

Surfing plasmonic waves
Plasmonic crystal based solid substrate for Surface Enhanced Raman Spectroscopy

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Abstract

The optical properties of nanoparticles used for enhancement of Raman signals in Surface Enhanced Raman Spectroscopy (SERS) strongly depend not only on the composition, shape and size of the particles, but also on the properties of the surrounding medium. Complex multistep synthesis methods are applied to prepare monodispersed, coated or core-shell particles that resist of aggregation, of aspecific binding of analytes or allow to collect them by external magnetic fields for easy separation and concentration [1]. Nanohole array based solid SERS substrates help to overcome these difficulties. They provide a regularly distributed array of hot spots and offer the facile phase separation advantage of heterogeneous reaction systems. In these structures, enhanced electrical field is generated when incident light excites an active plasmonic mode of nanoholes, which can be exploited for several plasmonic applications. The availability of cheap, reliable and easy to use substrates would pave the road to the development of bio-analytical tests that can be used in clinical practice.

SERS based analysis of biomarkers is expected to provide not only higher sensitivity [2] and specificity, but also multiplexing capacity and markedly improved detection speed compared to the conventional analytical methods [3]. Several studies forecast the potential of Raman-SERS to yield innovative biotechnological applications in the field of cancer diagnosis and monitoring [4-6].

We present here the SERS activity of 2-D plasmonic crystals deposited by the combination of soft-lithography and plasma deposition techniques on transparent substrates. The special lithographic process enables accurate control of the structural and chemical parameters of the crystal surfaces. In this way the plasmonic resonance spectral position was tuned to the excitation wavelength of the monochromatic light source. Samples were characterized by atomic force microscopy, scanning electron microscopy, reflectance measurements and tested for SERS activity using known Raman reporter dye molecules. The transparent support material allowed SERS detection from support side opening the possibility to use these substrates combined with microfluidic devices. In order to demonstrate the potential for bioanalytical applications, the SERS active gold surface was functionalized with thiol modified (ssDNA) capture oligonucleotides. Concentration dependent signal of a complement, Raman-reporter labeled target nucleotide (21 bp WT1 gene sequence) was detected on the surface after annealing reaction.

Based on our results, the excellent Raman enhancing properties accompanied by the ease of functionalization as well as controllability and low cost of the production procedure make this kind of nanostructures promising candidates for bioanalytical applications.

References

- [1] H.T. Zhang, J. Ding, G.M. Chow, Z.L. Dong, *Langmuir*, 24 (2008) 13197-202.
- [2] D. Graham, *Angew. Chem. Int. Ed.* 49 (2010) 9325 – 9327.
- [3] C. Kirschner, K. Maquelin, P. Pina, N.A. Ngo Thi, L.P. Choo-Smith, G.D. Sockalingum, C. Sandt, D. Ami, F. Orsini, S.M. Doglia, P. Allouch, M. Mainfait, G.J. Puppels, D. Naumann, *J. Clin. Microbiol.* 39 (2001) 1763-70.
- [4] C.T. Nguyen, J.T. Nguyen, S. Rutledge, J. Zhang, C. Wang, G.C. Walker, *Cancer Letters* 292 (2010) 91–97.
- [5] K. Hering, D. Cialla, K. Ackermann, T. Dörfer, R. Möller, H. Schneidewind, R. Mattheis, W. Fritzsche, P. Rösch, J. Popp, *Anal. Bioanal. Chem.* 390 (2008) 113–124.
- [6] G.L. Liu, F.F. Chen, J.A. Ellman, L.P. Lee, *Conf. Proc. IEEE Eng. Med. Biol. Soc.* 1 (2006) 795-8.

Figures

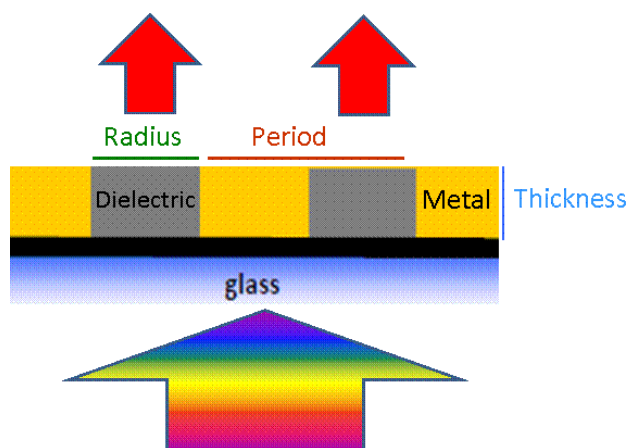


Figure 1: Nanohole array and tunable parameters

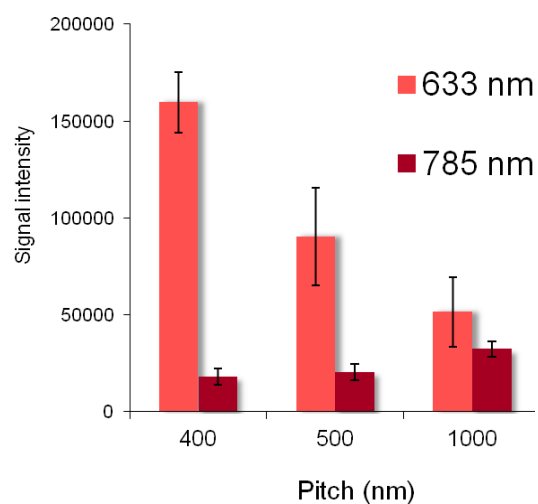


Figure 2: Tuning of the structure by changing geometric parameters

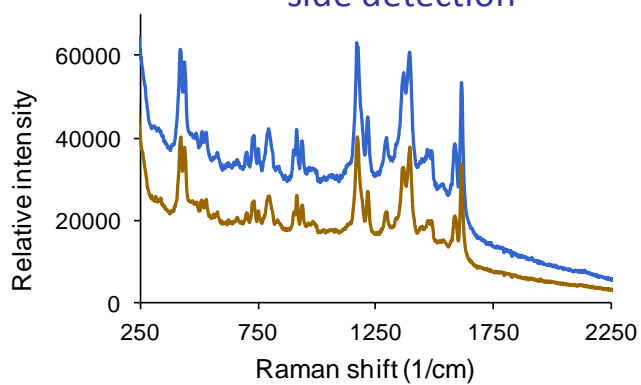
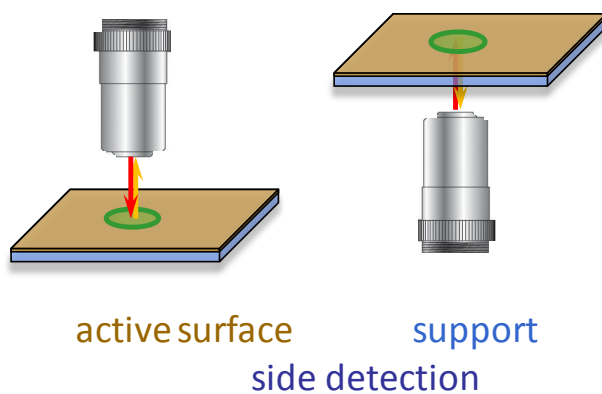


Figure 3: SERS detection of dried malachite green drop from active surface and support side on the nanoarray substrate.