Ocean Salinity Sensing Using Long-Period Fiber Gratings Functionalized with Layer-by-Layer Hydrogels

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ABSTRACT: Rapid, accurate, and real-time measurements of ocean salinity are of great importance for a host of scientific, commercial, and defense applications. We demonstrate a highly sensitive, fast-responding fiber-optic salinity sensor that integrates long-period fiber gratings (LPFGs) with ionically strength-responsive hydrogel. The submicron-thick hydrogel was synthesized via layer-by-layer electrostatic assembly of partially quaternized poly(4-vinylpyridine) (qP4VP) and poly(acrylic acid), followed by chemical cross-linking. Spectroscopic ellipsometry measurement of a hydrogel made of 37% quaternized qP4VP showed robust and reversible swelling/deswelling in solutions with salt concentrations ranging from 0.4 to 0.8 M (22.8–44.7 g/kg) around pH 8.1. The swelling/deswelling process induced large changes in the refractive index of the hydrogel, leading to resultant shift in the resonance wavelength (RW) of LPFGs. The salinity-dependent optical response of the hydrogel-coated LPFGs is in good agreement with ellipsometry measurement. LPFGs coated with the hydrogel exhibited a sensitivity of 7 nm RW shift/M (125.5 pm/%e) with a measurement time less than 5 s. The shift in the resonance wavelength correlated linearly with salt concentration, making quantification of measured salinity straightforward.

INTRODUCTION

Ocean salinity has gained heightened attention in the study of marine biology and global ocean currents. The long-term surface salinity of ocean is also one prime parameter in monitoring global climate change as well as fresh water circulation. The marine organisms and submarine activities are mainly affected by the salinity in the marine environment. The mass of marine salinity is around 35 g/kg, and the concentration of salinity is typically measured by the conductivity temperature depth system based on the relationship between the amount of chloride ions and the electrical conductivity in the ocean. One major drawback is that this method is vulnerable to electric interference. Even though the Global Remote Sensing System can obtain the large area, real-time, and surface salinity data of the global ocean, the capability of this system has disadvantages such as limited sensing depth, unacceptable, costs and the specific design of hardware/software. Recently, researchers have shed light on the optical fiber-based sensors for salinity owing to the desirable advantages such as low cost, compact size, pollution free, remote sensing, corrosion resistance, antielectromagnetic interference, and so on. Basically, the refractive index (RI) of seawater will vary in the marine salinity, which means that the accurate salinity can be measured indirectly by the refractive index. The various optical fiber sensors for salinity based on the refractive index have been proposed and demonstrated, including fiber gratings, fiber interferometers, fiber surface plasma resonance (SPR), optical refraction and photonic crystal fiber (PCF), etc. It should be noted that the salinity sensors based on interference are fabricated by fiber tapering and/or splicing procedures, which implies that the fiber structures are more fragile, easily damaged, and need armored in the harsh underwater environment. For the SPR-based sensors, a thin metallized film of nanometers in thickness is required to deposit on the surface of the optical fiber. The sensors for salinity are not allowed to work under seawater for long hours, due to strongly corrosion of the seawater. Optical refraction-based sensors possess a complex prism system and the overall size of the probe is relatively heavy and large, which is difficult to apply in the ships or laboratories. In addition, the refractometers integrated with PCF have the challenge in loading aqueous samples into the tiny air holes of the cross-sectional PCF, which leads to a longer response time.

Long-period fiber gratings (LPFGs)-based sensors have been in use for salinity based on surrounding medium refractive index for years. The long-period fiber gratings have a period of gratings typically in the range 100 μm to 1 mm that promotes coupling between the propagating core mode and
co-propagating cladding modes. The high attenuation of the cladding modes results in a series of attenuation bands centered at discrete wavelengths in the transmission spectrum, with each attenuation band corresponding to a specific cladding mode. The phase matching condition between the guided mode and the forward propagating cladding modes is given by \( \beta_{01} - \beta_{cl}^{(s)} = \frac{2\pi}{\Lambda} \), where \( \Lambda \) is the grating period, \( \beta_{01} \) and \( \beta_{cl}^{(s)} \) are the propagation constants for the fundamental core mode and the \( n \)th cladding mode, respectively. The effective refractive indexes of the core and cladding are obtained by \( n_{eff,co} = \frac{n_d}{\lambda_0} \) and \( n_{eff,clad} = \frac{n_d^{clad}}{\lambda_0} \), so the expression of the resonance wavelength (RW) is \( \lambda_{res} = \left( n_{eff,co} - n_{eff,clad}^{(s)} \right) \Lambda \). The dependence of \( \lambda_{res} \) on \( n_{eff,co} \) and \( n_{eff,clad}^{(s)} \) makes LPFGs a highly sensitive index transduction platform. The higher sensitivity of LPFGs is generally obtained by the special design in the fiber structures\(^{21-24} \) such as tapered, etched or D-shaped fibers, etc., that causes the fragile mechanical property and complicated fabrication for LPFGs. Scientific interest in LPFGs integrated with stimuli-responsive nanofilm have emerged in recent years for multifunctionality and enhanced sensitivity by surface refractive index increment.\(^{25-28} \) As a frontier in the functional nanofilm, layer-by-layer (LbL) technique provides a highly controllable means to build uniform thin films of unlimited functionalities with conformity to any shape of the substrate.\(^{29,30} \) Refractive indices of polyelectrolyte LbL coatings with tunable physicochemical properties have been reported to be strongly affected by concentration of ionic strength.\(^{31,32} \) For example, ionic strength-responsive chitosan (CHI)/poly(acrylic acid) (PAA) polyelectrolyte multilayers on LPFGs for salinity sensing were recently explored. Even though a dramatic improvement of sensitivity showed a great promise, two opposite relations with a turning around point between resonance wavelength shift and concentration of salinity were discovered, due to two-component polyelectrolytes in multilayers.\(^{33} \) Meanwhile, weakly charged groups of CHI and PAA led to pH cross-sensitivity in the salinity measurement. One of the most effective approaches to address the challenges associated with pH cross-sensitivity and nonlinear correlation between RWs and salinity is to develop single-component surface-bound hydrogels by postassembly chemical cross-linking and release one of the two types of polyelectrolytes based on LbL strategy.\(^{34,35} \) A novel ionic strength-responsive quaternary polymer with cross-linkable groups was first synthesized and then assembled at the surface of LPFGs within quaternized poly(4-vinylpyridine) (qP4VP)/PAA LbL films via LbL.

Quaternized poly(4-vinylpyridine) (qP4VP) is characterized by one of highly cationic polyelectrolytes with strong permanent charge of quaternary ammonium groups,\(^{36} \) and also it is not responsive to temperature.\(^{37} \) In the process of qP4VP synthesis, amino groups were introduced to the side chain that confers chemically cross-linking ability to qP4VP, to build up single-component hydrogel coatings. As a stimuli-responsive coating, the nanoscale thickness and single chemistry component of qP4VP hydrogel induce the significant and fast volume response to the ionic strength in the aqueous solution, and the cross-linking networks impart hydrogel stability and reversibility. Here, we show that quaternary ionic strength-responsive hydrogel can be integrated with LPFGs to improve the saline sensitivity by apparent swelling or shrinking volume response and measure the surface refractive index to detect salinity in the seawater. As we know, NaCl is the main component of inorganic salts (several orders of magnitude larger than other salts) in seawater.\(^{38} \) Thus, the cross-sensitivity of other salts to NaCl is only about 15%. Most importantly, such errors can always be compensated mathematically,\(^{39} \) so we use NaCl solution as the experimental sample instead of the real seawater.

In this paper, a novel salinity sensor employing long-period fiber gratings (LPFGs) coated with nanoscale overlays of partially quaternized poly(4-vinylpyridine) (qP4VP) hydrogel is proposed, to achieve high sensitivity, specificity, and fast responsiveness in salinity sensing. This was followed by chemical cross-linking of the coating to retain qP4VP. PAA was released from the film to yield a qP4VP hydrogel, eliminating pH cross-sensitivity. Furthermore, the swelling/deswelling mechanism of salinity response of \( [q_{37}P4VP]_n \) hydrogel on LPFGs is proposed to understand the salinity response based on the salt-induced changes in refractive index and thickness of hydrogel coating by spectroscopic ellipsometry. The paper provides significant insights into the mechanism of salinity response and the synergistic effect between a 150-layer qP4VP hydrogel coating and LPFGs, which endure our robust sensor with particular properties such as high-salinity sensitivity, linear response, reversibility, and repeatability.

## RESULTS AND DISCUSSION

Figure 1 illustrates the use of \(^1\)H NMR and Fourier transform infrared (FTIR) to determine the degree of quaternization of qP4VP. After 300 min of reaction (see Experimental Section), the overall quaternization degree of qP4VP of 37 ± 1% was calculated from the ratio of intensities of \( f \) and \( d \) protons in \( ^1\)H NMR spectrum of q37P4VP-p in D\(_2\)O; \( b \) FTIR spectrum of q37P4VP-p.
To enable a quantitative study of the film growth, the same deposition procedure was used to assemble LbL films at the surface of precleaned silicon wafer. An increase in dry thickness of $[q_{37}P4VP/PAA]_{10}$ film as a function of bilayer number measured via spectroscopic ellipsometry is shown in Figure 2a.

The thicknesses of polymer films were 72.2 and 46.2 nm for $[q_{37}P4VP/PAA]_{10}$ film and $[q_{37}P4VP]_{10}$ hydrogel, respectively. The FTIR spectra of a $[q_{37}P4VP/PAA]_{150}$ multilayers (top) and a $[q_{37}P4VP]_{150}$ hydrogel after releasing PAA (bottom) are shown in Figure 2b. The characteristic bands at 1642 and 1601 cm$^{-1}$ corresponding to pyridinium and pyridine functional groups are indicative of partial quaternization of the polycation. The spectrum of $[q_{37}P4VP/PAA]_{150}$ multilayers has two additional bands: one at 1715 cm$^{-1}$ associated with C=O stretching of protonated carboxylic groups and another at 1570 cm$^{-1}$ associated with antisymmetric vibrations of $-COO^-$ groups of PAA. These two bands completely disappeared in the spectra after the release of PAA, confirming successful synthesis of single-component $[q_{37}P4VP]_{150}$ hydrogel coating. The same procedure was employed to deposit $[q_{37}P4VP]_{150}$ on the surface of LPFGs. As shown in Figure 3, the resultant $[q_{37}P4VP]_{150}$ hydrogel had a uniform dry thickness of ~910 nm, as observed in the scanning electron microscopy (SEM) image of the cross-section of the coated fiber.

LPFGs integrated with $[q_{37}P4VP]_{150}$ were tested at room temperature of 25 °C by immersing it in sodium chloride aqueous solutions with the concentration from 0.4 to 0.8 M at an interval of 0.1 M and pH 8.1 that simulates the marine environment. Figure 4 shows the RW of LPFGs in response to different salinities. The salinity response of pristine LPFGs without coating was also performed to compare and contrast the sensitivity of the LPFGs with and without the hydrogel thin film. A linear fitting to the experimental data showed a high coefficient of correlation (0.99226 for $[q_{37}P4VP]_{150}$-coated LPFGs and 1 for pristine LPFGs, averaged for all five measured RWs). A sensitivity of 2 nm/M in RW shift for the pristine LPFGs (Figure 4, circles) was deduced from the slope of the linear fitting curve. This linear correlation is most likely due to the linear dependency of 0.0099 RIU/M for the RI of the sodium chloride solution on concentration at room temperature. On the other hand, the $[q_{37}P4VP]_{150}$-coated LPFGs (Figure 4, squares) showed a sensitivity of 7.08 nm shift/M, which is 3 times higher than that of the pristine LPFGs. The corresponding transmission spectra of the $[q_{37}P4VP]_{150}$-coated LPFGs for salinity response are shown in the inset of Figure 4.

Figure 5a shows the real-time RW shift of the coated LPFGs as a function of time upon immersion in sodium chloride solutions with concentrations from 0.8 to 0.4 M. A consistent and reproducible response for four cycles of alternate salinity

Figure 2. (a) Dry thickness as a function of bilayer number during deposition of a $[q_{37}P4VP/PAA]_{10}$ LbL film as well as $q_{37}P4VP$ hydrogel at a surface of silicon wafer as measured by spectroscopic ellipsometry; (b) FTIR spectra of as-deposited $[q_{37}P4VP/PAA]_{150}$ films (top) and $[q_{37}P4VP]_{150}$ hydrogels after cross-linking and removal of PAA (bottom).

Figure 3. Cross-sectional SEM image of a dry $[qP4VP]_{150}$ coating deposited on LPFGs.

Figure 4. RW shift of $[q_{37}P4VP]_{150}$-coated LPFGs (blue square) and pristine LPFGs (black circle) for salinity response in different concentrations. Solid lines stand for the linear fitting to the experiment data. The inset shows the corresponding transmission spectra of $[q_{37}P4VP]_{150}$-coated LPFGs in buffer solution (0.01 M) and varied sodium chloride solutions.
was achieved within a 0.01 nm variation at any given concentration. The ionic strength-responsive hydrogel combined with LPFGs showed good reproducibility and stability as a robust salinity sensor, where chemical cross-linkage in the hydrogel on LPFGs plays a paramount role. It is important to establish the quantitative correlation between the RWs and salt concentrations in Figure 4, where the real-time measurement of salinity in the seawater is desirable. Given the sweeping speed of the optical spectrum analyzer (OSA) was limited, it is worth to note that the measurement time of the [q37P4VP]150-coated LPFGs to salinity was less than 5 s, it is faster than those of the polyacrylamide and polyimide hydrogel on Bragg gratings designed salinity sensors, whose whole measurements need to wait 30 min. Over the past 250 years, there has been ongoing reduction in ocean pH, and pH value of ocean is not usually constant due to the rising atmospheric carbon dioxide and environmental pollution, etc. It is thus important to develop a pH-insensitive hydrogel to eliminate the pH cross-sensitivity for an ocean salinity sensor.

To understand the interaction between ionic strength and hydrogel, the refractive index and thickness of [q37P4VP]30 hydrogel deposited on silicon wafer were measured in sodium chloride solution with different concentrations from 0.4 to 0.8 M using spectroscopic ellipsometry. The [q37P4VP]30 coating has the refractive index increment \((dn/dc)\) up to 0.04 RIU/M in Figure 6a, which is more than 4 times higher than the 0.0099 RIU/M of the RI dependence on salt water concentration itself. An increase in ionic strength leads to increased water uptake and swelling in the hydrogel, thus its density and the refractive index correspondingly decrease as shown in Figure 6a. The mechanism of salinity responsiveness of [q37P4VP]150 hydrogel is proposed and shown in Figure 6b. The quaternary ammonium groups of the [q37P4VP]150 hydrogel carry permanent positive charge in aqueous solution. The corresponding electrostatic repulsion between charged groups and additional osmotic pressure arising from counterions within induce hydrogel swelling (i.e., a decrease in RI), resulting in a blue shift in RW of LPFGs. A common line of arguments to explain this type of dependences is that as concentration of salt increases, positively charged groups of [q37P4VP]150 hydrogel attract surrounding Cl\(^-\) ions, resulting in the decrease of electrostatic repulsion due the electrostatic screening effect of Cl\(^-\) ions. The subsequent volume shrinking of [q37P4VP]150 hydrogel takes place in the solutions with higher salinity, leading to an increase of effective RI and thus a red shift in RW of the LPFGs. This standard explanation might not be completely applicable in this case because of the very low values of the Debye screening length in high-salinity solutions studies in this work (≈5 and 3.5 Å for 0.4 and 0.8 M NaCl solutions, respectively). It is likely that another well-
known phenomenon, i.e., a decrease in solubility of polyelectrolyte chains in salt solution, known as a salting-out effect played a significant role in hydrogel shrinking in the high-salt solution.\textsuperscript{47,48} Importantly, variations in solution salinity caused almost linear changes in the RI of the coatings and therefore provided a broad dynamic range for RW-based salinity detection in the range of solution salinity similar to that in seawater. Moreover, the effect was robust, i.e., fully reversible and highly repeatable as demonstrated by the consistent salinity response in cyclic measurements using the \([\text{q37P4VP}]_{150}\)-coated LPFGs.

## CONCLUSIONS

In this work, we presented a sensitive and fast salinity sensor based on \([\text{qP4VP}]_{150}\) hydrogel-coated LPFGs. The response of the coated LPFGs in terms of RW shift shows a linear correlation \((R^2 = 0.999)\) with salt concentrations from 0.4 to 0.8 M \((22.8 - 44.7 \text{ g/kg})\), making quantification of measured salinity straightforward. Additionally, the hydrogel-coated LPFGs show good performance in reproducibility and stability in various salt solutions with a fast measurement time (less than 5 s) in cyclic tests, due to the open, chemically cross-linked molecular network and a relatively low, micron-scale thickness of the hydrogel coating. Specifically, it was found that the \([\text{q37P4VP}]_{150}\)-coated LPFGs have no response to varying pH around 8.1 typical of marine environment. The salinity sensitivity of the \([\text{q37P4VP}]_{150}\)-coated LPFGs was 7 nm/M \((125.5 \text{ pm/‰})\), 3 times higher than that of the pristine LPFGs. The robust ionic strength responsiveness of \([\text{q37P4VP}]_{150}\) hydrogel markedly amplified the refractive index increment from 0.0099 RIU/M to 0.04 RIU/M in the salt concentration from 0.4 to 0.8 M. Several features of this sensing scheme, including high sensitivity, reproducibility, stability, and fast response, have made stimuli-responsive hydrogel integrated with LPFGs a novel and robust platform for salinity detection in the range of solution salinity similar to that of seawater. Moreover, the effect was robust, i.e., fully reversible and highly repeatable as demonstrated by the consistent salinity response in cyclic measurements using the \([\text{q37P4VP}]_{150}\)-coated LPFGs.

## EXPERIMENTAL SECTION

**Materials.** Sodium chloride (NaCl), sodium hydroxide standard solution (0.1 M, NaOH), poly(acrylic acid) (PAA, \(M_w \sim 1.2 \text{ kDa}\)), branched polyethylenimine (BPEI, \(M_w = 750 \text{ kDa}, M_n = 60 \text{ kDa}\)), poly(methacrylic acid) (PMAA, \(M_w = 60 \text{ kDa}\)), poly(4-vinylpyridine) \((\text{P4VP}, M_w = 160 \text{ kDa})\), glutaraldehyde, sodium acetate buffer (NaOAc), sodium dihydrogen phosphate \((\text{NaH}_{2}\text{PO}_{4})\), and disodium phosphate \((\text{Na}_{2}\text{HPO}_{4})\) were obtained from Sigma-Aldrich. Hydrochloric acid \((1 \text{ N standard solution, HCl})\) was purchased from Acros Organics. Hydrogen peroxide (30% in water, \(\text{H}_2\text{O}_2\)) was obtained from Fisher Scientific Inc. Cross-linkable quaternized poly(4-vinylpyridine) \((\text{qP4VP}, 160 \text{ kDa})\) was synthesized, as described in section 2.3. All chemicals were used without further purification steps. All solutions were prepared using ultrapure water (Milli-Q, <18.2 M\(\Omega\) cm). For LbL deposition, qP4VP and PAA solutions were prepared at a concentration of 0.2 mg/mL in 10 mM sodium phosphate buffer and adjusted to pH 6.5. The salinity solutions were prepared by adding sodium chloride powder to the phosphate buffer solutions at pH 8.1.

**LPFGs Fabrication.** The LPFGs were fabricated using point-by-point irradiation of a focused CO\(_2\) laser beam. The CO\(_2\) laser with a closed loop kit has excellent power stability (<1%) to guarantee reproducible LPFGs structure. LPFGs were inscribed with the aid of 120° Au-coated Si reflection mirror pair via a motorized translation stage with 0.2 μm minimum incremental motion. The entire LPFGs fabrication was controlled by computer interface to ensure synchronized operations on laser irradiation and translation stage. The employed optical fiber was SMF-28 (from Corning Optical Communications Inc.). The LPFGs coupled with LP\(_{0\text{10}}\) cladding mode were fabricated with parameters of 247 μm in period and 5 cm in length. A broadband light source was connected to one end of the LPFGs and an optical spectrum analyzer (OSA) to the other for the measurement of the transmission spectra of the LPFGs in real time during the fabrication process.

**Synthesis of Cross-Linkable qP4VP.** The synthesis of cross-linkable quaternized qP4VP polymers, where \(i\) is the percentage of the quaternized groups, was performed in several steps, as illustrated in Scheme 1. At the first step, a small number (~5%) of Boc-protected cross-linkable groups were introduced in the polymer to yield P4VP-p. At the second step, the polymer was quaternized with ethyl bromide to a desired degree of quaternization \(i\) to obtain Boc-protected qP4VP-p. Finally, the protecting Boc groups were removed to yield qP4VP containing a fraction of amino groups, which could be used to chemically cross-link the polycation after its assembly within LbL films.

A Schlenk flask was sequentially filled with 1.50 g of poly(4-vinylpyridine), 0.107 g of 2-(Boc-amino) ethyl bromide, and 30.0 mL of anhydrous methanol. The solution was degassed by three freeze–thaw cycles, transferred into a round-bottom flask with a reflux condenser, and then refluxed on an oil bath overnight under argon atmosphere. The solution was cooled to ambient temperature, and 4.0 mL of ethyl bromide was added. The mixture was refluxed on an oil bath for 2–6 h. During that time, 5.0 mL aliquots were sampled at 120, 180, 190, 220, 240, 300, and 360 min of the reaction time. All of the samples were frozen in liquid nitrogen to stop the reaction and dried under...
vacuum. The resultant varying degrees of quaternization of the protected polymers were determined using 1H NMR.

The deprotection procedure was performed as follows. qP4VP-p (0.150 g) was dissolved in 5.0 mL of methanol in a Schlenk flask. The solution was degassed by three freeze–thaw cycles, and 1.0 mL of concentrated hydrochloric acid was added drop-by-drop using a syringe. The mixture was heated at 60 °C for 1 h under argon atmosphere, dried under vacuum, and kept in a vacuum desiccator filled with Drierite overnight.

The hydrogels with various quaternization degrees were deprotected and deposited onto silicon substrates, 37% quaternization of qP4VP hydrogel exhibited the highest sensitivity in the region of salt concentration from 0.4 to 0.8 M, and it was selected to construct the hydrogel via LbL on LPFGs.

**Hydrogel Deposition on LPFGs.** LPFGs were mounted and fastened between two holders on an optical stage. It was dipped into a container with a V-shaped groove holding the polyelectrolyte solutions during the LbL assembly. The LPFGs were cleaned with 7.5% H2O2 solution for 20 min, followed by thorough rinsing with deionized water, then were dipped to polyelectrolyte solutions with the application of three consecutive 1 min rinsing cycles in 10 mM sodium phosphate buffer after each polymer adsorption step.

The entire procedure of hydrogel preparation is shown in Scheme 2. Prior to q37P4VP/PAA film construction, a prime two-bilayer BPEI/PMAA film was deposited on the LPFGs and annealed at 140 °C for 30 min. The q37P4VP/PAA LbL film was then deposited on LPFGs by sequential dipping in 0.2 mg/mL of q37P4VP and PAA solutions for 5 min at pH 6.5. The deposition was repeated for 150 cycles, yielding a [BPEI/PMAA]1−[q37P4VP/PAA]150 multilayer. The multilayer was then cross-linked via a 30 min exposure to 0.1 mg/mL of glutaraldehyde buffered solution at pH 6.5. After cross-linking, the assembled PAA was selectively released from the film upon exposure to 2.0 M NaCl solution at pH 7.5 overnight.

**1H Nuclear Magnetic Resonance (1H NMR) Spectrometry.** The quaternization degree of qP4VP polymers was determined using a VARIAN Mercury 300 NMR spectrometer using D2O as a solvent. The data were processed with a VarianJ software.

**Fourier-Transform Infrared (FTIR) Spectroscopy.** The spectra were recorded using a Bruker Tensor II spectrometer equipped with an mercury cadmium telluride detector by accumulation of 96 scans within a spectral range of 1900–900 cm−1 at a resolution of 4 cm−1.

**Spectroscopic Ellipsometry.** Refractive indices and thicknesses of LbL films deposited on silicon wafer were determined using a variable angle spectroscopic ellipsometer (M-2000, J.A. Woollam Co., Inc.) equipped with a temperature-controlled liquid cell. Dry measurements were performed at four incidence angles: 45, 55, 65, and 75°. The measurements in the liquid cell required the angle of incidence of 70° because of specific cell geometry. Thickness of native oxide on silicon wafer was measured prior to depositing LbL films.

For fitting of ellipsometric data of dry films, a three-layer model was used where the first two layers are silicon substrate and oxide layer. Third layer was characterized as a Cauchy material with a thickness d. The dependence of refractive index was stated as \( n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \), where \( \lambda \) is wavelength; A, B, and C are coefficients. For the fitting of swollen film data, a four-layer model was used where three layers are considered as dry films, and solution environment was considered as the fourth layer. It was characterized as a semi-infinite transparent Cauchy medium with fixed refractive index value. The refractive index of each solution was determined prior to each measurement for a bare silicon wafer installed to liquid cell. All four variables A, B, C, and thickness d were fitted simultaneously to get the closest theoretical description of the experimental data.

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**Notes**
The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation under grant number ECCS-1611155 and DMR-1610725.

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