Quantum dot-embedded microspheres for remote refractive index sensing

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We present a refractometric sensor based on quantum dot-embedded polystyrene microspheres. Optical resonances within a microsphere, known as whispering-gallery modes (WGMs), produce narrow spectral peaks. For sensing applications, spectral shifts of these peaks are sensitive to changes in the local refractive index. In this work, two-photon excited luminescence from the quantum dots couples into several WGMs within the microresonator. By optimizing the detection area, the spectral visibility of the WGMs is improved. The spectral shifts are measured as the surrounding index of the refraction changes. The experimental sensitivity is about five times greater than that predicted by the Mie theory. © 2008 American Institute of Physics.

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Optical microspherical cavity resonators have recently been applied in biosensing.^{1,2} The resonance modes, known as whispering-gallery modes (WGMs), arise from confinement of light within a resonant cavity through total internal reflection. The resonance shift due to local refraction index changes can detect near-surface molecules without labeling. In most WGM sensor systems, light is coupled by intimate contact between the microresonator and an evanescent wave source,^{1–3} which precludes remote sensing. Linewidth changes in WGM peaks in optically trapped, dye-doped microspheres have also been reported as refractometric sensors.⁴ However, high power optical tweezing accelerates photobleaching of the organic dye⁵ and is unstable during fluidic change.

Here, we demonstrate a refractometric sensor based on a quantum dot (QD)-embedded microresonator. The use of QDs as a local light source within the microresonator enables remote optical excitation and interrogation of the sensor element. As the local light source, QDs have unique advantages of high quantum yield and resistance to photobleaching.⁶ We applied two-photon excitation to locally excite a small volume of the QDs for enhanced WGM resonance contrast. The QD-embedded polystyrene microspheres are immobilized on a microscope cover slip and the spectral shifts of the WGM resonances are monitored as the bulk index around the sensor changes.

Linearly polarized 170 fs pulses with a central wavelength of 800 nm (Coherent Mira 900F) are incident upon a microscope objective (Nikon 50×0.8 numerical aperture) through a dichroic mirror and focused on an immobilized QD-embedded microsphere. Two linear polarizers are used to control the excitation power while maintaining constant polarization. Luminescent light is collected by the objective in reflection geometry. A spectrograph (PI-Acton SpectraPro 2300i) with thermoelectrically cooled charge coupled device (CCD) camera (PI-Acton PIXIS 100) operates in both imaging and spectroscopy modes. The equivalent wavelength pitch between two adjacent pixels of the CCD is 0.04 nm.

Microspheres (sulfate latex, diameter of 9.6 μm , and standard deviation of 0.71 μm , Molecular Probes, Inc.) are infused with CdSe/ZnS (core/shell) QDs with emission peak at 550 nm. The QDs are prepared colloiddally via organometallic synthesis, as reported in literature.⁷ The QDs are embedded in the microspheres following a reported procedure in which QDs passively diffuse into microspheres swollen by chloroform in butanol.⁸ The concentration of QDs is 2.5 mg/l in chloroform and the ratio of the chloroform to butanol with microspheres by volume is 1:4. After 48 h of infusion at room temperature, the particles were resuspended in butanol to lock the QDs in the polystyrene (PS) matrix.⁹ The QD penetration is less than the diffraction limit of our confocal microscope (~ 122 nm) and is likely a few QD diameters.

A thin film of polyethyleneimine (PEI) immobilizes the microspheres on the glass cover slip electrostatically, as shown in Fig. 1(a). The immobilized microspheres are stable during the experimental fluidic changes. A paraffin donut traps the immersion liquid on the cover slip. Figure 1(b) is a

(a)

FIG. 1. (a) Sample layout; (b) bright field image of QD-embedded microsphere; (c) dark field image of QD-embedded microsphere with excitation at the lower point on the equatorial plane, and an intensity maximum at the upper point on the equatorial plane.

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FIG. 2. WGM spectra of different detection areas in water immersion. (a) The WGM spectrum from the entire area over the slit of spectrograph. (b) The WGM spectrum from only the opposite position to the excitation of the microresonator.

bright field image of an immobilized microsphere.

In analogy to previous results on localized WGM excitation showing two maximum emission locations (at the excitation point and opposite to the excitation point),¹⁰ two-photon excitation allows a well-controlled, local coupling of QD luminescence to the microresonator. Figure 1(c) shows a dark field image of the locally excited microresonator, in which the lower excitation area and an upper emission maximum are easily distinguished. To quantify the contrast of the WGM peaks, the visibility is defined as $V = (I_{\text{peak}} - I_{\text{background}}) / (I_{\text{peak}} + I_{\text{background}})$.¹¹ Previous research indicates that the visibility of WGMs can be optimized by locating the excitation at the equator of the microresonator. Because only a portion of the luminescence from the QDs couples into the WGMs within the microresonator, the visibility of the WGMs from the emission area opposite to the excitation should be greater. The spectra are recorded from an area including both bright spots [Fig. 2(a)] and from only the area opposite to the excitation [Fig. 2(b)]. Both spectra clearly show WGM peaks with seven paired transverse magnetic (TM)/transverse electric (TE) modes across the QD luminescence. As expected, the spectrum including the excitation area includes a relatively large background signal from uncoupled luminescence and has a visibility of 0.24. The visibility from only the area opposite to the excitation is 0.76 and yields a visibility enhancement of over three times.

The refractive index of the immersion fluid is changed by adding ethanol into water. The refractive index of each mixture can be estimated by the weight fraction of ethanol in water.¹² The experiments use mixtures with refractive indices of 1.333, 1.343, 1.352, and 1.362. Following each addition of ethanol, the mixture is placed at room temperature for 3 min to reduce thermal effects and allow mixing. Figure 3 shows the WGM spectra for all of the mixtures. The WGMs of the same mode number redshifted and broadened with increasing liquid index of refraction.

According to the Mie theory, a resonance occurs when an eigenmode, either TE or TM, dominates the scattering

FIG. 3. WGM spectra from a microresonator for ethanol water mixtures of different ratios by weight: (a) 52.0% ethanol water mixture, $n_e = 1.3621$; (b) 27.9% ethanol water mixture, $n_e = 1.3522$; (c) 15.2% ethanol water mixture, $n_e = 1.3434$; and (d) pure water, $n_e = 1.3330$. The solid arrows represent TM modes and the dotted arrows represent TE modes.

field.¹³ The dimensionless size parameter describes the relative sphere size $x = 2\pi a / \lambda$, where a is the sphere radius and λ is the vacuum wavelength. For a WGM with angular mode number l and radial mode number i , the resonance size parameter is denoted as x_l^i . The size parameters in the experiments are around 100 and the size parameters of WGMs in bare microspheres can be asymptotically expressed as the power expansion of $\nu^{1/3}$ (Ref. 14)

$$n_s x_l^i = \nu + \frac{\alpha_i}{2^{1/3}} \nu^{1/3} - \frac{mp}{\sqrt{m^2 - 1}} + \frac{3\alpha_i}{10 \times 2^{2/3}} \nu^{-1/3} + \frac{m^3 p (2p^2/3 - 1) \alpha_i}{2^{1/3} (m^2 - 1)^{3/2}} \nu^{-2/3} + O(\nu^{-1}), \quad (1)$$

where $\nu = l + 1/2$, $m = n_s / n_e$ is the relative refractive index between the sphere and the immersion medium, $p = 1$ for TE mode, $p = 1/m^2$ for TM mode, and α_i is the i th zero of the Airy function. For the size parameter in the experiments, the linewidths of the second radial modes ($i = 2$) are about 5 nm, so only the first order radial modes are considered.

Theoretically, a given refractive index change of the immersion medium results in larger spectral shifts for a WGM of lower angular mode number. Conversely, a WGM of lower angular mode number has a broader linewidth. According to the theory, TM modes shift more than the corre-

FIG. 4. Comparison between experimental and theoretical sensitivities of the WGM sensor. The sensitivities of the shifts for the four WGMs in Fig. 3 marked as TM a, TE a, TM a-5, and TE a-5 modes are 165.6 nm/RIU, 155.2 nm/RIU, 177.7 nm/RIU, and 170.1 nm/RIU, respectively. The theoretical WGM sensitivities of a PS microresonator with a radius of 5 μm for TM 88, TE 88, TM 83, and TE 83 modes (at 523.3, 525.9, 553.2, and 556.1 nm in water) are 32.3 nm/RIU, 24.9 nm/RIU, 38.6 nm/RIU, and 28.1 nm/RIU, respectively.

spondent TE modes. So, the smaller peak in each TM/TE pair in Fig. 3 is the TM mode. This observation is also verified by calculation of the mode spacing.

We compare the experimental results with theoretical results from Eq. (1) by using a 5 μm radius microsphere, which provides a close match to the observed spectrum in water. Four calculated WGM peaks were chosen, as marked in Fig. 3. As shown in Fig. 4, the theoretical sensitivities of the modes are around 30 nm/RIU (refractive index unit) and the experimental sensitivities are around 160 nm/RIU. The sensitivity enhancement may result from the embedded CdSe ($n=2.45$) QD layer. As has been shown theoretically¹⁵ and experimentally,¹⁶ a high refractive index layer will move the confinement of the WGM energy closer to the surface and yield resonance modes more sensitive to refractive index changes. Here, the thin QD-embedded layer will not move the confinement out of the polystyrene core, and thus, will not significantly shift the modal position.¹⁵ However, due to modal location nearer the surface, the modes will be more sensitive to refractive index changes.¹⁷ The full effects of the QD layer are under continued investigation.

The characterization of multiple WGM shifts improves the estimation of the refractive index change compared to a single WGM shift. By linearly fitting the shift of each WGM independently, the fitted refractive indices of the immersion medium are calculated from each line function. The averages of the fitted refractive index changes from water to the water/ethanol mixtures for all of the 14 modes are 0.0102, 0.0190, and 0.0289 and the standard deviations are 2.2×10^{-4} , 1.9×10^{-4} , and 1.3×10^{-4} , respectively. With the equivalent wavelength pitch of 0.04 nm and the sensor element sensi-

tivity of about 160 nm/RIU, the minimum detectable refractive index change can be estimated as 2.5×10^{-4} RIU. The standard deviations of the fitted refractive indices are less than the minimum detectable refractive index change limited by the spectrometer. Thus, the pitch between two adjacent CCD pixels is the major limitation of the sensor system. If the detection limit of the resonance shifts can be improved to 0.1 pm, a detection limit on the order of 10^{-7} RIU can be achieved.

In summary, we demonstrate a remote refractometric sensor based on WGM shifts within a QD-embedded microsphere. The QDs serve as a local broadband light source to couple light into the microresonator. Due to their high quantum yield and resistance to photobleaching, QDs provide a strong and stable signal. By using localized two-photon excitation, the visibility of WGMs is improved by exclusion of the excitation volume. The measured shifts due to the refractive index change in the immersion fluid show more than a fivefold enhancement over the theoretical calculation for an uncoated microresonator. By averaging the relative shifts of all of the modes within the QD emission spectrum, the random error can be reduced. The improved sensitivity and accuracy of WGM based refractometric sensors offer a promising opportunity for the development of remote microscale elements for biomedical and environmental applications.

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