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Humidity Responsive Photonic Sensor based on a Carboxymethyl Cellulose Mechanical Actuator

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Abstract

We describe an intuitive and simple method for exploiting humidity-driven volume changes in carboxymethyl cellulose (CMC) to fabricate a humidity responsive actuator on a glass fiber substrate. We optimize this platform to generate a photonic-based humidity sensor where CMC coated on a fiber optic containing a fiber Bragg grating (FBG) actuates a mechanical strain in response to humidity changes. The humidity-driven mechanical deformation of the FBG results in a large linear change in Bragg resonance wavelength over the relative humidity range of 5 % to 40 %. The measurement uncertainty over this relative humidity range is ± 2 % ($k = 1$).

Introduction

Measurement of humidity refers to a determination of the amount of gaseous water within a local environment.¹⁻⁴ Often the water-vapor content is expressed in units of relative humidity (RH) which is simply the ratio of water vapor partial pressure to the saturation water vapor partial pressure at a specific temperature.¹ Like temperature, humidity is an important parameter for controlling the quality of manufactured goods from starting materials to usage across a diverse array of industries including semiconductor and pharmaceutical manufacturing. In pharmaceutical production and storage, uncontrolled changes in humidity can lead to pseudo-polymorphic transitions⁵ of the drug substance resulting in a form of the active ingredient that could have widely different and inappropriate pharmacokinetics.⁶ On a more prosaic level, good humidity control in building environmental conditions is important for the comfort and well-being of the occupants and in the detection of possible mold-growth conditions. Consequently, the development of novel humidity sensors, whether based on electrical or optical devices, is necessary to facilitate the desired environmental controls for industrial and residential settings. Optical sensing methods encompass direct absorption spectroscopy, cavity ring down spectroscopy, fluorescence spectroscopy, light attenuation measurements, interferometric interrogation of Fabry-Perot cavities, strain induced shift in Bragg resonances, and refractive index sensing using evanescent coupling of waveguide field.^{1, 7} Molecular spectroscopic measurements provide the most definitive measurements,⁸ but the instrumentation cost, size and complexity can be a hindrance for routine application. Simple fiber-based humidity sensors

such as those relying on polyimide-mediated strain transduction in fiber Bragg grating (FBG) sensors provide a cost-effective means for optical measurement of relative humidity over a wide humidity and temperature range.^{9–10}

Tight control of low humidity levels (below 10 % RH) is necessary in many industrial and technical applications (including industrial processes such as Li-ion battery production, the operation of environmental test chambers, and control of airline cabin environments). However, low humidity environments have been specifically challenging for many measurement systems.^{1, 3, 7} Optical humidity sensors have the potential to address these shortcomings as well as allowing RH measurements in other challenging environments including those with electromagnetic interference and where remote detection is required. As the commercially available polyimide FBG sensors do not permit measurement in this low humidity range, it is necessary to develop new transduction layers to incorporate onto these sensors.

We discuss our efforts to develop a fiber-optic sensor for low humidity environments. In this work, we detail the modification of an untreated FBG sensor with a carboxymethyl cellulose (CMC) transduction layer. We observed humidity-based mechanical actuation of our test fibers. Finally, we measured the optical response, over a range of RH values, of a fiber with an optimized coating thickness of carboxymethyl cellulose.

Materials and Methods*

Carboxymethyl cellulose (molecular weight = 2.5×10^5 g/mol) was purchased from Sigma Aldrich (Lot: A0328062). FBG sensors with acrylic coating were purchased from Advanced Optics Solutions. The coating surrounding the FBG sensors was mechanically stripped. The fiber was dip-coated into an aqueous solution (5 % by mass) of CMC and allowed to dry. Different coating thicknesses were achieved by changing the number of times the fiber was immersed into the solution. The thinnest coating was produced from a single immersion of the fiber.

The prepared sensors were interrogated inside an environmental chamber where temperature and humidity were independently monitored using a calibrated Vaisala humidity probe (model HMP40S). The relative humidity in the measurement chamber (Figure S1, Supporting Information) was varied by changing the mixing ratio of dry (RH = 5 %) air with water saturated (RH = 85 %) air. As FBG sensors are also sensitive to temperature, the temperature within the chamber was maintained at 23.5 °C. A CMC-FBG sensor was probed using a custom-built interrogator that has been described in detail elsewhere.¹¹ Briefly a small amount of laser light (New Focus, 1550 nm) was immediately picked up from the laser output for wavelength monitoring (HighFinesse WS/7) while the rest, after passing through the photonic device via an optical circulator (ThorLabs), was detected by a large sensing-area power meter (Newport). Five consecutive scans were recorded at each humidity level.

*Disclaimer: Certain commercial fabrication facility, equipment, materials or computational software are identified in this paper in order to specify device fabrication, the experimental procedure and data analysis adequately. Such identification is not intended to imply endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the facility, equipment, material or software identified are necessarily the best available

Example data are shown in Figure S2 (Supporting Information). Data were analyzed to extract the mid-point of the full width at half maximum of the FBG response curve.

Results and Discussion

We have prepared a humidity-responsive actuator based on the water adsorption-desorption properties of carboxymethyl cellulose (CMC) (Figure 1). CMC was chosen as it is an abundant, naturally sourced material that displays stronger water adsorption properties than other cellulosic polymers.¹² This actuator is constructed when a glass fiber (120 μm in diameter) is dip coated in CMC and allowed to dry. The thickness of the CMC on the fiber is determined by the concentration of the CMC solution and the number of dip-coat cycles (Figures S3, S4, and S5 in the Supporting Information). As the CMC-fiber is exposed to dry environments, water desorbs from the CMC, which subsequently contracts. The glass fiber bends to relieve the strain brought on by the CMC contraction (Figure 1). As its environment becomes less humid, the curvature of the CMC-fiber increases. We observe more pronounced curvatures for fibers with thicker coating. Our design is one of many in which variants of cellulose are being exploited in the production of smart materials.^{13–15}

We have optimized the CMC-fiber platform for use as a photonic humidity sensor by coating a fiber optic, featuring a Fiber Bragg Grating (FBG), with CMC. We expected that the strain induced by the mechanical actuation affected by CMC would result in a significant change in the reflected Bragg wavelength. We tested the effect of CMC thickness on the FBG fiber response to humidity.

Figure 2 shows the wavelength response of CMC-FBGs with the thinnest CMC layer over a relative humidity range of 5 % to 85 %. The humidity response of the other fibers is shown in the Supporting Information. In the data shown, featuring the response of our narrowest CMC coating (4 μm), we observe a redshift of 221 pm over a relative humidity range of 5 % to 85 %. Data taken for a CMC coating of 30 μm (Figure S4, Supporting Information) show a change of 520 pm over the full 80 % range of relative humidity studied. The fiber with the thickest coating (70 μm) shows the largest observed curvature at low RH values. However, the FBG response of this sensor is only 100 pm over the full range of relative humidity values measured. The two thicker coatings (30 and 70 μm) also displayed hysteresis over the course of the experiments with different signal changes that were dependent upon whether the relative humidity was being increased or decreased (Figures S4 and S5, Supporting Information). We found that a CMC coating of 4 μm was able to produce a maximum response to changes in RH with no observable signal hysteresis (Figure 2 top panel).

For the 4 μm CMC-FBG we observe a redshift of 146 pm over the linear response range of RH = 5 % to 40 % (Fig 2 top panel). At relative humidity values above 40%, the response to changes in RH decreases. Similar observations were made for the CMC-FBG fibers with thicker coatings as well and is likely an intrinsic property of CMC. We expect that different cellulose variants will have different humidity response curves and that these could be exploited to cover the full range of RH. For the linear range of the 4 μm CMC coated fiber, we observe a relative humidity sensitivity of 4.6 pm/%, which is comparable to commercially-available polyimide coated fiber sensors.^{9–10} We calculated the uncertainty of

our device response by comparing the fit residual to the data with the Vaisala-measured relative humidity. The impact of hysteresis is folded into this analysis by including the up and down cycles in the fit analysis. The standard deviation in the relative humidity response was found to be $\pm 2\%$ ($\sigma = 1$). We expect that the calibration uncertainty in measured RH could be further improved by limiting the impact of strain and vibrations caused by air currents within the measurement chamber.

Kronenberg and coworkers have evaluated the strain relationship for polyimide coated FBG fibers.¹⁰ Using Young's modulus for the fiber and the polymer, they were able to mathematically relate the response of the coated fiber to the hygroscopic expansion coefficient (β_{coating}) of the polymer. They found β_{coating} of polyimide to be around $8 \times 10^{-5} \text{ \%}^{-1}$. Performing a similar analysis and using values of Young's modulus for CMC films from the literature,^{16–17} we find β_{coating} of CMC to be roughly $9 \times 10^{-3} \text{ \%}^{-1}$. One of the reasons why CMC gives a lower response to humidity than polyimide is that the Young's modulus for polyimide is an order of magnitude larger than that of CMC. CMC may show a stronger response by crosslinking the polymers (using citric acid or some other suitable reagent) or by using another additive to increase the CMC's elastic modulus. As the CMC molecules are held together non-covalently, crosslinking will have the added benefit of increasing the long-term reusability of the sensor. One benefit to using CMC instead of polyimide is that CMC-coated fibers show a linear response region below RH = 10 %. Achieving, maintaining, and monitoring this low humidity range is critical for a number of industrial processes.³

We measured the sensor response time by monitoring the frequency of the probe laser locked to the FBG sensors as it was cycled in and out of the environmental chamber (Figure 2 bottom right panel). For this measurement, a dither locking scheme was implemented. As shown in Fig 2 (bottom right panel), instantaneous change in relative humidity from 27 % to 45 % results in a fast rehydration of the sensor leading to 56 pm redshift in ≈ 10 s. Upon reinsertion in the environmental chamber, the dehydration process is considerably slower taking a full minute to return to baseline. The sensor response time is likely limited by diffusion rate of water in cellulose and could be significantly improved by reducing the coating thickness. However, reduced thickness will likely result in reduced actuation limiting the range and sensitivity of the fiber sensors. Use of cellulosic coatings in on-chip photonic sensors such as a photonic crystal cavity where the evanescent field of the cavity is used to probe slight changes in the refractive index of the coating and strain changes in the silicon may help in lowering the detection limit while reducing the coating thickness.

Summary

We demonstrated that carboxymethyl cellulose's humidity driven volume changes can be used to actuate a mechanical strain in an optical fiber, which can be read out as a frequency change in the photonic device's resonance. Our results indicate that CMC coated fibers show a linear dependence on humidity over the relative humidity range of 5 % to 40 % that has a response time of a minute. Our results suggest the sensor performance at low RH can be improved by reducing the cellulose coat thickness while higher RH ranges may be better detected by coatings of other cellulose-based polymers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
(upper panel) Response of the CMC-fiber to humid and dry environments. (lower panel)
Light microscope image of a CMC-fiber.

Figure 2.

(left panel) Response curve of the 4 μ m CMC-fiber to changes in relative humidity (filled circles: fit data in linear range; open circles: unfit data outside of the linear range). (left panel inset) The linear fit to the data is compared to the measured humidity. (right panel) Response time of the CMC-FBG fiber instantaneously moving from an environment at an RH of 27 % to an environment at RH = 45 % (at 20 seconds) and then returning to the RH = 27 % environment (at 40 seconds).