ACS APPLIED MATERIALS & INTERFACES

Research Article

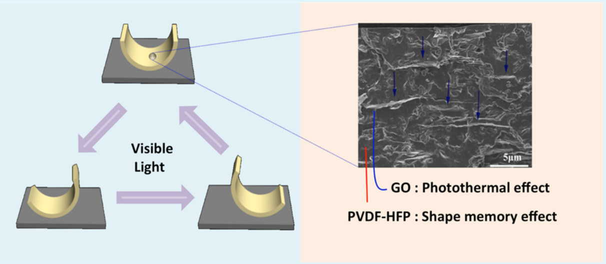
www.acsami.org

Light-Powered Tumbler Movement of Graphene Oxide/Polymer Nanocomposites

Li Yu and Haifeng Yu*

Department of Material Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

Supporting Information



ABSTRACT: Photoresponsive lamina and flexible graphene oxide/polymer nanocomposite films were fabricated using a simple solution casting method. Fast, stable, and reversible photomechanical behavior of the nanocomposite films upon irradiation with visible light was observed based on the photothermal effect of graphene oxide and the shape memory effect of the polymer matrix. According to the principle of equilibrium apparatus, light-powered tumbler movement was achieved in these films by imitating the structure of a wobbly man. Although photodriven contraction, expansion, bending, twisting, oscillation, and cilia movement have been realized in photomechanical materials, novel forms of complicated motion are still a bottleneck problem limiting their practical applications. This work would have a significant impact on photomechanical materials in device applications for advanced functions.

KEYWORDS: *photoinduced 3D movement, graphene oxide, polymeric nanocomposites, photothermal effect, shape memory effect*

INTRODUCTION

As one of the photomechanical materials, light-responsive polymers showing the capability to directly convert light energy into mechanical work have sparked enormous interest because they may play an important role in smart actuators, artificial muscles, and microelectromechanical systems (MEMS).[1−3] Compared to other stimuli-driven methods like electricity,[4] magnetism,[5,6] heat,[7,8] and moisture,[9] light is one clean energy source that can be controlled remotely, instantly, and precisely in one uncontacted way.[10−12]

Recently, a variety of photomechanical polymer materials have been developed based on hydrogels,[13] liquid-crystalline elastomers (LCEs),[14−16] and shape memory polymers (SMPs).[17,18] Multiple forms of movement mode involving contraction,[19] expansion,[20] bending,[21] twisting,[22] oscillation,[23] and cilia movement[24] have been achieved in these photomechanical polymer materials. A diversity of actuation devices such as soft robots,[25] inchworm walkers,[26] motors,[27] and smart curtains[28] have been designed based on these simple movement modes. However, complex micro- and macrostructures of photomechanical polymer materials are usually required, limiting their practical applications. Furthermore, novel light-driven forms of motion still remain challengeable to meet the requirement of device applications for advanced functions.

Here, we report a facile strategy to fabricate light active and flexible nanocomposite films based on graphene oxide (GO) and SMPs. These photoresponsive nanocomposite films show fast, stable, and reversible photomechanical behavior under visible-light due to the photothermal effect of GO and the shape memory effect of the polymer matrix. Moreover, complex structures can be conveniently manipulated in these films due to the unique shape programming process of the polymer matrix. This characteristic should be absolutely beneficial for their application as functional devices. Notably, light-powered tumbler movement was achieved in nanocomposite films by imitating the structure of a wobbly man. Our approach would provide photomechanical materials with imitating the structure of moving objects and contribute to developing complicated movement for full-plastic devices driven by light.

RESULTS AND DISCUSSION

The GO/poly(vinylidenefluoride-hexafluoro propylene) (PVDF-HFP) nanocomposite films were fabricated by directly casting a mixed solution of PVDF-HFP containing homogeneously dispersed GO on dry and clean glass substrates, as shown in Figure 1A. Graphite oxide was synthesized according to the modified Hummers method. GO was prepared by dispersing graphite oxide in dimethylformamide (DMF) and following ultrasonic treatment. The chemical composition and microstructure of GO are shown in Figures S1 and S2. A variety of oxygen-containing functional groups on the surface of GO were confirmed by FTIR and Raman spectra, which makes it stably homodispersed in DMF. The AFM image demonstrates that the thickness of GO flakes is about 1 nm, indicating that graphite oxide has been fully exfoliated in DMF solution.[29]

As shown in Figure 1B, the obtained nanocomposite film was flexible and suitable for fabricating a photoactuator. Here, GO may function as a light absorbent and nanoscale thermal source

Received: December 19, 2014
Accepted: January 26, 2015
Published: January 26, 2015

DOI: 10.1021/am508970k
ACS Appl. Mater. Interfaces 2015, 7, 3834−3839

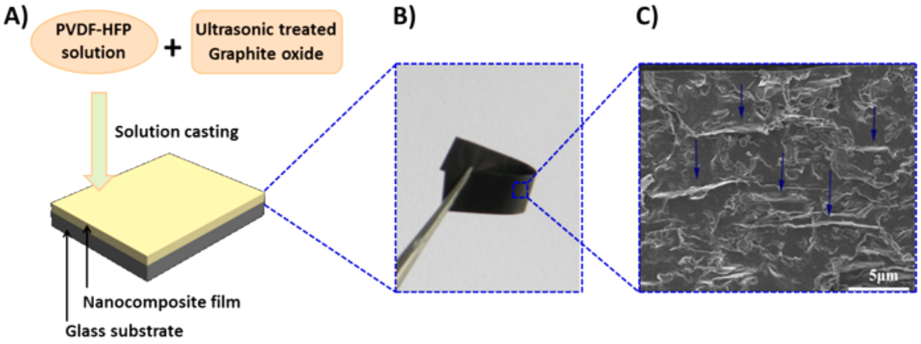


Figure 1. (A) Schematic illustration of the fabrication process of GO/PVDF-HFP nanocomposite film. (B) Optical image of the lamina and flexible GO/PVDF-HFP nanocomposite film with thickness of 50 μm. (C) SEM image of the fracture morphology of the nanocomposite film with 3 wt % GO.

to trigger the shape memory effect of the nanocomposite film. Compared to carbon nanotubes (CNTs) and gold nanoparticles, it exhibited good absorption in the visible region and was more easily homodispersed in solvents with a high concentration. These advantages should be beneficial for uniform dispersion of GO in films (Figure 1C). Furthermore, the excellent dispersion property of GO flakes could provide the nanocomposite film with unique photothermal features and high thermal conductivity, which would help for the improvement of photomechanical properties of the fabricated actuators.[21]

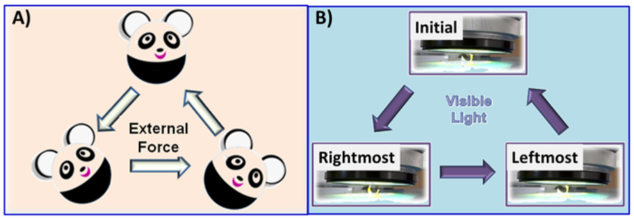


Figure 2. (A) Cartoon of typical tumbler movement of a wobbly man induced by mechanical force. (B) One oscillation cycle for the tumbler movement of GO/PVDF-HFP nanocomposite film induced by visible light (450 nm, 54 mW/cm^2).

Then we try to imitate the structure of a wobbly man using the nanocomposite film. As shown in Figure 2A and Video S1, three-dimensional (3D) tumbler movement mode is so special that it never falls down. When a mechanical force is applied, it starts to oscillate and slowly recover to the initial stationary state. Usually, two structural features play an important role in this interesting movement. One is that the lower part is much weightier than the upper one, making it difficult to turn down; the other is that the shape of the lower part is an arc, enabling the tumbler and smooth platform to exhibit linear contact in the vibrational motion. Usually, SMPs exhibit complex shape transitions by facile utilization of the shape programming process compared to hydrogels and LCEs. Therefore, the nanocomposite film was programmed from a flat square to a cylinder shape with $F = 0.6$ to imitate the two structural features of the nondownable doll. Here, a factor F was introduced to quantitatively characterize the bending degree of the films, which can be calculated by eq 1:

$$F = \frac{L_0 - L}{L_0} \qquad (1)$$

where L_0 and L are the linear length of the nanocomposite film before and after the shape programming process, respectively.

As shown in Figure 2B, the nanocomposite film started to oscillate upon irradiation of visible light (450 nm, 54mw/cm^2), similarly to special tumbler movement. Before irradiation, the film kept balance at its initial state. Once the light was switched on, it oscillated to the rightmost position, and then it returned to the initial state. But it never stopped at the initial position upon photoirradiation. Finally, it reached the leftmost place. The entire process can be defined as one oscillation cycle, which was completed within about 2 s, indicating an oscillation frequency of 0.5 Hz. As shown in Video S2, the tumbler movement of the nanocomposite film lasted for about 1 min without obvious fatigue. In fact, the oscillation cycle was repeated for several hours as long as the visible light was irradiated.

This light-powered tumbler movement of the nanocomposite film can be elucidated base on its photomechanical behavior and general principle of a lever. In the initial state, the film ($F = 0.6$) is simultaneously subjected to the gravity and the bracing force with equal magnitude in opposite directions, and the action falls into a straight line (see in Figure 3A). Thus, the film is in an equilibrium state before light irradiation. As shown in Figure 3B, the film ($F = 0.6$) unfolds to a state of $F = 0.5$ upon visible-light irradiation because of its photomechanical behavior. During the unfolding process, the equilibrium of the film is inevitably broken because of its asymmetry in shape. As a result, the film rocks to the right, and the contact line

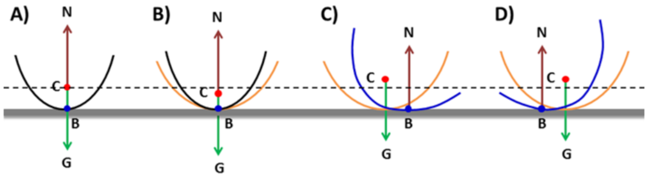


Figure 3. Schematic illustration of the light-powered tumbler movement. G and N represent the gravity and the bracing force. C and B represent the barycenter of the film and contact point between the platform and nanocomposite film, respectively. (A) Initial equilibrium state of the nanocomposite film. (B) Photoinduced unfolding behavior of the nanocomposite film. (C) Contact point shifts to right side of the barycenter due to the broken equilibrium of the film induced upon irradiation of visible light. (D) Contact point shifts to left side of the barycenter due to motion inertia of the film when it recovers to its initial state.

between the platform and the film simultaneously shifts to the right side of the gravity center, as shown in Figure 3C. At the same time, a left-rotation force moment is produced to enable the film to recover to its initial position after reaching the rightmost position. Due to the existence of motion inertia, the film will not stay at its initial state but continue rocking to the extreme left, as shown in Figure 3D. In this case, the contact line shifts to the left side of the gravity center and the action line of gravity and bracing force exhibits a displacement. This causes the film to generate a right-rotation force moment, driving the film to rotate to the reverse side. In this way, one cycle of the tumbler movement is achieved.

As shown in Video S1, the oscillating amplitude of one tilting doll gradually decreased under the function of friction. Then, it got to the initial stationary state after releasing the acquired energy from the applied mechanical force. If the external mechanical force is continuously applied, the tilting doll will uninterruptedly oscillate. Similarly, such continuous tumbler movement was maintained because visible-light acted as an external force always exerting on the nanocomposite film in the whole process, as shown in Video S2. Just like the movement of one daruma doll shown in Video S1, the tumbler movement of the nanocomposite film was gradually terminated once removing the visible-light source and the film folded to its initial state with F = 0.6. From the viewpoint of practical applications, reproducibility is one of the most significant characteristics of the tumbler movement in the nanocomposite film, which was investigated by turning on and off the visible light in cycles. The tumbler movement occurred immediately as visible light was turned on, while it gradually disappeared as the visible light was turned off, indicating good reproducibility.

In the dynamic condition of the tumbler movement (see in Figure 3), it is difficult to directly characterize the reversible photomechanical behavior of the nanocomposite film. As mentioned above, two structural features of one titling doll are the precondition for this interesting movement mode. When the nanocomposite film was programmed from the square shape (a permanent shape, shape A) to the cylinder shape with F = 0.4 (a temporary shape, shape B), it exhibited plane rather than linear contact with the platform. Therefore, the tumbler movement was not obtained because one structural feature was not satisfied.

As demonstrated in Figure 4A, the nanocomposite film (F = 0.4) showed reversible photomechanical behaviors of unfolding and folding. When the GO/PVDF-HFP nanocomposite film (left side) was placed directly under visible light (450 nm, 54 mw/cm^{-2}), it rapidly unfolded with F decreasing to 0.2, achieving an intermediate shape (shape C). This photoresponsive behavior was completed within 5 s. A further increase of exposure time made no effect on the photomechanical behavior. When the photoirradiation was stopped, the sample quickly folded and returned to shape B because of the shape memory effect of PVDF-HFP. Figure 4B shows the initial five cycles of shape shifting between shape B and shape C when the light was turned on or off without any decay, indicating the stability of the reversible photomechanical behavior. Furthermore, Video S3 clearly demonstrates two cycles of reversible photomechanical behaviors of the film. This photoresponsive behaviors are the result of a combination of the shape memory effect with the photothermal effect, which is far different from the photoactuation of LCEs based on photochemically induced phase transition behaviors.[14−16,21] Although the reversible shape-memory effect caused by heat with or without the external force has been reported recently,[30,31] this two-way reversible shape-memory effect triggered by visible light has never been reported. For comparison, pure PVDF-HFP film with the same shape programming process exhibited no response to visible light, demonstrating that GO played a key role in the photomechanical behavior.

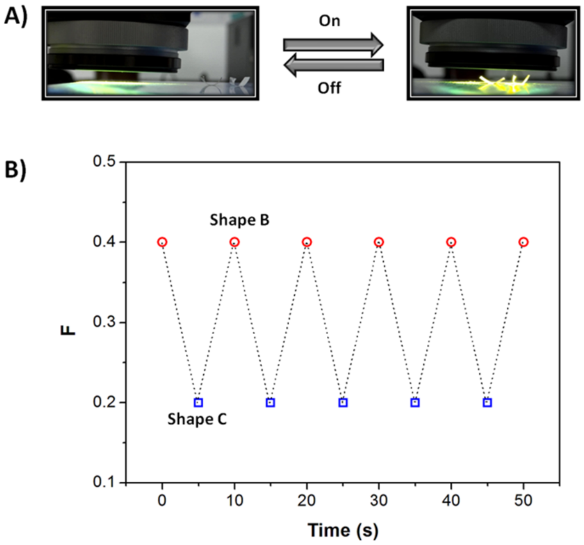


Figure 4. (A) Reversible photomechanical behavior of GO/PVDF-HFP nanocomposite film when turning visible light on and off (450 nm, 54 mW/cm^{-2}). Size and thickness of the nanocomposite film and the pure PVDF-HFP film are the same (1 mm × 1 mm and 50 μm). (B) Initial five cycles of the shape shifting between shape B and shape C when turning visible light on and off.

To clarify the reversible photomechanical behavior of the nanocomposite film, we first focus on the photothermal effect of GO. For comparison, the temperature of the nanocomposite film and pure PVDF-HFP film were measured with one infrared thermometer as visible light was turned on or off. As shown in Figure 5A, the temperature of the nanocomposite film was increased by 20 °C upon light irradiation. On the contrary, no obvious increase in temperature was observed in pure PVDF-HFP film. This verifies that GO exhibits good photothermal feature and may function as an effective nanoscale thermal source. Figure 5B shows that the temperature almost decreased to the room temperature after stopping the light irradiation. The rapid rise and decay of temperature were obviously detected because of high thermal conductivity of the nanocomposite film by incorporation with GO. Moreover, the time for the rise or decay of the temperature was close to that of photomechanical behavior, indicating that the photothermal effect of GO should be the most key to achieve reversible photomechanical behavior of the nanocomposite film.

Then, the shape memory effect of the PVDF-HFP copolymer was systematically investigated based on its microstructure and thermal property. As shown in Figure 6A, PVDF-HFP mainly exhibited three peaks at 2θ = 18.2°, 19.7°, and 26.4°, corresponding to 100, 110, and 021 diffractions all from the PVDF a phase.[32] Figure 6B shows the thermal property of the PVDF-HFP copolymer, three typical peaks at T_1 = 40.4 °C, T_2 = 75.5 °C, and T_3 = 131.2 °C, corresponding to melting points occuring in the heating process. From XRD and DSC curves of the copolymer, it is easy to know that that PVDF segments are crystallizable, and the HFP segment contributes to a broad

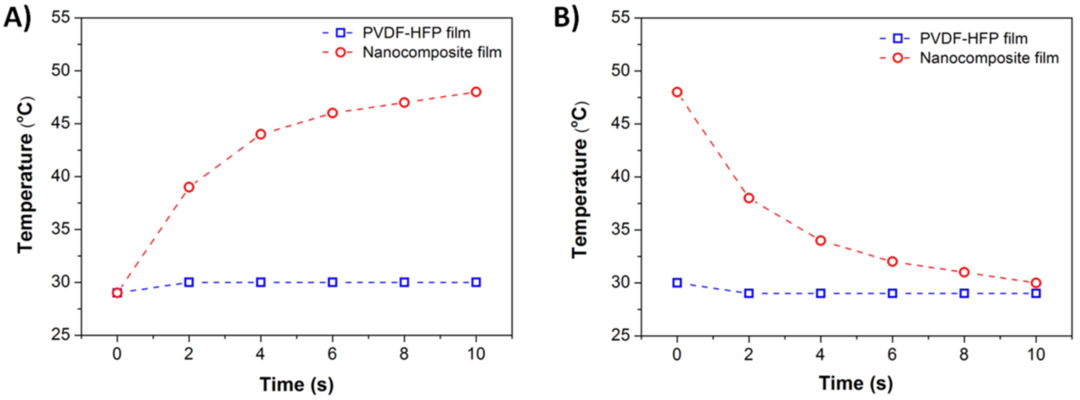


Figure 5. Change in temperature of films as a function of time upon irradiation with visible light (450 nm, 54 mw/cm^2) (A) and removal of the light (B).

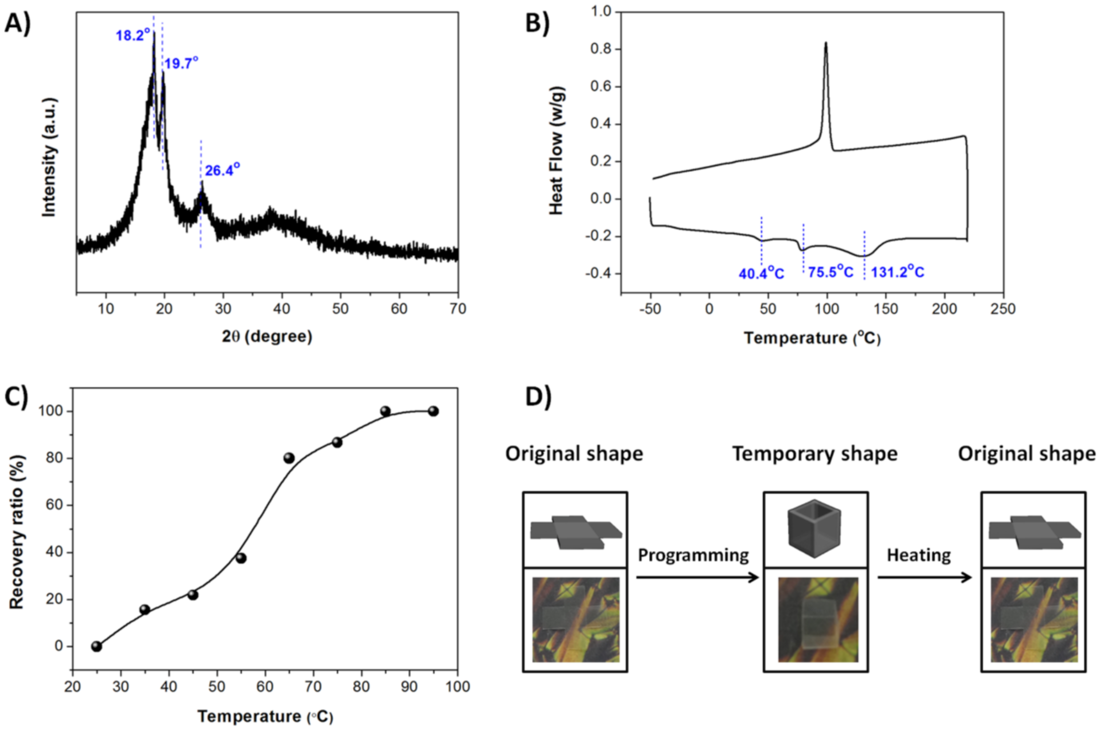


Figure 6. Shape memory effect of the pure PVDF-HFP film without GO. (A) XRD curve of PVDF-HFP copolymer. (B) Thermal properties of PVDF-HFP copolymer characterized by DSC. (C) Recover ratio of PVDF-HFP copolymer as a function of the temperature. (D) Direct shape changes of PVDF-HFP copolymer for expressing traditional one-way shape memory effect.

melting transition of PVDF crystallites. The shape memory effect of PVDF-HFP was characterized by a bending test according to previous reports.[9] Detailed information about the test protocol for quantifying the shape memory effect is given in the Materials and Methods section. In each shape memory cycle, the shape fixity (R_f) of the PVDF-HFP copolymer was almost approaching 100%. The shape recovery ratio (R_c) was evaluated in the temperature region from 25 to 95 °C (Figure 6C). As PVDF-HFP possessed a broad melting transition, it showed a distinctive recovery ratio at different temperatures. From room temperature to 45 °C, the recovery ratio was very small. When the temperature was set in the region of 45 to 75 °C, the recovery ratio significantly increased from 20% to 80%. When the temperature was higher than 75 °C, the recovery ratio almost reached 100%.

According to the microstructure and thermal property of the PVDF-HFP copolymer, the shape memory effect can be elucidated as follows. The PVDF-HFP copolymer has three crystal phases of $CrPs_1$, $CrPs_2$, and $CrPs_3$, corresponding to melting points of T_1 = 40.4, T_2 = 75.5, and T_3 = 131.2 °C, respectively. For the copolymer, $CrPs_1$ and $CrPs_2$ are switchable domains, and $CrPs_3$ acts as the physically cross-linked networks determining the permanent shape. To directly express the shape memory effect of PVDF-HFP, an origami-like PVDF-HFP sheet was programmed into a cubic box at 95 °C and fixed by cooling down to 25 °C under constant external force (Figure 6D). The shape of the PVDF-HFP copolymer changed from a cubic box to origami-like sheet when it was heated up to 95 °C. The shape of the PVDF-HFP film did not change reversibly from an origami-like sheet to a cubic box by cooling, which is known as the traditional one-way shape memory effect.[33] Additionally, it also reveals that complex structure can be conveniently manipulated in PVDF-HFP film due to the unique shape programming process for SMPs.

On the basis of the photothermal effect of GO and shape memory effect of PVDF-HFP, the possible mechanism of reversible photoactuation behavior for the GO/PVDF-HFP nanocomposite film can be proposed correspondingly. In the nanocomposite film, GO functions as the only photoabsorbent and nanoscale heat source since PVDF-HFP is inert to visible light. It must be mentioned here that characteristic melting points of PVDF-HFP were not influenced by the incorporation of GO as shown in Figure 7A. When visible light is switched on, GO can effectively absorb light and transfer it into thermal energy, thereby instantly heating the nanocomposite film from 28 to 48 °C. In this case, only the crystal phase $CrPs_1$ is melted (higher than T_1, but lower than T_2), leading to the shape change from shape B to shape C (Figure 7B). Meanwhile, the crystal phase $CrPs_2$ remains and acts as an internal skeleton to promise that crystal phase $CrPs_1$ returns to its original state in the crystallization process.[31] Therefore, shape C recovers to shape B after removing visible light by cooling the film down from 48 to 28 °C.

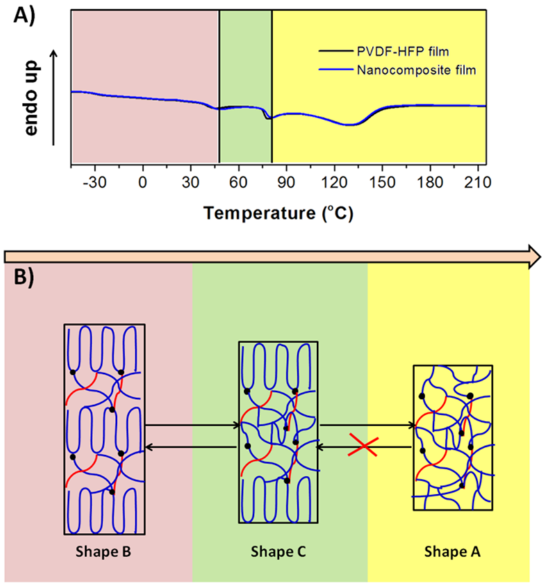


Figure 7. Possible mechanism for the reversible photomechanical behavior of the GO/PVDF-HFP nanocomposite film. (A) DSC curves of pure PVDF-HFP and the GO/PVDF-HFP nanocomposite with a GO content of 3 wt %. (B) Scheme illustration of the microstructure of the nanocomposite film showing the two-way and one-way shape memory effect.

Further, to prove our conjecture, we adopted near-infrared (NIR) light (808 nm, 1.5 W/cm^{-2}) to explore the photomechanical behavior of the nanocomposite film. Upon NIR irradiation, the temperature of the film rapidly increased from 28 to 80 °C (higher than T_2, but lower than T_3). In this case, the nanocomposite film directly changed from shape B to shape A because both of the crystal phases $CrPs_1$ and $CrPs_2$ are melting (Figure 7B). After removal of the NIR light, the nanocomposite film did not show an obvious change in shape, although the temperature decreased to 28 °C. Thus, the nanocomposite film did not exhibit reversible photomechanical behavior but a light-driven one-way shape memory effect as both of the crystal phases $CrPs_1$ and $CrPs_2$ were melting, which agrees with our conjecture.

CONCLUSIONS

In summary, light-powered tumbler movement was successfully obtained in GO/PVDF-HFP nanocomposite films by imitating the structural feature of a tilting doll. The imitating process can be conveniently performed due to the unique shape programming process of SMPs. Visible light acted as both a trigger and an external force for starting and maintaining the tumbler movement. The tumbler movement can be completely reversible by turning the visible light on and off in cycles because of the interesting photomechanical behavior of the nanocomposite film, which was attributed to the incorporation of the photothermal effect of GO with the shape memory effect of PVDF-HFP. It is expected that more complicated movement can be achieved in photomechanical nanocomposite films for full-plastic devices of advanced functions driven by visible light.

MATERIALS AND METHODS

Materials. PVDF-HFP, density 1.78 g/cm^3, and DMF were purchased from Sigma-Aldrich and used as received. GO was prepared according to our previous report.[29]

Fabrication of Nanocomposite Films. PVDF-HFP (3.0 g), GO, and DMF (25 mL) were mixed and heated to 80 °C and stirring to obtain a homodispersed solution. The mixture was cast onto a glass substrate and heated at 220 °C until DMF was completely evaporated. For the investigation of photoinduced tumbler movement and reversible photomechanical behaviors, the nanocomposite film with 3 wt % GO was fabricated with a shape of 1 cm × 1 cm and a thickness of around 50 μm.

Shape Programming Process. A flat nanocomposite film with a square shape of 1 cm × 1 cm was programmed to a cylinder shape, as shown in Figure S2.

Test Protocol for Quantifying the Shape Memory Effect of PVDF-HFP.[5] The PVDF-HFP film was folded to a bending shape with a bending angle of 180° at 95 °C and then cooled down to 25 °C to fix the shape under constant external force. The bending angle θ for the PVDF-HFP film was measured when a fixed temperature was reached. The shape recovery ratio (R_c) for fixed temperature was calculated by eq 2:

$$R_c = \frac{180 - \theta}{180} \tag{2}$$

where θ is the bending angle after being elevated to fixed temperatures. Shape memory behaviors of PVDF-HFP were investigated in the region from 25 to 95 °C at intervals of 10 °C.

Characterization. Scanning electron microscopy (SEM) observation was performed with a Hitach S-4800. Atomic force microscopy (AFM) was obtained by one scanning probe microscope in tapping mode. Raman spectroscopy was recorded on a microspectrometer (Horiba Jobin Yvon, LavRAM Aramis). X-ray diffraction (XRD) measurement was recorded with a D8-discover Bruker X-ray diffractometer using Cu Ka radiation (0.154 nm). Photocontrolled actuation was recorded using a CEL-M500 mercury lamp with color filters.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1 and S2: chemical composition and structure of GO. Figure S3: schematic illustration of the shape programming process of the nanocomposite film for photoactuators. Supporting Videos S1−S3: The oscillation movement of the tumbler induced by mechanical force; light-powered tumbler movement of the nanocomposite films; reversible photomechanical behavior of the nanocomposite film upon the irradiation and removal of visible light. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yuhaifeng@pku.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was mainly supported by National Natural Science Foundations of China (51322301 and 51303007) and the China Postdoctoral Science Foundation (2012M520111).

■ REFERENCES

(1) Ikeda, T.; Mamiya, J. I.; Yu, Y. Photomechanics of Liquid-crystalline Elastomers and other Polymers. *Angew. Chem., Int. Ed.* **2007**, *46*, 506−528.

(2) Pei, Z.; Yang, Y.; Chen, Q. M.; Terentjev, E. M.; Wei, Y.; Ji, Y. Mouldable Liquid-Crystalline Elastomer Actuators with Exchangeable Covalent Bonds. *Nat. Mater.* **2014**, *13*, 36−41.

(3) Li, M.; Keller, P.; Li, B.; Wang, X. G.; Brunet, M. Light-driven side-on Nematic Elastomer Actuators. *Adv. Mater.* **2003**, *15*, 569−572.

(4) Osada, Y.; Okuzaki, H.; Hori, H. A Polymer Gel with Electrically Driven Motility. *Nature* **1992**, *355*, 242−244.

(5) He, Z. W.; Satarkar, N.; Xie, T.; Cheng, Y.-T.; Hilt, J. Z. Remote Controlled Multishape Polymer Nanocomposites with Selective Radiofrequency Actuations. *Adv. Mater.* **2011**, *25*, 3192−3196.

(6) Kumar, U.; Kratz, K.; Wagermaier, W.; Behl, M.; Lendlein, A. Non-Contact Actuation of Triple-Shape Effect in Multiphase Polymer Network Nanocomposites in Alternating Magnetic Field. *J. Mater. Chem.* **2010**, *20*, 3404−3415.

(7) Miaudet, P.; Derre, A.; Maugey, M.; Zakri, C.; Piccione, P. M.; Inoubli, R.; Poulin, P. Shape and Temperature Memory of Nanocomposites with Broadened Glass Transition. *Nature* **2007**, *318*, 1294−1296.

(8) Gall, K.; Dunn, M. L.; Liu, Y.; Stefanic, G.; Balzar, D. Internal Stress Storage in Shape Memory Polymer Nanocomposites. *Appl. Phys. Lett.* **2004**, *85*, 290−292.

(9) Zakharchenko, S.; Puretskiy, N.; Stoychev, G.; Stamm, M.; Ionov, L. Temperature Controlled Encapsulation and Release Using Partially Biodegradable Thermo-Magneto-Sensitive Self-Rolling Tubes. *Soft Matter* **2010**, *6*, 2633−2636.

(10) Sun, L.; Huang, W. M.; Ding, Z.; Zhao, Y.; Wang, C. C.; Purnawali, H.; Tang, C. Stimulus-Responsive Shape Memory Materials: A Review. *Mater. Des.* **2012**, *33*, 577−640.

(11) Feng, Y. Y.; Qin, M. M.; Guo, H. Q.; Yoshino, K.; Feng, W. Infrared-Actuated Recovery of Polyurethane Filled by Reduced Graphene Oxide/Carbon Nanotube Hybrids with High Energy Density. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10882−10888.

(12) Loomis, J.; Fan, X. M.; Khosravi, F.; Xu, P.; Fletcher, M.; Cohn, R. W.; Panchapakesan, B. Graphene/Elastomer Composite-based Photo-thermal Nanopositioners. *Sci. Rep.* **2013**, *3*, 1900−1909.

(13) Li, W.; Wang, J. S.; Ren, J. S.; Qu, X. G. 3D Graphene Oxide-Polymer Hydrogel: Near-Infrared Light-Triggered Active Scaffold for Reversible Cell Capture and On-Demand Release. *Adv. Mater.* **2013**, *25*, 6737−6743.

(14) Zhang, Y. Y.; Ma, Y.; Sun, J. Q. Reversible Actuation of Polyelectrolyte Films: Expansion-Induced Mechanical Force Enables cis-trans Isomerization of Azobenzenes. *Langmuir* **2013**, *29*, 14929−14925.

(15) Li, C.; Liu, Y.; Huang, X. Z.; Jiang, H. R. Direct Sun-Driven Artificial Heliotropism for Solar Energy Harvesting Based on a Photo-Thermomechanical Liquid-Crystal Elastomer Nanocomposite. *Adv. Funct. Mater.* **2012**, *22*, 5166−5174.

(16) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. Fast Liquid-Crystal Elastomer Swims into the Dark. *Nat. Mater.* **2004**, *3*, 307−310.

(17) Xie, T. Recent Advance in Polymer Shape Memory. *Polymer* **2011**, *52*, 4985−5000.

(18) Behl, M.; Zotzmann, J.; Lendlein, A. Shape-Memory Polymers and Shape-Change Polymers. *Adv. Polym. Sci.* **2010**, *226*, 1−40.

(19) Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. Remotely Actuated Polymer Nanocomposites-Stress-Recovery of Carbon-Nanotube-Filled Thermoplastic Elastomers. *Nat. Mater.* **2004**, *3*, 115−120.

(20) Palffy-Muhoray, P. The Diverse World of Liquid Crystals. *Phys. Today* **2007**, *60*, 54−60.

(21) Yu, L.; Cheng, Z. X.; Dong, Z. J.; Zhang, Y. H.; Yu, H. F. Photomechanical Response of Polymer-Dispersed Liquid Crystals/Graphene Oxide Nanocomposites. *J. Mater. Chem. C* **2014**, *2*, 8501−8506.

(22) White, T. J. Light to Work Transduction and Shape Memory in Glassy, Photoresponsive Macromolecular Systems: Trends and Opportunities. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 877−880.

(23) Jiang, W. T.; Niu, D.; Liu, H. Z.; Wang, C. H.; Zhao, T. T.; Yin, L.; Shi, Y. S.; Chen, B. D.; Ding, Y. C.; Lu, B. H. Photoresponsive Soft-Robotic Platform: Biomometic Fabrication and Remote Actuation. *Adv. Funct. Mater.* **2014**, *48*, 7598−7604.

(24) Van Oosten, C. L.; Bastiaansen, C. W. M.; Broer, D. J. Printed Artificial Cilia from Liquid-Crystal Network Actuators Modularly Driven by Light. *Nat. Mater.* **2009**, *8*, 677−682.

(25) Cheng, F. T.; Yin, R. Y.; Zhang, Y. Y.; Yen, C. C.; Yu, Y. L. Fully Plastic Microrobots Which Manipulate Object Using Only Visible Light. *Soft Matter* **2010**, *41*, 3447−3449.

(26) Moua, M.; Kohlmeyer, R. R.; Chen, J. Wavelength-Selective, IR Light-Driven Hinges Based on Liquid Crystlaine Elastomer Composites. *Angew. Chem., Int. Ed.* **2013**, *52*, 1−5.

(27) Yamada, M.; Kondo, M.; Mamiya, J. I.; Yu, Y. L.; Kinoshita, M.; Barrett, C. J.; Ikeda, T. Photomobile Polymer Materials: Towards Light-Driven Plastic Motors. *Angew. Chem., Int. Ed.* **2008**, *47*, 4986−4988.

(28) Zhang, X. B.; Yu, Z. B.; Wang, C.; Zarrouk, D.; Seo, J.-W. T.; Cheng, J. C.; Buchan, A. D.; Takei, K.; Zhao, Y.; Ager, J. W.; Zhang, J. J.; Hettick, M.; Hersam, M. C.; Pisano, A. P.; Fearing, R. S.; Javey, A. Photoactuators and Motors based on Carbon Nanotubes with Selective Chirality Distributions. *Nat. Commun.* **2014**, *5*, 2983−2991.

(29) Shang, J. W.; Zhang, Y. H.; Yu, L.; Luan, X. L.; Shen, B.; Zhang, Z. L.; Lv, F. Z.; Chu, P. K. Fabrication and Enhanced Dielectric Properties of Graphene-Polyvinylidene fluoride Functional Hybrid Films with a Polyaniline Interlayer. *J. Mater. Chem. A* **2013**, *1*, 884−890.

(30) Chung, T.; Romo-Uribe, A.; Mather, P. T. Two-Way Reversible Shap Memory in a Semicrystalline Network. *Macromolecules* **2008**, *41*, 184−192.

(31) Behl, M.; Kratz, K.; Zotzmann, J.; Nochel, U.; Lendlein, A. Reversible Bidirectional Shape-Memory Polymers. *Adv. Mater.* **2013**, *25*, 2034−2057.

(32) Guan, F. X.; Pan, J. L.; Wang, J.; Wang, Q.; Zhu, L. Crystal Orientation Effect on Electric Energy Storage in Poly(vinylidene fluoride-co-hexafluoropropylen) Copolymers. *Macromolecules* **2010**, *43*, 384−392.

(33) Zhang, H. J.; Xia, H. S.; Zhao, Y. Optically Triggered and Spatially Controlled Shape-Memory Polymer-Gold Nanoparticle Composite Materials. *J. Mater. Chem.* **2012**, *22*, 845−849.