## 2D and 3D Plasmonic Nanostars for Bio-sensing Applications - Single Molecule Detection

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Nanostars are complex plasmonics nanostructures, where the central core and petal parameters are the main factors which determine the LSPR in the nanostar. Plasmonic Au nanostars offer great potential for biomedical application due to their biocompatibility and plasmon tunability over visible and near IR region. SERS based signal detection and molecular identification (concentration ranging from 1M to single molecule) has been investigated in the past. SERS spectroscopy provides highest sensitivity among all other analytical techniques. Up to date, SERS has been investigated in a variety of gold nanostructures/particles fabricated by top-down or bottom-up techniques. Fabrication of gold nanostructures, due to its surface stability, offers a potential application in the growing field of nanoscale bio-sensors and opto/plasmonic devices [1-5].

Herein, we report on the fabrication of novel biosensor SERS device based on plasmonic nanostars by e-beam lithography technique (EBL) and reactive ion etching (RIE) techniques. To date, Electron beam lithography is an advanced top-down nanopatterning technique in which patterns of sub-10 nm range of complex geometries are fabricated with a control over size, shape and distance between the structures. A set of periodic arrays of Au nanostars of branch length 80 nm, width 30nm, centre diameter 70 nm and inter-particle separations ranging from 6 nm to 200 nm were fabricated. Figure1(a, b) represents the typical SEM micrograph of 2D and 3D nanostar with 150 nm star size and 100 nm inter-particle separations, respectively. The fabrication process was optimized by finely tuning the particle size and shape in order to maximize the SERS enhancement. In order to assess the versatility of the nanostructures for bio-sensing applications, a monolayer of cresyl violet (CV) was deposited over the surface by means of chemisorption technique and SERS measurements were performed. Typical SERS spectra on and out of the 2D nanostar array is shown in Figure 2. Red trace refers to the SERS spectrum of CV molecules deposited on star nanostructures when the excitation laser power and integration time were fixed to  $60 \,\mu\text{W}$  and  $30 \,\text{s}$ . Low intense peaks (black trace) were observed for gold marker. Inset shows the background Raman spectrum of Au nanostructures without any molecule, showing no Raman bands within the spectral range, which confirms the absence of surface contamination. The average SERS enhancement factor was found to be about  $10^8$  with respect to the gold marker (see in the inset). In this work, we have shown the fabrication of complex 2D and 3D nanostar structures associated with EBL and RIE techniques and experimentally investigated the SERS studies on nanostar structures. The advantage of nanostar structures over other nanostructures is due to the localization of strong EM fields at branch tips and in the gaps (dips) between branches. These structures are providing a novel strategy towards the biological and chemical high sensing capability.

## References:

F. De Angelis, G. Das, P. Candeloro, M. Patrini, M. Galli, A. Bek, M. Lazzarino, I. Maksymov, C. Liberale, L. C. Andreani and E. Di Fabrizio, Nature Nanotechnol. 5 (2010) 67-72.
G. Das, F. Mecarini, F. Gentile, F. De Angelis, H. G. M. Kumar, P. Candelero, C. Liberale, G. Cuda, E. Di Fabrizio, Biosens. Bioelectron 24 (2009) 1693.

[3] C. Haynes, A. Mcfarland, and R. Duyne, Anal. Chem 77 (2005) 338A.

[4] Jeremy N. Munday and Harry A. Atwater, Nano Lett (2010).

[5] m.chirumamilla et al., Microelectron.Eng. 97 (2012) 189-192.



*Figure 1* (a,b): SEM micrographs of 2D and 3D nanostars with 150 nm size and 100 nm inter-particle spacing, respectively.



*Figure 2:* SERS spectra of 150 nm 2D Au nanostar structure (red trace) and Au marker (black trace) after depositing a monolayer of Rhodamine-6G. The SERS background coming from bare nanostar structures illustrated in the inset.