Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

Configurable Swellability of Hydrogel Microstructure for Structural-Color-Based Imaging Concealment/Encryption

Method:

Sample Fabrications: For the metal-hydrogel-metal (MHM) nanocavities, the 100 nm-thick aluminum (Al) film was first deposited on a clean 2-inch silicon (Si) wafer (from Kaihuajingxin Electronics Co., Ltd.) using thermal evaporation to achieve total reflection in the visible light wavelength range. Polyvinyl alcohol (PVA, with Mw between 10,000 ~ 26,000 g/mol and alcoholysis degree of 87~89 %, from Alfa Aesar) was dissolved in deionized (DI) water to prepare a 10 wt% hydrogel solution. For the hydrogel resist layer, the 10 wt% PVA solution was spin-coated on the Al/Si substrates at the speed of 3000 r.p.m. for 40 s to form a 360 nm-thick uniform film. The hydrogel microstructures were patterned on the resist layer through grayscale electron-beam lithography (G-EBL, Elphy Quantum system, from Raith Gmbh) at the exposure dose of 200~5620.5 $\mu C/cm^2$ and the acceleration voltage of 5 kV. After exposure, the PVA patterns were developed with DI water for 60 s and then dried with N_2 gas. Finally, a 10 nm-thick platinum (Pt) film was coated on the top using a sputtering instrument.

Characterization: The topographic changes of PVA microstructures in the dry state (40 % RH) and moist state (100 % RH) with varied exposure doses were characterized by environmental atomic force microscope (e-AFM, CypherESc system, from Oxford). Since the blowing N_2 gas may impact the scanning tip during e-AFM, the ideal dry state of 0 % RH is not conducted in e-AFM test. The morphologies of the G-EBL patterned MHM nanocavities were observed using optical microscopy and scanning electron microscopy (SEM, Sigma 300 system, from Carl Zeiss). During the reflectance spectra measurement, the samples and the commercial humidity sensor (Thorlabs TSP01) were placed in a self-made transparent quartz box to ensure that the ambient humidity remained stable. The gas humidifier (MF-R5 system, from Zhongke Huanyi (Beijing) Measurement Technology Co., Ltd.) was used to control the mixing ratio between dry N_2 (~0 % RH) and moisture (~100 % RH) for tunable ambient humidity. The reflectance spectra and the reflected images of the MHM nanocavities under varying levels of ambient humidity were collected by a fiber-based spectrometer (from Shanghai Fuxiang Optical Co., Ltd.). After humidity change, the reflectance spectra were collected after waiting for 15 s to make sure the completed swelling/shrinkage of MHM pixels.

Resolution calculation: Pixels per inch (PPI) is selected to indicate the resolution capability of this high-density image concealment/encryption. It can be calculated as：

$$PPI = \frac{\sqrt{Horizontal\, pixel\, count^2 + Vertical\, pixel\, count^2}}{Diagonal\, size(in\, inches)}$$

Based on this, structures with the width of 4 μm in Fig. 5 indicates the density of 6,350 PPI. Fig. S8 with the periods of 1 μm means the density of 25,400 PPI. (Ref. Furey, Edward "Pixels Per Inch PPI Calculator" at https://www.calculatorsoup.com/calculators/technology/ppi-calculator.php from CalculatorSoup, *https://www.calculatorsoup.com* - Online Calculators)

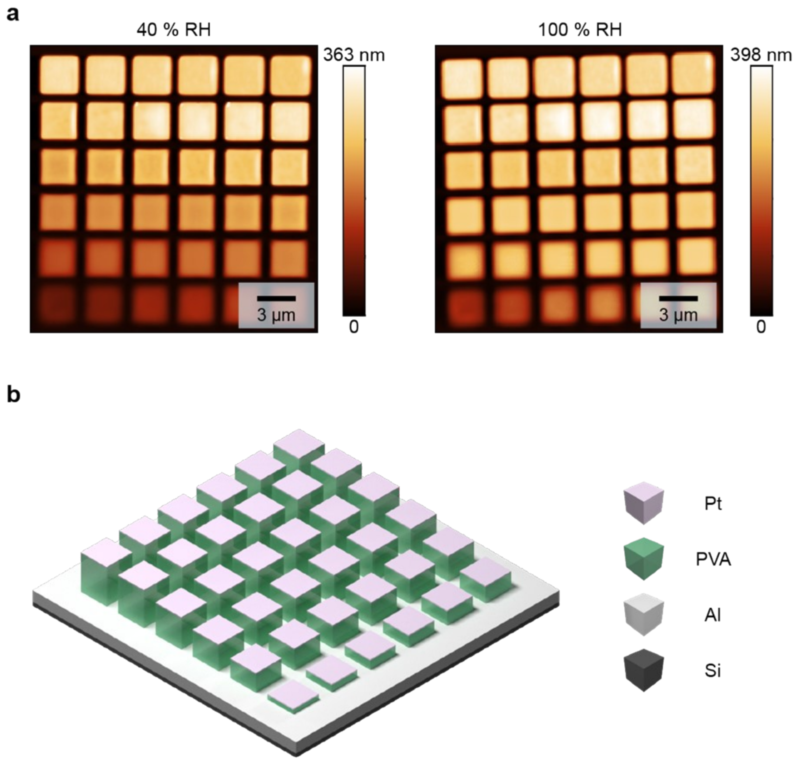


Figure S1. (a) e-AFM images of hydrogel structures with controlled ambient humidity at 40 and 100 % RH. **(b)** Schematics of the proposed MHM nanocavities with varied insulator thicknesses for multi-color displays.

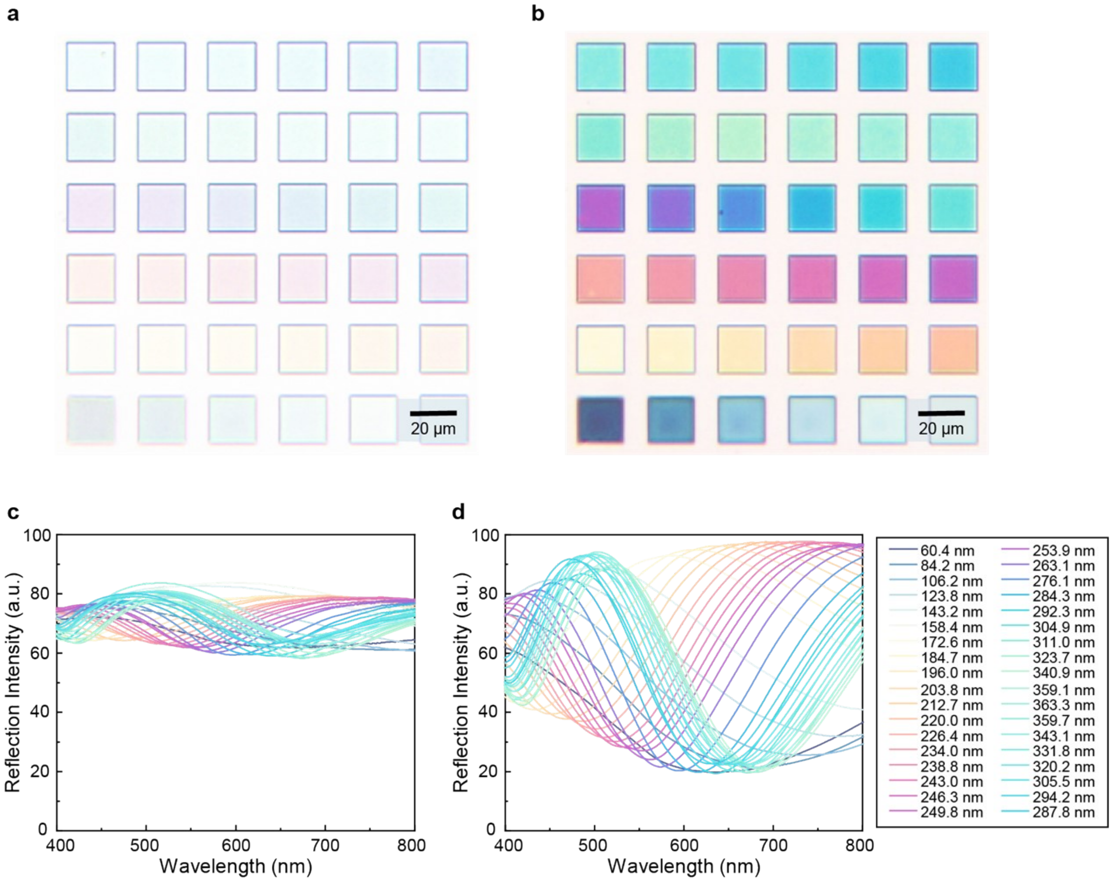


Figure S2. Optical microscopy image of the hydrogel nanocavities with varied insulator thickness **(a)** before and **(b)** after depositing Pt on the top. Reflectance spectra of nanocavities with different PVA thickness **(c)** before and **(d)** after depositing Pt on the top.

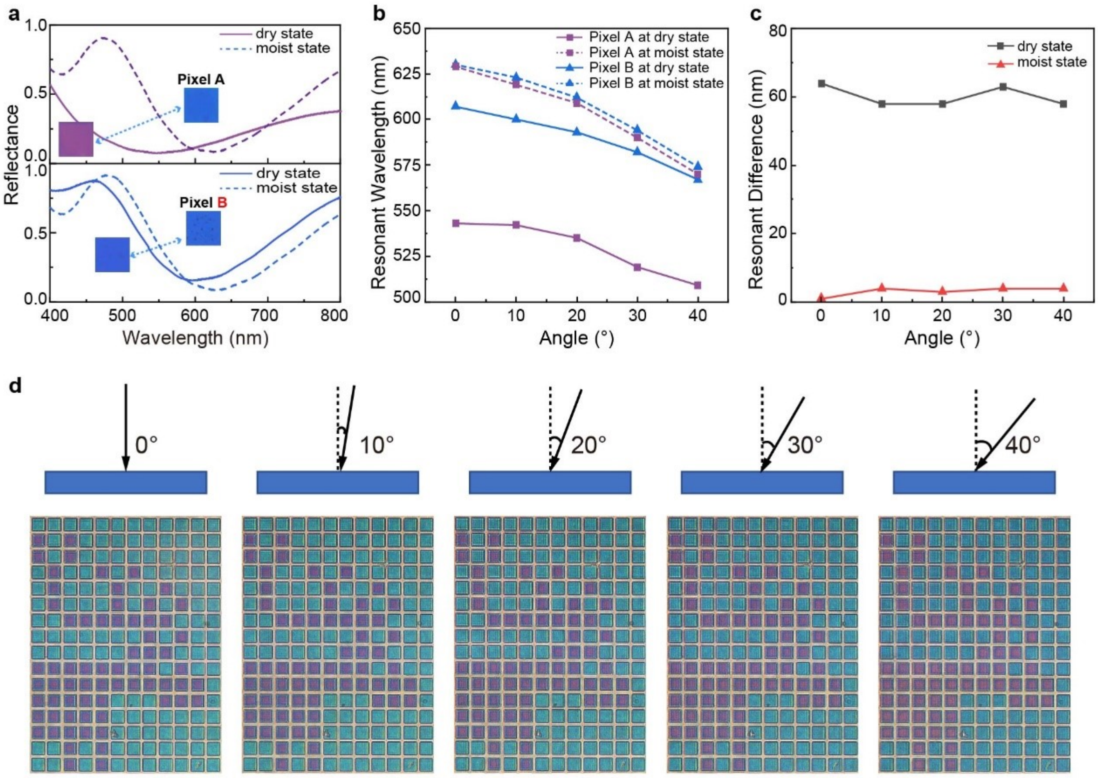


Figure S3. (a) Reflectance spectra of the marked Pixel A and B measured with normal incidence measured at 40 and 100 % RH, respectively. **(b)** Resonance shifts of pixel A and B at dry and moist states with varied incident angle from 0^o to 40^o. **(c)** Resonant difference between pixel A and B at dry (the black line) and moist (the red line) states. **(d)** Optical microscopy images of the “deer” image at 40 % RH with the incident angle of 0^o, 10^o, 20^o, 30^o, 40^o, respectively.

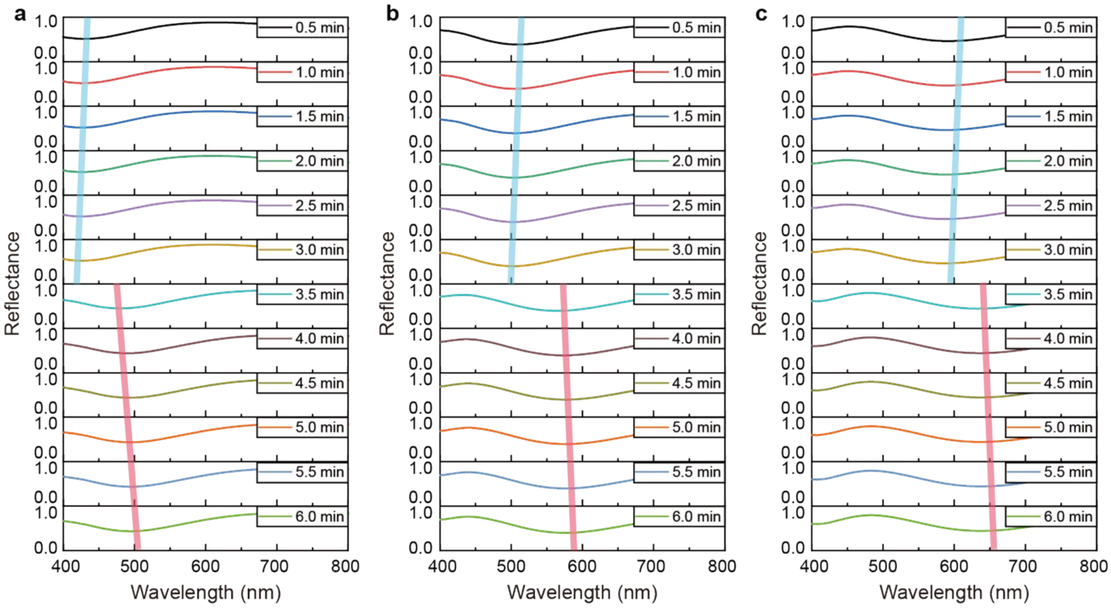


Figure S4. Reflectance spectra of the first cycle of the repeatability test. **(a)** h = 184.7 nm **(b)** h = 234.0 nm **(c)** h = 276.1 nm.

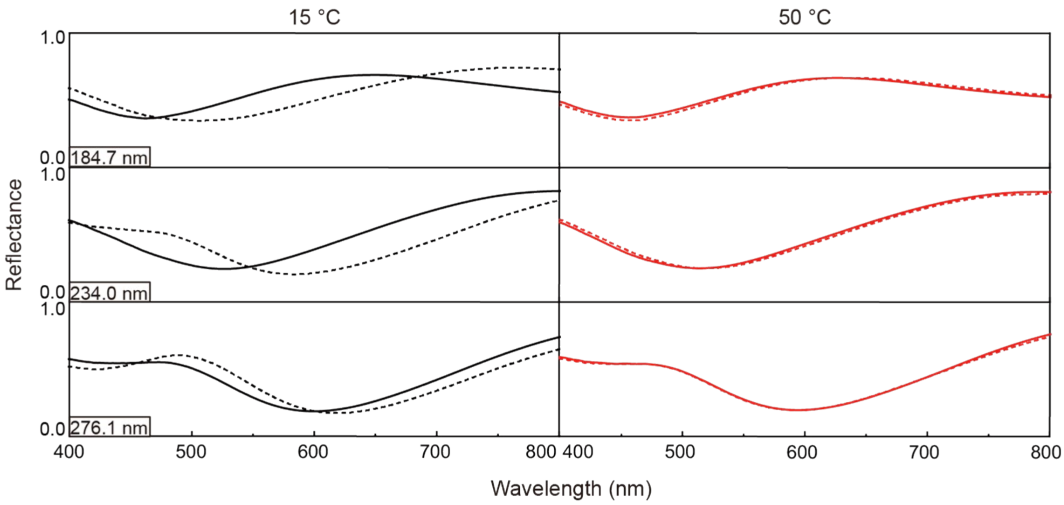


Figure S5. Reflectance spectra of MHM pixels with h = 184.7, 234.0 and 276.1 nm at 40 % RH (marked as sold line) and 100 % RH (marked as dash line), measured at 15 ^{o}C (left) and 50 ^{o}C (right), respectively.

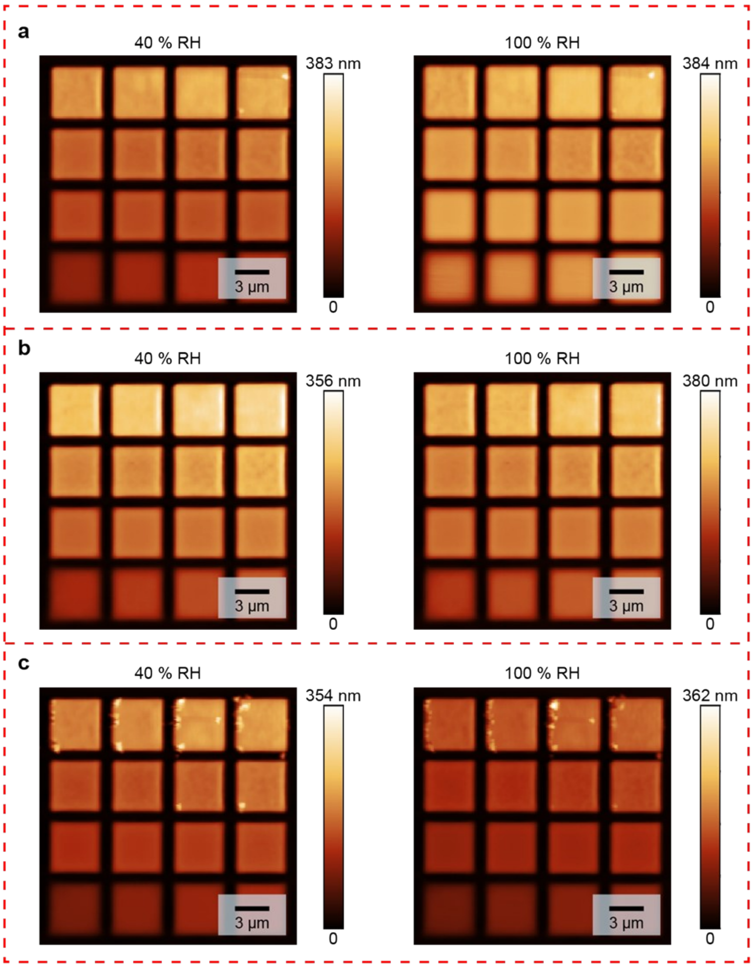


Figure S6. e-AFM images of PVA pixels with controlled ambient humidity at 40 and 100 % RH with the second exposure doses: **(a)** 0 μC/cm^2; **(b)** 500 μC/cm^2; **(c)** 1000 μC/cm^2.

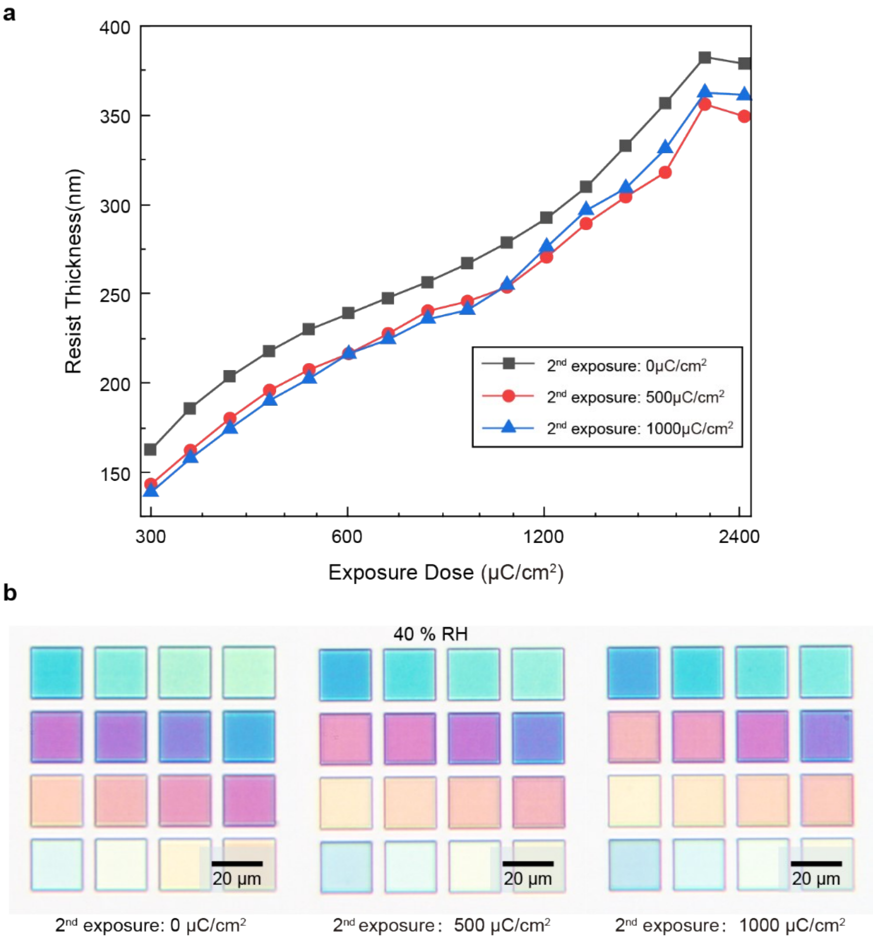
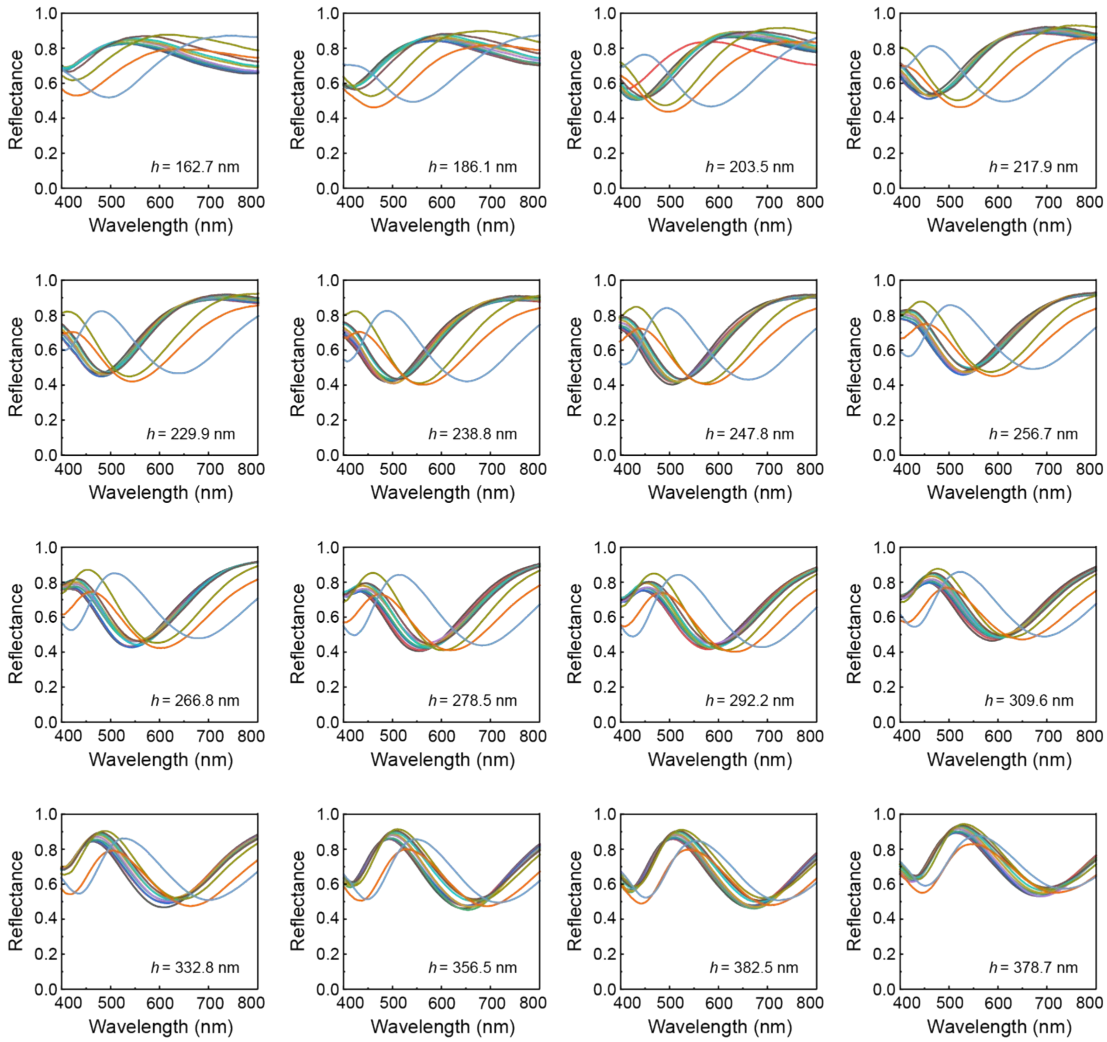
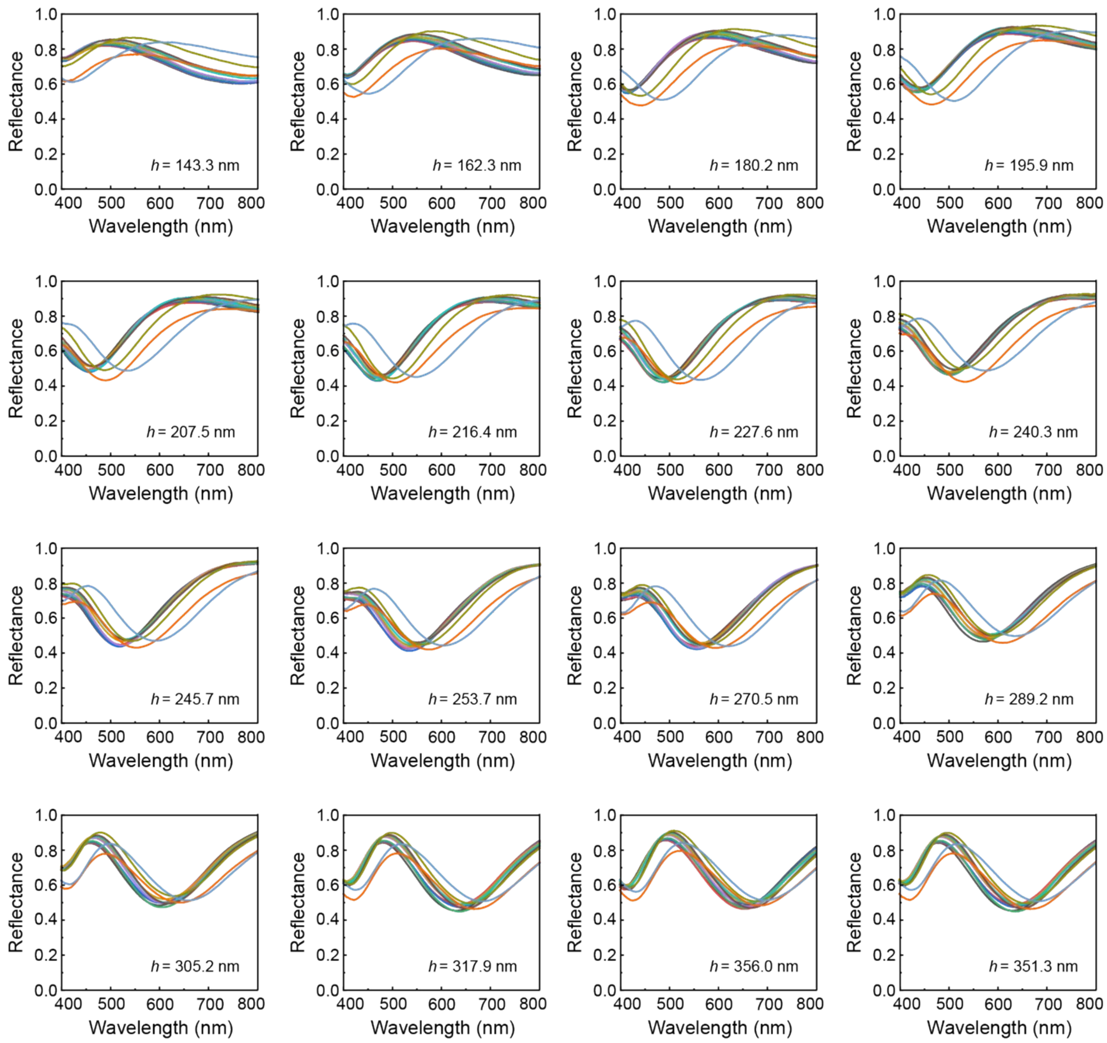


Figure S7. (a) Thickness change of MHM nanocavities with the second exposure dose of 0, 500 and 1000 μC/cm^2. **(b)** Optical microscopy images of MHM nanocavities with the second exposure dose of 0, 500 and 1000 μC/cm^2.

a


Reflectance
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
500
600
700
800
h = 162.7 nm
h = 186.1 nm
h = 203.5 nm
h = 217.9 nm
h = 229.9 nm
h = 238.8 nm
h = 247.8 nm
h = 256.7 nm
h = 266.8 nm
h = 278.5 nm
h = 292.2 nm
h = 309.6 nm
h = 332.8 nm
h = 356.5 nm
h = 382.5 nm
h = 378.7 nm

b



h = 143.3 nm
h = 162.3 nm
h = 180.2 nm
h = 195.9 nm
h = 207.5 nm
h = 216.4 nm
h = 227.6 nm
h = 240.3 nm
h = 245.7 nm
h = 253.7 nm
h = 270.5 nm
h = 289.2 nm
h = 305.2 nm
h = 317.9 nm
h = 356.0 nm
h = 351.3 nm
Reflectance
Wavelength (nm)

c

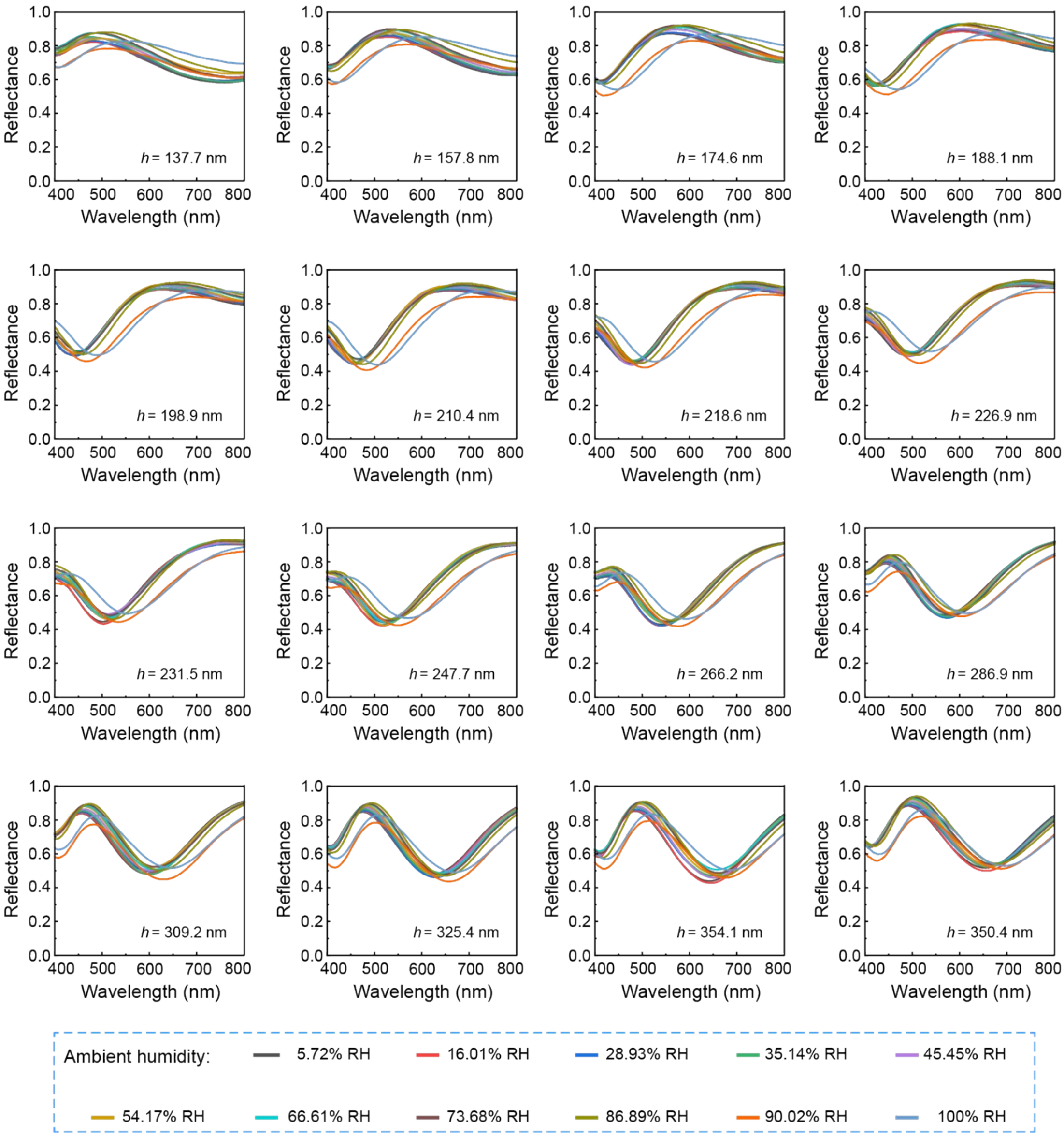


Figure S8. Reflectance spectra of MHM nanocavities with varied *h* at different ambient humidity. Second exposure dose: **(a)** 0 μC/cm^2; **(b)** 500 μC/cm^2; **(c)** 1000 μC/cm^2.

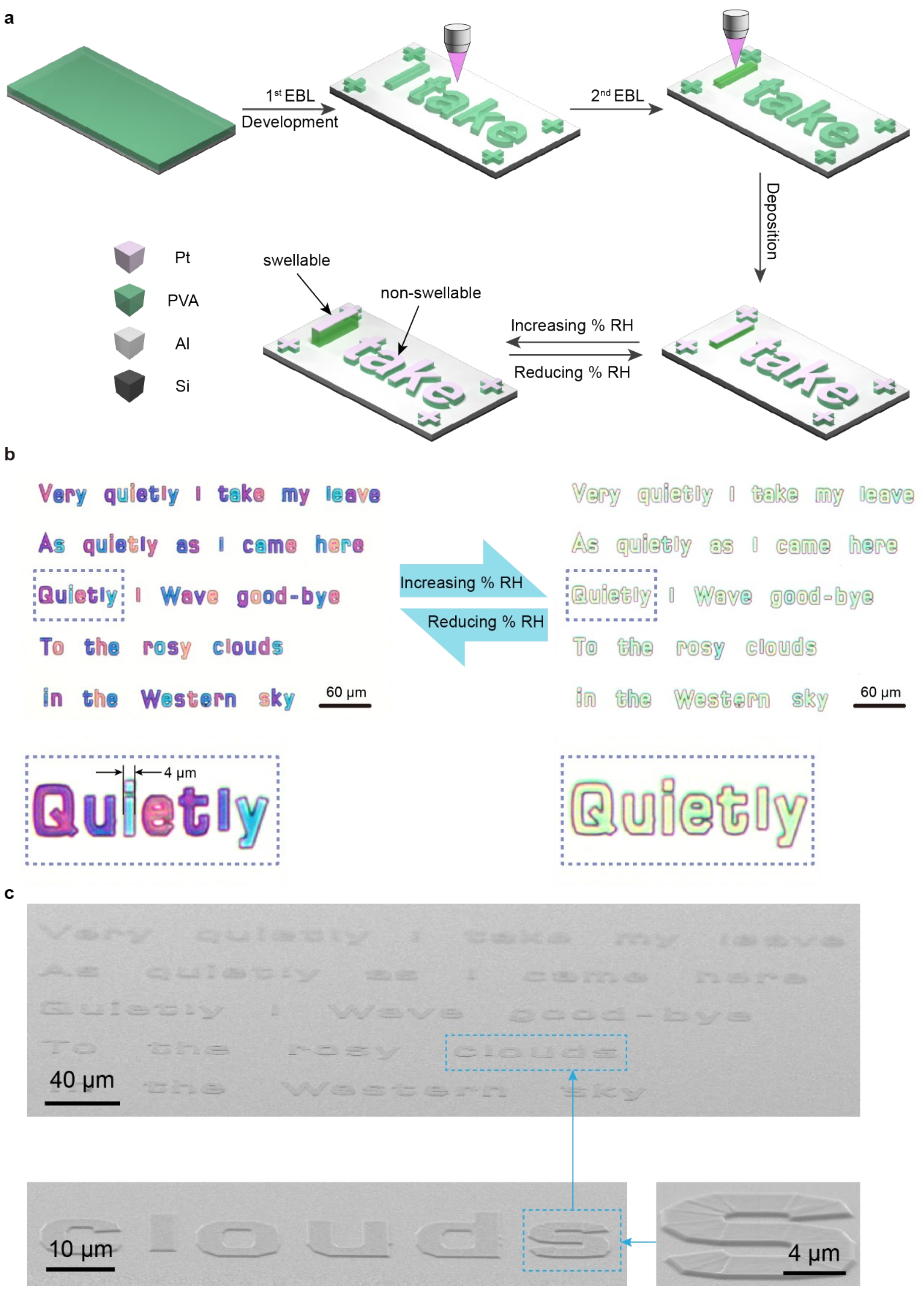


Figure S9. (a) Fabrication process flow of the double exposure structure. **(b)** Optical images of the excerpt of the poem *Saying Good-bye to Cambridge Again* without the second exposure, which is tunable by switching humidity between 40 and 100% RH. **(c)** SEM images of the corresponding structures.

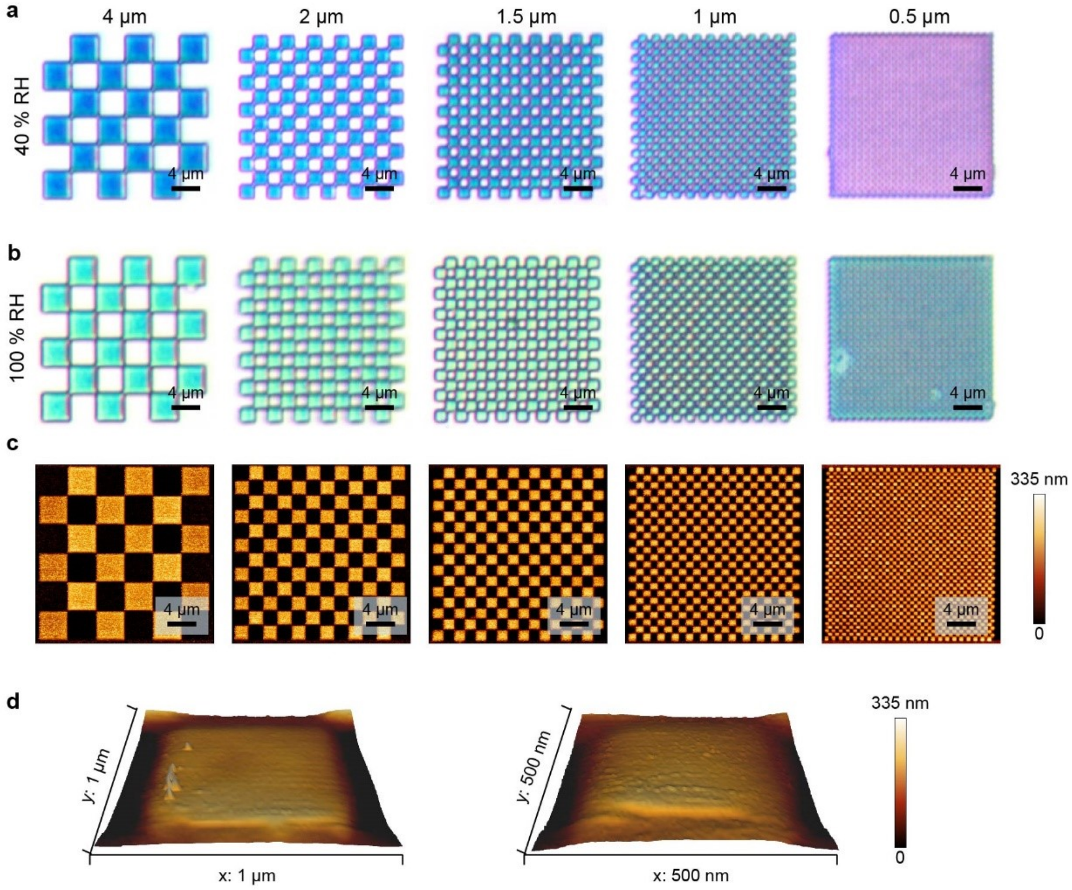


Figure S10. Optical images of checkerboard patterns with the pitch of 4, 2, 1.5, 1 and 0.5 μm, captured at **(a)** 40 % RH and **(b)** 100 % RH. **(c)** AFM images of the corresponding structures. **(d)** Zoomed-in AFM images of patterns with the pitch of 1 and 0.5 μm.