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Ultra-Stretchable Graphene-Based Molecular Barriers for Chemical Protection, Detection, and Actuation

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Abstract

A wide range of technologies require barrier films to impede molecular transport between the external environment and a desired internal microclimate. Adding stretchability to barrier films would enable the applications in packaging, textiles, and flexible devices, but classical barrier materials utilized dense, ordered molecular architectures that easily fracture under small tensile strain. Here, we show that textured graphene-based coatings can serve as ultra-stretchable molecular barriers expandable to 1500% areal strain through programmed unfolding that mimics the elasticity of polymers. These coatings retain barrier function under large deformation and can be conformally applied to planar or curved surfaces, where they are washfast and mechanically robust to cycling. These graphene-polymer bilayer structures also function as sensors or actuators by transducing chemical stimuli into mechanical deformation and electrical resistance change through asymmetric polymer swelling. These results may enable multifunctional fabrics that integrate chemical protection, sensing and actuation, with further applications as selective barriers, membranes, stretchable electronics, or soft robotics.

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Supporting Information

Supporting Information, including Figure S1–S26, Table S1, Movie S1–S3, and detailed description of numerical modeling with relevant Python codes, is available free of charge from the ACS Nano home page (<http://pubs.acs.org/journal/ancac3>).

Author Contributions

P.-Y.C., M.Z., M.L., I.Y.W., and R.H.H. conceived the idea and designed the experiments. P.-Y.C., M.Z., and M.L. fabricated the ultra-stretchable chemical barriers and performed solvent contact assays. P.-Y.C., M.Z., and M.L. applied the graphene barrier on gloves and tested its improved chemical protection. P.-Y.C. fabricated graphene-based chemoresistive sensor and relevant characterization. P.-Y.C. and M.Z. fabricated the functional actuators and characterized their bending behaviors. P.-Y.C., M.Z., and R.H.H. developed the numerical modeling. P.-Y.C., M.Z., M.L., I.Y.W., and R.H.H. co-wrote the paper, and all authors discussed the results and commented on the manuscript.

Smart Graphene Molecular Barriers

Keywords

Graphene oxide membrane; ultra-stretchable molecular barriers; broad-range chemical rejection; chemoresistive sensors; chemomechanical actuators

Electronics, food and drug packaging, and personal protective equipment often require barrier layers that inhibit the transport of small molecular species either into, or out of, an internal space for which some specified “microclimate” is desired.¹ Conventional molecular barriers include specialty polymer films,² ceramic films,³ amorphous carbon or SiO_x coatings,^{4,5} and metallization layers.⁶ Many traditional barrier materials are not flexible, and essentially none are stretchable, but rather fail under modest tensile strain or develop pores or cracks that degrade barrier function. Stretchability would be a desirable feature in some applications, including protective fabrics,^{7,8} wearable electronics,^{9–11} packaging/encapsulation of complex shapes or mechanically dynamic devices,^{12,13} lightweight inflatables,² and stretchable food/drug wrapping.¹⁴ Stretchability is easily achieved through elastomeric films, but elastomers as a general class of materials consist of molecular chains that are disordered in the relaxed state and thus have significant free volume and very poor barrier properties. In general, it is difficult to combine effective barrier performance (requiring dense, ordered, space-filling materials) with high stretchability (achieved by reversible molecular reorganization in response to external forces) because of the conflicting requirements on the desired molecular structures. Recent studies have reported progress in improving stretchability and barrier function in a single composite material. Holder *et al.* imparted some stretchability (10%) to molecular barriers made of polyethyleneimine-clay composites by addition of polyglycidol layers.¹⁵ Xiang *et al.* reported a poly(ethylene oxide)/tannic acid layer-by-layer assembly that achieved barrier performance at 100% extension that is superior to thick rubber films, and the barrier performance was stable upon 20x cycling.¹⁶ An additional factor is chemical resistance, as common polymer-based barriers are not stable against the full spectrum of target permeants, which include organic liquids that dissolve or swell the polymer matrix.¹⁷ High grade durable polymer barriers are

normally heavyweight films that sacrifice mechanical flexibility. Moreover, current technologies provide only passive protection, and many smart technologies could benefit from add-on functions that sense, identify, and/or adapt to chemical exposures.¹⁸ Major challenges remain for the development of multi-functional or “smart” molecular barriers that are lightweight, stretchable, durable, and integrated with sensing or actuating features that report on or adapt to environmental conditions or other stimuli.

The present article explores the use of graphene-based materials in smart, stretchable barrier technologies. The ideal graphene sheet is known to be a highly effective molecular barrier, and assembled multilayer films of graphene,^{19–21} graphene oxide (GO)^{22,23} or reduced graphene oxide (rGO)²⁴ have shown promise as protective coatings with both chemical resistance and high barrier performance under some conditions.^{25–27} Unfortunately, graphene is strong under tension but not stretchable, and multilayer rGO or GO films in the dry state are neither stretchable nor strong, but rather undergo brittle failure under tension due to weak intersheet van der Waals forces.²⁸ A possible route to high-performance stretchable barriers is through pre-compression of such multilayer films to form textured coatings capable of programmed unfolding.²⁹ Potentially suitable graphene texturing methods have been developed for other purposes.³⁰ One method uses relaxation of pre-stretched elastomer substrates to compress graphene films into complex out-of-plane micro-textures.^{30,31} These textured films have been shown to exhibit enhanced hydrophobicity,³⁰ electrochemical activity,^{31,32} and photosensitivity,^{33,34} but their barrier properties have not been measured, either in the textured, compressed state, or after relaxation or cycling back to the expanded planar state. Because of the extreme local deformations experienced by graphene-based films under high compression, it is not clear if the intrinsic graphene barrier properties are maintained, or if they would survive mechanical relaxation or cycling stresses.

In addition to stretchable barriers, the asymmetric architecture of textured 2D material coatings on soft elastomeric substrates displays stimuli-responsive behaviors that can be utilized for chemomechanical sensors and actuators. Our sensing concept is based on the solvent-specific swelling of silicone elastomers,³⁵ which can be transduced into electrical signals due to the deformation of textured graphene-based films (if electrically conductive forms such as graphene or rGO are used). This substrate swelling can also result in the spontaneous development of curvature.³⁶ This chemomechanical actuation is dramatic and can also be utilized in origami-like actuators to generate three-dimensional architectures under external chemical stimuli.³⁷ The present work clarifies and models the underlying actuation mechanism for these systems, and the chemomechanical devices are proposed as sensors and actuators that can be naturally integrated into stretchable barrier layers to establish smart materials for more comprehensive management of chemical risk.

Here we show that graphene-elastomer bilayer architectures can be utilized as multifunctional molecular barriers with ultrahigh stretchability (Scheme 1). We first deposited large-area GO multilayer films on pre-stretched latex substrates followed by a biaxial contraction. The two-layer devices can be stretched and relaxed up to 1500% areal strain for 500 cycles and were evaluated as protective layers against a variety of small-molecule organic liquids under extreme deformation. The functionality of the bilayer devices can also be modified by selecting different elastomeric components. Bilayer films

with rGO coatings on PDMS for example exhibit solvent-specific swelling behaviors that can be relaxed and cycled without mechanical damage (Scheme 1). This swelling induces systematic changes in both the shape and electrical resistance that are distinctive for each organic solvent. These chemoresistive and chemomechanical behaviors can be utilized for real-time identification of chemical species. Surprisingly, we show through experiments and modelling that the actuation is not due to the expected bimetallic strip mechanism with graphene and polymer as the two active layers.³⁸ Instead, graphene acts as a molecular barrier on one side of the device causing asymmetric solvent uptake into the polymeric substrate, which results in a non-uniform swelling that causes the bilayer structures to bend. This chemomechanical actuation is demonstrated in an electronic device to report chemical exposure, and could be integrated with barrier layers that are based on the same layered material platform. These bilayer devices composed of elastomers and textured 2D films are also of great interest for further exploitation for the applications including lightweight personal protective equipment,³⁹ wearable electronics,⁴⁰ and soft robotics.⁴¹

RESULTS AND DISCUSSION

Ultra-stretchable graphene-elastomer bilayer structures

An ultra-stretchable graphene-elastomer bilayer was prepared by depositing a pre-stacked planar multilayer GO film onto a pre-stretched elastomeric substrate followed by relaxation, allowing the resulting surface instability to deform the GO coating out-of-plane (see overview sketch in Figure S1). This procedure starts with an aqueous stock suspension containing monolayer GO sheets with lateral dimension from 0.5 - 5 μm (Figure S2a).^{42,43} The GO suspension was first drop-cast and air-dried on a polystyrene (PS) substrate, assembling into a GO thin film with planar morphology. The thickness of GO film was adjusted by the concentration of GO dispersion (Figure S2b), and the multilayered structure of GO membrane can be observed in Figure S2c. The PS substrate was dissolved in dichloromethane (DCM) and rinsed to obtain a freestanding GO film, which was transferred as a patch onto an inflated latex balloon serving as a model for a general elastomeric substrate to be enhanced by an active barrier layer. The pre-strain and total contraction were controlled by the volume of water or air in the inflated state. Treatment of the latex by O_2 plasma was necessary to achieve an adherent conformal patch (Figure S2d,e).⁴⁴ Figure S3 shows examples of the textures created by latex relaxation on different sections of the balloon.

The topographical features of crumpled GO structure were systematically controlled based on the pre-strain on the elastomer film and/or the thickness of GO film. For instance, a thin stiff coating with thickness h deposited on a uniaxially pre-stretched elastomeric substrate will buckle with a characteristic wavelength of $\lambda = 2\pi h \left(\bar{E}_c / 3\bar{E}_s \right)^{1/3}$,⁴⁵ where the plane-strain elastic modulus $\bar{E}_i = E_i / (1 - \nu_i^2)$ is given in terms of the Young's modulus E and Poisson's ratio ν_i of the coating (c) or latex substrate (s), respectively. This classical treatment in the limit of small deformations gives qualitative insight into the isotropic crumpled structures formed here through biaxial deformation. In particular, we find a characteristic texture length scale of the crumpled structures that varies from 1.2 to 3.5 μm

as the GO coating thickness varies from 0.2 to 1.2 μm (Figure S4). Nevertheless, it should be noted that these surface features are generated by extreme biaxial deformations, *i.e.*, areal strains, which can be defined in Equation 1:

$$\text{Areal Strain} = \Delta A / A_0 \times 100\% \quad (1)$$

, where ΔA is the change ($A_f - A_0$) of superficial area of GO films between the inflated (A_f as the planar GO film is attached) and deflated states (A_0 as the GO film is fully compressed). These areal strains (1500%) corresponding to uniaxial strains in each direction of $\epsilon_x = \epsilon_y = 300\%$. In this large deformation limit, the characteristic wavelengths and amplitudes likely exhibit a more complicated dependence on the magnitude of pre-strain, which will be examined more thoroughly in future work.

An important consequence of these accordion-like composite structures is that they can be unfolded by in-plane mechanical deformations, which diminishes the effective strain on the coating. In particular, the peak strain on the coating ϵ_{peak} that can be sustained before fracture is governed by the pre-strain ϵ_{pre} in Equation 2:⁴⁶

$$\epsilon_{peak} = \sqrt{\epsilon_{pre} \epsilon_c} \frac{(1 + \xi)^{1/3}}{\sqrt{1 + \xi_{pre}}} \quad (2)$$

, where the critical buckling strain $\epsilon_c = 1/4(3E_s/E_c)^{2/3}$ and $\xi = 5\epsilon_{pre}(1 + \epsilon_{pre})/32$. In these studies, the cumulative pre-strain is considerable ($\epsilon_1 = \epsilon_2 = 300\%$), enabling the composite structure to undergo large deformations without fracturing the GO coating. Figure 1a shows a continuous evolution of the GO coating actuated by re-inflating the underlying latex balloon to different stages. For instance, as the latex balloon was gradually re-inflated to 275 cm^3 , the superficial area of the GO coating increased from 0.25 cm^2 (deflated state) to 4.00 cm^2 (inflated state). Simultaneously, the crumpled features unfolded and texture length scale increased from 2.5 to 10.0 μm with reduction in Z-amplitude (Figure S5). The conformal GO coating was subjected to 100 - 500 cycles of inflation/deflation during which we did not observe changes in the relaxed state topography (Figure S6a-c and Movie S1). The interlayer spacing by XRD also remained constant during compression and expansion (Figure S7). For extremely large mechanical deformations with areal strains that exceed the pre-strain, the GO coating fractures and detached from the latex substrate (Figure S6d).

Chemical barrier performance of stretchable GO coatings

Unfoldable GO coatings were then evaluated as molecular barriers under varying degrees of mechanical stretching. It should be noted that properly fabricated planar GO films (in the dry state) have been shown to be impermeable to organic solvents,^{22,23} but it was unclear whether these barrier properties would be maintained after extreme mechanical deformation. A solvent contact assay was developed to (i) rapidly test permeation by organic solvents known to dissolve or weaken the underlying elastomer, and (ii) test permeation at various stages of film contraction/expansion by partial inflation. In control experiments, unprotected latex balloons were placed in contact with nine organic solvents, including dichloromethane

(DCM), trichloroethylene (TCE), chlorobenzene, chloroform, cyclohexane, dimethyl sulfoxide (DMSO), ethyl ether, tetrahydrofuran (THF), and hexane (Figure 1b and Figure S8). In all nine cases, the latex balloon immediately burst (within 5 seconds or less). In contrast, GO-protected balloons at areal strains of 500%, 900%, and 1500% were impervious to attack by all nine solvents for over 100 seconds, which was the duration of the experiment.

A higher resolution measurement of molecular permeation across these GO films was performed using TCE, a small-molecule industrial solvent (kinetic diameter ~ 5.6 Å) and important persistent and volatile environmental toxicant.⁴⁷ The GO-based barriers were stretched to 600% or 1500% of their deflated dimension and brought into direct contact with a liquid TCE bath for over 12 hours. The water reservoir on the back side of the barrier was collected for gas chromatography at different time points to quantify TCE concentration and thus permeation rate. For unprotected balloons, TCE was able to diffuse across the latex and rapidly accumulated over a period of 12 hours, reaching a final concentration of $1.6 \cdot 10^{-4}$ g/mL, corresponding to an approximate TCE flux of $1.94 \text{ nmole s}^{-1} \text{ cm}^{-2}$. In contrast, GO-protected balloons allowed very low TCE permeation over 12 hours (Figure 1c), indicating excellent barrier properties. A cross-sectional SEM image of GO-latex bilayer composite is shown in Figure 2a. By harnessing the surface instability during balloon deflation, an extended, interlocked interface between GO coating and latex substrates can be observed. The convoluted GO coating on elastomeric substrate were further challenged by mechanical stresses occurring during use and cleaning operations, including hand rubbing, autoclave sterilizing, machine laundering, and spray washing (Figure 2b and Figure S9). These coatings remain mechanically intact with unaffected barrier properties, indicating they are durable and washfast under these conditions of simulated use stress (Figure S10).

These results suggest that stretchable GO films could be utilized in next-generation protective fabrics. As a proof of concept, GO coatings were deposited on a pre-inflated general purpose chemical safety (nitrile) glove (Figure 2c,d). Deflation led to a crumple-textured GO patch conformally adhered on the outer surface. PS beads were filled in a nitrile glove and utilized as indicators to report in DCM penetration (Figure S11a,b). This glove was then contacted with DCM, a common industrial extraction solvent.⁴⁸ With the textured GO layer, the glove can withstand direct contact with bulk liquid DCM for over 30 minutes without penetration (see Figure 2e, Figure S11c,d). The demonstration also provides evidence that the GO barrier properties are independent of substrate selection.

Real-time chemical identification and reporting using rGO-elastomer bilayer films

In addition to the barrier function, these textured-graphene-elastomer bilayer composites show intriguing chemoresistive and chemomechanical behaviors of interest for chemical exposure sensing and actuation (Scheme 1). For these experiments, a planar GO film was deposited on a thermally-responsive PS substrate (*i.e.*, shrink film) and actuated at about 140 °C (above the T_g of PS) to 20% of its original area (see detailed fabrication in Figure S12), inducing the formation of isotropic crumple texture (Figure S13a). Chemical reduction using hydrazine hydrate solution (2 wt.%) was performed to achieve electrical conductivity in rGO without disrupting the crumple texture (Figure S13b).⁴³ The rGO flake size is about

$1 \times 1.5 \mu\text{m}^2$ as shown in Figure 13c. Afterwards, an uncured PDMS solution was infiltrated into the microtextural features and cross-linked at 80 °C, followed by an etching step in DCM to remove the PS substrate. PDMS was selected as the elastomer in this application due to its extensive physiochemical database in the literature,³⁵ which will prove to be advantageous in the development of a mathematical model of the chemomechanical behavior (see paragraphs below). Note that this etching step swells the PDMS, but the compression-induced texture allows the rGO coating to survive the swelling intact (Figure S14). After rinsing in DCM and ethanol, a freestanding, stretchable, electrically conductive textured-rGO-PDMS two-layer film was produced (Figure 3a). The texture length scale of rGO-PDMS films is about 7.7 μm , which is similar as the length scale (7.39 μm) of GO-latex sample under similar areal strain (~300%) (Figure S13d). We used PDMS in the later part of the work in order to have control of the thickness by in-house fabrication and due to the known literature database on solvent-induced swelling of PDMS.

Two methods reported in this manuscript (plasma treatment and attachment vs. liquid elastomer precursor back-infiltration) exhibit different attachment mechanisms for the two different polymer substrates. The back-infiltration of uncured PDMS liquid is useful in that it maximizes the contact area between rGO micro-textures and elastomeric substrates, forming an extended, interlocked interface (cross-sectional SEM in Figure 3b). The rGO-PDMS bilayer microstructures also remain intact after multiple cleaning processes (Figure S15). On the other hand, the latex substrate was prefabricated (not polymerized *in situ*), so we needed another method to enhance adhesion, and found the plasma treatment was useful. In general, the adhesion techniques would need to be chosen for each polymer of interest. Both methods (balloon compression and elastomer back-infiltration) can achieved similar crumpled topographies and bilayer microstructures that can provide strong adhesion and increased mechanical durability. Both structures can remain intact after daily mechanical stress (rGO-PDMS in Figure S15 and GO-latex in Figure 2b).

In response to organic solvent exposure, rGO-PDMS bilayer displayed a range of solvent-specific actuation behaviors. In particular, after the bilayer film is brought into contact with liquid organic solvents, the PDMS layer absorbs the solvent and swells, driving a partial unfolding of the upper-layer textured rGO and modulation of its electrical resistance (Figure 3c). For instance, as the PDMS substrate swelled, the texture length scale of rGO layer increases from 12.8 μm (Figure 3a) to 19.1, 17.9, 16.8, 14.5, and 13.2 μm for diisopropylamine, THF, DCM, acetone, and DMSO, respectively (Figure 3d and Figure S16a,b). We observed that rGO expansion increases the resistance between two gold electrodes at the edges, which may be a consequence of longer electron transport pathways.

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A panel of responses was developed by measuring the resistance from the sensors upon exposure (at the 300-second mark) to different organic analytes (Figure 3e). For each profile, the normalized resistance change ($\Delta R/R_0(\%)$) was calculated in Equation 3 from the resistance reading in response to the analyte, using:

$$\Delta R/R_0(\%) = (R_f - R_0)/R_0 \quad (3)$$

where R_f is the resistance value at equilibrium of the sensor after exposure to the analyte, and R_0 is the baseline resistance.⁴⁹ We demonstrate in Figure S17a,b that the resistance increase is mainly attributed from substrate swelling/expansion that leads to elongated electron transport pathways. The contact resistance between gold electrodes and rGO film is relatively small and does not affect the sensitivity of chemo-resistive devices. Based on the resistance change, the device can identify the presence of liquid diisopropylamine (> 56%), chloroform (35%), THF (32%), DCM (19%), chlorobenzene (18%), acetone (8%), and DMSO (0%), which is well correlated with the swelling ratio (S) and solubility parameters (δ) reported in the literature (see Figure S18a and Table S1).³⁵ The only exception was diisopropylamine which has a very similar solubility parameter as PDMS ($\delta = 7.3 \text{ cal}^{1/2} \text{ cm}^{-3/2}$) and a high swelling ratio ($S = 2.2$). The large substrate expansion caused the delamination of gold electrodes and thus incorrect resistance reading beyond 60%. Next, the rate of normalized resistance change, $[(R_f - R_0)/R_0]/t (\% \text{ min}^{-1})$, were calculated and summarized in Figure S18b. With the additional information about rate of resistance change, organic solvents with similar resistance changes can be distinguished, including chloroform ($0.98\% \text{ min}^{-1}$) and THF ($1.25\% \text{ min}^{-1}$), DCM ($0.76\% \text{ min}^{-1}$) and chlorobenzene ($0.64\% \text{ min}^{-1}$). The rate of resistance change and the response time can be simply customized by changing the thickness of PDMS layer (Figure S18c). By decreasing the thickness of PDMS layer from ~ 4 to < 1 mm, the rate of resistance change can be increased from 0.012 to 0.09 $\% \text{ s}^{-1}$, and the response time can be reduced from 1500 to 200 seconds. These chemoresistive behaviors are highly stable after repeated cycling, with resistance profiles that are the same magnitude and rate after multiple exposures to DCM (Figure 3f).

Chemomechanical actuation using rGO-PDMS bilayers

Finally, rGO-PDMS bilayer films were fabricated to investigate chemomechanical actuation. In response to solvent exposure, the initially flat rGO-PDMS films immediately bend upwards (towards the GO side, defined as positive) in response to organic solvents and reach a maximum curvature within a few seconds (Figure 4a,b). Classically, analogous bending behaviors in bilayer substrates are treated using the Stoney model, which describes the resulting curvature in terms of surface tension between the bottom layer (*e.g.*, PDMS) and the top layer (*e.g.*, rGO).^{50,51} This mechanism has been used to interpret analogous behavior in systems that exhibit solvent swelling (rather than thermal expansion) based on polymer substrates with thin graphene coatings as the two contrasting layers.³⁸ However, we observed that the rGO-PDMS bilayers did not remain in the maximally curved shape, but began to flatten back after ~ 200 seconds while still in contact with the solvent (Figure 4b), which is not a behavior consistent with the Stoney mechanism. We further observed that during solvent drying, the initially flat rGO-PDMS films immediately bend downwards to a maximum curvature (towards the PDMS side, defined as negative) within a few seconds (Figure 4b). Similarly, this curvature slowly return to the planar state after extended drying times, over ~ 200 seconds (Figure 4b).

To explain this dynamic mechanical behavior, we considered the possibility that actuation was driven not by tensile stress in the GO coating, but by its chemical barrier property, which only permits solvent permeation from the bottom of the bilayer. The resulting diffusion of solvent should induce transient concentration gradients within the PDMS

substrate, which over time fade to a uniform concentration as full solvent saturation is approached. The initial concentration gradients represent an asymmetry within the PDMS substrate, in which the lower regions experience high solvent uptake and swelling, but this swelling is resisted by the largely unaffected upper region near the GO film. A rough estimate of the diffusion time for solvent uptake is $\tau = h^2/D \sim 100$ s (for $h = 0.1$ cm and $D \sim 10^{-4}$ cm²/s), which is comparable to the experimentally observed timescale for actuation. Several additional control experiments corroborate the proposed mechanism. First, if the rGO-PDMS film is brought into contact with solvent from the graphene side, there was no actuation (curvature). Second, if the solvent is carefully applied onto only one side of PDMS film (even without graphene coating), the film also exhibits a transient bending behavior. Finally, if solvent is allowed to penetrate freely from both sides of the PDMS, the bending diminishes. Previous studies have also shown that compressed GO films do not significantly resist extension, but rather spontaneously relax in the presence of solvents.³² These additional observations all support our hypothesis that actuation is caused by asymmetric swelling of the elastomer substrate related to the one-sided solvent uptake driven by the graphene barrier function on the top surface, and the observations clearly rule out the Stoney model mechanism.

A coupled transport-mechanics model was developed to quantitatively describe the multistage curvature actuation. A flow chart of simulation logic is shown in Figure S19. Concentration profiles of solvent can be obtained by numerical solution of the diffusion equation (Fick's Second Law) (Equation 4),

$$\frac{\partial \bar{C}}{\partial t} = D \frac{\partial^2 \bar{C}}{\partial \bar{z}^2} \quad (4)$$

where $\bar{C}$ is the mole fraction (C/C_0) in comparison to the saturated concentration within PDMS (C_0), D is the diffusion coefficient, $\bar{z}$ is the distance (z/h) from the uncoated side normalized by the film thickness (h), and t is time. Boundary conditions are schematically illustrated in Figure S20: for the uptake process, we set a constant concentration at the uncoated surface ($\bar{z}=0$) to represent liquid contact and zero flux from the impermeable rGO coating ($\bar{z}=1$); for the drying process, constant evaporation flux at the uncoated side and again no flux at the rGO layer. A detailed description of numerical modeling including the Python codes is provided in supporting information. To predict the actuation, we modeled the PDMS as a stack of two equal thickness layers with average solvent concentration in each layer ($\bar{C}_{i,upper}, \bar{C}_{i,bottom}$) obtained by integration of the Equation 3 solution (Figure S21). The concentration profiles in each actuation stage are shown in Figure S22, and the asymmetry of solvent distribution results in different swelling percentages (L_i/L_0) in the bottom half ($\bar{z}=0 - 0.5$) and upper half ($\bar{z}=0.5 - 1$) of PDMS substrate (Figure S23). The mismatched swelling behavior bends the rGO-PDMS film toward the side with lower expansion percentage, and the curvature can then be calculated using Timoshenko's model (Equation 5), which is used to describe the development of curvature upon heating of bimetallic strips composed of two metals with unequal thermal expansion coefficients:⁵²

$$\kappa = \frac{12\varepsilon_m}{h/2} \frac{M_{upper}}{M_{bottom}} \left[1 + 14 \frac{M_{upper}}{M_{bottom}} + \frac{M_{upper}^2}{M_{bottom}^2} \right]^{-1} \quad (5)$$

where ε_m is the mismatch strain approximated by $(L_{bottom} - L_{upper})/L_0$, h is the thickness of PDMS layer, M_{upper} is the biaxial modulus of upper PDMS layer, M_{bottom} is the biaxial modulus of bottom layer. The ratio of biaxial modulus between upper and bottom PDMS layers (M_{upper}/M_{bottom}) is defined as n , and the values of n for different analytes are recorded in Table S1. The simulated curvature results are shown as solid lines in Figure 4b and fit well with the experimental data points (empty dots) along the multistage curling process. This model was then fit to experimental results with diisopropylamine, THF, benzene (see Figure 4b). In agreement with the model, the organic solvents with higher PDMS swelling factor, S , exhibited a larger mismatch in the swelling percentages and thus a larger curvature of bilayer film (κ : diisopropylamine ($S = 2.1$) > THF ($S = 1.4$) > benzene ($S = 1.3$)).

This chemical-responsive actuation could be optimized to produce extremely large deflections in response to solvent exposure. For instance, one end of an rGO-PDMS rectangle was fixed to a Teflon substrate with a tiny hole as an entrance for solvent molecules (Figure 4c, S25). After contact with an organic solvent, the unbalanced swelling induced a counterclockwise bending, and in this experiment one arm of the rGO-PDMS actuator extends out of the organic liquid pool into the air on the order of a centimeter (Figure 4c). In this configuration, the solvent can continuously diffuse upward into elastomer while also evaporating from the top portion (Figure S25). The concentration profiles and thus the chemomechanical actuator shape thus reach a steady state with maximal deflection height within several seconds after contact with the organic liquid (Figure 4d). The degree of actuation is independent of thickness of rGO layer from 0.6 μm to 1.2 μm , and the deflected height can be pre-programmed by altering the thickness of rGO-PDMS bilayers. Figure 4e further demonstrates a promising prototype actuator that provides analyte-specific deflections (*e.g.*, ~1 cm for diisopropylamine, ~0.8 cm for chloroform, ~0.2 cm for acetone) as observable signals for prompt chemical identification and adopt complex structures at the macroscale.

Chemical-responsive functional actuators

The ability to change shape and control the 3D structures from planar sheets can aid in assembly and add functionality to an object. We adapted the dimension of rGO-PDMS film to a square-shaped sheet (3 cm $\times$ 3 cm) and introduced the spills of diisopropylamine to trigger a rapid transformation that is reminiscent of the *Mimosa pudica*'s touch-induced leaflet folding (Figure 4f).⁵³ These rGO-PDMS materials are capable of imparting spontaneous motion (less than 7 seconds) in response to chemical stimulus (Movie S2). Another potential application for this actuator with a conductive rGO layer suggests in a chemical-responsive electrical switch. Figure 4g and Movie S3 shows a protective switch that can be activated by a chemical spill. The electrical connection for a LED monitor with a warning signal was made *via* the conductive rGO layer when the actuator underwent an

angle increase upon chemical exposure. This self-folding behavior is reversible and recovers the initial planar geometry after solvent drying. During this process, the rGO coating still acts as a transport barrier, and solvent molecules in the PDMS matrix cannot diffuse across the membrane. Compared with other polymer-based actuators,^{54,55} the graphene-elastomer bilayer structures represent an exciting class of soft multifunctional actuators which could manipulate objects and provide electrical connections to transmit signals for electronic devices.

CONCLUSIONS

This article presents a generalized fabrication strategy to create molecular barrier materials with ultrahigh stretchability. Traditional approaches struggle to meet the conflicting requirements for high-density space-filling crystal structures (for barrier properties) and macromolecular mobility (for stretching). The proposed concept uses graphene nanosheets with their high in-plane atomic density, but replaces the requirement for molecular mobility with conformational shape changes between 2D folded and unfolded states. These configurational transitions allow the stiff, space-filling graphene sheets to mimic the elastic behavior of polymers. Single-layer graphene has been studied extensively and can reasonably be expected to retain its molecular barrier properties before and after folding, but extended monolayers are not likely to be a practical solution for most large-area barrier applications. In contrast, tiled nanosheet coatings are scalable for large-scale barrier applications. Nevertheless, weak van der Waals interactions between nanosheets could result in high mobility and restacking after extreme mechanical deformations, which might compromise the overall barrier fidelity. In this article, we show that pre-compression of multilayer GO films give highly complex fractal-like microtextures that allow expansion up to 1500% areal strain without film damage. Indeed, these films are largely impermeable to a variety of organic liquids in both the pre-compressed and expanded states. Moreover, the films are durable and washfast through simulated stresses of cleaning and use and can be cycled at least 500 times while maintaining barrier properties. In the course of this work, we discovered that some of these graphene-polymer bilayer devices show chemoresistive and chemomechanical behaviors in the presence of organic solvents. Solvent uptake into PDMS occurs one-directionally in these devices, as top-side entry is inhibited by the graphene barrier, leading to asymmetric swelling in the polymer and spontaneous curvature that can be utilized for real-time identification of chemical species. The chemical-responsive curvature actuation can be pre-programmed for the fabrication of multifunctional actuators that can adapt their macroscale shape and provide electrical connections to transmit signals for environmental monitoring.

The general principle of a stretchable graphene-based barrier can be implemented in a variety of ways. We envision the use of pristine graphene or rGO to form stretchable products that are absolute barriers - impermeable to all species.²⁴ The use of (unreduced) GO with its gallery spaces expanded by hydration may result in stretchable “breathable” barriers (selectively permeable to perspiration water vapor),²³ and this combination of stretchability and breathability is an attractive target for next-generation protective fabrics. The GO-based forms may also find technological use in high flux water treatment membranes where texturing dramatically increases the active transport area per superficial

device area. Further development of this stretchable barrier technology should address vapor permeability, humidity effects, incorporation in multi-layer constructs such as fully imbedded barrier layers, and wear-induced nanosheet release. Our work also opens another application area for 2D materials, and the approach may possibly be extended to other 2D materials (*e.g.*, MoS₂ in Figure S26). Finally, we envision these textured-graphene-based bilayer films integrated into responsive devices, including personal monitoring equipment, wearable electronics,⁴⁰ and soft robotics.⁴¹

METHODS

Materials

Anhydrous acetone, benzene, chlorobenzene, chloroform, cyclohexane, dichloromethane (DCM), dimethyl sulfoxide (DMSO), ethanol, ethyl ether, hexane, hydrazine monohydrate, tetrahydrofuran (THF), trichloroethylene (TCE), were purchased from Sigma-Aldrich. Latex-based balloons are purchased from Amazon (Zuru X-Shot). Laboratory nitrile gloves are bought from Kimberly-Clark Professional. Clear heat shrink films were purchased from Grafix. Polydimethylsiloxane (PDMS) is made from SYLGARD® 184 silicone elastomer kit. All water was deionized (18.2 MΩ, mill-Q pore). All reagents were used as received without further purification.

Fabrication of ultra-stretchable GO-latex bilayer materials

GO suspensions were prepared by a modified Hummer's method, purified, and characterized as described previously.⁴² The concentration of stock GO suspension is about 2.3 mg mL⁻¹, and a C/O atomic ratio of approximately 1.8. Different concentration of GO suspensions was prepared by diluting with water. PS film was cut into 36 cm² squares and washed with ethanol. Once dry, samples were treated with pure oxygen plasma for 30 minutes followed by slow venting of the chamber. Next, 40 μL cm⁻² of GO suspension were drop-cast onto the substrates. After the planar GO films were obtained, we intentionally dissolve the PS substrate in DCM and wash the detached GO membranes with DCM, acetone, and ethanol sequentially. The free-standing GO membranes are then carefully transferred onto a plasma-treated, inflated latex balloon. The extent of substrate expansion can be controlled by the amount of water or air. After drying at room temperature, the latex balloon was then slowly deflated and the upper layer of GO coating was deformed into highly convoluted structures.

Fabrication of multifunctional reduced GO (rGO)-PDMS bilayer materials

Shrink film was cut into 16 cm² squares and washed with ethanol. Once dry, samples were treated with pure oxygen plasma for 30 minutes. Next, 150 μL of GO suspension were drop-cast onto the shrink films. Once dry, the planar GO samples were placed and allowed to shrink in an oven at 140 °C for 0.5 hours. The sample was shrunk without any clamps or constraints for 2D biaxial deformation. Afterwards, the samples were removed from the oven and allowed to cool for approximately 30 minutes on the bench top. Hydrazine in dilute aqueous solution (2 wt.%) was prepared and stirred overnight. The crumple-textured GO samples were immersed fully in the hydrazine solution, and the reduction was allowed to proceed at 80 °C for 12 hours. The reduced samples were sequentially rinsed with water and ethanol and dried in an oven at 70 °C. The dark brown-colored rGO samples were then

infiltrated with uncured PDMS mixture; the elastomer and curing agent were mixed at 10:1 ratio. After degassing, the PDMS was cured at 70 °C for 2 hours. The shrunk PS substrate was then dissolved and rinsed in DCM. The final rGO-PDMS bilayer films were achieved and can be cut into desired size and shape for further investigation. The gold electrodes were fabricated *via* depositing conductive gold paste (Ted Pella) on the rGO films. A copper wire was connected with conductive gold electrode and connect with the electrodes of portable standard multimeter. After the gold paste is dried, a thin layer of epoxy was covered on the electrodes to stabilize the adhesion.

Characterization

Surface morphology of the crumpled GO or rGO samples was investigated using a field emission scanning electron microscope (SEM) (LEO 1530 VP) operating at 10.0 kV for low-, medium- and high-resolution imaging. Before the SEM imaging, the crumpled graphene structures were coated with a layer of AuPd (~2 nm). Transmission electron microscopy (TEM) was performed using a JEOL 2100F TEM/STEM at an acceleration voltage of 200 kV with GO nanosheets on lacey carbon grids. TCE containing aqueous samples were analyzed using a Shimadzu GC-2010 with a Restek Rxi-624Sil MS column following the US EPA 551.1 method. The interlayer spacing before and after compression were identified by X-ray diffraction spectrometry (XRD) on a Bruker AXS D8 Advance instrument with Cu KR radiation ($\lambda = 1.5418 \text{ \AA}$). The change of resistance of rGO-PDMS samples in response to chemical exposure was measured by using a portable standard multimeter (Fluke).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Ultra-stretchable GO-latex layered composite can serve as a broad-spectrum chemical barrier

(a) Continuous evolution of GO surface topography driven by re-inflation of underlying latex balloon to different stages. The superficial area of the crumpled GO film was expanded to 600%, 900% or 1500% areal strain. The thickness of GO film is $\sim 1.2 \mu\text{m}$. (b) The barrier performance of ultra-stretchable GO-latex layered composites is illustrated as a “heat map” covering nine chemical compounds and three stretching states. The balloons without conformal GO protective membrane burst within 5 seconds after contact with solvent liquid baths. The balloons with protective GO layer survived under direct liquid contact after under extreme substrate stretching. (c) GC measurements of TCE concentration in inner water reservoir after permeation across the GO-latex barrier.

Figure 2. Mechanical stability and technological application of stretchable GO-based barriers
 (a) Cross-sectional SEM image of GO-latex bilayer film. (b) Surface morphology of crumpled GO films after stresses associated with model cleaning and handling processes: hand rubbing (light blue), autoclave sterilizing (light brown), machine laundering (red), and spray dish washing (dark blue). (c)(d) The fabrication of stretchable GO-nitrile rubber materials for chemically protective gloves. (e) The GO-coated nitrile gloves can stay in contact with DCM bath over 30 minutes without the swelling of PS beads as indicator of penetration.

Figure 3. rGO-PDMS chemoresistive device can sense and identify organic liquid solvents
 (a) Photograph and SEM images of as-fabricated rGO-PDMS film. (b) Cross-sectional SEM image of rGO-PDMS film. (c) The rGO-PDMS film can be fabricated into a chemoresistive device that changes electrical resistance in contact with different organic solvents. The PDMS substrate absorbs the solvent molecules and swells; the conductive rGO layer transduces the swelling extent into electrical signals. (d) SEM images of conformal rGO coating under the swelling of PDMS substrate in different chemical solvents. (e) Electrical resistance profiles recorded by a rGO-PDMS chemoresistor exposed to seven organic

liquids. (f) Cycling stability of a rGO-PDMS chemoresistive device under multiple cycles of DCM exposure.

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Figure 4. rGO-PDMS bilayers undergo rapid actuation in response to organic solvent exposure
 (a) rGO-PDMS bilayer exhibits chemomechanical behaviors in the form of reversible curvature change: when wetting in the organic solvent bath (solvent is diisopropylamine), the flat films begin to swell and bend toward the graphene side then relax back to planarity; while drying, the swollen bilayers gradually contract and bend toward the PDMS side before relaxing back to planarity. Both schematic figures and photos are shown. (b) The experimental data (empty dots) and simulated results (solid lines) of the reversible curvature actuation of rGO-PDMS bilayers in response to the exposure of diisopropylamine, benzene, and THF. (c) The degree of chemically-induced actuation is highly dependent on the thickness of PDMS layer (solvent is diisopropylamine). (d) The profile of deflected heights of rGO-PDMS actuator for different thicknesses of rGO and PDMS. (e) The profile of deflected heights varies with solvent. (f) A square-shaped rGO-PDMS actuator can mimic the touch-induced folding of *Mimosa pudica*'s leaflets (organic solvent diisopropylamine). (g) An "on-and-off" rGO-PDMS switch that activates a LED display in response to THF solvent.

Scheme 1. Multifunctionality of graphene-elastomer layered materials toward smart molecular barrier technologies

Fabrication steps of graphene-elastomer layered materials and their potential applications in stretchable chemical barriers, chemoresistors, and stimuli-responsive actuators that can be integrated into smart protective barriers.