Supporting Information

Unraveling the Mechanism of Coloration and Prolonged Discoloration in Abnormally Thermochromic PDMS Nanocomposites

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Supplementary Text
Figs. S1 to S25

Calculation of fractions of voids and water moisture based on the effective medium theory

We use Bruggeman effective medium approximation[1] to calculate the effective refractive index of the composite. When the composite consists of i components, with each component having a refractive index n_i and a volume fraction Φ_i, the effective refractive index of the composite can be calculated from the equation:

$$\sum_i \Phi_i \left(\frac{n_i^2 - n_{eff}^2}{n_i^2 + 2n_{eff}^2} \right) = 0 \#(1-1)$$

At 100 ℃, the composite consists of PDMS (n = 1.378 @589 nm), SiO_2 (n = 1.458 @589 nm), and air in voids (n = 1.000 @589 nm) (Figure 4A). The volume fraction ratio of SiO_2 to PDMS is 4:6. Importing the known parameters to equation (1-1), we calculate that the volume fraction of voids is 9.69%. After cooling to 20 ℃ and in equilibrate state, the voids are occupied by both air and moisture (n = 1.33 @589 nm) and the refractive index of PDMS and the same silica-PDMS film increases to 1.406 and 1.395 @589 nm. We assume the volume fraction of the void remains to be 9.69% at 20 ℃ considering the volume decreases only by 6.82% for PDMS based on the thermal expansion coefficient (Fig. S24). We calculate that the volume fractions of air and moisture are respectively 6.54% and 3.15% at 20 ℃. We then convert the weight percentage of moisture to be 2.39%.

Rayleigh scattering model

We apply Rayleigh scattering theory to calculate the scattering by air voids in PDMS matrix. When the incident light is unpolarized with irradiance I_0, the irradiance I_s of scattered light is:

$$I_s = \frac{8\pi^4 N a^6}{\lambda^4 r^2} \left| \frac{n^2 - 1}{n^2 + 2} \right|^2 (1 + cos^2\theta) I_0, \#(1-2)$$

where N is the number density of particles, a is the size of scattered particles, λ is wavelength of light, r is the distance between the scattered particles and observer, n is the refractive index of the particles, and θ is the scattering angle.[2] According to equation (1-2), the ratio of scattered light to incident light, I_s/I_0, is proportional to λ^{-4}. By setting the coefficient to be a constant, we obtain the spectra in wavelengths of 420 nm to 800 nm.

Multiple scattering model

To calculate the reflectance spectra of silica-PDMS film, we use a multiple scattering model developed by Manoharan Group.[3,4] In this model, the light propagates into the film and the trajectories of photons are recorded. We obtain the reflectance and transmittance spectra by

calculating the percentage reflected or transmitted out of the sample. More details on the simulation principles and Python codes are well documented in the reference.[3,4] In our simulation, the SiO_2 nanoparticles are distributed in PDMS matrix with a disordered packing. Input parameters include the refractive index of SiO_2 nanoparticles and PDMS matrix, size and volume fraction of nanoparticles and thickness of the sample.

To understand how the arrangement of SiO_2 nanoparticles affects the coloration, we decouple the volume fraction from structure factor following our previous work.[5] The structure factor is obtained from Percurs-Yevick approximation, which is a function of volume fraction. We use two structure factors in the simulations: one is Percurs-Yevick structure factor with volume fraction of 64% to represent a hard-sphere close packing state with short-range order; the other one is set to be 1, meaning there is no correlation between particles.

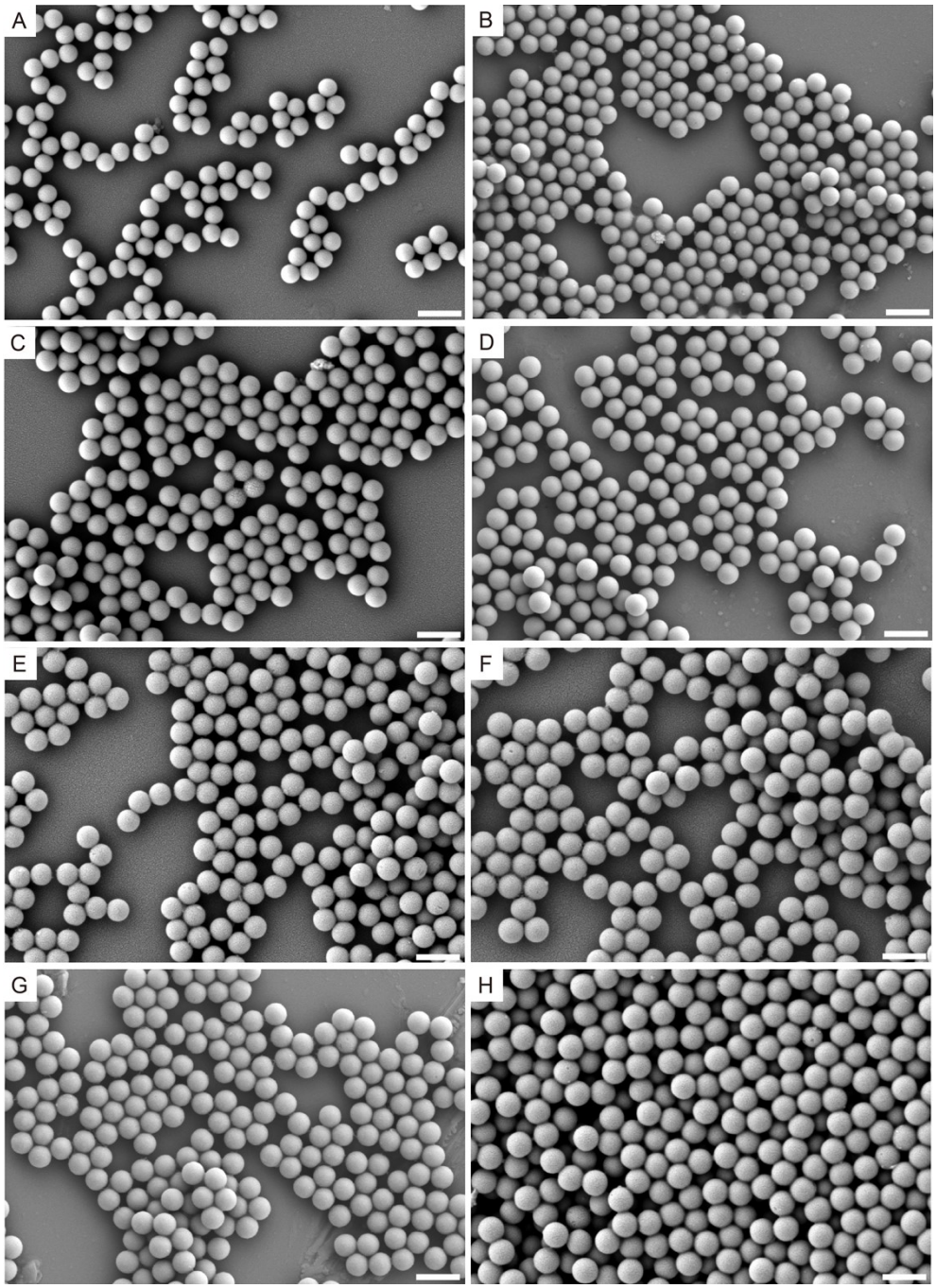

Fig. S1. SEM images of silica nanoparticles with various diameters before (A, C, E, G) and after (B, D, F, H) surface modification. (A, B) 219 ± 4 nm, (C, D) 241 ± 5 nm, (E, F) 264 ± 6 nm, and (G, H) 286 ± 6 nm. Scale bars: 500 nm.

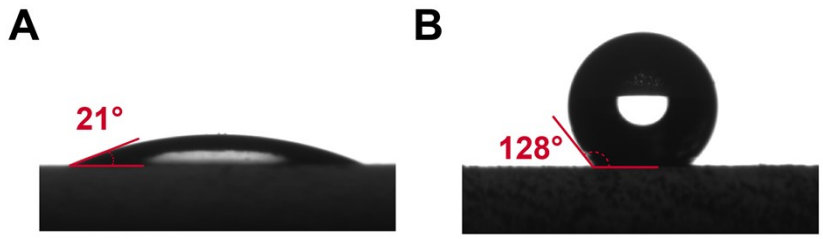

Fig. S2. Water contact angle measurements of unmodified (A) and modified SiO_2 (B) films. Both films are made by spin-coating an ethanol solution of SiO_2.

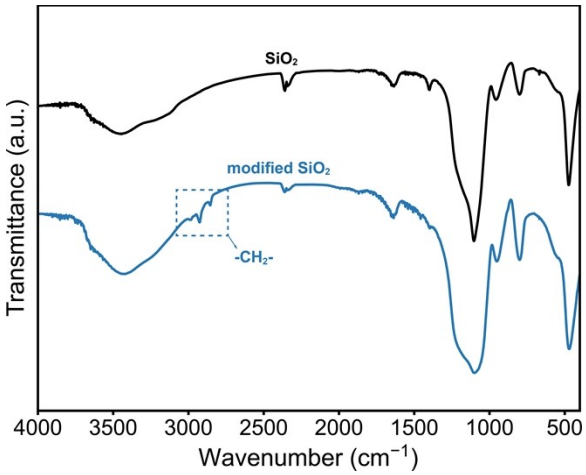

Fig. S3. FTIR spectra of unmodified and modified SiO_2 nanoparticles.

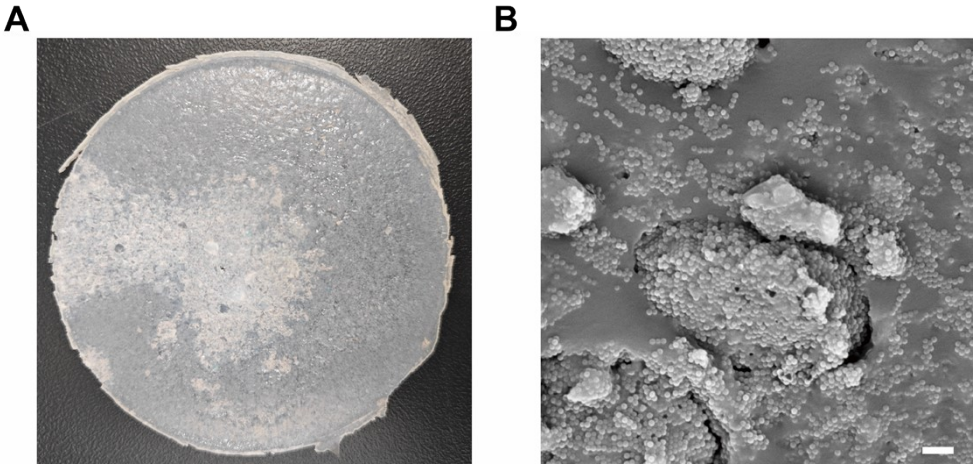

Fig. S4. (A) Photograph of PDMS film blended with unmodified SiO_2 nanoparticles. (B) Cross-sectional SEM image of the film. Scale bar: 2 μm.

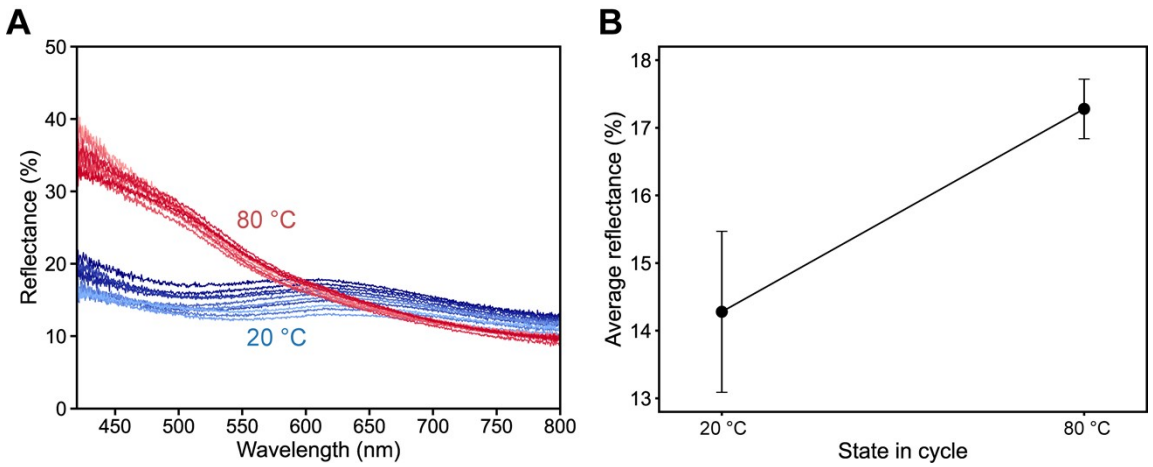

Fig. S5. (A) Reflectance spectra of sample with 40% v/v SiO_2 particles of 240 nm in 10 heating and cooling cycles. (B) Average reflectance calculated from the reflectance spectra for ten cycles.

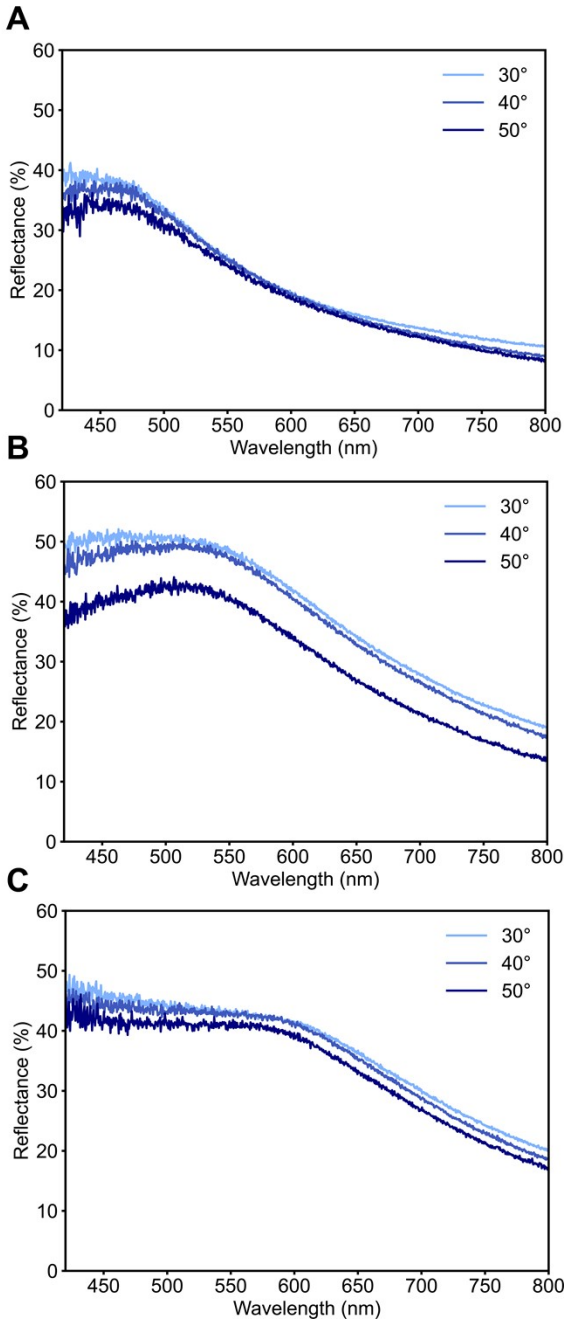

Fig. S6. Angle-resolved reflectance spectra of heated silica-PDMS films containing 40 %v/v SiO_2 of nanoparticles with diameters, (A) 220 nm, (B) 260 nm, and (C) 280 nm. The incident light is normal to the sample surface with varied detection angles from 30° to 40° and 50°.

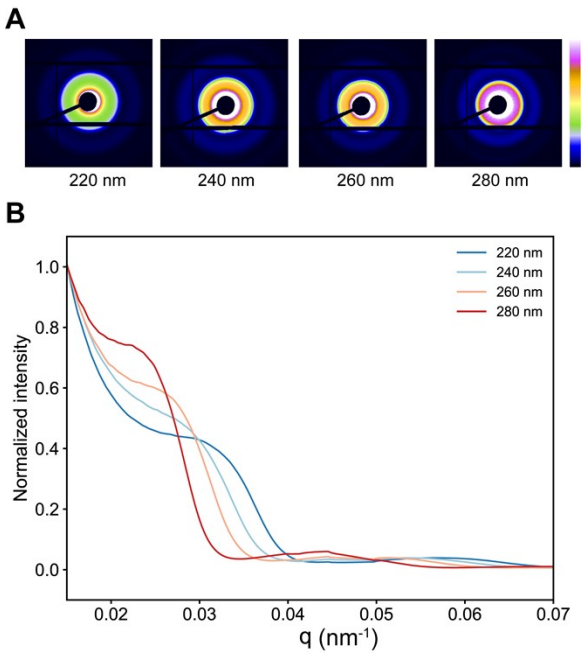

Fig. S7. (A) 2D USAXS images of silica-PDMS films with different particle size, volume fraction is 40 %v/v. (B) 1D curves of the sample integrated from 2D images in q space.

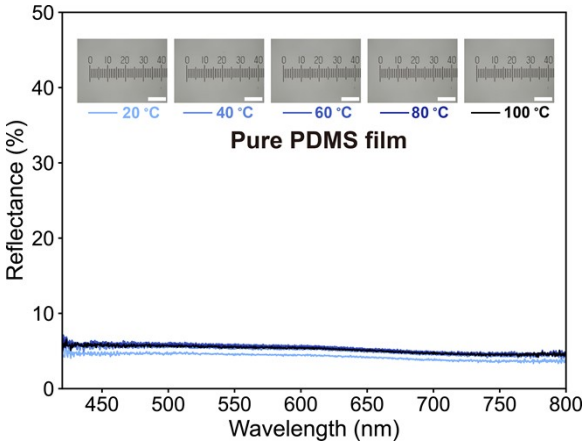

Fig. S8. Equilibrated reflectance spectra and microscopic images of a pure PDMS film from 20 ℃ to 100 ℃. Scale bars in insets: 500 μm.

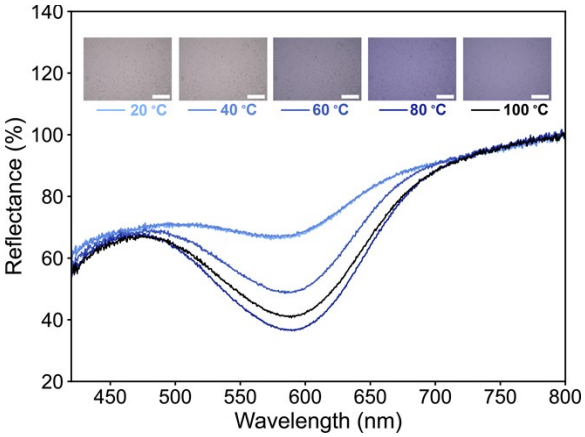

Fig. S9. Equilibrated reflectance spectra and microscopic images of commercial thermochromic pigmentary powder (Shengzhen Huancaibs) from 20 ℃ to 100 ℃. Scale bars in insets: 500 μm.

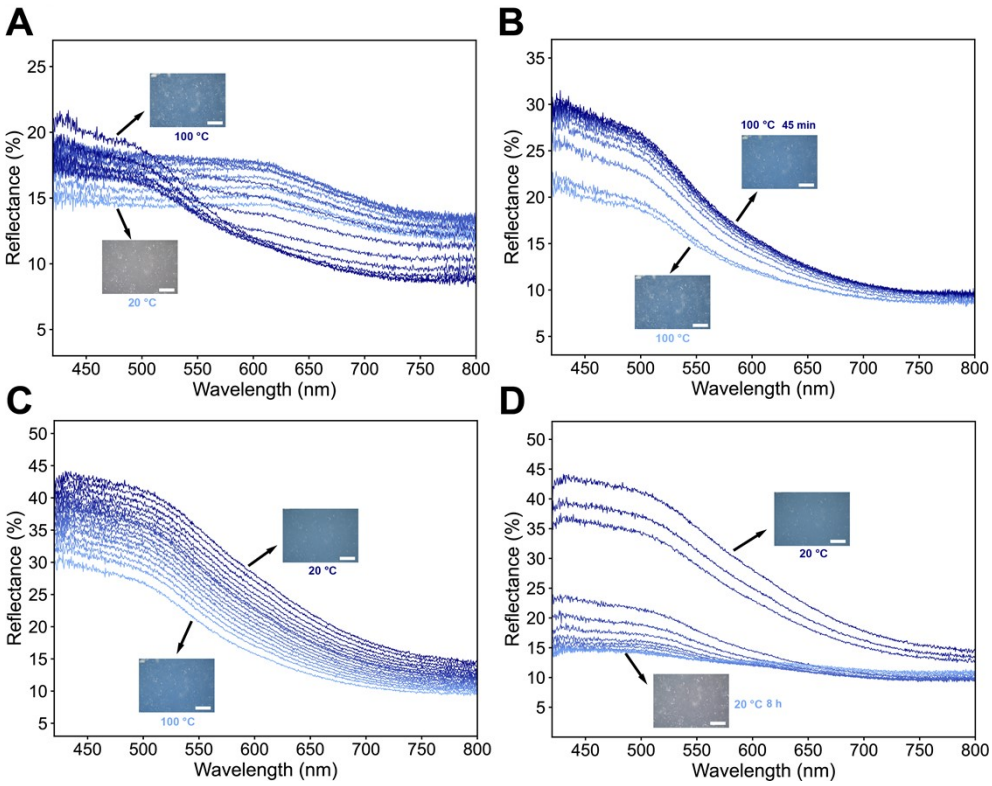

Fig. S10. Reflectance spectra of the silica-PDMS film with 40% v/v 240 nm SiO_2 particles in a heating and cooling circle. (A) Reflectance spectra measured every 2.5 minutes at a heating rate of 2 ℃/min. (B) Reflectance spectra measured every 5 minutes at 100 ℃ for 45 min. (C) Reflectance spectra every 2.5 minutes at a cooling rate of 2 ℃/min. (D) Reflectance spectra measured every 1 hour at 20 ℃ for 8 hours. Scale bars: 500 μm.

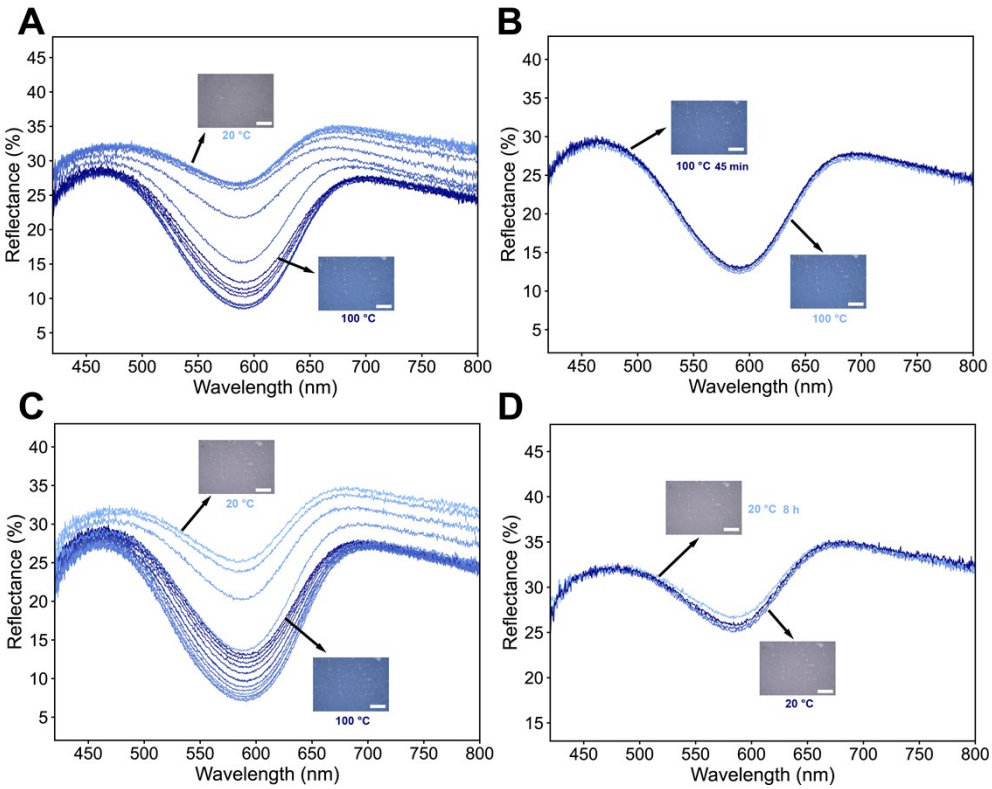

Fig. S11. Reflectance spectra of the TPM film during a heating and cooling circle. (A) Reflectance spectra measured every 2.5 minutes at a heating rate of 2 ℃/min. (B) Reflectance spectra measured every 5 minutes at 100 ℃ for 45 min. (C) Reflectance spectra every 2.5 minutes at a cooling rate of 2 ℃/min. (D) Reflectance spectra for 8h, measured at 0 h, 4 h, and 8 h at 20 ℃. Scale bars: 500 μm

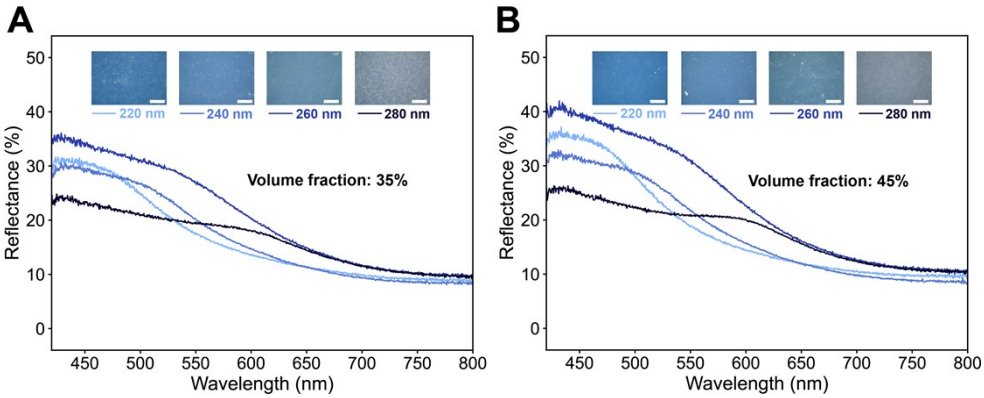

Fig. S12. Equilibrate reflectance spectra of silica-PDMS films with varied sizes and volume fractions of silica nanoparticles at 100 ℃. (A) Volume fraction is fixed at 35% with particle diameters of 220 nm, 240 nm, 260 nm, and 280 nm. (B) Volume fraction is fixed at 45% with particle diameters of 220 nm, 240 nm, 260 nm and 280 nm. Scale bars: 500 μm.

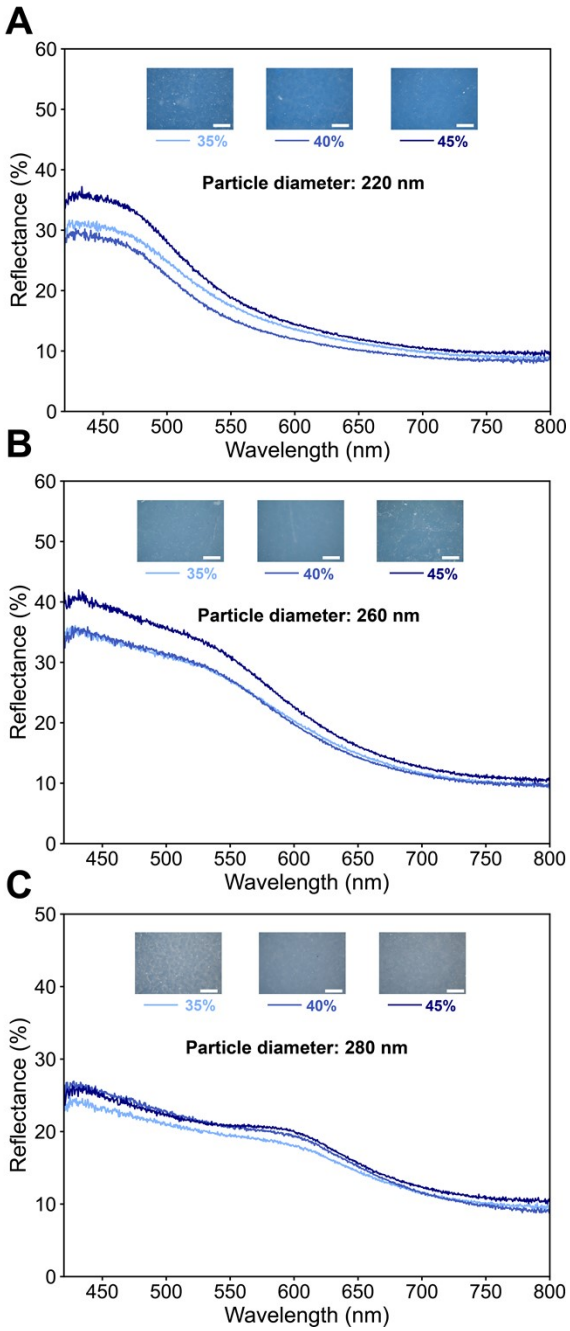

Fig. S13. Equilibrate reflectance spectra of silica-PDMS films with varied sizes and volume fractions of silica nanoparticles at 100 ℃. (A) Particle diameter is fixed at 220 nm with volume fractions of 35%, 40% and 45%. (B) Particle diameter is fixed at 260 nm with volume fractions of 35%, 40% and 45%. (C) Particle diameter is fixed at 280 nm with volume fractions of 35%, 40% and 45%. Scale bars: 500 μm.

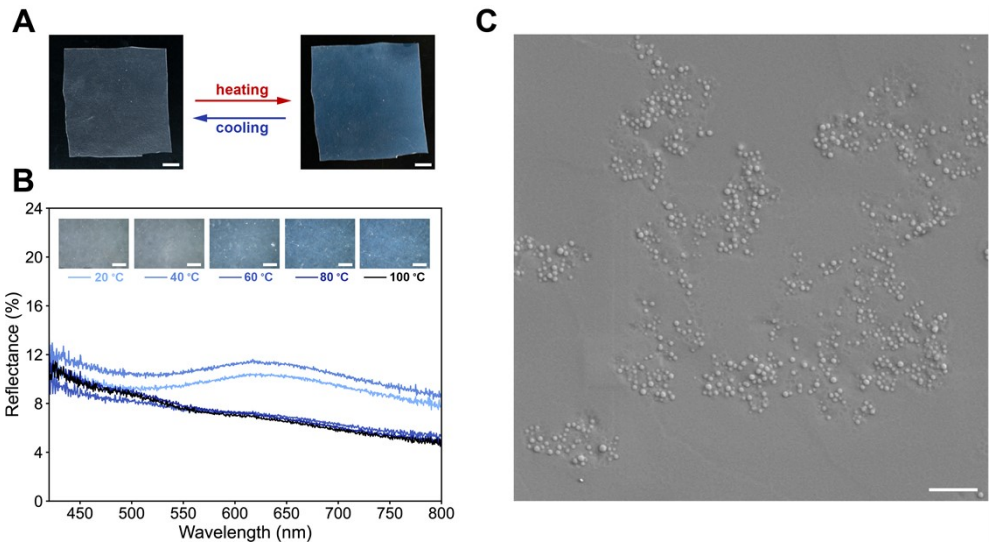

Fig. S14. Characterization of silica-PDMS film with SiO_2 of 240 nm diameter and volume fraction of 5%. (A) Photos of the film with SiO_2 of 240 nm diameter and volume fraction of 5% on 20 ℃ and 80 ℃ heating stage. The film is placed on a black background. Scale bars: 5 mm. (B) Stable reflectance spectra and microscopic photos at various temperature. Scale bars: 500 μm. (C) Cross-sectional SEM image of the film, Scalebar: 2 μm.

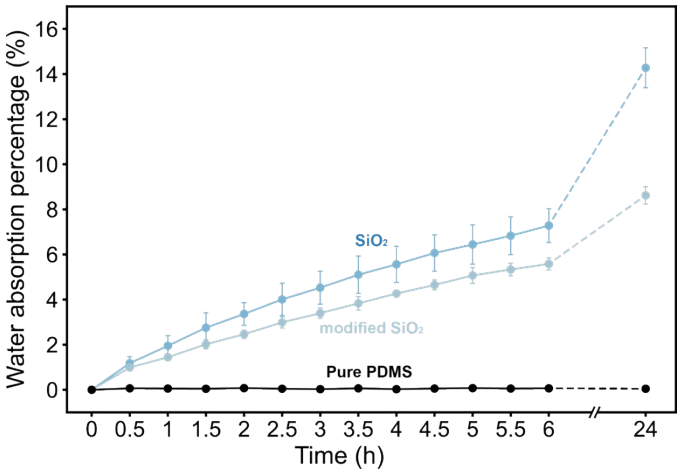

Fig. S15. Water absorption weight percentage of pure PDMS, unmodified and modified SiO_2 nanoparticles at relative humidity of 100% and 20 ℃.

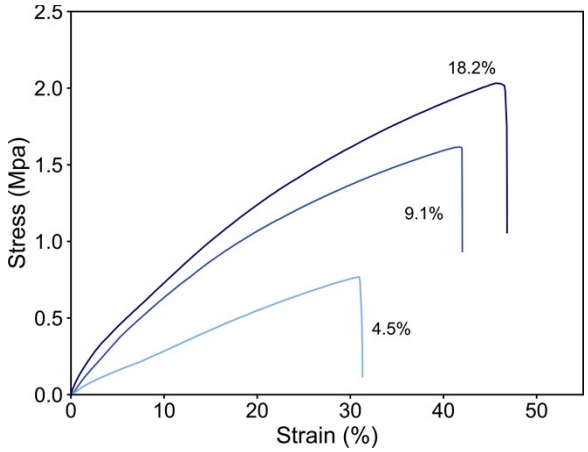

Fig. S16. Stress-strain curves of silica-PDMS films with 4.5%, 9.1% and 18.2% w/w crosslinker.

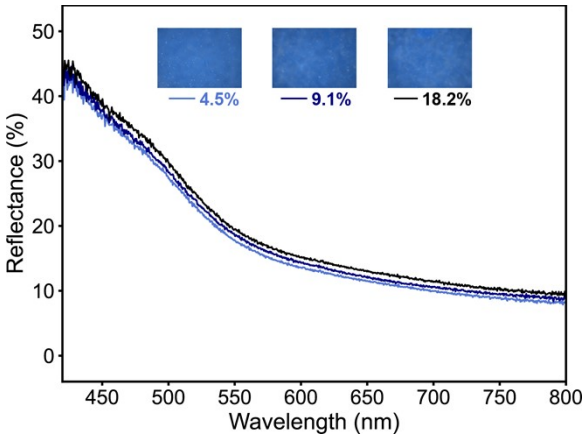

Fig. S17. Reflectance spectra of silica-PDMS films with crosslinker percentages of 4.5%, 9.1%, and 18.2% w/w when equilibrated at 100 ℃。

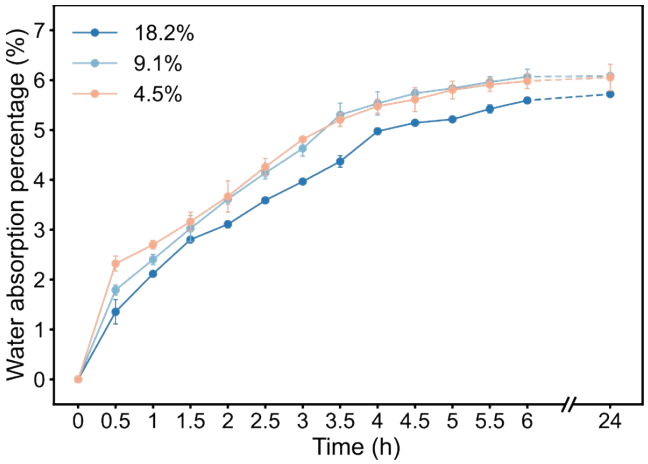

Fig. S18. Water absorption weight percentage of silica-PDMS films with crosslinker ratios of 4.5%, 9.1%, and 18.2% at Rh = 75%.

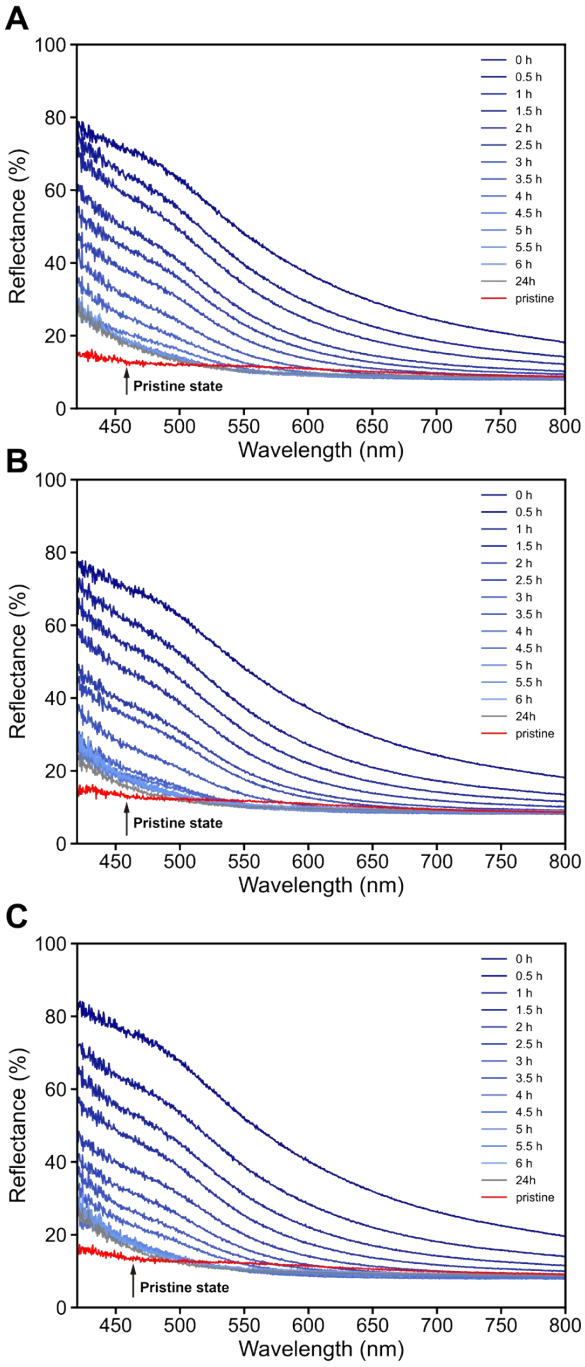

Fig. S19. Dynamic reflectance spectra of silica-PDMS films with different crosslinker densities of PDMS after taken equilibrated at 100 °C to the ambient temperature (around 20 °C, Rh = 75%). The weight percentage of the crosslinker is (A) 4.5% w/w, (B) 9.1% w/w, and (C) 18.2% w/w.

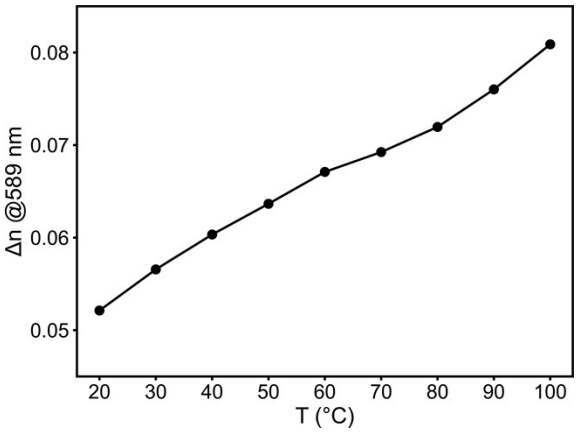

Fig. S20. Refractive index contrast between silica nanoparticles and PDMS at different temperature.

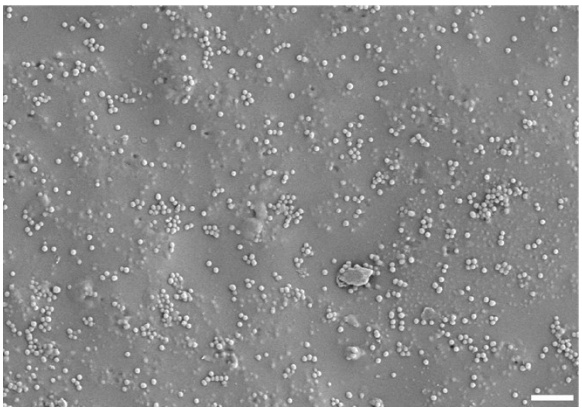

Fig. S21. Top view SEM image of silica-PDMS film with 40% v/v silica nanoparticles (240 nm). Scale bar is 2 μm.

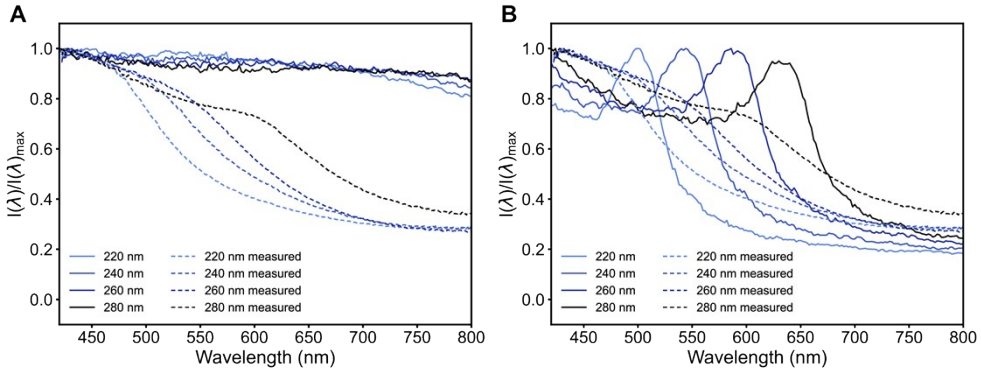

Fig. S22. Simulated and measured spectra of silica-PDMS films with different particle sizes and a fixed volume fraction of 40%. (A) The spectra are calculated with the structure factor of 1. (B) The spectra are calculated with the Percus-Yevick structure factor with volume fraction of 64%.

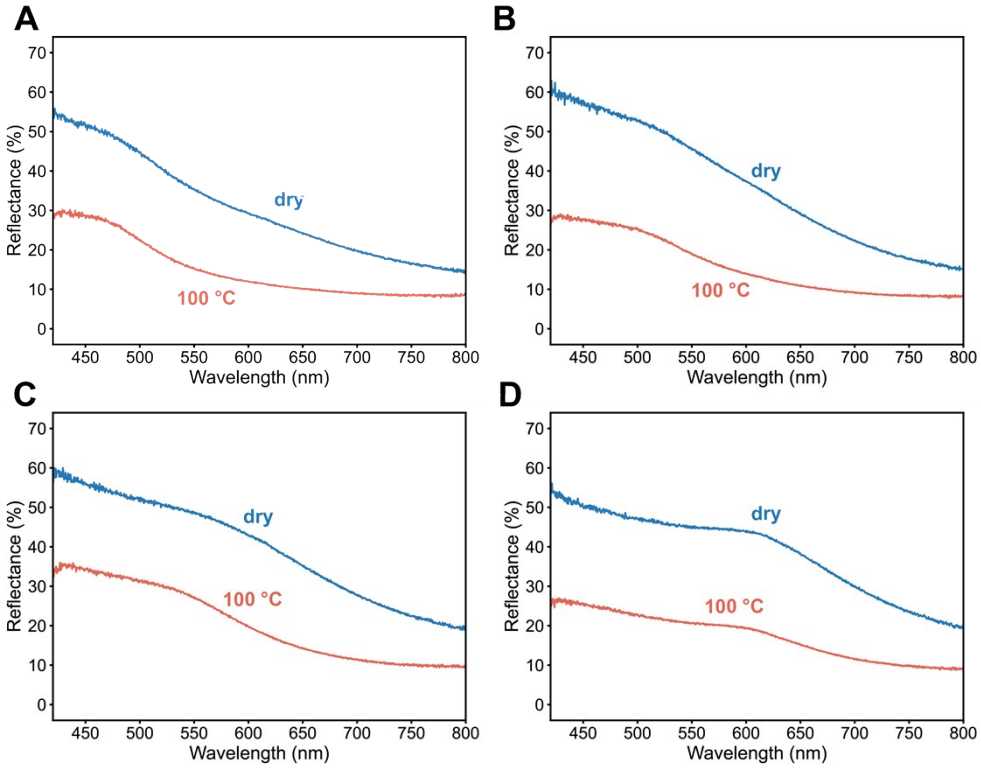

Fig. S23. Comparison of reflectance spectra of silica-PDMS films between 100 ℃ equilibrated state and completely dry state at 20 ℃. The particle diameters and volume fractions are: (A) 220 nm, 40%, (B) 240 nm, 40%, (C) 260 nm, 40%, (D) 280 nm, 40%.

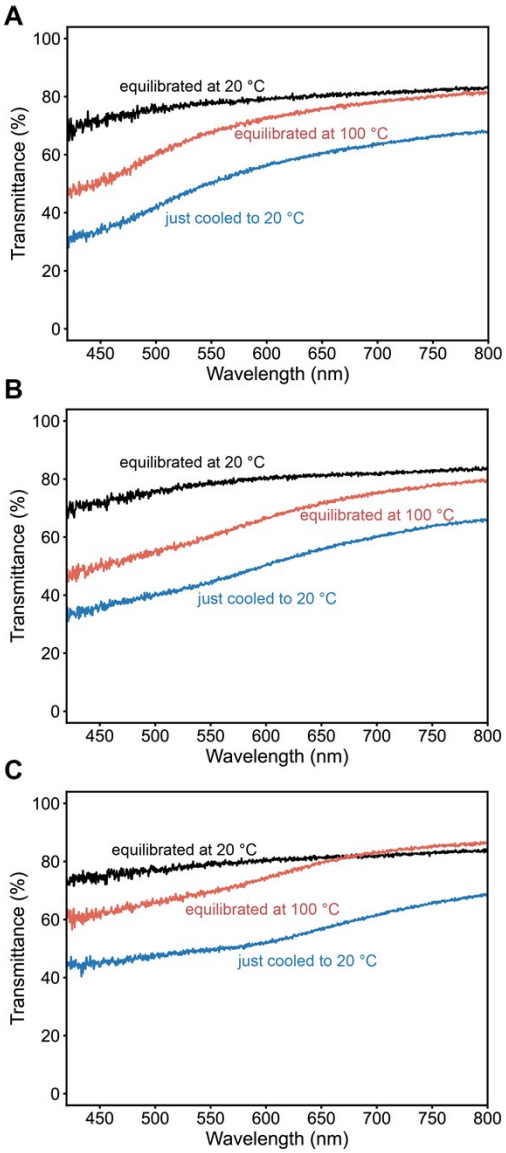

Fig. S24 Transmittance spectra of silica-PDMS films at 3 different states. The diameters and volume fractions are (A) 220 nm, 40%. (B) 260 nm, 40%. (C) 280 nm, 40%.

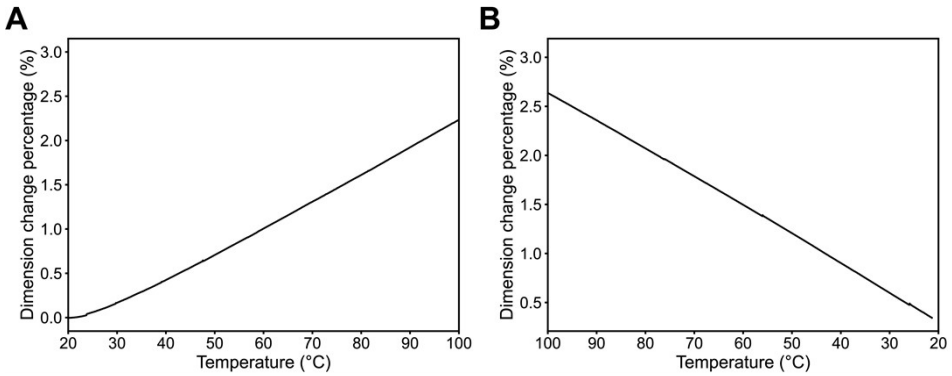

Fig. S25. Linear dimensional change percentage ($^{\Delta L/L_0)}$ of pure PDMS in heating (A) and cooling (B). Heating and cooling rate: 5 ℃/min. The calculated linear expansion coefficient is 3.05×10^{-4} and the linear shrinkage coefficient is 2.84×10^{-4}.

1. D. a. G. Bruggeman, *Annalen der Physik*, 1935, **416**, 636–664.

2. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, 2008.

3. V. Hwang, A. B. Stephenson, S. Barkley, S. Brandt, M. Xiao, J. Aizenberg, V. N. Manoharan, Designing Angle-independent Structural Colors Using Monte Carlo Simulations of Multiple Scattering. *Proc Natl Acad Sci USA* **118**, e2015551118 (2021).

4. A. B. Stephenson, M. Xiao, V. Hwang, L. Qu, P. A. Odorisio, M. Burke, K. Task, T. Deisenroth, S. Barkley, R. H. Darji, V. N. Manoharan, Predicting the Structural Colors of Films of Disordered Photonic Balls. *ACS Photonics* **10**, 58–70 (2023).

5. M. Xiao, A. B. Stephenson, A. Neophytou, V. Hwang, D. Chakrabarti, V. N. Manoharan, Investigating the Trade-off Between Color Saturation and Angle-independence in Photonic Glasses. *Opt. Express* **29**, 21212 (2021).