REVIEW ON CRUMPLED GRAPHENE: UNIQUE MECHANICAL PROPERTIES

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Abstract. Bulk carbon nanomaterials based on graphene and other \(sp^2\) carbon nanopolymorphs are structures with a low density but high resistance to compression. These materials are promising candidates for supercapacitors, electronics, energy storage devices, etc. due to their unique properties such as extremely high specific surface area, high conductivity and stability against graphitization. In this review, after a brief overview of the structure of graphene and its mechanical properties, recent developments in the fabrication and understanding of mechanical properties of three-dimensional graphene nanostructures are discussed.

1. INTRODUCTION

Graphene, a two-dimensional (2D) material with a single-atomic thickness, is the building unit for graphite (see Fig. 1) [1]. It has been studied theoretically for a long time as a building block of graphitic materials [2,3]. Since the first successful isolation of graphene in 2004 [4], its remarkable physical, mechanical, chemical, and optical properties have been the subject of intensive investigations to implement them in many applications such as graphene-based electronics [5,6], optics [7], photovoltaics [7,8], spintronics [9], hydrogen storage [10,11], thermal [12] and composite materials [13], to name a few. Very recently, graphene and graphene-based materials have also been utilized as electrode materials in energy related devices on which promising results were demonstrated [14-18].

Significant progress has been made recently in the fabrication and understanding of graphene-based nanostructures. Various graphene nanostructures have been developed and incorporated as key components in supercapacitors, lithium-ion batteries, solar cells, and fuel cells. The other important goal is the production of energy supporting devices which hold the key role to sustain our energy demand well into the future.

The curvature imposed on a graphene sheet by external confinement or forces concentrates largely on the ridges [19,20] and leads to considerable changes in various properties of the material. Graphene is very easy to bend and many researchers have discussed how to introduce ripples, folds or wrinkles in graphene sheets in a controllable fashion and how to use such corrugations [21-31] (see Fig. 2). In fact, wrinkling is a very general physical phenomenon demonstrated by thin sheets and membranes [32-35]. Such one-or two-dimensional (2D) ripples can strongly affect the electronic properties of graphene by inducing effective magnetic fields and changing local potentials [24,25,29]. Moreover, crumpled graphene flakes, which can be characterized by various distribution of folds and

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ripples, are one of the main structural units for bulk nanomaterials and should be carefully studied.

For a perfectly elastic sheet, the work done in crumpling is stored in the elastic energy of these focused deformations, which is partitioned in finite fractions of bending and stretching energies [19]. For most familiar examples of crumpled sheets such as plastic, paper, or metal foils, the strains at ridges exceed the yield strain and the ridges become irreversibly creased into folds. As this aspect is scientifically intriguing and crumpled materials can have potential use for structural applications due to the good combination between properties, density and an easy way to process, further understanding of potential of this field is one of the main goals in the future. The final issue is to better describe the crumpling phenomenon and to establish the link between the macroscale mechanical behavior and the developed complicated internal mesostructure. It is also required to investigate various initial configurations of foils with different thickness and made of different materials. Understanding the mechanics of an interacting set of folds is a formidable challenge, and it is crucial to obtain experimental insights into their three-dimensional (3D) arrangement.

When subjected to deforming forces, thin sheets of stiff materials tend to crumple, forming distinctive patterns characterized by network of sharp folds and cone singularities. These patterns form due to the interaction between low bending resistance and high in-plane stiffness. As buckling occurs, ridges form structures that concentrate curvature at singularities and narrow folds. It is a challenge to experimentally probe the interior geometry of a 3D crumpled object. Ref. [36] studied, by laser profilometry, the statistics of folds and vertices of a uniform crumpled sheet. However, unfolding the sheet leads to a loss of spatial information about the interactions of the folds and of its final crumpled configurations. Graphene structure, consisting of six graphene flakes with interlayer distance two times larger than that of graphite, folded by compressive forces acting along the sheets was studied in [37] (Fig. 3). This work showed that large in-plane strain of graphene sheets results in formation of folds with sharp edges and high energy. The same simulation was carried out for the six times larger interlayer distance between graphene sheets. It was shown that in this case the sharp folds could not be observed under the same loading conditions. This can be explained by the van der Waals forces acting between graphene flakes in the bulk graphene structure with smaller distance between the sheets leading to the strong folding. Graphene offers a unique platform to explore crumpling due to the existence of defects and self-adhesion properties.

Many attempts have been done nowadays in the going from crumpled and folded sheet of graphene to various bulk carbon nanostructures both by experiment and simulation. The synthesis of new 3D sp²-bonded carbon forms, such as fullerites (Fig. 4), entangled carbon nanotubes (Fig. 5), crumpled graphene (Fig. 6), graphene foams, carbon nanotube (CNT)-based thin films and other hybrid carbon nanostructures can be based on the unique properties of this carbon polymorphs [38-45].
The above-mentioned graphene-based materials demonstrate high thermal conductivity [46], field-emission [47], stimulus-responsive behavior [48], superhydrophobicity [40,49] and capacitance [50,51], which opens fascinating perspectives for their applications. Such materials, if prepared in a facile and cost-effective way [49], shall have significant implications for both academic and industry communities [52,53]. It is noted that another way to produce new carbon materials is grain boundary engineering [54].

This review intends to summarize the very recent status and progress in the studies of graphene-based nanostructures addressing their mechanical properties. The brief overview of production methods for various structures will be presented as well as experimental and numerical results on their properties. It will be suggested that these novel 3D carbon nanostructures are very promising candidates for numerous applications.
The search for new forms of matter produced at the nanoscale with required properties constitutes one of the fundamental challenges of nanotechnology. The possibility of existence of highly connected, fully covalent sp\(^2\)-bonded 3D carbon forms such as schwarzites [46,55,56], polybenzenes [57] and hollow graphites [58] recently has been demonstrated theoretically. Nowadays, there is clear evidence that random carbon structures, taking the aspect of highly porous, fully 3D sp\(^2\) graphite-like carbon, are formed under special controllable conditions [59]. It was shown that high pressure and high temperature treatment can be successfully used for production of solid C\(_{60}\) fullerites with astonishing mechanical properties [60,61]. In Ref. [49], a simple approach to produce 3D graphene-based porous materials with ultra-high specific surface area and excellent bulk conductivity was presented. As can be seen from structure analysis, these nanomaterials mainly consist of defected/wrinkled...
Crumpling a thin sheet of material into a small volume requires energy for creating a network of deformations such as vertices and ridges. By the large-scale computer simulations, the crumpling of thin sheets by external forces was studied [67]. This work showed the role of self-avoidance for the crumpling process. Scaling properties of a single elastic vertex or ridge and sheet crumpling were analyzed theoretically in [68], where a numerical model that can be purely elastic or elasto-plastic was introduced.

The direct measurements of the configurations of a fully elastic sheet evolving during the dynamic process of crumpling under isotropic confinement was presented in [69] with the aim to study dynamic evolution of 3D spatial configurations of crumpling sheets. The formation of a network of ridges and vertices into which the energy is localized was observed. It was shown that the evolution of this crumpled structure involves movements of ridges and vertices.

Programmable chemical functionalization by doping a pristine graphene sheet in a certain pattern with hydrogen atoms to precisely control its folding morphology and produce the nanocages was developed in [77]. Molecular dynamics simulation was performed to create a cubic graphene nanocage by warping the top graphene layer downward and the bottom graphene layer upward to mimic the drug delivery vehicle, which opens up a new avenue to control the 3D architecture of folded graphene.

The other type of bulk carbon nanostructures is densely compacted CNT bulk materials which can be used in thermoelectric devices [71-73]. This is why production of solid structures that are composed entirely of CNTs [74] is of high importance. Some physical properties of bulk samples are needed when we extend future applications of CNTs to a larger scale such as microelectromechanical systems. Nevertheless, the solidified property of pure CNTs is poor, and the bulk CNT materials compacted by the conventional sintering method usually exhibit loose microstructure and inferior mechanical and physical properties [75, 76]. The output of CNTs is restricted by previous nanotube growth methods such as arc discharge [76]. Hence, CNTs are only used as a reinforced second phase added into matrix materials, e.g., ceramics [77]. Catalytic chemical vapor deposition (CVD) leads to large yields of CNTs at a low cost of production compared with other synthesis methods such as the carbon arc discharge [77] or laser vaporization methods [78]. Therefore, the preparation of bulk CNT materials has become feasible now. Furthermore, the cylindrical
tubular structure may be damaged during conventional powder sintering because a long soaking time at elevated temperatures is needed to densify the microstructures of the CNT compact. It was recently reported that CNTs were embedded into a ceramic matrix and this composite was synthesized by the spark plasma sintering method [77,79]. The pristine tubular structure of the nanotube remained unchanged after the spark plasma sintering processing. The method of preparation of pure CNT bulk materials by spark plasma sintering was proposed in [72], where the thermal conductivity of the resultant materials was evaluated and analyzed to explore the physical elements associated with individual CNTs.

The other reported class of carbon bulk nanopolymorphs is fullerite structures. It is well known that fullerites at ambient conditions adopt a close-packed face centered cubic lattice [80,81]. In this structure, there are no links between the C_{60} molecules. When high pressure is applied, often accompanied by annealing, strong covalent bonds are formed between neighbouring molecules and the material forms polymers with well-defined ordering. Polymers C_{60} could thus find various technological applications, for example, hard and super-hard materials [82].

The materials fabricated using the approach developed in [49] can naturally include not only crumpled graphene flakes but also some portions of other basic carbon nanopolymorphs such as fullerenes and CNTs. The structure and properties of materials that consist of different building units were studied in [83-85] (see Fig. 9). It was shown that the type of structure can significantly affect properties of 3D nanopolymorphs. Furthermore, the
structure consisting of graphene flakes is very close to the crumpled graphene. From the other point of view, it is better to produce more inhomogeneous structure to simulate crumpled graphene, consisting of small pieces of different sizes and shapes (see Fig. 10) or from mixed building units [84].

3. MECHANICAL PROPERTIES OF 2D AND 3D GRAPHENE

The covalent bonds between nearest-neighbor carbon atoms in graphene are formed by $sp^2$-hybridised orbitals. These strong bonds give graphene its extraordinary mechanical strength, making it possible to have stable free-standing graphene sheets, being only one atomic layer thick. The mechanical properties of 2D graphene under strain have been investigated extensively using both experimental and simulation methods [86-98]. It was shown that carbon-based nanostructures such as CNTs and nanofibers can fail near their ideal strengths due to exceedingly small dimensions [87].

The first systematic experimental analysis of elastic properties and strengthening behavior of graphene was done in [86]. In this work, a graphene membrane was mechanically deposited onto a substrate with arrays of circular wells and loaded by tip of atomic force microscope (Fig. 11). It was experimentally found that the graphene showed both nonlinear elastic behavior and brittle fracture. The graphene was characterized by the Young’s modulus of $E=1$ TPa and the third-order elastic stiffness of $D=2$ TPa. Brittle fracture of graphene occurred at a critical stress equal to its intrinsic strength of 130 GPa. This value is the highest ever measured for real materials.

The above-mentioned experimental data on the Young’s modulus and the intrinsic strength exhibited by pristine graphene are consistent with further computer simulations done by other researchers. Stability range and mechanical properties were investigated for both pristine graphene (Fig. 12) and graphene with Stone-Walles defect (Fig. 13) [93-96]. Fig. 12 shows that graphene can stay stable until ~40% tension along the zigzag direction, ~30% tension along the armchair direction.
tension along the armchair direction and ~40% of shear. For example, quantum mechanics and quantum molecular dynamics calculations gave the following limiting values for uniaxial loading along the zigzag (armchair) direction:

$$\epsilon_{xx} = 0.38 \text{ and } \sigma_{xx} = 168 \text{ GPa}$$

$$\epsilon_{yy} = 0.19 \text{ and } \sigma_{yy} = 120 \text{ GPa}$$

Density functional perturbation theory was employed to calculate the dispersion curves of uniaxially loaded graphene and the phonon instability was found at $$\epsilon_{xx} = 0.266, \sigma_{xx} = 121 \text{ GPa}$$ for the zigzag direction and $$\epsilon_{yy} = 0.194, \sigma_{yy} = 110 \text{ GPa}$$ for the armchair direction [87]. In molecular dynamics study of graphene nanoribbons oriented along the armchair direction, the critical parameters $$\epsilon_{yy} = 0.3, \sigma_{yy} = 175 \text{ GPa}$$ were reported [98]. It is well known that defects can considerably affect the mechanical properties and strength of materials [94,99-101].

Superior mechanical properties of single-layer graphene suggest that 3D sp²-bonded structures will exhibit interesting properties. Such materials can be divided into two groups. One group consists of fully sp²-bonded structures such as schwarzites [46,55,56], polybenzenes [57], and hollow graphites [58], while the other is represented by graphite, fullerites and tubulenes aggregated into 3D solids by means of weak van der Waals bonds. Below the discussion of mechanical properties of the materials belonging to the second group is presented.

In early experiments, very hard and stiff materials were synthesized (stable under ambient condi-
fullerites, in both the face centered cubic and simple cubic phases, as a function of pressure up to 1 GPa over the temperature range from 150 to 335K was measured [108]. According to the measurements, at zero pressure, the samples had the density 1.66 g/cm³, and the room-temperature bulk modulus 6.8 GPa for the fcc phase and 8.7–9.5 GPa for the simple cubic phase. For both phases, the bulk modulus increased rapidly with the pressure. A considerable difference in elasticity under pressure for fullerites C₆₀ and C₇₀ was demonstrated using an ultrasonic technique in the temperature range 77–340K at pressure up to 2.5 GPa [109]. The non-Hookean stress-strain response of carbon fiber crystallites was investigated in relation to changes in crystallite orientation with respect to the tensile stress direction [110]. It was found that the ratio of the tensile stress of the fiber to that of the crystallites is close to the crystallite volume fraction rather than the ratio of the fiber density to the crystallite density.

It can be seen that all the materials are compression-resistant just like paper balls as compressive stress makes them stiffer and harder [83-85,111]. Crumpled sheets have large resistance to compression and their elastic energy is focused into a complex network of localized structures. At moderate compression, the force-compression relations of crumpled sheets for both self-avoiding and phantom sheets are found to obey universal power-law behavior. However, self-avoiding sheets are much stiffer than phantom sheets and, for a given compression, develop many more folds [67]. The same behavior has been observed for crumpled graphene [67] which is very close to the structure consisting of the bended flakes.

The results of hydrostatic compression for three structures, consisting of bended graphene flakes, short CNTs and fullerites are shown in Fig. 15 [83]. Note that the structure consisting of fullerences represents the fullerite and the structure consisting of bended graphene flakes is very close to the crumpled graphene. Pressure-strain and pressure-density curves for all the materials show very different behavior for loading as well as for the unloading. The inset in Fig. 15a demonstrates that fullerite shows linear relation between $p$ and $\varepsilon$ up to $\varepsilon = 0.08$, while the structures build from CNTs and graphene flakes show nonlinear relation with $p=\varepsilon^2$ even for small $\varepsilon$. Deformation of CNTs and graphene flakes is accompanied by the formation of new sp² bonds at the edges of structural units even at relatively small densities, resulting in gradual increase in the rigidity of these materials. From the slope of the pres-
Fig. 15. Pressure as the function of (a) strain and (b) density for the material consisting of bended graphene flakes (red thin line), CNTs (black solid line), and fullerenes (blue dashed line). The density range for graphite ($\rho = 2.09\text{–}2.23 \text{ g/cm}^3$) is shown by grey dashed vertical lines and for diamond ($\rho = 3.47\text{–}3.55 \text{ g/cm}^3$) by green dotted vertical lines. (c–e) Pressure as the function of density for loading (solid lines) and unloading from different strain levels (dashed lines) for the structure consisting of graphene flakes, CNTs and fullerenes, respectively. The threshold density (the elasticity limit) is denoted by $\rho^*$. Reprinted with permission from [83].

The effect of the loading scheme and temperature on the mechanical properties of bulk carbon clearly seen that graphene flakes can be easily deformed at any loading scheme, while the fullerenes preserve their spherical shape until quite high densities [85]. Calculations of the elastic properties of CNTs confirmed that they are extremely rigid in the axial directions and are most likely to distort perpendicular to the axes. It can also be seen that the collapse of the CNTs took place under all loading conditions at the densities lower than for the breaking and collapse of the fullerenes.

To understand the mechanical behavior of considered nanostructures, the structural changes during deformation were analyzed [84, 85]. The structural transformations of the single unit (graphene flake, CNT and fullerene) are shown in Fig. 16. It is
nanostructures was studied [84]. A temperature range of 300–3000K for the three loading schemes was considered. Additionally, the structure build as a mixture of graphene flakes, CNTs and fullerenes was simulated. Fig. 17 shows the pressure (stress) as a function of density for the four materials consisting of graphene flakes, CNTs, fullerenes and mixture of different structural units. Two different temperatures were taken as the examples for the hydrostatic, biaxial and uniaxial compressions. It shows that there is almost no effect of temperature under hydrostatic compression, while temperature slightly affects the strengthening behaviour under biaxial and uniaxial compression. Surprisingly, the greatest effect of temperature is observed for mixed structure. The changes of the curve shape and even
the increase of final value of stress for uniaxial compression can be seen. The effect of loading schemes strongly depends on the type of structural units. It is observed that fullerite could be deformed more easily using hydrostatic compression than under uniaxial and biaxial compressions; mixed structure shows average mechanical properties compared to the other nanostructures, which is determined by the interactions of the structural units; while the mechanical properties of crumpled graphene are only slightly affected by the loading scheme.

In our recent work [84], the parameters of the constitutive relationships describing the deformation of bulk carbon nanostructures (including crumpled structure were) found for various temperatures and densities.

The pressure-density (stress-density) nonlinear curves can be well fitted by the power law

\[ p = A \left( \frac{\rho}{\rho_0} \right)^a, \quad \sigma_p = A \left( \frac{\rho}{\rho_0} \right)^a, \quad \sigma_\perp = A \left( \frac{\rho}{\rho_0} \right)^a, \quad (1) \]

where \( p \) is the pressure, \( \sigma_p \) is the averaged stress under biaxial compression, \( \sigma_\perp \) is the averaged stress under uniaxial compression, \( A \) and \( a \) are constants, and \( \rho_0 \) and \( \rho \) are the initial and current densities, respectively. To achieve a better fit, the constants \( A \) and \( a \) were taken different for the two density ranges 1 < \( \rho \) < 1.5 g/cm\(^3\) and 1.5 < \( \rho \) < 3 g/cm\(^3\). As an example, the constitutive relation parameters for the case of hydrostatic compression of three different structures are given in Table 1.

### Table 1. Constitutive relation parameters for hydrostatic compression for three structures with different structural units [84].

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>( T ) (K)</th>
<th>( A_{\rho&lt;1.5} )</th>
<th>( a_{\rho&lt;1.5} )</th>
<th>( A_{\rho&gt;1.5} )</th>
<th>( a_{\rho&gt;1.5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene flake</td>
<td>300</td>
<td>0.041</td>
<td>3.8</td>
<td>0.018</td>
<td>5.38</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>0.066</td>
<td>3.73</td>
<td>0.034</td>
<td>4.85</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.096</td>
<td>3.18</td>
<td>0.046</td>
<td>4.62</td>
</tr>
<tr>
<td>CNT</td>
<td>300</td>
<td>0.014</td>
<td>7.52</td>
<td>0.023</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>0.024</td>
<td>6.6</td>
<td>0.035</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.04</td>
<td>5.9</td>
<td>0.059</td>
<td>4.43</td>
</tr>
<tr>
<td>fullerene</td>
<td>300</td>
<td>0.023</td>
<td>7.0</td>
<td>0.057</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>0.014</td>
<td>8.0</td>
<td>0.076</td>
<td>4.21</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.027</td>
<td>6.94</td>
<td>0.078</td>
<td>4.3</td>
</tr>
</tbody>
</table>

### 5. CONCLUSIONS

The experimental data and computer simulation results presented in this review show that 3D carbon nanostructures are of great interest nowadays because they are promising candidates for numerous applications. 3D assembly of 2D graphene materials can lead to a variety of porous and non-porous structures with other unique properties. The possible applications of graphene-based material include transparent flexible electrodes, solar cells, graphene/polymer composites for mechanical parts, energy storage, sensors and actuators, organic electronics, and supercapacitors. In addition, 3D graphene also provides a new material platform for lithium ion batteries, catalysis, water purification, biomedical devices, etc.

The design of bulk nanostructures proposed in the literature potentially allows the production of a wide variety of new carbon allotropes with outstanding properties. The attempts made to create bulk carbon structures with novel properties have been done by experiment and computer simulations in recent years.

A number of future research directions become possible, such as systematic investigations of the effects of crumpling on the electrical and electrochemical properties of graphene and on the strengths and fracture mechanisms of graphene-based 3D structures. Also, the ridges and vertices in the crumpled graphene are highly deformed and microscopically patterned, which can potentially lead to other new properties and functions, such as patterned chemical reactions. Furthermore, by controlling the microscopic patterns of graphene with a...
simple macroscopic tool, one can develop new graphene-based systems with novel tunability and flexibility to make nanoscale mechanisms visible at the macroscale.

Though studies in this area are in their infancy, several intriguing results and remarkable trends have been reported serving as a basis for further progress. The core issues such as the homogeneous distribution of individual graphene platelets, their orientation, connectivity, and bonding with each other still require additional studying. The other unresolved issue is how to overcome the energy barrier of the folding process to fold the graphene with the specific morphology. Thermo-mechanical treatment including severe plastic deformation at elevated temperatures can be applied to activate structural reconstruction in 3D graphene to change its properties in a controllable fashion.

With further understanding of the role of graphene in electron transfer in bulk nanostructures, and reducing the cost of crumpled graphene preparation, carbon bulk nanomaterials could be promising in the future design of various devices.

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