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Photothermal actuated origamis based on graphene oxide-cellulose programmable bilayer

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The design and construction of 3D architectures enabled by stimuli-responsive soft materials can yield novel functionalities for next generation soft-bodied actuating devices. Apart from additive manufacturing processes, origami inspired technology offers an alternative approach to fabricate 3D actuators from planar materials. Here we report a class of near-infrared (NIR) responsive 3D active origamis that deploy, actuate and transform between multistable structural equilibria. By exploiting the nonlinear coefficient of thermal expansion (CTE) of graphene oxide (GO), graphene oxide/ethylene cellulose (GO/EC) bilayers are readily fabricated to deliver precise origami structure control, and rapid low-temperature-triggered photothermal actuation. Complexity in 3D shapes are produced through heterogeneously patterning GO domains on 2D EC thin film, which allows us to customize 3D architectures that adapt to various robotic functions. The strategy also enables the construction of material systems possessing naturally inaccessible properties, such as remotely controlled mechanical

metamaterials with auxetic behavior and bionic flowers with rapid blooming rate. Harnessing deformability with multiple degrees of freedom (DOF) upon light irradiation, this work leads to breakthroughs in the design and implementation of shape-morphing functions with soft origamis.

Introduction

The combination of soft smart materials and advanced manufacturing technologies has given birth to diverse shape programmable 3D architectures ranging from macroscopic to mesoscopic^{1, 2} scales. Complementary to the well-known additive 3D printing technology, origami, the centuries-old art exploiting 2D to 3D transformations, has been infused with planar engineering methods to enable top-down parallel formation of 3D geometries from 2D sheets. Taking inspiration from papercrafts (i.e. origami, kirigami and pop-up book), thin-film materials are firstly assigned or tailored as planar precursors, then reconfigured into target 3D shapes through deterministic transformation induced by internal stress³⁻⁵ or external modulation.⁶⁻⁹ Moreover, instead of static 3D structures, “active origamis” with autonomous and controllable deformability have been implemented in advanced research fields such as soft robotics,¹⁰ flexible electronics¹¹ and biomedicine.¹² These systems ingeniously leverage existing actuator techniques to achieve reversible and multimodal locomotion in 3D architectures, among which photothermal-mechanical transduction is a promising energy conversion route possessing advantages of wireless stimulation and remote motion control.¹³

The assembly strategy namely “asymmetric bilayer” has been widely adopted to fabricate energy-efficient photothermal actuators (PTAs), where mismatched coefficient of thermal expansion (CTE) between counterpart layers will lead to bending or torsion under selected light irradiation.^{13, 14} Carbon allotropes, including graphite,¹⁵ carbon nanotube (CNT),¹⁶⁻²¹ graphene²²⁻²⁸ and graphene oxide (GO),^{29, 30} are considered as superior active materials for bilayer PTAs due to their excellent photothermal conversion efficiency and heat conductivity. Apart from the prevalent flat-shaped bimorph PTAs, several recent works have demonstrated self-curing or rolling bilayer PTAs

possessing 3D geometries under ambient conditions,¹⁹⁻²³ yet they only provide limited precision in geometrical control and undesirable actuating speed while responding to external stimuli. As a result, significant challenges still exist in delivering PTA origamis with high DOF to perform exquisite robotic tasks in a programable manner.

Herein we report an innovative strategy using 2D precursors to devise complex active origamis that exhibit various 3D architectures at room temperature. By studying the humidity-dependent negative thermal expansion behavior of GO assemblies,³¹ PTAs based on the graphene oxide/ethylene cellulose (GO/EC) bilayer are successfully prepared to deliver rapid, reversible and low power triggered photothermal actuation. Patterning GO onto ethylene cellulose (EC) substrate in a heterogeneous manner leads to segmented bilayer domains with variant bending directions and degrees, whilst curvature control in each domain is facilitated by manipulating residue thermal stress along the interface between GO self-assembly and EC. Our PTA-based active origamis are soft, lightweight, and can sustain multistable shape transformations attributing to the photo-thermo-mechanical transducing behavior of the bilayer. Benefitted from the versatility and simplicity of our planar fabricating process, various shape formats from tubular bimorph to complex morpho-functional origamis are demonstrated, which elucidates the pathway towards agile control in soft robotics, self-propelling mechanical metamaterials as well as biomimetic applications.

Results and discussion

Generation of shape programmable bilayer origamis

Identifying materials set with larger CTE mismatch is pivotal to deliver intensive deformation and fast actuation kinematics in PTA. While most intrinsic negative thermal expansion (NTE) materials display small NTE effect (e.g. graphene has a negative yet tiny CTE value about -7 ppm K^{-1} at 300 K),³² GO is an exception in which the NTE behavior is highly correlated with water molecules' reversible removal/intercalation between adjacent atomic layers, and its non-constant CTE shows more negative value in humid environment than in dry state (-130 ppm K^{-1} for 25% and -68 ppm K^{-1}

Fig. 1 Fabrication, characterization and geometry control of bimorph 3D-PTAs. (a) Schematics of the 3D-PTA fabrication process. (b-c) Optical and confocal microscopic images of GO surface (b) before and (c) after 90 °C thermal annealing. Histograms beside color palette represent height distribution and surface roughness. (d) Cross-sectional SEM images of GO/EC bilayer (top) and magnification of condensed GO stack (bottom). (e) Photographs of bimorph 3D-PTAs with various EC thickness. Label unit: μm. (f) Experimental results and theoretical prediction of bimorph curvature variation over EC thickness change. Bimorphs with each EC thickness were fabricated in ten sets with error bars presented. Scale bars: 100 μm in (b-c), 20 μm for top and 2 μm for bottom image in (d).

for 2% relative humidity(RH)).³¹ On the other hand, cellulose is a cluster of environment-friendly soft matters which can serve as soft substrates for flexible electronics^{33, 34} and energy storage devices.³⁵ Among all its derivatives we selected EC for PTA construction considering its highly positive CTE ($\sim 150 \text{ ppm K}^{-1}$)³⁶ and favorable mechanical properties (refer to tensile test results in Note S1 and Fig. S1-S2, ESI†). Based on these material-level advancements, central to yielding room temperature-stable 3D architectures is to facilitate the bilayer's preparation at a non-ambient temperature.

As an illustrative example to showcase the facile fabrication protocol of our 3D-PTA, a bimorph with 5:1 aspect ratio (25 mm:5 mm) was firstly produced as depicted in Fig. 1a. Here EC thin film served as a planar precursor with GO dispersion uniformly casted on top and dried in ambient environment. Then the composite underwent a $T_0 = 90\text{ }^{\circ}\text{C}$ vacuum oven annealing process, through which GO/EC bimorph was monolithically formed with eliminated internal stress. During annealing the sample was sandwiched between glass plates to enhance lamination and maintain flatness. Thereafter, the action of taking the bimorph back to ambient condition ($T \approx 25\text{ }^{\circ}\text{C}$, $\text{RH} \approx 70\%$) introduced a negative temperature gradient as $\Delta T = T - T_0 = -65\text{ }^{\circ}\text{C}$, upon which GO with negative CTE expanded, while EC with positive CTE contracted, and the beam scrolled towards EC side to reach its mechanics equilibrium guided by the inbuilt stress. Surface morphology evolution in GO has been observed assisted by optical confocal microscope. As differentiated between Fig. 1b and Fig. 1c, GO thin film prior to thermal treatment exhibited a root mean square (rms) surface roughness of c.a. $0.97\text{ }\mu\text{m}$, while the post-annealing sample was roughened to be c.a. $1.53\text{ }\mu\text{m}$. The enhancement in surface wrinkling implied an increased lateral interlocking of 2D lamellae attributed to an irreversible free water loss as confirmed by peak shift in X-ray diffraction (XRD) spectrum (Fig. S3, ESI†). The self-assembling nature of individual GO sheets also resulted in a condensed interlamellar stacking and a coherent GO/EC interface (characterized by SEM in Fig. 1d).

3D-PTAs require predictable degrees of cylindrical curling (assessed by curvature, Fig. S4a, ESI†) to deliver high-fidelity geometries with reliable repeatability. We hereby developed a theoretical model (see derivation and discussion in Note S2 and Fig. S5, ESI†) to understand the governing parameters in the determination of coil curvature, and to provide design guidelines for more complicated 3D structures. The describing equation reveals that the ultimate curvature (κ) in GO/EC bimorph is related to the fabrication conditions, both materials' thermal and mechanical properties, as well as their spatial geometries:

$$\kappa = \frac{(\alpha_2 - \alpha_1)\Delta T}{t_2} \frac{6(m+1)}{3(m+1)^2 + (m^3n+1)\left(\frac{1}{mn} + 1\right)}$$

where $m = t_1/t_2$, $n = E_1/E_2$; α_1 , t_1 , E_1 are CTE, thickness and Young's modulus of EC, while α_2 , t_2 , E_2 are the corresponding parameters of GO, respectively. Specifically, the product of temperature gradient (ΔT) and CTE mismatch is linearly proportional to curvature, while film thickness and Young's modulus of GO and EC affect the self-rolling magnitude in nonlinearity. In view of the complexity in precisely modifying the physical properties of both materials, realizing geometric control through adjusting the thickness ratio of GO/EC is expected to be feasible. Experimentally we achieved spatially varying curvatures via altering the thickness of EC film while fixing the dosage of GO dispersion (a 1.5 mg cm^{-2} dose leads to c.a. $10 \text{ }\mu\text{m}$ thickness in GO layer, examined by SEM in Fig. 1d). When $20 \text{ }\mu\text{m}$ thick EC was applied, the GO/EC bilayer rolled up intensively into a tubular shape with a curvature as high as $3.87 \pm 0.13 \text{ cm}^{-1}$ (see curvature evaluation method in Fig. S4b, ESI[†]). The bimorph's curvature decreased monotonically against the increment in EC layer's thickness, and finally ended up bending with a smaller curvature of $0.85 \pm 0.16 \text{ cm}^{-1}$ when EC was as thick as $70 \text{ }\mu\text{m}$. These experimental results as captured in Fig. 1e are in good agreement with the predictive mechanics model we developed (Fig. 1f), where curvature becomes a nonlinear polynomial function of EC's thickness when that of GO is a constant of $10 \text{ }\mu\text{m}$. The model predicts an extreme curvature of 11.24 cm^{-1} at a 2.5:1 (GO:EC) thickness ratio (Fig. S6, ESI[†]), indicating that further employing thinner EC film will lead to even more intensive self-rolling in bimorph configurations. The influence of RH on curvature is discussed in Fig. S7 (ESI[†]).

Photothermal actuation: performance and mechanism

Actuation in PTA is the macroscopic portrayal of nanoscale mechanisms. Given that a complete energy transducing loop consists of both photothermal and thermo-mechanical conversion processes, the combination of GO and EC provides a simple yet efficient solution to achieve both functionalities simultaneously. Contemporary structural model of GO can be interpreted as an atomically thin, sp^2 -carbon dominated basal plane decorated with disordered oxygen-containing groups either in plane or on edge. The monolayer nature of the GO used in this work is characterized via atomic force

Fig. 2 Photothermal actuation of bimorph 3D-PTAs. (a) Illustration for NIR triggered thermohydration effect in GO. (b) Morphology change of the bimorph under increasing NIR intensity. Label unit: mW cm⁻². (c) Thermogram of the bimorph exposing to 140 mW cm⁻² NIR. (d) Corresponding curvature and temperature change of the bimorph as functions of light power density. (e) Diagram recording dynamic curvature and temperature variation during the actuation process under 140 mW cm⁻² NIR.

microscopy (AFM) as shown in Fig. S8 (ESI[†]). Although oxidation introduced defects in GO inevitably segment conjugated π network into nanoclusters,³⁷ in phase lattice vibration still substantially exists as confirmed by the strong G band in Raman spectroscopy³⁸ (Fig. S9a, ESI[†]), which in turn ensures sufficient near-infrared (NIR) absorption (Fig. S10a, ESI[†]) and photothermal energy transfer through photon-phonon interaction. Concomitantly, as validated by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S9b, ESI[†]), the enriched oxygen-functional groups in GO provide hydrophilic sites for ultrafast water diffusion and reversible hydration/dehydration upon thermal provoked RH changes.³⁹ At room temperature, the abundant water molecules locating at hydrophilic region act as supportive pillars that hold adjacent GO sheets apart, and the desorption of water under thermal condition will cause vertical collapse and transverse contraction within the stacked GO assembly,³¹ resulting in macroscale thermo-mechanical transduction as illustrated in Fig.

2a. With GO serving as the NIR-active and negative CTE layer, EC in contrast exhibits positive thermal expansion when receiving heat flux from GO across their compact interface, and is highly transparent over the spectrum, which enables omnidirectional NIR absorption in GO.

The actuation performance of bimorph 3D-PTA (GO:EC 10 μm :30 μm) under NIR irradiation was studied as benchmark (see the spectrum of light source in Fig. S10b, ESI†). When light intensity stepwise increased, the bimorph gradually uncurled itself to a specific curvature corresponding to each power input (Fig. 2b), suggesting the presence of thermomechanical equilibrium states in the photothermal trajectory, and the onset of complete flattening was under 140 mW cm^{-2} NIR exposure with an average bimorph temperature as low as 44.5 $^{\circ}\text{C}$ (Fig. 2c). The trends of curvature decrement and temperature rise against power density ramp are plotted in Fig. 2d, wherein each data set can be fitted into a quasi-linear extrapolation. Fig. 2e and Movie S1 (ESI†) record the dynamic actuation of a bimorph exposed to 200 mW cm^{-2} NIR. The PTA unrolled c.a. 430° within 5 s, then returned rapidly from the temporary flat state to its initial curvature after NIR was switched off. The total actuation amplitude of our 3D-PTA excels significantly when compared to most of the NIR-driven actuators,^{25-28, 40} as well as those actuated by UV⁴¹⁻⁴³ or visible light,^{17, 18, 44} without detriment to actuation rate (see comprehensive Ashby plot comparison in Fig. S11, ESI†). NIR with lower intensity could also fully straighten the bimorph, but the actuation speed would be attenuated (Fig. S12, ESI†). Future attempts to improve the actuating speed of GO/EC PTA could be carried out by hybridizing GO with carbon nanotubes (CNTs)²⁰ or graphene nanosheets to achieve higher thermal conductivity in the photothermal active layer.

Conventional planar PTAs are strain-free at room temperature and strained to deform (bend/twist) consequent to heating. In contrast, self-rolling PTAs endure internal stress in ambient environment; they are expected to fully flatten only when being heated up till their curing temperature T_0 attributing to the complete relaxation of accumulated stress.²⁰ Our 3D-PTAs manifested a low temperature actuating performance during photothermal heating. As shown in Fig. 2d, the temperature of the bimorph PTA increased almost linearly when NIR irradiation increased from 0 to 200 mW cm^{-2} ,

Fig. 3 Actuation mechanism analysis based on in-situ thermal XRD and FEA results. (a) XRD patterns of thin-film GO sample through consecutive temperature elevation. (b) Temporal trace of d-spacing for characteristic peaks in (a). (c) FEA results showing longitudinal normal stress distribution within the cross section of GO/EC bilayer at various temperatures. Here positive values in the color palette represent tensile stress while negative ones stand for compression. (d) Diagram of quantified stress distribution extracted from FEA. GO is entirely compressed; EC is extended in upper part while slightly compressed in its downside. The neutral plane in GO/EC bilayer is fixed at c.a. 20 μm beneath the interface irrelevant to temperature change.

while its actuation started to saturate (fully unroll) from 45 °C (140 mW cm^{-2} NIR) onwards, way before reaching $T_0 = 90 \text{ °C}$. Besides, the PTA's recovery (rerolling) rate was slower than that of its actuation (unrolling, Fig. 2e). These phenomena indicate that the actuation mechanism cannot be simply explained by linear-CTE modulation, whereas the peculiar thermohydration trait of GO may play a role in the apparent temperature-curvature asymmetry. The first clue we reasoned was that RH decreases nonlinearly with temperature increment (refer to Antoine equation and RH change against temperature in Fig. S13a, ESI†). Concurrently, water desorption in GO was more drastic in the low temperature region than higher temperature during thermal gravimetric analysis (TGA). As shown

in Fig. S13b (ESI†), 11% of total weight was lost at 50 °C, while the overall weight loss at 90 °C only increased up to 15%. We further employed in-situ thermal XRD to provide direct evidence of microstructural evolution in GO over consecutive heating. The fingerprint peak depicting hydrophilic region shifted from 11.4° to 13.5° when temperature raised from 30 °C to 110 °C (Fig. 3a), and could revert to 11.7° (Fig. S14, ESI†) upon cooling back to 30 °C. Meanwhile, enhancement in peak intensity was observed along temperature rise due to water desorption triggered better alignment in stacked GO sheets. Similar to the trend of weight loss, d-spacing between adjacent GO atomic layers also declined in a monotonical yet nonlinear manner through heating up (Fig. 3b). Considering temperature increment from 25 °C to 90 °C as the whole thermal trajectory, d-spacing decrement at 50 °C constitutes 79% of the total structural collapse of layered GO assembly. The above results solidly confirm that water removal/insertion at hydrophilic sites is substantial and reversible, and such mass transportation process is more prominent in low temperature region (< 50 °C). Therefore, it is expected that GO layer can generate sufficient thermal contraction at around 50 °C, which is macroscopically reflected as low temperature actuating behavior in GO/EC bilayers.

Stress distribution within GO/EC bilayer was then investigated by finite element analysis (FEA). In the simulation, different CTE values were assigned to GO in a set of 10 °C intervals. We probed the cross section of the bilayer (Fig. 3c) and extracted its longitudinal normal stress distribution along thickness direction as plotted in Fig. 3d. It is visualized that, at room temperature (25 °C), the bimorph is strongly strained with GO being compressed (negative stress) while EC being stretched (positive stress) owing to their mutual confinement. Axial stresses accumulate at the bearing interface within the composite and progressively recede towards both surfaces. Heat, or photothermal effect, contributes to the relaxation and flattening of the bimorph by releasing mismatch strain. The simulation result reveals that the internal strain can be freed by c.a. 80% at 50 °C, which correlates well with the experimental observation of the low temperature onset of actuation.

Self-propelling origami architectures and mechanical metamaterials

We further exemplify the versatility of our 3D-PTAs by constructing multi-DOF origami architectures beyond standard bimorphs. Planar geometries, such as triangular and annular rings, are able to transform into sophisticated 3D architectures by programming the shape and relative position of self-rolling domains in 2D (dimensional specifications of 2D layouts are available in Fig. S15, ESI†). For instance, EC thin film can be blade cut into an equilateral triangular ring (Fig. 4a1) followed by drop casting GO dispersion on its front. The as formed triangular bilayer consists of three equivalent beams, which will collectively and symmetrically bend inwards (Fig. 4a2) subsequent to thermal annealing and cooling. Being processed in 2D yet functions in 3D, such origami geometry with 3 DOF could be potentially used to trap moving objects given its ability to switch between open and closed states. Moreover, each individual beam in the triangular origami could be independently controlled if more precise NIR sources such as NIR lasers are employed. Another characteristic feature of our planar process is that one 2D precursor may end up having disparate 3D shapes ascribing to arbitrary GO layouts. Assigning GO on top, or beneath EC at specific regions will dictate localized, bidirectional curvatures (positive or negative), meanwhile the relative coverage of each GO domain also affects the ultimate contour of complex 3D architectures. We exemplified such vision via patterning GO underneath EC in shaded area while maintaining it above in bare region according to prescribed graphic design (Fig. 4b1, c1, d1). As shown in Fig. 4b2, still utilizing the triangular EC substrate, the domains were programmed in a way that each beam bend convexly by half while concavely in the other bisection. Such 2D plot renders a periodically undulating 3D frame structure which is highly distinct to its gripper-like counterpart. Another set of practice was carried out with respect to annular rings. In Fig. 4c1 and 4d1 we designed two annuli with identical 2D geometry but variant styles of GO assignment, with alternating GO domains equidistantly patterned in one sample yet unequally in the other. Although both consequent 3D shapes look undulatory, they show inherent divergence in spatial symmetry, as the 3D annulus in Fig. 4c2 is centrosymmetric while the one in

Fig. 4 Various shape programmable 3D architectures derived from 2D layouts. (a-e) Graphic designs, room temperature stable 3D modes and high temperature planar states of (a) an equilateral triangular ring encoded with only positive curvature; (b) an equilateral triangular ring encoded with alternating positive and negative curvatures; (c) an annulus programmed with central symmetry; and (d) an annulus programmed with axial symmetry. (e) FEA macroscopic prediction of the centrosymmetric annulus. The color scale represents vertical displacement of the elements. (f) Weight-lifting performance of a centrosymmetric annulus origami as functions of resisting load. (g) Photograph of the origami lifting 1,020 mg load. (h) Graphic design and 3D state of a wavy strip with equidistant domains. (i-l) 3D-PTA enabled mechanical metamaterials including (i, j) an assembly strategy for ultra-positive Poisson's ratio and (k, l) an assembly strategy for negative Poisson's ratio. The length direction of the stripe is regarded as axial direction for Poisson's ratio calculation. All demonstrations shown above were fabricated with 10 μm GO and 30 μm EC. Reversible actuations were performed under 200 mW cm^{-2} NIR irradiation. Scale bars : 1cm in (a-d) and (f), 0.5 cm in (g).

Fig. 4d2 is axisymmetric. Apart from microscale stress analysis, FEA can also predict macroscopic deformation of the origamis. We developed an annular model with the characterized thermal/mechanical parameters being assigned (Fig 4e). The planar outline represents the strainless annulus at 90 $^{\circ}\text{C}$, while its 3D architecture at room temperature (color scheme) could be closely

simulated in consistence with the experimental result. Therefore, FEA can serve as a powerful tool for fast prototyping of unexplored 3D origami architectures. Furthermore, all above mentioned active origamis can reversibly actuate owing to the collective motions of GO/EC domains (Movie S2, ESI†), which enables metamorphoses between their 3D modes and flattened 2D states (Fig. 4a3, b3, d3, e3), and characterizes them as self-deployable structures which can transform into space-efficient flat formats as needed. As cycling durability is important for PTAs, we exposed the 3D origamis to 200 continuous actuation cycles and found the geometry remained almost unchanged as shown in Fig. S16a (ESI†). Despite their inherent compliance and lightweight nature, the actuations of these 3D architectures are by no means limited to unloaded modes. We examined the weight-lifting performance of a centrosymmetric annulus, which weighs merely 14.8 mg, by quantifying its actuation strokes and specific works under various normal loads (Fig. 4f, refer Fig. S16b, ESI† for experimental details). Under a moderate load of 170 mg (1.67 mN), the PTA could fully revert to its 3D state from flatness with a c.a. 8 mm stroke (20,000% of flat thickness). Peak specific work capacity of 3.38 J kg^{-1} occurred at 1,020 mg resisting load (Fig. 4g), revealing the high thrust-to-weight ratio (c.a. 69) achieved by our 3D-PTA origamis for robotic functionalities. Compared with other stimuli-responsive origamis (summarized in Table S2), our PTA-based origami architectures are lightweight, less power consuming, remotely actuated, and render larger stroke as well as a moderate thrust-to-weight ratio.

The concept of shape programming can be further expanded by integrating individual 3D-PTA units into one assembly with multiple DOF, which is conducive to yielding materials with conventionally inaccessible mechanical properties and functionalities, that is to say, mechanical metamaterials.⁴⁵ Here we constructed metamaterials characterized with unusual Poisson's ratio utilizing the wavy-strip 3D-PTAs (Fig. 4h) as unit building blocks, through which strong heterogeneities in Poisson's ratios were established via differential assembling strategies. For instance, when four initially separated PTA strips were bonded together at their contacting hinges (Fig. 4i), they constituted a system which collapsed vertically while only slightly extended in lateral

direction under NIR activation (Fig. 4j), leading to a highly positive Poisson's ratio of 3.6. Furthermore, the entirety could be reconfigured into a re-entrant honeycomb structure⁴⁶ endowed with auxetic behavior by joining 3D-PTA stripes with NIR-nonresponsive stiff paper as solid, bracing connections (Fig. 4k). It exhibited expansion in both length and width when stimulated by light irradiation (Fig. 4l), since the straightening and alignment of wavy units along horizontal direction will motivate vertical repelling through hinging motions, and a negative Poisson's ratio of -2.4 was obtained. The deformation of auxetic metamaterials are commonly driven by mechanical force induced stretch or compression due to the restricted usage of passive structural materials. In contrast, guided by our active origami scheme, untethered mechanical metamaterials capable of shape encoding, self-propelling and remote control have been realized, as both aforementioned meta-structures can rapidly switch between their high temperature and room temperature stable configurations without physical contact (Movie S3, ESI[†]).

Biomimetic Origami

Biological systems can skillfully adopt origami approach to create tissue and organs.⁴⁷ For example, early-stage plant organs, such as flower buds (Fig. 5a), are generally configured into folded status with deterministic folding patterns. These contractive conformations will subsequently unfold and flatten during organism maturation. In our case, we constructed botanical analogies with shape programmable 3D-PTAs and replicated the aforementioned plant growth processes harnessing photothermal effect. A double-layered origami flower was firstly designed planarly in a floral form as depicted in Fig. 5b (dimensions specified in Fig. S17, ESI[†]). Since the initial petal curvature can be encoded by EC paper's thickness, we chose 50 μm and 30 μm EC papers for outer and inner petals respectively to showcase the concept of spatial bio-gradient. As shown in Fig. 5c-d, translation from 2D layouts into 3D petals was achieved through annealing induced curvature rendering process, and both petal groups exhibited uniform curvature owing to the excellent repeatability of our 3D-PTA generation protocol. Similarly, temperature variation serves as the trigger for shape-morphing in this

Fig. 5 Biomimetic origami flower manifesting photothermal-triggered bloom. (a) Photograph of gold climber (*Tristellateia australasiae* A.Rich) buds and flowers revealing morphological differences before and after organism maturation. Photograph was taken by author. (b) 2D graphical design for inner and outer layers of the origami flower. (c) Side view and (d) top view of already formed inner and outer petal groups at room temperature 3D states. (e) Morphology evolution of the origami flower along increasing NIR intensity. Scale bars: 1 cm in (c-e).

plant-inspired system. By applying NIR with a crescendo of intensity, the artificial flower could mimic a series of intermediate blossom states until fully flattened (Fig. 5e, thermogram available in Fig. S18, ESI[†]), which declares its thermomechanical multistability. The rapid and reversible dynamic deforming process under 200 mW cm^{-2} NIR was recorded in Movie S4 (ESI[†]). The awing blooming rate of the origami bionic device is much faster than many flowers in nature including the much admired *cereus* or *epiphyllum*.

Conclusions

Our GO/EC bilayer system relies on a combination of material properties and geometrical design to produce spatially programmable and dynamically reconfigurable active origamis. The as derived mechanics model and FEA prediction allow us to precisely program origamis from planar processes, and the mechanism for fast, low temperature, and fully reversible photothermal actuation has been investigated in nanoscale considering thermohydration effect. By introducing novel features, such as domain patterning and multistable shape-morphing, into the fabrication of soft 3D-PTA origamis, this technique provides a platform on which tunable functionalities can be achieved on demand for soft robotics, mechanical metamaterials, artificial bio-systems and beyond.

Experimental

Materials preparation

8 wt% EC powder (Sigma-Aldrich 200654) was dissolved into toluene/ethanol (4:1 volume ratio) binary solvent with stirring and 70 °C water bath. The as formed viscous EC solution was bar coated onto polyethylene terephthalate (PET) film, heated at 60 °C to fully evaporate the solvent, and subsequently peeled off to obtain EC films (thicknesses varying from 20 to 70 μm controlled by bar coating spacer). GO flakes were synthesized from commercial graphite powder (Sigma-Aldrich 282863) via a modified Hummers method.⁴⁸ GO dispersion of 9 mg/ml was obtained by diluting and 30 mins ultrasonication. GO thin films were prepared on silicon wafers for XRD characterization through drop casting, air drying and 12 hours 90 °C vacuum oven annealing. The film could be peeled off from substrate for mechanical and optical tests.

Materials characterization

Optical confocal microscope (ZEISS, Smartproof5) was used to characterize surface morphology and rms roughness of GO assembly. Field emission SEM (JEOL 7600) was used to reveal the cross section of GO/EC bilayer. AFM (Oxford Instrument, Cypher S) was employed to determine the layer thickness and relative surface area of GO. Structural/chemical information of GO including lattice

vibration modes and degree of oxidation are revealed by Raman spectroscopy (Thermo Scientific, iS 50) and XPS (Kratos Analytical, AXIS Supra+). Light absorbance was measured by a UV-Vis-NIR spectrophotometer (PerkinElmer, Lambda 950). Heat induced weight loss in GO was monitored by TGA (TA Instruments, Q500). In-situ thermal XRD experiment was performed by Bruker D8 DISCOVER (Cu-K α radiation, $\lambda = 1.5406 \text{ \AA}$) with $1 \text{ }^{\circ}\text{C min}^{-1}$ heating rate and 30 minutes temperature stabilization before each scanning run.

Finite element analysis

FEA was conducted using a commercial finite element software (ANSYS Workbench) with steady-state thermal module. For stress distribution analysis (Fig. 3c-d) we constructed a representative volume element with real scale thickness (GO/EC $10 \text{ }\mu\text{m}/30 \text{ }\mu\text{m}$) yet shrunken lateral dimension of $100 \text{ }\mu\text{m} \times 100 \text{ }\mu\text{m}$ to enhance the fineness of hexahedron meshing. For macroscopic shape prediction (Fig. S14, ESI †) the model was built with identical thickness, area and materials assignment according to real condition. Mechanical parameters of GO and EC are indicated in Note S1, ESI † , while disparate CTE values of GO in all temperature intervals are adopted from Kotov group's work.³¹ $90 \text{ }^{\circ}\text{C}$ was set as environmental temperature for strainless models, then thermal stresses and deformations were calculated and visualized under arbitrary thermal condition.

Fabrication and characterization of 3D-PTA origamis

EC film was blade cut into specific shapes, followed by drop casting GO dispersion at predesigned regions. After air drying and 12 hours $90 \text{ }^{\circ}\text{C}$ vacuum oven annealing, 3D architectures could be immediately obtained upon cooling back to room temperature. $90 \text{ }^{\circ}\text{C}$ was selected as annealing temperature since it could deliver sufficient temperature gradient (ΔT) for 3D-PTA fabrication, yet was not too high to expedite thermal reduction in GO. A NIR light source (Philips BR125 250W) was utilized as stimulus, whose power density at different distance was measured by a NIR power meter (Linshang LS122A). Emission spectrum of the light source was determined by a spectroscopy CCD

detector (Princeton Pixis 100B). Photothermal actuation of the samples were recorded by a digital camera, while an infrared camera (Fluke Ti200) was employed for temperature tracking.

Conflicts of interest

The authors declare no conflict of interest.

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