

Light-driven Self-sustained Rolling of Cylinder Hydrogels with Fast and Anisotropic Responses

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Electronic Supplementary Information

Abstract Achieving continuous motions typically requires dynamic external stimuli for cyclic deformation, or crafted geometries with intricate modules to form a self-regulated feedback loop upon static stimulation. It is still a grand challenge to realize self-sustained motion in soft robots subject to unchanging environment, without complex geometry or a control module. In this work, we report soft robots based on an anisotropic cylindrical hydrogel showing self-regulated, continuous rolling motions under constant light irradiation. The robots are animated by mirror-symmetry-breaking induced by photothermal strain gradient. The self-sustained motion is attributed to the fast and reversible deformation of the gel and the autonomous refresh of the irradiated region during the rolling motion. The hydrogel robots can reach a rolling speed of $1.27 \text{ mm} \cdot \text{s}^{-1}$ on a horizontal surface and even climb a ramp of 18° at a speed of $0.57 \text{ mm} \cdot \text{s}^{-1}$ in an aqueous environment. Furthermore, the hydrogel robots can overcome an obstacle, with rolling direction controllable through irradiation angle of the light and local irradiation on selective regions. This work suggests a facile strategy to develop hydrogel robots and may provide unforeseen inspirations for the design of self-regulated soft robots by using other intelligent materials.

Keywords Self-sustained motions; Light-driven; Rolling; Anisotropic hydrogels; Soft robots

Citation: Zhu, Q. L.; Cheng, H. L.; Liu, W. X.; Xiao, Y. B.; Wu, X. L.; Breu, J.; Hong, W.; Wang, Z. J.; Zheng, Q.; Wu, Z. L. Light-driven self-sustained rolling of cylinder hydrogels with fast and anisotropic responses. *Chinese J. Polym. Sci.* 2025, 43, 548–555.

INTRODUCTION

Natural organisms flexibly adapt to their external environment and convert constant stimuli to complex motions and other functionalities.^[1–3] These fascinating phenomena have garnered significant interest from many researchers, leading to the rapid development of soft bionics and robots by using various intelligent materials, such as hydrogels, liquid crystal elastomers (LCEs), and shape memory polymers (SMPs).^[4–22] While contemporary soft robots made of LCEs and SMPs can mimic the continuous motions of life, they usually rely on heterogeneous or dynamic external stimuli for cyclic deformation.^[9,11,12,14] In recent years, there have been notable advancements in designing soft robots capable of continuous motions such as rolling and swimming under constant conditions.^[23–31] However, the

soft robots with self-regulated rolling movements often necessitate structures of complex designs (e.g., kirigami structures, helical or tubular configurations)^[27,28,32,33] and/or assembly of dissimilar responsive elements.^[7,26,27,32,34–40] For example, Cheng *et al.* prepared a light-driven petal-like rolling robot by introducing kirigami patterns into a light-responsive LCE film.^[28] To simplify the complex geometry, Cai *et al.* prepared an anisotropic LCE rod and achieved continuous rolling on a hot plate that built up a temperature gradient.^[29] However, the use of heat stimulation poses limitations on the direction control of soft robots. Moreover, the high temperature required for actuation severely restricts their applications, particularly in an aqueous environment. Overcoming these challenges to achieve self-sustained motions with controlled directions is important for the development of untethered soft robots with simplified geometry and broad applications.

Hydrogels, characterized by their high water content and responsiveness to various stimuli, have garnered substantial interest in the development of soft robots capable of executing tasks in aqueous environments.^[14,41–43] Among various stimuli, light emerges as an effective means to remotely pow-

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Special Topic: Smart Elastomers and Actuators

Received June 15, 2024; Accepted July 5, 2024; Published online October 21, 2024

er the hydrogel robots.^[4,9,11,35,44–46] Herein, we report a light-powered soft robot made of cylinder hydrogel showing self-regulated rolling motion under water. The anisotropic hydrogel cylinder with highly oriented nanosheets (NSs) and randomly dispersed gold nanoparticles (AuNPs) exhibits a fast and isochoric deformation upon heating. Under inclined light irradiation, the gel bends toward the light source due to photothermal strain gradient, which breaks the rotational symmetry and thereby animates the gel robot to roll on a flat surface. The self-sustained motion is attributed to the fast, reversible deformation and the refreshed irradiation region of the gel. Notably, the gel robot sustains continuous rolling even on a slope of 18°. Furthermore, we demonstrate its capacity of crossing obstacles and executing turning maneuvers through light modulation. These results indicate that the gel robot has the possibility of moving on 3D terrains with versatile motions.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAm, the monomer) was bought from Aladdin Chemistry Co., Ltd. *N,N'*-methylenebis(acrylamide) (MBAA, the crosslinker) was purchased from Sigma Aldrich. Lithium phenyl-2,5,6-trimethylbenzoylphosphine (LAP, the photo-initiator) was synthesized according to the reported protocol.^[47,48] Fluorohectorite $[\text{Na}_{0.5}]^{\text{inter}}[\text{Li}_{0.5}\text{Mg}_{2.5}]^{\text{oct}}[\text{Si}_5]^{\text{tetr}}\text{O}_{10}\text{F}_2$ nanosheets (NSs) were synthesized by melt synthesis according to the literatures.^[49,50] The NS powers spontaneously swelled and delaminated into single lamellae of 1 nm thickness when immersed in deionized water. The NSs had a high charge density of 1.1 nm^{-2} and a high aspect ratio of *ca.* 20000. The obtained suspension with 1.0 wt% of NSs showed a nematic phase at room temperature. Gold nanoparticles (AuNPs) were synthesized by reduction process as reported in the literature,^[51] the average size of synthesized AuNPs was about 9.5 nm.

Synthesis of Anisotropic Hydrogels

The suspension of NSs (content of 1.0 wt%) was obtained by adding 0.1 g of NS powder into 9.9 g of water and shaking with a speed of 60 r/min for 1 month at room temperature. The precursor solution was prepared by mixing the NIPAm of 10.1 wt%, MBAA of 0.28 wt%, LAP of 0.11 wt%, and AuNPs of 0.35 wt% into the suspension of NSs (89.16 wt%). The precursor solution was injected into transparent rubber tubes with inner diameter of 1.0, 1.3, 1.5, or 2.0 mm at a flow rate of $11 \text{ mm}\cdot\text{s}^{-1}$, and immediately exposed to 365 nm ultraviolet (UV) light for 90 s to complete the photopolymerization. The ordered structure of NSs was permanently immobilized by the network to produce an anisotropic cylindrical hydrogel. The obtained cylindrical hydrogels were swelled in large amount of water to remove the residuals and reach the equilibrium state at room temperature.

Characterizations

The precursor solutions and anisotropic hydrogels were observed under a polarizing optical microscope (POM; LV100N POL, Nikon) with and without 530 nm tint plate. Small angle X-ray scattering (SAXS) measurements of hydrogels were conducted on the Xeuss SAXS system (Xenocs SA). The wavelength of X-ray was 0.154 nm, and the sample-to-detector distance was 1370 mm. *In situ* SAXS measurements were performed to the

anisotropic gel during heating and cooling at the beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF), in which X-ray wavelength was 0.124 nm and the sample-to-detector distance was 1954 mm. The intensity-azimuthal plots were used to calculate the orientation degree (π) of NSs according to $\pi = (180 - H)/180$, where H is the half width of the peak of the azimuthal plot from the selected equatorial reflection.

RESULTS AND DISCUSSION

Aqueous suspension of NSs containing prescribed amounts of AuNPs, monomer, and photoinitiator is in a nematic phase and used to prepare responsive poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel. NSs within the precursor can be easily oriented by external force or shear flow.^[50,52] The precursor solution is injected into a transparent rubber tube at a flow rate of $11 \text{ mm}\cdot\text{s}^{-1}$, which leads to orientation of NSs along the tube; the tube is then immediately exposed to UV light to initiate the polymerization of the precursor. The aligned structure of NSs is fixed by the polymer network, and anisotropic cylindrical hydrogel is thus obtained (Fig. 1a). The resultant hydrogel exhibits strong birefringence along the shear direction under polarized optical microscopy (POM), and the cross-section of the gel shows a Maltase cross, indicating that the NSs are concentrically aligned along the cylinder (Fig. 1b and Fig. S1 in the electronic supplementary information, ESI). The synthesis process has been optimized through systematic experiments; flow rate of $11 \text{ mm}\cdot\text{s}^{-1}$ and NS content of 1.0 wt% are used for the synthesis of anisotropic gels (Figs. S2 and S3 in ESI). The alignment of NSs within the gel is also confirmed by SAXS measurement. When the gel is exposed to the X-ray beam orthogonally, 2D SAXS image shows an elliptical diffusion pattern with its longer axis orthogonal to the shear direction. The orientation degree of NSs within the gel calculated from the intensity-azimuthal plot is 0.84 (Fig. S3 in ESI). The highly oriented NSs endow the hydrogel with a fast and isochoric deformation upon heating. When immersed in a water of 40 °C for 5 s, above the lower critical solution temperature of PNIPAm (LCST, 32 °C), the gel contracts by 0.78 in length (parallel to the alignment of NSs) and expands by 1.14 in diameter (Fig. 1b and Fig. S4 in ESI). The isochoric deformation of the gel is attributed to the increased electrostatic permittivity of the media after the release of water molecules previously bound to the PNIPAm chains; this increased permittivity enhances electrostatic repulsion between the NSs.^[53–56] When the temperature drops below the LCST, the gel rapidly recovers its original state. The varying anisotropic structure of NSs during the isochoric deformation of the gel is monitored by *in situ* SAXS measurements (Fig. S5 in ESI). Upon heating, the 2D scattering pattern becomes less elliptical, corresponding to a reduced orientation degree of 0.72.

AuNPs, as a high-efficiency photothermal agent, show a characteristic absorption peak at 520 nm (Fig. S6 in ESI), endowing the gel with response to light. As shown in Fig. S7 (in ESI), upon light irradiation (light wavelength, 520 nm; light intensity, $1.1 \text{ W}\cdot\text{cm}^{-2}$), the local temperature of the gel raises above the LCST within 3 s. Due to the limited depth of light penetration, a photothermal gradient and resultant strain gradient are generated, driving the gel to bend toward light. As shown in Figs. 1(c) and 1(d), the gel with a diameter of 1.5 mm bends toward light with a bending angle of 58° after 3 s

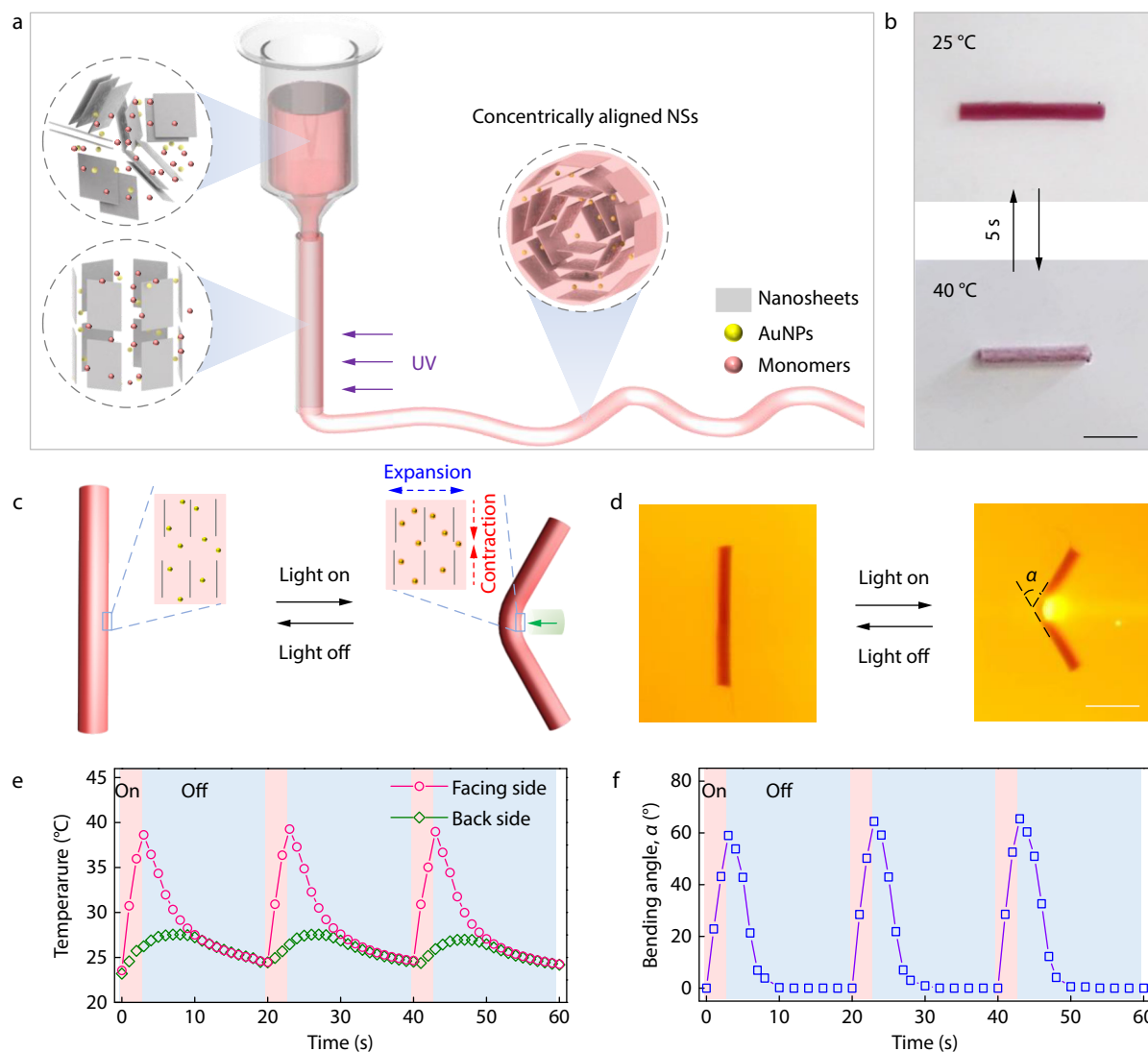


Fig. 1 (a) Preparation of anisotropic cylinder hydrogel with concentric alignment of NSs induced by shear flow before photopolymerization. Crosslinker and photoinitiator are omitted for simplicity. (b) Thermal response of the anisotropic cylinder gel. (c, d) Schematics (c) and photos (d) for photothermal bending of the anisotropic gel. (e, f) Varying local temperatures (e) and bending angle (f) of the gel under cyclic light irradiation. Green arrow in (c) represents the direction of light irradiation. Light intensity, $1.1 \text{ W}\cdot\text{cm}^{-2}$; gel diameter, 1.5 mm; gel length, 20 mm. Scale bar: 10 mm.

of light irradiation and recovers the initial state within 15 s after switching off the light. Under light irradiation, the local temperature of illuminated side of the gel increases to 45°C in 3 s, causing the contraction in length of the irradiated region, whereas the unilluminated side keeps a temperature below the LCST and the dimensions of this side remain unchanged (Fig. 1e). The light-induced asymmetric strain in the cross-section bends the gel toward the light. Under cyclic light irradiation, the hydrogel exhibits fast and repeated photothermal bending and unbending (Fig. 1f).

An interesting phenomenon is that constant light irradiation on the central of the cylindrical hydrogel results in continuous rolling motion. When a cylindrical gel (diameter, 1.5 mm; length, 20 mm) is irradiated on its center by a light spot (diameter, 8 mm; intensity, $1.1 \text{ W}\cdot\text{cm}^{-2}$) from the top (irradiation angle, 90°), the gel rolls to left or right randomly with a rolling speed of $1.27 \text{ mm}\cdot\text{s}^{-1}$. When the gel is exposed to the

light at an angle of 80° , it bends and rolls continuously with a specific direction (toward the light) with the speed of $0.93 \text{ mm}\cdot\text{s}^{-1}$ (Fig. 2a). The animation of gel robot is attributed to the mirror symmetry-breaking of the gel induced by out-of-plane bending under light irradiation. When the cylindrical gel is placed on a horizontal surface, the gravity and the balanced supporting force are distributed homogeneously along the length, without lateral force or torque on the gel. When exposed to the light spot with an oblique irradiation angle, the gel bends toward the light with a lateral bending angle θ , i.e., bending toward x-axis direction in Fig. 2(b). Consequently, the gravity and the support force no longer align, generating a torque that drives the cylindrical gel to roll toward the bending direction. With the friction between the gel and the substrate, the continuous rolling results in directional motion of the cylinder gel. As expected, the rolling direction can be controlled by adjusting the irradiation direction of the light

(Movie S1 in ESI). It is worth noting that the irradiation region is autonomously refreshed during the rolling, which is crucial for the morphing and motion of the gel under constant condition. The temperature of the irradiated side is consistently higher than the other side, which guarantees the self-sustainability of the rolling of the gel robot. The kinematics is further confirmed by the simulated temperature distributions of the gel during its rolling motions (Fig. 2c and Movie S2 in ESI).

Under constant light irradiation, the gel robot starts to roll with an increasing speed, then moves forward with an almost constant rolling speed of $0.93 \text{ mm}\cdot\text{s}^{-1}$ (Fig. 2d). However, upon closer examination, the lateral bending angle θ and the rolling speed v exhibit oscillatory behaviors, displaying opposite trends as functions of the irradiation time. This periodic oscillation should arise from the mismatch between the rapid photothermal heating process and the relatively slow cooling process (Fig. 2d). During the motion, the bent gel induced by photothermal gradient provides the actuated torque, driving

the gel robot roll toward light. However, a larger θ corresponds to a higher temperature of the irradiated region, necessitating more time of cooling and shape recovery, which hinders the rolling motion. Therefore, the value of θ is closely related to the rolling state of the gel robot. When θ is smaller than a threshold, approximately 19° in this case, the irradiated region has sufficient time to recover, affording gradually speeding up of the gel robot (Fig. 2c(ii)). However, when θ exceeds 19° , the recovery of lateral bending deformation requires an extended cooling time. This slow deformation recovery at large θ constrains the rolling motion, leading to a reduction in v (Fig. 2c(ii)). Numerical simulations found the same variation trends of θ and v , along with the temperature distribution of the gel during the rolling. As the temperature of the lateral side of the central gel increases, θ rises from 19° to 28° but v decreases from $1.1 \text{ mm}\cdot\text{s}^{-1}$ to $0.73 \text{ mm}\cdot\text{s}^{-1}$ (Figs. 2c and 2e). This reduced v , in turn, provides sufficient time for the actuation of the freshly irradiated region and the recov-

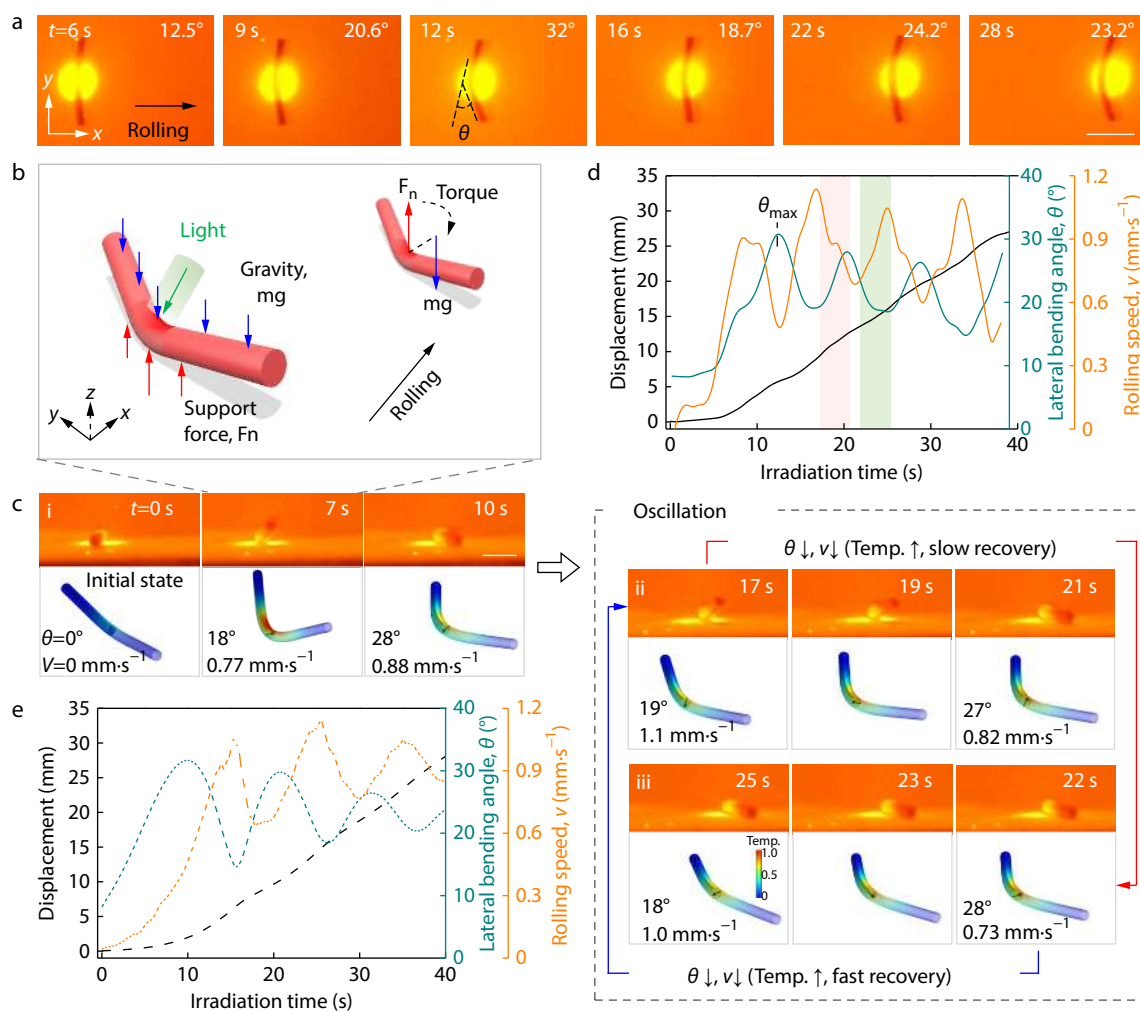


Fig. 2 (a) Continuous rolling of the cylindrical gel on a flat surface under constant light irradiation. Irradiation angle of light is 80° ; (b) Schematic for the mechanism of rolling motion of the gel robot under light irradiation; (c) Photos of the rolling motion of the gel robot taken from side view and numerical simulations of the self-sustained rolling motion. Snapshots of simulated configurations with related θ and v of the gel during the motion are showed under the photos. Color scale represents the temperature distribution of the gel during the motion. (d) Displacement, lateral bending angle θ and rolling speed v of the gel robot as a function of the irradiation time; (e) Simulated displacement, θ and v of the gel robot as a function of irradiation time. Gel length, 20 mm; gel diameter, 1.5 mm; light intensity, $1.1 \text{ W}\cdot\text{cm}^{-2}$. Scale bar: 10 mm.

ery of the lateral bending deformation, which tends to decrease θ . Conversely, as θ decreases, the gel exhibits fast recovery and increased v (Fig. 2c(iii)). As shown by the simulation results, v increases as θ decreases, accompanying with decreased local temperature of the gel (Fig. 2e). The maximal v is determined by the time of the actuation and recovery of the gel. In brief, the gel robot demonstrates self-sustained rolling motion characterized by oscillations in θ and v under constant light irradiation, which is, to the best of our knowledge, different from the rolling motions of other cylindrical materials with a uniform speed.^[7,27,29,37–39] One major reason is the varying contact of the two ends of the gel robot on the flat substrate upon local irradiation with a light spot, when compared to the uniform light irradiation or heating on the total cylindrical LCEs or SMPs. This rolling velocity of our gel robot is comparable or superior to that of LCE-based rolling robots (Fig. S8 in ESI). Experiments and numerical simulation results demonstrate that the self-sustained motion is attributed to the fast, reversible deformation of anisotropic gel and refreshed irradiated region during the rolling. In contrast, the isotropic PNIPAm hydrogel without NSs fails to sustain continuous rolling motion under spot light irradiation (Fig. S9 in ESI).

Effects of the length and the diameter of cylindrical gels, as well as the intensity and the irradiation angle of light beam on the rolling motions are systematically investigated. As

shown in Fig. 3(a) and Fig. S10(a) (in ESI), with the increase in gel length from 10 mm to 30 mm, the gel robot exhibits continuous rolling with an increased speed from 0.4 mm·s⁻¹ to 1.0 mm·s⁻¹ under constant light irradiation (intensity, 1.1 W·cm⁻²; spot diameter, 8 mm; irradiation angle, 80°). Extremes in gel length is detrimental to the effective rolling motion. When the gel length increases to 40 mm, the rolling becomes discontinuous. At the beginning, the gel bends toward the light and then suddenly lies down on the surface with a maximal θ ($\theta_{\max}$) of 45°. Meanwhile, the two sides of the gel neighboring the irradiated region again contact the substrate, resulting in an increased friction. Consequently, the gel with extreme long length cannot timely recover from the bending. Prolonged irradiation and photothermal heating of the same irradiated region keep θ unchanged, making the gel fail to roll continuously. A cylinder gel with the length of 20 mm, capable of self-sustained rolling, is selected as the model for the following discussions. Fig. 3(b) and Fig. S10(b) (in ESI) show the effects of gel diameter on $\theta_{\max}$ and the rolling speed of the gel robots. The gel diameter influences the rolling motions through photothermal gradient within the soft robots. When the diameter is smaller than 1.0 mm, the light has penetrated through the majority of the gel depth. The internal stress induced by the photothermal gradient is insufficient to bend the cylindrical gel, leading to failure of animating the gel robot. With an increase in the diameter to 1.5

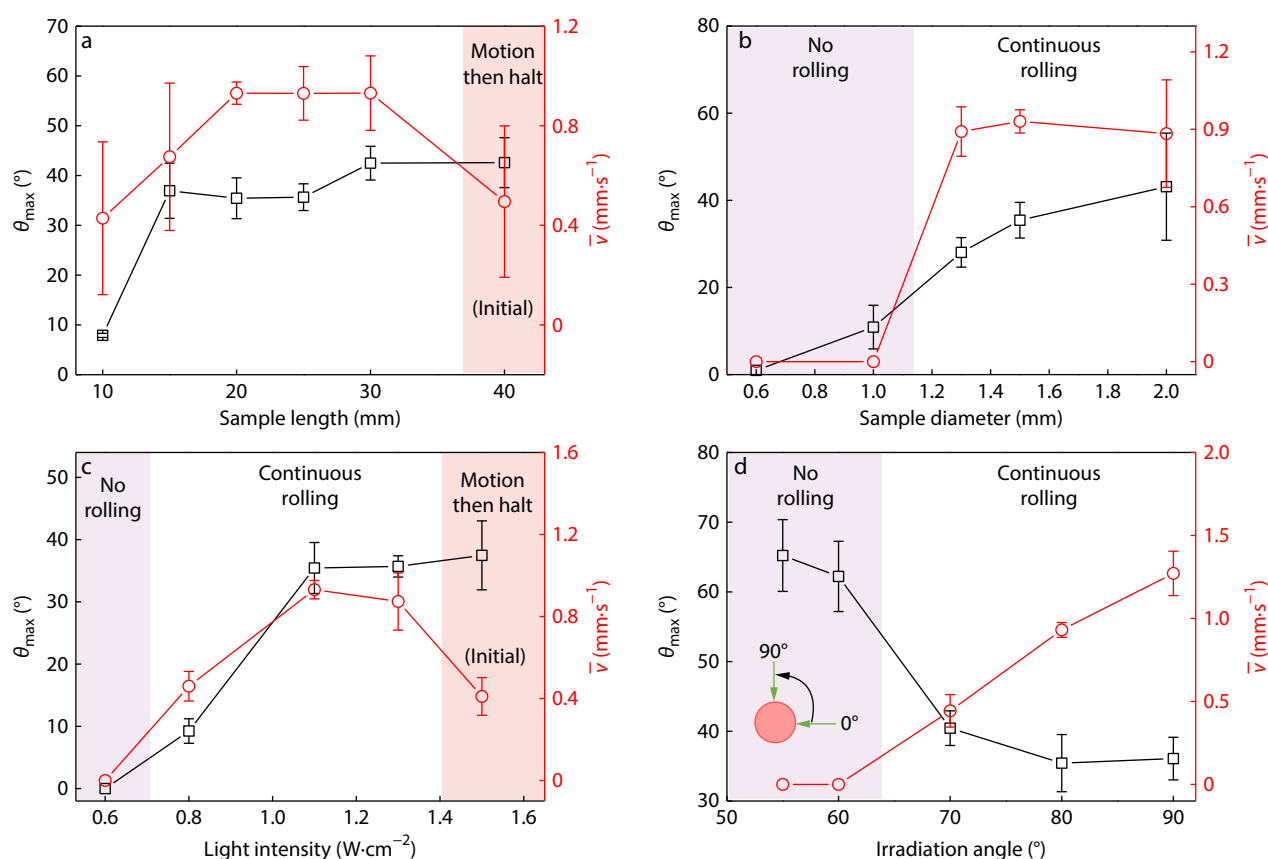


Fig. 3 Effects of length (a) and diameter (b), as well as light intensity (c) and irradiation angle (d) on rolling motion. After investigation, length and diameter are set as 20 and 1.5 mm, respectively; light intensity and irradiation angle of light are set as 1.1 W·cm⁻² and 80°, respectively. The data points in the "motion then halt" region represent results obtained during the initial motion.

mm, the cylindrical gel exhibits continuous rolling with a speed of $0.93 \text{ mm}\cdot\text{s}^{-1}$.

As expected, the light intensity also affects the rolling motions of the gel robots (Fig. 3c and Fig. S10c in ESI). When the light intensity is lower than $0.8 \text{ W}\cdot\text{cm}^{-2}$, the photothermal gradient is too weak to animate the rolling of the gel robot. As the light intensity increases from $0.8 \text{ W}\cdot\text{cm}^{-2}$ to $1.3 \text{ W}\cdot\text{cm}^{-2}$, the hydrogel robot exhibits continuous rolling with increasing θ_{max} from 9° to 30° and increasing speed from $0.5 \text{ mm}\cdot\text{s}^{-1}$ to $0.93 \text{ mm}\cdot\text{s}^{-1}$. With the further increase in power intensity to $1.5 \text{ W}\cdot\text{cm}^{-2}$, the rolling motion becomes unstable. At the beginning of light irradiation, the gel bends and rolls toward light quickly. However, due to the excessive thermal energy input compared to energy dissipation to surrounding water, the local temperature of the irradiated region increases and the corresponding bending cannot recover to original state, leading to gradual cessation of the motion. In the following, the light intensity is kept as $1.1 \text{ W}\cdot\text{cm}^{-2}$ for continuous motion of the gel robot. The gel robot exhibits continuous rolling over a wide range of irradiation angles, showing the robustness of the motions. As depicted in Fig. 3(d) and Fig. S10(d) (in ESI), when the irradiation angle increases from 70° to 90° , the

gel robots exhibit continuous rolling with an increasing speed from $0.45 \text{ mm}\cdot\text{s}^{-1}$ to $1.27 \text{ mm}\cdot\text{s}^{-1}$. However, when the irradiation angle is lower than 60° , the gel only bends toward the light with a θ_{max} of 62° , and the torque is insufficient to drive the gel to roll.^[57] In this case, the gel rod only bends toward light and lacks motion ability upon light irradiation. To afford the gel robot with controllable motion direction and moderate rolling speed, the irradiation angle of the light is set as 80° in this work.

Unlike other soft robots that require complex geometries to provide friction bias for climbing,^[28,32] the gel robot in this work can climb up on a slope without additional aids. As shown in Fig. 4(a), the gel robot smoothly maneuvers along an 18° slope at a speed of $0.57 \text{ mm}\cdot\text{s}^{-1}$ under light irradiation with an angle of 90° . However, when the slope increases to 25° , the gel robot succumbs to gravity and falls down along the slope (Fig. 4b, Fig. S11 and Movie S3 in ESI). The versatility of the gel robot extends its ability to traverse obstacles. The unique cocked ends of the rolling gel enable it to negotiate an obstacle with a height of 2 mm (Fig. 4c and Movie S4 in ESI). In addition, the control of motion directions can be realized by irradiation on selective region of the gel robot. When

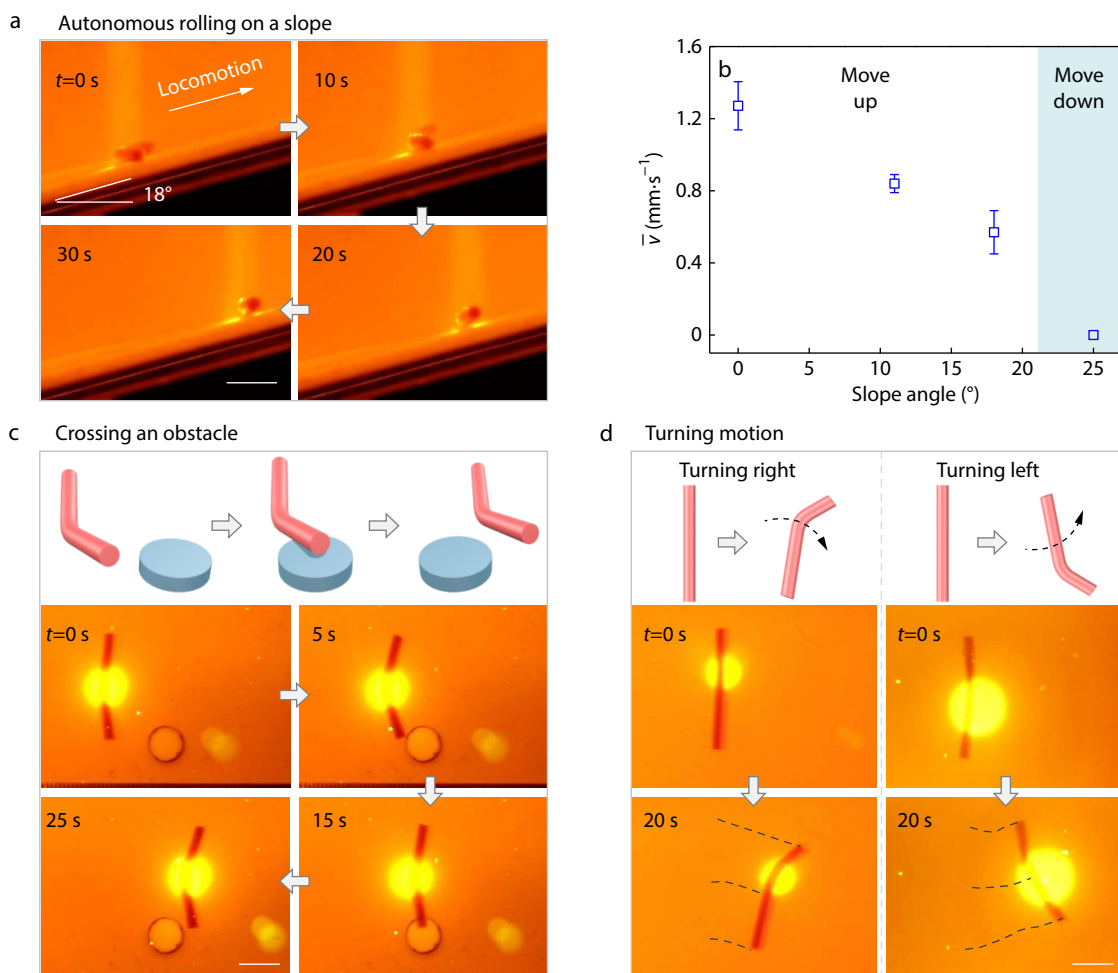


Fig. 4 (a) Autonomous rolling motion of the gel robot on a slope with angle of 18° . Irradiation angle, 90° ; (b) Rolling speed of a gel robot as a function of the slope angle; (c) Crossing an obstacle of the gel robot; (d) Light-driven turning motion of the gel robot. Light intensity, $1.1 \text{ W}\cdot\text{cm}^{-2}$; irradiation angle in (c) and (d), 80° . Scale bar: 10 mm.

the gel is irradiated on the center, symmetric bending of both arms leads to forward rolling. The gel shows asymmetric bending when irradiated on the region deviated the central, enabling turning to some extent of the gel robot during the rolling motion (Fig. 4d). When the light spot is biased to one side, the asymmetric bending and resultant temporal configuration dictate the gel robot to turn right or left (Movie S5 in ESI). These results indicate that the gel robots with a simple structure have versatile locomotion and potential applications under aqueous conditions.

CONCLUSIONS

In summary, we have achieved an untethered, self-regulated rolling motion of hydrogel robots through a simple design. The cylinder gel with concentric alignment of NSs exhibits fast and reversible deformation upon heating. Under light irradiation, the photothermal bending breaks the mirror symmetry of the gel and animates the soft robot to roll autonomously on a flat surface in aqueous environment. Experimental and simulation results reveal that the self-sustained rolling arises from the collective contributions of the fast, reversible deformation of the gel and the autonomous refresh of the irradiated region during the motions of gel robots. By adjusting light intensity and irradiation angle, the rolling motion can be automatically triggered and the speed could be turned. Furthermore, the gel robot is capable of rolling on an 18° slope, traversing obstacles, and turning right or left on demands. This work proposes a straightforward method to achieve self-regulated motions of soft and active materials under constant conditions, which may provide inspirations for the designs of other untethered soft robots.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-024-3196-3>.

Data Availability Statement

The data that support the results of this study are available from the corresponding author upon reasonable request. The contact information of corresponding author: wuziliang@zju.edu.cn (Z.L.W.), wangzj@icredd.hokudai.ac.jp (Z.J.W.).

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52325302 and 52173012) and Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering (No. 2022SZ-FR005). We acknowledge BL 16B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) for the SAXS measurements.

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