Silver nanoparticle arrays enhanced spectral surface plasmon resonance optical sensor

Wei Zhang[1,2], Weixiang Ye[1,2], Cheng Wang[1,2,3], Wenbin Li[1,2], Zhao Yue[1,2], Guohua Liu[1,2]

[1]*College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300071, People's Republic of China*
[2]*Key Laboratory of Photo-electronic Thin Film Devices and Technology of Tianjin, Nankai University, Tianjin 300071, People's Republic of China*
[3]*Department of Mechanical Engineering, Columbia University, New York 10027, USA*
E-mail: liugh@nankai.edu.cn

An on-chip spectral surface plasmon resonance (SPR) optical sensor with a silver nanoparticle (Ag NP) array has been designed. Dextran (Dex)-capped Ag NP (Dex-Ag NP) arrays were initially self-assembled on the gold (Au) sensing film. The large perturbations and increased penetration depth of the evanescent field, which is caused by the use of the Dex-Ag NP array self-assembled on the Au sensing film, can effectively enhance the SPR spectral shift response. Compared with the bare Au sensing film configuration, the Au sensing film with a Dex-Ag NP array configuration improves sensitivity from 5492 to 6613 nm/RIU.

1. Introduction: Surface plasmon resonance (SPR) optical sensors are known to be extremely sensitive to the refractive index of the dielectric medium within the penetration depth of the evanescent field. This remarkable property has been widely applied for sensitive and real-time detection of biomolecule interactions [1–4]. Most of the spectral SPR optical sensors use surface plasmon polaritons (SPPs), which are excited on continuous gold (Au) or silver (Ag) films in the attenuated total internal reflection geometry [2]. The SPPs will then form an electric field that exponentially decays into its surrounding medium with a penetration depth in the range of hundreds of nanometres. As a result, this evanescent field is highly sensitive to the refractive-index change of the surrounding medium.

Many sensitivity-enhancement methods for SPR optical sensors have been proposed and reported [5]. One of them, the nanomaterials enhancement method has been commonly applied for improving the sensing performance of SPR optical sensors by using nanomaterials. Plasmonic nanoparticles (NPs), especially gold NPs (Au NPs) and silver NPs (Ag NPs) exhibit strong absorption in the visible and near-infrared wavelength regions by exciting the localised SPR (LSPR) electric field [6–9]. Therefore they could be used for the development of electric field enhancement units. Moreover, Ag NPs demonstrate superiority over Au NPs when only plasmonic characteristics are taken into account [10]. However, Ag NPs are less stable than Au NPs, and for electric field enhancement units this drawback has to be circumvented.
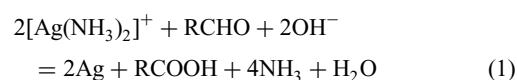
In this Letter, we propose an on-chip spectral SPR optical sensor with an Ag NP array. Coupling the LSPR electric field of the Dex-Ag NP array with surface plasmon waves generated from Au sensing film could to be an efficient way to obtain a larger field enhancement, thereby resulting in higher sensitivity. In addition, these dextran-modified Ag NPs have high stability by using the long-chain dextran as a stabilising agent. The performances of the proposed SPR optical sensor were demonstrated by testing different concentrations of ethanol–water solutions. The results illustrated that the Au sensing film with the Dex-Ag NP array could be an efficient way to obtain a larger field enhancement, thereby resulting in a higher sensitivity.

2. Materials and methods

2.1. Materials: In the experiment several chemical reagents were used to synthesise Dex-Ag NPs and their self-assembly monolayer (SAM) on the Au sensing film. The reagents such as silver nitrate ($AgNO_3$), ammonia ($NH_3 \cdot H_2O$), sodium hydroxide (NaOH), toluene (C_7H_8), acetone (CH_3COCH_3), ethanol (CH_3CH_2OH), glucose ($C_6H_{12}O_6$) and dextran (Dextran T150 K, $M_w = 150\ 100$, $M_n = 957\ 000$) were all obtained from Sigma-Aldrich. 1,4-Benzenedithiol ($C_6H_6S_2$) was from TCI (Japan). All materials were used without further purification. Deionised (DI) water was used to prepare all solutions. All the other chemical reagents, not mentioned above, were of analytical reagent grade and used as received.

2.2. Synthesis of Dex-Ag NPs and their self-assembly: It has been reported that the large-sized Ag NPs and their arrays have a stronger excited LSPR electric field [11]. Therefore Dex-Ag NPs with a mean diameter of 30 nm were chosen to construct Ag NP arrays on the Au sensing film and were synthesised using our previously reported protocol [12] with minor modification. The 30 nm Dex-Ag NPs solution was synthesised by using $[Ag(NH_3)_2]OH$ reagent as a precursor. Dextran was the stabiliser and glucose acted as a reducing agent. In this work, 5 ml of the $[Ag(NH_3)_2]OH$ reagent solution(4 μmol/ml), 2 ml of dextran (0.19 nmol/ml) and glucose (4 mM) solution were mixed with 23 ml of water in a round-bottom flask (225 ml) and then the mixture was heated to 60 °C in an oil bath and stirred using a Teflon magnetic rotor at 100 rpm. The main synthesis reaction of the Ag NPs can be summarised as follows

$$2[Ag(NH_3)_2]^+ + RCHO + 2OH^-$$
$$= 2Ag + RCOOH + 4NH_3 + H_2O \qquad (1)$$

Au sensing films were fabricated as follows: a 3 nm Ti layer was sputtered on glass chips as the adhesion mediator, then a 30 nm-thick Au film was deposited over the Ti layer. To form the Dex-Ag NPs SAM, Au sensing films should be treated as follows: first, they were sonicated in ethanol and acetone for 5 min each, then treated by cyclic voltammetry in 1 M NaOH for 20 min and later in 500 mM H_2SO_4 for 30 min. Secondly, the cleaned Au sensing films were incubated in 50 mM 1,4-benzenedithiol for 20 h, and then they were rinsed with toluene to remove the excess of 1,4-benzenedithiol. Finally, the dithiol-modified Au sensing films were covered with only one droplet of Dex-Ag NPs

liquid for 5 min before removing the liquid by spin coating. The sulphydryl group of the 1,4-benzenedithiol can link with the Dex-Ag NPs, thus forming a SAM of Dex-Ag NPs on the Au film surface of the glass substrate.

The morphology of the Dex-Ag NPs and their SAM on the Au sensing films were characterised by transmission electron microscopy (TEM) and atomic force microscopy (AFM), respectively. The TEM image of the synthesised Dex-Ag NPs with a mean diameter of 30 nm is presented in Fig. 1a; the size distribution of the Dex-Ag NPs is presented in Fig. 1b, which shows a Gaussian distribution [13]; the AFM image of the Au sensing film with the Ag NP array is presented in Fig. 1c, which clearly demonstrates the surface morphology and the microstructure of the well-dispersed SAM of the Dex-Ag NPs on the Au sensing film.

2.3. Sensor device: On the basis of our previous spectral SPR module [14, 15], the SPR sensor is used with the Kretschmann configuration and the incident SPR angle of the light is 69°. The prepared Au sensing films were deposited on a piece of BK7 glass substrate (nBK7 ≃ 1.5168) and covered by the Dex-Ag NPs SAM, which was attached with a microfluidic channel fabricated by polydimethylsiloxane (PDMS) and polymethylmethacrylate (PMMA). In this device, a travelling-wave magnetic micropump [16] was used to drive the target liquids into the channel. A polarised polychromatic light was imported to the prism and SPR absorption is achieved by total reflection at the Au/glass interface. The SPR optical signals which interacted with the Au sensing films were captured by a mini-spectrometer (Ocean Optics Maya 2000pro). The obtained optical signals can be displayed and monitored by a computer connected to the mini-spectrometer. The diagram of the proposed SPR optical sensor is shown in Fig. 2.

3. Experiments and discussion: In this work, we compared the performance of our SPR optical sensor in a bare Au sensing film configuration and the Au sensing film with a Dex-Ag NPs array configuration. The liquid samples to be detected were ethanol–water solutions, of which the ethanol concentration changes in the range of 10–60% (volume ratio) with known RI values. The mini-spectrometer was used to detect the reflective intensity distribution on the spectrum from 600 to 1100 nm, the
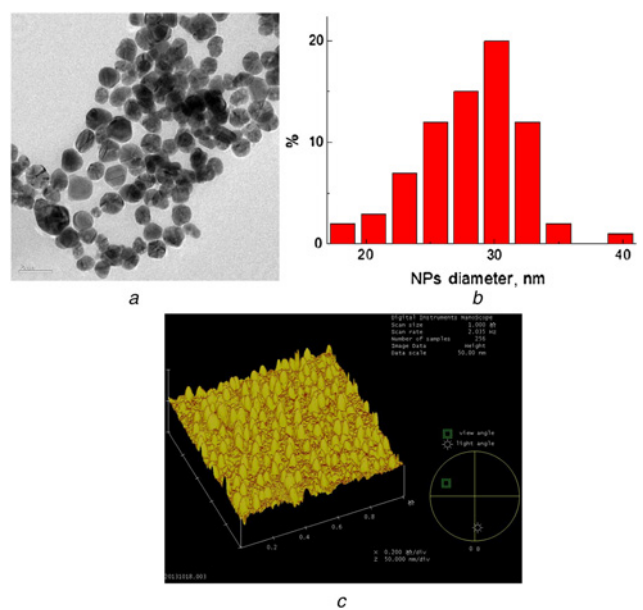
Figure 2 *Diagram of the proposed SPR optical sensor*

spectrometer grating is HC-1, the slit width is 250 μm and the integration time is 20 ms. The SPR-dip with a typical shape can be fitted by the fuzzy control filtering approach to calculate the accurate resonance wavelength [17]. The spectral shift of the SPR response of the Au sensing film configuration and the Au sensing film with the Dex-Ag NPs array configuration are shown in Figs. 3a and b. As can be seen from the Figures, the resonant wavelength of the SPR-dip shifts to the infrared region approximately linearly with the increasing RI value of the sample. The linear relationships between the spectral shift of the SPR response and the RI value of the ethanol–water solutions are shown in Fig. 4, and the average sensitivities (k_{slope}) of these two configurations were calculated to be 5492 and 6613 nm/RIU, respectively.

Experimental results demonstrated that the Au sensing film with the Dex-Ag NPs array configuration led to a significant

Figure 1 *Characteristics of dextran-capped Ag NPs and their SAM*
a TEM image of dextran-capped Ag NPs
b Size distribution of Dex-Ag NPs
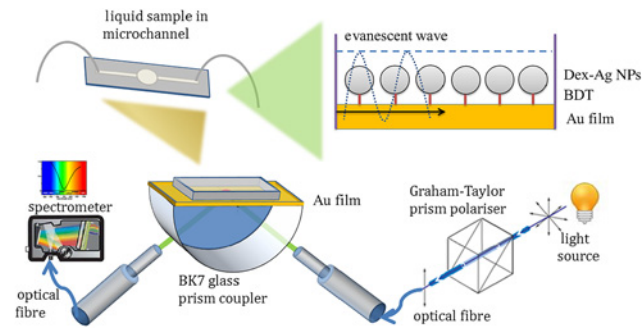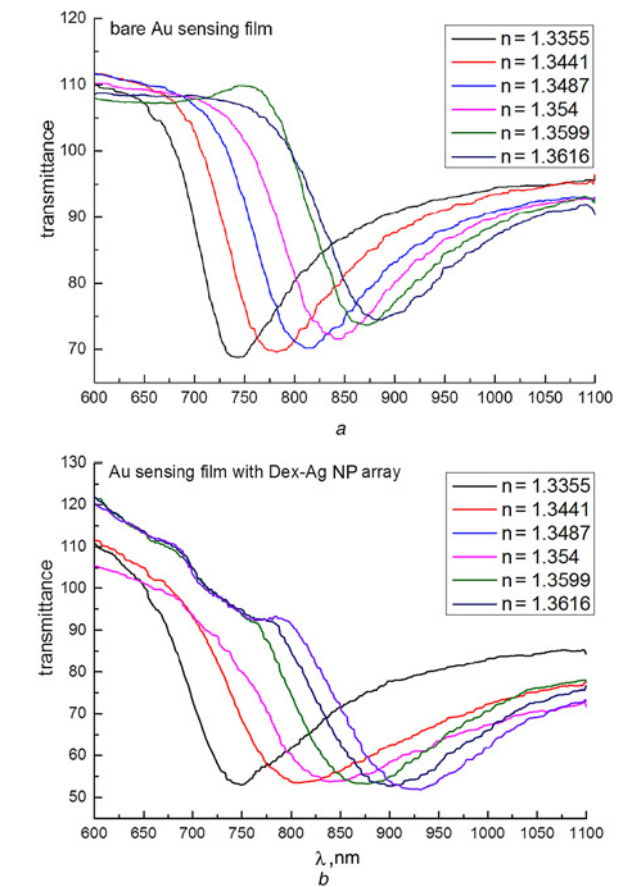c AFM image of SAM on the Au sensing film

Figure 3 *SPR spectral shift responses*
a Bare Au sensing film configuration
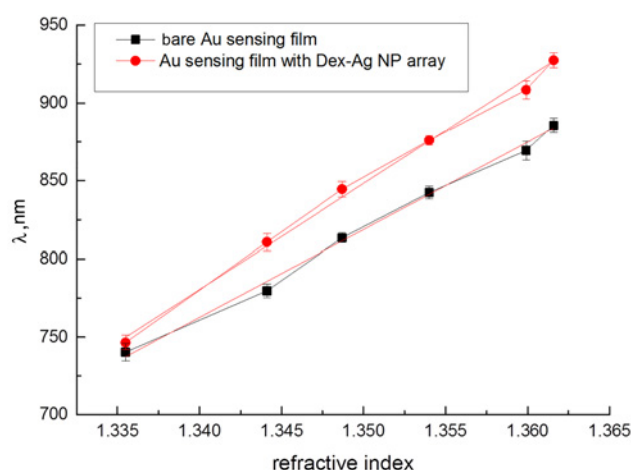b Au sensing film with Dex-Ag NPs array configuration

Figure 4 *Linear relationships between the spectral shift of SPR response and ethanol–water solutions*

improvement in sensitivity. As we know that the Dex-Ag NPs will excite a large electric field on the surface of the NPs because of the strong LSPR absorption in the visible and near-infrared wavelength regions, and the SPR sensitivity is closely related to the excited electric field, the larger the electric field, the more sensitive the SPR sensor to the change of its surrounding medium [18]. Therefore, the Au sensing film with the Dex-Ag NP array configuration enhanced the SPR sensitivity, which could be attributed to two aspects: first, the electric field enhancement by coupling the LSPR electric field excited on the surface of Dex-Ag NP array with the SPW excited on the Au sensing film, thereby enhancing the penetration depth of the evanescent field; secondly, the large surface mass loading of the Dex-Ag NP array leading to large perturbations on the Au sensing film surface, thereby magnifying the SPR signals.

4. Conclusion: In summary, we developed a new Au-based film with improved spectral sensitivity for the optical sensor by coating the film with the self-assembly array of Ag NPs. Manufacturing of the Dex-Ag NP array on Au sensing film has been discussed. The large perturbations and increased penetration depth of the evanescent field on the Au sensing film surface with the Dex-Ag NP array led to an enhancement in SPR spectral shift response. Hence the sensor significantly improves the sensitivity of the film. Furthermore, the proposed Dex-Ag NP array-modified Au sensing film can be easily and inexpensively produced and can be further optimised, and could be widely utilised in designing high-performance spectral SPR optical sensors.

6 References

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