#### MATERIALS SCIENCE

# Near-infrared light-responsive dynamic wrinkle patterns

Fudong Li, Honghao Hou, Jie Yin, Xuesong Jiang\*

Dynamic micro/nanopatterns provide an effective approach for on-demand tuning of surface properties to realize a smart surface. We report a simple yet versatile strategy for the fabrication of near-infrared (NIR) light-responsive dynamic wrinkles by using a carbon nanotube (CNT)-containing poly(dimethylsiloxane) (PDMS) elastomer as the substrate for the bilayer systems, with various functional polymers serving as the top stiff layers. The high photonto-thermal energy conversion of CNT leads to the NIR-controlled thermal expansion of the elastic CNT-PDMS substrate, resulting in dynamic regulation of the applied strain ( $\varepsilon$ ) of the bilayer system by the NIR on/off cycle to obtain a reversible wrinkle pattern. The switchable surface topological structures can transfer between the wrinkled state and the wrinkle-free state within tens of seconds via NIR irradiation. As a proof-of-concept application, this type of NIR-driven dynamic wrinkle pattern was used in smart displays, dynamic gratings, and light control electronics.

#### **INTRODUCTION**

Micro/nanoscale surface patterns that can endow materials with unique and intriguing physical, chemical, and biological properties have attracted growing scientific interest (1-9), with a particular focus on the exploitation of dynamic surface patterns to realize a controllable adjustment of surface properties such as optical characteristics, friction, wettability, and adhesion (3, 10-23). Among numerous alternative processes for generating patterned surfaces, especially with dynamic morphology, surface wrinkles of a stiff skin bound to an elastomeric substrate have been harnessed to create reversible patterns that are responsive to external stimuli and provide unique dynamic characteristics of surface morphology and properties. Wrinkles occur to minimize the total energy of the bilayer system when the compressive strain  $(\varepsilon)$ , caused by the modulus mismatch between the skin layer and the substrate induced by thermal, mechanical, or osmotic stimuli, exceeds the critical threshold ( $\varepsilon_c$ ), defined by the mechanical properties of the bilayer system (24-28). According to linear buckling theory, the characteristic amplitude (A) of the sinusoidal wrinkles can be predicted on the basis of the applied strain  $\varepsilon$  in the system (13), as in Eq. 1

$$\ln(A^2 + h_{\rm f}^2) = \ln 4\varepsilon + \left(\ln 2h_{\rm f} + \frac{2}{3}\ln\overline{E_{\rm f}} + \frac{2}{3}\ln 3\overline{E_{\rm s}}\right)$$
(1)

Here, A,  $h_f$ ,  $\varepsilon$ , and  $\overline{E}$  represent the amplitude of the wrinkles, the thickness of the skin layer, the applied strain, and the plane-strain modulus, respectively, and the subscripts f and s refer to the skin layer and the substrate in the bilayer system. For a given thermally induced wrinkle system, the compressive strain can be estimated as

$$\mathbf{\varepsilon} = (\alpha_{\rm s} - \alpha_{\rm f}) \times \Delta T \tag{2}$$

where  $\alpha_s$  and  $\alpha_f$  are the linear thermal expansion coefficients for the substrate and the skin layer, respectively, and  $\Delta T$  represents the temperature variation. If the parameters  $h_f$  and  $\overline{E_s}$  are fixed, then the modulus of the top layer ( $\overline{E_f}$ ) and the applied strain ( $\varepsilon$ ) can be used as control parameters for the regulation of the formation and size of wrinkle patterns.

School of Chemistry and Chemical Engineering, State Key Laboratory for Metal Matrix Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China.

\*Corresponding author. Email: ponygle@sjtu.edu.cn

Copyright © 2018 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

Downloaded from http://advances.sciencemag.org/ on April 6, 2018

By precisely regulating the modulus of the top layer  $(\overline{E_f})$  and the applied strain ( $\epsilon$ ), a series of dynamic wrinkles with responsive morphology have been developed on the basis of bilayer systems; for example, the wrinkle pattern can be tailored reversibly through externally imposed stimuli such as wetting and dewetting of the solvent (4, 29-32) and the stretch and release of prestrain (3, 33-38). Seki et al. (39) and Lu et al. (40) demonstrated the light-erasable wrinkles on a poly(dimethylsiloxane) (PDMS) substrate, respectively, in which the top azobenzene-containing polymer layer could be softened and compressive stress released by the trans/cis photoisomerization of azobenzene moieties upon illumination. By regulating the modulus and cross-linking density of the skin layers via the dynamic chemistry, such as the reversible Diels-Alder reaction, photodimerization, and supramolecular chemistry, our group recently developed a facile strategy for the fabrication of multiresponsive dynamic wrinkling patterns (13, 41, 42). To mimic the wrinkling phenomenon of finger skin after prolonged exposure to water, Sun and co-workers (29) demonstrated three types of moisture-responsive wrinkles by tailoring the cross-link degree/gradient of the polyvinyl alcohol top layer to allow for moisture-dependent changes in the modulus and swelling degree. In these works, much attention was paid to the design and fabrication of complicated stimulus-responsive materials as the skin layer in the bilayer system to realize a dynamic patterned surface, in which the surface morphology is always dependent on physical or chemical properties of the top layers. This means that the morphology and surface composition cannot be regulated independently of each other.

Here, by controlling the applied strain ( $\varepsilon$ ) via near-infrared (NIR) light radiation, we demonstrated a simple and general strategy for the fabrication of NIR-responsive dynamic wrinkle patterns based on bilayer systems, in which the PDMS substrate was modified by incorporating a small amount of single-walled carbon nanotubes (CNTs), and varieties of functional polymers can serve as the top stiff layers (Fig. 1A). Owing to the high photon-to-thermal energy conversion efficiency and absorption ability in the NIR region, the thermal expansion of the elastic CNT-PDMS substrate can be easily tuned by the NIR irradiation, resulting in the regulation of the applied strain ( $\varepsilon$ ) of the bilayer system dynamically to obtain the reversible wrinkle patterns. As a noncontacting and harmless stimulus, NIR provides an expedient and efficient approach to spatially and temporally tuning the surface features and inherently has the unique advantages of ultrarapid



Fig. 1. Schematic illustration of NIR-driven dynamic wrinkle pattern fabrication. (A) Fabrication process of NIR-driven dynamic wrinkles. RT, room temperature. (B) Temperature variation of CNT-PDMS in NIR on/off switch. (C) Atomic force microscopy (AFM) images to test reversibility of the NIR-driven wrinkles. NIR intensity is approximately 1.5 W/cm<sup>2</sup>.

response, controllable operability, and region selectivity for the resulting dynamic wrinkling pattern over other stimuli such as solvents (4, 29), temperature (13), electrical and magnetic fields (43, 44), and mechanical force (3, 35). This NIR-responsive dynamic wrinkle provides a facile and general approach for the fast morphology control of a functional surface on demand and may find potential applications in smart displays, dynamic gratings, and light control electronics.

#### RESULTS

Strategy for the fabrication of NIR-driven dynamic wrinkles The key strategy for the fabrication of the NIR-driven dynamic wrinkle patterns is illustrated in Fig. 1A. The PDMS elastomer containing a small amount of CNTs (CNT-PDMS) served as the substrate owing to its high thermal expansion coefficient. The incorporation of 0.05% CNT reduced the transparency of the PDMS elastomer to an acceptable level (fig. S1) and had no obvious effect on the mechanical performance of the PDMS elastomer. The Young's modulus and thermal expansion coefficient ( $\alpha_s$ ) of the obtained CNT-PDMS (0.05%) are approximately 2 MPa and  $3 \times 10^{-4}$ /°C, respectively. Upon exposure to NIR irradiation  $(\lambda = 808 \text{ nm}, 1.5 \text{ W/cm}^2)$ , the surface temperature of the CNT-PDMS elastomer monitored by an infrared camera increased rapidly and could reach over 100°C from room temperature after irradiation for 3 min (Fig. 1B and figs. S2 and S3). The rapidly increasing temperature of the CNT-PDMS elastomer containing a small amount of CNT (0.05%) by NIR irradiation should be ascribed to two factors: the high photon-to-thermal conversion efficiency of the CNTs and the low thermal conductivity of the PDMS substrate. The heating rate and the maximum temperature of CNT-PDMS depend on the CNT contents and NIR light intensity. The surface temperature of pure PDMS elastomer without CNTs remained almost unchanged after NIR irradiation. After removing NIR irradiation, the samples cooled to room temperature at a rate that was lower than the heating rate (Fig. 1B and figs. S3 and S4).

The CNT-PDMS was used as the substrate for bilayer systems, and various functional polymers could be coated onto the CNT-PDMS elas-

tomers as the top stiff layers for designing the functional surface. For example, random fluorinated copolymer poly(styrene-co-perfluorooctyl acrylate) (PSF;  $M_{\rm n}$  (number-average molecular weight) = 24,600 g mol<sup>-1</sup>,  $M_{\rm w}$  (weight-average molecular weight)/ $M_{\rm n}$  = 1.44; fig. S7) was spincoated on CNT-PDMS as the stiff layer with the thickness of 122 nm. Upon heating to 80°C for 3 min, an equibiaxial compressive stress σ was generated upon cooling the bilayer sample to room temperature, owing to the considerable mismatch between the modulus and thermal expansion ratio of the elastic CNT-PDMS substrate and the stiff top layer of the functional polymer ( $\alpha_s \gg \alpha_f$ ), which induced the wrinkle pattern as a result of the release of the localized stress to minimize the total energy of the system (13). Apart from heating the bilayer system to a certain value in an oven, the irradiation of the samples by NIR for 2.5 min could also induce the formation of the wrinkles with the characteristic wavelength ( $\lambda$ ) of 12.5  $\mu$ m and amplitude (A) of 560 nm, owing to the excellent photon-to-thermal energy conversion effect of CNTs (fig. S10). This photon-to-thermal energy conversion effect of CNTs was further confirmed by the fact that the effect of NIR irradiation on thermal expansion of the CNT-PDMS substrate was similar to that of directly heating. Through this approach, various wrinkle patterns with tunable characteristic wavelength ( $\lambda$ ) and amplitude (A) could be prepared by tuning the thickness of the top layer, in good agreement with linear buckling theory (fig. S11) (26). It should be noted that the wrinkle pattern on this bilayer system can be temporarily erased by NIR irradiation. The NIR irradiation can again induce the thermal expansion of the CNT-PDMS substrate, resulting in the decrease in the compressive strain of the bilayer systems and the disappearance of the wrinkles. After removing the NIR source and cooling to room temperature, the smooth surface is restored to the original wrinkled state (Fig. 1, A and C). Because the thermal expansion of the elastic CNT-PDMS substrate can be easily tuned by NIR irradiation, the wrinkle pattern for this bilayer system with CNT-PDMS as the substrate can be easily controlled by the NIR on/off cycles. This strategy provides a versatile and general method for the fabrication of NIR-responsive dynamic wrinkles, and various materials [for example, amorphous polymer polymethyl methacrylate (PMMA), poly (n-butylacrylate-co-anthracene-containing styrene) (PAN), and natural polymer gelatin] can be used as the skin layers to realize the real-time dynamic transformation of surface morphology (fig. S12).

#### The dynamics of wrinkle extinction and formation

We investigated the dynamics of wrinkle extinction and formation through NIR switchable on/off cycles for the case where the skin layer material is PSF with the thickness of 122 nm. We observed the dependence of the evolution of the wrinkle pattern on NIR irradiation via a profile measurement microscope. As illustrated in Fig. 2 (A to C) and movie S1, the wrinkle was gradually reduced by NIR radiation and completely disappeared after irradiation for 20 s. We suppose that the driving force for this effect originates from the photon-to-thermal energy conversion of CNTs, which causes the thermal expansion and deformation of the CNT-PDMS substrate when irradiated by NIR light. According to linear buckling theory, the critical strain ( $\varepsilon_c$ ) for the generation of the wrinkle in the given PSF/CNT-PDMS bilayer system is approximately 1.3%, and the critical strain for the elimination of the wrinkle ( $\varepsilon_{c}$ ) is approximately 0.5% (the details of the calculation are shown in section S2.2) (25, 27). When irradiated by NIR light for 20 s, the CNT-PDMS length increased by ~0.6% compared to the initial length, owing to thermal expansion caused by photon-to-thermal energy conversion (section S2.2), which exceeded to the critical elimination strain and consequently resulted in the disappearance of the wrinkles (45). The dependence of the characteristic amplitude of the wrinkles  $(A/A_0)$ , where A and  $A_0$  represent the actual amplitude and initial amplitude of the wrinkle patterns, respectively) decreased sharply

with the increasing NIR irradiation time as a result of the thermal expansion of the CNT-PDMS substrate (Fig. 2G). By contrast, the wavelength of the wrinkle ( $\lambda$ ) remained constant, which may be explained by the fact that the parameters that determine  $\lambda$  (the thickness and mechanical properties of the skin layer and the substrate) remained almost unchanged. After cessation of the NIR irradiation, the PSF/ CNT-PDMS bilayer system gradually cooled down to room temperature and shrank to the original state, resulting in the recovery to the original wrinkled state (Fig. 2, D to F). The recovery rate was slower in contrast to the disappearing process because of the slower heat dissipation compared to the excellent photon-to-thermal energy conversion efficiency of the CNT-PDMS, which was consistent with the temperature variation in the NIR on/off switch (Fig. 1B). It is noted that the dynamic wrinkles are highly reversible, and the disappearance/ formation process of the wrinkles could be conducted for more than 1000 NIR on/off cycles without damaging the characteristic morphology of the wrinkles.

To understand the effect of CNTs on the wrinkle extinction dynamics, we decreased the CNT content in PDMS to 0.025%. It took approximately 30 s or longer to fully erase the wrinkle pattern by NIR irradiation. This should be ascribed to the lower efficiency of the photon-to-thermal energy conversion caused by the lesser content of CNTs in PDMS. The PDMS substrate that does not contain CNTs cannot be heated by NIR irradiation (Fig. 1B), and consequently, a wrinkled pattern cannot be smoothed out by NIR irradiation, confirming that the photon-to-thermal energy conversion by the CNTs is necessary to erase the wrinkles. NIR light intensity is another key factor that determines



Fig. 2. Dynamics of wrinkle extinction/formation process via NIR switchable on/off cycle. (A to C) Optical images of wrinkle disappearance behavior via NIR irradiation. (D to F) Optical images of the wrinkle formation process after cessation of NIR irradiation. (G) Deformation of CNT-PDMS and the corresponding amplitude variation of wrinkles as a function of NIR irradiation time. (H) Extinction/formation cycles. The skin layer is PSF with the thickness of ~122 nm, and the CNT content in the PDMS substrate is 0.05%. NIR light intensity is approximately 1.5 W/cm<sup>2</sup>. Scale bar, 100  $\mu$ m.

the erasing rate. When the light intensity declined from 1.5 to 0.75 W/cm<sup>2</sup>, erasure time increased from 20 to 70 s (fig. S13).

#### Strategy for the formation of NIR-driven, hierarchical patterns

On the basis of this simple and general strategy for NIR-driven dynamic wrinkles by tuning the applied strain, in this work, we demonstrated a series of multiresponsive dynamical, hierarchical patterns with various topographies by using ultraviolet (UV) light-responsive materials as skin layers, whose modulus can be controlled by reversible photodimerization. A copolymer containing anthracene moieties [PAN,  $M_n$  = 14,400 g·mol<sup>-1</sup>,  $M_w/M_n = 1.52$ ) was spin-coated on CNT-PDMS as the top layer with the thickness of 180 nm. The modulus and crosslinking density of the PAN top layer can be regulated by UV-induced reversible photodimerization of the anthracene moieties (29, 30). Upon heating at 80°C, the PAN/CNT-PDMS was irradiated by 365-nm UV light through a photomask for 40 min (fig. S14). The top layer of PAN at exposed regions that underwent the photodimerization of anthracenecontaining styrene (AN) became cross-linked and stiff, showing a high modulus, whereas the unexposed region remained unchanged and soft. After stopping the illumination of 365-nm UV light and cooling down to room temperature, wrinkles occurred in the exposed region, owing to the considerable mismatch of the modulus and thermal expansion coefficient between the exposed skin layer and the elastic CNT-PDMS, whereas the unexposed region remained in its initial smooth state because the soft uncross-linked PAN could not accumulate sufficient compressive stress to trigger wrinkle formation (Fig. 3, A and B). It should be noted that the wrinkle is highly ordered and perpendicular to the boundary between the exposed and unexposed region, owing to the boundary effect (40, 45, 46).

### The dynamics of hierarchical wrinkle extinction and formation

As shown in Fig. 3 (B to D) and movie S2, when the hierarchically ordered wrinkle pattern was irradiated by NIR light, the pattern was reduced gradually until it completely disappeared after 15 s. In comparison to the isotropic wrinkles (fig. \$15), this hierarchically anisotropic pattern could be erased more quickly by NIR irradiation, which may be ascribed to the unexposed area of soft PAN being able to lead to fast release of the compressive stress. After removing NIR irradiation, the erased pattern gradually restored the initial state of the anisotropic wrinkles because the bilayer sample shrank to the original state as the temperature gradually decreased (Fig. 3, E to G). In addition to the thermal erasure of the wrinkle pattern by real-time NIR irradiation, this striped wrinkle can be permanently erased by 254-nm UV light irradiation, owing to the reversible photodimerization of anthracene moiety (AN). Upon irradiation by 254-nm UV light, the photocleavage of the AN dimer leads to an uncross-linked and soft PAN layer and the spontaneous release of compressive stress, resulting in wrinkle extinction (Fig. 3H). The wrinkle-free surface remains fixed other than returning to the initial wrinkled state after the cessation of the 254-nm UV light irradiation, which represents a kind of typical relatively statically reversible pattern. The PAN/CNT-PDMS bilayer system without the pattern can be further used to generate other real-time dynamic wrinkle patterns by selective irradiation through different photomasks such as a circular ring and a circular pattern (Fig. 3, I and J, and fig. S16). Therefore, by controlling the photodimerization of the top layer and photon-to-thermal energy conversion of the CNT-PDMS substrate, we can realize multiple regulation of the wrinkle patterns.



**Fig. 3. NIR-driven controlled wrinkle pattern and its real-time dynamics. (A)** Schematic illustration of controlled wrinkle formation. The inset at the bottom is the reversible chemical reaction in the skin layer via UV light irradiation with different wavelengths. (**B** to **D**) Optical images of stripe wrinkled pattern's disappearing behavior via NIR radiation. (**E** to **G**) Optical images of recovery evolution process after NIR being removed. (**H**) Optical image of hierarchical wrinkle pattern (**G**) erased by irradiation of 254-nm UV light for 5 min. Scale bar, 100 μm. (**I** and **J**) Optical images of the extinction/formation process of circular ring pattern. The NIR intensity is 1.5 W/cm<sup>2</sup>. The CNT content in PDMS is 0.05%. Scale bar, 621 μm.

#### NIR-controlled dynamical light grating

Because of the versatility of this approach for dynamic control of surface morphology, together with good reversibility and sensitive responsiveness, this NIR-driven dynamic wrinkle pattern is well suited for the development of a new type of smart materials that can change their physical properties in optical and electronic devices. For example, the NIR-responsive dynamic wrinkle pattern shown in Fig. 2 can be used as the optical grating for dynamically tuning light diffraction, which is a challenge in the field of light control (17, 47-52). The optically transparent materials with a surface micropattern can cause light diffraction when a light beam passes through these samples (Fig. 4A). The experiments were performed in transmission mode, using a green laser beam ( $\lambda = 532$  nm), and the distance between the wrinkled sample and the screen was d = 1.0 m. As shown in Fig. 4B and movie S3, when a green laser beam passed through the wrinkled sample, a diffraction ring pattern (concentric rings) was observed, and the distance between the central light spot and the inner ring (radius of the inmost circle, r) was similar to that of the adjacent diffraction rings. Upon NIR radiation, the green ring diffraction quickly disappeared from the outside ring to the inner light ring as a result of the gradual wrinkle extinction, and only a light spot remained after the wrinkles were completely erased within 20 s. When the NIR light was removed, the diffraction gradually recovered to its initial pattern, owing to the regeneration of the wrinkles. It was noted that the recovery rate was slower than that mentioned before, and we assumed that the CNT-PDMS substrate could absorb the green laser, leading to the slower recovery rate (fig. S6). We further investigated the influence of the morphology and size of wrinkles and the laser beam on the diffraction patterns. When one-dimensional anisotropic wrinkles were used to replace the disordered wrinkled samples, the distinguishing discrete laser spots were obtained instead of concentric rings. With the decrease of the wavelength of the wrinkles, the size of diffraction patterns increases gradually. The laser beam imposed an effect on the diffraction patterns as well. The red laser beam ( $\lambda$ = 650 to 660 nm) leads to the larger size of diffraction patterns than the green

laser beam because of the longer wavelength of red laser (fig. S17). The light diffraction can be switched by NIR on/off for many cycles, and to the best of our knowledge, this is the first example of the realization of a NIR-controlled dynamical light grating.

#### Dynamic wrinkle pattern applied to fabricate smart windows, dynamic displays, and light-controllable electronics

Furthermore, the dynamic wrinkle pattern can enable the capacity for switchable optical windows. Figure 5A demonstrates a representative result of switchable optical transparency in the wrinkled and wrinkle-free states of our reversible wrinkle system that undergoes on/off cyclic NIR irradiation. The as-prepared wrinkled surface was opaque with a frosted glass-like appearance, and the covered letter could not be observed. The opacity is due to the extensive scattering of light by the micro/nanoscale surface structures (*14, 24*). As the sheet was irradiated by NIR for 20 s to eliminate the wrinkle pattern, it became transparent and showed a clear transmitted image as a result of the absence of the wrinkles.

By using photosensitive materials as the skin layer, the NIR-driven dynamic wrinkle pattern can also be used for recording information. The initial sample coated with PAN as the top layer with the thickness of 180 nm was a transparent surface. As shown in Fig. 5B, after the initial wrinkle-free sample (i) was selectively exposed to 365-nm UV light, a specific pattern showing a positive letter "S" was obtained, which can be identified and is visible to the naked eye, owing to the light scattering of the wrinkle (ii). The initial wrinkle-free sample could be converted into a fully wrinkled surface via irradiation by 365-nm UV light without photomasks (iii). The fully wrinkled surface could be selectively erased by 254-nm UV light because of dedimerization and could write other information [a negative letter "T" (iv)]. The samples with specific information could temporarily be erased by NIR irradiation (v) and swiftly restored to their original state; this may find potential application in dynamic information record and dynamic no-ink display, such as the fabrication of dynamic QR codes and bar codes.



Fig. 4. Illustration of the NIR-responsive wrinkle pattern serving as a dynamic light grating. (A) Schematic demonstration of the NIR-controlled dynamic light grating. (B) Evolution process of light diffraction patterns upon the NIR on/off switch. NIR light intensity is 1.5 W/cm<sup>2</sup>.

### SCIENCE ADVANCES | RESEARCH ARTICLE



Fig. 5. Schematic representation of the NIR-driven smart windows, information record, and electronic devices. (A) Images of switchable transparency due to the reversibility of the wrinkled/wrinkle-free surface. The Shanghai Jiao Tong University logo is underlying the sample. The insets are AFM images. Scar bars, 100 µm. (B) Demonstration of dynamic information record through controlled wrinkle formation via different photomasks. (C) Schematic showing of NIR-driven electronics. (D) Optical images of the extinction/formation cycle of a gold-PAN/CNT-PDMS sample. Scale bar, 100 µm. (E) Electrical resistance as a function of NIR radiation time. NIR light intensity is approximately 1.5 W/cm<sup>2</sup>.

Figure 5C presents a proof-of-concept device for light-controllable electronics realized by the NIR-driven wrinkle patterns. A conductive wrinkled sample prepared by sputtering gold on the wrinkled PAN/ CNT-PDMS bilayer system was placed on two pieces of separated indium tin oxide (ITO) glass to fabricate NIR-driven dynamic electronics. Owing to the change of conformal contact between the conductive sample and ITO glass, the electrical resistance will be controlled by tuning the morphology of the surface wrinkles through NIR irradiation. As shown in Fig. 5D, the gold-coated PAN/CNT-PDMS bilayer system can also achieve a switchable erasure/generation cycle via the NIR on/off switch. The initial resistance was approximately 16.1 ohms in the wrinkled state, while it gradually dropped upon NIR irradiation. After the wrinkle pattern fully disappeared, the resistance decreased by 15% compared to the initial state, which implies its potential application in light-operated electronics (Fig. 5E). The sample can be cycled for more than 100 times via controlling the NIR on/off state while still retaining its capacities.

#### DISCUSSION

In summary, we demonstrated a novel NIR-responsive dynamic wrinkle pattern with excellent reversibility and sensitive response by using a CNT-containing PDMS substrate for bilayer systems, in which the applied strain can be regulated by NIR-induced thermal expansion of the CNT-PDMS substrate, owing to the efficient photon-to-thermal energy conversion of CNT. The erasure and generation of the wrinkles are

controlled by NIR on/off switches, and various functional materials can be used as the skin layer for fabricating a smart surface for the desired function. This NIR-responsive dynamical wrinkle can be used as a dynamic platform for the realization of the dynamic light gratings, no-ink displays, and NIR-controlled electronics. We believe that our strategy can be extended to a general method to provide real-time responsive wrinkles by the introduction of various responsive materials into the elastic substrate, such as other NIR-responsive materials (for example, graphene, metal nanoparticles, organic dyes, and conjugated polymers) and electromagnetic-responsive compounds. Furthermore, the NIR-driven wrinkling strategy is expected to expand the applications to prepare the dynamic anisotropic wrinkles by exploring more versatile elastic substrate materials, for example, liquid crystalline elastomers (53, 54). We envision that the real-time dynamic strategy for preparing NIR-responsive wrinkle patterns can be applied in situ for on-demand tuning of surface properties.

#### MATERIALS AND METHODS Materials

Single-walled nanotubes were purchased from Alpha Nano Technology Co. Ltd. and were directly used. 9-Anthracenemethanol and 4-vinylbenzyl chloride purchased from China National Pharmaceutical Group were used directly without further purification. Styrene, n-butyl acrylate, and perfluoroalkyl ethyl acrylate obtained from China National Pharmaceutical Group were washed by saturated sodium hydroxide solution to remove retarder and then were dried by magnesium chloride.

#### Fabrication of CNT-PDMS sheet

Eight milligrams of single-walled CNTs, 16 g of PDMS base agent, and 20 ml of toluene were added into a flask and then were processed by ultrasound for 12 hours. Then, the mixture solution was left standing for 1 hour. Most well-distributed solution was taken out and dried in a vacuum oven at 70°C for 10 hours to completely remove the residual solvent. Then, the obtained CNT-containing PDMS base was mixed with 1.6 g of curing agent (PDMS base to curing agent at 10:1 weight ratio). The mixture was poured into a petri dish, degassed for 1 hour, and then cured at 70°C for 4 hours.

#### **Preparation of PSF**

PSF was synthesized by free radical copolymerization shown in fig. S7. Styrene (0.05 mol, 5.2 g) and perfluoroalkyl ethyl acrylate (0.0067 mol, 3.45 g) were dissolved in 10 ml of toluene, and then 88 mg of 2,2-azobisisobutyronitrile (AIBN) was added [1 weight percent (wt %) total monomer weight]. After the mixture totally dissolved, the polymerization reaction was performed at 70°C for 12 hours under nitrogen protection. The reaction mixture was precipitated in cold methanol. The filtered solid was washed by methanol six times. Then, it was dried in a vacuum oven at 70°C for 24 hours to obtain the product.

#### **Preparation of AN**

9-Anthracenemethanol (0.017 mol, 3.471 g) and 4-vinylbenzyl chloride (0.020 mol, 3.04 g) were dissolved into 50 ml of dried tetrahydrofuran (THF) solvent. Sodium methanolate (0.12 mol, 6.48 g; exceeding five times) was added into a mixture solution and then was heated to reflux for 24 hours under nitrogen protection (fig. S8). After cooling to room temperature, the mixture solution was filtered to remove sodium methanolate. The solution was precipitated in 500 ml of cold methanol three times to obtain light yellow solid. After solid was filtered, it was dried in a vacuum oven at 50°C for 24 hours.

#### **Preparation of PAN**

PAN was synthesized by free radical copolymerization (fig. S9). AN (0.005 mol, 1.62 g) and *n*-butyl acrylate (0.0125 mol, 1.6 g) were dissolved into 15 ml of toluene, and then 32 mg of AIBN was added into the mixture (1 wt % total monomer weight). After the mixture totally dissolved, the polymerization reaction was performed at 70°C for 12 hours under nitrogen protection. The mixture solution was precipitated in 200 ml of cold petroleum ether three times to obtain light yellow solid copolymer. The filtered product was dried at 70°C for 24 hours.

#### Fabrication of NIR-driven dynamic wrinkle pattern

The toluene solution of PSF was spin-coated on the CNT-PDMS sheet. By varying the concentration of the solution and the spinning speed, a series of samples with different thicknesses of the skin layer were obtained. These samples were heated to 80°C for 3 min and cooled down to room temperature to gain various wrinkle patterns.

### Fabrication of NIR-driven dynamic, hierarchical wrinkle pattern

The toluene solution of PAN was spin-coated on the CNT-PDMS sheet. The thickness of the skin layer could be controlled via varying the solution concentration and the spinning speed. These samples were heated to 80°C and exposed to 365-nm UV light for 40 min. After cooling down to room temperature, wrinkles occurred. Photomasks were used to precisely control wrinkle patterns.

#### Characterization

Surface patterns and their erasure/regeneration process were recorded by a profile measurement microscope (VF-7501, KEYENCE). AFM was also carried out to measure wrinkles in tapping mode by using silicon cantilevers with a force constant of 40 N/mv (E-Sweep, Seiko Instruments Inc.). The laser source used in the experiments was a laser diode controller ( $\lambda = 808$  nm; LE-LS-808-1000TFCB, LEO Photonics). <sup>1</sup>H nuclear magnetic resonance spectra were recorded on a Varian Mercury Plus spectrometer (400 MHz) with deuterated chloroform (CDCl<sub>3</sub>) and dimethyl sulfoxide-*d*<sub>6</sub> as the solvent and tetramethylsilane as an internal standard at room temperature. The cross-linking dynamics of PAN was recorded via a TU-1091 spectrophotometer (Persee). Average molecular weight was measured by gel permeation chromatography (LC-20A, Shimadzu) using THF as an eluent.

#### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/4/4/eaar5762/DC1

section S1. Experimental section

- section S2. Results and discussion
- fig. S1. Image of CNT-PDMS that retains good transparency.
- fig. S2. UV-vis-NIR spectrum of CNT-PDMS.

fig. S3. The temperature variation during NIR on/off switch monitored by an infrared camera. fig. S4. Temperature variation during NIR light radiation with different intensities monitored by an infrared camera.

- fig. S5. Temperature variation during 365-nm UV light radiation.
- fig. S6. Temperature variation during the exposure of green laser beam.
- fig. S7. The synthesis route to PSF.
- fig. S8. The synthesis route to AN.
- fig. S9. The synthesis route to PAN.
- fig. S10. Wrinkles occur through NIR radiation.
- fig. S11. Various wrinkles across different scales.
- fig. S12. Various functional polymers served as the skin layers, including PSF, PMMA, PAN and gelatin.
- fig. S13. Control experiments of the NIR-driven dynamic wrinkle pattern.
- fig. S14. UV-vis spectra of dimerization of PAN.

fig. S15. The evolution process of PAN/CNT-PDMS wrinkles during NIR on/off cycles. fig. S16. The extinction/formation process of the circular wrinkle pattern via NIR on/off switch fig. S17. The influence of the morphology and size of wrinkles and the laser beam on the diffraction patterns.

movie S1. Video of the fully wrinkled pattern's disappearance/formation behavior. movie S2. Video of the striped wrinkled pattern's disappearance/formation cycle. movie S3. Video of the diffraction ring/light spot switch corresponding to the wrinkled/ wrinkle-free state of surface pattern.

#### **REFERENCES AND NOTES**

- L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, Super-hydrophobic surfaces: From natural to artificial. *Adv. Mater.* 14, 1857–1860 (2002).
- X. Yao, Y. Song, L. Jiang, Applications of bio-inspired special wettable surfaces. *Adv. Mater.* 23, 719–734 (2011).
- S. G. Lee, D. Y. Lee, H. S. Lim, D. H. Lee, S. Lee, K. Cho, Switchable transparency and wetting of elastomeric smart windows. *Adv. Mater.* 22, 5013–5017 (2010).
- H. S. Kim, A. J. Crosby, Solvent-responsive surface via wrinkling instability. Adv. Mater. 23, 4188–4192 (2011).
- A. Schweikart, N. Pazos-Pérez, R. A. Alvarez-Puebla, A. Fery, Controlling inter-nanoparticle coupling by wrinkle-assisted assembly. *Soft Matter* 7, 4093–4100 (2011).
- N. A. Patankar, Mimicking the lotus effect: Influence of double roughness structures and slender pillars. Langmuir 20, 8209–8213 (2004).
- X. Gao, X. Yan, X. Yao, L. Xu, K. Zhang, J. Zhang, B. Yang, L. Jiang, The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography. *Adv. Mater.* 19, 2213–2217 (2007).

- 8. L. Jiang, X. Gao, Water-repellent legs of water striders. Nature 432, 36 (2004).
- P. Vukusic, J. R. Sambles, C. R. Lawrence, R. J. Wootton, Structure colour. Now you see it—now you don't. *Nature* 410, 36 (2001).
- C. C. A. Ng, A. Magenau, S. H. Ngalim, S. Ciampi, M. Chockalingham, J. B. Harper, K. Gaus, J. J. Gooding, Using an electrical potential to reversibly switch surfaces between two states for dynamically controlling cell adhesion. *Angew. Chem. Int. Ed.* **51**, 7706–7710 (2012).
- M. A. Cole, N. H. Voelcker, H. Thissen, H. J. Griesser, Stimuli-responsive interfaces and systems for the control of protein–surface and cell–surface interactions. *Biomaterials* 30, 1827–1850 (2009).
- D. Ge, E. Lee, L. Yang, Y. Cho, M. Li, D. S. Gianola, S. Yang, A robust smart window: Reversibly switching from high transparency to angle-independent structural color display. *Adv. Mater.* 27, 2489–2495 (2015).
- H. Hou, J. Yin, X. Jiang, Reversible Diels–Alder reaction to control wrinkle patterns: From dynamic chemistry to dynamic patterns. *Adv. Mater.* 28, 9126–9132 (2016).
- T. Ohzono, H. Monobe, R. Yamaguchi, Y. Shimizu, H. Yokoyama, Dynamics of surface memory effect in liquid crystal alignment on reconfigurable microwrinkles. *Appl. Phys. Lett.* **95**, 14101 (2009).
- P. Kim, Y. Hu, J. Alvarenga, M. Kolle, Z. Suo, J. Aizenberg, Rational design of mechano-responsive optical materials by fine tuning the evolution of strain-dependent wrinkling patterns. *Adv. Opt. Mater.* 1, 381–388 (2013).
- N. Bowden, W. T. S. Huck, K. E. Paul, G. M. Whitesides, The controlled formation of ordered, sinusoidal structures by plasma oxidation of an elastomeric polymer. *Appl. Phys. Lett.* **75**, 2557–2559 (1999).
- T. Ohzono, K. Suzuki, T. Yamaguchi, N. Fukuda, Tunable optical diffuser based on deformable wrinkles. *Adv. Opt. Mater.* 1, 374–380 (2013).
- K. Suzuki, Y. Hirai, T. Ohzono, Oscillating friction on shape-tunable wrinkles. ACS Appl. Mater. Interfaces 6, 10121–10131 (2014).
- Y. Rahmawan, C.-M. Chen, S. Yang, Recent advances in wrinkle-based dry adhesion. Soft Matter 10, 5028–5039 (2014).
- K. Suzuki, T. Ohzono, Wrinkles on a textile-embedded elastomer surface with highly variable friction. Soft Matter 12, 6176–6183 (2016).
- H. Monobe, T. Ohzono, H. Akiyama, K. Sumaru, Y. Shimizu, Manipulation of liquid filaments on photoresponsive microwrinkles. ACS Appl. Mater. Interfaces 4, 2212–2217 (2012).
- T. Ohzono, H. Monobe, Morphological transformation of a liquid micropattern on dynamically tunable microwrinkles. *Lanamuir* 26, 6127–6132 (2010).
- T. Ohzono, H. Monobe, K. Shiokawa, M. Fujiwara, Y. Shimizu, Shaping liquid on a micrometre scale using microwrinkles as deformable open channel capillaries. *Soft Matter* 5, 4658–4664 (2009).
- J. Rodríguez-Hernández, Wrinkled interfaces: Taking advantage of surface instabilities to pattern polymer surfaces. Prog. Polym. Sci. 42, 1–41 (2015).
- C.-M. Chen, S. Yang, Wrinkling instabilities in polymer films and their applications. *Polym. Int.* 61, 1041–1047 (2012).
- N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, G. M. Whitesides, Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer. *Nature* **393**, 146–149 (1998).
- C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. VanLandingham, H.-C. Kim, W. Volksen, R. D. Miller, E. E. Simonyi, A buckling-based metrology for measuring the elastic moduli of polymeric thin films. *Nat. Mater.* **3**, 545–550 (2004).
- Q. Wang, X. Zhao, Beyond wrinkles: Multimodal surface instabilities for multifunctional patterning. MRS Bull. 41, 115–122 (2016).
- S. Zeng, R. Li, S. G. Freire, V. M. M. Garbellotto, E. Y. Huang, A. T. Smith, C. Hu, W. R. T. Tait, Z. Bian, G. Zheng, D. Zhang, L. Sun, Moisture-responsive wrinkling surfaces with tunable dynamics. *Adv. Mater.* **29**, 1700828 (2017).
- N. Gao, X. Zhang, S. Liao, H. Jia, Y. Wang, Polymer swelling induced conductive wrinkles for an ultrasensitive pressure sensor. ACS Macro Lett. 5, 823–827 (2016).
- J. Y. Chung, A. J. Nolte, C. M. Stafford, Diffusion-controlled self-organized growth of symmetric wrinkling patterns. *Adv. Mater.* 21, 1358–1362 (2009).
- J. Huang, M. Juszkiewicz, W. H. de Jeu, E. Cerda, T. Emrick, N. Menon, T. P. Russell, Capillary wrinkling of floating thin polymer films. *Science* **317**, 650–653 (2007).
- S. Yang, K. Khare, P.-C. Lin, Harnessing surface wrinkle patterns in soft matter. Adv. Funct. Mater. 20, 2550–2564 (2010).
- W.-K. Lee, W.-B. Jung, S. R. Nagel, T. W. Odom, Stretchable superhydrophobicity from monolithic, three-dimensional hierarchical wrinkles. *Nano Lett.* 16, 3774–3779 (2016).
- J. M. Taylor, C. Argyropoulos, S. A. Morin, Soft surfaces for the reversible control of thin-film microstructure and optical reflectance. *Adv. Mater.* 28, 2595–2600 (2016).

- T. Ohzono, M. Shimomura, Geometry-dependent stripe rearrangement processes induced by strain on preordered microwrinkle patterns. *Langmuir* 21, 7230–7237 (2005).
- T. Ohzono, M. Shimomura, Ordering of microwrinkle patterns by compressive strain. Phys. Rev. B 69, 132202 (2004).
- J. Genzer, J. Groenewold, Soft matter with hard skin: From skin wrinkles to templating and material characterization. Soft Matter 2, 310–323 (2006).
- T. Takeshima, W.-y. Liao, Y. Nagashima, K. Beppu, M. Hara, S. Nagano, T. Seki, Photoresponsive surface wrinkle morphologies in liquid crystalline polymer films. *Macromolecules* 48, 6378–6384 (2015).
- C. Zong, Y. Zhao, H. Ji, X. Han, J. Xie, J. Wang, Y. Cao, S. Jiang, C. Lu, Tuning and erasing surface wrinkles by reversible visible-light-induced photoisomerization. *Angew. Chem. Int. Ed.* 55, 3931–3935 (2016).
- H. Hou, F. Li, Z. Su, J. Yin, X. Jiang, Light-reversible hierarchical patterns by dynamic photo-dimerization induced wrinkles. J. Mater. Chem. C 5, 8765–8773 (2017).
- 42. F. Li, H. Hou, J. Yin, X. Jiang, Multi-responsive wrinkling patterns by the photoswitchable supramolecular network. *ACS Macro Lett.* **6**, 848–853 (2017).
- N. Wu, L. F. Pease III, W. B. Russel, Toward large-scale alignment of electrohydrodynamic patterning of thin polymer films. *Adv. Funct. Mater.* 16, 1992–1999 (2006).
- D.-M. Drotlef, P. Blümler, P. Papadopoulos, A. del Campo, Magnetically actuated micropatterns for switchable wettability. ACS Appl. Mater. Interfaces 6, 8702–8707 (2014).
- W. T. S. Huck, N. Bowden, P. Onck, T. Pardoen, J. W. Hutchinson, G. M. Whitesides, Ordering of spontaneously formed buckles on planar surfaces. *Langmuir* 16, 3497–3501 (2000).
- W. Ding, Y. Yang, Y. Zhao, S. Jiang, Y. Cao, Well-defined orthogonal surface wrinkles directed by the wrinkled boundary. *Langmuir* 9, 3720–3726 (2013).
- Z.-g. Zheng, R. S. Zola, H. K. Bisoyi, L. Wang, Y. Li, T. J. Bunning, Q. Li, Controllable dynamic zigzag pattern formation in a soft helical superstructure. *Adv. Mater.* 29, 1701903 (2017).
- X. Wang, J. Vapaavuori, X. Wang, R. G. Sabat, C. Pellerin, C. G. Bazuin, Influence of supramolecular interaction type on photoresponsive azopolymer complexes: A surface relief grating formation study. *Macromolecules* 49, 4923–4934 (2016).
- C. Harrison, C. M. Stafford, W. Zhang, A. Karim, Sinusoidal phase grating created by a tunably buckled surface. *Appl. Phys. Lett.* 85, 4016–4018 (2004).
- H. Park, H. Cho, A. S. Lee, S. Yu, J. H. Lee, K. Y. Cho, S. M. Hong, C. M. Koo, Multidirectional wrinkle patterns programmed by sequential uniaxial strain with conformal yet nontraceable masks. *Macromol. Rapid Commun.* 38, 1700311 (2017).
- S. Schauer, R. Schmager, R. Hünig, K. Ding, U. W. Paetzold, U. Lemmer, M. Worgull, H. Hölscher, G. Gomard, Disordered diffraction gratings tailored by shape-memory based wrinkling and their application to photovoltaics. *Opt. Mater. Express* 8, 184–198 (2018).
- S. Peng, W. Li, J. Zhang, Diffraction-pattern based on spontaneous wrinkled thin films. Mater. Trans. 1, 1–5 (2017).
- L. Yang, K. Setyowati, A. Li, S. Gong, J. Chen, Reversible infrared actuation of carbon nanotube-liquid crystalline elastomer nanocomposites. *Adv. Mater.* 20, 2271–2275 (2008).
- C. Li, Y. Liu, C.-w. Lo, H. Jiang, Reversible white-light actuation of carbon nanotube incorporated liquid crystalline elastomer nanocomposites. *Soft Matter* 7, 7511–7516 (2011).

#### Acknowledgments

Funding: We thank the Shanghai Municipal government (17JC1400700) and the National Natural Science Foundation of China (51373098 and 21522403) for their financial support. Author contributions: XJ. and J.Y. conceived the experimental system and analyzed the figures and data; F.L. carried out the material synthesis and characterization; and H.H. performed part of material synthesis. All authors contributed to the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 23 November 2017 Accepted 16 February 2018 Published 6 April 2018 10.1126/sciadv.aar5762

Citation: F. Li, H. Hou, J. Yin, X. Jiang, Near-infrared light-responsive dynamic wrinkle patterns. Sci. Adv. 4, eaar5762 (2018).

## **Science** Advances

#### Near-infrared light-responsive dynamic wrinkle patterns

Fudong Li, Honghao Hou, Jie Yin and Xuesong Jiang

*Sci Adv* **4** (4), eaar5762. DOI: 10.1126/sciadv.aar5762

ARTICLE TOOLS	http://advances.sciencemag.org/content/4/4/eaar5762
SUPPLEMENTARY MATERIALS	http://advances.sciencemag.org/content/suppl/2018/04/02/4.4.eaar5762.DC1
REFERENCES	This article cites 54 articles, 1 of which you can access for free http://advances.sciencemag.org/content/4/4/eaar5762#BIBL
PERMISSIONS	http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. 2017 © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. The title Science Advances is a registered trademark of AAAS.