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Atomistic modeling of the stiffness, strength and charge-induced actuation of graphene nanofoams

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ABSTRACT

To exploit the excellent electrical and mechanical properties of graphene, three-dimensional nanoporous graphene architectures have appeared recently. These graphene nanofoams are conductive and have very large internal surface areas, making them attractive for application as low-voltage electrochemical actuators. The key feature that connects the excess-charge-modified interatomic bond length to the overall strains is the three-dimensional spatial distribution of the graphene ribbons. This is governed by the competition between interlayer van der Waals forces and intralayer charge-affected covalent interactions. Here we explore this competition through atomistic modeling of ordered graphene hexagonal honeycombs. We modify the adaptive intermolecular reactive empirical bond order (AIREBO) potential to account for the excess-charge-induced change in equilibrium bond length of the carbon atoms. We use the charge-strain results of single graphene ribbons obtained by density functional theory (DFT) calculations to calibrate the atomistic AIREBO potentials. We investigate the effect of edges stresses and excess charge on the dimensional and morphological changes of free-standing graphene ribbons. We study the effect of internal surface area and relative density on the actuation stroke and work density and compare the graphene nanofoams with several nanoporous gold systems. Our results reveal that the graphene nanofoams have a smaller actuation stroke per unit charge density than random nanoporous gold, but that more mechanical work can be generated.

1. Introduction

In order to fully exploit the unique properties of graphene, three-dimensional graphene-based porous materials have appeared recently as a promising material for application in biomedicine [1], actuators [2,3], sensors [4–7], energy storage devices [8], catalysis [9], imaging [10] and quantum computing [11]. Graphene nanofoams can have exceptionally large specific surface areas, which, combined with their excellent electrical and mechanical properties, make these materials promising candidates for actuation applications.

Ordered and disordered graphene nanofoams have been produced by several techniques, yielding different microstructural morphologies. Biener et al. [2] produced centimeter-sized monoliths of disordered graphene nanofoams with pore sizes of several micrometers and specific surface areas up to 3000 m²·g⁻¹. The ligaments of the foam, with thicknesses of approximately 500 nm, consist of agglomerates of individual graphene layers curved and intertwined in a disorderly fashion, allowing the graphene layers to be maximally accessible by the electrolyte. As a result, all graphene ribbons fully contribute to the macroscopic charge-induced actuation, yielding positive and negative strains as large as 2.2% by cycling the potential between −1V and +1V, respectively. The foams are found to be mechanically robust with Young’s moduli ranging...
from 0.3 to 1 GPa. Huang et al. [12] used hydrophilic silica spheres as a template on which the graphene sheets self-assemble to form disordered nanofoams with controllable pore sizes (30–120 nm), cell walls consisting of 2–3 monolayers of graphene and specific surface areas around 851 m²g⁻¹. Lee et al. [13] produced disordered foams using chemical vapor decomposition. The average pore size obtained is 40–50 nm, while the thickness of the foam is limited to 550 nm. Xiao et al. [14] fabricated ordered nanofoams which have a three dimensional interconnected network of hollow ligaments. The pore size is around 500 nm and the multi-layered graphene walls of the ligaments have a thickness varying from 5 nm to 20–30 nm. Qiu et al. [15] fabricated ordered honeycomb structures having porosities of 99.98%, with cell-wall lengths in tens of micrometers and cell wall thicknesses of 10 nm. These foams are found to have excellent energy absorption capability and are able to elastically recover even when compressed to 80% strain.

Nanoporous graphene actuators operate in an electrochemical environment, exploiting their high surface-area capacitance to inject charge [2,16]. In case of isolated monolayer graphene, the excess charge is injected on all atoms, modifying the carbon–carbon bond strength and thus changing the equilibrium spacing, resulting in in-plane deformations of the graphene sheet. When the ligaments consist of aggregates of graphene ribbons that are distorted and curved, as in [2], most of the individual graphene layers are accessible by the electrolyte, resulting in uniform actuation of the ligaments. However, when the ligaments of the graphene nanofoams consist of multiple monolayers stacked together (as in [13–15,17,18]), only the outer (surface) layers have full access to the electrolyte and thus accumulate excess charge, leading to a miss-match in equilibrium spacing between the surface and inner graphene layers of the ligament. In that case, the van der Waals interactions between neighboring layers dictate the level of constraint imposed on the charged surface layers and thus control the overall deformation of the ligaments. In addition to the actuation strain, also the specific work density is an important actuation performance index. Here, the overall stiffness and strength of the three-dimensional graphene structure come into play, quantifying, together with the actuation strain, the amount of work the actuator can do against an applied load [19]. Both the actuation strain as well as the mechanical properties will depend on the competition between the intralayer covalent interactions and the interlayer van der Waals forces. The goal of this letter is to explore this competition by analyzing the stiffness, strength and actuation strain of regular graphene honeycomb structures (similar to the materials synthesized in [15]) as a function of relative density and internal surface area.

2. Atomistic model

When negative charge is injected on a graphene monolayer, the bond length of the carbon atoms increases, creating an in-plane stretching of the ribbon. The opposite happens when positive charge is injected, i.e., the bond length decreases resulting in contraction [2,16,20]. Density functional theory (DFT) simulations have been carried out on graphene monolayers, providing detailed information on the subatomic quantum-mechanical interactions and the effect of excess charge on the interatomic bonds [16,20]. To bridge the gap between this subatomic scale and the macroscopic scale of graphene nanofoams, we will develop an atomistic model by modifying the adaptive intermolecular reactive empirical bond order (AIREBO) potential [21,22] to account for the charge-induced change in equilibrium bond length of the carbon atoms. The atomistic potential parameters are calibrated to the charge-induced strain of graphene monolayers obtained by DFT computations [16]. Using this modified potential we calculate the actuation strains of single graphene ribbons and their collective response in graphene honeycombs. Full details of the model and its calibration can be found in section S1 of the supporting information.

3. Results

Besides the amount of strain $\epsilon_c$, the performance of an actuator is also expressed in terms of the amount of work it can do against an external load (tensile or compressive). The maximal work density can be written in terms of $\epsilon_c$ and the stiffness $E^*$ as [19,23]

$$W_V^{\text{max}} = \frac{1}{4} E^* \epsilon_c^2.$$  

(1a)

under the assumption that the stress induced by the load is smaller than the failure stress ($\sigma_f^*$) of the material. If this is not the case, the maximal work output is limited by the failure stress of the material, leading to

$$W_V^0 = \sigma_f^* (\epsilon_c - \sigma_f^*/E^*).$$  

(1b)

To quantify the performance of the graphene nanofoam actuator in terms of the above indices, we will explore how the stiffness $E^*$, failure stress $\sigma_f^*$ (in compression and tension) and the overall actuation strain $\epsilon_c$ scale with the relative density and the internal surface area. However, before doing so, we will first study the actuation response of a single graphene layer.

Graphene ribbons

The ligaments of disordered nanofoams produced by Biener et al. [2] and the ordered honeycombs by Qiu et al. [15] are made of several graphene layers. In the former, the layers are disorderly arranged and in the latter they are stacked on top of each other in an orderly fashion. As the individual graphene layers are the building blocks of these foams, we first study the actuation response of a single graphene layer.

Actuation strains are calculated for pristine and perturbed (with initial atomic coordinates having random deflections normal to the plane of the ribbon) graphene ribbons with widths ranging from 2 to 10 nm and a length of 10 nm. First, uncharged pristine ribbons are relaxed at 0 K. The equilibrium spacing of the atoms at the edges have a larger equilibrium spacing than those at the center, resulting in an overall expansion of the ribbon and a compressive edge stress of $-21.2$ eV/nm, see section S2.
of the supporting information for details. The expansion (termed ‘equilibrium strain’) increases for smaller widths \( w \) leading to a \( 1/w \) scaling (see section S3 and Fig. S2 of the supporting information). For the perturbed ribbons, the edges buckle under the influence of the compressive edge stress, resulting in a full relaxation of the stresses, leading to zero equilibrium strain, as shown in Fig. S2. Then, a charge of \(-33.7\) and \(+33.7\) \( \mu C/cm^2 \) (equal to \(-0.05 \, |e|/\text{Atom} \) and \(0.05 \, |e|/\text{Atom} \), respectively) is applied to all atoms of the relaxed, pristine ribbons and then relaxed again at 0 K. Relative to the initial equilibrated configuration, the ribbons contract upon positive charge injection and expand with negative charge, see Fig. 1(b), without buckling. In a second exercise the pristine ribbons are given an initial random perturbation normal to the plane of the ribbon ranging from \(-0.1\) \( \text{Å} \) to \(0.1\) \( \text{Å} \), then a charge of \(-33.7\) and \(+33.7\) \( \mu C/cm^2 \) is applied and finally the sample is relaxed at 0 K. The ribbons are found to undergo buckling-induced shape changes, see Fig. 1(a), and dimensional changes that are of the same magnitude as the pristine ribbons (see Fig. 1(b)). To investigate the effect of charge injection on the mismatch between surface and inner atoms, we have computed the edge stresses in the presence of charge. We found that the edge stresses are only mildly affected by charge \((-21.2\) versus \(-21.0\) eV/nm, see section S2 of Supplementary Information for details), indicating that the actuation of the ribbons is predominantly due to the charge-induced modification of the bond length of the inner atoms.

It should be noted that hydrogen passivation or bond reconstruction can modify the graphene edges [24–26], which will affect the edge stress and the shape of the uncharged ribbons. Upon charging, however, the overall actuation strain is predominantly due to the modified bond length of the inner atoms (see Fig. 1(b)), so that changes in edge stress are not expected to affect the actuation strains. Further investigations are needed to confirm this.

The actuation strains do not only depend on the presence and distribution of the excess charge, also the reverse is true: the charge distribution will change when the graphene structure changes shape. This two-way coupling seems relevant for the isolated graphene ribbons studied where large changes of shape occur due to edge buckling (Fig. 1(a)). However, these shape changes remain localized to the edges and, if important, will only affect the charge distribution for ribbons smaller than 5 nm. For larger widths the actuation strain is dominated by the atoms in the inner regions which remain flat. We have therefore neglected the effect of edge buckling on the charge-distribution.

**Graphene honeycombs**

Hexagonal honeycombs are assembled from continuous graphene layers, with ligaments (struts) that consist of several layers stacked on top of each other, as shown in Fig. 2(a). We study three different-sized honeycombs with strut lengths of 8, 16 and 25 nm; named \(L_8\), \(L_{16}\) and \(L_{25}\), respectively. For a given strut length, the number of layers is varied from 2 to 18 to generate samples of different relative densities. Due to the geometry of the hexagonal architecture, it is not possible to create initial registries in which the interatomic and interlayer distance coincide with the equilibrium spacing (equal to 1.38 \( \text{Å} \) and 3.42 \( \text{Å} \), respectively) [22]. As a result the interlayer distance is slightly different in some regions of the samples with deviation varying from \(-9\) to \(20\)%. In addition, the interatomic bond length at the corners of the hexagons is altered within \(-6\) to \(20\%) deviation to get a proper structural alignment between the connecting layers. Due to this the samples will contain a prestress prior to loading.

To study the tensile and compressive stress–strain behavior of the honeycombs, a unit cell is identified (see Fig. 2(a)). The unit cell features periodic boundary conditions in the \(x\)- and \(y\)-directions and free edges in the \(z\)-direction. The width of the ribbon in the \(y\)-direction is \(2\) \( \text{nm} \). The samples are pulled/compressed along the \(z\)-direction. The atomic interactions in the honeycomb are modeled by the AIREBO potential as discussed in section S1 of Supplementary Information (see Appendix A). First, the samples are relaxed to a minimum energy configuration at \(T = 0\) K using the conjugate gradient method. Subsequently, the degrees of freedom of the atoms (along the pulling direction) in 5 atomic layers on both sides are fixed and an equal displacement, in increments, is prescribed to
Fig. 2. (a) A unit cell of a graphene honeycomb with struts consisting of 4 layers and, a zoomed and slightly rotated view of the region marked with a red box in the honeycomb. Each graphene layer consist of carbon atoms arranged in a hexagonal lattice oriented in such a way that the zigzag edges are parallel to the z-axis. (b) Compressive and tensile stress–strain curves of L25 samples with different number of layers. The solid lines are curve fit to the data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. (a) Compressive and tensile Young’s modulii of the L8 (triangles), L16 (squares) and L25 (circles) honeycombs as a function of relative density (i.e., for different number of layers). The solid lines are linear curve fits to the data. (b) Delamination stresses of L8, L16 and L25 honeycombs for different numbers of layers. The solid lines are linear curve fits to the data. Inset: Delamination of the layers at the junctions at 6% tensile strain for the 6-layered L8 sample.

the atoms at both ends. Energy minimization is applied after each displacement increment. Lateral contraction in the x- and y-directions is allowed [27]. The samples are subjected to a total strain to failure. The strain is calculated as the ratio of the change in length and the length at the initial relaxed configuration. Unit cells of different size in the z-direction were tested and it was found that a 1 × 1 unitcell is sufficient to get converged, size-independent stiffness values [28,29]. Fig. 2(b) shows the average virial stress–strain results for the L25 samples with different strut thicknesses. At zero strain the samples contain a pre-stress as discussed above, which increases with the number of layers due to the increase in the number of structural deviations from the equilibrium configuration. The Young’s modulus in tension is calculated from the slope of the stress–strain curve at positive strains and the one in compression at negative strains. The relative density $\rho^*$ is calculated from the strut length $L$, the number of layers $n$ and the spacing $t$ between the graphene layers according to $\rho^* = \frac{\sqrt{3}}{2} (nt/L) - \frac{1}{3} (nt/L)^2$. Fig. 3(a) shows that both stiffnesses increase linearly with relative density, indicating that the struts deform by stretching, which is in agreement with the affine deformation behavior of the struts observed in our atomistic calculations. It should be noted that the mechanical tests on the graphene honeycombs prepared by Qiu et al. [15] show a quadratic dependence of stiffness on the density of the samples, which is due to the fact that the struts have a much larger slenderness ratio (2000–4000) than the slenderness ratios of the struts used in our computational study (4–18). The values of the Young’s moduli in compression are a factor 1.6 higher than the values in tension, which is due to the asymmetric stiffness of the interlayer LJ potential, as explained below.

The equilibrium interlayer spacing between individual graphene layers in the honeycomb is 3.42 Å. At interlayer distances less than 3.42 Å the layers are subject to a strong repulsive force accompanied by a high stiffness, while for distances larger than 3.42 Å the layers feel a relatively weak attractive force accompanied by a lower stiffness. The ratio of the average stiffness in compression to that in

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1 Lateral contraction is allowed in LAMMPS while using periodic boundary conditions [27].
tension of the LJ potential in the 1% strain neighborhood of the equilibrium interlayer spacing (3.42 Å) is 1.4, close to the ratio of stiffnesses shown in Fig. 3(a). At larger tensile strain values, the interlayer LJ bonds are broken resulting in the gradual delamination of the struts at the junctions (see inset of Fig. 3(b)). The delamination starts at the junctions close to the ends where the displacement is applied, and with an increase in strain the delamination also appears in the other junctions. Fig. 2(b) shows that the tensile failure stress is independent of the number of layers. To investigate this further, we plot the tensile failure (delamination) stress, \( \sigma_d \), as a function of relative density for different cell sizes (L8, L16 and L25) in Fig. 3(b). The delamination stress depends solely on the length of the cell wall \( L \) and decreases with increasing \( L \), see Fig. 3(b). The delamination stress \( \sigma_d^* \) can be written in terms of the delamination force (per unit out-of-plane width) \( F_d \) by neglecting the shear force \( F_s \) (see Fig. S3 of supplementary information), resulting in

\[
\sigma_d^* = \frac{F}{2L \cos \gamma} = 2F_d \cos \gamma/2L \cos \gamma = F_d/L, \quad (2)
\]

which is independent of the number of layers (see Fig. S3 of the Supplementary Information for the decomposition of the force components in a honeycomb). Using the result for L16 from Fig. 3(b), the delamination force per unit out-of-plane width \( F_d \) can be found to be 1.28 GPa (16 nm) = 20.5 N/m. Then, by using this in Eq. (2), the delamination stress for the L8 and L25 honeycombs are predicted to be 2.5 and 0.75 GPa which are in close agreement with the atomistic results of 2.5 and 0.96 GPa, respectively.

Fig. 2(b) shows that, in contrast to tension, the failure stress in compression depends greatly on the strut thickness. As depicted in the inset of Fig. 4(a), buckling is the dominant failure mode in compression. To analyze this, we assume the struts to be pin jointed at the junction and by using the multi-beam shear model [30,22], the critical buckling stress \( \sigma_b^* \) can be found to be

\[
\sigma_b^* = \frac{nt}{2L \cos \gamma} \sigma_b = \frac{-1}{2L \cos \gamma}\left(nD_{\text{bend}}k^2 + (n-1)Gt \right), \quad (3)
\]

where \( \gamma = 30^\circ \), \( D_{\text{bend}} \) is the monolayer bending modulus per unit out-of-plane width, \( G \) is the interlayer shear modulus and \( k = 2\pi/L \) (see section S5 of the Supplementary Information for the derivation). For the L16 and L25 samples the critical buckling stress predicted by Eq. (3) is in close agreement with the atomistic results (see Fig. 4(a)). For the L8 case the atomistic results are slightly overestimated, which is due to the fact that for these values of \( nt/L \), the struts become very stocky and beam theory can no longer be applied.

In contrast to the honeycombs studied so far, the honeycombs fabricated by Qiu et al. [15] consist of struts that are assemblies of finite-sized graphene ribbons. To explore this, we have generated two L8 samples with struts made of finite-sized segments of length 8 and 16 nm. The segments are separated by a gap of 2.4 Å. To investigate whether the location of the gaps affects the Young’s modulus of the sample, we performed tensile tests on three different realizations of honeycombs with the location of the gaps varying in each realization. The tensile test procedure is the same as that followed for the unsegmented samples. The resulting stress–strain curves are shown in Fig. 4(b). The slope of the stress–strain curve (Young’s modulus) is not affected much in case of discrete segments and it is independent of the location of the gaps. However, in the segmented samples, the stress–strain curves become serrated with intermittent stress drops due to discrete interlayer sliding events. With the increase in strain the interlayer sliding events increase the gap between the segments, finally leading to strut failure by severe sliding, see Fig. S4 of the Supplementary Information. This is in contrast to the failure in the unsegmented samples where failure occurs by the gradual delamination at the junctions, leading to a flat stress–strain curve after delamination, see Figs. 2(b) and 4(b). Note that for the 6-layered L8 sample shown in Fig. 4(b), the stress-drop at around 4% strain is due to the spontaneous sliding of layers.

Next, we perform actuation simulations of the L8, L16 and L25 honeycombs having different number of layers (and thus different relative densities). The samples are initially relaxed at 0 K with periodic boundaries on all sides. Then, charge is injected in increments on the atoms of the surface layers of the hexagons through the modified AIREBO potential. After every charge increment the sample is relaxed at 0 K. The charge-strain response is linear, see Fig. 5(a). For a specific strut length, the magnitude of the strain is inversely proportional to the number of layers \( n \), see Fig. 5(b). In addition, we found that for a specific number of layers the magnitude of the strain is independent of the cell size, in correspondence to our previous studies on nanoporous gold showing that the actuation strain is independent of relative density and varies only with the thickness of the cell walls [31,23]. Finally, we have also performed actuation calculations (not shown) on the segmented samples, depicting that the curves are more serrated (as also shown in Fig. 4(b)), but that the strain–charge slopes are unaffected.

### 4. Summary and conclusions

We have modified the AIREBO potential to account for the excess charge by fitting the potential to the charge-induced strain of graphene layers obtained by DFT calculations. The morphological changes in graphene layers due to edge stresses and external charge were investigated. In contrast to the equilibrium strain, the charge-strain response of the ribbons does not show a dependence on specimen size (see Fig. 52 and Fig. 1(b)), emphasizing that the charge-induced actuation strain is due to the expansion or contraction of the interatomic bond lengths of all carbon atoms and not only those at the edges. Mechanical tests on graphene honeycombs reveal that the Young’s modulus \( E^* \) scales linearly with relative density, indicating that the struts predominantly deform by stretching. Due to the asymmetry of the non-bonded interactions between neighboring graphene layers, the Young’s modulus \( E^* \) in compression is larger than that in tension (see Figs. 2(b) and 3(a)). The honeycombs fail by buckling of struts in compression and by delamination of graphene layers in tension (see Figs. 4(a), 3(b)). The buckling stresses of the
Fig. 4. (a) Buckling stresses of the L8, L16 and L25 honeycombs as a function of nt/L. The solid lines are the theoretical predictions of the buckling stress according to Eq. (3). Inset: Buckled configuration of the 6-layered L8 sample at 6% compressive strain. (b) Stress–strain curves of unsegmented and segmented samples for the 6-layered L8 sample. The colors distinguish the different realizations. The samples with segments of 16 nm correspond to the colored dotted lines and those with segments of 8 nm to the colored solid lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (a) Actuation strains of the L8 honeycombs with different number of layers as a function of the surface charge density. (b) The strain of the L8 sample is inversely proportional to the number of layers n (symbols: atomistic calculations, solid line: n\(^{-1}\) scaling relation).

honeycombs predicted by a multi-beam shear model are in close agreement with the atomistic results (see Eq. (3) and Fig. 4(a)), showing a linear dependence on nt/L. On the other hand, the delamination stress solely depends on the length of the strut, and it decreases with an increase in strut-length, which is consistent with a strut-thickness independent delamination force, see Eq. (2) and Fig. 3(b).

Upon actuation, the strain scales linearly with the injected charge density and the strain per unit surface charge is inversely proportional to the strut thickness (see Fig. 5).

As indicated before, the performance of an actuator depends on the actuation stroke as well as the ability of the structure to do work against an applied load. The load should be limited not to exceed the failure stress of the material. The actuation strain \(\epsilon_c\) of graphene honeycombs, however, is found to be much smaller (by one order of magnitude) than the failure strain \(\epsilon_f = \sigma_f^* / E^*\), so that the work performance of the graphene honeycombs is evaluated in the elastic limit. The ratio of volume and surface area, \(V_s / A_s\), for the hexagonal honeycombs is equal to nt/2, so that the magnitude of the actuation strain per unit charge density can be described by the scaling law

\[
\frac{d\epsilon_c}{dq_a} = c_1 n^{-1} = c_1 \left( \frac{2V_s}{A_t} \right)^{-1},
\]

where \(c_1 = -5.35 \times 10^{-3} \text{ m}^2/\text{C}\). Besides the actuation strain the performance of an actuator depends on its Young’s modulus, see Eq. (1a). The compressive \(E^*\) scales linearly with the relative density of the honeycomb (see Fig. 3(a)) through the relation

\[
\frac{E^*}{E_g} = c_2 \rho^*,
\]

where \(c_2 = 0.259\) and \(E_g = 1.025 \text{ TPa}\) [10] is the Young’s modulus of one graphene layer. Note that \(c_1\) and \(c_2\) are constants which depend on the morphology of the structure.
Substituting Eqs. (4) and (5) in Eq. (1a), we arrive at

\[ W'_v^{\text{max}} = c_3 E_s \rho^{*} \left( \frac{V_s}{A_d} \right)^{-2} q_a^2, \]

with \( c_3 = c_1^2 C_s/16 = 4.63 \times 10^{-7} \text{m}^4/\text{C}^2 \). Figure S5(a) shows the work density as a function of the strut thickness for different relative densities and a charge density of 26.92 \( \mu \text{C/cm}^2 \). Clearly, to maximize \( W'_v^{\text{max}} \), a small number of graphene layers should be combined with large relative densities.

It is now insightful to compare the graphene nanofoams with the nanoporous gold structures studied in [23]. A first important index is the amount of strain that can be generated per unit injected surface charge, \( d_{e_c}/dq_a \). Comparing Eq. (4) with that for nanoporous gold [23],

\[ \frac{d_{e_c}}{dq_a} = d_1 \left( \frac{V_s}{A_d} a \right)^{-1}, \]

with \( d_1 \) equal to 5.9 \( \times \) 10^{-2}, 3.9 \( \times \) 10^{-2}, 3.4 \( \times \) 10^{-2} m^2/C for cubic lattices, gyroids and nanoporous gold, respectively, yields the ratio

\[ \frac{(d_{e_c}/dq_a)_{\text{graphene}}}{(d_{e_c}/dq_a)_{\text{gold}}} = \frac{c_1 t}{(2d_1 a)}, \]

reaching values of −0.082, −0.117 and −0.135 (with the minus sign being related to the opposite sign of the strain upon injection of charge) for cubic lattices, gyroids and nanoporous gold, respectively. These values clearly show that larger strains can be generated per unit charge density for gold nanostructures compared to graphene honeycombs. Note that the above analysis only holds for quantum-mechanical charging effects, neglecting the electrostatic contributions to strain which might be operative at larger charge densities [16,32,33]. Next we compare the stiffness (Eq. (5)) to that for nanoporous gold [23],

\[ \frac{E^*}{E_s} = d_2 \rho^{*}, \]

with \( E_s = 79 \text{ GPa} \) and \( (d_2, \beta) = (0.33, 1), (0.84, 2) \) and \( (1.83, 3.9) \) for cubic lattices, gyroids and nanoporous gold, respectively, and neglecting the size-effects for the cubic lattice. This leads to a ratio of

\[ \frac{E^*_{\text{graphene}}}{E^*_{\text{gold}}} = \frac{c_2 E_s}{d_2 E_s} \rho^{*(1-\beta)}, \]

which clearly indicates the difference in inherent stiffness between graphene and gold, \( E_s/E_{\text{gold}} = 13.0 \), and the effect of morphology, leading to bending-dominated scaling for the gyroids and npg with \( \beta \)-values larger than 1. This results in much lower stiffnesses of these structures at small relative densities: for \( \rho = 0.1 \) the ratio in Eq. (7d) becomes equal to 10.2 for the gold lattice, 40 for the gold gyroid and 1458 for nanoporous gold. Finally, the different scaling for actuation strain and stiffness culminates in the difference between the work densities, shown in Fig. S5(b) of the Supporting Information. Their ratio can be written as

\[ \frac{W'_v^{\text{max}}_{\text{graphene}}}{W'_v^{\text{max}}_{\text{gold}}} = \frac{c_3 E_s \rho^{*(1-\beta)}/d_3 E_s a^2}{c_4 E_s \rho^{*(1-\beta)}}, \]

with \( d_3 = d_2 a^2/4 \), leading to \( \alpha \) values of 0.068, 0.055 and 0.034 for cubic lattices, gyroids and npg. Fig. S5(b) shows this ratio as a function of relative density for the graphene honeycombs relative to the gold lattice, gold gyroid and nanoporous gold. The prefactor \( \alpha \) in Eq. (7e) is considerably smaller than 1 as a result of the quadratic contribution of the actuation strain per unit charge density which is smaller for graphene than for gold. For gold lattices, which also have a stretching dominated deformation mode as graphene (i.e., \( \beta = 1 \)), this leads to the highest work density. The gold gyroids feature a bending dominated deformation mode (\( \beta = 2 \)), which leads to higher stiffnesses for the graphene hexagon, especially at small densities. However, this cannot compensate for the smaller actuation stroke of graphene for a typical relative density of 0.1. The stiffness of nanoporous gold scales with relative density power 3.9, leading to a much higher work density for graphene by a factor of 27 for a relative density of 0.1. The above analysis shows that the actuation stroke per unit charge density is higher for the gold structures. However, also the ability of the nanoporous structures to accumulate charge (related to the capacitance) should be taken into account. Here, the graphene may do better than the gold structures, with reported values of \( q_a = 26.92 \mu \text{C/cm}^2 \) [16] for graphene and \( q_a = 7.7 \mu \text{C/cm}^2 \) for nanoporous gold [34].

Our results provide a fundamental understanding of the physical mechanisms that couple the electrochemical injection of charge at the nanoscale to the overall actuation stroke and work output of graphene nanofoams. Key mechanisms that set the nanofoams of graphene apart from that of gold are the ratio between the inherent graphene and gold stiffness, the sub-atomic quantum-mechanical strain-charge ratio of the graphene ribbons and gold surfaces and the different architectural morphologies that control bending versus stretching dominated mechanical properties. The results can be used as guidelines for the synthesis of nanoporous actuators having optimal actuator strokes and work densities.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.eml.2015.09.006.

References


