Nanorod-mediated surface plasmon resonance sensor based on effective medium theory

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We investigate a nanorod-mediated surface plasmon resonance (SPR) sensor for sensitivity enhancement. The theoretical model containing an anisotropic layer of nanorod is investigated using four-layer Fresnel equations and the effective medium theory. The properties of the nanorod-mediated SPR curves versus the metal thin film thickness \(d_f\), length \(l\), and diameter \(D\) of the nanorod are studied in the environment with refractive indices of 1.00 and 1.33. Compared to the conventional thin metal film SPR configuration, the nanorod-mediated SPR sensor presents a larger resonance angle shift and the sensitivity increases with increasing refractive index of the target analyte. Besides the theoretical analysis, we fabricate different Ag nanorod array/Ag film substrates by oblique angle deposition and characterize their SPR responses using a laboratory-made SPR setup in air and in deionized (DI) water. Compared with the Ag film sample, the SPR angles observed for Ag nanorods/Ag film samples shift to larger angles in air (for shorter nanorods), while it is hard to observe the SPR angle in DI water, which is qualitatively consistent with theoretical results. We believe that the nanorod-mediated SPR sensor is able to improve the sensitivity and the theoretical discussion is helpful for sensor fabrication. © 2009 Optical Society of America

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1. Introduction

Surface plasmon resonance (SPR) sensors have widely been recognized as valuable tools for investigating chemical and biological binding events on a surface [1–3]. A surface plasmon (SP) is a charge density wave propagating along the interface between two media, where one is a metal (silver or gold) and the other is a dielectric. The resonant interaction occurs as a result of the momentum matching between incident photons at a specific incident angle (resonance angle) and SPs, which is accompanied by radiative and thermal damping of the incident light energy. The resonance angle is very sensitive to refractive index change of the dielectric, in other words, the surrounding medium around the metal film. By measuring the shift of the resonance angle, researchers have successfully monitored biological and chemical reactions [4–6].

A conventional SPR sensor is usually based on the attenuated total reflection configuration [7], in which an incident beam is coupled through a prism on a glass slide coated with the metal thin film. To improve the performance of conventional SPR sensors, sensitivity enhancement has been of tremendous interest in SPR sensor development. By optimizing the properties of the metal film and those of the prism, the light launching conditions, and the immobilization efficiency of the biocapturing elements on the sensor surface, efforts have been made by use of fiber optic sensor [8–10], change of prism material [11,12], double layers, such as gold–silver [9,13] and indium tin oxide (ITO)–silver [14], and biochemical arrays [15]. In recent years, localized surface plasmon
(LSP), i.e., electrons collectively oscillating in the metal nanostructures, have drawn intensive attention for SPR signal amplification [16–26]. These LSPs allow strong optical coupling of incidence light into resonance, and the momentum matching is usually achieved at higher momentum than bulk SP modes. Based on this knowledge, modified SPR sensing systems, such as metallic nanoparticles conjugated with target analytes [19,21] or used as local resonators [26], two-dimensional nanohole array SPR sensors [22], and metallic nanowires regularly patterned on a metal film, where LSPs inside the nanowires strongly interact with SPs inside the metal film [16–18,20,23–25,27], have been proposed theoretically and experimentally. These studies show that interactions among LSPs, SPs, and the analytes on the nanostructures can lead to various properties, such as narrow SPR curve width or additional shift of resonance angle.

In this study, a nanorod-mediated SPR sensor is proposed and the influence of different structural parameters on its performance is investigated. We believe that the nanorod surface will provide more surface area for analyte adsorption, thus increasing the dynamic range; more importantly, the LSPs will be generated inside the nanorods under certain structural conditions; therefore, the SPR properties can be enhanced due to the interaction between LSPs and SPs. In doing so, a theoretical model is constructed based on four-layer Fresnel equations. Instead of using the rigorous coupled-wave analysis reported in most previous studies [16,18,20,23,25], the effective medium theory was used by treating the anisotropic nanorod layer as a layer with an effective dielectric constant [28]. To make the theoretical results relate to real nanorod fabrication, we introduce an oblique angle deposition (OAD) method to determine some structural parameters, which will be described in detail in Section 2. OAD is a physical vapor deposition in which the incident vapor has a large angle with respect to the normal direction of the substrate [29,30]. By changing the vapor incident angle and film thickness, we can make tilted Ag nanorods on the substrate. Our study is useful to understand the properties of an anisotropic nanorod layer in an SPR sensor. It also provides suggestions for highly sensitive SPR sensor design.

2. Theoretical Model

A. Nanorod-Mediated Surface Plasmon Resonance Sensor Model

In typical SPR sensors, the reflectance versus angle of incidence of the monochromatic light is the fundamental data for analyzing signals caused by the refractive index changes. Kretschmann was the first to provide a theoretical equation of the SPR curve for a prism–metal film–sensing layer structure by using three-layer Fresnel equations [31]. Figure 1(a) illustrates our model of a SPR sensory system with a Kretschmann attenuated total reflection configuration. Since we have incorporated an anisotropic nanorod layer into our sensing system, we consider a modified four-layer model with the structure of prism–metal film–nanorods–sensing layer: a glass prism (layer 1), a metal thin film with a thickness of \(d_f\) (layer 2), a layer of aligned nanorod array, which has the same orientation with respect to the surface normal (layer 3), and a sensing layer, which can be air or the target analyte (layer 4). We define that the effective medium layer with a thickness of \(d_e\) is composed of the nanorods and the voids between, and the voids have the same material as the sensing layer. The tilting angle, length of nanorod, and diameter of nanorod are \(\beta\), \(l\), and \(D\), respectively. A monochromatic light beam containing wave vector \(\vec{k}\) incident on the interface between metal thin film and glass prism, and the reflectance \(R\) will be measured as a function of angle of incidence \(\theta\).

![Fig. 1. (Color online) (a) Schematic of prism-metal film-nanorods-sensing layer model. (b) Incident plane and the plane defined by nanorods and normal direction of interface are all in the \(xz\) plane. The \(x', y', z'\) system has each axis parallel to one of the optical axes defined by the nanorod. (c) Multireflected ray in anisotropic nanorod layer.](image-url)
B. Four-Layer Fresnel Equations

To be consistent with most SPR literature, we adopt the Fresnel formula; however, we believe that one could also use the N-layer matrix method to deal with this problem [32,33]. With the four-layer model in Fig. 1(a), using three-layer Fresnel equations, we can obtain four-layer Fresnel equations and the reflectance \( R \) of the light relating to \( p \) polarization can be derived as follows:

\[
R = |r_{1234}|^2, \quad (1)
\]

with

\[
r_{1234} = \frac{r_{12} + r_{23} \exp(2ik_2d_f)}{1 + r_{12}r_{23} \exp(2ik_2d_f)}, \quad (2)
\]

\[
r_{23} = \frac{r_{23} + r_{34} \exp(2ik_3d_e)}{1 + r_{23}r_{34} \exp(2ik_3d_e)}, \quad (3)
\]

\[
r_{12} = \frac{k_{1x} \varepsilon_2 - k_{2x} \varepsilon_1}{k_{1x} \varepsilon_2 + k_{2x} \varepsilon_1}, \quad (4)
\]

\[
r_{23} = \frac{k_{2x} \varepsilon_3 - k_{3x} \varepsilon_2}{k_{2x} \varepsilon_3 + k_{3x} \varepsilon_2}, \quad (5)
\]

\[
r_{34} = \frac{k_{3x} \varepsilon_4 - k_{4x} \varepsilon_3}{k_{3x} \varepsilon_4 + k_{4x} \varepsilon_3}, \quad (6)
\]

\[
k_j = \sqrt{\frac{\varepsilon_j}{c^2} - k_z^2} \quad \text{for} \quad j = 1, 2, 3, 4, \quad (7)
\]

\[
k_x = \sqrt{\varepsilon_1 \frac{\omega}{c} \sin \theta}, \quad (8)
\]

\( k_x \) is the component of the incident wave vector parallel to the interface and remains constant in each interface; \( \omega \) and \( \lambda \) are the angular frequency and the wavelength of the incident light; and \( c \) is the speed of light in vacuum.

Since we have introduced an anisotropic layer (layer 3) into this four-layer model, the dielectric constant \( \varepsilon_3 \) is a tensor, which makes the calculation of \( r_{23} \) and \( r_{34} \) complicated. Thus, we need to investigate the wave propagation in this anisotropic layer, determine the effective dielectric constant, and modify the four-layer Fresnel equations accordingly.

C. Wave Propagation in an Anisotropic Nanorod Layer

Figure 1(b) shows a \( p \)-polarized light beam with wave vector \( \mathbf{k} \) incident on the interface between the glass prism (layer 1) and the metal thin film (layer 2). The plane of incidence defined by the incident beam and surface normal of the interface is taken to be parallel to the plane defined by the direction of the tilted nanorods and the surface normal of the interface and is defined as the \( xz \) plane, as shown in Fig. 1(b). Consequently, the components of the dielectric tensor \( \varepsilon_3 \) in the coordinate system \( xyz \) are all nonzero. To simplify the representation of the tensor \( \varepsilon_3 \), we rotate the system \( xyz \) by an angle of \( \beta \) around the \( y \) axis and make each axis of the new system \( x'y'z' \) parallel to one of the principal axes defined by the nanorod, as shown in Fig. 1(b). The dielectric constants in three principal axes, \( \varepsilon_x, \varepsilon_y, \) and \( \varepsilon_z \), only depend on the material and the shape of nanorods. For a cylindrical and spheroid-shaped nanorod, the dielectric constant tensor

\[
\varepsilon_3' = \begin{pmatrix}
\varepsilon_x' & 0 & 0 \\
0 & \varepsilon_y' & 0 \\
0 & 0 & \varepsilon_z'
\end{pmatrix}
\]

(10)

and \( \varepsilon_x' = \varepsilon_y' \). Thus, the dielectric constant tensor \( \varepsilon_3 \) in the \( xyz \) coordinates can be written as

\[
\varepsilon_3 = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{pmatrix} = \begin{pmatrix}
\varepsilon_x \sin \beta + \varepsilon_z \sin \beta \\
\varepsilon_x \cos \beta + \varepsilon_z \sin \beta \\
0
\end{pmatrix} \begin{pmatrix}
0 & -\varepsilon_x' \sin \beta \cos \beta + \varepsilon_z' \sin \beta \cos \beta \\
\varepsilon_y' \sin \beta + \varepsilon_z' \cos \beta & 0 \\
-\varepsilon_x' \sin \beta \cos \beta + \varepsilon_z' \sin \beta \cos \beta & 0
\end{pmatrix}.
\]

(11)

Using Maxwell’s equations, the wave vector \( k_{3z} \) propagating in the anisotropic layer and the effective dielectric constant of this layer in terms of \( k_{3z} \) can be derived, and the equations are [32,34,35]

\[
k_{3z \pm} = \frac{-k_x \varepsilon_{xz} \pm \sqrt{k_x \varepsilon_{xx} \sqrt{(\omega / c)^2 \varepsilon_{zz} - k_z^2)}}}{\varepsilon_{zz}}, \quad (12)
\]

where \( r_{12}, r_{23}, \) and \( r_{34} \) are the reflectance amplitudes given by the Fresnel formula relating to \( p \) polarization for adjacent layer interfaces; \( \varepsilon_j \) and \( k_{jz} \) are the dielectric constant and the wave vector component perpendicular to the interface in layer \( j (j = 1, 2, 3, 4) \).
\[ \varepsilon_{3\pm} = \varepsilon_1 \sin \theta \]
\[ + \left[ -\sqrt{\varepsilon_1} \sin \theta \sqrt{\varepsilon_{xx} + \sqrt{\varepsilon_x \varepsilon_z}} \sqrt{\varepsilon_{zz} - \varepsilon_1 \sin \theta} \right]^2. \]

(13)

We note that the wave vector \( k_{3z} \) has two solutions, which is consistent with the phenomenon of non-symmetrical reflection that occurs when the wave propagates from an anisotropic to an isotropic medium [36]. The solution \( k_{3z=+} \) corresponds to the reflected ray in a backward direction, \( k_+ = k_x \hat{x} + k_{3z=+} \hat{z} \), whereas the solution \( k_{3z=-} \) corresponds to the reflected ray in a forward direction, \( k_- = k_x \hat{x} + k_{3z=-} \hat{z} \), as illustrated in Fig. 1(c) [36].

Considering the nonsymmetrical reflection, we derive the reflectivity and transmittance coefficients for the interfaces between the anisotropic layer and the isotropic layer and, finally, obtain the modified Fresnel equations as follows:

\[ r_{34} = r_{23} + \frac{t_{23A} r_{34B} t_{32C} \exp[i(k_{3z=+} - k_{3z=-})d_e]}{1 - r_{32C} r_{34B} \exp[i(k_{3z=+} - k_{3z=-})d_e]}, \]

(14)

with

\[ r_{23A} = \frac{k_{2x} \varepsilon_{3z=+} - k_{3z=+} \varepsilon_2}{k_{2x} \varepsilon_{3z=+} + k_{3z=+} \varepsilon_2}, \]

(15)

\[ t_{23A} = \frac{2k_{2x} \varepsilon_2}{\sqrt{\varepsilon_2} k_{2x} \varepsilon_{3z=+} + k_{3z=+} \varepsilon_2}, \]

(16)

\[ r_{34B} = \frac{\sqrt{\varepsilon_3-} \varepsilon_{3z=-} \varepsilon_4 - k_{4x} \varepsilon_{3z=-}}{\sqrt{\varepsilon_3-} \varepsilon_{3z=-} \varepsilon_4 + k_{4x} \varepsilon_{3z=-}}, \]

(17)

\[ r_{32C} = \frac{\sqrt{\varepsilon_3-} \varepsilon_{3z=-} \varepsilon_2 - k_{2x} \varepsilon_{3z=-}}{\sqrt{\varepsilon_3-} \varepsilon_{3z=-} \varepsilon_2 + k_{2x} \varepsilon_{3z=-}}, \]

(18)

\[ t_{32C} = \frac{\sqrt{\varepsilon_2} k_{3z=+} \varepsilon_{3z=+} + k_{3z=+} \varepsilon_3}{\sqrt{\varepsilon_2} k_{3z=+} \varepsilon_{3z=+} + k_{3z=+} \varepsilon_3}, \]

(19)

D. Effective Medium Theory

Now the problem is reduced to the calculation of effective dielectric constants along the three principal axes, \( \varepsilon_x, \varepsilon_y, \) and \( \varepsilon_z \). This can be accomplished by means of the effective medium theory, which has been validated by the Kim and Yoon study on the nanowire-mediated SPR sensor [37] and applied in some other works [36,38]. The theoretical formulations due to Maxwell–Garnett (MG) and Bruggeman (BR) are well known and widely used [39]. The MG theory applies to particles embedded in a host, while the BR theory presumes structural equivalence between two constituents. In this study, we take the metal as the host; thus the MG theory is used, which yields [34,38]

\[ \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_i - \varepsilon_m)} = (1 - f_m) \left[ \frac{\varepsilon_s - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_s - \varepsilon_m)} \right]. \]

(20)

for \( i = x', y', z' \),

where \( \varepsilon_m \) and \( \varepsilon_s \) are the dielectric constants of metal and sensing material, respectively, \( f_m \) is the volume fraction of metal, and \( L_i \) is the depolarization factor.

In this paper, we consider three shapes of the nanorod: prolate spheroid, oblate spheroid, and sphere. The corresponding depolarization factor \( L_i \) can be calculated as follows [40]:

\[ L_{x'} = \frac{1 - e^2}{e^2} \left[ \frac{1}{2e} \ln \left( \frac{1 + e}{1 - e} \right) - 1 \right], \]

(21)

\[ e = \sqrt{1 - r^2} \text{(prolate spheroid)}, \]

(22)

\[ L_{y'} = \frac{g}{2e^2} \left( \frac{\pi}{2} - \tan^{-1} \frac{g}{e} \right) - \frac{g^2}{2}, \]

(23)

\[ g = \sqrt{1 - e^2} \text{(oblate spheroid)}, \]

(24)

\[ L_{z'} = L_y' = \frac{1}{3} \text{(sphere)}, \]

(25)

\[ L_{z'} = L_y' = \frac{1}{2} \left( 1 - L_{x'} \right), \]

(26)

where \( r \) is the aspect ratio of the nanorod.

E. Parameters for Numerical Calculation

To determine the dielectric constant of the Ag layer \( \varepsilon_2 \), as well as the effective dielectric constant \( \varepsilon_3 \), the Drude model is used as [31]

\[ \varepsilon_2 = \varepsilon_2^{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \]

(27)

where \( \omega_p \) and \( \gamma \) are the plasma frequency and the damping frequency, respectively, and \( \varepsilon_2^{\infty} \) is the background frequency of the metal at a frequency of infinity. Those parameters are \( \varepsilon_2^{\infty} = 2.48, \omega_p = 1.35 \times 10^{16} \text{rad/s}, \) and \( \gamma \) = 7.62 \times 10^{15} \text{rad/s} \) for Ag [41]. In our calculation, other constants are determined as follows: the refractive indices of an air and glass prism are 1 and 1.51, respectively; the wavelength of the incident light is \( \lambda = 632.8 \text{nm} \); and the speed of light is \( c = 3 \times 10^8 \text{m/s} \).

As we can see, to calculate reflectance \( R \), we need six structural parameters: tilting angle \( \beta \), the volume fraction of metal \( f_m \), the thickness of the effective medium layer \( d_e \), the thickness of the film \( d_f \), the diameter of nanorod \( D \), and the length of nanorod \( l \). First, from previous SPR experimental results
(not shown), we know that the thickness of the film \( d_f \) plays a significant role in SPR properties. Second, during OAD deposition, by changing the vapor incident angle \( \alpha \), deposition rate, and film thickness, we can control the tilting angle \( \beta \), the volume fraction of metal \( f_m \), the diameter of nanorod \( D \), and the length of nanorod \( l \). For most of our experiments reported thus far, we fix the vapor incident angle as \( \alpha = 86^\circ \); thus the tilting angle \( \beta \) and volume fraction of metal \( f_m \) are fixed. There is an empirical formula for the relationship between vapor incident angle \( \alpha \) and the tilting angle \( \beta \):

\[
\beta = \alpha - \arcsin \left( \frac{1 - \cos \alpha}{2} \right) \quad \text{[42]},
\]

indicating that a large vapor incident angle \( \alpha \) will result in a large tilting angle \( \beta \). Figure 2(a) is a representative scanning electron microscope (SEM) (FEI Inspect F) image of the cross section of Ag nanorods fabricated by OAD. The tilting angle can be measured by ImageTool, and the statistically averaged \( \beta \) is \( 73^\circ \) [30]. Figure 2(b) shows an atomic force microscope (AFM) (Veeco Dimension 3100) image of the Ag nanorods and the scan size is 1 \( \mu \)m \( \times \) 1 \( \mu \)m. The bearing analysis can reveal how much of a surface lies above or below a given height by giving the depth, which is the difference between the tallest point and the measured point in Fig. 2(c). The ratio between the area under the bearing curve and the whole area will be \( f_m \), which has been calculated as 0.4. From our previous study, if the vapor incident angle \( \alpha \) decreases, the density of the nanorods will increase and, thus, the volume fraction will increase. In this calculation, the vapor incident angle \( \alpha \) is fixed as 86°; we therefore fix \( \beta = 73^\circ \) and \( f_m = 0.4 \). Since we have assumed that the nanorod has the shape of a spheroid, the thickness of the effective medium layer \( d_e \) is determined by tilting angle \( \beta \), diameter \( D \), and length \( l \) of the nanorod, as shown in Fig. 2(d). A simple geometry calculation can be accomplished as follows:

\[
d_e = \frac{2}{B} \left( \frac{Ax + DL}{4} \sqrt{B - x^2} \right),
\]

where

\[
A = \frac{1}{4} (L^2 - D^2) \sin \beta \cos \beta,
\]

\[
B = \frac{1}{4} (D^2 \cos^2 \beta + L^2 \sin^2 \beta),
\]

\[
x = A \sqrt{\frac{B}{A^2 + \frac{DL}{16}}},
\]

To investigate how the other structural parameters, such as thickness of the film \( d_f \), the diameter of nanorod \( D \), and length of nanorod \( l \) influence the SPR properties, we carry out the calculation by varying these parameters in the following range: \( d_f = 30, 40, 50 \) nm; \( D = 5, 10, 30, 50, 70, 100 \) nm; \( l = 10, 20, 40, 60, 80, 100, 150, 200 \) nm. All the calculations were performed by MATLAB 6.1.

### 3. Results and Discussion

#### A. Typical Nanorod-Mediated Surface Plasmon Resonance Properties

SPR detection can be performed in three different environments. One is under ambient conditions: either detecting the chemical vapor or dried liquid solution and the refractive index should be changed from 1 to higher. The second is to detect chemical molecules in the aqueous solution, which has a refractive index
close to 1.33. The third is to detect biomolecules from mixtures of biomedium, which has a refractive index between 1.3 and 1.5. We will first discuss SPR detection with the refractive change ranging from 1 to 1.33. A set of typical SPR curves ($d_f = 40 \text{ nm}$, $D = 30 \text{ nm}$) for different lengths of nanorod calculated by this effective-medium-theory-based four-layer model is shown in Fig. 3. In general, the SPR curve can be characterized by three parameters: reflectance minimum at resonance $R_m$, SPR resonance angle $\theta_r$, which is defined as the angle associated with the reflectance minimum, and width $w$ at half of the dip height. Figure 3(a) shows the SPR curves corresponding to the refractive index of sensing layer $n = 1.00$. As we can see, when the length of nanorod increases from $l = 10 \text{ nm}$ to $l = 20 \text{ nm}$, the reflectance minimum $R_m$ and width $w$ decrease, while the SPR resonance angle $\theta_r$ redshifts. With further increase of length $l$, the reflectance minimum $R_m$ and width $w$ increase, while the SPR resonance angle $\theta_r$ blueshifts. When $l = 200 \text{ nm}$, the SPR dip becomes inconspicuous. Figure 3(b) shows the SPR curves generated with the same structure, but the surrounding refractive index changes from $n = 1.00$ to $n = 1.33$ (water). Obviously, all SPR angles redshift with an increasing reflectance minimum and a broadened width.

For a detailed comparison of SPR curves in air ($n = 1.00$) and in water ($n = 1.33$), we summarize the reflectance minimum $R_m$, SPR resonance angle $\theta_r$ and width $w$ of the nanorod-mediated SPR curves with film thickness $d_f = 40 \text{ nm}$ as a function of the length of nanorod $l$ in Fig. 4. In air [Fig. 4(a)], reflectance minimum $R_m$ increases with increasing diameter of nanorod $D$ at a fixed length of nanorod $l$, as shown in Fig. 4(a). For different diameters of nanorod $D$, $R_m$ first decreases until the aspect ratio $r$ approaches 1, and then begins to increase. Figure 4(b) shows that SPR angle $\theta_r$ behaviors differently at different diameters of nanorod $D$ and varies in the range between 43.5° and 48.5°. At $D = 5 \text{ nm}$, $\theta_r$ increases with increasing $l$; at $D = 10 \text{ nm}$, $\theta_r$ decreases first and then increases with increasing $l$; at $D > 10 \text{ nm}$, $\theta_r$ reaches maximum as the aspect ratio $r$ approaches 1, at which point it begins to decrease. The SPR width $w$ almost overlaps at $D = 5$ and 10 nm, and it increases with increasing $l$, as shown in Fig. 4(c). The trend becomes different at $D > 10 \text{ nm}$, and the $w - l$ behavior has almost the opposite trend compared to the $\theta_r - l$ relation: $w$ decreases first until the aspect ratio is close to 1 and then increases with increasing $l$. The minimum width $w$ for different $D$ ranges from 0.5° to 0.75°.

In water, the SPR signal cannot be obtained under the following conditions: $D = 50 \text{ nm}$ and $l = 40$, 60, 80, 120 nm; $D = 70 \text{ nm}$ and $l > 10 \text{ nm}$; or $D = 100 \text{ nm}$. Figure 4(d) shows the reflectance minimum $R_m$ obtained under specific conditions for water. It increases with increasing length of nanorod $l$ at $D = 5$ and 10 nm and is close to 1 at $D > 10 \text{ nm}$. The SPR angle $\theta_r$ shifts to a larger angle ranging from 71° to 82.5° when the surrounding dielectric constant increases to $n = 1.33$ [Fig. 4(e)]. At $D = 5$ and 10 nm, $\theta_r$ follows the same trend as that in air, except that $\theta_r$ decreases slightly at $l > 150 \text{ nm}$. At $D = 30 \text{ nm}$, $\theta_r$ locates its maximum at the smallest length of nanorod ($l = 10 \text{ nm}$) and then decreases with increasing length of nanorod $l$, except for a peak at $l = 60 \text{ nm}$. There is an overall trend that $\theta_r$ converges for different diameters of nanorod $D$ at a large length of nanorod $l (l = 200 \text{ nm})$. Figure 4(f) shows that width $w$ becomes apparently broad in water, as we observe in

![Fig. 3.](image)

![Fig. 4.](image)
Fig. 3(b). At $D = 5$ and 10 nm, $w$ has a minimum of about 4° at $l = 10$ nm and then quickly increases to 12° at $l = 100$ nm. After that, it decreases slightly with $l$. At $D = 30$ nm, $w$ is around 11° and has a slightly higher value at $l = 100$ nm. At $D > 30$ nm, $w$ is randomly distributed and larger than 10°. From the above discussion, we find that most configurations of the nanorod-mediated SPR structure at $D > 30$ nm will lose the SPR signal in water. Therefore, the discussion will be focused on $D = 5, 10$, and 30 nm in the following sections since, for the real applications, most sensing processes will be performed in aqueous solutions.

To find out how reflectance minimum $R_m$ and width $w$ change with film thickness $d_f$, we plot them as a function of the length of nanorod $l$ for $d_f = 30, 40$, and 50 nm at $n = 1.00$ in Fig. 5. According to Fig. 5(a), at $D = 5$ and 10 nm, when $d_f = 30$ nm, $R_m$ reaches a minimum at $l = 40$ nm; when $d_f = 40$ nm, $R_m$ has a minimum at $l = 20$ nm; when $d_f = 50$ nm, $R_m$ does not have a minimum, and increases with increasing $l$ monotonically. The general trend is that smaller $d_f$ has its minimum $R_m$ at larger $l$. At $D = 30$ nm, $R_m$ has the minimum located at $l = 20$ nm for all film thicknesses $d_f$. Figure 5(b) shows that the trends of width $w$ stay the same when the film thickness $d_f$ changes to $d_f = 30$ and 50 nm, as described in Fig. 4(e). One should note that the width $w$ decreases with increasing $d_f$ for fixed diameter $D$ and length $l$ of the nanorod. In other words, by changing the film thickness $d_f$, we find that reflectance minimum $R_m$ and width $w$ have a trade-off relationship; i.e., a small reflectance minimum $R_m$ can be obtained at the expense of a large width $w$.

In terms of the diameters of nanorod $D$, at a fixed film thickness $d_f$ and a fixed length of nanorods $l$, the reflectance minimum $R_m$ increases with increasing $D$, except that at $d_f = 30$ nm and $l < 40$ nm, a larger $D(D = 30$ nm) makes the $R_m$ decrease, as shown in Fig. 5(a). For the width $w$, it decreases with increasing $D$ under the following conditions: $l > 20$ nm and $d_f = 30$ nm; $l > 40$ nm and $d_f = 50$ nm. As a matter of fact, when $d_f = 50$ nm and $l > 40$ nm, the values of $w$ are close to each other, whereas $D$ varies.

B. Dynamic Range and Sensitivity Enhancement

We have thus far discussed the effect of nanorod length, nanorod diameter, and film thickness on SPR curves by inspecting its reflectance minimum $R_m$ and width $w$ at a specific refractive index $n = 1.00$. Practically, for chemical or biological sensors, small SPR angle $\theta_r$, small reflectance minimum $R_m$, and narrow width $w$ are desirable for sensing applications. However, it is more important to examine how the SPR signal, i.e., the position of SPR angle $\theta_r$, shifts with the change of refractive index $n$. There are two important parameters associated with sensing: the dynamic range and the sensitivity. First we calculate the dynamic range, which is defined as the detectable refractive index change, by plotting the SPR angle $\theta_r$ as a function of refractive index $n$, for $d_f = 30, 40$, and 50 nm from $n = 1.00$ to $n = 1.34$. Since their dynamic ranges have the same trends, the discussion will focus on the structure with $d_f = 40$ nm. Figures 6(a)–6(c) compare the dynamic ranges for different lengths of nanorod $l$ at $D = 5$, 10, and 30 nm, respectively. As shown in Fig. 6(a), SPR angle $\theta_r$ redshifts with increasing length of nanorod $l$ at the fixed refractive index $n$. More interestingly, at a fixed $l$, SPR angle $\theta_r$ not only redshifts, but also has an increasing slope, which is defined as the local sensitivity $s$ of the SPR sensor $s = \frac{dn}{d\theta}$ with increasing $n$. This means that this nanorod mediated SPR structure has an increasing sensitivity $s$ when the refractive index $n$ increases. Figure 6(b) shows a similar trend, except in the case of $D = 10$ nm, $l = 10$ nm, which corresponds to the spheres with a diameter of 10 nm. In this case, SPR angle $\theta_r$ is overlapped with that of the structure $D = 10$ nm, $l = 40$ nm at $n < 1.25$. With further increasing of refractive index $n$, the sensitivity increases rapidly. At $D = 30$ nm [Fig. 6(c)], the phenomenon becomes more interesting. First, at $l = 20$ and 40 nm, i.e., as the aspect ratio $r \rightarrow 1$, the SPR angle $\theta_r$ redshifts and the slope increases with increasing refractive index $n$ when $n \leq 1.30$. From $n = 1.30$ to $n = 1.34$, SPR angle $\theta_r$ blueshifts with $n$, thus the slope suddenly becomes negative. In other cases, for $l = 10, 60$, and

![Fig. 5. (Color online) (a) Reflectance minimum $R_m$ and (b) SPR curve width $w$ as a function of length of nanorod $l$ at different film thickness $d_f = 30, 40, 50$ nm and diameter of nanorod $D = 5, 10, 30$ nm.](image-url)
80 nm, SPR angle $\theta_r$ redshifts and the slope increases with refractive index $n$ when $n \leq 1.32$. With further increasing of the refractive index $n$, $\theta_r$ slightly redshifts or blueshifts, which means it becomes more difficult to differentiate SPR angle shift due to the change of refractive index $n$. Figure 6(d) shows a typical comparison for different diameters of nanorod $D$ at a fixed length of nanorod $l = 20$ nm. As we can see, SPR angle $\theta_r$ and the sensitivity $s$ increases with increasing $D$ at a fixed refractive index $n$, except that $\theta$ begins to blueshift when $n \geq 1.30$ at $D = 30$ nm.

In real SPR sensor applications, we are more concerned about the local sensitivity $s$ around some certain refractive index $n$. In other words, how much is the smallest amount of analyte we can measure when the refractive index $n$ is changed in only a very small range? We still take the structure with $d_f = 40$ nm as an example and consider the sensitivity $s$ when the refractive index $n$ changes from $n = 1.00$ to $n = 1.05$ (in air) and from $n = 1.30$ to $n = 1.34$ (in water), as shown in Figs. 7(a) and 7(b), respectively. From $n = 1.00$ to $n = 1.05$, the sensitivity $s$ increases with increasing diameter of nanorod $D$ at a fixed length of nanorod $l$, but it changes differently with $l$ when $D$ is fixed (Fig. 7(a)): at $D = 5$ nm, $s$ increases with increasing length of nanorod $l$ monotonically; at $D = 10$ nm, $s$ first decreases to its minimum at $l = 20$ nm and then increases with $l$; at $D = 30$ nm, $s$ is much larger than that at $D = 5$ and 10 nm and it reaches its maximum around $r \to 1$ before it decreases with $l$. From $n = 1.30$ to $n = 1.34$ (Fig. 7(b)], at $D = 5$ and 10 nm, $s$ shows trends similar to those from $n = 1.00$ to $n = 1.05$ and is higher than that at $D = 30$ nm. Corresponding to the negative slope described in Fig. 6(c), at $D = 30$ nm, the sensitivity $s$ becomes negative around $r \to 1$, although the absolute value is larger than those when $r > 1$ or $r < 1$.

When we are dealing with the SPR curves generated by the theoretical model, we have no difficulties recognizing the SPR signal even if the reflectance minimum is close to 1. However, in the real measurements, we need to consider the signal-to-noise ratio and the significance of the SPR dip; thus, we set a positive threshold to detect the SPR signal.
reasonable threshold for $R_m$ and require $R_m < 0.6$ as a valid SPR signal for the following sensitivity comparison. To see the enhancement by incorporating the nanorod structure into the SPR configuration, we compare the sensitivity $s$ among the nanorod-mediated SPR configurations with $d_f = 30, 40, \text{ and } 50 \text{ nm}$, $D = 5, 10, \text{ and } 30 \text{ nm}$ and the conventional SPR configurations composed of Ag film with thicknesses of $30, 40, \text{ and } 50 \text{ nm}$, as shown in Figs. 8 and 9. The sensitivity $s$ calculated when the refractive index $n$ changes from $n = 1$ to $n = 1.05$ is plotted in Fig. 8(a). First, sensitivity behaviors are similar as the film thickness changes from $d_f = 40 \text{ nm}$ to $d_f = 30, 50 \text{ nm}$. Second, sensitivity $s$ of the nanorod-mediated SPR configurations is higher than that of the conventional Ag film SPR configuration. In this case, the best configuration is the nanostructure with $d_f = 30 \text{ nm}$, $D = 30 \text{ nm}$, and $l = 20 \text{ nm}$. Since the sensitivities for all the conventional SPR configurations are very close, we take the most commercially used film structure with $50 \text{ nm}$ thickness as a comparison with the best nanostructure, and their SPR curves are plotted in Fig. 8(b). From $n = 1$ to $n = 1.05$, SPR angle $\theta_s$ shifts $2.91^\circ$ for the film structure and $3.74^\circ$ for the nanostructure, although the width increases in the case of the nanostructure. It has been reported that the broadening in the SPR curve is caused by the excited LSPs, which involve a large number of damping modes and the decreased effective mean free path of conduction electrons [16,40]. From $n = 1.3$ to $n = 1.34$, the negative values of the sensitivity are filtered out due to the large $R_m$ and the data are plotted in Fig. 9(a). The configuration with the highest $s$ is the nanostructure with $d_f = 50 \text{ nm}$, $D = 10 \text{ nm}$, and $l = 10 \text{ nm}$, which corresponds to the spheres with diameter of $10 \text{ nm}$. It is compared with the $50 \text{ nm}$ film structure in Fig. 9(b), and the SPR dips indicate a shift of $4.47^\circ$ for the film structure and $8.54^\circ$ for the nanostructure. The enhancement is almost twofold at the expense of the broadened width.

Regarding biomolecule detection, researchers normally use $n = 1.45$ as the dielectric constant of the protein layer [43,44]. From Fig. 6 it can be seen that the SPR angles are close to $80^\circ$ when the refractive index is 1.34, which means this configuration has limitations for higher refractive index measurement. To solve the problem, we can replace the glass prism ($n = 1.51$) by a prism with higher refractive index, such as 1.78. If we take the structure with $d_f = 50 \text{ nm}$, $D = 10 \text{ nm}$, and $l = 10 \text{ nm}$ as an example, and assume the surrounding medium has a small change from $n = 1.45$ to $n = 1.46$, the SPR dip shifts from the above structure and the traditional Ag film, $50 \text{ nm}$, are plotted in Fig. 10. As we can see, the SPR dips indicate a shift of $0.78^\circ$ for the film structure and $1.46^\circ$ for the nanostructure. The enhancement is still almost twofold at the expense of broadened width. To find the optimized structure, one can calculate the shift by taking a range of the film thickness $d_f$ and the diameter and length of the nanorods $D$ and $l$.

C. Preliminary Experimental Results

1. Morphologies of Ag Nanorods with Different Lengths

To visualize the Ag nanorods, Ag nanorods with nominal thicknesses of $d = 200, 300, 600, \text{ and } 800 \text{ nm}$ grown on the Si substrate were observed with a

![Fig. 9. (Color online) (a) Sensitivity comparison between the nanorod-mediated SPR sensor and the conventional SPR sensor, and (b) the corresponding SPR curves from $n = 1.30$ to $n = 1.34$. The refractive index of the prism is 1.51.](image)

![Fig. 10. (Color online) SPR shift comparison between the structure with $d_f = 50 \text{ nm}$, $D = 10 \text{ nm}$, $l = 10 \text{ nm}$ and the Ag film with a thickness of $50 \text{ nm}$ from $n = 1.45$ to $n = 1.46$. The refractive index of the prism is 1.78.](image)
SEM. Cross sections and top views of these samples are shown in Figs. 11(a)–11(d). For the Ag nanorods with \( d = 200 \) nm, there are islands with random shapes on the surface and small anisotropy can be seen from the cross section [Fig. 11(a)]. When the nominal thickness \( d \) increases to 300 nm, the size of those islands increases and the nanorods start to grow [Fig. 11(b)]. As the growth continues, the nanorods can be clearly identified from samples with \( d = 600 \) and 800 nm, as shown in Figs. 11(c) and 11(d). By rough estimation, the average diameter of the Ag nanorods with \( d = 200, 300, 600, \) and 800 nm are \( D = 93, 93, 70 \) and 70 nm, respectively; the averaged lengths are \( l = 70, 209, 535 \) and 744 nm, respectively.

2. Surface Plasmon Resonance Measurements of Ag Film and Ag Nanorods/Ag Film

In the experiments, we fix the incident light wavelength at 632.8 nm, scan the incident angle onto the sample, and collect the reflected light by a line camera. The optical path is shown in Fig. 12. The incident light beam first goes through a neutral density (ND) filter, then is reflected from a mirror and goes into a polarizer, which turns the incident light into \( p \)-polarized light. Since \( s \)-polarized light is treated as the background, a half-wave plate is placed behind the polarizer so that the \( p \)-polarization state and \( s \)-polarization state can be easily switched. To filter out the spatially varying “noise” intensity of the input Gaussian beam, a space filter is used, which contains an aspheric lens and a 10 \( \mu \)m pinhole. Then the beam goes through the aperture, lens 1 and lens 2, and incidents onto a semicylindrical prism. Though the incident beam has the shape of a cone, which contains a small range of incident angles on the backside of the prism, the subtle bending at the curve surface of the prism will be ignored. The sample is attached on the backside of the prism by using the index matching fluid (Cargille Laboratories, Cedar Grove, New Jersey), and the reflected beam goes through lens 3 and enters a linear CCD camera. The sample and the camera can be rotated to search the SPR resonance angle when necessary.
SPR measurements of Ag nanorods with a nominal thickness of 200 nm on Ag film with a thickness of 40 nm were first performed in air. The SPR reflectance is defined as the ratio between the reflectance from $p$-polarized incident light and that from $s$-polarized incident light. Since the tilted Ag nanorods are anisotropic, two different incident configurations, the incident light parallel to the nanorod tilting direction (configuration A) and the incident light antiparallel to the nanorod tilting direction (configuration B), are taken for the measurement and the tilted nanorods are within the plane of incidence [Fig. 13(a)]. The SPR curves measured in configurations A and B almost overlap with each other [Fig. 13(b)]. This is consistent with our theoretical model and Smith’s study, where the reflectance of an anisotropic nanorod layer is independent of the sign of the incident angle if the nanorods are lying in the plane of incidence [35]. The SPR angles $\theta_r$ measured at different locations for different orientations are shown in Fig. 13(c). The standard deviations (SD) for orientations A and B are 0.009° and 0.005°, respectively, and the difference between the averaged SPR angles $\theta_r$ for different orientations is only 0.023°, which we believe will not affect the shift due to the analyte. For the Ag nanorods with $d = 500$ nm on 40 nm thick Ag film, we did not observe any SPR signal [Fig. 13(b)].

From the theory developed previously, in the case of Ag nanorods 200 nm/Ag film 40 nm ($D = 93$ nm, $l = 70$ nm), the minimum reflectance, SPR resonance angle, and the width in air are 0.9, 47.2°, and 0.8°, respectively. However, the experimental results show that the minimum reflectance, SPR resonance angle, and width in air are 0.2, 42.5°, and 0.2°, respectively. We believe that the inconsistency is caused by the difference between the theoretical model and the actual morphology of the Ag nanorods 200 nm/Ag film 40 nm. As a matter of fact, it is hard to treat the islands with the random shapes on the surface as the “spheroids.” In the case of Ag nanorods 500 nm/Ag film 40 nm, the morphology should be something between Figs. 11(b) and 11(c), which is close to the theoretical model. However, according to the theory, if the length of the nanorods is larger than 200 nm, the minimum reflectance is very close to 1 and the SPR signal cannot be observed.

Efforts have also been made on SPR measurements of Ag film and Ag nanorods/Ag film in DI water. Ag film with a thickness of 50 nm was fabricated and a thin layer of Ti film (1 nm) was deposited prior to the Ag deposition to enhance the adhesion in water. Figures 14(a) and 14(b) show the reflectance of 50 nm Ag film in air and in water, and the SPR angles are 41.96° and 67.38°, respectively. The curve is a little noisy; we believe that this is caused by the linear CCD camera.
Ag nanorods with $d = 200$ nm were deposited onto Ag film 50 nm/Ti film 1 nm and measured in air. As shown in Fig. 14(c), the SPR angle is 42.16°. The curve looks noisier and one possible reason is the increasing surface roughness. However, we could not find any SPR signal when the Ag nanorods were in contact with DI water. According to the theory, if the nanorods have a diameter larger than 70 nm, the SPR signal cannot be observed in water. In summary, the nanorods under examination have a large diameter and length, which makes it difficult to produce a significant SPR dip, either in air or in water. However, those preliminary experimental results seem to qualitatively agree with the predictions from our theory.

4. Conclusions

In conclusion, we have carried out theoretical modeling of a nanorod-mediated SPR sensor using anisotropic effective medium theory and have studied the impact of various structural parameters, such as the metal thin film thickness $d_f$, length $l$, and diameter $D$ of the nanorod on the properties of this SPR sensor. Compared with the conventional SPR configuration, the nanorod-mediated SPR sensor shows a larger resonance angle shift, and its sensitivity increases with increasing refractive index of the target analyte. According to the calculation, the sensor with $d_f = 30$ nm, $D = 30$ nm, and $l = 20$ nm performs best when the refractive index changes from $n = 1$ to $n = 1.05$, while in another index changing range, $n = 1.3$ to $n = 1.34$, the sensor with $d_f = 50$ nm, $D = 10$ nm, and $l = 10$ nm enhances the sensitivity by twofold. By replacing the prism with a higher refractive index, the model can be applied to a biological analyte with a refractive index of around $n = 1.45$. The results suggest that a nanorod-mediated SPR sensor should be designed based on estimated index changes induced by target interactions. Experimental investigation has been carried out for the Ag nanorod-mediated SPR sensor. For measurements in air, the SPR angles of the Ag nanorods 200 nm/Ag film 40 nm sample have a SD smaller than 0.01°, but no signal was observed for the Ag nanorods 500 nm/Ag film 40 nm sample. Efforts have also been put on the measurements in DI water, but no SPR signal is observed for the Ag nanorods/film structure. According to the theory, if the nanorods have a diameter larger than 70 nm and the measurement is performed in water, the reflectance minimum will be too close to 1 and will be difficult to see experimentally. Though we have not experimentally verified the enhancement by the Ag nanorods/film structure, the theory can still predict some results to some extent. We believe that the OAD technique is able to produce nanorods with a smaller diameter, and the experiments are under investigation.

We have to mention that we used the bulk refractive index of silver in the theoretical model. However, since the thickness of the thin silver film is within 100 nm, its refractive index should be different from the bulk material. Taking this factor into account, we believe that there will be more space for modeling improvement and further instructions for SPR sensor fabrication.

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