Nanolayer characterization through wavelength multiplexing of a microsphere resonator

Mayumi Noto, Frank Vollmer,* David Keng, Iwao Teraoka, and Stephen Arnold

Microparticle Photophysics Laboratory, Polytechnic University, 6 Metrotech Center, Brooklyn, New York 11201

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We optically characterize nanolayer (<150 nm) formation in situ on a silica microsphere in an aqueous environment by simultaneously following the shifts of whispering-gallery modes at two wavelengths. This approach was inspired by layer perturbation theory, which indicates that these two measurements can be used to determine independently both the thickness and the optical dielectric constant. The theory is verified for extreme cases and used to characterize a biophysically relevant hydrogel nanolayer with an extremely small excess refractive index of 0.0032.© 2005 Optical Society of America

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It is common in optics to create nanoscopic dielectric layers from inorganic insulators, semiconductors, and metals; however, as biophotonics1 looms more strongly, soft condensed biofunctional layers formed at an aqueous–solid interface and made of DNA, protein, lipids, and hydrogels are gaining strong appeal. This appeal is being driven by the need for biosensors and for investigation of biomolecular interactions as they relate to drug discovery. Although techniques outside of optics, such as neutron reflection, have been used to gauge the thickness of these layers, new methods to monitor the formation of such layers and to characterize them in a noninvasive manner are greatly needed. We show in what follows that wavelength-multiplexing experiments on microspherical optical cavities can reveal independently both the thickness and the optical dielectric constant for adsorbed layers.

Our experimental approach is driven by the predicted theoretical effect that a nanoscopic layer has on the shifts of whispering-gallery modes (WGMs) in a microsphere. In particular, the ratio of the shifts between resonances stimulated at separated wavelengths can be used to determine the thickness of a layer. In addition, the dielectric constant of the layer can be evaluated by use of this thickness and the shift at either wavelength. The theoretical approach we employ here is distinct from recent work2 on individual dipole perturbations, in which the sensitivity of such a system for the detection of single biomolecular adsorption events was estimated. Although the latter theory has been successfully applied to sensitivity issues associated with the identification of mismatches in DNA,3 for the current work our interest is in the perturbations by a dielectric layer.

In what follows we first outline our perturbation theory. Our approach will be to turn the microsphere perturbation problem into a quantum analog4 and perturb the analog potential by adding a layer. Then we present experiments that test this theory. Finally we attempt to determine the thickness and refractive-index perturbation for a thin hydrogel layer.

Although the full theory will appear elsewhere,5 here we outline its basic components. Our approach resembles first-order perturbation theory in quantum mechanics. We concentrate on TE modes. Representing the electric field in terms of a scalar function $E = L\Psi$, where $L$ is a dimensionless angular momentum operator, allows us to easily reduce the problem of solving the vector wave equation to the solution of a Schrödinger-like equation for the radial part of $\Psi$, $\Psi_r$.6 The effective energy $E_{\text{eff}}$ for this quantum analog is the square of the free-space wave vector $E_{\text{eff}} = k_0^2$, and the effective potential $V_{\text{eff}} = k_0^2(1 - n^2) + l(l + 1)/r^2$, where $n$ is the radial refractive-index profile and $l$ is the angular momentum quantum number of a particular mode. A layer perturbation corresponds to changing $n^2$ from the surface out to a thickness $t$ by $\delta(n^2)$. The first-order perturbation is

$$\delta E_{\text{eff}} = \langle \psi_r | \delta V_{\text{eff}} | \psi_r \rangle,$$

where $\psi_r$ is constructed from appropriate quasi-normalized functions.7 After substituting for the major components in expression (1) we find that the fractional perturbation in effective energy is

$$\frac{\delta(k_0^2)}{k_0^2} = -\frac{2t}{R} \left[ \frac{\delta(n^2)}{n_s^2 - n_m^2} \right] \left[ \frac{L}{t} \left[ 1 - \exp(-t/L) \right] \right].$$

where $n_s$ and $n_m$ are the refractive indices of the sphere (silica, 1.47) and its environment (water, 1.33), respectively; $R$ is the sphere radius; and $L$ is the evanescent field length, with $L = (\lambda/4\pi)(n_{\text{eff}} - n_m^2)^{-1/2}$. The fractional wavelength shift $\delta \lambda/\lambda$ is related to $\delta(k_0^2)/k_0^2$ through $\delta \lambda/\lambda = -\lambda/2[\delta(k_0^2)/k_0^2]$, where $n_{\text{eff}}$ is the effective index for propagation within the WGM. Since our sphere has an ~200-μm radius and is much larger than either of the laser wavelengths, $n_{\text{eff}}$ varies by only ~1% between radial modes and will be approximated by its grazing incidence value $n_s$. Equation (2) may seem awkward; however, it has a particularly simple structure when one considers that the principal wavelength dependence is contained within the evanescent field length in the rightmost factor on the right-hand side. By a judicious choice of the wavelength regions to be used, the leftmost factor on the right-hand side
can be considered relatively constant. Consequently, by taking a ratio of the fractional shift at one wavelength $\lambda_1$ to that at a longer wavelength $\lambda_2$, we arrive at a particularly simple expression that provides the design principle for our surface analysis approach. This ratio $S$ is

$$ S = \left( \frac{\delta \lambda}{\lambda_1} \right) \approx \frac{L_1[1 - \exp(-t/L_1)]}{L_2[1 - \exp(-t/L_2)]}. $$

(3)

For an ultrathin layer (i.e., $t/L_1, t/L_2$ << 1), $S$ approaches 1, whereas for a thick layer (i.e., $t/L_1, t/L_2$ >> 1), $S$ approaches $L_1/L_2$, which with $n_{\text{eff}}$ taken constant is just $\lambda_1/\lambda_2$. For our experiments this ratio is (760 nm/1310 nm) = 0.58. For our chosen wavelengths, $S$ falls off in an approximate exponential fashion in between the two extreme cases with a characteristic length of $t_c = 192 \mu m$ [i.e., $S \approx (L_1/L_2) + (1 - L_1/L_2)\exp(-t/t_c)$]. Measuring $S$ therefore allows us to estimate $t$. With $t$ in hand, Eq. (2) gives $\delta(n^2)$.

We performed wavelength-multiplexing experiments while forming nanolayers on a silica microsphere surface. Light from two current-tunable distributed-feedback lasers with nominal wavelengths of 760 and 1310 nm was coupled to a single-mode fiber (Nufern 780-HP) (Fig. 1). A portion of the fiber was acid eroded down to a 3-$\mu m$ diameter to facilitate coupling to the WGMs of a silica microsphere.\(^9\) The microsphere and fiber were contained within a temperature-controlled 1-ml cuvette containing buffer solution and a magnetic stirrer. Beyond this cuvette the fiber was led to an InGaAs detector. By scanning both lasers with a synchronous ramp, we observed that the light from each independently stimulates WGMs in the microsphere and yields a distinct transmission spectrum with a superposition of resonant dips from each. By observing which resonances disappear as either laser is shut off, the resonances are easily associated with the 760- and 1310-nm region. In this way, resonances can be identified and tracked.

As a test of our perturbation theory we constructed two experiments at the extreme limits. First we built a monolayer of bovine serum albumin (BSA) ~3 nm thick.\(^{10,11}\) The microsphere surface was treated with 3-aminopropyltrimethoxysilane, and BSA with a final concentration of $1 \mu M$ was injected into 10-mM phosphate-buffered saline (pH of 7.4). The shifts of resonances at two wavelengths, $\lambda_1 = 760$ nm and $\lambda_2 = 1310$ nm, are shown in Fig. 2(a). The BSA reached Langmuir-like saturation (i.e., monolayer formation\(^8\)) at $\delta \lambda/\lambda \sim 1 \times 10^{-5}$. The two resonances from each wavelength region shifted almost the same amount. As a second test case we injected NaCl into the water surrounding a sphere. We sequentially increased the salt concentration by 0.1-M increments starting with de-ionized water. Figure 2(b) shows the time trace of the resonance shifts in $\delta \lambda/\lambda$ from each wavelength region. In this case the fractional shift at 760 nm is considerably less than that at 1310 nm. Figure 3 summarizes the experimental results and the layer theory prediction. For a BSA monolayer, $t/L \ll 1$, and $S$ in Eq. (3) should approach 1. The experiment yields a slope of 1.04. For the NaCl experiment, $t/L \gg 1$, and $S$ should approach the ratio of the wavelengths, 0.58. The experimental result was 0.54. Our limiting tests are in reasonable agreement with theory. We are now in a position to demonstrate the usefulness of our approach by attempting to evaluate the optical properties of biophysically relevant hydrogel.

Poly-L-lysine (PLL) is a hydrogel that takes on extremely positive charge in water and is consequently favored as a means for adsorbing biomolecules with a negative charge. However, the physical properties

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**Fig. 1.** Experimental setup for wavelength multiplexing of a microcavity. LD, laser diode.

**Fig. 2.** (a) Resonance shifts at two wavelengths [$\lambda_1 = 760$ nm (thin curve) and $\lambda_2 = 1310$ nm (thick curve)] owing to BSA adsorption. (b) Resonance shifts at the same wavelengths owing to two sequential injections of NaCl by 0.1-M increments.
Wavelength-multiplexing experiments have created a new window of opportunity for the WGM resonator. For the first time to our knowledge, a WGM resonator was applied to study a commonly used biofunctional layer. It will be interesting to measure the change in $S$ as a self-assembled monolayer forms on a surface. As the layer density increases, the morphology of the molecules in the layer may change. This phase transition will lead to a change in the layer thickness, and a real-time measurement of $S$ should reveal this transition.

Our method can be extended to individual particles. However, the spherically symmetrical theory that generated Eq. (2) cannot be used. Instead a Green’s function approach must be applied. This alternate direction is in the works. The result shows promise for looking at heterogeneous structures such as adsorbed bacteria.

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*Present address, Rowland Institute, Harvard University, Cambridge, Massachusetts 02142.

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