed nanoparticle to increase their size and reduce the size of the gaps between them.

Figure 1 shows a typical substrate following adsorption of gold nanospheres on the block-copolymer film (step #2). The image demonstrates the uniformity of the substrate and hints to the commensurate alignment of the nanoparticle array and the block-copolymer domain array. A low concentration of vacancies (i.e. domains with no nanoparticle) and a few instances of dimerization (i.e. two particles per domain) can be observed. The formation of the hexagonal array of metal nanoparticles is optimal when the domain size is close to the nanosphere size. However, this condition results in arrays with inter-particle separations that are too large for optimal SERS performance.



nanospheres arrayed over a block-copolymer templating film.

The inter-particle separation is reduced by electroless deposition of metal on the immobilized nanospheres (step #3). As the growth time increases, the particle diameter increases and the gaps between particles decrease in size. Simultaneously, the collective plasmonic response of the substrate to incoming optical radiation changes as the coupling between adjacent nanoparticles increases. As shown in Figure 2, the coupling between nanoparticles can

improve the SERS enhancement by the metal nanosphere array. However, the fabrication conditions that lead to the optimal SERS substrate enhancement factors are dependent on the spectrometer wavelength. Conveniently, the process outlined above can be easily regulated to produce the substrate that best fits the costumer's Raman spectrometer.

Thus far, uniform substrates were fabricated over up to 4 inch silicon wafers. The SERS substrate enhancement factor (probing adsorbed thiol monolayers) is routinely $>8\cdot10^4$ for excitation with a 633nm laser and $>5\cdot10^5$ with a 785nm laser. 1,2-bis(4-pyridyl)ethylene has been detected down to 10^{-9}M concentration.

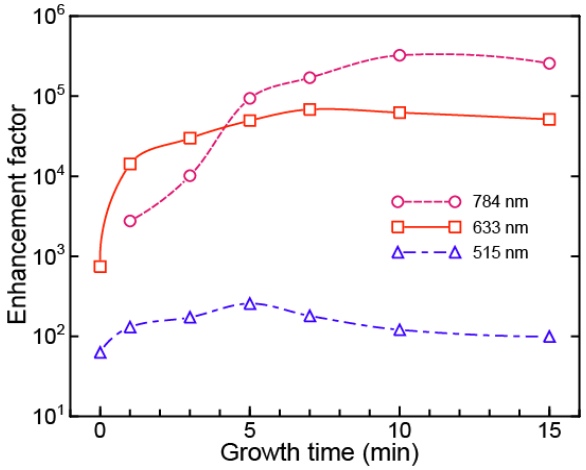


Figure 2: SERS substrate enhancement factor of nanoparticle array substrates as a function of overgrowth time and spectrometer wavelength.Figure 1: SEM image of gold