Ultrasensitive chemical sensors based on whispering gallery modes in a microsphere coated with zeolite

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We propose a highly sensitive chemical sensor by functionally coating a zeolite film on the external surface of an optical microsphere. Using the perturbation theory, a model is developed to calculate sensor sensitivity and analyze the impact of the zeolite film thickness. The quality factor and detection limit are also investigated by using an approximate model. Simulations show that a zeolite coating can effectively increase sensitivity. The results provide physical insights for the design and optimization of various parameters for desired sensor performance.

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1. Introduction

Increasing research activities have been focused on optical microspheres with whispering gallery modes (WGMs) used as refractive index optical sensors for broad applications such as the detection of biological materials, and measurement of chemical composition or concentration changes [1–6]. Hanumegowda *et al.* developed a refractometric optical sensor based on fused silica microspheres, which has a sensitivity of nearly 30 nm/refractive index unit (RIU) [3]. Zhu *et al.* developed an optical microsphere resonator biosensor using an aptamer as the receptor for the detection of thrombin [4]. Vollmer *et al.* reported specific detection of proteins absorbed on a spherical surface by observing the resonant wavelength shift of WGMs [5], and they found that the theoretical shift for a single protein can be extremely sensitive [6]. They also described a perturbation theory for the wavelength shift of WGMs in a transparent sphere [7,8]. In addition, they examined properties of WGMs in a microsphere coated with a high-refractive index layer, and found that the high-refractive index layer would enhance the sensitivity of WGM wavelength shift sensors [9,10]. But sensitivity is still low because all the reported microsphere sensors utilize the evanescent field leaked into the surrounding medium to detect the refractive index change. Also, it remains challenging to obtain a stable output signal in practical applications of the microsphere sensors, especially for gas detection, which is mainly due to the microsphere small surface-to-mass ratio and poor adsorbability to most chemical molecules. Furthermore, an optical microsphere has no selectivity to mixtures and requires time-consuming surface treatment or sample separation for measurement.

Most recently, it was discovered that the unique combination of optical and chemical properties of zeolite could be used to develop ultrasensitive optical

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chemical sensors [11–13]. And the WGMs in zeolite-based microcavities have also been experimentally demonstrated, such as microlasers based on zeolite containing embedded dyes [14], and the fiber-taper-coupled zeolite cylindrical microcavity [15]. Zeolite is a class of crystalline aluminosilicate materials with uniform subnanometer- or nanometer-scale pores determined by their crystal structures. With very large surface-to-mass ratio, zeolite pores can adsorb chemical molecules of specific size from the ambient efficiently and selectively [16,17]. Then the adsorbed analyte molecules are organized and oriented in the pores, which causes a refractive index change of the zeolite that can be examined by various optical methods. Hence, with the zeolite coating as an effective sample concentrator, an optical probe integrated with a sensitive photonic device can be used to develop chemical sensors.

This study proposes an ultrasensitive chemical sensor by functionally coating a zeolite film on an optical microsphere. To our knowledge, a chemical sensor based on a zeolite-coated microsphere has not been reported previously. The concept of the sensor and a brief introduction to its operating principle are included in Section 2. In Section 3, the model to calculate sensitivity is developed based on the perturbation theory presented by Teraoka and Arnold [8–10]. The detection limit, coupling efficiency, and free spectral range (FSR) are also considered in Section 3. In Section 4, the influences of the zeolite coating on the sensitivity, quality factor, and detection limit are investigated in detail. Lastly, important results are summarized in Section 5.

2. Sensor Concept

As shown in Fig. 1, this study proposes an ultrasensitive chemical sensor by functionally coating a thin layer of zeolite film on an optical microsphere, and the coated microsphere is closely coupled with a tapered fiber. The size of the fiber and its distance to the microsphere should be precisely determined and controlled to obtain a desired WGM excitation in the microsphere. Then a series of resonance bands can be detected in the fiber transmission spectrum in the laser illumination.

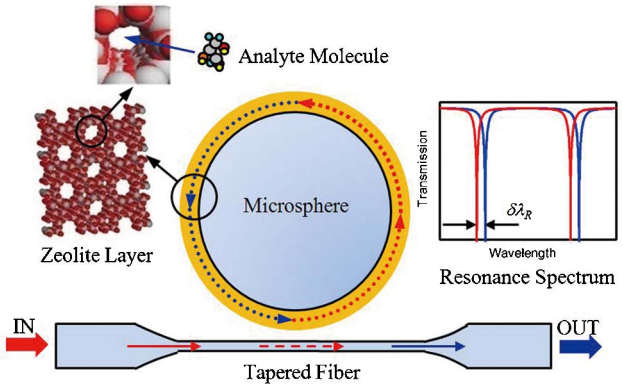

Fig. 1. (Color online) Proposed zeolite-coated microsphere sensor.

The proposed sensor detects the molecular adsorption-induced refractive index change of the zeolite, which is different with most microsphere sensors that use the evanescent field of WGMs to detect the refractive index change of the surrounding medium. With selective adsorption of the target analyte molecules from the environment, the refractive index of the zeolite thin film increases. On the other hand, the release of adsorbed molecules from the zeolite pores results in a decrease in the zeolite refractive index. The refractive index of zeolite was reported to change dramatically on loading and unloading of guest molecules in the zeolite cavities [18]. And the wavelengths of the resonant bands are very sensitive to the refractive index change. Ultrasensitive detection of the target chemicals can thus be achieved by monitoring the resonant wavelength shift ($\delta\lambda_R$ in Fig. 1) in the transmission spectrum. In addition to the advantages of microsphere sensors, such as small size and capability of multiplexing, zeolite-coated microsphere sensors have ultrahigh sensitivity, good selectivity and stability, and capability of *in situ* detection of most chemicals, including gases. The operating temperature of the proposed sensor should be well controlled because the zeolite adsorbing selectivity is sensitively affected by temperature [12].

The primary performance factor of the proposed sensor is detection sensitivity. Other important factors include detection limit, coupling efficiency, and FSR. These performance factors depend on a number of parameters, such as the microsphere size, zeolite film thickness, tapered fiber size, and its distance from the microsphere.

3. Theory

A. Whispering Gallery Modes in a Microsphere

Over the years, the WGM modal structures and resonance spectra of the microspheres have been widely studied [19–21]. The WGM is characterized by a set of integers: l, m, and v, which represent angular, azimuthal, and radial mode numbers, respectively. For an ideal sphere, modes with the same l and v, but arbitrary m have the same resonant wavelength. When $m = l$ and $v = 1$, the modes are frequently called fundamental WGMs. Also, a WGM has either TE or TM polarization, and the two polarizations can be selectively excited by controlling the polarization in the tapered fiber. In general, the resonance spectrum of the WGMs is determined by the size of the microsphere and spatial distribution of the refractive index inside/outside the microsphere. Considering an ideal microsphere with the radius of a_0 and refractive index of n_s, surrounded by a medium with the refractive index of n_0, the characteristic equation to specify the resonant wavelengths λ_R of the WGMs in the resonance spectrum is expressed by [8]

$$\eta_s \frac{\chi_l'(n_0 k a_0)}{\chi_l(n_0 k a_0)} = \frac{\psi_l'(n_s k a_0)}{\psi_l(n_s k a_0)}, \tag{1}$$

where $k = 2\pi/\lambda_R$ is the resonant wave vector; $\eta_s = n_0/n_s$ (TE modes), n_s/n_0 (TM modes); and ψ_l and χ_l are the spherical Ricatti–Bessel function and spherical Ricatti–Neumann function, respectively. If the microsphere is coated with a zeolite film of thickness h and refractive index n_{cl}, the characteristic equation to specify λ_R can be given as [9,10]

$$\eta_0 \frac{\chi_l'(n_0 k a_1)}{\chi_l(n_0 k a_1)} = \frac{B_l \psi_l'(n_{cl} k a_1) + \chi_l'(n_{cl} k a_1)}{B_l \psi_l(n_{cl} k a_1) + \chi_l(n_{cl} k a_1)}, \tag{2}$$

where $a_1 = a_0 + h$ is the total radius of the whole microsphere including the zeolite film; $\eta_0 = n_0/n_{cl}$ (TE modes), n_{cl}/n_0 (TM modes); B_l is a coefficient, and its expression is given by

$$B_l = \frac{\eta_{cl}\psi_l'(n_s k a_0)\chi_l(n_{cl} k a_0) - \psi_l(n_s k a_0)\chi_l'(n_{cl} k a_0)}{\psi_l'(n_{cl} k a_0)\psi_l(n_s k a_0) - \eta_{cl}\psi_l(n_{cl} k a_0)\psi_l'(n_s k a_0)},$$
$$\eta_{cl} = \begin{cases} n_s/n_{cl}, & \text{TE modes} \\ n_{cl}/n_s, & \text{TM modes} \end{cases}. \tag{3}$$

For a given value of l, there are multiple values of λ_R that satisfy the characteristic equations. These resonant modes are called the first-order mode, the second-order mode…, and the vth order mode in the decreasing value of λ_R.

According to Eq. (1), when a refractive change δn_0 occurs in the surrounding medium, a shift $\delta\lambda_R$ in the resonant wavelength would take place correspondingly. When the sphere is coated with a zeolite film, both changes in n_0 and n_{cl} will cause the wavelength shift, according to Eq. (2). But, as described previously, the proposed sensor mainly detects the molecular adsorption-induced refractive index change of the zeolite. So, only δn_{cl} is considered for the zeolite-coated microsphere. $\delta\lambda_R$ can be calculated by substituting the refractive index change into Eqs. (1) or (2). But, it is difficult to derive an explicit formula to describe the relation between $\delta\lambda_R$ and δn_{cl} (or δn_0) from the characteristic equations.

B. Sensitivity

The sensitivity S, is defined as $S = \delta\lambda_R/\delta n$. For an uncoated microsphere, $\delta n = \delta n_0$, and for a zeolite-coated microsphere, $\delta n = \delta n_{cl}$. The sensitivity can be calculated by

$$S = \frac{\delta\lambda_R}{\delta n} = -\frac{\lambda_R}{\delta n} \cdot \frac{\delta k}{k_0}, \tag{4}$$

where k_0 is the wave vector before the refractive index change and δk is the wave vector shift induced by δn. If the refractive index change is uniform and $\delta(n^2) \ll 1$, the fractional shift $\delta k/k_0$ can be calculated by the perturbation theory developed by Teraoka and Arnold [8–10]. In the case of an uncoated microsphere, $\delta k/k_0$ is given as [9,10]

$$\left(\frac{\delta k}{k_0}\right)_{\text{TE}} = -\frac{\delta(n_0^2)\int_0^\infty T_0^2(r)\mathrm{d}_r}{2\int_0^\infty [n(r)T_0(r)]^2\mathrm{d}_r}, \quad \text{TE modes}, \tag{5a}$$

$$\left(\frac{\delta k}{k_0}\right)_{\text{TM}} = -\frac{\delta(n_0^2)[-T_0(a_0)T_0'(a_0^+) + n_0^2 k_0^2 \int_0^\infty T_0^2\mathrm{d}_r]}{2n_0^4 k_0^2 \int_0^\infty T_0^2(r)\mathrm{d}_r}, \quad \text{TM modes}, \tag{5b}$$

where $n(r) = n_s(r < a_0)$, $n_0(r > a_0)$ a_0^+ is infinitesimally greater than a_0, $T(r)$ is the function to describe the electric field distribution of WGMs along the radial direction, and T_0 denotes the field before the refractive index change. For an uncoated microsphere, $T(r)$ is expressed as

$$T(r) = \begin{cases} \psi_l(n_s k r) & r < a_0 \\ D_l \chi_l(n_0 k r) & r > a_0 \end{cases}, \tag{6}$$

where D_l is the coefficient, and $D_l = \psi_l(n_s k a_0)/\chi_l(n_0 k a_0)$. Substituting (5) and (6) into (4), and considering $\delta\ (n_0^2) \approx 2n_0\delta n_0$ if $\delta(n_0^2) \ll 1$, the sensitivity S_0 for the TE and TM modes in an uncoated microsphere can be, respectively, expressed as

$$(S_0)_{\text{TE}} = \frac{n_0 \lambda_R I_0}{n_s^2 I_s + n_0^2 I_0}, \tag{7a}$$

$$(S_0)_{\text{TM}} = \frac{\lambda_R^2 [n_0 k_0 I_0 - D_l^2 \chi_l(n_0 k_0 a_0)\chi_l'(n_0 k_0 a_0)]}{2\pi n_0^2 (I_s + I_0)}, \tag{7b}$$

where

$$I_s = \int_0^{a_0} [\psi_l(n_s k_0 r)]^2 \mathrm{d}_r, \quad I_0 = \int_{a_0}^{\infty} [D_l \chi_l(n_0 k_0 r)]^2 \mathrm{d}_r. \tag{7c}$$

In the situation of a zeolite-coated microsphere, using the perturbation theory, $\delta k/k_0$ can be derived:

$$\left(\frac{\delta k}{k_0}\right)_{\text{TE}} = -\frac{\delta(n_{cl}^2)\int_{a_0}^{a_1} T_0^2(r)\mathrm{d}_r}{2\int_0^\infty [n(r)T_0(r)]^2\mathrm{d}_r}, \quad \text{TE modes}, \tag{8a}$$

$$\left(\frac{\delta k}{k_0}\right)_{\text{TM}} = -\frac{\delta(n_{cl}^2)[T_0'(a_1^-)T_0'(a_1) - T_0'(a_0^+)T_0(a_0) + n_{cl}^2 k_0^2 \int_{a_0}^{a_1} T_0^2\mathrm{d}_r]}{2n_{cl}^4 k_0^2 \int_0^\infty T_0^2(r)\mathrm{d}_r}, \quad \text{TM modes}, \tag{8b}$$

where $n(r) = n_s(r < a_0)$, $n_{cl}(a_0 < r < a_1)$ and $n_0(r > a_1)$; a_1^- is infinitesimally smaller than a_1. For the zeolite-coated microsphere, $T(r)$ is given as

$$T(r) = \begin{cases} A_l\psi_l(n_s kr) & r < a_0 \\ B_l\psi_l(n_{cl}kr) + \chi_l(n_{cl}kr) & a_0 < r < a_1 \\ C_l\chi_l(n_0 kr) & r > a_1 \end{cases}, \quad (9a)$$

where A_l and C_l are the coefficients determined by

$$A_l = \frac{B_l\psi_l(n_{cl}ka_0) + \chi_l(n_{cl}ka_0)}{\psi_l(n_s ka_0)}, \qquad C_l = \frac{B_l\psi_l(n_{cl}ka_1) + \chi_l(n_{cl}ka_1)}{\chi_l(n_0 ka_1)}. \quad (9b)$$

Substituting (8) and (9) into (4), and considering $\delta(n_{cl}^2) \approx 2n_{cl}\delta n_{cl}$ if $\delta(n_{cl}^2) \ll 1$, the sensitivity for the TE and TM modes in a zeolite-coated microsphere can be expressed by

$$S_{\mathrm{TE}} = \frac{n_{cl}\lambda_R I_{cl}}{n_s^2 I_s + n_{cl}^2 I_{cl} + n_0^2 I_0}, \quad (10a)$$

$$S_{\mathrm{TM}} = \frac{\lambda_R^2[n_s n_0 k_0 I_{cl} + n_s C_l^2\chi_l(n_0 k_0 a_1)\chi_l'(n_0 k_0 a_1) - n_0 A_l^2\psi_l(n_s k_0 a_0)\psi_l'(n_s k_0 a_0)]}{2\pi n_s n_0 n_{cl}(I_s + I_{cl} + I_0)}, \quad (10b)$$

where

$$I_s = \int_0^{a_0} [A_l\psi_l(n_s k_0 r)]^2 \mathrm{d}_r, \qquad I_0 = \int_{a_1}^{\infty} [C_l\chi_l(n_0 k_0 r)]^2 \mathrm{d}_r, \quad (10c)$$

$$I_{cl} = \int_{a_0}^{a_1} [B_l\psi_l(n_{cl}k_0 r) + \chi_l(n_{cl}k_0 r)]^2 \mathrm{d}_r. \quad (10d)$$

The unit of sensitivity is nm/RIU.

C. Detection Limit

The detection limit, defined as the smallest detectable change of the refractive index, is proportional to $1/(S \times Q_{\mathrm{tot}})$ [22], where Q_{tot} is the total quality factor of the sensor system defined as the ratio of the resonant wavelength to the full width at half-maximum of the resonance. In practical applications of the sensor, various noises can perturb the resonance spectrum. In these cases, the accurate detection of the resonant wavelength shift becomes difficult for a broad resonance linewidth. This suggests that a narrow resonance (thus a high Q_{tot} value) is preferred to achieve a small detection limit. The total quality factor is calculated by [23]

$$\frac{1}{Q_{\mathrm{tot}}} = \frac{1}{Q_{\mathrm{in}}} + \frac{1}{Q_{\mathrm{ex}}}, \quad (11)$$

where Q_{in} is the intrinsic quality factor that is related to the quality of the resonator itself, and Q_{ex} is the extrinsic quality factor that describes the light coupling condition between the resonator and the tapered fiber. Q_{ex} can be calculated by using the coupled mode theory, and it was found that Q_{ex} increases with the coupling distance between the fiber and resonator [21].

Q_{in} is calculated by $Q_{\mathrm{in}} = 2\pi n/\alpha\lambda_R$, where α is the lumped loss of light in the resonator. The losses include the scattering loss from surface irregularities, optical absorption loss due to molecular resonances, Raleigh scattering loss, and tunneling loss [24]. Tunneling loss is due to the curvature of the waveguiding boundaries in the direction of propagation, and it is also referred to as the whispering gallery loss. The tunneling and scattering loss are small for the well-fabricated and air-clad microsphere with a radius larger than 15 μm. The optical absorption loss of the optical fiber grade glass is about 0.2 dB/km at the wavelength of 1550 nm. This corresponds to a very high absorption-limited Q_{in} factor, on the order of 10^{11} [21]. In our case, the proposed sensor utilizes the nanoporous zeolite coating as an intermediate film to translate the molecule adsorption to the refractive index change. This coated zeolite film improves the sensitivity. But, unfortunately, the zeolite film may impair the Q_{in} factor due to its possible large absorption loss of light. Considering a microsphere ($a_0 > 15$ μm) coated with a defect-free and smooth-surface film, the Q_{in} factor is mainly determined by the material absorption loss of the microsphere and the film [25,26], which can be estimated by

$$\frac{1}{Q_{\mathrm{in}}} \approx \eta_1 \frac{1}{(Q_{\mathrm{in}})_{h=0}} + \eta_2 \frac{1}{(Q_{\mathrm{in}})_{h \geq h_0}}, \quad (12a)$$

where $(Q_{\mathrm{in}})_{h=0}$ is the quality factor of the microsphere before coating and $(Q_{\mathrm{in}})_{h \geq h_0}$ is the quality factor of the coated microsphere with the film thickness lager than the threshold h_0 (discussed in detail in

Section 4). For a defect-free film with a smooth surface, $(Q_{\text{in}})_{h\geq h_0} \approx 2\pi n_{cl}/\alpha_{cl}\lambda_R$, where α_{cl} is the optical absorption loss of the film; η_1 and η_2 denote the fractions of light energy traveling in the microsphere and the film, which can be calculated by

$$\eta_1 = \frac{n_s^2 I_s}{n_s^2 I_s + n_{cl}^2 I_{cl} + n_0^2 I_0},$$
$$\eta_2 = \frac{n_{cl}^2 I_{cl}}{n_s^2 I_s + n_{cl}^2 I_{cl} + n_0^2 I_0} \quad \text{(TE modes)}, \tag{12b}$$

$$\eta_1 = \frac{I_s}{I_s + I_{cl} + I_0}, \qquad \eta_2 = \frac{I_{cl}}{I_s + I_{cl} + I_0} \text{(TM modes)}. \tag{12c}$$

The sum of η_1 and η_2 is nearly 1 because the fraction of light energy in the surrounding medium is negligible.

D. Other Main Performance Factors

In addition to high sensitivity and a small detection limit, high coupling efficiency is also important for accurate sensing, because it implies a deeper resonant peak and a better signal-to-noise ratio. Two conditions must be met to achieve the maximum (100%) coupling efficiency: (i) the propagation constant of the WGM is matched with the propagation constant of the appropriate mode in the tapered fiber [27] and (ii) the coupling distance is adjusted to meet $Q_{\text{ex}} = Q_{\text{in}}$, which is commonly referred to as the case of critical coupling [23]. The FSR, defined as the difference between two adjacent resonant wavelengths, is another important parameter. A small FSR will impose a limit on the dynamic range of the refractive index measurement as it becomes difficult to differentiate the corresponding order of the resonance peaks. A small FSR also makes it hard to multiplex a number of microspheres to form a sensor array. It was found that the FSR is mainly determined by the size of the microresonator [28]. Large resonators are preferred for achieving high quality factors (thus an enhanced detection limit), but they usually have a small FSR (thus a small detection range). The trade-off between the detection limit and the detection range should be decided by the specific sensing requirements.

4. Results and Discussion

In the studied case, a silica microsphere of $n_s = 1.452$ coated with a zeolite film is considered. The whole device is assumed to be immersed in nitrogen with a refractive index of $n_0 = 1.0$. Considering that isopropanol molecules are mixed with the nitrogen, the zeolite film will adsorb the isopropanol molecules, which leads to an increase in the refractive index. As found by Zhang *et al.*, the refractive index n_{cl} of zeolite increases from 1.336 in pure nitrogen to 1.402 in 5353 parts per million isopropanol vapor in nitrogen [13]. The parameters that have a significant impact on the sensitivity are the microsphere radius a_0 and the zeolite film thickness h. Figure 2 shows the sensitivity for the WGMs of two polarizations and $v = 1$ and 2 as a function of the zeolite film thickness. The radius of the microsphere is $a_0 = 25\ \mu$m, and the mode numbers l are chosen to have a similar resonant wavelength, $\lambda_R \approx 1550$ nm, which corresponds to the center wavelength of the tapered fiber operating wave band.

As shown in Fig. 2, the sensitivity increases with the zeolite film thickness for the WGMs of $v = 1$, until it reaches a threshold thickness h_0, above which sensitivity reaches the highest value S_{MAX}. While, there is an oscillation of the sensitivity changes for the WGMs $v = 2$. The threshold thickness for the modes of $v = 2$ is larger than that of $v = 1$. In Fig. 2, $h_0 \approx 3\ \mu$m for the modes of $v = 1$, as compared with $h_0 \approx 4.5\ \mu$m for the modes of $v = 2$. Figure 2 also shows that the sensitivity changes are similar for two polarizations, and S_{MAX} for the TE modes is slightly larger than that of the TM modes. Figure 3 shows the sensitivity for the TE modes of $v = 1$ in microspheres of different radii. From Fig. 3, the sensitivity of a larger sphere increases more slowly with the thickness and its threshold thickness is larger. The sensitivity can be increased by about 2 orders of magnitudes if the microsphere is coated with a zeolite film thicker than the threshold thickness. For instance, at the microsphere radius of 25 μm, S increases from $S_0 = 15.17$ nm/RIU at $h = 0\ \mu$m to $S_{\text{MAX}} = 1138.60$ nm/RIU at $h = 3\ \mu$m, which presents an increase of about 75 times.

The sensitivity changes can be explained by the electric field distributions along the radial direction $T_0(r)$. Figure 4 shows $T_0(r)$ for TE modes of $v = 1$ and 2, in the microsphere of $a_0 = 25\ \mu$m coated with zeolite films of various thicknesses. All the curves in Fig. 4 are normalized for comparison, and the curves for the TM modes are similar to those for the TE modes. At $h = 0\ \mu$m, the evanescent field in

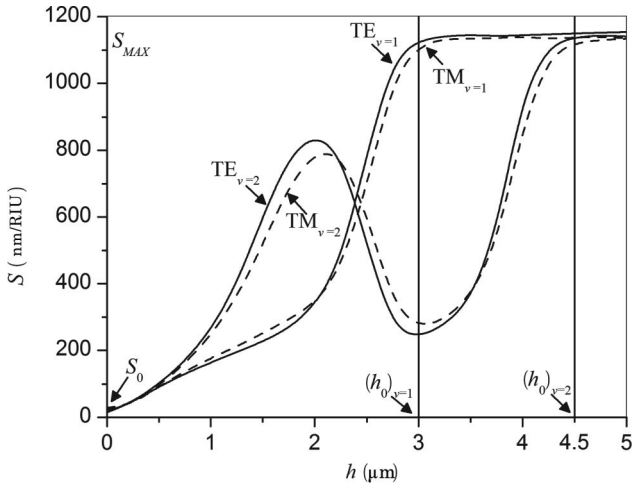

Fig. 2. Sensitivity of TE modes (solid curves) and TM modes (dashed curves) of two orders ($v = 1, 2$) as a function of the zeolite film thickness.

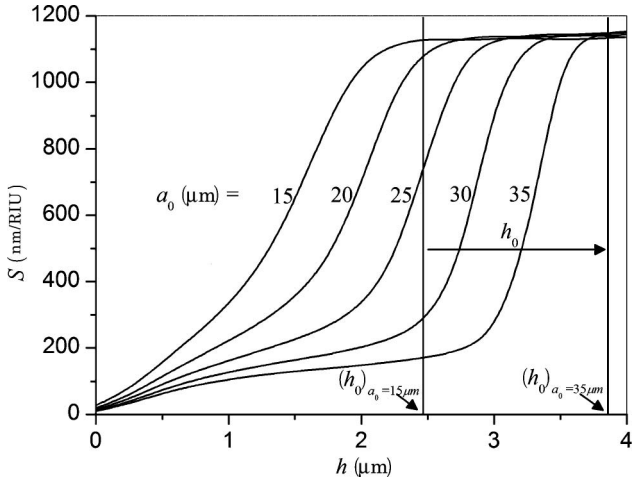

Fig. 3. Sensitivity for TE modes of $v = 1$ in microspheres of different radii as a function of the zeolite film thickness.

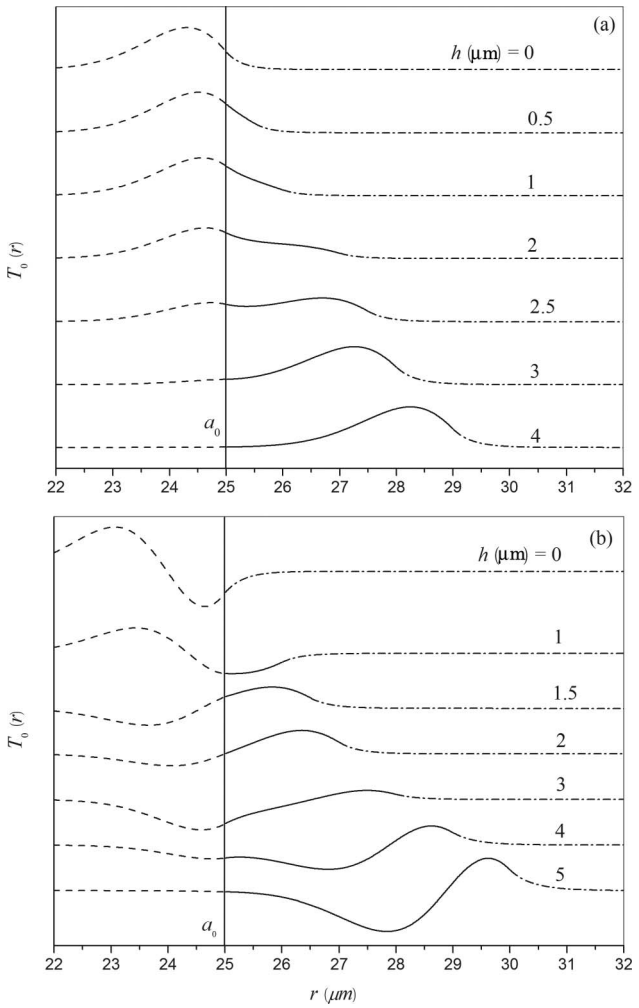

Fig. 4. Electric field distribution along the radial direction for TE modes in the microsphere of $a_0 = 25$ μm coated with zeolite films of various thicknesses. Modes of the (a) first order ($v = 1$) and (b) second order ($v = 2$). The dashed and solid curves represent the internal field in the microsphere and the zeolite film, and the dashed-dotted curves represent the evanescent field in the surrounding medium.

the surrounding medium is the key to explain the refractive index changes of the surrounding medium. As shown in Fig. 4, the evanescent field is just a very small part of the whole field, which implies a small sensitivity. If the microsphere is coated with a zeolite film, the electric field inside the zeolite film is the main factor for sensitivity, because the refractive index change is transferred from the surroundings into the zeolite film. For the modes of $v = 1$, with h increasing from $0 \sim 3$ μm, $T_0(r)$ gradually shifts into the zeolite film, which implies the increase of sensitivity. If the zeolite film is thicker than 3 μm, most of the electric field is inside the film, which corresponds to the highest sensitivity. While for the modes of $v = 2$, with h increasing, the electric field has a rebound from the zeolite film into the microsphere (when $h = 2$–3 μm), which implies the oscillation of sensitivity in Fig. 2.

After the sensitivity is determined, we can easily calculate the wavelength shift by $\delta\lambda_R = \delta n \times S$. Figure 5 shows $\delta\lambda_R$ as a function of δn for TE modes of $v = 1$, at $a_0 = 25$ μm with zeolite films of various thickness. The solid curves represent results by $\delta\lambda_R = \delta n \times S$. Hence, the slopes of the lines are actually the sensitivity. The discrete spots represent the actual values of $\delta\lambda_R$ that are numerically calculated based on the resonance conditions (1) and (2). Figure 5 indicates that errors between the solid lines and the actual values are very small and can be ignored, regardless of the zeolite film thickness, if $\delta n < 0.01$. While for $\delta n > 0.01$, the errors may be significant when $0 < h < h_0$ ($h_0 = 3$ μm at $a_0 = 25$ μm in the example). This can be explained by the following statements. The perturbation theory uses the field distribution $T_0(r)$ before the refractive index change to replace $T(r)$ after the change [9,10]. But the refractive index change may have a significant impact on the field distribution, as shown in Fig. 6. If the microsphere is uncoated ($h = 0$), a refractive index change of the surrounding medium has little

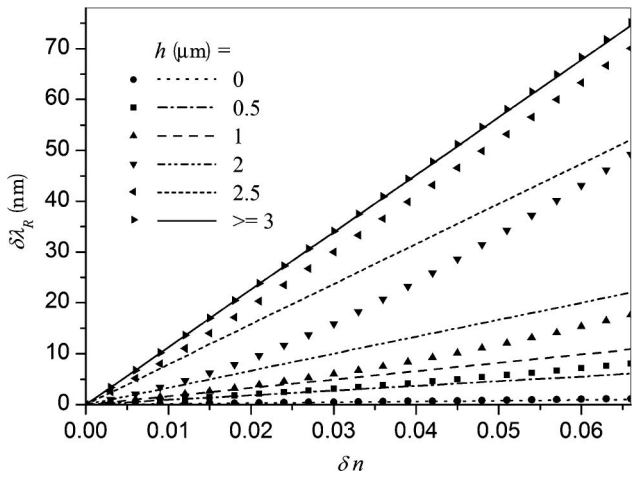

Fig. 5. $\delta\lambda_R$ as a function of δn for TE modes of $v = 1$ at $a_0 = 25$ μm with various coating thicknesses. The lines represent $\delta\lambda_R = \delta n \times S$. The discrete spots represent the actual values of $\delta\lambda_R$ calculated by Eqs. (1) and (2).

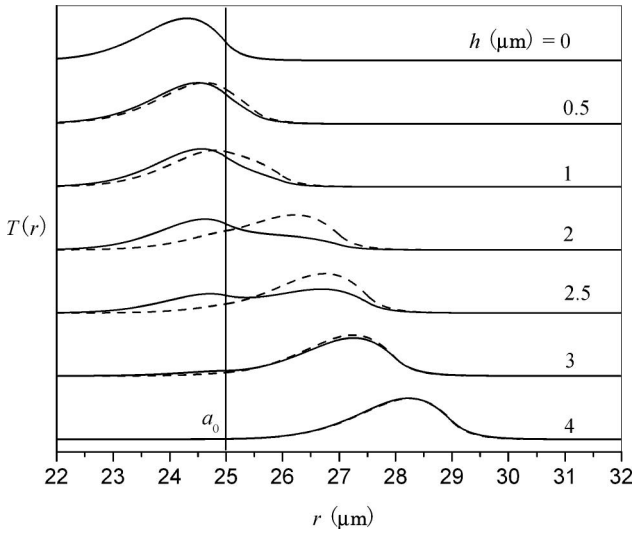

Fig. 6. Electric field distribution along the radial direction for TE modes of $v = 1$ before (solid curves) and after (dashed curves) a refractive index change of $\delta n = 0.06$.

impact on the field distribution (top curve in Fig. 6). While, if the microsphere is coated with a zeolite film ($0 < h < h_0$), the refractive index change of the zeolite film has a significant impact on the field distribution. Thus, in these cases, the actual sensitivity changes with the refractive index of the zeolite film. Figure 6 also shows that if $h > h_0$, the field distribution remains almost unchanged even at $\delta n = 0.06$, and, therefore, the sensitivity is almost a constant. In other words, the zeolite-coated microsphere has a linear sensing characteristic in a much greater range of refractive index changes if the coating thickness is larger than the threshold value.

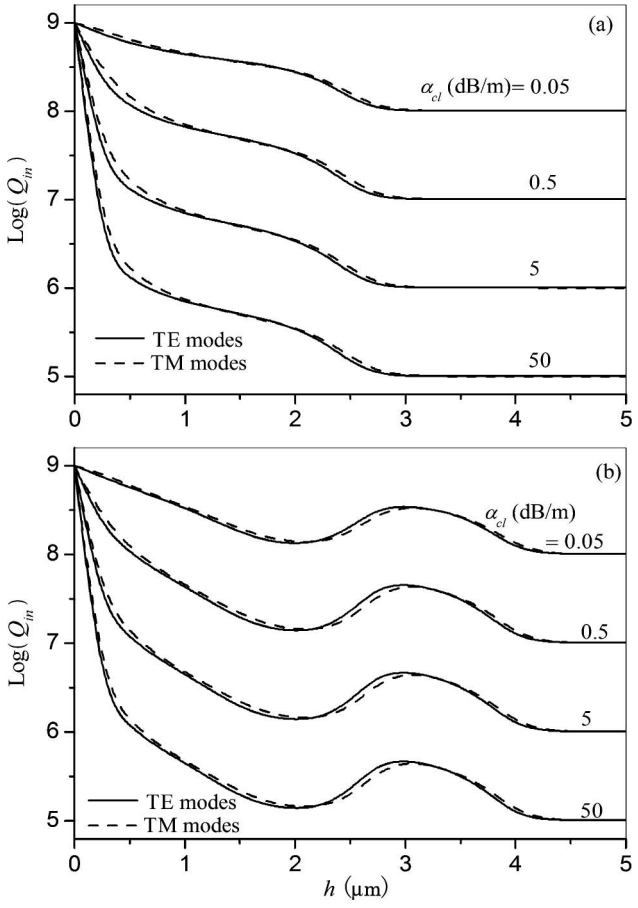

Fig. 7. Q_{in} for the WGMs of (a) $v = 1$ and (b) $v = 2$ as a function of h at $\lambda_R \approx 1550$ nm. The solid and dashed curves represent the quality factors for the TE and TM modes, respectively.

The aforementioned analysis demonstrates that the sensitivity of the proposed sensor increases with the electric field (thus the light energy) in the zeolite film. But, as the fraction of light energy in the film increases, the Q_{in} factor may be significantly decreased due to the possible significant light loss in the film, which eventually leads to the impairment of the detection limit. Especially when the light energy is mostly distributed in the film, the Q_{in} factor reaches the minimum value, which is almost completely determined by the film absorption loss (i.e., $Q_{\text{in}} \approx 2\pi n_{cl}/\alpha_{cl}\lambda_R$). Figure 7 shows Q_{in} as a function of h by calculating Eq. (12), for the WGMs of $v = 1$ and 2 in a zeolite-coated silica microsphere of $a_0 = 25$ μm, at $\lambda_R \approx 1550$ nm. The quality factor of the microsphere before zeolite coating is taken to be about 10^9 [25], and α_{cl} is assumed to be 0.05, 0.5, 5, and 50 dB/m, which corresponds to $(Q_{\text{in}})_{h \geq h_0} \approx 10^8$, 10^7, 10^6, and 10^5, respectively. From Fig. 7, the intrinsic quality factor decreases with the film thickness for the WGMs of $v = 1$, which is significant for a large optical absorption loss of the film. While for the WGMs of $v = 2$, there is an increase of the intrinsic quality factor when $h = 2 \sim 3$ μm. When the film thickness exceeds the threshold h_0, the light energy is almost completely confined in the film (thus $\eta_2 \approx 1$), and the Q_{in} factor reaches the minimum value, $(Q_{\text{in}})_{h \geq h_0}$. Considering the critical coupling (thus, $Q_{\text{ex}} = Q_{\text{in}}$) between the tapered fiber and the zeolite-coated microsphere, the total quality factor is $Q_{\text{tot}} = Q_{\text{in}}/2$. Figure 8 shows $S \times Q_{\text{tot}}$ as a function of h, which is inversely proportional to the detection limit. Figure 8 illustrates that a larger $S \times Q_{\text{tot}}$, i.e., the smaller detection limit, occurs at a smaller optical absorption loss of the film. For example, $S \times Q_{\text{tot}}$ decreases quickly to ~0.6 and ~0.06 m with the film thickness increasing, at $\alpha_{cl} = 5$ and 50 dB/m. While, $S \times Q_{\text{tot}}$ basically increases with h to a much larger value at $\alpha_{cl} = 0.05$ dB/m. So it is important to ensure a relatively small optical absorption loss of the film for a small detection limit.

The optical absorption loss of zeolite films is influenced by many factors, such as the zeolite structure type, coating uniformity, crystal sizes, and molecular species adsorbed in the zeolite pores. To date, a number of zeolites (e.g., LAU, FAU, and MFI) have been successfully grown into continuous films on substrates of different materials and various geometries. But, as a result of the polycrystalline nature of zeolite films and the current lack of suitable optical models, there have been no quantitative studies reported on the optical absorption loss of zeolite films in the

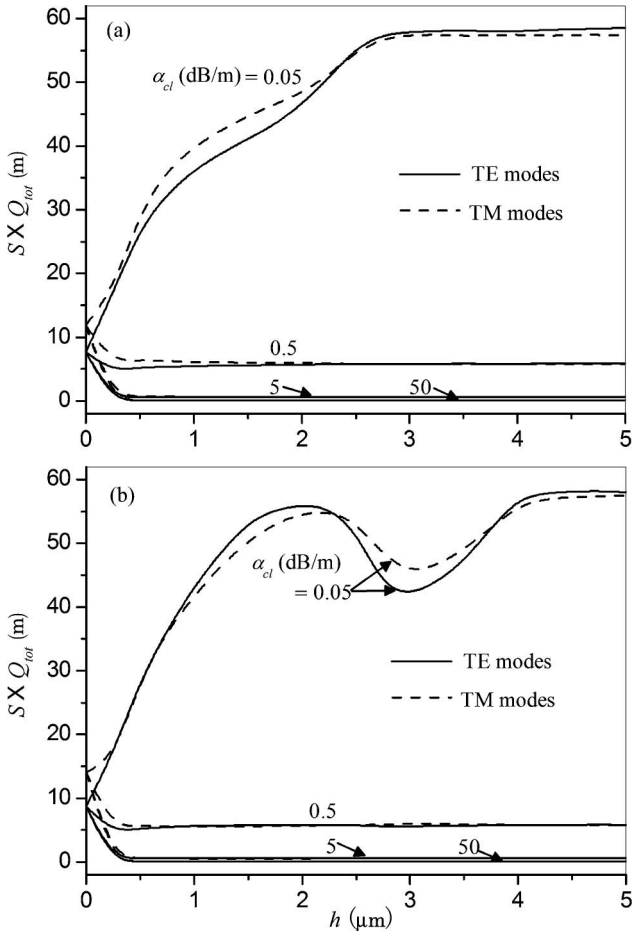

Fig. 8. $S \times Q_{\text{tot}}$ for the WGMs of (a) $v = 1$ and (b) $v = 2$ as a function of h at $\lambda_R \approx 1550$ nm. The solid and dashed curves represent the values for the TE and TM modes, respectively.

near-IR region (~1550 nm). Further experiments can be conducted to study the optical attenuation properties of zeolite films through the WGMs excited in zeolite-coated microspheres and the approximate model based on Eq. (12).

5. Conclusions

This study proposes a chemical sensor based on a zeolite-coated microsphere. A numerical model is derived to calculate the sensitivity. Based on the numerical model, the influence of the zeolite film is investigated, which shows that the sensitivity can be increased by nearly 2 orders of magnitudes if the microsphere is coated with a zeolite film. It is also demonstrated that the zeolite-coated microsphere has a linear sensing characteristic in a wide range of refractive index changes if the coating thickness is larger than a threshold value that increases with the sphere radius. The possible influences of a zeolite coating on the quality factor and detection limit are also discussed by an approximate model. The predictions by our models can effectively guide the selection of various parameters for the fabrication and application of the proposed sensor.

In our future work, the optical absorption loss of zeolite films will be experimentally investigated in detail for a number of zeolite types, based on the platform of the proposed device and models in this study.

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