Supplementary Materials for

Anisotropic Mechano-Adaptive Cavitation in Elastomer for Unclonable Covert–Overt Anti-counterfeiting

Huaixia Zhao, Boya Li, Yangxin Wang, Xiaozhuang Zhou, and Jiaxi Cui

Correspondence to: jiaxi.cui@uestc.edu.cn; zhaohx@njtech.edu.cn

Section S1. Fabrication Methods

The *a*-DPDMS-0.2-100 films with different elastic moduli. The same protocol described in the main text was used to prepare the samples. The PDMS precursors with different base/curing agent ratios (10:1.2, 10:0.9, and 10:0.6) led to the samples with different moduli (2.2, 1.5, 0.8 MPa). All obtained films were transparent.

Patterning *a*-DPDMS-PDMS hybrid films (Chinese character and barcode). The *a*-DPDMS-0.2-100 (std) film was fabricated and cut into designed shapes of Chinese characters. These obtained *a*-DPDMS pieces were then put into PDMS precursors in the designed way respectively, followed by annealing at 70°C for 1 hour to fix these pieces into four thin PDMS films. After that, these PDMS films were coated with PDMS precursor, followed by being combined layer by layer into one hybrid sample. The hybrid sample was then annealed at 70°C for 10 hours, resulting in transparent hybrid film.

The fabrication of the patterning hybrid film with barcode follows the similar processing. The pieces of *a*-DPDMS bars with designed widths were fixed onto the substrate in the designed orders with the PDMS precursor as the adhesive (70°C for 1 hour). After that, the fixed pieces were completely covered with more PDMS precursor and followed by degasing and curing process (70°C for 10 hours), resulting in the transparent hybrid film.

Patterning isotropic DPDMS-PDMS hybrid films (crossed cubic spaces).

To a mould with crossed cubic spaces, normal PDMS precursor and the PDMS/water emulsion were separately injected. After degassing, the mould was removed and the confluent casting was pre-cured in a sealing condition at 70°C for 4 hours. The sample was then exposed to air at 70°C for another 20 hours curing. A transparent sample was obtained.

Patterning *a*-DPDMS-PDMS hybrid films (crossed cubic spaces). To a mould with crossed cubic spaces, normal PDMS precursor and the PDMS/water emulsion were separately injected. After degassing, the mould was removed and the confluent casting was pre-cured in a sealing condition at 70°C for 20 minutes, after which the pre-cured coating was peeled off from the substrate, followed by pre-stretching with 100 % elongation under the sealing condition for 4 hours curing at 70°C. The stretched sample was then exposed to air at 70°C for another 20 hours curing. A transparent sample was obtained.

Patterning *a*-DPDMS-PDMS hybrid films (the programmable 2D codes). As shown in Fig. S12, in order to get the patterns shown in Figures 4d and 4e, two *a*-DPDMS-PDMS pieces (piece i and piece ii) with different cubic spaces patterns was integrated into one hybrid film with commercial PDMS as the adhesive. With parallel stretch, 4×4 2D code was displayed on the piece i layer. With subsequent perpendicular stretch, the pattern on the piece ii layer appeared. Together with the 4×4 2D code on the piece i layer and the patterns on the piece ii layer, a 5×5 2D code was thus displayed on the hybrid sample after the two-steps stretching.

Patterning *a*-DPDMS-PDMS hybrid films (flowers). In the preparation of the flowers patterns, the same protocol as that for preparing anisotropic crossed cubic spaces patterns was employed but a mould with a flower-shaped space was used. Briefly, the PDMS/water emulsion and normal PDMS precursor were subsequently put into the different regions of the mould, followed by degasing, mould-removing, pre-stretching, step curing and evaporation, resulting in transparent films.

Section S2. Fig.S and related results

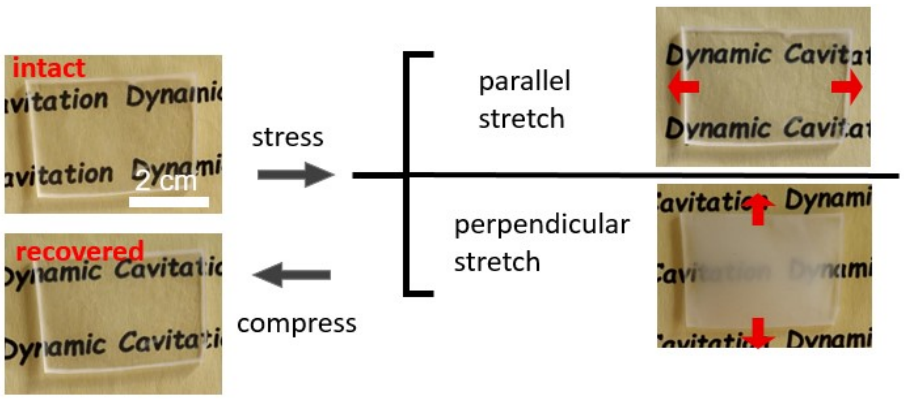

Fig. S1 Photographs of the as-prepared film *a*-DPDMS-0.2-100 (std) after different treatments.

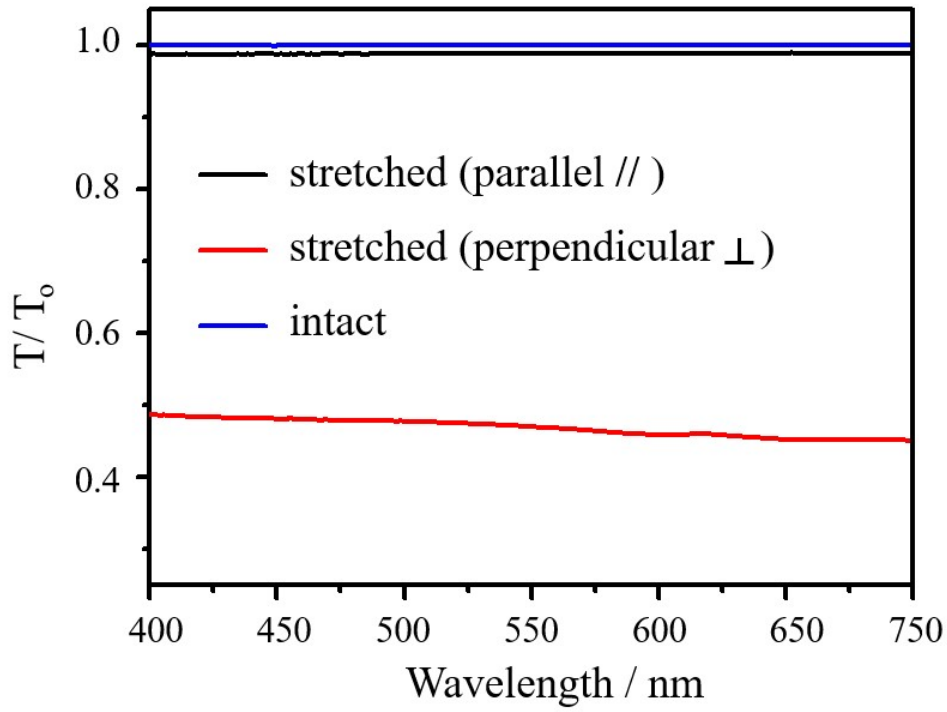

Fig. S2 Corresponding transmittances of the film *a*-DPDMS-0.2-100 (std) after different treatments.

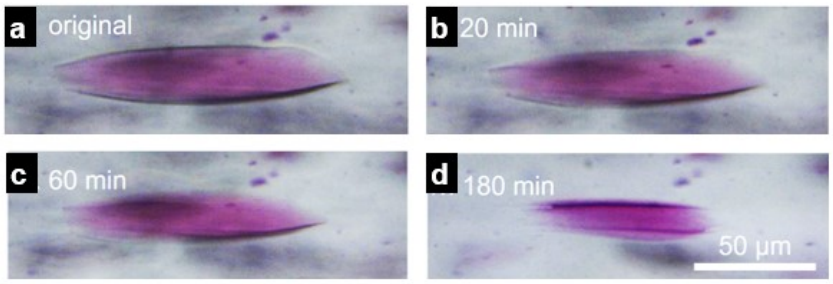

Fig. S3 Optical microscope images of an elliptical water droplet entrapped in a PDMS matrix at different evaporation time. The coating was procured at 70°C for 20 min, then peeled off from the substrate and stretched by 100% elongation, followed by curing at 70°C in a sealed condition for 4 hours. The images were then captured at 70°C in air with the situ-observation under optical microscope.

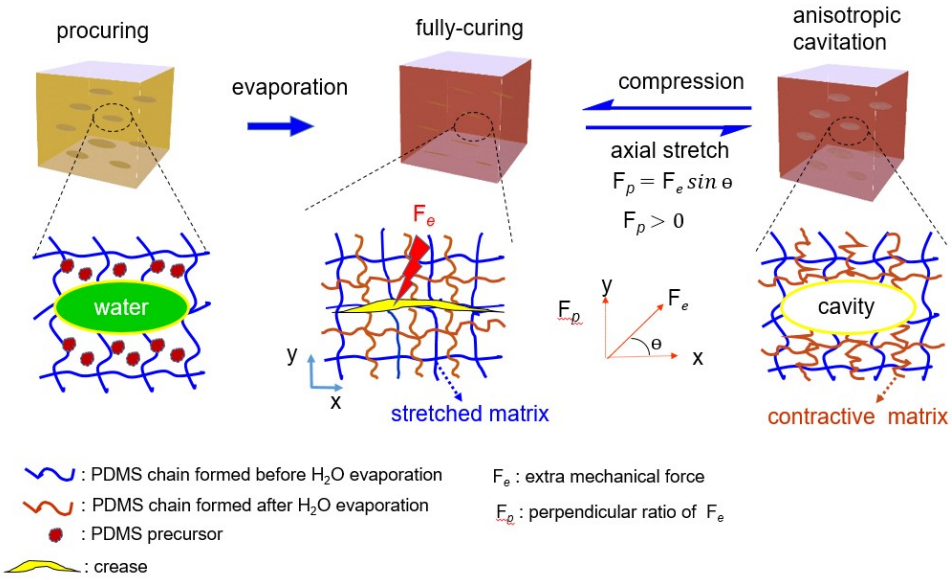

Fig. S4 The schematics of mechanisms resulting in the anisotropic cavitation.

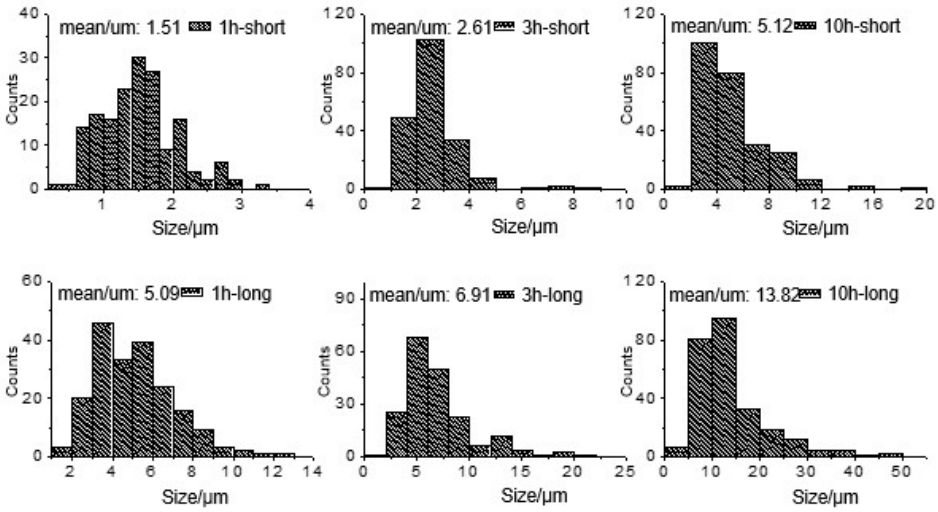

Fig. S5 The size distributions of the ellipsoidal cavities in the *a*-DPDMS-0.2-100 films fabricated with different sealing times. The labels show the sealing time and the size data collected at different aspects. The films were stretched by 150% in Y-direction before testing, and then released.

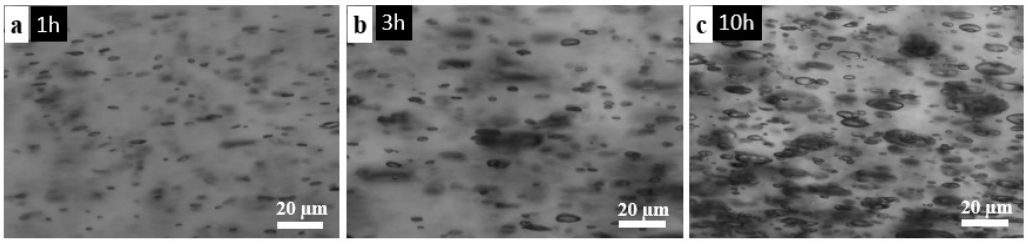

Fig. S6 Optical microscope images of the cavities in the *a*-DPDMS-0.2-100 films fabricated with different sealing times (1, 3, or 10h). Before imaging, the tested films were stretched by 150% in Y-direction, and then released.

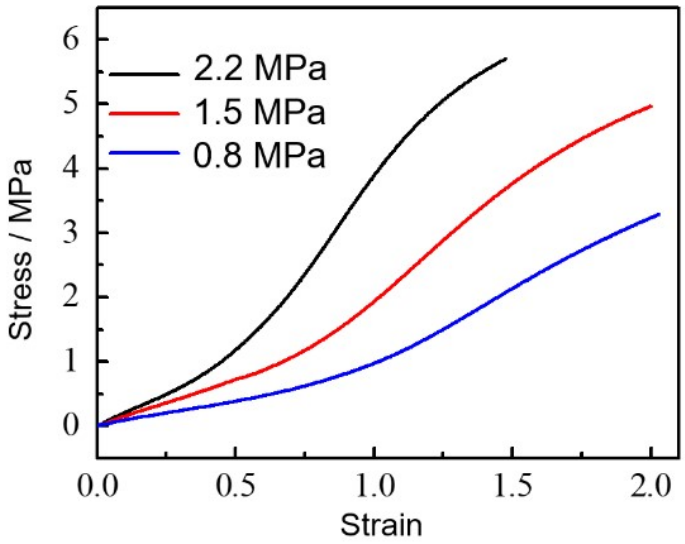

Fig. S7 The tensile tests of the anisotropic films *a*-DPDMS-0.2-100 (2.2 MPa), *a*-DPDMS-0.2-100 (1.5 MPa), and *a*-DPDMS-0.2-100 (0.8 MPa).

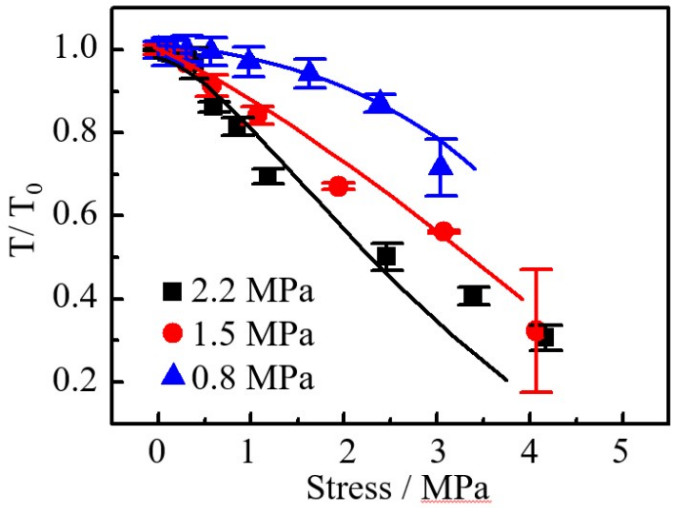

Fig. S8 Optical transmittance changes of anisotropic films *a*-DPDMS-0.2-100 (2.2 MPa), *a*-DPDMS-0.2-100 (1.5 MPa), and *a*-DPDMS-0.2-100 (0.8 MPa) as function of stress. T: Ttransmittance after treatment; T_o: Transmittance before treatment.

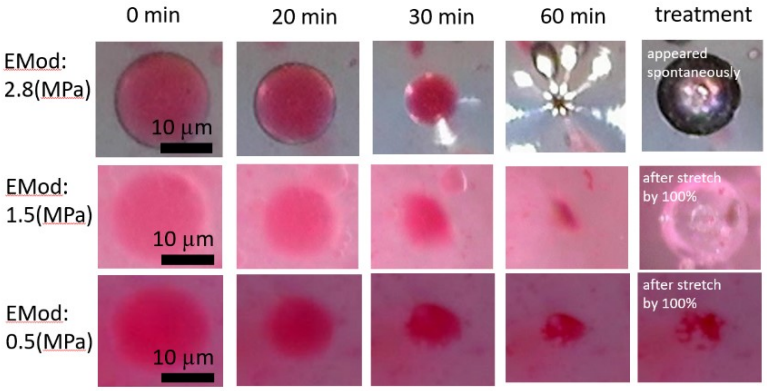

Fig. S9 Optical microscope images of the water inclusions, the formed crease, and the cavities in PDMS matrices with different elastic moduli. The only difference for the fabrication of these tested DPDMS films here from that of *a*-DPDMS films is the absence of pre-stretching in the curing process.

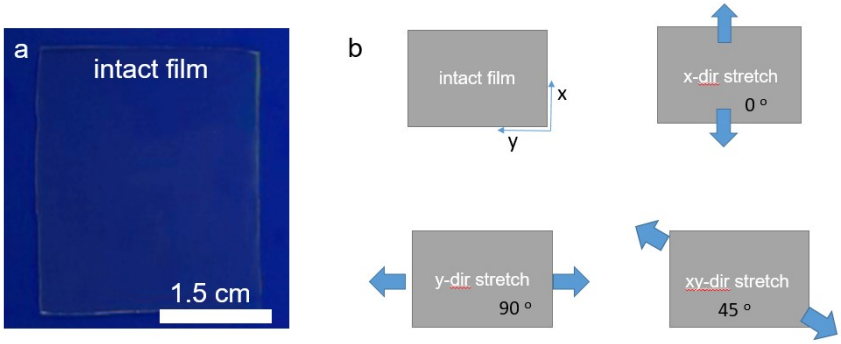

Fig. S10 The photograph of the intact *a*-DPDMS-PDMS hybrid film (Chinese character) (a) and the schematics for the mechanical treatment for this film as shown in Fig. 3 (b).

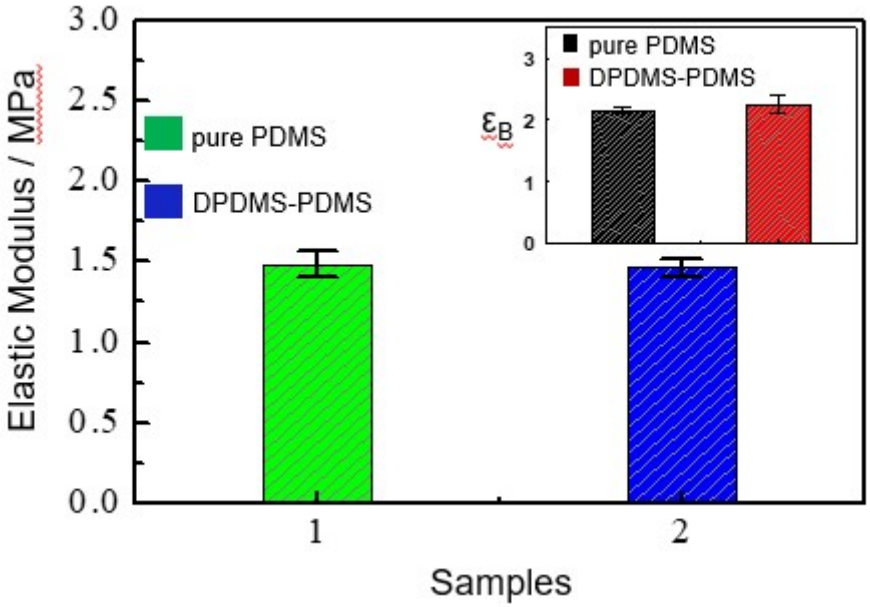

Fig. S11 The mechanical properties of the normal pure PDMS elastomer and the DPDMS-PDMS hybrid film shown in Fig. 4 (c).

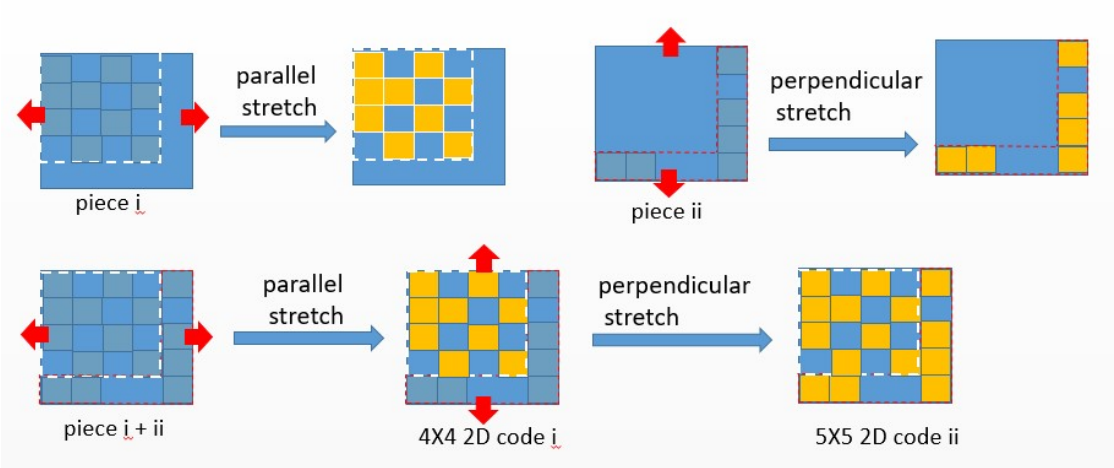

Fig. S12 The schematics for the fabrication and the mechanical adaptive response of the patterned sample shown in Fig. 4 (d, e).