Patterning Of Plasmonic Structures For (Bio)Sensing

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The electromagnetic field confinement and enhancement that can be achieved with nanostructures sustaining localised surface plasmon modes make them excellent candidates as nanoscale sensing devices for biological applications. In this communication we will show a highly-specific, label-less, localised-surface-plasmon based immunosensor for the detection of stanozolol, an anabolic agent (mis)used in sports, horse racing and as a growth promoter in animals for human consumption. We will also discuss further improvements in sensitivity that can be achieved when using optimised nano-patterned substrates that further enhance and confine the electromagnetic field.

Among their multiple potential applications [1], noble metal nano-structures sustaining localised surface plasmons (LSPs) have recently shown to be well suited for sensing purposes [2-4]. This method of sensing is advantageous when compared to conventional flat extended film surface plasmon resonance (SPR) systems [5,6] in the simplicity of the system and in the minimum detectable number of molecules involved in the binding event. Whilst LSP sensors have shown current prominence with recent demonstrations of single-particle sensing [3,4], their real-life application has not been greatly exploited. In fact, of the reported systems in the literature, emphasis has been on model systems like biotin/streptavidin and with large proteins like IgGs and albumins [3,8,9], where the huge affinity and the large size of the molecules are highly advantageous for the operation of the sensor.

In this communication we show a demonstration of label-less, quantitative detection of stanozolol (Sz, Mw 328) down to the nM range. The system basically consists of isolated gold nano-particles with a diameter of 100 nm, randomly arranged and chemically immobilized on top of a glass substrate through the use of a sylilating agent. The chemical conditions chosen

[10] allow for a consistent control of the density of gold dots, and avoid clustering of the gold particles, thus limiting the spectral broadening of the ensemble's resonance. The immobilized gold particles are coated with a Sz-BSA conjugate. Binding of the anti-Sz antibody can be observed by a shift in the resonance wavelength, measured after just 30 min incubation and 15 s recording the signal in a setup as sketched in Fig. 1. The response of the sensor has been shown to be specific and to allow for quantitative detection of concentrations of Sz in the range 1 nMº–10 µM in a competitive mode.

Further improvements to the sensitivity of this LSP-based sensor are possible through careful optimisation of the electromagnetic field landscape created by the metallic nanoparticles. In particular, by using patterned samples it is possible to create spots where the electromagnetic field is further increased and localised, at the expense of higher processing complexity.

Large electromagnetic field enhancement factors, which in turn result in enhanced sensitivities can be achieved by taking advantage of the near-field coupling between closely spaced metal nanoparticles [11]. The hot spot observed in the inter-particle nanometre gap can be seen as a consequence of the hybridization of the single-particle localized plasmon modes [12]. Although the enhancement factors reported in the literature (based on theoretical models) can reach unprecedented values, the structures proposed are far from being manufacturable with today's state-of-the-art lithographic techniques.

In this communication we propose several different nanoparticle arrangements, based on arrays of dimers and on discrete chains of nanoparticles that can be fabricated with existing lithographic techniques, yet produce significant field enhancement as compared to isolated nanoparticles. In figure 2 we show SEM micrographs of samples fabricated with electron-beam lithography combined with lift-off of a thin gold layer.

The use of arrays of dimers, as shown in fig. 2 (left), not only results in a higher sensor sensitivity (in the form of a larger resonance peak shift for a given change in dielectric function), it also results in the appearance of multiple peaks (see fig. 3), that can further increase overall reliability and sensitivity of the system if a spectral analysis can be performed [13]. On the other hand, the use of finite nanoparticle chains can create very strong field enhancements at the extremity of the chain (see fig. 4) [14].

References:

[1] Barnes, W.L., Dereux, A., Ebbessen, T.W., Nature 424 (2003), 824–830.
[2] Okamoto, T., Yamaguchi, I., Kobayashi, T., Opt. Lett. 25 (2000), 372–374.
[3] Raschke, G., Kowarik, S., Franzl, T., Sönnichsen, C., Klar, T.A., Feldmann, J., Nichtl, A., Kurzinger, K., Nano Letts. 3 (2003), 935–938.
[4] McFarland, A.D., Van Duyne, R.P., Nano Letts. 3 (2003), 1057–1062.
[5] Xu, H., Käll, M., Sens. Actuators B 87 (2002), 244–249.
[6] Xinglong, Y., Dingxin, W., Zibo, Y., Sens. Actuators B 91 (2003), 285–290.
[7] Lyon, L.A., Musick, M.D., Smith, P.C., Reiss, B.D., Peña, D.J., Natan, M.J., Sens. Actuators B 54 (1999), 118–124.
[8] Frederix, F., Friedt, J.M., Choi, K.H., Laureyn, W., Campitelli, A., Mondelaers, D., Maes, G., Borghs, G., Anal. Chem. 75 (2003), 6894–6900.
[9] Haes, A.J., Van Duyne, R.P., J. Am. Chem. Soc. 124 (2002), 10596–10604.
[10] Kreuzer, M.P., Quidant, R., Badenes, G., Marco, M.P., Biosens. Bioelectr. 21 (2006), 1345-1349
[11] Kottmann, J., Martin, O.J.F., Optics Expr. 8 (2001), 655
[12] Nordlander, P., Oubre, C., Prodan, E., Li, K., Stockman, M., Nano Lett. 4 (2004), 899.
[13] Enoch, S., Quidant, R., Badenes, G., Opt. Expr. 12 (2004), 3422-2427
[14] Ghenuche, P., Quidant, R., Badenes, G., Opt. Lett. 30 (2005), 1882-1884

Figures:

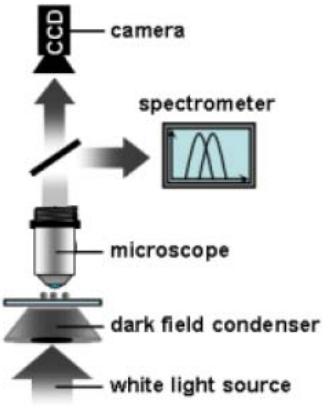

Fig. 1: Schematic setup for LSP sensing

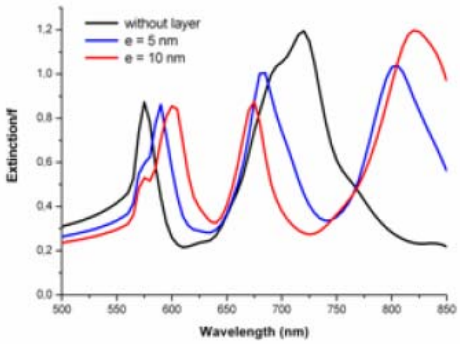

Fig. 3: Extinction spectra of a dimer matrix as a function of the thickness e of a dielectric layer located on top of it.

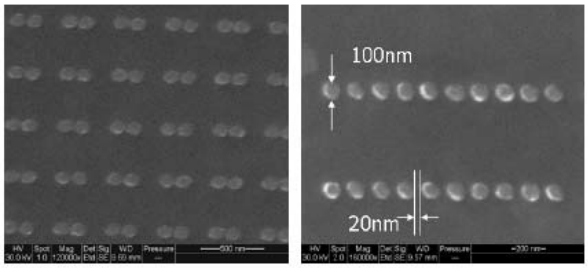

Fig. 2: SEM micrographs of 100 nm diameter gold dots with 20 nm spacing, fabricated using e-beam lithography and lift-off

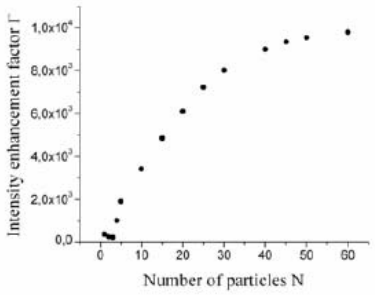

Fig. 4: Intensity enhancement factor as a function of the number of particles in a chain.