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Ultrathin thermoresponsive self-folding 3D graphene

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Graphene and other two-dimensional materials have unique physical and chemical properties of broad relevance. It has been suggested that the transformation of these atomically planar materials to three-dimensional (3D) geometries by bending, wrinkling, or folding could significantly alter their properties and lead to novel structures and devices with compact form factors, but strategies to enable this shape change remain limited. We report a benign thermally responsive method to fold and unfold monolayer graphene into predesigned, ordered 3D structures. The methodology involves the surface functionalization of monolayer graphene using ultrathin noncovalently bonded mussel-inspired polydopamine and thermoresponsive poly(*N*-isopropylacrylamide) brushes. The functionalized graphene is micropatterned and self-folds into ordered 3D structures with reversible deformation under a full control by temperature. The structures are characterized using spectroscopy and microscopy, and self-folding is rationalized using a multiscale molecular dynamics model. Our work demonstrates the potential to design and fabricate ordered 3D graphene structures with predictable shape and dynamics. We highlight applicability by encapsulating live cells and creating nonlinear resistor and creased transistor devices.

INTRODUCTION

Two-dimensional (2D) nanomaterials, including graphene, boron nitride, and transition metal dichalcogenides, have been extensively studied due to their promising applications in flexible electronics, energy conversion and storage, plasmonics, and sensing (1, 2). The majority of prior work involves devices in which these 2D materials are in an inherently planar geometry (3). However, some applications such as wearable electronics, biological or dispersible sensors, and actuators could benefit from curved and folded architectures that feature small form factors (4, 5). In addition, it has been suggested that the physical and chemical properties of these 2D materials could be strongly affected by the introduction of curvature, folds, and creases (6, 7).

There have been a number of previous reports of folding or wrinkling of graphene, which leverage the atomically thin and extremely low bending stiffness of graphene (8). For example, previous studies have shown that suspended graphene sheets can fold under intense mechanical stimulation (9) or when curved templates are used during growth (10) or transfer (11, 12). Elsewhere, interfacial forces (13) and prestretched or thick gradient cross-linked polymer-graphene bilayers have been utilized to induce wrinkling or folding of graphene (14, 15). Although these methods are inspiring, they offer only limited precision and tunability in the three-dimensional (3D) geometries that can be formed or require harsh conditions or significantly thicken the folded graphene due to their reliance on thick substrates or multilayer structures (16, 17).

In contrast, theoretical studies suggest that such folding could be precisely controlled resulting in novel 3D geometries such as flowers, capsules, knots, rings, and boxes (18, 19). These approaches necessitate that folding be carried out with patterned graphene (20, 21). Manual folding of kirigami-patterned graphene has been demonstrated, and shapes such as springs, stretchable electrodes, and hinges have been

formed using external mechanical forces (22). However, controlled self-folding in response to external environmental stimuli, such as mild temperature compatible with biological systems, has yet to be demonstrated. Such controlled self-folding is extremely difficult to achieve with pristine graphene because graphene by itself is highly chemically inert and does not respond to most external stimuli. Hence, surface functionalization of graphene is necessary, while at the same time, it is also important that the sp^2 hybridization and excellent intrinsic electrical properties of graphene are retained.

Here, we report a strategy to modify the surface of graphene to endow it with thermoresponsive properties and pattern the functionalized graphene into ultrathin self-folding precursors. First, we used polydopamine (PD), a mussel-inspired bioadhesive, to functionalize the surface of graphene in a noncovalent manner (23). PD also enables a wide variety of chemical reactions for subsequent functionalization due to its reactive catechol/quinone groups (24, 25), so that responsive polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM) used in this study, can be further grafted to the surface (26, 27). We patterned the functionalized monolayer graphene into a variety of sizes and shapes using photolithography and plasma etching. Then, we released the functionalized graphene patterns from the substrate, and upon heating above the lower critical solution temperature (LCST) of PNIPAM, the 2D precursors self-folded into ordered 3D microstructures induced by the molecular conformational change of the grafted polymer brushes. Note that the functionalized graphene is extremely thin, in the range of 5 to 10 nm. In addition, the noncovalent method preserves the intrinsic properties of graphene and its low bending stiffness (28). Because the designs of the 2D precursors can be readily controlled using computer-aided design photomasks, we anticipate that this general approach is highly tunable and can be used to fabricate a range of 3D carbon structures of relevance in foldable electronics, biosensing, and molecular robots (29); and we highlight some applications.

RESULTS

Surface functionalization of graphene

Graphene is a highly chemically inert material due to the sp^2 hybridization of the carbon atoms on the basal plane (30), and thus, covalent functionalization of pristine graphene typically requires highly reactive

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chemicals and harsh conditions (31). Moreover, covalent functionalization usually introduces a large number of defects in graphene, which has an adverse effect on its intrinsic electrical properties and stability (32). Therefore, in this study, we developed a mild and eco-friendly method to noncovalently functionalize graphene and introduce stimuli-responsive properties.

In the first step, we self-polymerized dopamine on the graphene surface via pH-induced oxidation at room temperature (33), which resulted in a very thin layer (~ 5 nm in the dry state) of PD on the surface of graphene (Fig. 1A). The PD layer makes the surface of monolayer graphene hydrophilic (34) and allows further covalent attachment of other molecules and polymers containing functional groups that can react with PD. The strong attachment of PD to the surface of graphene is mostly due to physical interactions, such as π - π stacking and hydrophobic forces (24). In the second step, we used the PD thin film as an intermediate active layer to graft the PNIPAM chains. The chemical grafting mechanism is mainly a result of the reaction between the amine end groups of PNIPAM and the functional groups on PD, as discussed in a previous report (35).

We investigated the structure of monolayer graphene before and after surface functionalization using Raman spectroscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The Raman spectrum of the pristine monolayer graphene shows the characteristic G and 2D band at 1591 and 2693 cm^{-1} , respectively, and there is also a very weak D band at 1350 cm^{-1} . The intensity ratio I_{2D}/I_G is 2.0, which indicates high-quality monolayer graphene (Fig. 2A) (36). To investigate the time dependence of the reactions and tune the thickness of the grafting layers, we varied the polymerization time of PD from 2 to 4 hours (denoted as PD2 and PD4) and that of PNIPAM from 12 to 18 and 24 hours (denoted as PNIPAM12, PNIPAM18, and PNIPAM24). Spectra taken after functionalization at different time points for PD and PNIPAM indicate that the peak intensity and I_{2D}/I_G ratio is largely preserved, suggesting that there is no significant bond breakage in the monolayer graphene during functionalization (fig. S1) (37).

The AFM results indicated that the thickness increases from about 0.8 nm for pristine monolayer graphene to 6.0 and 6.9 nm for G-PD2 and G-PD4, respectively (Fig. 2B and fig. S2). The surface of G-PD was relatively uniform, which indicates a strong interaction between PD and the graphene surface. After further grafting of PNIPAM, the thickness of the G-PD-PNIPAM further increased to 8.5, 8.9, and 9.6 nm for grafting reaction times of 12, 18, and 24 hours. In subsequent experiments, unless specifically mentioned, the functionalization of graphene was done with PD grafting time of 2 hours and PNIPAM grafting time of 18 hours, and we refer to these samples as G-PD and G-PD-PNIPAM, respectively.

We characterized the chemical composition of the functionalized graphene using XPS (fig. S3 and table S1). After surface functionalization with PD and PNIPAM, there are significant changes to the C1s (Fig. 2C), N1s (Fig. 2D), and O1s (fig. S4) peaks. For instance, the C1s peak of graphene mainly corresponds to graphite-like sp^2 carbon (284.2 eV) (38), whereas that of G-PD can be decomposed to sp^2 C-H on the aromatic rings at 284.0 eV, C-O/C-N species at 285.6 eV, and C=O/C=N species at 287.9 eV (39). After PNIPAM grafting, the C1s peak can be decomposed into three peaks, the major one at 285.6 eV for CH_x , another one at 286.7 eV for the C-C=O groups, and the third one at 288.4 eV for the N-C=O groups (40). The Raman, AFM, and XPS data together provide strong evidence for the noncovalent surface functionalization of graphene by PD and PNIPAM to a tunable thickness of less than 10 nm.

Fabrication of self-folding microstructures

We observed that after surface functionalization of the graphene, it was endowed with thermoresponsive properties due to the PNIPAM brushes, so that it could behave as an ultrathin shape-changing material. We developed a process to selectively pin down parts of the 2D self-folding precursors while releasing others using a patterned aluminum (Al) sacrificial layer. The parts of the graphene in contact with the underlying SiO_2/Si substrate remain pinned due to strong van der

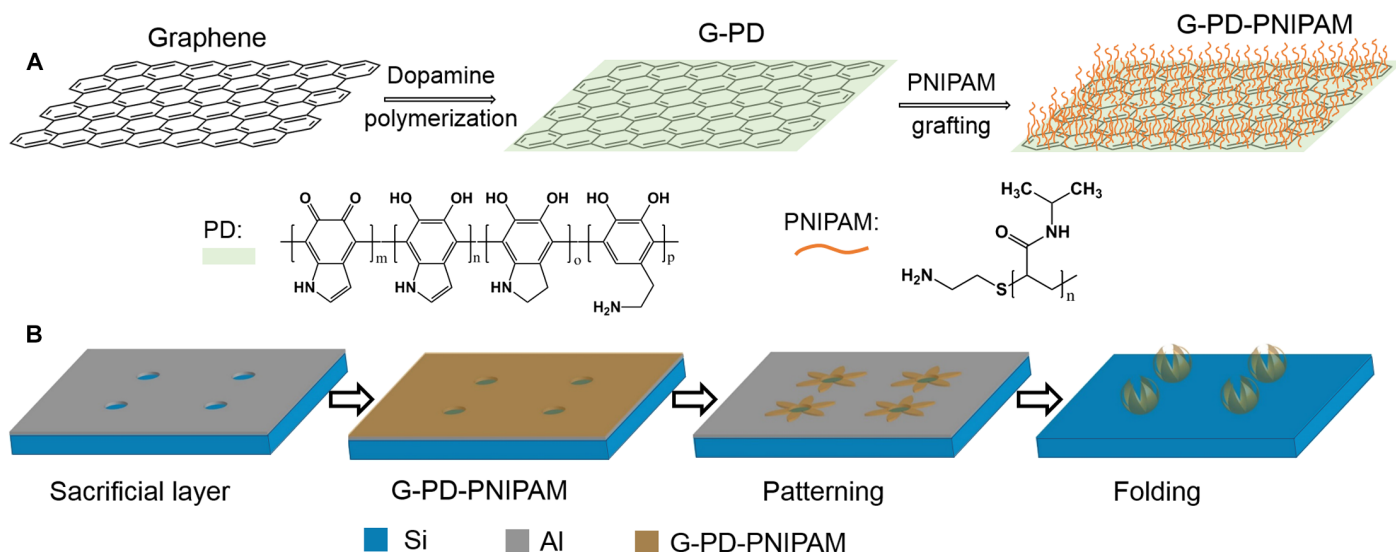


Fig. 1. Surface functionalization and patterning of monolayer graphene. (A) Schematic illustration of the surface functionalization process of graphene. In the first step, dopamine was self-polymerized on the surface of graphene to form a thin layer of PD, and then, the amine-terminated PNIPAM chains were grafted on the PD. (B) Schematic illustration of the fabrication and folding process of graphene microstructures. First, a patterned Al sacrificial layer was deposited. Then, monolayer graphene was transferred onto the substrate and functionalized using PD and PNIPAM. The functionalized graphene layer was patterned using photolithography and plasma etching. Finally, folding was induced by heating above the LCST of PNIPAM.

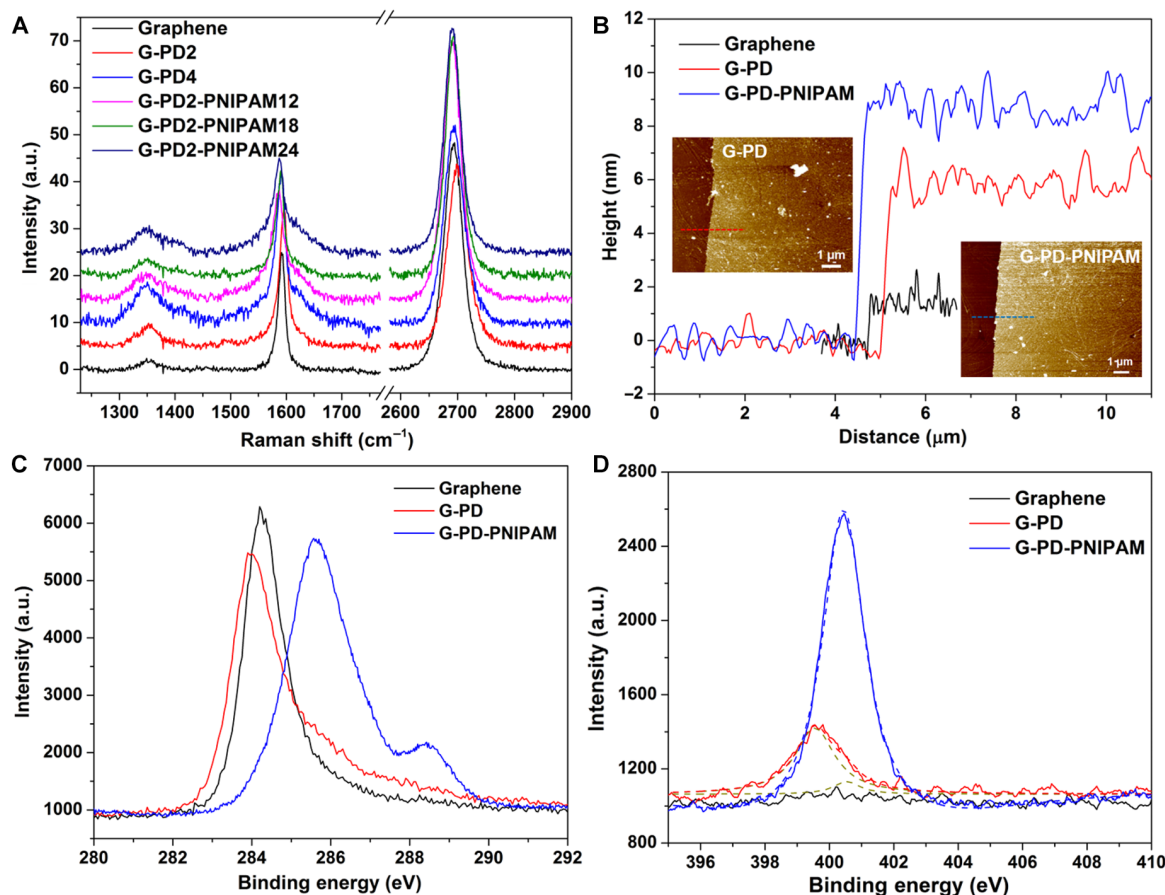


Fig. 2. Characterization of the functionalized graphene. (A) Raman spectra of graphene and functionalized graphene with PD and PNIPAM. PD_x and PNIPAM_x denote self-polymerization times of PD and grafting times of PNIPAM for *x* hours, respectively. a.u., arbitrary unit. (B) Representative AFM line scans of the graphene and functionalized graphene measured from the AFM images (insets). (C and D) XPS spectra (solid line) and peak fitting (dotted line) of graphene and functionalized graphene at the (C) C1s and (D) N1s binding energy regions.

Waals adhesion, whereas the graphene in contact with the Al is released during Al dissolution (Fig. 1B). Selective pinning prevents the folded structures from being washed away, which facilitates characterization, imaging, and device fabrication. If needed, free-floating or untethered self-folded graphene microstructures could also be fabricated using an unpatterned sacrificial layer.

We triggered the self-folding of the microstructures by increasing the temperature to approximately 45°C in aqueous media. The shape of the 2D patterned graphene precursors has a strong influence on their 3D shape after folding. We observed that the flower tends to fold its free petals toward the center and go from an open to a closed state (Fig. 3, A to C), which is useful for the encapsulation of cargo within the ultrathin graphene (41). For the dumbbell shape (Fig. 3, D to F), the two circles fold inward; this shape was inspired by the Venus flytrap. We could also self-fold a graphene box using a cruciform precursor (Fig. 3, G to I). In this case, we pinned the center face and released the other five faces. In addition, a rigid SU8 epoxy segment was placed between the two hanging faces to serve as a rigid folding hinge, and its dimensions could be varied without significantly altering the folding (fig. S5).

The scanning electron microscopy (SEM) images of the representative folded structures in the dry state are shown in fig. S6. It can be seen that the functionalized graphene microstructures are stable and uniform and tend to collapse onto the substrate upon drying due to cap-

illary forces. Note that, unlike the previous one-of-a-kind serial folding demonstrations with graphene, this process is highly parallel and structures can be triggered to fold en masse (fig. S7). In addition, using control experiments, we verified that the grafting of thermoresponsive PNIPAM to the surface of graphene is necessary for folding; the pristine graphene and G-PD dumbbell do not show any self-folding behavior at an increased temperature (fig. S8). Furthermore, the thickness of functionalized graphene can be varied in a wide range, down to as low as 5 nm; these ultrathin precursors are still capable of self-folding induced by a temperature increase (fig. S9).

We could achieve selective folding of the graphene microstructures by selective functionalization of different spatial regions with PD and PNIPAM; we observed that only those functionalized regions folded upon heating. The self-folding of the graphene dumbbell with only the right circle functionalized (Fig. 4, A and B) and the graphene flower with the alternating three petals functionalized (Fig. 4, C and D) demonstrate this selectivity. These results indicate a previously unachievable high degree of tunability and control over self-folding monolayer graphene. We observed that the extent of self-folding can be tuned by the temperature for regular-shaped functionalized graphene microstructures and that the extent of folding increased with temperature in the range of 35° to 45°C (fig. S10). The Raman spectrum of the folded functionalized graphene is shown in fig. S11.

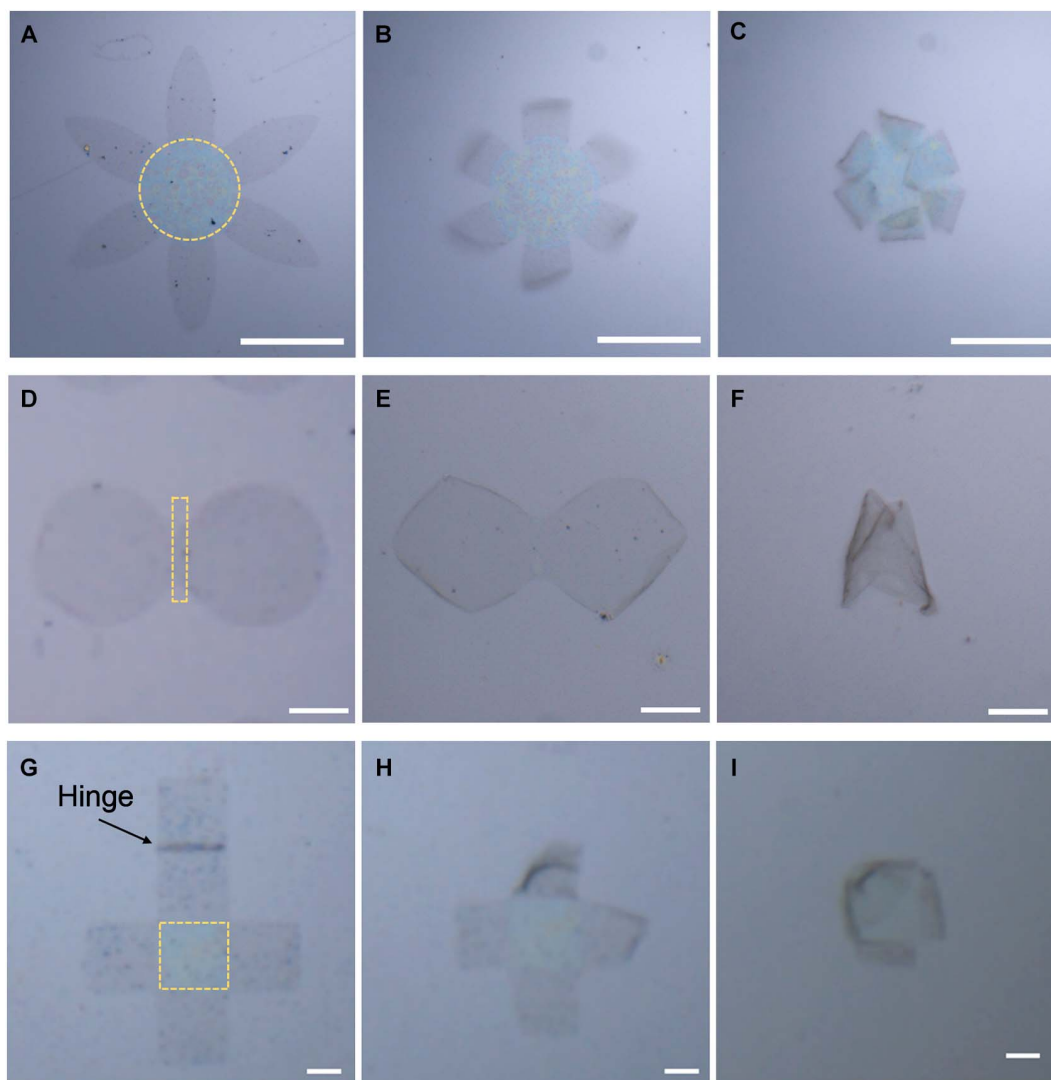


Fig. 3. Temperature-induced self-folding. Optical microscope snapshots of the self-folding of ultrathin graphene microstructures with different geometries: (A to C) flower, (D to F) dumbbell, and (G to I) box. The first column is at room temperature and before folding, the second column is a folding intermediate, and the third column is the folded structure after heating to 45°C. All the optical images were taken in an aqueous environment. Yellow dash lines indicate the pinned down area. Scale bars, 100 μm . The dimension of the rigid SU8 hinge in (G) has a length of 200 μm and a width of 25 μm .

We also achieved reversibility in self-folding by temperature control (Fig. 4E). For example, we could unfold a closing graphene flower by cooling it down from 45° to 25°C, which is consistent with the reversible switching behavior of PNIPAM from collapsed to swollen state at these temperatures. However, note that when the ultrathin graphene petals touched each other during folding, they irreversibly bonded due to the strong van der Waals interactions and were unable to unfold. We found that by adding a rigid polymer layer (SU8) to the petals, we could attenuate the influence of the van der Waals interaction and reduce adhesion between petals, which results in more reversible self-folding but increases the thickness of the precursors (at the rigid panels) to more than 100 nm (Fig. 4F).

One of the highlights of our approach is that the self-folding process utilizes benign thermoresponsive conditions compatible with cell biology. We demonstrate this feature by encapsulating live cells within the self-folding flower. We observed that unlike bare graphene, high densities of cells could be cultured on G-PD-PNIPAM similar to that on a

glass substrate, indicating good cell affinity (fig. S12). To encapsulate live cells inside the self-folded graphene microstructures, we first patterned the functionalized graphene into a flower-shaped precursor, and then, the cells were cultured on it. The elevated temperature during cell culture (37°C) induced the folding of the functionalized graphene flowers and encapsulated cells inside the petals (Fig. 4G). We confirmed that the cells are alive after encapsulation within the ultrathin functionalized graphene (Fig. 4H). This result suggests that the self-folding process is biocompatible and can be used to capture biological cargo.

Moreover, by decreasing the size of the functionalized graphene flower to 60 μm , even a single cell can be encapsulated inside (Fig. 4, G and H, insets), which is useful for single cell analysis (42). In addition, because of the ultrathin and flexible nature of the functionalized self-folded graphene, it can conform with the surface of the cell, which is important for biosensing applications. For example, we performed Raman characterization of a live cell encapsulated in the functionalized graphene, and the results indicate that the Raman signals from the

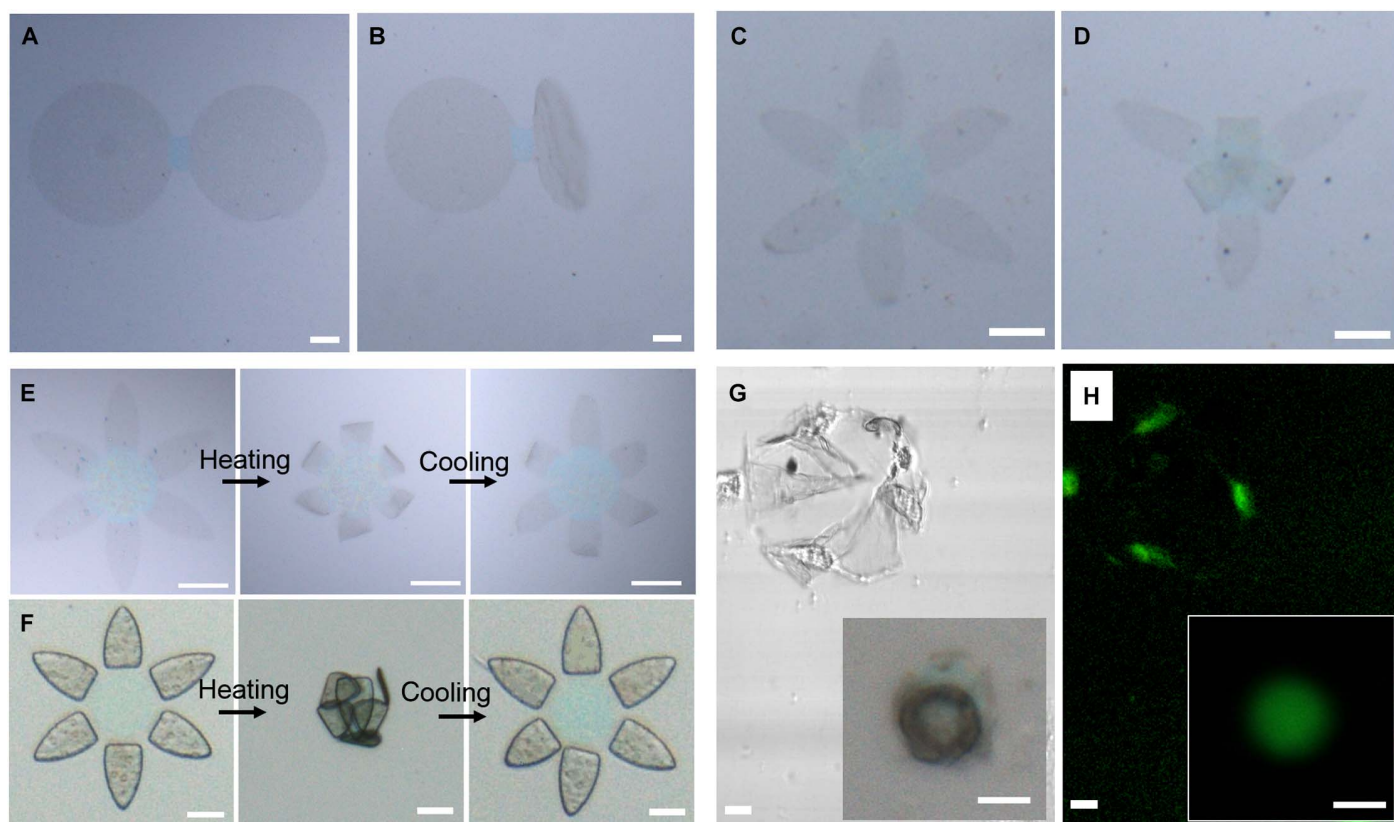


Fig. 4. Selective folding, reversibility, and live cell encapsulation. (A to D) Selectivity of self-folding in graphene microstructures induced by heating. (A) Optical microscope image of a dumbbell with only its right circle functionalized and (C) a flower with alternating three petals functionalized. (B and D) Optical images of folded structures indicating that only the functionalized regions self-fold on heating. (E and F) Reversibility of the temperature-induced self-folding. The sequence in (E) shows the folding and unfolding of a functionalized graphene flower, whereas the sequence in (F) shows the folding and unfolding of a flower with rigid SU8 petals, with better stability and reversibility but with increased thickness. (G and H) Encapsulation of live breast cancer cells within the functionalized graphene flowers. (G) Bright-field and (H) corresponding fluorescence image of encapsulated cells. Cells were stained with a live/dead (calcein AM/ethidium homodimer-1), and green fluorescence indicates viability. Insets in (G) and (H) show the encapsulation of a single breast cancer cell with a 60- μm flower. Scale bars, 50 μm , except for (G) and (H), which are 10 μm .

relevant biological molecules (for example, proteins and phospholipids) in the cell are significantly enhanced (fig. S13).

Multiscale simulations of folding

We developed a mesoscale coarse-grained molecular dynamics (MD) model of the G-PD-PNIPAM structure with its numerical parameters assigned on the basis of the mechanical characterization of different materials learnt from the full atomistic MD simulations. This model was used as an efficient tool to simulate the effect of the thermal stimulus on the structure deformation to gain an in-depth understanding of the folding mechanism and rationalize the self-folded 3D shapes. For a film with a bilayer structure, in which the two layers have different swelling/shrinking properties, it is well known that the strain mismatch will induce the film to bend or form 3D structures (43). Such strain mismatch-induced folding has been demonstrated for various materials, such as metals, semiconductors, and polymers (44, 45). However, for ultrathin materials, such as graphene and other 2D materials, such folding has not been achieved or well studied before.

The G-PD-PNIPAM in this work can be simplified as a bilayer material modeled by an elastic network composed of coarse-grained mass beads connected by elastic springs that define both the mechanical stiffness and equilibrium volume of the material (details in Materials and Methods and the Supplementary Materials). The bottom layer con-

sists of a monolayer graphene and thin PD film, which is inert and does not actively swell or shrink due to change in temperature, and thus, the bottom layer is considered as a passive layer only for mechanical stiffness; the top layer consists of PNIPAM brushes, which will shrink when temperature is increased above LCST, and thus, the top layer is considered as an active layer with its equilibrium volume change during the simulation.

We conducted a full atomistic computational study on PNIPAM and PD using MD simulations (details in Materials and Methods) to provide the required mechanical property and structural parameters for the coarse-grained MD model. Figure 5A shows the aggregate structure of PNIPAM brushes (see also fig. S14) at different temperatures: swollen and hydrated at 275 K and shrunken and dehydrated at 325 K. Because of the hydrophobic effect, the total volume of the material at 325 K is only 51% of that at 275 K (fig. S15). Subsequently, tensile tests (see the Supplementary Materials for details) were performed to estimate the Young's modulus of PNIPAM (46), and the results show that the Young's moduli are 94 and 243 MPa at 275 and 325 K, respectively (table S2). In addition, the Young's modulus of PD is around 5 GPa according to our previous simulation (47, 48) and experimental results (49). Although graphene is extremely stiff, the bending stiffness of the graphene layer is negligible due to its small thickness compared to other layers.

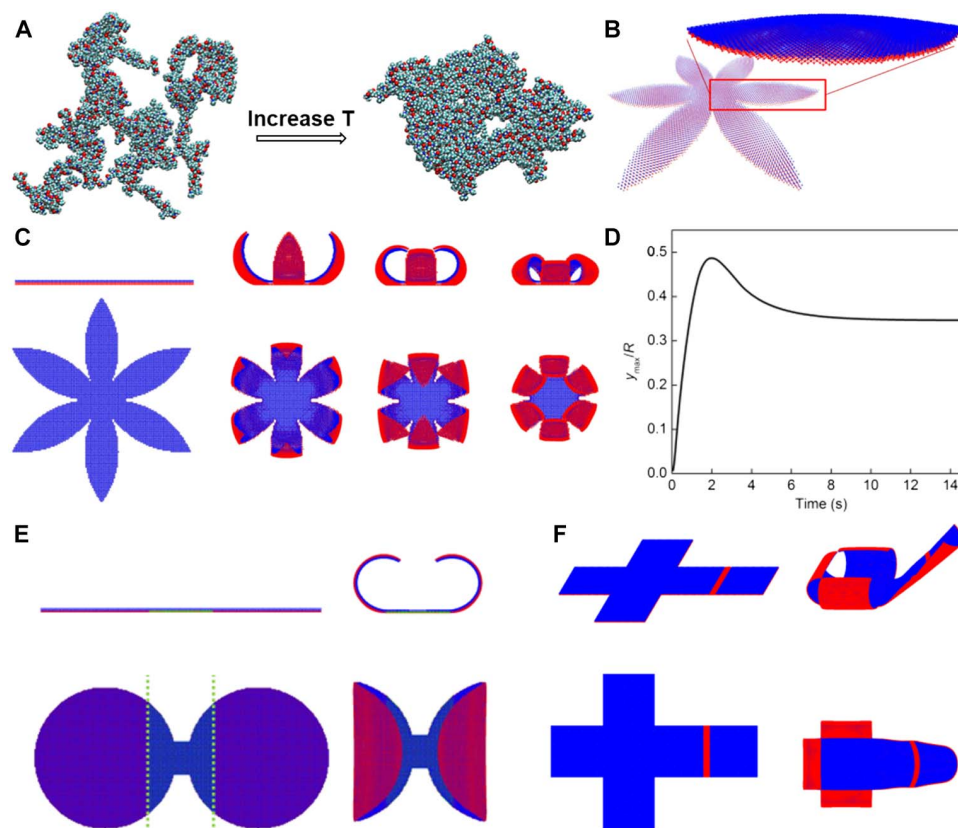


Fig. 5. Multiscale modeling of the temperature-driven self-folding of the functionalized graphene. (A) Top view of the aggregation of an array of PNIPAM brushes with increasing temperatures in full atomistic MD simulations (cyan, C; red, O; blue, N; white, H). (B) A representative mesoscale coarse-grained model of the flower-shaped functionalized graphene. (C) Simulation snapshots of the coarse-grained model during the folding process of the functionalized graphene flower. The first row is the side view, and the bottom row is the top view. (D) Plot of the height versus the overall initial radius of the flower pattern over time. (E and F) Flat and folded states of the dumbbell and box shaped graphene from simulation. The top row is the side/tilted view, and the bottom row is the top view. The coarse-grained structure is colored according to different materials: blue for the PNIPAM layer and red for the PD-graphene layer. A certain region of the bottom layer of coarse-grained beads is fixed by adapting the same boundary condition as in the experiments.

We parametrized the elastic springs in the coarse-grained model according to the full atomistic simulations (see Materials and Methods and the Supplementary Materials for details), and the overall geometry of the model was of three sets of different shapes: flower, dumbbell, and box. Note that this model enables us to define the equilibrium volume and material stiffness as an explicit function of the temperature and, thus, allows us to efficiently simulate its temperature response. The deformations of the multilayered G-PD-PNIPAM structures of these shapes are summarized in Fig. 5. We found that the folding is induced by shrinking of the PNIPAM layer to 51% of its original volume, when the temperature increases from 275 to 325 K. The entire folding process of the flower shape can be closely monitored (Fig. 5C), and the entire deformation process can be traced by the overall height of the folded structure, showing that the folded structure can first reach a peak height and then coil to reach equilibrium after a certain amount of time (Fig. 5D). The simulation and experiment results are consistent. For instance, for the self-folding graphene flower, the average lateral size and height in the folded state measured by confocal microscopy were found to be $131 (\pm 14)$ and $58 (\pm 17)$ μm (Fig. 3C), and those values are 125 and 52 μm (Fig. 5C) in the simulation. A qualitative comparison was conducted between the simulation and experimental results for self-folding structures with different sizes (fig. S16).

We also theoretically investigated the effect of the modulus ratio between the top and bottom layers on their folding behavior. We observed that similar fully folded geometries could be achieved by a range of stiffness ratio of the two layers (fig. S17), suggesting the consistent geometry of the folded structure. Similarly, the modeling of the folding process of the dumbbell shape, which folds toward the center, is shown in Fig. 5E. Figure 5F shows the folding of the patterned functionalized graphene into a box shape; it is worth mentioning that in the simulation, the box is not fully closed, but in the experiment, because of the small perturbation of water flow at elevated temperature, the ultrathin faces can fold more toward the center, which results in a more closed box. We have also used this material model to design other material systems with different deformation ratio and material stiffness. It was suggested by these simulations that we can also change the fixed boundary condition and distribution pattern of the PNIPAM layer to create different folded geometries.

Nonlinear resistors and creased transistors

Apart from its applicability as ultrathin encapsulating devices, self-folding can also be used as a means to tune the electrical properties of graphene. We measured the conductivity of the functionalized

graphene microstructure using the four-point probe method, and the gold electrodes were placed directly on graphene before it was functionalized with PD and PNIPAM. The I - V curve for G-PD-PNIPAM in the flat state shows a linear behavior with a sheet resistance of 430 ohm/sq, which is approximately the same as that measured on pristine monolayer graphene (fig. S18) and similar to that reported previously in the literature (50). This result further confirms that the functionalization is noncovalent in nature and does not compromise the excellent conductivity of graphene.

In contrast, the electrical properties change dramatically after folding and crease formation. We measured the I - V characteristics of self-folding functionalized graphene dumbbells (Fig. 6A). After self-folding and drying, the right circle folds on top of the left circle forming a crease, the diameter of which was measured by AFM to be around 18 nm (fig. S19). Note that we insulated the two graphene layers in the flat region with a 100-nm-thick SU8 layer to eliminate interlayer tunneling. After folding, the I - V curve becomes nonlinear, and there is a significant increase in resistance by approximately threefold from 2.08 kilohms to a voltage-dependent resistance ranging from 5.47 to 7.67 kilohms (Fig. 6, B and C), with the maximum resistance at around 0 V. We attribute this increase in resistance to the introduction of a folding crease region. Previously, it has been reported that folded graphene nanochannel structures also showed nonlinear I - V curves with increased resistance (51, 52), which is consistent with our observations. In our approach, the magnitude of resistance increase can also be tuned by changing the dimension of the folding crease (fig. S18).

We also fabricated back-gated graphene field-effect transistors (FETs) to further study the effect of folding crease on the electronic properties of graphene (Fig. 6D). All the measurements were done at room temperature under ambient conditions. Before folding, the transfer curve (Fig. 6E) shows that the drain current (I_d) gradually decreases with increasing gate voltage (V_g), and the Dirac point is approximately +90 V, which indicates that the graphene is heavily p-doped. This behavior is also observed in pristine graphene FETs (fig. S20), and a possible reason for this shift in the Dirac point is the adsorption of water molecules from air and the polymer residue from the transfer process (53).

After folding, the transfer curve shows that in addition to the Dirac point at around +90 V, there is a new minimum observed at around -30 V. A similar feature has been observed in a previous report (54), and it is believed that the new minima are related to the folding crease, which induces strong gauge fields and alters the charge carrier densities. In addition, the I_d is almost one order of magnitude lower than that of the flat state at the same drain voltage, which indicates a significant increase in the resistance of the graphene channel due to the folding crease (Fig. 6F and fig. S20). We rationalize this observation by noting that the folding crease behaves as a tunnel barrier for the current flow; the exact mechanism for the formation of these barriers in folded graphene or nanoribbons is still in debate. Plausible explanations have been previously attributed to the formation of an energy band gap due to the confinement (55) and the formation of a series of quantum dots induced by a disorder potential (56).

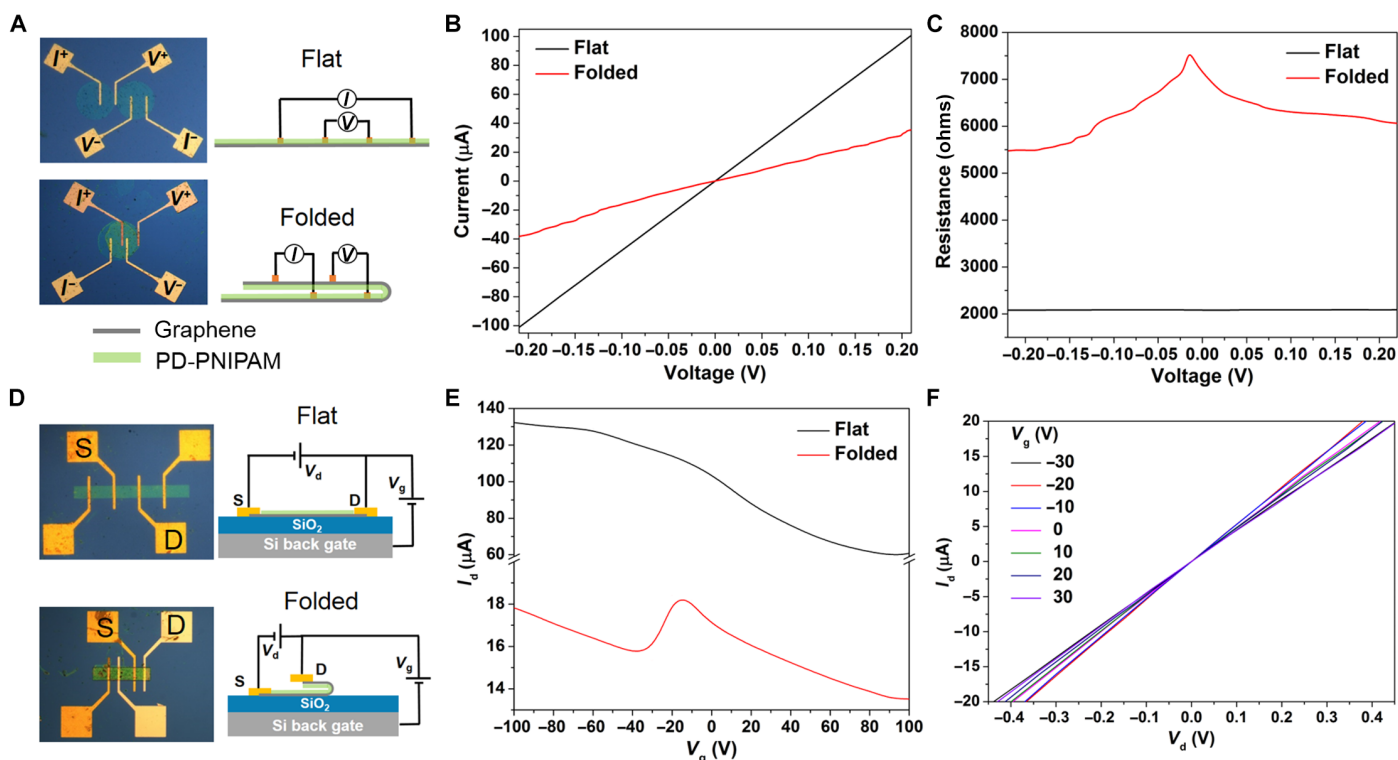


Fig. 6. Graphene-based nonlinear resistors and creased transistor devices. (A) Optical images and circuit diagrams of the measured resistor devices in the flat (top) and folded (bottom) states. (B) Representative I - V curves of a graphene dumbbell before and after folding. (C) R - V curves of the same samples as shown in (B). (D) Optical images and circuit diagrams of the measured graphene FETs in the flat (top) and folded (bottom) states. (E) The transfer curves of the functionalized graphene FET as a function of back-gate voltage in the flat (black line) and folded (red line) states. (F) Output curves of the functionalized graphene FET in the folded state as a function of drain voltage with varying gate voltages.

DISCUSSION

Graphene has been extensively studied in its planar form, and the ability to manipulate graphene and fold the atomically thin sheet into 3D shapes represents a new direction with the possibility to create new types of devices. However, because graphene is chemically inert, it is very challenging to achieve this transformation without altering the intrinsic properties of graphene. Here, we showed how this can be done using a noncovalent functionalization method. Our method has several unique advantages compared with previous reports: First, the noncovalent nature of PD surface functionalization does not compromise the electrical property of graphene; second, the polymer layer is ultrathin, and its thickness can be accurately controlled by tuning the PD polymerization time and polymer brush length; and third, the functionalization is confined within one side of the monolayer graphene surface and can also be performed on selective regions of graphene when combined with patterning techniques. Hence, the process is highly tunable, and a variety of folding shapes can be formed. Finally, this process is benign and does not require harsh processing conditions and is compatible with cell biology and physiological conditions.

As highlighted, we envision a number of applications. First, because of the versatility of the surface functionalization and patterning techniques, a variety of origami and kirigami shape-changing structures could be formed. In addition, the temperature responsiveness of PNIPAM is reversible and has been widely utilized to form a range of actuators, so it is anticipated that our approach could extend these to graphene hybrids. Because of the compatibility with living systems, this approach could be used to encapsulate and deliver cells or other biologicals. Moreover, because of low bending rigidity, we believe that the graphene can be conformably coated on the surface of 3D objects with intimate contact, which is very important for ultrasensitive detection, biosensing, and drug delivery (57). Finally, programmed crease formation driven by self-folding can be used to design novel electrical and field effect devices where the properties of graphene can be tuned on the basis of folding geometries.

MATERIALS AND METHODS

Surface functionalization of graphene

Monolayer graphene on the patterned substrate was immersed in a dilute aqueous solution of dopamine (2.0 mg/ml) (Sigma-Aldrich), buffered to a typical marine environment pH of 8.5 (10 mM tris-HCl), for 2 or 4 hours. A thin layer of PD formed on the graphene surface via self-polymerization. The coated surface was washed thoroughly with deionized water and dried with N₂ gas.

The PD-coated graphene was then immersed into a solution of amine-terminated PNIPAM (2.0 mg/ml) (*M_n*, 5500; Sigma-Aldrich) dissolved in 10 mM tris-HCl buffer (pH 8.5). The grafting reaction was carried out at 60°C for 3 hours and then cooled down to room temperature and further kept for 12, 18, or 24 hours. The functionalized graphene was thoroughly washed with deionized water and dried with N₂ gas.

Characterization of the functionalized graphene

Raman measurements were done using a Jobin-Yvon T64000 triple monochromator spectrometer with an Olympus microscope. The excitation line was the 514.5-nm line of a Spectra-Physics Ar-Kr laser. XPS data were acquired with a PHI 5400 XPS using Mg K α X-rays (energy = 1253.6 eV). The peaks in the high-resolution scan were

fitted with Shirley backgrounds and a Gaussian-Lorentzian mixed function. AFM was performed in tapping mode with ~300 kHz Si cantilevers on a Bruker AFM (Dimension FastScan). The scan rate was set at 0.5 Hz, and the sampling was at least 512 samples per line by 512 lines.

Fabrication of self-folding graphene microstructures

The functionalized graphene was patterned into various shapes, including flower, dumbbell, and box, by photolithography, and the graphene in unwanted areas was removed using an oxygen plasma [radio frequency (RF) power, 60; time, 30 s] (PE-100; Plasma Etch Inc.). The functionalized graphene was released from the substrate by dissolving the underlying Al layer with dilute NaOH (5 mM). The solution also contained 3 mM sodium dodecyl sulfate surfactant to reduce the adhesion of graphene to the surface and prevent the graphene from permanently sticking to itself. A previous study showed that the presence of surfactant molecules does not measurably affect the mechanical and electrical properties of graphene (22). Folding of the functionalized graphene was induced by increasing the temperature after dissolving the Al sacrificial layer. The solution was heated to 45°C using a hot plate, and the temperature was monitored during the entire process with a thermometer.

Characterization of folded graphene microstructures

Optical microscope images were taken in aqueous condition using a Nikon AZ100 microscope equipped with a mercury lamp (Nikon C-HGFI). SEM images were taken with the FEI Quanta 200 microscope. The resistance of the graphene microstructures was measured using the conventional four-point probe method, where a constant current was generated from the Keithley 220 current source, and the voltage was measured using a Keithley 2182A Nanovoltmeter. We fabricated back-gated graphene transistors on a Si/SiO₂ substrate (p⁺-doped, $\rho \sim 0.001$ to 0.005 ohm cm; Silicon Materials Inc.). We evaporated 5 nm of Cr (adhesion layer) and 50 nm of Au for source and drain contacts to the graphene. The transport channel defined by the two electrodes deposited on graphene was 125 μ m wide and 230 μ m long. All the measurements were performed at room temperature.

Full atomistic modeling and equilibration

To obtain the required coefficients for our coarse-grained MD model, full atomistic MD simulations of PNIPAM were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) (58). The full atomistic PNIPAM model consists of 36 PNIPAM chains with a chain length of 20-mer. In the initial configuration (fig. S14), the longitude direction of each PNIPAM chain is faced to the *x*-direction of the simulation box, and the PNIPAM chains are separated by a distance of 30 Å in both the *y* and *z* directions. The simulations were conducted in the presence of explicit water, and the mass of the PNIPAM chains was around 10% of the mass of the water molecules in the PNIPAM-water system. In the simulation, the CHARMM (Chemistry at Harvard Macromolecular Mechanics) General Force Field (CGenFF) was adopted (59), and the CGenFF code was used to create the parameter file (60). Periodic boundary conditions were applied in all three directions. After energy minimization, which was performed with the conjugate gradient algorithm, the PNIPAM-water system was equilibrated with the isothermal-isobaric (NPT) ensemble at a temperature of 275 K and pressure of 1.013 bar in the *y* and *z* directions for 20 ns. To study the temperature effects on the structural and mechanical

properties of PNIPAM, another PNIPAM-water system was equilibrated with the NPT ensemble at a temperature of 325 K and pressure of 1.013 bar in the y and z directions for 20 ns. More details can be found in the Supplementary Materials.

Coarse-grained modeling and equilibration

The face-centered cubic lattice was used to model the location of the mass beads (which locate at corners and face centers), and an elastic spring was used to model the interaction between the nearest neighboring beads. The effect of the temperature on the PNIPAM brush layer was implicitly simulated by tuning the equilibrium length constant of the lattice structure as

$$a(t) = a_{\text{end}} + (a_0 - a_{\text{end}}) \exp\left(-\frac{t}{t_0}\right)$$

In the above equation, $a_0 = 4 \mu\text{m}$ is the initial lattice length at low temperature, $a_{\text{end}} = 0.71 a_0$ is the equilibrium length constant at high temperature, which reflects the 49% in-plane volume change for one length dimension, and t_0 is the time constant used in the simulations to reflect how quick the PNIPAM responds to the temperature change. More details can be found in the Supplementary Materials.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/10/e1701084/DC1>

Additional experimental details

Raman spectra of the functionalized graphene

AFM characterization of the functionalized graphene

XPS characterization of functionalized graphene

Optical and SEM imaging of the self-folding graphene structures

Raman spectra of folded graphene

Cell encapsulation and Raman analysis

Full atomistic modeling of the folding behaviors

Electrical properties of folded graphene structures

fig. S1. Raman spectra of PD with different thickness (self-polymerization for 2 and 4 hours) on the Si substrate.

fig. S2. Surface morphology of graphene and functionalized graphene.

fig. S3. Chemical composition of functionalized graphene studied by XPS.

fig. S4. High-resolution O1s XPS spectra and peak fitting (dotted lines) of graphene, G-PD, and G-PD-PNIPAM.

fig. S5. Effect of the rigid hinge on the self-folding of functionalized graphene box.

fig. S6. Characterization of the self-folding graphene microstructures using SEM.

fig. S7. Highly parallel self-folding of ultrathin 3D graphene microstructures.

fig. S8. Control experiments of self-folding on pristine graphene and G-PD.

fig. S9. Self-folding of functionalized graphene with 5 nm thickness.

fig. S10. The folding process of half-functionalized graphene dumbbell with increasing temperature.

fig. S11. Raman spectra of a graphene flower in the flat and folded regions.

fig. S12. Cell viability with the live/dead assay.

fig. S13. Single cell encapsulation and Raman study.

fig. S14. Initial configuration of the PNIPAM-water system in the MD model.

fig. S15. Top view of the aggregation behavior of an array of (36 chains in total) PNIPAM brushes at different temperatures in MD simulations.

fig. S16. Comparison between the coarse-grained MD model and the experiment results for a functionalized graphene flower with different size.

fig. S17. The effect of mechanical properties of the two layers on self-folding.

fig. S18. Electrical measurements on pristine graphene and functionalized graphene dumbbell.

fig. S19. Dimension of the folding crease measured by AFM.

fig. S20. Output and transfer curves of the pristine and functionalized graphene FET.

table S1. XPS data analysis of graphene, G-PD, and G-PD-PNIPAM at the C1s, N1s, and O1s peaks.

table S2. Tensile test results of PNIPAM from the MD simulations.

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Ultrathin thermoresponsive self-folding 3D graphene

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