Tailoring Graphene to Achieve Negative Poisson's Ratio Properties

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Graphene, a one-atom-thick carbon allotrope featuring excellent mechanical, electronic, and thermal conductivity properties, is widely regarded as one of the possible wonder materials of the 21st century.[1] Here, we show that its already remarkable properties may be further improved through modification of its nanostructure. In particular, negative Poisson's ratio (auxetic behavior), that is the anomalous property of becoming wider rather than thinner when stretched, may be imparted to graphene at ambient conditions through the introduction of vacancy defects thus resulting in the thinnest auxetic material known so far with potential applications ranging from smart nanoelectromechanical devices to the design of nanocushions or nanodomes and smart nanofiltration. We indicate that this effect results from a de-wrinkling mechanism, which mimics the behavior exhibited by a crumpled sheet of paper when it is stretched.

Due to its unusual properties, graphene may well end up being used in various applications. In recent years, significant advances have been made in the design of devices utilizing grapheme-based materials ranging from superior chemical and molecular sensors,[2] to electronic equipment[3] and nanooscillators.[4] In fact, graphene is forecasted to be a potential replacement for a number of existing materials, especially if one is able to produce it with sufficient purity. As with other materials, the properties of graphene are highly dependent on the quality of the sample prepared. Prima facie, one might be concerned that the presence of defects will weaken the remarkable mechanical and electrical properties of this superstrong highly conductive ultrathin material, to the extent that it would become unusable in practical applications. However, it is known that in some cases, defects in graphene are beneficial and are introduced intentionally at the required size and concentration to bring about a desired quantified change in some property of graphene.[5]

Materials with a negative Poisson's ratio,[6–8] auxetics,[9] constitute another class of systems, which are becoming increasingly popular as a result of their remarkable properties. For example, it is now known that auxetics normally have the natural tendency to form dome-shaped conformations, i.e., synclastic curvature,[10] which may be of use in the manufacture of curved body parts for aircrafts or automobiles. They also offer better indentation resistance when compared to their conventional counterparts, making them ideal for use in superior protective equipment. A number of materials and model systems have now been found to exhibit a negative Poisson's ratio. These range from foams[11] to single metal crystals[12] and from model phases[13] and macrostructures[14] to nanomaterials.[15,16] Despite recent works attempting to discover auxeticity in graphene-based and related carbon-based materials, a route to convert graphene to a material with significant auxetic characteristics at ambient conditions is still to be identified. In fact, prior art on the subject has dealt mainly with auxeticity in nanotubes,[17–23] or, in the case of single layer graphene, potential auxeticity at nonstandard conditions, such as very high temperatures[24] or resonance under fully blocked boundary conditions with C–C bonds approximated by auxetic Timoshenko beams.[25] Also, work reported so far which looked into the effect of vacancy defects on the Poisson's ratio of graphene[26,27] did not result in auxeticity, although the work by Dettori et al.[26] did suggest a lowering of the Poisson's ratio when vacancy defects at low concentrations are introduced.

This Communication presents the results of extensive molecular dynamics simulations that show how the conformation of graphene can be modified through the introduction of defects so as to make it amenable to exhibit a negative Poisson's ratio.

In particular, molecular dynamics simulations at 300 K for different extents of uniaxial stress corresponding to a maximum of 10% uniaxial strain were performed upon systems having different concentrations of double vacancy defects of the 5–8–5 type (see **Figure 1**a and Supporting Information) which correspond to having p% of the atoms removed, where p% = 0.5%, 1.0%, 2.0%, and 3.0%. More specifically, a pristine graphene sheet having 28 800 carbon atoms, with dimensions ca. 25 nm × 29 nm was first constructed and positioned in the xy-plane with the armchair conformation being aligned parallel to the x-direction. As discussed in more detail in the Supporting

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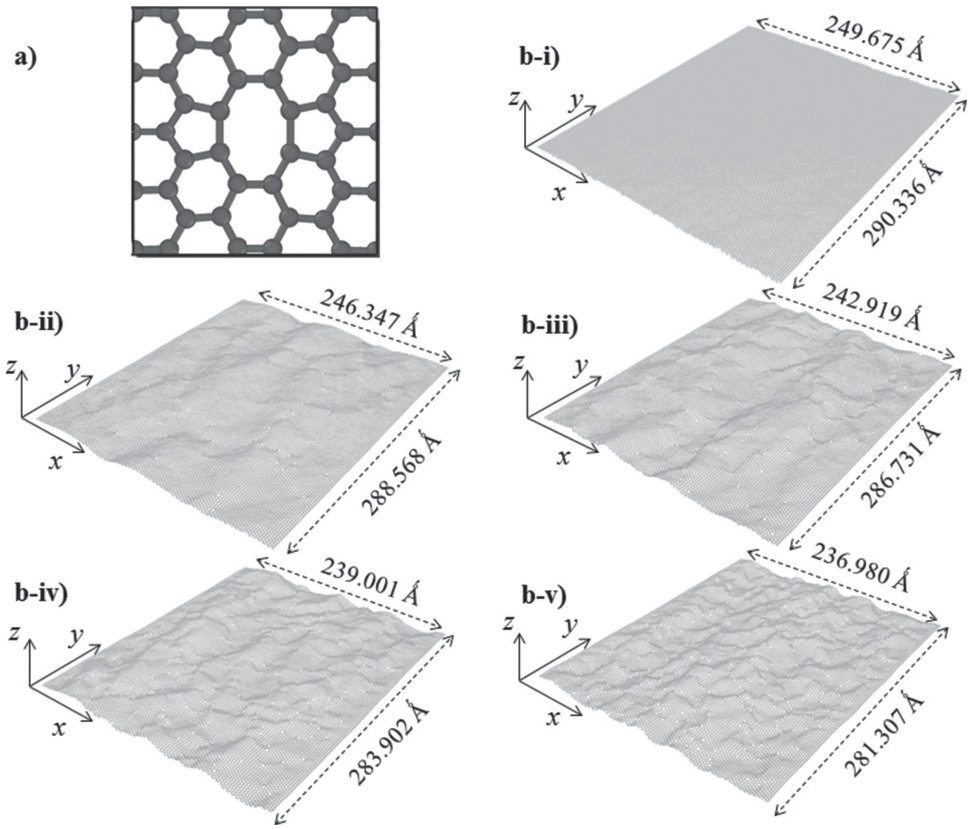

Figure 1. a) A representation of a 5–8–5 double vacancy defect in graphene and b) typical images of different systems at increasing defect concentration: i) $p = 0\%$, ii) $p = 0.5\%$, iii) $p = 1.0\%$, iv) $p = 2.0\%$, and v) $p = 3.0\%$. Note that as the concentration of defects increases, the graphene sheets adopt a more wrinkled conformation thus achieving a shape which resembles that of a wrinkled paper model.

Information, standard periodic boundary conditions[28] were applied in the *y*-direction while in the *x*-directions, some constraints on the atoms at the leftmost and rightmost edges were applied to permit loading and ensure that the system remains aligned in the *xy*-plane during the simulations. With these conditions, the structure being modeled corresponds to an infinite graphene nanoribbon, which can be stretched through a set of parallel rollers in the *x*-direction.

The defects were then generated by deleting 72, 144, 288, and 432 pairs of neighboring atoms (corresponding to 0.5%, 1.0%, 2.0%, and 3.0% of the atoms, respectively) in a random and nonoverlapping manner and then using a bond reconstruction process to ensure that all defects are truly of the 5–8–5 type. For each system, an energy expression was then set up using the adaptive intermolecular reactive empirical bond order (AIREBO)[29] potential with periodic boundary conditions being used in the *y*-direction. Uniaxial loading was simulated by applying forces parallel to the *x*-direction on the atoms at the boundaries parallel to the *y*-direction. This procedure was used in an attempt to obtain a realistic graphene-like material, which could easily be studied under constant uniaxial stress conditions applied in the *x*-direction. Moreover, the atoms on which the stretching forces acted directly were further constrained so as not to move in the third direction. This was done so as to ensure that the graphene sheet behaves, as much as possible, as if it was gripped to horizontal rollers, i.e., similar to what happens in real-life mechanical testing. These constraints also ensure that the system remains parallel to the *xy*-plane throughout the simulation and also that the stress applied is purely uniaxial. These simulations were then repeated twice, to obtain three independent sets of results, each corresponding to different initial structures that have the same concentration of double-vacancy defects. Pristine graphene was also studied in order to ensure the reliability of the methodology used.

Typical images of the systems having various extents of defects in the unstretched state clearly suggest that as the extent of defects increases, the graphene sheets adopt a more wrinkled and crumpled conformation (see Figure 1b) with a higher density of ripples having more pronounced amplitude than in the pristine form. This observation is clearly supported through the distributions of the modulated out-of-plane *z*-coordinates of the atoms, which increase significantly as more defects are introduced. It should be noted that in all cases studied, our simulations suggest that the out-of-plane dimension of the wrinkles is significantly larger than the amplitude of the thermal fluctuations of the individual atoms. This is evident by looking at the trajectories of the molecular dynamics simulations (e.g., in Video S1 in the Supporting Information, which illustrates the atomic motions present in a typical sample of graphene at 300 K with 3% defects simulated over a period of 6.25 ps). As a result, the imperfect graphene nanoscale systems with their wrinkled and crumpled conformations resemble the shape of a

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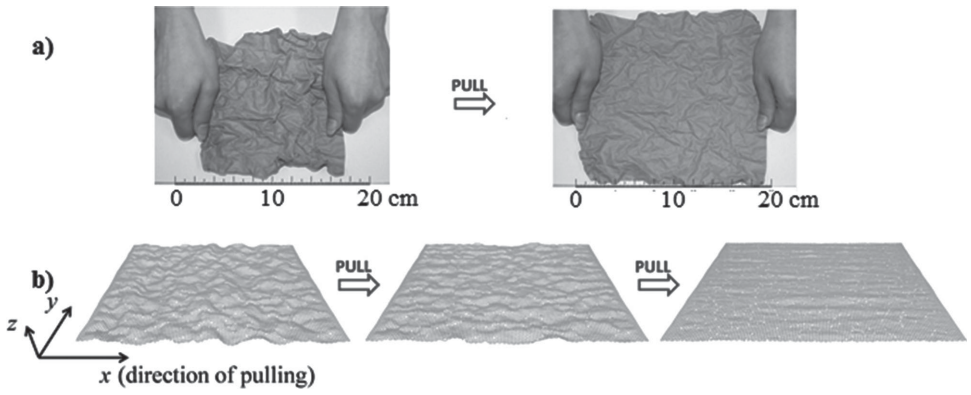

Figure 2. a) Typical images of a crumpled sheet of paper at different levels of applied strain and b) typical images of a graphene sheet having 3.0% defects at different levels of applied strain. Note that both systems undergo a de-wrinkling process so as to assume a more planar conformation resulting in an in-plane negative Poisson's ratio.

macroscale highly wrinkled sheet of paper, which can be shown to exhibit significant negative Poisson's ratios, an effect which is known[30] and can be easily verified (see **Figure 2**a and Video S2 in the Supporting Information). In fact, tests we performed on various sheets of crumpled papers clearly confirm auxeticity, with the measured Poisson's ratios typically ranging between ca. –0.5 and ca. –1.3. As evidenced in Figure 2a, this effect, which was measured on crumpled paper where the extent of crumpling is comparable to that of the graphene with vacancy defects studied here, is obviously the result of the de-wrinkling and unfolding that occurs when a paper is being stretched, rather than from some intrinsic property of the paper itself. This type of behavior may be regarded as the disordered equivalent of the well-known auxetic egg-rack mechanism.[31]

In fact, our simulations clearly confirm that, even at ambient conditions, through the introduction of defects, graphene can be made to mimic the behavior of the wrinkled paper model and exhibit auxetic properties. More importantly, the extent of auxeticity can be fine-tuned since extent of auxeticity increases with increasing defect concentration. Evidence that the de-wrinkling mechanism is leading to auxetic behavior, even in these nanoscale crumpled imperfect graphene sheets, may be directly obtained from the results of the simulations (see Figure 2b and **Figure 3**). In fact, the molecular dynamics simulations performed at various extents of uniaxial loading show that upon pulling in the *x*-direction, the systems flatten out. This is evident from the images in Figure 2b, as well as the narrowing of the distributions of the modulated out-of-plane *z*-coordinates of the atoms at increasing strains. For example, in the case of systems with 3.0% defects, it was found that at 10% axial strain in the *x*-direction, there is an increase in the *y*-dimension by ca. 1.3%, i.e., they exhibit a negative Poisson's ratio. It is also clear that once the system flattens out, the auxetic properties in the plane of the graphene sheets are no longer manifested. This is particularly evident in the systems with a low concentration of defects. For example, the system with 1.0% defects is only auxetic until a strain of ca. 2%–3%, a point which corresponds to a system that has already become planar, i.e., no longer possesses the geometric features, which are essential for a negative Poisson's ratio to be manifested. This further confirms the paradigm that auxetic behavior necessitates the presence of particular geometric features to be present in the system, and that an amenable deformation mechanism must take place.

It should be emphasized that the finding that graphene can be turned to an auxetic form simply through the introduction of double vacancy defects of the 5–8–5 type is in line with the work by Dettori et al.[26] and Wang et al.,[32] which have suggested a lowering of the Poisson's ratio with the introduction of defects at low concentrations (though not sufficient enough to result in a negative Poisson's ratio). At the same time, it indicates that some of the predictions made by Tapia et al.[27] based on a purely mechanical FEA-based model that vacancy defects increase the Poisson's ratio of defective hexagonal systems are not fully applicable to real graphene-like materials. This is probably due to the fact that the formulation of the model by Tapia et al. was not amenable to any crumpled conformation similar to the one reported here, conformation of which is essential for achieving a negative Poisson's ratio.

This is very significant as it suggests a clear route for turning regular conventional graphene to an auxetic form through the introduction of defects so as to produce one of the thinnest auxetic materials known so far which may be made to achieve tailored anomalous negative Poisson's ratio properties unattainable in pristine graphene under ambient conditions. However, this result should not be considered as a mere scientific curiosity, since it is obvious that the ability of converting graphene-like materials to an auxetic form is likely to result in a number of novel applications of this already exceptional material (e.g., enhanced nanoelectromechanical sensors, nanocushions, nanodomes, etc.) For example, the potential of using the imperfect graphene for making nanodomes can be easily demonstrated through the crumpled paper macromodel equivalent, which can be easily turned into a bowl-shaped conformation as opposed to its original noncrumpled form, which is much less amenable to adopting a synclastic curvature.

Before concluding, it is important to note that, despite the limitations one normally associates with force-field-based modeling studies, the work presented here provides a blueprint on how graphene and other sheet-like materials can be transformed to an auxetic state. Given the current level of experimental techniques used for modification of nanostructures, it is envisaged that the manufacturing and testing of such imperfect

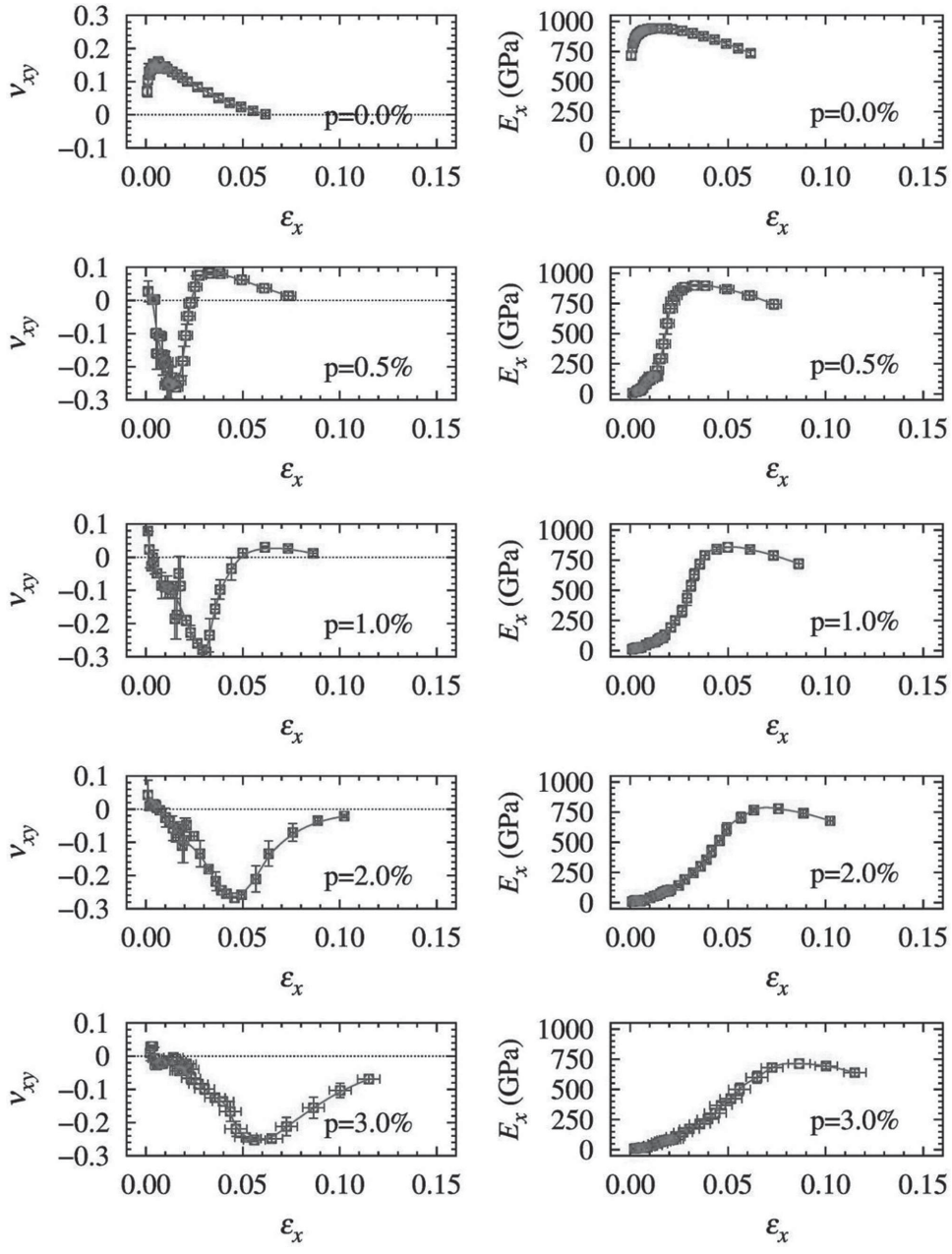

Figure 3. The averaged in-plane Poissons's ratios and Young's moduli (calculated from the differential strains) plotted against the engineering strain for stretching in the *x*-direction as obtained from the simulations of pristine graphene (p = 0.0%) and the imperfect graphene systems (p = 0.5%, 1.0%, 2.0%, and 3.0%).

materials is not unlikely and may potentially lead to the production of a real manmade nanoscale auxetic material having truly multifunctional characteristics. Also, it is important to highlight that the discovery reported here, i.e., that crumpled sheet-like materials have the potential to exhibit a negative Poisson's ratio is not only applicable solely to graphene with 5–8–5 type defects, but also to other similarly shaped materials, including membranes, for which a negative Poisson's ratio has already been reported.[30,33–35] It is also likely that imperfect graphene with other forms of defects at sufficiently high concentrations may also exhibit negative Poisson's ratio.

To conclude, the work presented here shows, for the first time, how graphene can be modified to mimic the behavior of a highly and densely wrinkled paper model to the extent that it can exhibit auxetic behavior under ambient conditions. It is hoped that this result will stimulate further research in this field, especially work of an experimental nature, which should provide definite evidence that graphene with defects and structurally similar materials can assume a crumpled sheet conformation and indeed exhibit a negative Poisson's ratio, with all the benefits that this brings with it. It is also hoped that this study will start to pave the way for a new gen-

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eration of products incorporating auxetic graphene, which would combine the useful properties associated with such a multifunctional materials from a mechano-electro-thermal point of view.

Supporting Information

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

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