Photoresponsive Biomimetic Soft Robots Enabled by Near-Infrared-Driven and Ultrarobust Sandwich-Structured Nanocomposite Films

Yi Yu, Ran Peng, Zihe Chen, Li Yu,* Jinhua Li, Jianying Wang, Xinyu Liu, Qian Wang,* and Xianbao Wang*

1. Introduction

Robotics is a booming field attracting researchers from various backgrounds like chemical engineering, material science, artificial intelligence, and nanotechnology. Conventional robots made of rigid materials are able to carry out special work but sometimes can hardly deliver desired adaptability, dexterity, and safety in contact with human beings and surrounding circumstances.[1,2] To address this issue, soft robots, built up of stimuli-responsive functional soft matters with a wide range of elastic moduli have emerged in recent years.[3–5]

In biological systems, shape-shifting behavior of living creature tissues plays an essential role in their activities for adapting to ecological environments, such as curling/uncurling behavior of inchworm body to crawl on demand,[6] folding/unfolding motion of venus flytrap leaf to grasp a prey,[7] and hierarchical expansion/contraction behavior of octopus skin to defend against the harm.[8] These functionalities offer myriads of inspiration for designing and fabricating bioinspired soft robots. By emulating shape-changing behaviors of living creatures, a series of biomimetic soft robots including artificial grippers,[9–11] gecko/caterpillar-inspired walkers,[12–14] and fish/dolphin-like swimmers[15,16] powered by stimuli such as temperature,[17] humidity,[18] light,[19] electric field,[20] and magnetic field[21] have been devised based on soft actuators. Among these stimuli-responsive counterparts,
photoresponsive soft actuators, possessing optical-to-mechanical energy conversion capability, have been considered as an ideal candidate for designing biomimetic soft robots because of their superior features. For example, light would enable remote, instant, and precise control of photoresponsive soft actuators by a noncontact way, and shape-changing (photomechanical) behaviors of soft actuators are able to be modulated by physical parameters of the stimulating light source such as intensity, wavelength, and polarization.

The bilayer structure simply composed of a photoactive and a photopassive layer offers a promising platform for creating photoresponsive soft robots (Table S1, Supporting Information). Materials of distinct chemical structures and compositions, and broad mechanical properties can be selected as the building blocks to assemble photoresponsive soft actuators featuring of ultrasensitivity, programmability, and superior compatibility. However, the molecular photoswitches (e.g., azobenzene) or functional nanomaterials with photothermal effect (e.g., carbon nanotubes or graphene) usually have to be incorporated into the soft matrix to form the photoactive layer, which needs complicated synthesis procedures. To simplify the fabricating process, some work directly utilize compounds containing molecular photoswitches or functional nanomaterials with photothermal effect (e.g., carbon nanotubes or graphene) as the photothermal layer. Nevertheless, weak interferential interaction between the photoactive and photopassive layer of the soft actuators can hardly achieve stable actuating performance under extreme conditions in their real-world applications, like in low-temperature environments and ultralarge deformation scenarios.

To overcome the aforementioned limitations, we report a facile approach to mass-produce photoresponsive sandwich-structured nanocomposite films using commercially available low-density polyethylene (LDPE) film and polyimide (PI) adhesive as raw materials. A thin layer of Au is sandwiched by the two films and works as the photothermal conversion layer. In our concept, the photoresponsive actuation behavior of sandwich-structured PI/Au/LDPE nanocomposite film originates from the mismatch of the coefficient of thermal expansion (CTE) between the LDPE film and PI adhesive stimulated by the functional Au layer with photothermal effect. The performance (actuating curvature) of the bilayer actuator stimulated by infrared light is investigated systematically by experiments, and the design of the actuator via tuning the thickness of the PI film and LDPE film in the temperature range of −60 °C to 90 °C is conducted by finite element analysis (FEA).

Based on the dexterous geometry design, remote and precise-driven mode, reversible and stable actuation behavior, and ultrarobust mechanical properties of the sandwich-structured PI/Au/LDPE nanocomposite films, we have designed photoresponsive biomimetic soft robots that can be implemented under distinct circumstances with pre-engineered functionalities such as artificial flytrap, caterpillar-inspired walker, and dolphin-like swimmer.

2. Results and Discussion

Figure 1a schematically shows the procedure for fabricating photoresponsive PI/Au/LDPE nanocomposite film for devising biomimetic soft robots in detail. Briefly, A thin layer of Au film is thermally evaporated onto a piece of LDPE film. Then, photoresponsive PI/Au/LDPE nanocomposite film is prepared by directly pasting a PI adhesive on the surface of the Au-coated LDPE film. Finally, the sandwich-structured PI/Au/LDPE nanocomposite film can be tailored into a pre-engineered geometry on demand which is beneficial for designing and fabricating biomimetic soft robots with desired functionalities such as creeping and locomotion (Figure 1b). As shown in the cross-sectional scanning electron microscope (SEM) image (Figure 1c), PI/Au/LDPE nanocomposite film possesses a compact structure where the thicknesses of the LDPE film (bottom layer) and PI adhesive (top layer) are around 36 and 82 μm. The excellent adhesion performance of the PI adhesive enables high stability of the sandwiched structure. Noted that, the Au film (middle layer) cannot be observed because its thickness is far less than that of the LDPE film and PI adhesive. The thickness and uniformity of the Au layer deposited on the LDPE layer were characterized by an atomic force microscopy (AFM) and the SEM (energy dispersive spectrometer [EDS] mode), showing ~9 nm Au was deposited with decent uniformity, as shown in Figure S2, Supporting Information, and 1d.

![Figure 1](image-url)
In our design, the three layers of the PI/Au/LDPE nanocomposite film, i.e., LDPE film, Au, and PI adhesive, all play key roles in the photoresponsive actuation behavior. For instance, over the temperature range of 30–90 °C, LDPE film presents much larger CTE in contrast to PI adhesive (Figure 2a and Table S2, Supporting Information). Thus, LDPE film and PI adhesive can act as the active layer and passive layer, respectively, to enable the actuation behavior of the PI/Au/LDPE nanocomposite film.\[18,40\] Meanwhile, Au with excellent absorption in near-infrared radiation (NIR) region (Figure 2b) can directly convert light energy into thermal energy and induce the mismatch of CTE between the LDPE film and PI adhesive for stimulating the actuation behavior of the PI/Au/LDPE nanocomposite film.\[41\] To evaluate the photothermal effect of the Au layer, the temperature of the PI/Au/LDPE nanocomposite film under distinct NIR light intensities was recorded by an IR thermal imager (inset of Figure 2c). Under NIR light irradiation, the temperature of the PI/Au/LDPE nanocomposite film displays no change at a relatively lower intensity (<0.37 W cm\(^{-2}\)) and starts to rise from 25 to 83.9 °C as the NIR light intensity increases from 0.37 to 0.65 W cm\(^{-2}\) (Figure 2c). The photothermal effect of the Au nanofilm is further verified by slighter change in the temperature of the PI/LDPE composite film (without Au layer) even under high intensity NIR irradiation (0.65 W cm\(^{-2}\)).

Reversible photoresponsive actuation behavior of the PI/Au/LDPE nanocomposite film is shown in Figure 2e and Movie S1, Supporting Information. Upon exposure to NIR light (0.65 W cm\(^{-2}\)), flat PI/Au/LDPE nanocomposite film bends toward the direction of NIR light source. The curvature \(\kappa\) reaches a maximum value of 0.23 mm\(^{-1}\) within 8 s and keeps stable under continuous irradiation. After releasing NIR light source, the PI/Au/LDPE nanocomposite film gradually recovers to its initial flat state within 18 s. The response and recovery time is in accordance with that of for the temperature change of the PI/Au/LDPE nanocomposite film during the whole photoresponsive actuation process (Figure S3, Supporting Information). Moreover, reversible photoresponsive actuation behavior of the PI/Au/LDPE nanocomposite film well maintains after 1000 cycles of irradiation and relaxation, indicating its excellent fatigue resistance because of excellent thermal stability of the LDPE film and PI adhesive (Figure S4, Supporting Information).

To further illustrate and verify the working mechanism of the photoresponsive actuation behavior of PI/Au/LDPE nanocomposite film, we theoretically analyze its thermal-actuation behavior based on classical bimorph theory by neglecting the Au layer because the thickness of the Au layer is only around 9 nm which is far less than that of the LDPE film and PI adhesive. Attributed to the large difference of CTE between the LDPE film and PI adhesive in the temperature range of 30–90 °C (Figure 2a), the LDPE film expands much more than the PI adhesive, making the PI/Au/LDPE nanocomposite film bend toward the PI adhesive layer (inset of Figure 2d). Herein, the curvature \(\kappa = 1/\gamma\) (where \(\gamma\) is the curvature radius) is utilized for characterizing the degree of the bending deformation corresponding to the actuation performance of the PI/Au/LDPE nanocomposite film. According to classical bimorph theory, the curvature radius \(\gamma\) can be expressed as follow\[42\]:

\[
\gamma = \frac{6W_1W_2E_2t_1t_2(t_1 + t_2)(\alpha_1 - \alpha_2)}{(W_1E_1t_1^2)^2 + (W_2E_2t_2^2)^2 + 2W_1W_2E_1E_2t_1t_2(2t_1^2 + 3t_1t_2 + 2t_2^2)(T - T_{ref})}
\]

(1)

where \(W, E, t, \) and \(\alpha\) are the width, Young's modulus, thickness, and CTE of materials, respectively. The subscripts “1” and “2” refer to LDPE film and PI adhesive, respectively, \(T\) is the temperature of the PI/Au/LDPE nanocomposite film, whereas \(T_{ref}\) is the reference temperature 25.0 °C in our case. An FEA numerical model was also applied to predict the curvature of the bimetal actuator working at different temperature values, as demonstrated in the Supporting Information. The physical properties of the LDPE film and PI adhesive used for the calculation and numerical modeling are listed in Table S2 and S3, Supporting Information.

Based on both Equation (1) and the numerical modeling, we can calculate the theoretical curvature \(\kappa\) of PI/Au/LDPE nanocomposite film at a given temperature. As presented in Figure 2d and S5, Supporting Information, the photoresponsive actuation behavior of PI/Au/LDPE nanocomposite film agrees well with the theoretical results, indicating the reliability of the models. Figure 3a, b shows the numerical simulation results of curvature \(\kappa\) of the PI/Au/LDPE nanocomposite film working under the conditions of a given NIR intensity (temperature) but with different thicknesses of LDPE film (active layer) and PI adhesive (passive layer). Figure 3a shows the effects of both the thickness of LDPE film (active layer) and temperature on the curvature \(\kappa\) of the PI/Au/LDPE actuator in which the thickness of PI film keeps constant (82 \(\mu\)m), whereas the thickness of LDPE is in the range of 10–100 \(\mu\)m and the actuator works at −60 to 90 °C. The curvature \(\kappa\) shows negative values when the working temperature is lower than 25 °C and experiences positive values when the temperature is higher than 25 °C, indicating apparent heating- and cooling-induced actuation. In the heating-induced actuation temperature range (25–90 °C), \(\kappa\) increases with both temperature and thickness of the LDPE film due to higher expansion caused by the higher temperature and larger thickness of the active layer (LDPE); vice versa, for the low-temperature range (−60 to 25 °C) cases, where the contraction dominate the cooling-induced behavior where \(\kappa\) (absolute value, minus sign means opposite curve direction) increases with both decreasing temperature and thickness of the LDPE film. Figure 3b investigates the effect of thickness of PI film (passive layer) and working temperature on the curvature of the actuator, showing similar results as Figure 3a. As a result, the curvature \(\kappa\) can be predesigned by tuning the thickness of the LDPE film (active layer) (Figure 3a) or the PI adhesive (passive layer) (Figure 3b) for different applications.

However, the thickness effects of the actuation layers on the curvature \(\kappa\) are not investigated experimentally due to the availability of commercial films. Here, we investigate both heating- and cooling-induced actuation behavior of the PI/Au/LDPE nanocomposite film by experiments to expand the capability of actuator working at extreme-low temperature. Different from
heat-induced thermal-responsive actuation behavior, PI/Au/LDPE nanocomposite film presents minus curvature during the cooling process. This theoretical result is certified by the phenomenon that PI/Au/LDPE nanocomposite film bends toward...
the LDPE film side when it is immersed into the liquid nitrogen (−196 °C) (Figure 3ci,ii). At ultralow temperature, PI/Au/LDPE nanocomposite film reveals ultrarobust mechanical property with the fact that it is not fractured even when the bent nanocomposite film is further compressed (Figure 3ciii,ciiv). In addition, flexibility and photoresponsive actuation behavior of the PI/Au/LDPE nanocomposite film well remain after 50 cycles of immersing and compressing in the liquid nitrogen (Figure S6, Supporting Information). This feature of PI/Au/LDPE nanocomposite film gives a potential opportunity for devising soft robots which can be operated within ultralow temperature condition in the future.

The facile and scalable fabrication process, reversible and stable photoresponsive actuation behavior, and ultrarobust mechanical properties of the PI/Au/LDPE nanocomposite film offer a promising platform for exploring biomimetic soft robots. Venus flytrap has the capability of automatically closing the leaves upon mechanical stimulation and distinguishing the prey (insects) from random particles like dust (Figure 4a,b). Inspired by this unique feature of the flytrap, we fabricated a fully light-powered microdevice simulating the flytrap actuation behavior (Figure 4c and Movie S2, Supporting Information). Upon exposure to NIR (0.65 W cm⁻²), both the leaf and cilia of the artificial flytrap can close to trap the prey. Without photostimulation, the leaf and cilia gradually open and recover to their initial state. Moreover, the combination of remote and local control characteristics of photo-driven and geometry design of the PI/Au/LDPE nanocomposite film enables us to devise biomimetic soft robots possessing more complex locomotion under distinct circumstances. As shown in Figure 4d, we achieved a directionally moveable caterpillar-inspired walker by utilizing an asymmetric design of the PI/Au/LDPE nanocomposite film. The caterpillar-inspired walker has a serrated-shaped head and a regular-shaped tail. Triggered by NIR light, the caterpillar-inspired walker can curl its body due to the bending behavior of the PI/Au/LDPE nanocomposite film. After removal of the NIR light source, the caterpillar-inspired walker stretches out its body because of the relaxation behavior of the PI/Au/LDPE nanocomposite film. During this relaxation process, the caterpillar-inspired walker can move forward because the rectangular-shaped tail bears much larger frictional force (F₁) than that of the serrated-shaped head (F₂). The directional locomotion of the caterpillar-inspired walker can be observed in Figure 4e and Movie S3, Supporting Information, and the crawl speed is about 22.6 mm min⁻¹ (1.13 body length min⁻¹).

In addition, we designed a cruisable dolphin-inspired swimmer in which the head controls the moving direction and the tail provides the motivation (Figure 5a). Thanks to the hydrophobic surface property and low density of the PI/Au/LDPE nanocomposite film (1.1 g cm⁻³) (Figure 5b), the dolphin-inspired swimmer can float on the water. As shown in Figure 5c and Movie S4, Supporting Information, dolphin-inspired swimmer moves forward under constant NIR light (2.01 W cm⁻²) irradiation and
stops moving until the NIR light source is released. The moving direction of the dolphin-inspired swimmer can be facilely controlled in our integrated swimmer design. The dolphin-inspired swimmer can rotate by illuminating its head part. To illustrate the locomotion behavior of the dolphin-inspired swimmer under constant NIR light irradiation, we examined the photopowered deformation of its tail with detail. The tail originally stays at the surface of the water without light exposure; however, upon exposure to the NIR light (2.01 W cm$^{-2}$), the tail gradually immerses into the water because of the photo-induced bending behavior of the PI/Au/LDPE nanocomposite film (Movie S5, Supporting Information). Resulting from the heat transfer of the tail underwater, the temperature of the tail would decrease rapidly, therefore, making it tend to recover to its initial state. This recovery behavior of the tail can be hindered by the continuous NIR light irradiation which may lead to the vibration of the tail. The vibration behavior of the tail is similar to the swing of a dolphin tail provides the power source for the locomotion of the dolphin-inspired swimmer. Compared with previously reported photo-driven swimmers,[19,44–48] the dolphin-inspired swimmer has relatively higher moving speed of 600 mm min$^{-1}$. Moreover, the dolphin-inspired swimmer maintains a high moving speed of 450 mm min$^{-1}$ and excellent cruise capability even loading a cargo eight times its weight (Figure 5d and Movie S6, Supporting Information).

3. Conclusions

In summary, we demonstrate a facile and scalable approach to fabricate a sandwich structured PI/Au/LDPE nanocomposite film featuring reversible and stable photoresponsive actuation behavior. In our design, the Au film acts as the functional layer with photothermal effect, which stimulates the mismatch between the CTE of the LDPE film and PI adhesive, providing photoresponsive actuation behavior of the PI/Au/LDPE nanocomposite film. The dexterous geometry design of the PI/Au/LDPE nanocomposite film and its reversible and stable actuation properties enable remote control with high precision. The photoresponsive actuation performance of the PI/Au/LDPE nanocomposite film is in accordance with the classical bimorph theory. Design of the actuation curvature at a wide temperature range by tuning the thickness of the PI and LDPE was achieved by numerical simulations. Biomimetic soft robots with pre-engineered functionality and complex locomotion such as photoresponsive artificial flytrap, directionally moveable caterpillar-inspired walker, and dolphin-like cruisable and loadable swimmer were demonstrated. Moreover, the ultrarobust mechanical properties of the PI/Au/LDPE nanocomposite film in an ultralow temperature environment promise future applications of soft robots in low-temperature circumstances. The achievements within this work provide a stepping-stone...
for designing and fabricating the next generation of untethered and advanced functional biomimetic robotic devices.

4. Experimental Section

Fabrication of Sandwich-Structured PI/Au/LDPE Nanocomposite Film: The Au film was first thermally evaporated onto LDPE film (crystalline degree of 40.6%, Changyi packing Co.) by evaporation coating system (JSD-300) for 30 min at room temperature. The sandwich-structured PI/Au/LDPE nanocomposite film was obtained by pasting the PI adhesive (DuPont Co.) on the Au-plated LDPE film. As a reference, PI/LDPE composite film with Au layer coating was also prepared by directly pasting a PI adhesive on the surface of a LDPE film. Fabrication of the nanocomposite film was done at room temperature ≈25 °C and the original sandwich structured PI/Au/LDPE nanocomposite film was flat.

Fabrication of Photoresponsive PI/Au/LDPE Actuators: Evaluation of the photoresponsive actuation behavior of the sandwich-structured PI/Au/LDPE nanocomposite film was conducted on tailored films, in which large-sized sandwich-structured PI/Au/LDPE nanocomposite films were cut into rectangle pieces with 5 mm in width and 20 mm in length.

General Characterization: The sandwich structure of the PI/Au/LDPE nanocomposite film was observed by SEM (ZEISS Ultra) and atomic force microscope (Digital Instruments Dimension 3100 AFM). The thermal expansion coefficients of the LDPE film and PI adhesive were tested by thermomechanical analyzer (TMA, 420F3) in tension mode with heating rate of 5 °C min⁻¹ in the range from −60 to 90 °C. The thermal stability of the LDPE film and PI adhesive was measured with a TA-Q50 TGA under air atmosphere. The temperature of the photoresponsive PI/Au/LDPE actuator was measured by an IR camera (FLIR system, A645sc). The photoresponsive actuation behavior of the PI/Au/LDPE actuator and biomimetic soft robots was conducted using MDL-W-808 with the wavelength of 808 nm.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
Y.Y. and R.P. contributed equally to this work. This work was supported by the Hubei Provincial Department of Science and Technology (grant no. 2020CFB522), the National Science Foundation of China (grant nos. 52073081 and 51673060), Overseas Excellence Introduction Center for Discipline Innovation (grant no. D18025), and Fundamental Research Funds for the Central Universities (3132021216, 3132019336).

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
biomimetic soft robots, photosensitive actuation behavior, sandwich-structured nanocomposite films, ultrarobust mechanical properties

Received: January 19, 2021
Revised: June 23, 2021
Published online: July 23, 2021

[1] D. Rus, M. T. Tolley, Nature 2015, 521, 467.
[2] L. Yu, P. X. Si, B. Lukas, B. X. Zhao, Langmuir 2020, 36, 3279.
[3] E. W. Hawkes, S. M. Blumenschein, J. D. Greer, A. M. Okamura, Sci. Robot. 2017, 2, 3028.
[4] H. Shahsavani, A. Aghakhani, H. Zeng, Y. B. Guo, Z. S. Davidson, A. Priimagi, M. Sitti, P. Natl. Acad. Sci. USA 2020, 117, 5125.
[5] G. M. Whitesides, Angew. Chem., Int. Ed. 2018, 57, 4258.
[6] W. Wang, J. Y. Lee, H. Rodrigue, S. H. Song, W. S. Chu, S. H. Ahn, Sci. Robot. 2020, 5, 3279.
[7] Y. Forster, J. M. Soto, J. Dumas, L. Mahadevan, Nature 2005, 433, 421.
[8] J. H. Pikul, S. Li, H. Bai, R. T. Hanlon, I. Cohen, R. F. Shepherd, Science 2017, 358, 210.
[9] I. Must, E. Sinibaldi, B. Mazzolai, Nat. Commun. 2019, 10, 344.
[10] P. Rothemund, A. Aina, L. Belding, D. J. Preston, S. Kurihara, Z. G. Soo, G. M. Whitesides, Sci. Robot. 2018, 3, 7986.
[11] M. Kanik, S. Orguc, G. Varnavides, J. Kim, T. Benavides, D. Gonzalez, T. Akintilo, C. C. Tasan, A. P. Chandrakasan, Y. Fink, P. Anikeec,
Bioinspir. Biomim. 2014, 9, 046006.
[12] Y. Forterre, J. M. Soto, J. Dumas, L. Mahadevan, Nature 2005, 433, 421.
[13] J. H. Pikul, S. Li, H. Bai, R. T. Hanlon, I. Cohen, R. F. Shepherd, Science 2017, 358, 210.
[14] I. Must, E. Sinibaldi, B. Mazzolai, Nat. Commun. 2019, 10, 344.
[15] P. Rothemund, A. Aina, L. Belding, D. J. Preston, S. Kurihara, Z. G. Soo, G. M. Whitesides, Sci. Robot. 2018, 3, 7986.
[16] M. Kanik, S. Orguc, G. Varnavides, J. Kim, T. Benavides, D. Gonzalez, T. Akintilo, C. C. Tasan, A. P. Chandrakasan, Y. Fink, P. Anikeec,
Bioinspir. Biomim. 2014, 9, 046006.
[44] C. L. Huang, J. A. Lv, X. J. Tian, Y. C. Wang, Y. L. Yu, J. Liu, Sci. Rep. 2015, 5, 17414.

[45] S. Palagi, A. G. Mark, S. Y. Reigh, K. Melde, T. Qiu, H. Zeng, C. Parmeggiani, D. Martella, A. S. Castillo, N. Kapernaum, F. Giesselmann, D. S. Wiersma, E. Lauga, P. Fischer, Nat. Mater. 2016, 15, 647.

[46] H. M. Tian, Z. J. Wang, Y. L. Chen, J. Y. Shao, T. Gao, S. Q. Cai, ACS Appl. Mater. Interfaces 2018, 10, 8307.

[47] X. D. Wang, N. D. Jiao, S. Tung, L. Q. Liu, ACS Appl. Mater. Interfaces 2019, 11, 30290.

[48] Y. S. Zhao, C. Xuan, X. S. Qian, Y. Alsaid, M. T. Hua, L. H. Jin, X. M. He, Sci. Robot. 2019, 4, 7112.