

Making and Remaking Dynamic 3D Structures by Shining Light on Flat Liquid Crystalline Vitrimer Films without a Mold

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S Supporting Information

ABSTRACT: Making dynamic three-dimensional (3D) structures capable of reversible shape changes or locomotion purely out of dry polymers is very difficult. Meanwhile, no previous dynamic 3D structures can be remade into new configurations while being resilient to mechanical damages and low temperature. Here, we show that light-activated transesterification in carbon nanotube dispersed liquid crystalline vitrimers enables flexible design and easy building of dynamic 3D structures out of flat films upon irradiation of light without screws, glues, or molds. Shining light also enables dynamic 3D structures to be quickly modified on demand, restored from distortion, repaired if broken, in situ healed when microcrack appears, assembled for more sophisticated structures, reconfigured, and recycled after use. Furthermore, the fabrication, reconfiguration, actuation, reparation, and assembly as well as healing can be performed even at extremely low temperatures (e.g., $-130\text{ }^{\circ}\text{C}$).

Three-dimensional (3D) structures that combine sensing and actuation together to autonomously exhibit reversible shape morphing or continuous movement^{1,2} have been envisioned to serve essential functions in wide range of areas such as robotics,³ tissue engineering,⁴ and deployable devices in aerospace,⁵ to name a few. There are several critical issues to address to make such structures completely out of free-standing dry polymers. The first one is fabrication. Building dynamic 3D structures, especially hollow ones, with arbitrary configuration is hardly amendable to conventional polymer shaping techniques. Even though 3D printing has shown great promise,⁶ it involves special printers, professional programming, and careful material formulation. Whereas substantial progress has been made in 3D translation of static objects directly from 1D or 2D materials,^{7–9} making dynamic 3D structures with reversible shape change out of polymer films remains very scarce.^{2,3} The second one is reconfiguration. The geometric information which determines the final structure and shape morphing manner is always “genetically” imprinted in the material. Once the structure is formed, it can hardly be modified, deleted, or made into completely new configurations.^{10–13} The third one is maintenance. If the structure is damaged or deformed, it is almost impossible to be repaired, restored, or recycled, and the entire device has to be disposed. The fourth one is low-temperature resistance. One amazing potential of dynamic 3D structures lies in their application in harsh environment, such as robots which

can replace human beings to do work in outer space, in arctic regions, at high altitude, in heavy snow, and so on. So far few shape-morphing polymers can keep their dynamic features, needless to say to be mended or reconfigured at low temperature.

No currently used shape-morphing polymers for dynamic 3D structures can solve those problems. So far, most attention has been paid to hydrogels,^{1,14–20} which fail to work without water and lack mechanical strength. Other kinds of materials including shape memory polymers²¹ have been explored, but most of them adopt a bilayer or multilayer structure,^{9,18} which is susceptible to delamination. Recent efforts made it possible to make liquid crystalline networks into certain 3D shapes such as helices,^{22–24} cones or saddles,^{24,25} accordion configuration,²⁶ and even Miura-ori patterns.² Among them, only liquid crystalline elastomers with exchangeable links (xLCEs), which are one kind of vitrimers,^{27–29} have shown the potential to reconfigure into new 3D shapes once formed.³⁰ However, the utilization of a mold restricts their structures to very simple 3D shapes for demolding is extremely hard for complex structures. As direct heating will destroy all of the alignment information on the materials, to reconfigure the xLCE structure, a completely new mold has to be used, which is not only expensive but also lacks the capability to partially or in situ modify or repair the structures. Direct heating also faces other insurmountable barriers in a lot of scenarios, such as welding or healing the structures. Like other available LCEs, such xLCE materials cannot be used at low temperatures.

A new material platform has to be delivered to get rid of all these constrains existing in both LCEs and other shape-morphing materials. To this end, we prepared a light-sensitive composite by dispersing carbon nanotubes (CNTs) into xLCEs. Previously, CNTs have been used to trigger the actuation of common LCEs by light,^{31–34} but here we utilize it to fabricate, repair, assemble, and heal 3D structures as well as trigger actuations at low temperatures. As it has been shown that CNTs embedded in common vitrimers could remotely trigger localized transesterification,³⁵ we here employ such strong photothermal effects to induce fast exchange reaction in xLCEs. Therefore, IR light can replace direct heating to achieve alignment of CNT-xLCEs, which endows spatial control on the alignment of the materials. As a result, the material allows for easy fabrication of dynamic 3D structures by simply irradiating a stretched film under stress for a few seconds. The geometry information can be selectively or completely erased by light. New structure patterns can be rewritten into the recovered film, so that the dynamic 3D

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structures can be reshaped or reconfigured into various new shapes, which have reversible shape change between liquid crystal and isotropic phases. The dynamic 3D structures can be rapidly restored when squashed or mechanically deformed. Moreover, the materials are photoweldable, which enables replacement of damaged parts as well as strategic addition of other preformed building blocks. This kind of material also enables in situ photohealing of microcracks, which is valuable to enhance the durability of dynamic 3D structures and the cost of maintenance. The material is also recyclable. Furthermore, all of the light-manipulated processes can be carried out at a broad temperature range, even at extremely low temperatures (e.g., $-130\text{ }^{\circ}\text{C}$ in liquid nitrogen vapor).

To prepare CNT-xLCEs, similar to ref 30, the cross-linked liquid crystalline network was formed by the reaction between diglycidyl ether of 4,4'-dihydroxybiphenol and sebacic acid. Unlike ref 30, a solution of the starting materials was prepared first so that CNTs can be homogeneously dispersed in it with the help of a dispersant (PIM). After solvent evaporation, the mixture was cured in the presence of transesterification catalyst (triazobicyclodecene) at $180\text{ }^{\circ}\text{C}$ for 4 h (Figure 1A, see the

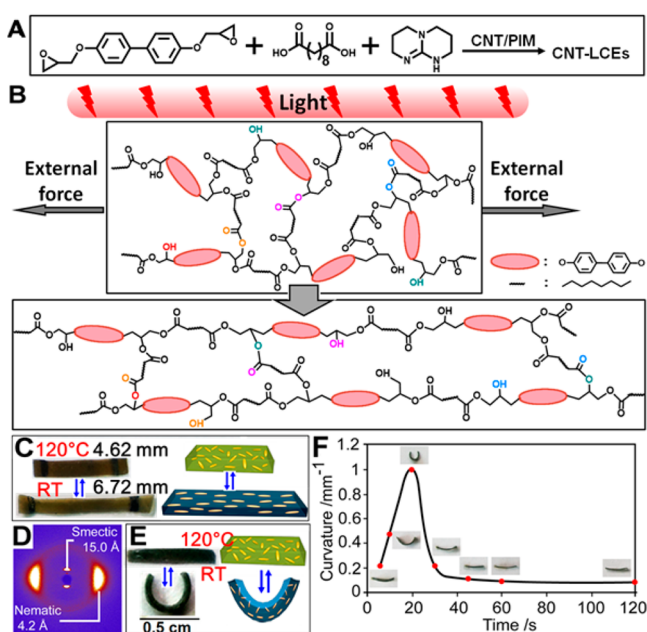


Figure 1. (A) Synthesis of CNT-xLCEs. (B) An illustration of alignment by light. (C) Reversible thermal actuation of CNT-xLCE aligned by shining light. (D) XRD image of CNT-xLCE aligned by light. (E) Reversible bending of a CNT-xLCE film. (F) Curvature change with irradiation time (thickness: 0.3 mm).

Supporting Information (SI) for the detailed preparation and characterization). The CNT-xLCEs have a similar thermal processability and thermal actuation capability as the neat xLCEs.³⁰ CNT-xLCE can be aligned and realigned by stretching at $180\text{ }^{\circ}\text{C}$ to activate transesterification, followed by cooling down (to room temperature, RT) while the sample is under stress.³⁰ The addition of CNTs does not affect the thermal actuation properties of xLCEs (Figure S7).

The CNT-xLCEs can be readily aligned by simply shedding infrared (IR) light (808 nm , intensity $0.84\text{ W}/\text{cm}^2$) on the stretched nonaligned films. A lot of wavelength can be chosen. We used IR light as a demonstration. Three different alignment procedures can be used, which are illustrated in SI. We used the

third method which is stretching upon light irradiation (Video S1). When light shines on the flat film which is under external stress, the temperature increases to more than $160\text{ }^{\circ}\text{C}$, and the transesterification is activated. At the same time, the polymer chains, accordingly the mesogens, align. Due to the accompanying light-induced transesterification, the new topology is adapted to an aligned state (Figure 1B). As shown in Figure 1C, the aligned film can reversibly change length between liquid crystalline phase RT and the isotropic phase ($120\text{ }^{\circ}\text{C}$). The X-ray clearly shows a broad reflection at wide angles and a strong sharp reflection at small angles (Figure 1D), indicating a good alignment. Light can also produce samples with reversible bending movement (Figure 1E), which may be used to enable folding of flat films into designed 3D structures. By controlling the amount of light energy to the film, we can generate a temperature gradient along the thickness of the film. From the top to the bottom, as a result, there is a reduction on the extent of alignment. As the light is turned off, the film bends toward the bottom part that is not exposed to light, offering large actuation amplitudes. The bending curvature depends on the film dimension and light intensity as well as the irradiation time. For example, a preliminary quantitative experiment shows that the curvature increases as the irradiation time increases from 5 to 20 s, but it decreases if the sample continues to be exposed to light for more than 20 s (Figure 1F). This is easy to understand since long time irradiation results in a homogeneous temperature distribution and total alignment of the whole film. Little fatigue was observed on the actuation of LCEs aligned by light after more than 20× of reversible bending—unbending or contraction—extension.

It is challenging to process common LCEs into dynamic 3D structures, because it demands spatial control on the long-range orientational ordering.^{2,24,36} The materials and alignment method presented here provide a unique opportunity to create dynamic 3D structures with great versatility, because different alignment modes can be written/programmed in one film (see sample in Video S1) without the worry of alignment loses due to direct heating. Two examples are given in Figure 2. As shown in Figure 2A, the right part of the film is horizontally aligned, while the left is vertically aligned, leading the right part to expand horizontally and the left part vertically. In Figure 2B, stretching of a triangular film at three vertexes while irradiated by light leads to a triangle capable of expanding and shrinking. Another two examples, a strip which combines bending—unbending and extension—contraction as well as a wavy film, which becomes straight at $120\text{ }^{\circ}\text{C}$, are shown in Figure S11.

Even though bending—unbending alone is enough to construct dynamic 3D structures (demonstrated in Figure S12), addition of contraction—extension mode can greatly increase the complexity of the shape morphing. As seen in Figure 2C, upon exposure to light, the flat film can form a chair when the four chair legs are programmed to bend downward and the chair back bends upward and extends vertically. The mechanical strength of the composite also allows dynamic 3D structures to generate stress and do physical work. A “Hercules” can easily lift four balls (Figure 2D and Video S2) or a glass plate (Figure S13A and Video S3) 5× heavier than “himself”. Moreover even an object 1000× heavier can be loaded onto “him” (Figure S13). Like the CNT-sensitized LCEs without exchangeable links,^{31–34} our dynamic 3D structures can also be actuated by light. Different from the alignment, a lower light intensity is used so as to raise the local temperature to $120\text{ }^{\circ}\text{C}$ instead of $180\text{ }^{\circ}\text{C}$. This enables real-time shape change and

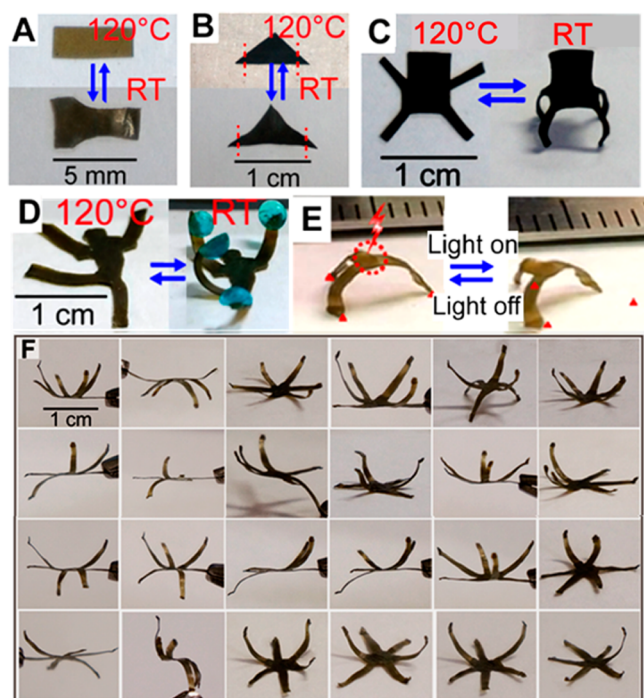


Figure 2. (A) Reversible actuation of a CNT-xLCE film with half vertical and half horizontal alignments. (B) Reversible shrinking and expanding of a CNT-xLCE triangle. (C) Reversible shape change of a chair. (D) A “Hercules” (18.5 mg) lifts four balls (72.6 mg). (E) A tripod rotates and returns back when the light turns on and off (light intensity: 0.47 W/cm²). (F) A six-petal “flower” is reconfigured repeatedly into more than 20 different dynamic 3D structures.

locomotion. This is conceptually demonstrated in Figure 2E. When the light is directed to a specific area, the tripod can rotate upon irradiation and return to the original spot when the light is off. In another case, a tripod can do push-ups continuously with the light on and off (Figure S14 and Video S4).

CNT-xLCE dynamic 3D structures can be readily reshaped, reconfigured, and even recycled. The programmed alignments (like “the genetic codes”) can be erased and reprogrammed over and over to generate various structures without a mold. As illustrated in Figure 2F, a six-petal “flower” was made into more than 20 different shapes by aligning each petal to contract or bend in different directions (details in SI). There are more variations if one continues to try. The transformation upon heating and cooling between each structure and the flat film (Figure S15) is reversible. Moreover, broken parts can be collected and recycled into a new film, as shown in Figure S16.

CNT-xLCE dynamic 3D structures are easy to restore when they are accidentally or purposely deformed or even squashed. There are two different mechanisms for restoration. If the deformation is done below 120 °C, the alignment information remains. Thanks to the shape memory effect of LCEs,^{30,37} dynamic 3D structures can be recovered just by reheating the structures to 120 °C and cooling them down to RT (Figure 3A(i)). When they are deformed at a higher temperature, for example, at 180 °C, all of the programmed alignments are lost. But as long as the films have the pristine integrity, their original structures can still be readily restored by shining light in the same way as they were previously programmed (Figure 3A(ii)).

Aligned CNT-xLCE parts can be assembled by photowelding without glues or adhesives due to light-induced transesterification. Fabrication of dexterous smart systems is always

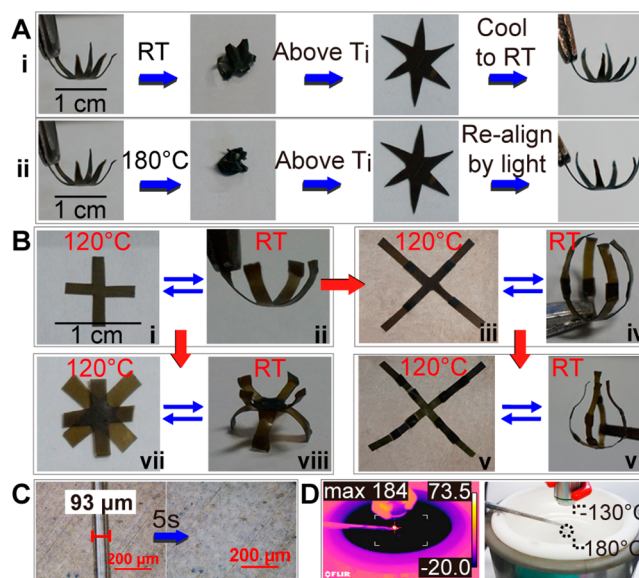


Figure 3. (A) Restoration of deformed dynamic 3D structures. (B) A simple cross (i) is made into a four-petal flower (ii); after welding each petal with another aligned film, respectively, the new shape looks like a ball (iv); a third film is photowelded onto each branch (v) so as to get a new structure (vi). Otherwise, the simple cross (i) can be attached to another cross to make a new flower with four petals up and four petals down (viii). (C) A cut healed by irradiation for 5 s. (D) IR image and optical photograph of the set for low-temperature experiments. The cross in the IR image shows the temperature of the light-irradiated area is ~184 °C.

accompanied by the necessary assembly and joining. It is very difficult to weld the aligned CNT-xLCE or xLCE by direct heating, because the alignment will disappear when the whole sample is heated to a temperature high enough for quick transesterification. With light, however, welding CNT-xLCEs can be achieved in seconds without losing alignment of the area unexposed to light (Figure S17A). Because the joint region is covalently linked, the welded film has a similar mechanical strength as the original one (Figure S18). When stretched, the film broke at bulk material instead of the overlap region. Moreover, the majority of the overlap region can be aligned again by light (Figure S17A). Therefore, if some part of the dynamic 3D structure is broken, replacement can be done by in situ photowelding. The welding also provides another way to spatially distribute alignment directions and gradients. For instance, films with different alignment directions can be joined together in a “zigzag” shape (Figure S19) capable of reversible actuation. As a demonstration on the versatility of making dynamic 3D structures by assembling, we show in Figure 3B that a simple cross can be welded into different dynamic 3D structures. More demonstrations are shown in Figure S19. By transmission welding,³⁵ CNT-xLCE can also be attached with other types of materials including epoxy-based and some non-epoxy-based polymers (Figure S20), which makes it convenient to add other functions to dynamic 3D structures.

Healing a microscale fracture is a sought-after property since small defects can lead to final macroscale structure failure. But for aligned CNT-xLCEs or xLCEs, similar to the welding, direct heating is unrealistic since it is not localized and will destroy all of the alignment of the actuator material. With light, and thanks to the light-induced transesterification, the healing can be carried out remotely and focused only on the small areas where the crack

is located. As shown in Figure 3C, a cut 93 μm wide vanished in 5 s, while a wider cut of 126 μm was healed in 10 s (Figure S21A) upon exposure to light. All of the healed samples have the mechanical strength similar to that of the sample without damages (Figure S22), and a hole with the diameter of 220 μm in the film can also be photohealed within 10 s (Figure S21B). The film is able to perform the original extension and contraction upon heating or exposure to light (Figure S23).

Another interesting feature in our dynamic 3D structures is that all of the alignment, reconfiguration, reparation, welding, healing, and actuation can be realized by shining light in an extremely cold environment. The photothermal effect of CNTs is very strong. Despite that the sample is placed in liquid nitrogen vapor (which can be as low as $\sim -130\text{ }^\circ\text{C}$), it can increase the local temperature to about 180 $^\circ\text{C}$ measured by an IR thermal imaging camera (Figure 3D) to effect all of the dynamic 3D structures' features. As an illustration, over liquid nitrogen vapor, we made a tripod out of flat film by light (Figure S25A). It moves on a glass plate when the light is turned onto a specific leg (Figure S25B and Video S5). Furthermore, when part of leg (i) was cut off, it was replaced by a new one using photowelding (Figure S25C, (i)). The length of leg (ii) was extended by transmission welding with a normal epoxy film, and leg (iii) was reshaped. As seen in Figure S25D, a pieced hole (iv) in leg (ii) was well photohealed within 10 s.

The concept demonstrated here is not restricted to the current system. The chemical composition can be adjusted to change the thermal, mechanical and actuation properties. CNTs can be replaced by other fillers with strong photothermal effects. As they are tether-free structures, they can also be incorporated into electronic, optical, or mechanical devices. Considering the robustness of this approach, it also may meet the increasing demand of the currently widespread mass customization and personalization paradigm.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterizations of CNT-xLCE; light-controlled alignment, fabrication of dynamic 3D structures, welding, healing, and recycling; low-temperature related experiments; related videos. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12531.

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Notes

The authors declare no competing financial interest.

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