Controlled Crumpling of Graphene Oxide Films for Tunable Optical Transmittance

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Bucking instability of thin films on substrates is ubiquitous in our daily lives, such as wrinkles on human skin and fruits (e.g., raisins), as well as blistering on painted walls. The former is a phenomenon of wrinkling under compression, where the compliant substrate (i.e., tissue/flesh) coherently deforms with the film (i.e., skin) without debonding; whereas the latter is a localized buckling-driven “delamination” with the compressed film (i.e., paint) partially and locally detaching from the stiff substrate (i.e., wall). Historically, these two types of buckling have been viewed negatively as a mechanism for structural and component failure. However, recently the potential benefits[1,2] of these instabilities are being recognized. For example, the first type of bucking instability, i.e., wrinkling in soft materials, has opened new vistas in surface patterning at both the micro- and nanoscales.[3,4] Such dynamically tunable wrinkling phenomena have found broad applications in thin film material properties measurement,[5] microfabrication,[6] stretchable electronics,[7] and optics devices.[8] Such surfaces can be used to tune a variety of surface topography-related properties, such as adhesion,[9] wetting,[10] friction,[11] and anti-biofouling.[12] Recent studies have also shown the potential impact of surface wrinkling in photonics, including light extraction enhancement in organic light-emitting devices,[13] light harvesting efficiency improvement in photovoltaics,[14] design of mechanoresponsive optical materials,[15] diffraction-free optical beams,[16] and multifunctional windows.[17,18]

However, so far there is limited work on harnessing the second and more severe type of buckling instability, i.e., delamination buckling, for functional applications at the small scales. Here we exploit delamination buckling of graphene oxide (GO) thin films to create new intricate periodic folding micropatterns, which are formed on optically transparent and highly pre-stretched silicone rubber (SR) substrates. The severity of the delamination blister patterns can be controlled in real-time by stretching the SR substrate and we can transition reversibly from a flat GO film that displays high optical transmittance to a completely crumpled film that is far less transparent to solar radiation. While one recent study[2] has investigated delamination buckling of chemical vapor deposition (CVD) deposited (few-layered) graphene films, GO-based coatings offer some unique advantages. A single layer of graphene (grown by CVD or other methods) has a transmission loss of ≈2.3% per layer[19] independent of incident wavelength. Consequently even for very thin graphene films (corresponding to thicknesses of ≈3–4 nm), the average transmission is already reduced to ≈80%, which could limit the maximum achievable modulation range for dynamic glazing applications. We have therefore focused on GO thin films rather than graphene because of its lower transmission loss per layer which enables us to achieve high optical transmission in the clear (unbuckled state) even with GO film thicknesses that are approximately one to two orders of magnitude thicker than traditional CVD grown (few-layer) graphene. Further the mechanically robust, solution-processed GO coatings used in this study could potentially be applied by a variety of methods (e.g., spray-coating, ultrasonic spray deposition, etc.) in a scalable and cost-effective manner over large area polymer substrates. A discussion of the relative merits of GO coatings versus the state-of-the-art electrochromics technology for dynamic facades is provided later in this Communication.

A schematic illustration of the spontaneous buckling delamination procedure utilized in this study is shown in Figure 1a. The buckling delaminated pattern is achieved through three steps: an SR substrate with thickness of ≈0.5 mm is first uniaxially stretched to a large strain of ≈400%; a GO film with thickness of ≈100 nm is then deposited through drop casting (see the Experimental Section) on the pre-stretched SR substrate; finally upon release of the substrate pre-strain, the GO film is under uniaxial compression and buckles spontaneously to form delaminated buckling patterns. Figure 1b shows a scanning electron microscopy (SEM) image of a typical periodic buckling pattern with blisters formed perpendicular to the pre-stretch direction. To investigate whether we have wrinkling without debonding or delamination buckling we performed high-resolution SEM imaging of the buckle pattern. The result (Figure 1c) indicates that the GO film has indeed delaminated from the SR surface in certain locations while in other places the film is still well-adhered to the substrate. The delaminated...
buckles exhibit typical amplitudes of $\approx 4–5 \mu m$ and delaminated widths of $\approx 1–2 \mu m$. Periodic cracks are also observed aligned orthogonal to the delaminated blisters in Figure 1b, which is due to the transverse tensile stress generated by the uniaxial compression of the substrate along its length. The spacing of these cracks will depend on the film thickness and material properties of the system such as film fracture strength and shear modulus of the substrate, as well as the compressive strain in the film. Since the delaminated pattern is a result of strain energy minimization,[19] the geometry of periodic blisters with periodicity $\lambda_d$ and amplitude $A_d$ described by $w(x) = \frac{A_d}{2} \left[1 + \cos\left(2\pi x / \lambda_d\right)\right]$ can be predicted, as shown in Equation 1 and 2:[20] (see the Supporting Information):

$$\lambda_d = \pi \lambda \left(36 E_f / \pi E_s \Gamma\right)^{1/3}$$  \hspace{1cm} (1)
$$A_d = \frac{2\lambda t}{3} \left(36 E_f / \pi E_s \Gamma\right)^{1/3} \left[\epsilon_{pre} (1 + \epsilon_{pre}) / 2\right]^{1/3}$$  \hspace{1cm} (2)

where $\lambda = 1 / \left[1 + \epsilon_{pre}\left(1 + \epsilon_{pre}\right) / 32\right]^{1/3}$, $t$ is the GO film thickness, $E_f = E_s / (1 - \nu_f^2)$ and $E_s = E_s / (1 - \nu_s^2)$ are the plain strain modulus of the film and substrate with $E_s$, $\nu_f$ and $E_s$, $\nu_s$ being the respective Young’s modulus and Poisson’s ratio. $\Gamma$ is the normalized interfacial toughness defined as $\Gamma = \Gamma / (E_s t)$.

For the studied system, we have $t = 100$ nm, $E_s = 32$ GPa, and $\nu_s = 0.2$ for GO film[21] and $E_s = 2$ MPa and $\nu_s = 0.49$ for SR.[22] The interfacial toughness $\Gamma$ can be estimated to be $\approx 50$ mJ m$^{-2}$ by assuming $\Gamma$ to be equal to the thermodynamic work of adhesion[23] (see the Supporting Information). For $\epsilon_{pre} = 400\%$, we obtain $\lambda_d = 1.3 \mu m$ and $A_d = 3.7 \mu m$, which are consistent with our experimental results (Figure 1c).

Based on the parameters given above, micromechanical modeling using the finite element method (FEM) was carried out to reveal the evolution of buckling delamination during the release of pre-strains using cohesive zone modeling. The results indicate that the buckling pattern experiences a transition from periodic wrinkling without film-substrate detachments at a small released strain (beyond the critical wrinkling strain; Figure S1, Supporting Information), to concurrent wrinkling-delamination with slightly increased strain release (Figure S1, Supporting Information), to growth of delamination at moderate released strain (i.e., beyond the critical buckling strain), to fully delaminated blisters at much larger strains (see Figure 1d). This indicates that wrinkling occurs first, followed by buckle delamination at the larger strains. Details regarding the simulation parameters are provided in the Experimental Section. Our simulations also indicate (Figure 1d) that even after delamination, the buckle amplitude continues to grow and the delaminated width decreases with further release of pre-strain. Therefore for the very large pre-strains used in the experiments (several hundred percent), the buckle pattern becomes very sharp with buckles that are several micrometers in height and spacing between buckles of the order of about a micrometer (Figure 1c). Note that the interfacial adhesion between the GO and SR substrate is an important parameter. Generally if the adhesion of GO film and substrate is enhanced, it will decrease the degree of delamination. In an extreme case, if the GO film is perfectly bonded to the substrate, when releasing the substrate pre-strain, the strong bonding will constrain the out-of-plane buckling, i.e., the buckle amplitude, and thus generate relatively low-aspect-ratio wrinkles. The other extreme is also not desired. Suppose there is weak

Figure 1. Uniaxial buckling of graphene oxide (GO) thin film. a) Schematic showing GO deposition on a uniaxially pre-stretched SR substrate. Strain release generates a uniaxial compressive stress in the GO skin causing spontaneous delamination buckling. b) Scanning electron microscopy (SEM) imaging of a typical delamination buckling pattern for an $\approx 100$ nm-thick GO film deposited on the SR substrate after strain release of $\approx 400\%$ in the uniaxial direction. The GO film buckles in a periodic repeating pattern. Large cracks in the GO film are also observed in the transverse direction. c) High-resolution SEM image of an individual blister showing sharp folds. The delaminated buckles exhibit typical amplitudes of $\approx 4–5 \mu m$ and delaminated widths of $\approx 1–2 \mu m$. d) Finite element modeling of the graphene/SR system under compressive stress showing the evolution of blisters from its initiation to fully delaminated buckles at larger strains. The delaminated blisters get taller (sharper) and more closely packed with further strain release.
adhesion between the GO and substrate — in such a case one global large blister will be generated upon compression instead of a number of periodic blisters. Therefore moderate GO-substrate adhesion is preferred so that the strain energy is released through the formation of periodic (high aspect ratio) delaminated buckles or blisters.

One possible limitation of utilizing uniaxial strains (as in Figure 1) to buckle the GO film is the presence of large periodic cracks that form orthogonal to the buckled pattern. Due to the Poisson’s ratio effect, when the pre-strain is released, the SR substrate and therefore the GO film will be in tension in the transverse direction which cracks the GO film as shown in Figure 1b. These cracks or gaps in the GO film will drastically reduce the opacity of the film which will in turn significantly lower the modulation range over which the film’s transmittance can be controlled. We therefore decided to investigate the feasibility of biaxial strains as a means to control the buckling of the GO film without cracking. Figure 2a shows a schematic illustration of this approach where the SR substrate is pre-stretched by the same amount along two mutually orthogonal directions. Figure S2 (Supporting Information) shows the test setup that was developed in our lab to simultaneously stretch the SR substrate in two orthogonal directions. In the next step, the GO film is drop cast onto the pre-stretched SR surface. Finally, the pre-strain in the SR surface is released resulting in the spontaneous crumpling of the GO film as it undergoes buckling delamination.

The typical buckling pattern of a GO film with thickness of ≈20 nm is shown in Figure 2b upon simultaneous release of biaxial pre-strain of ≈400% in the SR substrate, leading to an intricate flower-like folding pattern with both blisters and sharp folds. The corresponding FEM simulation (Figure 2c) shows the evolution of patterns under equi-biaxial compression, where short straight blisters are first developed and then evolved into an intermediate delaminated herringbone pattern. With further increase of the compressive strain, the pattern becomes distorted and forms a pattern that is qualitatively similar to the experimental observations. Note that the biaxial buckling pattern is far more complex compared to the uniaxial case since it involves the superposition of blister patterns along mutually orthogonal directions. Most importantly unlike the uniaxial case there is no indication of any cracking in the GO film even after the strain release as shown in Figure 2b. This is because biaxial strain generates compressive stress of equal magnitude in both the longitudinal and transverse directions which mitigates the cracking of the GO film. Further, the strain in the film is released effectively through delaminated blisters, which propagate orthogonally in the film–substrate interface to relieve the strain energy. The crack-free pattern implies that such biaxial buckle delamination in GO is highly effective at releasing the built-up strain in the structure. To quantify the buckled surface profile, we define the degree of buckling ($d_b$) of the surface as the ratio of the buckled surface area to its projected flat surface area. Atomic force microscopy (AFM) scans of the buckled surfaces (see the Experimental Section) were performed to measure the aforementioned $d_b$ parameter. The experimental measurement (Figure 2d) shows that $d_b$ increases non-linearly as the substrate pre-strain is changed from ≈50% to ≈400%. As indicated in Figure 2d, for substrate pre-strains above ≈200%, the measured surface area of the buckled surface increases non-linearly as the substrate pre-strain is increased. Test data at 50%, 100%, 200%, 300%, and 400% pre-strain are also shown on the plot along with the predictions.

Figure 2. Biaxial buckling of graphene oxide (GO) thin film. a) Schematic illustration of GO film deposited on a biaxially pre-stretched SR substrate. Strain release generates spontaneous delamination buckling of the GO film. b) Scanning electron microscopy imaging of the typical buckling pattern of GO film with thickness of ≈20 nm upon release of the biaxial pre-strain of ≈400% in the substrate. The flat GO film crumples forming an intricate flower-like folding pattern with blisters and sharp folds. This complex pattern results from the superimposition of periodic buckling patterns in two mutually orthogonal directions. c) Finite element simulation of delamination buckling of GO film on SR substrate under biaxial compression showing the evolution of buckling patterns with strains. d) Analytical modeling predictions for the effect of biaxial compression on the degree of buckling of GO films. Degree of buckling is defined as the surface area of the buckled surface normalized by the projected flat surface area. The degree of buckling shows a non-linear increase as the pre-strain is increased. Test data at 50%, 100%, 200%, 300%, and 400% pre-strain are also shown on the plot along with the predictions.
buckling pattern will significantly influence the light transmittance as shown later in this Communication.

Despite the complexity of the 2D delaminated patterns, some useful insights on how $d_b$ relates with pre-strain and film thickness can be obtained from the geometry of a simplified 2D wrinkled pattern described by $Z = A \cos(m \pi x/L_x) \cos(n \pi y/L_y)$, where $A$ is the amplitude (i.e., height) of the pattern and $m$ and $n$ are the number of waves in the projected length $L_x$ and $L_y$ along $x$ and $y$ directions, respectively. The ratio of the surface area to its projected area can be obtained as $d_b = 1 + \frac{\pi^2 A^2 \lambda_x^2 + \lambda_y^2}{2 \lambda_x^2 \lambda_y^2}$, with $\lambda_x = 2L_x/m$ and $\lambda_y = 2L_y/n$ being the wavelength along the respective $x$ and $y$ axes, which indicates that $d_b$ is a function of the amplitude and wavelength of the 2D pattern. Let us consider a simplified checkerboard pattern with $\lambda_x = \lambda_y = \lambda$ and thus $d_b = 1 + (\pi A/\lambda)^2$ to explore the effect of pre-strain and film thickness on the buckled profile of the GO film. For both wrinkling and delamination checkerboard patterns, we have $A/\lambda = \sqrt{\frac{\varepsilon(1+\nu)}{\pi}}$, with $\varepsilon$ being the applied strain in the GO film and thus $d_b \approx 1 + (1+\nu)\varepsilon$. When releasing the SR substrate with a pre-strain $\varepsilon_{pre}$, the applied strain in the film is $\varepsilon = \varepsilon_{pre}/(1+\varepsilon_{pre})$, which leads to $d_b \approx 1 + \frac{(1+\nu)\varepsilon_{pre}}{1 + \varepsilon_{pre}}$.

This simple analysis indicates that the degree of buckling of the films is strongly influenced by the substrate pre-strain. In Figure 2d we show predictions for $d_b$ versus pre-strain ($\nu = 0.2$ for the GO film$^{[21]}$) using this model and compare it to the experimental values obtained from our AFM scans of the buckled surface. The model predictions show good agreement with experimental data. Note that both the model predictions and experimental results indicate that the degree of buckling of the GO film does not change significantly in the 200–400% pre-strain range. This is because at these very large strains, the buckling pattern is fully developed and has saturated in terms of the maximum achievable surface area increases that are possible.

The simplified model also indicates that the degree of buckling is only dependent on the pre-strain in the substrate and the Poisson’s ratio of the film and independent of film thickness. To confirm this we varied the thickness of GO film and measured the topology of the buckled patterns by AFM. Figure 3a–c shows the experimentally measured buckled surface topographies for three different coating thicknesses of 20, 40, and 60 nm under the same substrate pre-strain of 400%. The corresponding SEM images are provided in Figure S3 (Supporting Information). The results (Figure 3a–c) indicate similar buckling patterns despite their different coating thickness, where the periodicity and fold height increase with the coating thickness. Fine buckles and folds with shallow height are observed in the thinnest coating of 20 nm (Figure 3a). As the coating becomes thicker, the pattern turns to being coarse with deeper amplitude (Figure 3b,c). Despite the different periodicities and amplitudes observed in the buckling patterns with different coating thickness, the experimental measurement shows that all three patterns collapse to nearly the same degree of buckling (Figure 3d) in terms of the buckled to flat surface area ratio,

![Figure 3](https://www.advmat.de)
which is in good agreement with our simplified theoretical model. Theoretically, $d_b$ scales with $A/\lambda$, where the buckle amplitude $A$ and periodicity $\lambda$ are dependent of the coating thickness. However, since both $A$ and $\lambda$ are proportional to the coating thickness, the thickness effect is canceled out when considering the buckled to flat surface area ratio in the aforementioned theoretical model.

The results so far indicate that the delamination buckling of GO films can be well-controlled by application and release of biaxial strains to the underlying SR substrate. To qualitatively study light transmittance through such surfaces, we placed a fully crumpled GO film on an SR substrate (optical image of the crumpled GO film is shown in Figure 4a) over a printed Rensselaer Polytechnic Institute (RPI) label. The GO film thickness was $\approx 40$ nm and the film was crumpled by releasing $\approx 300\%$ pre-strain in the underlying SR substrate. The crumpled GO film is highly opaque as indicated in the inset of Figure 4a. Images showing the opacity of crumpled GO in an architectural window setting are also provided in Figure S4 (Supporting Information). Next we applied a biaxial tensile strain to the SR substrate in two mutually orthogonal directions to unbuckle (or flatten out) the GO film. Figure 4b shows that the clarity of the RPI label is greatly improved at an applied biaxial strain of $\approx 200\%$. At 300% applied strain (Figure 4c), the GO film is significantly more transparent and the RPI lettering is clearly visible. Finally the film was over-stretched to $\approx 400\%$ strain (Figure 4d), i.e., the applied biaxial tensile strain exceeded the pre-strain. In this case, we see formation of cracks in the film and the RPI lettering in this case is nearly completely transparent as seen in the inset of Figure 4d. Note that these cracks are very different from the cracks previously observed (Figure 1b) for uniaxial buckling. In the uniaxial case, the cracks are created in the fully crumpled (i.e., opaque state) due to transverse tensile stresses. Here the cracks are created in the flat (i.e., clear state) by “over-stretching” the GO film. As a consequence, when the applied biaxial tensile strain was released the cracks that were formed disappeared and the film reverted back to the crumpled morphology in Figure 4a (the opacity of the GO film was also restored). This process of biaxially pulling and releasing the SR substrate was repeated several times and qualitatively the results appeared to be reversible in that the RPI logo could be successfully cycled between the highly opaque (Figure 4a) and highly clear (Figure 4d) states. Note that the flat or unbuckled GO films are highly transparent as shown in Figure S5 and S6 in the Supporting Information. GO typically contains various functional groups\cite{25–28} such as carbonyl ($\text{C}=\text{O}$), carboxyl ($\text{–COOH}$), epoxy ($\text{–O–C–O}$) and hydroxyl ($\text{–OH}$) groups. It has been shown theoretically and experimentally that the presence of these functional groups\cite{25–28} and the sp$^2$/sp$^3$ carbon ratio affects the band gap of GO. The band gap of GO varies\cite{27} from $\approx 3.5$ eV (for pristine GO) to $\approx 1$ eV (for reduced GO). Further, GO films with a C/O ratio\cite{27} of $\approx 2:1$ have a band gap of $\approx 3.0$ eV. It can be seen clearly from the X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectra (Figure S7 and S8, Supporting Information) that the C/O ratio for the GO material we use is $\approx 2:1$ and it contains the typical functional
groups like carbonyl, carboxyl, epoxy, and hydroxyl. Thus we expect the band gap of our GO material to also be around 3.0 eV. The energy of the visible light is in the range of 1.6–3.4 eV. Thus the majority of visible light photons do not have sufficient energy to bridge the band gap of GO. This results in a high transmission of visible light through the GO film. By contrast, the crumpled GO film is far more opaque and the reasons for this will be discussed later in this Communication.

For quantitative analysis of light transmittance through the GO films, the prepared samples were attached to the strain jig (Figure S2, Supporting Information) and the entire assembly was mounted in a Cary 6000i spectrophotometer, which was used to measure the percentage (%) normal transmission with respect to a background sample. The background used for each data point was the respective normal transmission of bare SR at that particular strain amount. The wavelength range for measurements was 200–1800 nm and scan rate was 909 nm min$^{-1}$ (see the Experimental Section for details). Figure 5a shows the normal transmittance data obtained for an ≈20 nm-thick GO film when it is completely flat (i.e., SR substrate is pre-strained to 400%), when the pre-strain is released in the uniaxial condition (and the film buckles with transverse cracks) and when the pre-strain is released in the biaxial condition (and the film crumples without cracking). The flat GO film shows very high average normal transmittance of over 90% in the visible region. This is the main advantage of working with GO since it provides very low transmission loss per layer enabling high transmittance values in the clear or transparent state. When the GO film is buckled by releasing the applied pre-strain (≈400%) in the uniaxial direction, the average normal transmittance in the opaque state (≈48%) is relatively high. This can be explained by the large cracks that form under this condition (Figure 1b) which limit the opacity of the coating in the buckled state. In contrast when the sample is pre-strained biaxially by 400% and the pre-strain is released, the average normal transmittance drops to ≈10% as the GO film crumples up without formation of cracks as shown in Figure 2b and is therefore far more opaque. Consequently, delamination buckling in the biaxial mode is preferred to the uniaxial mode since it provides a greater dynamic range for control of optical transmittance.

We also investigated the possibility of tuning the optical transmittance of the GO film in real-time mode by controlling the substrate strain. For this test, the biaxial pre-strain was ≈300% and the strain was fully released to increase the opacity of the film. Then a tensile (biaxial) strain was applied to the substrate to reduce the degree of buckling and flatten (or flatten) the film. As seen in Figure 5b, increasing applied biaxial tensile strains of 100%, 200%, 300%, and 400% allowed...
for the normal optical transmittance to be varied from the most opaque to the most transparent condition. In this way controllable mechanical strain applied to the soft polymer substrate can be used to fine tune the optical transmittance of the GO film. Moreover the response time of the system is nearly instantaneous and is limited only by the speed of the servo motors used to strain the sample. We also strained the baseline SR substrate (without the GO film) in the 0–400% range and there was a relatively small effect of the applied strain on the optical transmittance of the baseline SR material as shown in Figure S9 (Supporting Information).

The average normal transmittance in the visible region (for a typical GO film) is plotted in Figure 5c for three different values (200%, 300%, and 400%) of biaxial pre-strain to the film. The average values plotted in the figure were obtained by averaging the normal transmittance over the visible range (i.e., from $\lambda = 380$ to $\lambda = 780$ nm). The x-axis in the plot is the applied strain minus the substrate pre-strain. In the testing, the pre-strain is first completely released and the GO film is allowed to buckle and achieve its most opaque state. Then the substrate is strained biaxially in tension (this is the applied strain) to reduce the degree of buckling and flatten the film. As the applied strain is increased the opacity of the coating reduces as indicated in Figure 5c. When the applied strain is equal to the pre-strain, the GO film is completely flat and lacks any wrinkles or buckles. When the applied tensile strain exceeds the pre-strain, the GO film for the first time experiences a net tensile stress and develops cracks as shown in Figure 4d. The cracks further increase the transparency of the coating, indicating that the GO films can achieve a high degree of optical transparency in the clear state.

One of the key requirements for dynamic glazing is reactivity during extended cycling. To investigate this, the manual jig for straining the SR substrate was converted into an automated jig by attaching four servo motors and controlling the motors to biaxially deform the SR. Basic encoders were used to correlate the distance moved by each limb to the number of rotations of the motor. The motors were programmed to run for the desired number of cycles by straining (and releasing) each of the jaws at the same rate to maintain uniformity over the cycles. Figure 5d shows the average normal transmittance (in the visible range) of a typical GO film over 100 continuous strain and release cycles. While there is some change in the response from the first to the tenth cycle, there is little change in the subsequent cycling. SEM and optical microscopy characterizations of the GO film after cycling also showed no indication of damage such as cracking or changes to the morphology of the coating. We also explored CVD grown (few-layer) graphene films for dynamic glazing applications. The graphene films were grown by thermal CVD on copper substrates and then transferred onto the SR substrate using well-established wet-chemistry-based transfer methods.$^{[10]}$ However after a few delamination buckling cycles, we found that the CVD grown graphene films were extensively cracked and fragmented as shown in Figure S10 in the Supporting Information. This highlights the importance of using relatively thick GO films that are mechanically robust when subjecting the samples to aggressive delamination buckling conditions.

In addition to testing with a spectrophotometer which provides information on normal transmission we also performed tests using an integrating sphere setup to determine the diffuse transmission and diffuse reflectance. Most studies$^{[2,15,17,18]}$ that utilize surface roughness to control optical transmission have tended to focus on normal transmission measurements (as in Figure 5). However for dynamic glazing applications the diffuse transmission is also an important metric and should be considered. Figure 6a,b shows schematics of the integrating sphere setup that was used to record the diffuse transmittance and diffuse reflectance of the GO films as a function of the applied strain and the substrate pre-strain. The integrating sphere had two diametrically opposite opening ports, each measuring $=1$ in. in diameter. Diffuse transmittance was measured by mounting the sample in front of the sphere, while the other port remained closed. For measuring diffuse reflectance, both ports were kept open and the sample was mounted behind the integrating sphere. Additional details regarding the test procedures and instrumentation used are provided in the Experimental Section. The average diffuse transmission and diffuse reflectance in the visible range (from 380–780 nm) is plotted in Figure 6c for GO films of three different thicknesses. The x-axis in the plot is the applied strain minus the substrate pre-strain. Similar to the procedure for the tests in Figure 5c, the pre-strain is first completely released and the GO film is allowed to buckle and achieve its most opaque state. Then the substrate is strained biaxially in tension (this is the applied strain) to reduce the degree of buckling and flatten the film. As the applied strain is increased the transparency of the coating increases as indicated in Figure 6c. The achievable range for the average diffuse transmission in the visible region is from $\approx 57\%$ to $\approx 88\%$. This range is much lower than what we report in Figure 5 for the normal transmittance. This suggests that the increased opacity of the crumpled GO (with its intricate folding/wrinkling patterns) appears to result from refraction (i.e., bending of light) which scatters the incident light. Note that the diffuse reflectance (also plotted in Figure 6c) did not show significant sensitivity to the crumpling of the GO films, which indicates that it is the increased scattering (bending) and absorption of light in the rougher (and thicker) buckled GO films that is responsible for the reduced transparency of the GO in its buckled state.

We also explored the feasibility of coupling multiple GO films in parallel to increase the opacity of the GO coating. Note that increasing the thickness of a single GO film has a weak effect (Figure 6c) since the degree of buckling (Figure 3d) of the GO film is independent of the film thickness. However when two $=40$ nm-thick GO films are deposited and buckled on both sides of the SR substrate, the average (visible) diffuse transmittance of the combination reduces to $\approx 50\%$ as shown in Figure 6d. When two such SR substrates are used (i.e., a total of four $=40$ nm-thick GO films connected in parallel are buckled), the average diffuse transmittance in the visible region can now be reduced to $\approx 23\%$ (Figure 6d). The tradeoff is that in the clear (unbuckled) state the transparency for such a system is relatively low ($\approx 55\%$) for a total dynamic range of $\approx 30\%$. However as shown previously (Figure 5c) the transparency in the clear state can be further increased when the applied tensile strain exceeds the pre-strain. In this condition, the GO film experiences a net tensile stress and develops cracks (Figure 4d), which significantly boosts its transparency. It should be noted that such cracks are
created in the flat (clear state) by “over-stretching” the GO film. As a consequence, when the applied biaxial tensile strain is released such cracks disappear and the film reverts back to the crumpled morphology shown previously. Using this effect we were able to achieve an average diffuse transmission in the visible region as high as ≈65% by over-stretching the four GO films connected in parallel (Figure 6d). These results indicate that by appropriate control of the number of GO films and the applied substrate strain, it is possible to tune the optical transmittance of GO films over a reasonably wide range with fast response. Figure 6e summarizes the dynamic modulation range that is achievable for the different configurations of GO films tested in this study. Single GO films that offer a tunable visible diffuse transmission between 57% and 88% could be more suitable for privacy glass applications while multiple GO films connected in parallel which provide tunable visible diffuse transmission in the 23–65% range could be deployed for dynamic glazing in architectural or vehicular applications. The potential advantage of such a technology over electrochromics is faster response time. The switching time of electrochromics ranges from 3 to 40 min depending on the operation conditions. By contrast the response of the GO film is nearly instantaneous and only limited by the speed of the servo motors used to deform the SR substrate. Another aspect to consider is that electrochromics suffers from color neutrality issues due to wavelength-dependent absorptions. In particular, the deep blue color of electrochromics in their colored state can potentially disrupt the circadian rhythm of occupants and substantially modifies the color rendering of interior spaces. On the flip side electrochromics is attractive since it involves solid-state actuation without any moving parts and low power consumption. The GO coating on the other hand requires mechanical actuation of the underlying (soft) polymer substrate which necessitates use of servo motors (or other actuation mechanisms) to stretch and release the substrates. We would like to point out that exposure to sunlight in a dynamic glazing environment is not expected to reduce the GO coating. The photo energy used to reduce GO is typically on the order of ≈700 W cm⁻². In comparison, a typical south-facing window will experience a maximum of ≈0.09 W cm⁻² and an annual average of ≈0.0125 W cm⁻². Additionally, the inside cavity surfaces of a south facing glazing unit in the New York city climate will experience a maximum temperature of ≈42 °C and an annual average temperature of ≈16.5 °C, well below the temperatures used for reduction of GO by thermal annealing. We therefore do not anticipate that either the radiant flux or the ambient temperatures experienced by windows will be sufficient to reduce the GO films. However having said that, the effects of long-term cumulative exposure to irradiation and elevated temperatures on the GO structure will need to be investigated as part of future work.

**Experimental Section**

**Deposition of Graphene Oxide (GO) Film:** To prepare thin films of GO on silicone rubber (SR) substrates, GO dispersed in de-ionized water (from ACS Materials) was first diluted to a concentration of ≈0.25 mg mL⁻¹. The solution was then sonicated in an ultrasonic cleaner.
to ensure homogenous dispersion and centrifuged to ensure removal of heavier aggregates. A small amount (∼5% by weight) of a surfactant, sodium dodecylbenzenesulfonate (from Sigma–Aldrich), was also added to the GO solution, to enhance the adhesion of the GO films on the hydrophobic SR substrate. Different concentration, based on required film thickness, between 0.0025 and 0.04 mg mL$^{-1}$ of these GO solutions were prepared. Typically 1–2 mL of this solution was dropped onto the pre-strained transparent SR (∼0.5 mm) substrate and the solution was allowed to gently evaporate under a heat gun.

UV–vis-NIR Transmission Studies: Tests were performed using a Cary 60000 spectrophotometer, which was used to measure the percentage (%) normal transmission with respect to a background sample. The background used for each data point was the respective normal transmittance of bare SR at that particular strain amount. The aperture used was a 5 mm-diameter hole. The wavelength range for measurements was 200–1800 nm and scan rate was 909 nm min$^{-1}$. The system had a source and grating changeover at 350 and 800 nm, respectively, which accounts for the abruptness at those wavelength positions. The spectral bandwidth of the system was 2 nm and is a measure of the instrument resolution. The average% normal transmission values plotted for the visible range was averaged over 380–780 nm.

Diffuse Transmission and Diffuse Reflectance Measurements by Integrating Sphere Method: The custom-made experimental setup used for measuring diffuse transmittance and diffuse reflectance comprised of an integrating sphere (manufactured by Labsphere) of ∼20 cm diameter, a tungsten Halogen lamp of wavelength range 350–1050 nm (manufactured by Ocean Optics, model LS 1-CA) which was used as a light source. An optical fiber cable of ∼400 µm diameter (Ocean Optics, QP400-2-UV-VIS) was inserted inside the integrating sphere and the data were measured using a spectrometer (Ocean Optics, JAZ spectroscopy Suite). The integrating sphere had two diametrically opposite opening ports, each measuring 1 in. in diameter. The schematic of this setup is shown in Figure 6a (diffuse transmittance) and Figure 6b (diffuse reflectance). Diffuse transmittance was measured by mounting the sample in front of the sphere, while the other port remained closed. For measuring the diffuse reflectance, both the ports were kept open and the sample was mounted behind the integrating sphere. The references used for diffuse transmittance and reflectance were the diffuse transmittance of air (i.e., no sample in front of the sphere) and the diffuse reflectance of the material used for coating the interior of the integrating sphere, respectively. All measurements were normalized with respect to these references. The bare SR was used as the baseline, which was subtracted from the GO-coated SR response. The average transmittance was calculated by averaging the transmittance values in the visible range over 380–780 nm.

Atomic Force Microscopy (AFM) Study of Surface Topology: AFM was performed on the samples to measure the surface topology using a Veeco Dimension 3100. The samples were imaged in the contact mode using tips with a radius of curvature less than 25 nm and coated with Pt. A typical measurement included attaching the SR to the sample holder disc using a strong adhesive and mounting the disc on a magnetic chuck to ensure no drift.

FEM Simulation: The wrinkling and buckle induced delamination of GO film on SR are simulated using cohesive zone models in the finite element software ABAQUS. The GO film is modeled as a linear, isotropic, Hookean material with measured Young’s modulus 2 GPa and Poisson’s ratio $\nu = 0.2$. The SR substrate is a non-linear elastic elastomeric material and modeled as a hyperelastic almost incompressible Neo-Hookean material with measured Young’s modulus $E_s = 2$ MPa and Poisson’s ratio $\nu_s = 0.49$. The bottom of the substrate is pinned and periodic boundary conditions are applied during the simulation. A cohesive model is employed to model the delamination between the film and substrate, where a thin layer of cohesive elements is used to model the interface between the film and substrate. The constitutive response of the cohesive elements is defined in terms of linear elastic traction-separation laws, where the criterion for the damage initiation is based on the maximum nominal stress and the damage evolution is modeled based on the fracture energy.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.V.T., B.C.A., and S.S. contributed equally to this work. N.K. acknowledges funding support from the USA National Science Foundation (Award Nos. 1435783 and 1234641) and the John A. Clark and Edward T. Crossan Chair Professorship at the Rensselaer Polytechnic Institute.

Received: December 19, 2014
Revised: March 10, 2015
Published online: