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Universal sensitivity of propagating surface plasmon resonance in nanostructure arrays

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Abstract: A universal, geometry-independent sensitivity is derived by using a black box model of surface plasmon excitation for two-dimensional nanostructures. It is shown that the resonant wavelength of surface plasmons and dielectric property of interfacial materials dominate the sensitivity. Sensitivity data of nanostructure arrays, widely collected from independent research groups, comply well with our results. This analysis provides a conceptual and intuitive insight into the plasmonic sensing, covering various excitation arrangements under the same umbrella. The universal sensitivity offers a quantitative tool to evaluate and predict the performance of plasmonic sensors.

OCIS codes: (240.0240) Optics at surfaces; (240.6680) Surface plasmons.

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1. Introduction

Surface plasmon resonance (SPR) is collective oscillation of electrons excited by light at the metal/dielectric interfaces [1]. Such interaction leads to significant field enhancement and SPR is extremely sensitive to dielectric properties at the interface. Moreover, the spatial and spectral properties of SPR on nanostructures can be easily tuned by controlling the geometry [2,3]. These unique aspects give rise to prosperous research and applications of plasmonic nanostructures from biosensing, molecular imaging to surface-enhanced spectroscopy [4,5]. The merit of a plasmonic sensor is determined by its sensitivity, which indicates the sensor signal variation responding to a refractive index change of the bulk environment and provides an upper bound to the biosensing. Among the most common performance indicators is the wavelength sensitivity, which has been measured by numerous experiments [6]. For example, nanohole arrays in metal films with various configurations in terms of film thickness, hole size, periodicity and pattern exhibited distinct optical response and sensitivities [7–10]. Sensitivity expressions for regular and chirped diffraction gratings were derived with wavelength shifts being a function of the local structures and diffraction orders [11,12]. However, most of current results were associated with the single arrangement of individual exciting mechanism, thereby hindering the direct comparisons across various configurations. We need a coherent framework to enable sensitivity evaluation of plasmonic nanostructures from a generality point of view.

Since plasmonic sensing is essentially the interaction between surface plasmon (SP) and matters, one question raised naturally is whether and what fundamental physical properties intrinsically and generally rule the sensitivity irrespective of individual structure geometry. Spurred by this question, in this work, a universal geometry-independent sensitivity is established for generic two-dimensional plasmonic nanostructures by using a black box model of SPR excitation. Previous theoretical efforts have been put into flat metal films [13] and nanoparticles [14,15]. Here we focus on the sensitivity analysis of plasmonic structure arrays, which denote certain nanoscale elements (i.e. holes or slits) repeated in metal films, on behalf of one main class of plasmonic objects. This universal sensitivity expression helps us clarify a series of phenomena involved in plasmonic sensing. Our expression coincides well with a considerable amount of experimental and numerical results obtained independently by other groups, confirming the validity of our analysis. This analytical outcome can be exploited for sensitivity assessment and prediction for plasmonic nanostructures with diverse geometries and arrangements.

2. A black box model of SP excitation

Different geometry parameters always couple together to affect the spectral features. Thus, it is difficult to establish an analytical sensitivity expression applicable to generic two-dimensional plasmonic structures. To address this dilemma, we would like to first dwell on the essential physics of SP. The dispersion curve of SPs lies on the right of light line [16], which means freely propagating light cannot directly excite the SPR due to such a momentum gap [Fig. 1(b)]. Momentum-matching techniques (e.g. grating and subwavelength holes) are required to compensate the missing momentum for the excitation of SP oscillation. Indeed, these plasmonic structures constitute very different coupling mechanisms and their geometries have substantial impacts on sensor performance [17,18]. However, in essence, plasmonic sensing is the interaction between SPs and the dielectric analyte. Thus it is rational to evaluate the sensor performance based on the property of SP itself rather than specific excitation mechanism. Therefore we propose a black box model of SP excitation [Fig. 1(a)], where the specific coupling channel is simplified into a function to provide constant momentum Δk in the direction of SP propagation. Generally, exciting light with the frequency ω is input at the incident angle θ relative to the normal of SP plane (i.e. k_{sp} plane). The ψ is the angle between the incident plane and SP propagating direction.

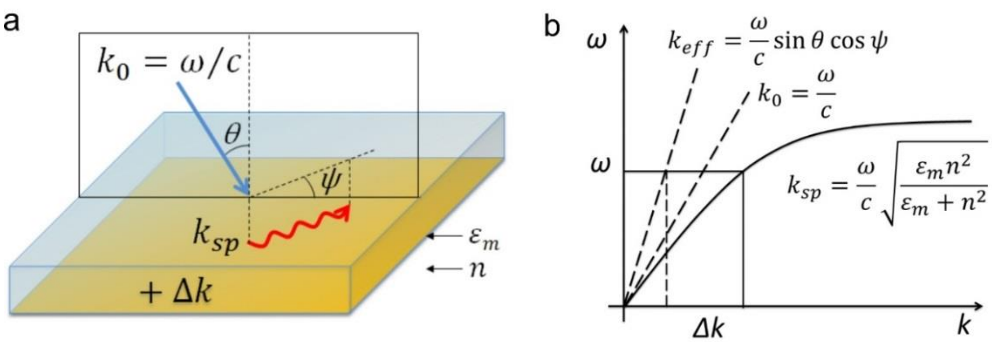

Fig. 1. Black box model of SP excitation. (a) Schematic diagram of a general three-dimensional SP black box. Except for the metal/dielectric interface, the plasmonic structures are invisible and simplified into a transfer function of adding momentum Δk to light. ω is the frequency of light and c is the velocity of light in vacuum. ε_m is the real dielectric constant of the metal and n is the refractive index of the dielectric. (b) Dispersion relation of SP. The momentum gap between the collinear wave vector component k_{eff} of incident light and SP requires additional momentum Δk.

We suppose in the first approximation that appearance of plasmonic structures do not change the dispersion relation of SPs at the metal/dielectric interface. By applying the momentum-matching condition [Fig. 1(b)], we get

$$\frac{\omega}{c}\sin\theta\cos\psi + \Delta k = k_{sp} = \frac{\omega}{c}\left(\frac{\varepsilon_m n^2}{\varepsilon_m + n^2}\right)^{1/2} \tag{1}$$

From this equation, we deduce the wavelength sensitivity S to refractive index,

$$S = \frac{2\pi\varepsilon_m^2}{\Delta k \cdot \varepsilon_m^{1/2}\left(\varepsilon_m + n^2\right)^{3/2} - \pi n^3 \dfrac{d\varepsilon_m}{d\lambda}} \tag{2}$$

According to this expression, an effective way to improve the sensitivity is decreasing Δk. For instance, a nanohole array has been used in the configuration of attenuated total reflection [19]. In the oblique incidence, much more in-plane momentum of incident light is coupled to SPs in comparison to the case of normal incidence. As a result, its sensitivity significantly increases to the level of prism-based sensors.

Another possible optimization method is to modify the structures' dispersion relation to further approach that of incident light. The guided SP modes of such structures have dispersion relations different from k_{sp}. However, Δk could become quite small to still dominate the sensitivity. A plasmonic nanorod layer has been demonstrated to support a guided mode [20]. Its dispersion curve is actually designed to approach that of incident light at the resonance wavelength, so extremely small Δk is required to excite SP and result in an extra-high sensitivity.

3. Analytical expression of wavelength sensitivity

To obtain an analytical sensitivity expression, Δk and ε_m need to be specified. Normal incidence is commonly adopted in most of experimental investigations because of its simplicity and practical consideration. In this case, the plasmonic structures provide all the necessary momentum for SP excitation, i.e. $\Delta k = \frac{\omega}{c}\left(\frac{\varepsilon_m n^2}{\varepsilon_m + n^2}\right)^{1/2}$. On the other hand, noble metals have free electron-like dielectric functions that vary quadratically with wavelength according to Drude model. At visible and near-infrared region, the real part of the dielectric function varies nearly linearly with wavelength, i.e. $\varepsilon_m \approx a\lambda + b$, where $a = -0.072, b = 34$ [21]. Substituting for Δk and ε_m in Eq. (2), we get an analytical sensitivity equation,

$$S = \frac{2\lambda\varepsilon_m^2}{n\left(2\varepsilon_m^2 + \varepsilon_m n^2 + bn^2\right)} \tag{3}$$

where λ is the resonance wavelength. This expression reveals that the sensitivity is dominated by the SPR wavelength and the dielectric property of materials involved in the interaction.

The sensitivities plotted for Au and Ag structures [Fig. 2] show a roughly linear increase as the SPR shifts to longer wavelength. Despite different dielectric properties [22], plasmonic structures with Au and Ag have almost equal sensitivities in the same dielectric (also see experimental data in Fig. 3). Given $|\varepsilon_m| \gg n^2$ at visible and near-infrared region, we can safely give an approximation $S \approx \lambda_m / n$, which confirms the SPR at the same wavelength show higher sensitivity in the analyte with lower refractive index. In particular, $S \approx \lambda_m$ in air ($n = 1$) and $S \approx 0.75\lambda_m$ in water ($n = 1.33$), which implies that measurements in air are more sensitive compared with that in aqueous solution. In addition, this analytical format of sensitivity can give us more insight into physics behind plasmonic sensing. For example, the SP penetration modulates the interaction: the longer penetration depth at the longer wavelength [16] provides a larger sensing volume and thus a higher interaction probability.

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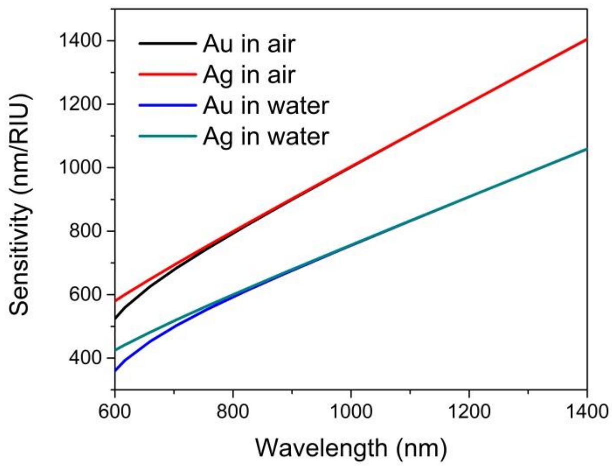

Fig. 2. Sensitivities of Au and Ag plasmonic sensors in air and water respectively.

4. Sensitivity quantification, comparison and prediction

The analytical sensitivity can be evaluated using those plasmonic sensors which are subject to the same principle of surface plasmon resonance. Typical embodiments of our model are plasmonic array structures including the tow-dimensional Bravais lattices of subwavelength apertures and arrays of nanoslits. They have different SPR wavelength expressions, e.g. $\frac{P}{\sqrt{i^2+j^2}}\left(\frac{\varepsilon_m n^2}{\varepsilon_m+n^2}\right)^{1/2}$ for square nanohole arrays [8], $\frac{P}{\sqrt{\frac{4}{3}(i^2+ij+j^2)}}\left(\frac{\varepsilon_m n^2}{\varepsilon_m+n^2}\right)^{1/2}$ for hexagonal nanohole arrays [8] and $\frac{P}{i}\left(\frac{\varepsilon_m n^2}{\varepsilon_m+n^2}\right)^{1/2}$ for nanoslit arrays [23], where P is lattice constant, i, j are the scattering orders in SP planes. From these wavelength expressions, we can mathematically derive their sensitivities, which are equivalent to Eq. (3).

We could validate our analytical results by using specific structures. However, this merely adds new instances of this universal model. Instead, we adopt a set of sensitivity data independently measured using metal nanostructure arrays with various geometries. A series of experimental and simulated data published by other groups (see appendix), are collected to quantify our theoretical values [Fig. 3]. It is observed that some experimental sensitivities are somewhat lower than theoretical values. This degradation can be partially attributed to coupling effects from substrates [24] and radiation damping induced by the appearance of nanostructures in real cases. Overall, our model predicts the correct range and trend of sensitivity change for plasmonic array structures.

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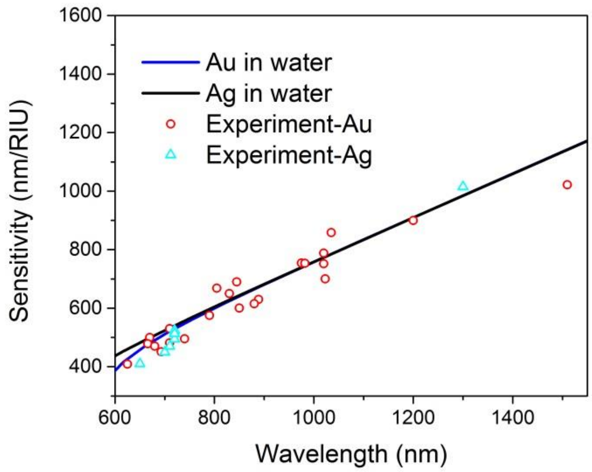

Fig. 3. Theoretical and experimental sensitivities of plasmonic nanostructure arrays.

Localized SPR (LSPR) in nanoparticles apparently has the same physical origin as those in two-dimensional plasmonic structures. The LSPR sensitivity for nanoparticles has been derived from a dipole polarizability resonance condition in the quasistatic limit [14]. This sensitivity also depends on the resonance wavelength and dielectric properties of the metal and medium. The theoretical sensitivities of both types are plotted in Fig. 4. Obviously, plasmonic array structures have much higher sensitivity in the visible range, whereas the nanoparticles' sensitivity is approaching parallel to the former at the near-infrared regime. Their difference can be attributed to stronger confinement of SP field in nanoparticles due to its localized nature, thereby providing less sensing volume and smaller sensitivity [26].

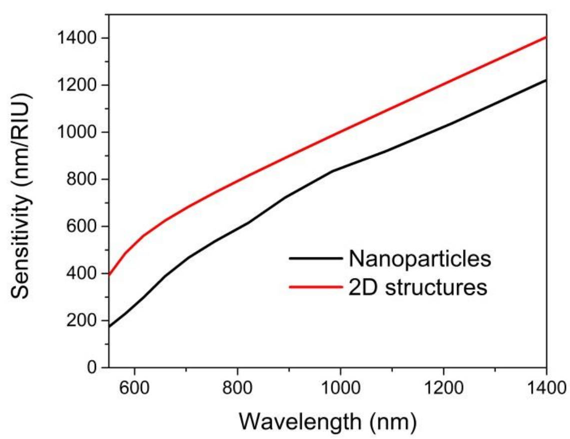

Fig. 4. Sensitivity comparison between two-dimensional plasmonic array structures and nanoparticles.

Our analysis reveals it is SPR that essentially determines the sensitivity of two-dimensional plasmonic sensors, whereas metal nanostructures mainly act as a coupling media to generate SPR. Beyond the Bravais lattices, quasicrystals (with long-range order but no short-range order) and aperiodic aperture arrays (without long-range or short-range order) were also demonstrated to support SPR [27–29]. Instead of reciprocal lattice vectors, quasicrystals and aperiodic structures are characterized by discrete Fourier transform vectors in their structure factors. Sharp transmission resonances appear at frequencies that closely match these discrete Fourier transform vectors [28]. These vectors in reciprocal space are in fact equal to different wave-vectors, corresponding to various SPR peak wavelengths in normal incident. In this context, our sensitivity expression is applicable to those two-dimensional aperture arrays that have discrete Fourier transform vectors in their geometrical structure factors. It is predicted that these non-periodic nanohole arrays would equally possess good optical performance thereby being used for sensing application.

5. Conclusions

In summary, a universal plasmonic sensitivity is established for generic two-dimensional nanostructures by using a black box model of SPR excitation. This expression defines plasmonic sensitivity based on the primary physical elements, rather than variable nanostructure geometries. The analytical model successfully explains a series of phenomena involved in plasmonic sensing. The previously published sensitivity data comply with and validate our theoretical results. This analysis provides a powerful and general tool to quantitatively evaluate and predict the performance of plasmonic nanostructure sensors.

6. Appendix: Sensitivity summary of two-dimensional plasmonic metal nanostructures

Publication	*SPR wavelength (nm)*	*Metal/Dielectric*	*Sensitivity (nm/RIU)*
Ref. 1	720	Ag/water	494
Ref. 1	720	Ag/water	524
Ref. 2	1023	Au/water	~700
Ref. 3	805	Au/water	668
Ref. 4	880	Au/water	615
Ref. 5	845	Au/water	690
Ref. 6	889	Au/water	630
Ref. 7	1200	Au/alcohol	900
Ref. 8	670	Au/water	~500
Ref. 9	710	Au/water	530
Ref. 10	650	Ag/water	410
Ref. 11	850	Au/water	600
Ref. 12	700	Ag/water	450
Ref. 13	710	Au/water	481
Ref. 14	710	Ag/water	470
Ref. 15	1532	Au/ water	1520
Ref. 16	740	Au/ water	495
Ref. 17	975	Au/ water	754
Ref. 18	1510	Au/ water	1022
Ref. 19	830	Au/water	650
Ref. 20	790	Au/water	575
Ref. 21	666	Au/water	478
Ref. 22	693	Au/water	451
Ref. 23	680	Au/water	470
Ref. 24	625	Au/water	409
Ref. 25	1300	Ag/water	1015
Ref. 26	720	Ag/water	513
Ref. 27	982	Au/water	753
Ref. 28	1035	Au/water	858
Ref. 29	1020	Au/water	788
Ref. 29	1020	Au/water	752

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