Title: Self-powered humidity sensor using chitosan-based plasmonic metal-hydrogel-metal filters

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Abstract

We introduce a tunable Fabry-Perot resonator that has Metal-Insulator-Metal structure, in which the insulator is chitosan hydrogel. The chitosan swells in response to changes in relative humidity; this change affects transmissive structural color of the multilayer structure. We utilize this tunable resonator for a humidity sensor combined with a photovoltaic cell. The change in current through the photovoltaic cell provides rapid precise measurement of RH, and the change in color of the multilayer provides an approximate, remotely-readable estimate. The response requires no power, so the device has numerous sensing applications.

1. Introduction

Chitosan is a semicrystalline biopolymer derived from chitin\cite{1}, and is biodegradable, biocompatible, and non-toxic\cite{2}. Chitosan-based devices have been evaluated in optics and nanoelectronics\cite{3,4}, particularly as planar optical waveguides for humidity sensors\cite{5} and gas sensors\cite{6}. Chitosan has remarkable film-forming properties\cite{7}, porous structure, and an ability to swell by absorbing water molecules from the air\cite{8}; this change affects both its electrical conductivity and its absorption spectrum. These changes have obvious application as a sensor of relative humidity (RH).

Structural colors found in nature\cite{9} have received great scientific interest and been reproduced by diverse structural colors\cite{10,11,12}. The simplest structural coloration mechanism consists of planar multilayered arrangements\cite{13-17}. In particular, the metal-insulator-metal (MIM) configuration based on a Fabry-Perot resonator has a high quality factor efficient band-pass filtering with scalability and cost-effective fabrication\cite{18-20}. However, conventional planar MIM resonators lack tunable function, because the resonance depends only on the geometry and optical parameters of the insulating layer.
Structural colors have been tuned using chemical\cite{21-26}, mechanical\cite{27,28} or electrical stimuli\cite{29,30}, polarization\cite{31,32}, and phase-change materials\cite{33}. However, tunable structural colors have a slow response\cite{21}, complicated mechanism\cite{27,28,33} and insufficient dynamic change. For those reasons, practical application of structural colors has been limited.

In this work, we propose tunable color filter composed of MIM multilayer, in which the insulator is chitosan hydrogel. This color filter can serve as a humidity sensors when combined with a photovoltaic (PV) cell. The structure uses chitosan film sandwiched between two ultrathin silver (Ag) layers deposited on a glass substrate. The key element is the chitosan insulating layer, in which the effective optical thickness $t_{\text{eff}}$ and refractive index $n_c$ change in response to RH; this trait can be exploited to obtain optical tunability of the resonance wavelengths. The corresponding resonance peak shift induces output current change of a PV cell, which is proportional to a change in the RH value of the environment. The special features of the proposed sensor are simple development, incorporation into PV cell, and potentially zero power usage, that make it a promising material for devices that monitor RH in enclosed spaces, workplaces and storage areas.

2. Results and Discussion

2.1 TMM Simulation of Ag-chitosan-Ag multilayer structures

We present a tunable MIM bandpass filter in which the sensitive insulating layer is composed of chitosan, which can adsorb water molecules from the air. The MIM structure mimics a Fabry-Perot resonator, which has a transparent layer between two reflecting surfaces. In this system, top and bottom 25 nm Ag layers serve as highly reflecting surfaces and chitosan serves as the cavity. Ag is chosen as the material of top and bottom layers because of its low material absorption in the visible regime and potential to excite surface plasmon resonance, and thereby enable high-quality band-pass filtering. The optical response of the resonator, defined as change of the resonant wavelength, is the result of variation of the physical parameters of the cavity,
i.e., $t_{\text{eff}}$ [nm] and refractive index $n_c$, in response to change in RH of the local atmosphere (Figure 1a). The measured and modeled $n_c$ of chitosan agree well (Figure S1).

To illustrate the spectra and colors of the filters, we used the Transfer-matrix method (TMM) to calculate the color gamut and transmission spectra of the samples that had a chitosan layer between Ag layers of 25-nm thickness on a silica substrate. $t$ was varied from 80 nm to 350 nm in increments of 30 nm. The color gamut of the samples on CIE 1931 Chromaticity Diagram (Figure 1b) showed a broad color spectrum, which can be expected from the high-Q features of a Fabry-Perot resonator[17]. Calculated transmission spectra were converted to visual representation (Figure 1c, insets at right) by applying a color weighting function (Figure S2).

The transmission peaks red-shifted as the thickness of the chitosan layer increased (Figure 1c, Figure S3). To aid in understanding, the electric field distributions (Figure 1d) were obtained for the chitosan layer at the 1st mode of the first sample, the 2nd mode of the seventh sample, and the 3rd mode of the tenth sample.

2.2 Comparison between calculated and measured colors

We performed thickness optimization of chitosan layer to achieve desired range of $t$ (i.e., 80 nm to 210 nm) in the MIM structure (Figure S3). $t$ was controlled by adjusting the concentration of the chitosan solution and the spin-coating speed. The chitosan solution was spin-coated on the glass substrate with the desired speed, then its thickness was measured using atomic force microscopy (AFM) in contact mode (Figure 2a).

We fabricated six MIM filters that used a chitosan layer prepared at spin-coating speeds of 1500 to 4000 rpm in increments of 500 rpm. Then the thickness of chitosan in each MIM sample was estimated by matching the transmission spectra from UV-Vis/IR spectroscopy with those of the simulation (Figure 2b). Overall, the estimated thickness tend to be thicker than that of the chitosan film on the glass substrate (Figure 2a). This discrepancy occurs because the chitosan layer in the sample is thicker in the central part in which the spectra were measured,
than in the off-center parts, so the spectra were red-shifted. This argument is supported by the match between the colors extracted from experiments (dashed line) match and the colors in center of optical microscopy images (Figure 2b, insets). Lastly, the experimental values of transmission may be lower than the simulated values because our measurement setup lacked an integrating sphere.

In colorimetric humidity sensor design, the sensing mechanism exploits the swelling/contraction of the polymer, because this response leads to changes of transmission spectra and colors of the multilayer film. In this work, we mainly focus on proof-of-concept of the proposed metal-hydrogel-metal structure as a colorimetric humidity sensor.

2.3 Self-powered humidity sensing with a PV cell

The changes in $t$ and $n_c$ of the swollen polymer in response to change of the physical parameters of the ambient medium provide a mechanism for sensing applications [33-35]. Here, we combined the MIM filters with a PV cell (Figure 3a-b) to achieve scalable RH sensing. The PV cell converts optical response of the filters to an electrical signal. The absorption spectrum of P3HT PV cell has a drastic decrease at wavelengths $600 \leq \lambda \leq 700$ nm (Figure 3c). This decrease enables manipulation of the absorption in the sensing system under varied RH by incorporating an MIM film that has resonance wavelength $\lambda_{res} = 600$ nm. As RH increases, the chitosan layer of sensing film starts to swell, so $\lambda_{res}$ red-shifts (Figure 3d).

The sensing film used is the 1st sample in Figure 2b. To compensate for the fabrication uncertainties and to take into account decrease in thickness with distance from the center, the initial thickness under ambient condition (RH $\sim$ 20%) for simulation was set to 155 nm, which is close to the average thickness of the film including the center and off-center parts (Figure 3d). The calculated transmission peaks red-shifted as RH increased, because the chitosan layer swelled. The sensing film affected its absorption of the PV cell, so its output current changed
Calculations suggest that a change in RH from 7.5 to 83.7% can reduce the light absorption of the PV cell to almost zero. The varied absorption of the PV cells directly affects its output current, and this change can be calibrated to allow estimation of the RH in the immediate environment.

$n_c$ of chitosan also varied with RH (Figure S1); this change affected both the transmission of the sensing film and the absorption of the PV cell. An increase in RH drove a decrease in $n_c$, and this change causes a blue-shift of the resonance wavelength, in opposition to the red-shift caused by swelling. This trade-off relation between $\text{eff}$ and $n_c$ affects our device by slowing the shift of $\lambda_{\text{res}}$ as RH increases. However, the blue-shift that is caused by the decrease of $n_c$ is effectively dominated by the red-shift that is caused by swelling of the chitosan, so this trade-off does have a weak influence on the design of the device (Figure S4).

For a test of the integrated device, we first measured the colors of the sensing film under a range of RH (Figure 4a). The color darkened as RH was increased from 7.5% to ~ 83.7%; this result is in good agreement with Figure 3d. Next, we estimated the output current of the integrated device with a change of RH from 5% (Dry condition) to 85% with a step of ~ 15%. Tests involved a sensing period of 1500 s and a recovery period of 3000 s. As a result of swelling of the chitosan layer, the output current changed under varied humidity conditions (Figure 4b). By the end of each recovery period, the sensing film had contracted back to its initial thickness, as confirmed by return of the output current to the initial level.

To quantify RH, we define the response $\Delta I/I_0$ where $\Delta I$ represents the change in electric current from the PV before and after humidity injection, and $I_0$ is the initial electric current in dry (5% RH) N₂ (Figure 4c). The transmission spectra of the sample were recorded before and after the tests (Figure S5). The first and second tests yielded slightly different absolute current measurements, possibly due to differences in initial input or environmental condition, but the responses matched well (Figure 4c). Therefore, these responses may correctly indicate
the RH in the environment. The trend line can be used to determine the relationship between $S$ and RH $h$ [%] as

$$S = -0.00002h^2 + 0.0046h - 0.0238,$$

with $r^2 = 0.9993$.

To further characterize our sensor, we compared its resolution with those of various types of RH sensors that use chitosan (Table S1). Our sensor can distinguish a change of 5% RH (Figure S6). Furthermore, its instant color changes in response to humidity changes enables rough estimation of RH (Figure 4a), so this change in color gives it utility as an instant RH indicator, to complement its accurate RH measurement that can be obtained from the change in output current. Moreover, the sensor does not require a specific light source, and can therefore may be used under arbitrary sources such as sunlight, office fluorescent lamps, and LEDs. The sensor’s independence of light source also gives the ability to operate in arbitrary surroundings without any electrical input.

However, our device suffers from a slow response time due to the sandwiched geometry of the chitosan layer. Future work could be aimed to reduce the response and recovery times. One possible design modifications is to change the existing MIM structure to a (metal-nanoparticle)-insulator-metal configuration to facilitate penetration of water vapor through the top layer. This chitosan-integrated device may have optical applications such as a phase modulator tuned by RH (Figure S7).

3. Conclusion

We proposed a modified tunable Fabry-Perot system and demonstrated its application in real-time colorimetric humidity sensors. The response of chitosan to the relative humidity of the ambient medium induces dynamic peak shift of the multiple-order resonances in the MIM structures. We calculated transmission spectra of the MIM structure and verified the simulation results by fabricating the device and characterizing it using AFM and UV-Vis/IR spectroscopy.
Finally, we applied the MIM structure to humidity sensors combined with a PV cell. Output current decreases as RH increases; the response can be described using an equation that can be used to estimate RH. We demonstrate a possible application of the system as a dynamic and real-time colorimetric humidity sensor and expect that the proposed MIM resonator can lead to development of a self-powered sensor.
4. Experimental Section

Materials: Medium-molecular-weight chitosan with a deacetylation degree of 75–85% and molecular weight of 190,000–310,000 Da, acetic acid (AA) (ACS reagent, ≥99.7%) and ammonium hydroxide (NH\textsubscript{4}OH) solution (puriss, 30–33% NH\textsubscript{3} in H\textsubscript{2}O) were purchased from Sigma-Aldrich and used without further purification. Isopropanol and acetone were purchased from J. T. Baker and used without further purification. A high purity (99.9%) Ag was obtained from E-tek. Glass was diced to a size of 2 cm by 2 cm, and used as substrate for preparing chitosan coatings.

Preparation of metal layer: Substrates were cleaned with deionized (DI) water, acetone and isopropanol, dried using an N\textsubscript{2} gun, then immediately loaded into a plasma cleaner (Cute-b, Femto Science) and placed under vacuum. Ultrathin bottom and top Ag layers were deposited using an E-beam Evaporator System (model KVE-C300160, Korea Vacuum Tech) using a high-purity Ag target under a base pressure of 5×10\textsuperscript{-6} Torr.

Chitosan films fabrication: Chitosan solution with concentration 1.5 wt% was prepared by dissolving the required amount of chitosan powder in 40 ml DI water that contained 1.5 wt% acetic acid. The solution was stirred under heating overnight with 2000 rpm at 65 °C, then centrifuged at 4000 rpm and 25 °C for 3 h. After centrifugation, the solution was pre-heated at 65 °C for 30 min then filtered through 1.2-μm (25 mm, Sterlitech) and 0.45-μm (13 mm, Whatman) Nylon membrane filters sequentially. To obtain thin polymer films, chitosan solution was spun using a spin-coater onto glass slides (square 20 mm × 20 mm) for 5 at in 1000 rpm, and then for 2 min at a specified speed. The polymer films were dried at ambient atmosphere for 2 h, then deprotonated by immersion in 3% ammonia solution for 10 min followed by thorough rinsing with distilled water.

Sample characterizations: Thickness of spin-coated chitosan films on glass wafers was measured in dry state by AFM (Park Systems, XE7). The measurements were performed at
ambient humidity (20 ± 5 RH%) and room temperature (20 ± 2°C).

**Simulation**: Transmission spectra were generated using TMM code developed by the authors. The refractive index of the SiO₂ substrate was set to 1.430. The refractive index of Ag for the simulation was obtained from measured data by P. B. Johnson[34]. Chromaticity simulations were executed using the color-related MATLAB toolbox named OptProp[35]. For color conversions, the CIE 1931 2° observer function with D50 was selected.

**Optical response measurements**: A UV-VIS Spectrophotometer (UV-2600Plus, Shimadzu, Japan) was used to measure the transmittance of the chitosan-based MIM filters. The transmittance of samples of various thicknesses (150, 160, 170, 190, 240 and 260 nm) of chitosan was measured with a glass reference. The thickness of chitosan was controlled by the rotation speed of spin-coating. The measurements were conducted at ambient humidity (20 ± 5 RH%) and room temperature (20 ± 2°C).

**Stimuli Response Measurements**: A xenon light source (LAX-C100, Asahi Spectra, USA) was employed as an ambient light source. The sensor device was placed in a chamber with a transparent window, then various RH (26, 41, 55, 70, 85) of humidity were supplied to the chamber by using a mass-flow controller (MFC). The desired level of humidity was provided by dry nitrogen (N₂) passed into a sealed glass bottle containing deionized water (DI water) and the flow rate was maintained at 500 sccm. To change the RH, dry N₂ gas and humid N₂ gas passed to DI water were mixed at specific ratio. The RH was confirmed using a humidity sensor (SHT31, Sensirion, Switzerland). The distance between the light source and the sensor device was 100 mm and the intensity of the light source was fixed at 235 W/m². The output current of organic PV cell was measured using a Sourcemeter (2400, Keithley, USA). The PV cell received no input voltage.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.J., K.K., N.R.-H. and A.I. contributed equally to this work. J.R. and N.R.-H. conceived the idea and initiated the project. N.R.-H. did initial design and preliminary experimental work. J.J., A.I. and C.J. continued and developed the simulation and experimental work. B.K. and J.-Y.L. provided the solar cell devices. K.K. and I.P. did the sensor-related work. All authors approved the final version of the manuscript. J.R. guided the entire project.

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Conflict of Interest

The authors have no conflict of interest.

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References


Figure 1. Color gamut, transmission spectra and field distribution calculated by TMM simulation. (a) Schematics of the proposed MIM filter that had thickness $t$ of chitosan. (b) CIE 1931 chromaticity diagram and (c) Transmission spectra of the MIM filters with the varied chitosan thickness ($t_n$, where $n$ is a sample code). Gray dashed lines connect the corresponding modes of Fabry-Perot resonance (insets: colors of corresponding samples). (d) Electric field distribution inside the cavity. (i) 1$^{st}$ mode of the second sample at a wavelength of 512 nm, (ii)
2nd mode of the seventh sample at a wavelength of 490 nm, (iii) 3rd mode of the tenth sample of 424 nm.

Figure 2. (a) Thickness of chitosan with respect to spin-coating speed used to prepare the samples. Thicknesses measured by AFM (triangles) and estimated by structural colors (diamonds). (b) Transmission spectra calculated using TMM (solid line) and obtained using UV-Vis/IR spectroscopy measurement of MIM filters having estimated thicknesses of chitosan $t_v$ where $v$ represents spin-coating speed. Insets: colors converted from simulation and measured spectra, and optical microscopy (OM) images.
Figure 3. (a) Schematic of experimental setup for humidity sensor application. (b) Humidity chamber and the sensor device, which is integrated with an organic PV cell and the adaptive
MIM filter. (c) Measured absorption spectrum of P3HT PV cell used in the sensor. (d) Calculated transmission spectra of the single sensing films (solid line) under varied RH conditions and the measured spectra of the sample 1 (dashed line) from Figure 2b. (e) Calculated absorption spectra of the PV cell combined with the sensing films as in (b). As the RH is increased, the absorption decreases.

Figure 4. (a) Swelling/contraction of the chitosan layer in the sensing film during RH modulation. Insets: corresponding structure colors measured in the chamber. (b) Output current generated by the proposed humidity sensor under varied RH condition. Unshaded area: recovery period, shaded area: sensing period. From the current, the film fully regains its original state (RH = 0 %) during the recovery period. (c) Response of the sensor under varied RH;
triangles: Test 1; circles: Test 2; yellow dashed line: trendline of the results.
The table of contents entry: The tunable interferometric colors are realized by silver-chitosan-silver Fabry-Perot resonators. The chitosan, one of polysaccharide, is stimuli-responsive to external vapor, so it is swollen and deswollen in response to humidity condition. With the properties of chitosan, the peak of transmission shifts as humidity changes. As proof of concept, we demonstrate a real-time colorimetric humidity sensor combined with a photovoltaic cell.

**Keyword:** tunable structural colors, metal-insulator-metal, interferometric colors, metal-insulator-metal, tunable color filter, structural colors, Fabry-Perot etalon

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