3D self-similar chain nanolens fabrication and their use in single molecule detection

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In this work, we report a novel process for the fabrication of nano-structures using e-beam lithography and electroless technique.[1] Theoretical proposal for a device with self similar chain of metallic nanoparticles based on plasmons was firstly proposed by Li et al[2] and showed drastic increase in the electric field on the smallest nanosphere gap. The fabrication difficulty for this device is twofold: the real nanoscale control (the radius of the smaller nanosphere has to be less than 10 nm) and the critical control in the gap distance between the last two sphere (around 5 nm). This is the first time, in our knowledge, that a fully fabrication control was reached and SERS measurement on such nanolens was obtained. A reproducible array pattern of nanolens are fabricated with different configuration (single lens, double lens etc.) on Si wafer. The lithographic result is shown in Figure 1. In order to control the electroless reaction, Si samples were pretreated in a 0.15M HF solution for 1 min. Si samples were immersed into the deposition bath (1 mM $AgNO_3$) for 40 sec, and thereafter rinsed with water and dried with N_2 flux. Silver nanoparticles are grown within this nano-patterned structure only. Novelty of this nanolens device is its potential in obtaining an enhancement of the electric field up to 3 orders of magnitude due to the multiplicative effect of the self-similar chain. In figure 2 is reported an SEM image of the 3D Silver lens after the local electroless reaction. SERS device was characterized by using several molecules including proteins and peptides. Raman mapping area of nanoLens structure and Raman spectra of the sample in/out of the nanostructure are shown in Figure 3a and Figure 3b, respectively. Various bands for R6G compound are observed at around 1649.5, 1574.9, 1508.9, and 1361.1 cm^{-1}, attributed to the xanthenes ring stretching of C-H, N-H, combination of νC-N and δN-H, and δC-H, respectively.[3] The broad band around 1183.6 cm^{-1} is related to the δC-H and δN-H vibration of xanthenes ring. The 3D-mapping analysis reveals the presence of R6G attached only to the metallic nanosphere. Using this SERS device we are able to detect very few molecules of R6G compound. The reproducibility of SERS device and the repeatability of SERS spectra on plasmonic nanostructure for few molecules detection open broad applications as a biomolecular sensor.

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1 M.V.T. Kortenaar, J.J.M. de Goeij, Z.I. Kolar, G. Frens, P.J. Lusse, M.R. Zuiddam, E. van der Drift, J. Electrochem. Soc. 148 (2001) C28-C33.
2 K. Li, M.I. Stockman, D.I. Bergman, Phys. Rev. Letts, 91 (2003) 227e footprint of the lens 402_1-227402_4.
3 L. Jensen, G.C. Schatz, The J. Phys. Chem. A, 110 (2006) 5973-5977.

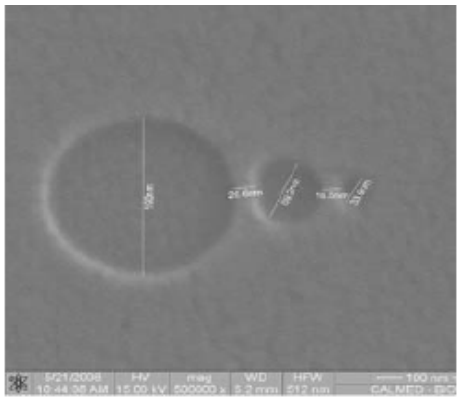

Fig 1. SEM of nanolithography defining the self similar chain

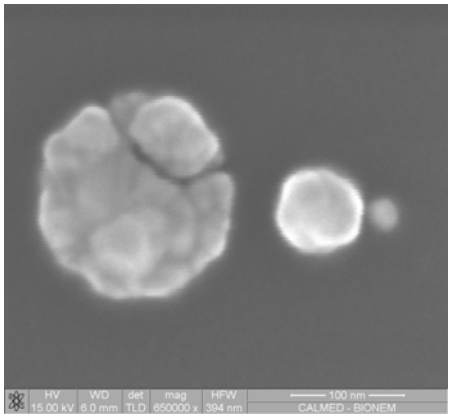

Fig 2. SEM of the 3D silver lens after electroless

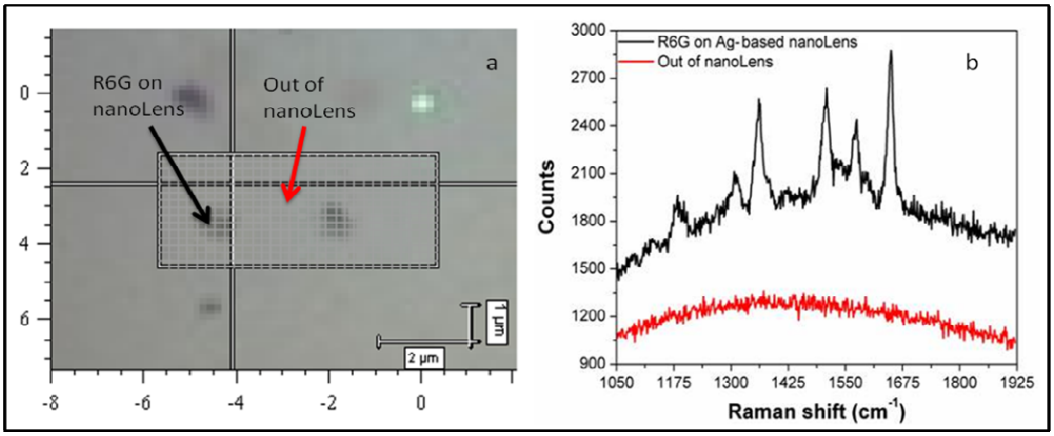

Fig 3a. Mapping area (each pixel is 100 nm) around the lens
Fig 3b. Raman spectra of R6G in and out the nanolens