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Roll up polymer/oxide/polymer nanomembranes as a hybrid optical microcavity for humidity sensing

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A hybrid optical microcavity from rolled-up polymer/oxide/polymer nanomembranes presents its excellent capability for environmental relative humidity detection. When exposed to a moist surrounding, poly (acrylic acid)/poly(ethylenimine) polymers swell greatly due to the absorption of water molecules, which thus leads to an increased wall thickness of the tubular optical microcavity and therefore presents a profound wavelength redshift of its whispering-gallery mode resonance. These experiments fit well with the calculation based on the Mie-scattering theory. Theoretical calculation also demonstrates that the thin walls of our tubular microcavities contribute to a high detection sensitivity compared to other microcavities. Our work could lead to new designs and applications of optical microcavities.

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1 Introduction

Optical microcavities¹ with whispering-gallery modes (WGMs) are widely used in the area of lasing, photovoltaics and optofluidic-/bio-sensing, mainly due to their selective and robust absorption enhancement at certain wavelengths.²⁻⁶ As one of the important sensing resonators, optical microcavities exhibit high sensitivity to the changes of the surrounding medium⁷ and the absorbents⁸ on their surfaces. Interestingly, such optical microcavities indicated that the WGMs could be tuned by the absorption and desorption of various molecules (for example, water molecules,⁹ DNA¹⁰ and virus¹¹) on their surfaces under certain control. This phenomenon inspires us that these microcavities can be used as optical sensors to detect the environmental relative humidity (RH). In order to enhance the humidity sensitivity of such optical microcavity with WGMs, surface modification¹² is one of the effective and easy methods to enrich the interactions between detected targets and the light evanescent field in a cavity. Based on previous studies,^{13,14} polymers with excellent water-sensitivity are always good candidates as the sensing material for surface

modification. These drive us to the exploration that uses polymers as the functional layers to improve the detection sensitivity based on optical microcavities.

In this article, we demonstrate that an optical microcavity (*i.e.*, self-rolled-up oxide tubular microcavity¹⁵⁻¹⁷) coated with poly(acrylic acid)/poly(ethylenimine)(PAA/PEI) polymers is used for the detection of environmental RH. This tubular microcavity with sandwiched polymer/oxide/polymer walls shows greatly enhanced humidity detection sensitivity compared to a pure oxide tubular optical microcavity. The sensitivity of up to 130 pm per RH% in our polymer modified tubular microcavity is ~10 times larger than sensors based on WGMs in other optical microcavities.^{18–20} Detailed calculations based on the Mie scattering²¹ theory indicate that such high sensitivity is closely related to the swelling of water-sensitivity polymers and the subwavelength thin-wall property of the tubular microcavity.

2 Experimental section

2.1 Preparation of sandwiched tubular microcavities

2.1.1 Fabrication of the oxide tubular microcavity. A uniform ARP-3510 photoresist (Allresist GmbH) layer with a thickness of ~2 μ m was spin-coated on the silicon substrate. The photoresist layer was then patterned to arrays of 80 μ m diameter circles by photolithography and used as the sacrificial layer. Pre-strained Y₂O₃/ZrO₂ bilayers with a thickness of 12/24 nm were deposited by electron beam deposition with an angle of 60°. The deposition rates were 3 Å s⁻¹ and 0.5 Å s⁻¹, respectively. Acetone was employed to selectively remove the



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Fig. 1 (a) Schematic image (upper) and optical microscopy image (below) of an oxide tubular microcavity after the ALD coating. The microtube consists of Y_2O_3/ZrO_2 layers wrapped by ALD coated Al_2O_3 monolayers. The thicknesses of $Al_2O_3/Y_2O_3/ZrO_2/Al_2O_3$ are 30/12/24/30 nm, respectively. (b) Sketch of the LBL coating process to obtain PAA/PEI polymer layers. The process was repeated twice. Both PAA and PEI solutions were diluted to 1 wt%. (c) SEM image of a PAA/PEI modified tubular microcavity. The inset shows the cross-section of the multilayers in the unrolled nanomembranes. The scale bar is 100 nm in the inset and the thickness of the PAA/PEI layer is 33.2 nm in vacuum. (d) Schematic diagram of PL measurement under different RHs. Tubular microcavities were placed in the sealed chamber with certain RH tuned by saturated salt solutions and the excitation laser was introduced through the transparent quartz window.

sacrificial layer and to release the strained Y_2O_3/ZrO_2 bilayers. To further strengthen the tubular microcavity, we wrapped the Y_2O_3/ZrO_2 microcavity with 30 nm Al₂O₃ monolayers by atomic layer deposition (ALD).²² The circular patterned Y_2O_3/ZrO_2 (the effective refractive index is around 1.68)²³ nanomembranes with a high effective refractive index and the ALD-coated Al₂O₃ (the effective refractive index is around 1.63) layer provide a good confinement of the incident light in both azimuthal and axial directions of the microtube. The final schematic diagram (upper) and optical microcavity are shown in Fig. 1(a).

2.1.2 LBL coating of PAA/PEI polymers. To form tubular microcavities with sandwiched polymer/oxide/polymer walls, the layer-by-layer (LBL) assembly was employed.²⁴ As shown in Fig. 1(b), the patterned microtube array immobilized on a glass slide was immersed in the 1 wt% PAA solution, deionized water and 1 wt% PEI solution in sequence, with times of 15 min, 1 min (4 times) and 15 min, respectively. The above process was repeated twice. Nitrogen protected annealing at 130 °C for 150 min was performed afterward. The scanning electron microscopy (SEM) image of a PAA/PEI modified tubular microcavity is shown in Fig. 1(c). The diameter of the sandwiched polymer/oxide/polymer tubular microcavity is ~7.2 µm and the PAA/PEI polymer layer is ~33.2 nm in vacuum with a calculated effective refractive index of 1.58.

2.2 Photoluminescence (PL) measurements under various RHs

Saturated salt solutions were used to offer controllable and stable RH for the following PL measurements. The RH of LiCl·H₂O, MgCl₂·6H₂O, Mg(NO₃)₂·6H₂O, NaCl, KCl and K₂SO₄

solutions are 12%, 33%, 52%, 75%, 97%, respectively.²⁵ A silica gel desiccant was used to dry the air in the sealed chamber for humidity detection down to \sim 5% RH.²² The whole detection setup is shown in Fig. 1(d). The experiment was done at room temperature^{26,27} and the excitation power was kept the same as the 514.5 nm laser line.

3 Results and discussion

3.1 WGM shifts of the unmodified/modified tubular microcavities under various RHs

The performances of both unmodified and PAA/PEI modified tubular microcavities as humidity sensors are demonstrated via PL spectra in Fig. 2. The PL spectrum (not shown) originates from defect-related emission centers in Y2O3/ZrO2 nanomembranes.²³ As shown in Fig. 2(a), for a certain azimuthal mode number, a main peak and a sub-peak are observed. Considering their differences in humidity detection sensitivity (Fig. 2(b)), the peaks are attributed to transverse-magnetic (TM) mode (main peak) and transverse-electric (TE) mode (sub-peak), respectively.⁷ Despite the good confinements of TM polarized and TE polarized waves that guarantee a high resolution to the tiny shifts of resonant wavelengths, the RH influence on resonant wavelengths in the pure oxide tubular microcavity (unmodified) is not distinct enough to be observed. The adsorption and desorption of water molecules on oxide microtube walls easily reach the saturation equilibrium state, then the WGMs position will not shift with the RH changing.⁸

When the pure oxide tubular microcavity is modified by PAA/PEI polymers, the resonant wavelengths red-shift considerably as presented in Fig. 2(b). This improved humidity detection capability is closely related to the LBL-coated PAA/ PEI polymers. LBL coating is a simple and versatile tool



Fig. 2 PL spectra from the centre of an ~7.2 μ m diameter tubular microcavity (Fig. 1(a)) acquired under increasing RH before (a) and after (b) PAA/PEI modification. Symbols mark the evolution of TM (circle) and TE (diamond) resonant wavelengths as a function of RH at the mode number of m = 63. The spectra are taken under excitation of the 514.5 nm line of an argon ion laser at room temperature.

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for constructing differently functioned thin films, based on the alternative absorption of monolayers of individual components.28 The electrostatic and van der Waals interactions between PAA and PEI molecules guarantee a uniform and thickness-changeable (PAA/PEI)2 composite layer, which is highly sensitive to water molecules.^{29,30} Along with the RH increasing, more water molecules are diffused into the PAA/ PEI polymers, thus causing the expansion of PAA/PEI layers. The expansion resultantly brings about an increase of microtube wall thickness and a decrease of PAA/PEI polymer's refractive index (n_p) . The refractive index of environmental air with more water molecules (n_{air}) is slightly increased. These three factors function simultaneously and eventually lead to the redshifts in resonant wavelengths in our sandwiched polymer/oxide/polymer tubular optical microcavity as shown in Fig. 2(b).

3.2 High RH sensitivity of the modified tubular microcavity

One of the biggest advantages of WGM-based humidity sensing in the PAA/PEI modified tubular microcavity is the high detection sensitivity. Our sandwiched polymer/oxide/ polymer tubular microcavity exhibits a total redshift of up to 12 nm (TE, m = 63) when the RH increases from 5% to 97% (Fig. 3(a), red and circle line), corresponding to an average sensitivity of 130 pm per RH%, which is about 10 times larger than sensors based on WGMs in other microcavities (*i.e.*, microsphere and/or microtoroid).¹⁶⁻¹⁸

Although TM mode presents better light confinement than TE mode and is more easy to be detected, the humidity detection sensitivity of TM mode is smaller than TE mode as shown in Fig. 3(a) (blue lines). When the RH changes from 5% to 97%, the total wavelength redshifts are 12 nm and 5.2 nm for TE and TM modes (m = 63), respectively. TE-polarized evanescent waves possess a deeper penetration depth in the surrounding medium and thus perform stronger interactions with the related changes, hence exhibit an enhanced response



Fig. 3 (a) Resonant wavelengths (azimuthal number m = 63) as a function of RH. The rectangles refer to the resonant wavelengths acquired from an unmodified tubular microcavity while the circles are acquired from our PAA/PEI modified tubular microcavity. The red and blue plots correspond to TE and TM modes, respectively. (b) Dependence of wavelength redshifts on azimuthal numbers for TE mode (red) and TM mode (blue). The vertical axis represents the accumulated redshift of the PAA/PEI modified tubular microcavity with RH increasing from 5% to 97% and the horizontal axis represents azimuthal numbers.

than TM mode.³¹ This enhanced response to the medium change is also the main source to the fast *Q* factor degradation of TE mode in our PAA/PEI modified tubular microcavity as shown in Fig. 2(b). The influences of azimuthal mode numbers (*m*) on the detection sensitivity of RH are also investigated as presented in Fig. 3(b). For both TE and TM modes, smaller azimuthal numbers correspond to larger redshifts with a nearly linear relationship. This RH detection sensitivity dependence on azimuthal numbers is due to the stronger light confinement in the tubular microcavity with larger azimuthal numbers.⁷ As has been proved in the previous study,⁹ water absorption and desorption are physical processes, so it can be expected that humidity sensing is reversible in the polymermodified rolled-up microtube.^{14,29,30,35}

3.3 Theoretical calculation based on the Mie-scattering theory

The WGM-based environmental RH detection model in the PAA/PEI modified tubular microcavity is shown in Fig. 4. Along with the increasing of environmental RH, the cavity experiences several changes. The most obvious one is the swelling of PAA/PEI polymer layers, which is schematized in the inset of Fig. 4(a). In this process, the oxide layer $Al_2O_3/Y_2O_3/ZrO_2/Al_2O_3$ is regarded as being rigid in the center of the microtube wall, taking into account their relatively strong stiffness compared to PAA/PEI polymers. Hence, only the PAA/PEI polymer layers inflate in the increased moist conditions, thus leading to a large improvement in the wall thickness and a slight decrease in the refractive index (n_p) of PAA/PEI polymers.²⁰ In the following calculations, we mainly focused on the influences of thickness alteration to resonant wavelengths,



Fig. 4 (a) Resonant wavelengths (TE, azimuthal number m = 63) as a function of polymer wall thickness (lines, calculation)/RH (red circles, experiment). The red line is acquired under a coefficient of humidity-induced thickness expansion of $\alpha = 0.33\%$ per RH%, and the dashed green lines are acquired under a coefficient of $(0.33 \pm 0.05)\%$ per RH%. The inset is a schematic of the PAA/PEI polymer swelling process, in which the yellow dashed lines refer to the inner and outer walls of the tubular microcavity before polymer swelling. The PAA/PEI modified microtube is surrounded by water molecules as shown in the inset. (b) Theoretical calculation of the effective refractive index $n_{\rm eff}$ of the microtube wall and the corresponding sensitivity $(\Delta \lambda/\lambda)$ as a function of wall thickness. The grey area refers to the wall thickness in our PAA/PEI modified tubular microcavity.

and temporarily ignored the decrease of the polymer refractive index (n_p) and the environmental moist air effective refractive index (n_{air}) .

We applied the Mie-scattering theory to calculate the function of polymer wall thickness to resonant wavelengths. The results are presented in Fig. 4(a) (TE, m = 63). The red line is acquired under a coefficient of humidity-induced thickness expansion of $\alpha = 0.33\%$ per RH%, ³²⁻³⁴ and the dashed green lines are acquired under a coefficient of $\pm 0.05\%$ per RH%. The experimental resonant wavelengths as a response to RH (red circles) are well fitted with our theoretical calculation, which discloses that the coefficient α of humidity-induced thickness expansion of PAA/PEI composite layers is in the range of 0.33 \pm 0.05% per RH%. Our calculation also demonstrates that the wall thickness increase is the dominant factor that affects the resonant wavelengths in our polymer modified tubular microcavity. As calculated by the Mie-scattering theory (lines in Fig. 4(a)), the resonant wavelengths follow a linear relationship with the polymer thickness, and the polymer thickness also follows a linear response with RH,³²⁻³⁴ thus the response of resonant wavelengths to RH is supposed to be linear. However, when RH reaches 52%, resonant wavelengths are smaller than the supposed linear wavelengths in our experiment as shown in Fig. 3(a) and 4(a) (red circles). When a large number of water molecules are diffused into the tubular microcavity, both the surface tension of water molecules and the hygroscopic strain^{34,35} inside the microtube could lead to a deformation of the thin-wall tubular microcavity, which resultantly leads to the nonlinear response at high RH.³⁶ We believe that through a further structural optimization to strengthen the microtube or thinning of the coating layer, the linear response range could be increased for practical applications.

Based on the resonance conditions of WGMs: $2\pi Rn_{eff} = \lambda_r m$ (*R* is the average radius of the microtube, λ_r is the resonant wavelength, $n_{\rm eff}$ is the effective refractive index of the microtube wall and m is the azimuthal number), the sensitivity of resonant wavelengths to changes in radius ΔR or $\Delta n_{\rm eff}$ is $\Delta \lambda_r / \lambda_r =$ $\Delta R/R + \Delta n_{\rm eff}/n_{\rm eff}$.³⁷ Here, the average radius of the microtube R nearly remains the same during the increase of RH in our experiment, mainly because of the symmetrical swelling of PAA/PEI polymers inside and outside the oxide layers. The asymmetrical swelling also brings about the doubled thickness increase (*i.e.*, doubled $\Delta n_{\rm eff}$) of the tubular microcavity wall, which acts as the main origin of the high RH detection sensitivity. A distinct feature of our hollow tubular microcavity is the subwavelength thin wall compared to other optical microcavities with WGMs.¹⁸⁻²⁰ Fig. 4(b) displays the effective refractive index $n_{\rm eff}$ of an optical microcavity and the corresponding sensitivity $(\Delta \lambda / \lambda)$ as a function of wall thickness. For both TM and TE modes, the sensitivity in thin-wall microcavities is much more higher than that in thick-wall microcavities. The water-sensitive PAA/PEI polymers, the doubled thickness alteration with RH changes, and the enhanced sensitivity in thin-wall optical microcavity, eventually make our PAA/PEI modified tubular microcavity a highly sensitive RH detector.

4 Conclusions

In conclusion, hybrid tubular microcavities from rolled-up polymer/oxide/polymer nanomembranes were fabricated and used to detect the environmental relative humidity based on the shifts of WGMs. Benefitting from the swelling of water-sensitive PAA/PEI polymers, the detection sensitivity of the PAA/PEI modified tubular microcavity is greatly enhanced, reaching the averaged value of 130 pm per RH%. Theoretical calculations based on the Mie-scattering theory were carried out, which demonstrate that the high sensitivity of our tubular microcavity mainly originates from the thickness alteration with RH and the thin-wall property of our tubular microcavity. Our work could lead to new designs and applications of optical microcavities.

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Notes and references

- 1 K. J. Vahala, Nature, 2003, 424, 839.
- 2 C. Czekalla, C. Sturm, R. Schmidt-Grund, B. Cao, M. Lorenz and M. Grundmann, *Appl. Phys. Lett.*, 2008, **92**, 241102.
- 3 J. Grandidier, D. M. Callahan, J. N. Munday and H. A. Atwater, *Adv. Mater.*, 2011, 23, 1272.
- 4 V. A. B. Quiñones, L. Ma, S. Li, M. Jorgensen, S. Kiravittaya and O. G. Schmidt, *Appl. Phys. Lett.*, 2012, **101**, 151107.
- 5 T. Beck, M. Mai, T. Grossmann, T. Wienhold, M. Hauser,
 T. Mappes and H. Kalt, *Appl. Phys. Lett.*, 2013, 102, 121108.
- 6 Z. Mi and P. Bianucci, *Curr. Opin. Solid State Mater. Sci.*, 2012, **16**, 52.
- 7 G. S. Huang, V. Quinones, F. Ding, S. Kiravittaya, Y. F. Mei and O. G. Schmidt, *ACS Nano*, 2010, 4, 3123.
- 8 J. Zhu, S. K. Ozdemir, Y. Xiao, L. Li, L. He, D. Chen and L. Yang, *Nat. Photonics*, 2010, **4**, 46.
- 9 J. Zhong, J. Wang, G. Huang, G. Yuan and Y. Mei, *Nanoscale Res. Lett.*, 2013, **8**, 1.
- 10 F. Vollmer, S. Arnold, D. Braun, I. Teraoka and A. Libchaber, *Biophys. J.*, 2003, **85**, 1974.
- 11 L. He, Ş. K. Özdemir, J. Zhu, W. Kim and L. Yang, *Nat. Nanotechnol.*, 2011, **6**, 428.

- 12 H. Im, N. C. Lindquist, A. Lesuffleur and S. Oh, *ACS Nano*, 2010, **4**, 947.
- 13 F. X. Gu, L. Zhang, X. F. Yin and L. M. Tong, *Nano Lett.*, 2008, **8**, 2757.
- 14 W. Li, G. Huang, H. Yan, J. Wang, Y. Yu, X. Hu, X. Wu and Y. Mei, *Soft Matter*, 2012, **8**, 7103.
- 15 Y. F. Mei, G. S. Huang, A. A. Solovev, E. B. Urena, I. Moench, F. Ding, T. Reindl, R. Fu, P. K. Chu and O. G. Schmidt, *Adv. Mater.*, 2008, **20**, 4085.
- 16 T. Kipp, H. Welsch, Ch. Strelow, Ch. Heyn and D. Heitmann, *Phys. Rev. Lett.*, 2006, **96**, 077403.
- 17 X. Li, Adv. Opt. Photonics, 2011, 3, 366.
- 18 B. Bhola, P. Nosovitskiy, H. Mahalingam and W. H. Steier, *IEEE Sens. J.*, 2009, **9**, 740.
- 19 Q. Ma, L. Huang, Z. Guo and T. Rossmann, *Meas. Sci. Technol.*, 2010, 21, 115206.
- 20 S. Mehrabani, P. Kwong, M. Gupta and A. M. Armani, *Appl. Phys. Lett.*, 2013, **102**, 241101.
- 21 T. Zhan, C. Xu, F. Zhao, Z. Xiong, X. Hu, G. Huang, Y. Mei and J. Zi, *Appl. Phys. Lett.*, 2011, **99**, 211104.
- 22 V. A. B. Quiñones, G. Huang, J. D. Plumhof, S. Kiravittaya,A. Rastelli, Y. Mei and O. G. Schmidt, *Opt. Lett.*, 2009, 34, 2345.
- 23 J. Wang, T. Zhan, G. Huang, X. Cui, X. Hu and Y. Mei, *Opt. Express*, 2012, 20, 18555.
- 24 G. Decher, Science, 1997, 277, 1232.

- 25 H. H. Yu, T. Cao, L. D. Zhou, E. D. Gu, D. S. Yu and D. S. Jiang, *Sens. Actuators, B*, 2006, **119**, 512.
- 26 M. Frenkel, M. Avellan and Z. Guo, *Meas. Sci. Technol.*, 2013, 24, 075103.
- 27 C. H. Seok, S. Ismail and A. M. Armani, *Opt. Lett.*, 2011, 36, 2152.
- 28 A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted and A. Hirsch, *Nat. Mater.*, 2002, 1, 190.
- 29 L. Shen, J. Fu, K. Fu, C. Picart and J. Ji, *Langmuir*, 2010, 26, 16634.
- 30 X. Wang, B. Ding, J. Yu, M. Wang and F. Pan, *Nanotechnology*, 2010, **21**, 055502.
- 31 J. Wang, T. Zhan, G. Huang, P. K. Chu and Y. Mei, *Laser Photonics Rev.*, 2014, **8**, 521.
- 32 H. Ardebili, E. H. Wong and M. Pecht, *IEEE Trans. Compon. Packag. Technol.*, 2003, **26**, 206.
- 33 M. R. Vanlandingham, R. F. Eduljee and J. W. Gillespie, J. Appl. Polym. Sci., 1999, 71, 787.
- 34 S. Schmid, S. Kuehne and C. Hierold, *J. Micromech. Micro*eng., 2009, **19**, 065018.
- 35 X. Wang, B. Ding, J. Yu and M. Wang, *J. Mater. Chem.*, 2011, **21**, 16231.
- 36 L. Ma, S. Kiravittaya, V. A. B. Quiñones, S. Li, Y. Mei and O. G. Schmidt, *Opt. Lett.*, 2011, 36, 3840.
- 37 A. M. Armani, R. P. Kulkarni, S. E. Fraser, R. C. Flagan and K. J. Vahala, *Science*, 2007, 317, 783.