



**Low-energy 3D sp<sup>2</sup> carbons with versatile properties  
beyond graphite and graphene**

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## Low-energy 3D $sp^2$ carbons with versatile properties beyond graphite and graphene

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Carbon materials with full  $sp^2$ -hybridized bonding, e.g. zero-dimensional (0D) fullerenes, 1D carbon nanotubes, and 2D graphene, possess outstanding and unparalleled properties, and have the unique scientific and technological importance. Theoretical design and experimental exploration of other types of novel  $sp^2$  carbon allotropes, especially with 3D architectures, is always a compelling scientific theme. Here we proposed a class of low-energy 3D  $sp^2$  carbons with exceptional properties, not only possessing excellent mechanical properties such as high 3D strength, rubber-like ultra-stretchability, and negative Poisson's ratio, but also covering the electronic properties of graphite-like metallicity and graphene-like Dirac cone, which are desirable properties across a broad range of potential applications. Furthermore, a design route was suggested to access these 3D  $sp^2$  carbons by polymerization of edge-functionalized graphene nanoribbon arrays.

### Introduction

The  $sp^2$ -hybridized carbon materials have attracted world-wide attention, from graphite, fullerenes, and carbon nanotubes (CNTs) to graphene. Fullerenes, CNTs, and graphene span a range of spatial dimensions from zero-dimensional (0D) to 2D, and are current research priorities for low-dimensional nanoscience and nanotechnologies. For instance, CNTs exhibit semiconducting or conducting behavior depending on the tube diameter and chirality,<sup>1, 2</sup> and are extraordinarily stiff with axial Young's modulus in the range of terapascal.<sup>3</sup> However, the superior properties of these low-dimensional carbons are limited in their expanding directions without bulk strength and robust construction, so that the interests on 3D  $sp^2$ -hybridized carbon allotropes are stimulated.

The 3D  $sp^2$  carbons have been expected to display unmatched bulk characteristics including superior 3D strength and exotic electronic properties,<sup>4</sup> however, the presently studied carbon

phases have the relatively low 3D strength. For example, the well-known graphene-based carbons (e.g., graphene aerogel, graphene foam, and graphene sponge)<sup>4</sup> can be considered as 3D disordered  $sp^2$  carbons, but they are composed of parallel, twisted, or curved multi-graphene sheets coupled by weak *van der Waals* interactions. Considering the disordered assembly of multi-graphene, 3D graphene-based carbons often have micron-scale open porosity, which further reduces their strength to only 15~361 MPa.<sup>5, 6</sup> As a result, the key for formation of strong 3D  $sp^2$  carbons is the rational design of a 3D covalently bonded network at the atomic level.

The first theoretical design of 3D  $sp^2$  crystalline carbon structure has been traced back to the 1980s.<sup>7</sup> This type of carbon, called H-6,<sup>8</sup> can be seen as the 3D connection of non-coplanar "Y"-shaped  $sp^2$  units. Later, the similar carbon structures such as typical BCT-4, K<sub>4</sub>, C-20 have been proposed.<sup>9-11</sup> However, some of them are dynamically unstable.<sup>12</sup> In addition to the carbon forms above, two classes of low-energy 3D  $sp^2$  crystalline carbons, i.e. the well-known negative-curvature schwarzite carbons as well as carbon nanotube superarchitectures, have been theoretically proposed with the structures composed of "5+6+7" or "5+6+8"  $sp^2$  rings at curved plane parts.<sup>13-19</sup> Since the 3D  $sp^2$  carbons were designed, the experimenters have tried their best to explore the evidence of existence for these  $sp^2$  carbons, and they may have found some clues about the schwarzite carbons and carbon nanotube superarchitectures.<sup>20, 21</sup>

The following challenge for theorists is to further search other novel 3D  $sp^2$  carbons with higher thermodynamic stabilities approach to experimental discovery as well as unusual properties beyond the known  $sp^2$  carbons. Here we report a new class of versatile 3D covalently bonded  $sp^2$  carbon allotropes. They are thermodynamically very stable, and have relative energies close to that of graphene, making them the most stable 3D  $sp^2$  carbons ever

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† Electronic Supplementary Information (ESI) available: Crystal structures information of 3D GNR polymers and previously proposed 3D  $sp^2$  carbons; calculated mechanical properties including elastic constants, bulk modulus, shear modulus, Young's modulus, and tensile strength; ground-state energies of other  $sp^2$  carbons not shown in Figure 2; calculated phonon dispersion curves of 3D GNR polymers; calculated electronic band structures of 3D GNR polymers; and calculated energy change during reactions from GNRs to 2D GNR polymers. See DOI: 10.1039/x0xx00000x

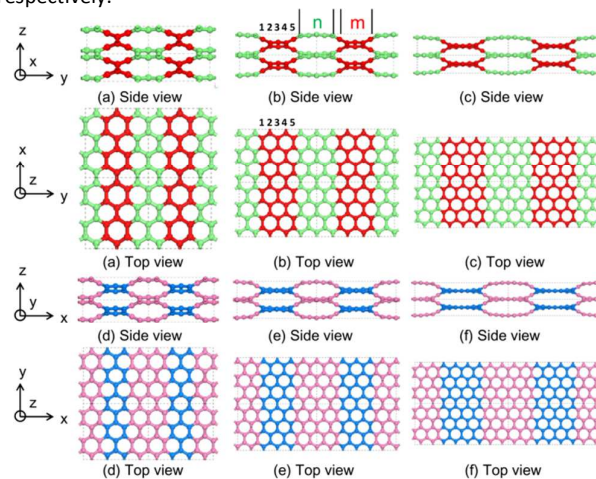
proposed theoretically as far as we know. They exhibit peculiar mechanical and electronic properties beyond graphite and graphene, such as high 3D strength, rubber-like ultra-stretchability, negative Poisson's ratio, graphite-like metallicity, and graphene-like Dirac Fermion, which is worthy of future pursuance. In addition, we also suggest a route to access this type of 3D  $sp^2$  carbons through polymerizing edge-functionalized graphene nanoribbon (GNR) arrays.

## Results and discussion

### Structures and stabilities of new 3D $sp^2$ carbons

CALYPSO and USPEX codes<sup>22, 23</sup> were used to search for new 3D  $sp^2$  carbons with high thermodynamic stabilities. In our extensive crystal structure searching, in addition to the previously discovered 3D  $sp^2$  carbons including  $K_4$ , C-20, H-6, BCT-4,  $sp^2$ -diamond, and GT-8,<sup>7-11, 24, 25</sup> we found a class of new 3D  $sp^2$  carbons with the lowest ground-state energy among the theoretical 3D  $sp^2$  modifications. Structurally, these 3D  $sp^2$  carbons can be seen as the 3D GNR polymers with the nanoribbon edges linked hand-in-hand (Fig. 1). As a result, these 3D  $sp^2$  carbons are named as 3D GNR polymers ( $m, n$ ), where  $m$  or  $n$  is the number of dimer lines across the ribbon width.<sup>26</sup> Detailed crystal structure parameters are listed in Table S1 (ESI†). Ground-state energy calculations indicate that the 3D GNR polymers possess higher energetic stabilities than previous 3D  $sp^2$  carbons including  $K_4$ , C-20, cR6, BCT-4,  $sp^2$ -diamond, Schwarzite, and CNT superarchitectures (Fig. 2). Notably, the ground-state energy of 3D GNR polymer (15,17) is only 0.064 eV/atom relative to graphite, and 0.038 eV/atom higher than that of graphene,

indicating its high stability. The dynamic and mechanical stabilities of 3D GNR polymers are verified through calculations of phonon dispersions with no imaginary frequency (Fig. S1†) and the elastic constants (Table S4†) meeting the Born stability criteria,<sup>27</sup> respectively.

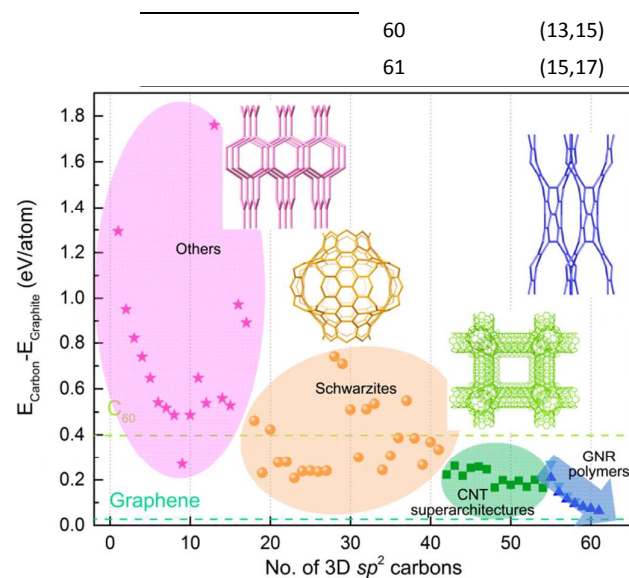


**Fig. 1** Crystal structures of 3D GNR polymers composed of GNRs with different widths. (a-f) 3D GNR polymers (3,3), (5,5), (7,7), (3,5), (5,7), and (7,9). The red, green, blue, and pink parts represent different GNR components, respectively. The  $m$  and  $n$  represent the number of dimer lines across the GNR width, such as  $m=5$  in (b).

**Table 1.** 3D  $sp^2$  carbons listed in Fig. 2.  $\Delta E = E_{\text{carbon}} - E_{\text{graphite}}$  is the calculated energy of 3D  $sp^2$  carbon relative to graphite, and  $\Delta E'$  is the relative energy from references for comparisons. Some of the structures are extracted from database SACADA.<sup>28, 29</sup>

3D $sp^2$ carbons	No.	Names in Ref.	Names in SACADA	$\Delta E$ (eV/atom)	$\Delta E'$ (eV/atom)
	1	$K_4$ <sup>30</sup>	srs	1.293	1.296 <sup>24</sup>
	2	C-20 <sup>30</sup>	xaa	0.951	0.947 <sup>24</sup>
	3	H-6 <sup>8</sup>	bto	0.822	
	4	cH6 <sup>31</sup>	eta	0.739	0.735 <sup>31</sup>
	5	$sp^2$ -diamond <sup>24</sup>	uta	0.647	0.646 <sup>24</sup>
	6	cR6 <sup>31</sup>	etb	0.542	0.539 <sup>31</sup>
	7	BCT-4 <sup>7</sup>	ths	0.518	0.589 <sup>24</sup>
	8	cT8 <sup>31</sup>	lig	0.487	0.431 <sup>31</sup>
Other $sp^2$ carbon	9	Triangular carbon <sup>32</sup>	$3^5T10$	0.270	0.23 <sup>32</sup>
	10	6(3)1-10 <sup>33</sup>	pcu-h	0.488	
	11	GT-8 <sup>25</sup>	clh	0.647	
	12	6(3)4-25 <sup>33</sup>	sqc326	0.539	
	13	dgn <sup>34</sup>	dgn	1.760	
	14	CT-12 <sup>25</sup>	sqc3051	0.559	
	15	Honeycomb carbon <sup>35</sup>	$3^3T38$	0.528	
	16	6(3)3-26 <sup>33</sup>	$3^3T5$	0.971	
	17	6(3)3-27 <sup>33</sup>	$3^5T2$	0.893	

	18	6.8 <sup>2</sup> P <sup>13</sup>	pbp	0.462
	19	6.8 <sup>2</sup> D <sup>13</sup>	pbz	0.231
	20	G688 <sup>15</sup>	pbg	0.423
	21	C <sub>168</sub> <sup>14</sup>	3 <sup>7</sup> T1	0.278
	22	C <sub>168</sub> D (Model H) <sup>15</sup>	—	0.280
	23	P8 <sup>36</sup>	mct	0.208
	24	C <sub>192</sub> D <sup>16</sup>	—	0.238
	25	C <sub>216</sub> D (Model K) <sup>15</sup>	—	0.241
	26	P7par <sup>37</sup>	3 <sup>6</sup> T5	0.236
	27	C <sub>216</sub> G (Model O) <sup>15</sup>	—	0.209
Schwarzites	28	fcc-(C <sub>28</sub> ) <sub>2</sub> <sup>38</sup>	kgz	0.741
	29	fcc-(C <sub>36</sub> ) <sub>2</sub> <sup>38</sup>	—	0.709
	30	fcc-(C <sub>40</sub> ) <sub>2</sub> <sup>38</sup>	—	0.511
	31	G8 <sup>39</sup>	3 <sup>4</sup> T13	0.300
	32	kgo <sup>34</sup>	kgo	0.512
	33	kgn <sup>34</sup>	kgn	0.536
	34	D8 <sup>36</sup>	pbz-m	0.243
	35	8-4-2-P <sup>40</sup>	3 <sup>4</sup> T15	0.307
	36	fcc-(C <sub>64</sub> ) <sub>2</sub> <sup>41</sup>	3 <sup>5</sup> T6	0.387
	37	6-1-3-P <sup>40</sup>	3 <sup>5</sup> T9	0.549
	38	c152 <sup>42</sup>	3 <sup>5</sup> T5	0.385
	39	6-1-1-P <sup>40</sup>	3 <sup>6</sup> T6	0.266
	40	c200 <sup>42</sup>	3 <sup>6</sup> T4	0.369
	41	IWPG <sup>16</sup>	3 <sup>16</sup> T1	0.335
CNT superarchitectures	42	8,0H-3D-A1 <sup>18</sup>	—	0.223
	43	8,0H-3D-A2 <sup>18</sup>	—	0.262
	44	8,0H-3D-B1 <sup>18</sup>	—	0.218
	45	8,0H-3D-B2 <sup>18</sup>	—	0.252
	46	8,0O-3D-A <sup>18</sup>	—	0.258
	47	8,0O-3D-B <sup>18</sup>	—	0.247
	48	6,6H-3D-A1 <sup>18</sup>	—	0.166
	49	6,6H-3D-A2 <sup>18</sup>	—	0.199
	50	6,6H-3D-B1 <sup>18</sup>	—	0.178
	51	6,6H-3D-B2 <sup>18</sup>	—	0.197
	52	6,6O-3D-A <sup>18</sup>	—	0.170
	53	6,6O-3D-B <sup>18</sup>	—	0.200
	54	6,6O-3D-C <sup>18</sup>	—	0.165
	3D GNR polymers	55	(3,3)	—
56		(5,5)	—	0.173
57		(7,7)	—	0.129
58		(9,9)	—	0.105
55		(3,5)	—	0.210
56		(5,7)	—	0.146
57		(7,9)	—	0.115
	58	(9,11)	—	0.095
	59	(11,13)	—	0.082



**Fig. 2** Ground-state energies of various  $sp^2$  carbon allotropes relative to graphite ordered according to Table 1. The insets are the crystal structures of previously reported  $sp^2$  carbons including Schwarzsites, CNT superarchitectures, and other allotropes. The light blue triangles: 3D GNR polymers (3,3), (5,5), (7,7), and (9,9). The dark blue triangles: 3D GNR polymers (3,5), (5,7), (7,9), (9,11), (11,13), (13,15), and (15,17). The wide 3D GNR polymers have energies close to that of graphene, making them the most stable 3D  $sp^2$  carbons theoretically proposed so far.

### Mechanical properties of new 3D $sp^2$ carbons

We calculated the ideal tensile strength of 3D GNR polymers (Tables S5† and S6†). Along the [100] and [010] directions (viz., the  $x$ - and  $y$ -axis), 3D GNR polymers show the structural characteristics of graphene, and possess superior tensile strengths of 108.1–123.0 GPa at tensile strains of 0.20–0.35. This is comparable with the in-plane intrinsic tensile strength of graphene reaching 130±10 GPa at a strain of 0.25,<sup>43</sup> but higher than that of diamond (~90 GPa) along [111] direction at a strain of 0.13.<sup>44</sup> While along the [001] direction (viz. the  $z$ -axis), which is perpendicular to the ribbon plane, 3D GNR polymers reveal the ultra-stretchability of up to 2.66-times the original length with high axial strength up to 52 GPa. As shown in Fig. 3, we compare the tensile behavior along the  $z$ -axis of 3D GNR polymers with common metals and ceramics. The ideal tensile strains of common metals and ceramics are usually less than 0.3, while 3D GNR polymers can endure a large tensile deformation with strain more than 1.3. These critical strain values can exceed diamond by a factor of >10 and graphene by a factor of >5.2 depending on the direction. This is mainly due to the expansion of nanoribbon wrinkles during tension (Fig. 3b). Interestingly, the stress–strain curve of 3D GNR polymer (3,5) demonstrates the characteristics of an elastomeric rubber during tension, whose stress–strain is nonmonotonic and the strain returns to zero once the stress is removed,<sup>45</sup> rather than that of brittle diamond (Fig. 3c). 3D GNR polymer (3,5) has the tensile strength of 52 GPa comparable to that of hard SiC and Al<sub>2</sub>O<sub>3</sub>, but with >12 times larger strain. As the ribbon width increasing, the tensile strains of 3D GNR

polymers decrease a little, but the tensile strengths decrease much more. For example, the 3D GNR polymer (9,11) has a high tensile strain of 1.35, and tensile strength of 15 GPa, which is similar to that of SiO<sub>2</sub>.

The change of Poisson's ratio of 3D GNR polymers during tension shows strong anisotropy. As shown in Fig. 3c, the  $z$ -axis Poisson's ratio of 3D GNR polymer (3,5) decreases when the  $x$ -axis stretched, and the Poisson's ratios drop to a negative value at a strain over 0.15 along the  $x$ -axis. This means that the  $z$ -axis would be also expanded when stretching the  $x$ -axis, similar to auxetic materials.<sup>46</sup> On the other hand, when  $z$ -axis is stretched, the Poisson's ratios of  $x$ -axis fluctuate in the range of 0.04–0.08, which approach that of cork (almost zero). There are two saddle points in the Poisson's ratio at strains of 0.49 and 0.94, respectively.

### Band structures of new 3D $sp^2$ carbons

Considering the full  $sp^2$  hybridization, the 3D GNR polymers are expected to have distinct and combined electronic properties of graphite and graphene. 3D GNR polymer (3,5) has a graphene-like Dirac cone with linear valence and conduction bands joined in a single point  $X_A$  of the Brillouin zone around the Fermi level, which is as yet firstly proposed 3D  $sp^2$  carbon with 2D graphene-like Dirac cone (Fig. 4a). The Fermi velocity of 3D GNR polymer (3,5) is estimated by the slope of the energy band. The slope of band in the  $k_y$  direction is ±25.2 eVÅ, equivalent to a Fermi velocity  $v_y = 0.61 \times 10^6$  m/s. While in the  $k_x$  direction, the Dirac cone is asymmetric with non-equivalent band slopes of 17.6 eVÅ ( $v_x = 0.42 \times 10^6$  m/s) and -28.5 eVÅ ( $v_x = 0.57 \times 10^6$  m/s), respectively. The Fermi velocity of 3D GNR polymer (3,5) is comparable to that of graphene ( $v = 0.82 \times 10^6$  m/s) when approaching a Dirac point along the  $\Gamma$ -K line.<sup>47</sup> 3D GNR polymers (3,3), (5,5), (7,7), (9,9), (5,7), (7,9), and (9,11) show metallic properties including certain characteristics of graphene-like linear dispersion (Figs. 4b and S2†). In addition, the smallest zigzag-edged 3D GNR polymer (2,2), initially proposed as one of the boron nitride allotropes,<sup>48</sup> recently has been computationally proven to be a novel topological node-line semimetal with a single nodal ring.<sup>49</sup> All in all, these 3D GNR polymers have a variety of intriguing electronic properties, covering those of graphene and graphite.

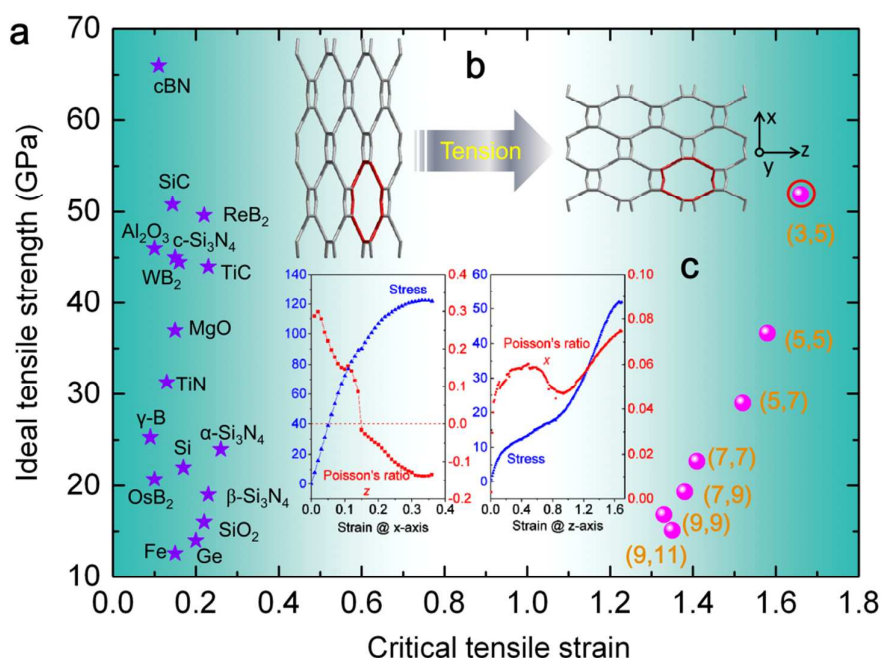
### A possible synthesis route of new 3D $sp^2$ carbons

Considering the structural similarities between GNR and 3D GNR polymers, we proposed a possible reaction pathway of edge-functionalized GNR arrays (H-GNR and Br-GNR) to form 3D GNR polymers (Figs. 5 and S3†) by the inspiration of the previous bottom-up production process of atomically precise GNRs,<sup>50</sup> where 10,10'-dibromo-9,9'-bianthryl monomers are assembled into GNRs through debromination (e-h in Fig. S3†) and dehydrogenation (i-n in Fig. S3†). Notably, during the bottom-up process, the dehalogenated intermediates are hand-in-hand linked with carbon bonds to form a class of non-coplanar hydrogenated linear polymers with full  $sp^2$  bonding<sup>50</sup> (i-k in Fig. S3†). This type of  $sp^2$

linear carbon polymers can cause people's imagination to use them as possible basic units for further 3D assembly.

Also, it is well-known that the electronic structures of GNRs can be further tailored based on edge termination engineering, that is,

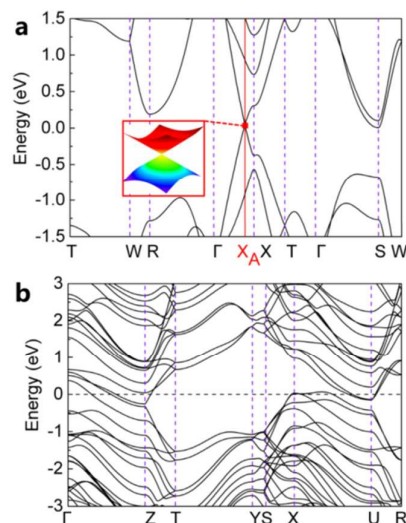
the edge-functionalized GNRs with atomic or functional-group terminations such as H, Cl, Br, OH, and SH.<sup>51</sup> Since the functional-groups (Cl, Br, OH, and SH) terminated GNRs have ripple-like edges with staggered functional groups, they are also a class of superior



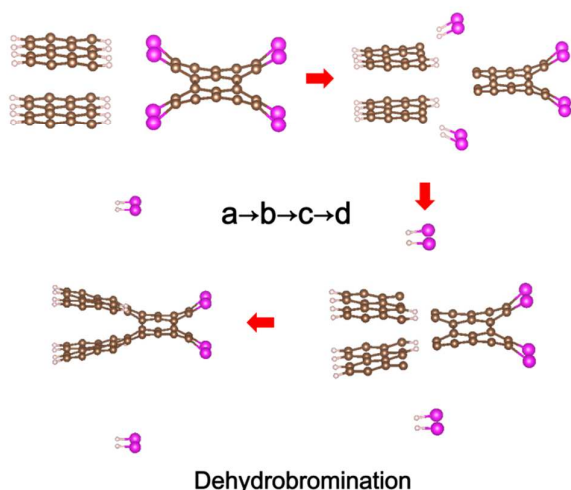
**Fig. 3** Ideal tensile strength and strain. (a) Critical tensile strength and tensile strain of 3D GNR polymers along the z-axis compared with these of common metals and ceramics. 3D GNR polymer (3,5) has a high tensile strength of 52 GPa comparable to that of ceramic materials such as SiC and Al<sub>2</sub>O<sub>3</sub>, but reveals the rubber-like ultra-stretchability of up to 2.66-times the original length. (b) Crystal structure changes of 3D GNR polymer (3,5) under tension along z-axis. (c) Simulated *in-situ* stress-strain and Poisson's ratio-strain curves of 3D GNR polymer (3,5) showing peculiar tensile-induced negative Poisson's ratio.

natural precursors for 2D or 3D assembly by functional-group polymerization. Furthermore, considering that specific nanoarchitectures can be engineered by manipulating the molecular assembly,<sup>52</sup> it is promising to form 3D covalently bonded *sp*<sup>2</sup> carbons based on edge-functionalized GNR building blocks.

As shown in Fig. 5 (a-d), H-terminated GNRs (i.e., H-GNRs) have a flat plane, while Br-terminated GNRs (i.e., Br-GNRs) possess innate "up and down" ripple-like edges originating from the repulsion of neighboring Br atoms.<sup>51</sup> Through the dehydrobromination procedure, the arranged H-GNR and Br-GNR arrays are expected to be seamlessly stitched into *sp*<sup>2</sup> GNR polymer fragments, and then topologically expand to 3D covalently buckled polymers with *sp*<sup>2</sup> hybridization. The calculations of reaction energy barrier (Fig. S3†) indicates that the dehydrobromination progress of edge-functionalized GNRs to form GNR polymer fragment has a moderate energy barrier between those of debromination and dehydrogenation procedures both taking place in bottom-up GNR synthesis,<sup>50</sup> which means feasible reaction to get full *sp*<sup>2</sup> carbons, i.e. polymerized GNR architectures. Herein we mainly emphasize the possible design strategy to form the GNR polymers. Our current polymers are composed of armchair-edged GNRs, and the similar design may also be extended to the zigzag-edged 3D GNR polymers.



**Fig. 4** Electronic band structures of 3D GNR polymers. (a) Band structure of 3D GNR polymer (3,5) with 2D graphene-like Dirac cone at X<sub>A</sub> point. The inset is the simulated Dirac cone in a 3D band structure. (b) Band structure of 3D GNR polymer (9,9) showing metallic properties. More distinct electronic properties of various 3D GNR polymers are shown in Fig. S2†.



**Fig. 5** Dehydrobromination to form GNR polymer fragment from H-GNR (left in a) and Br-GNR (right in a) arrays (a–d). The brown, magenta, and light pink spheres represent carbon, bromine, and hydrogen atoms, respectively.

## Theoretical

First-principles calculations on structural relaxation and predictions of mechanical properties (including elastic constants, Young's modulus, bulk modulus, shear modulus, tensile strength) were carried out using DFT as implemented in the CASTEP code.<sup>53</sup> The Vanderbilt ultrasoft pseudopotential<sup>53</sup> was employed with the tested energy cutoff 310 eV of the plane wave basis. The electron-electron exchange interaction was described by the LDA exchange-correlation functional of Ceperley and Alder as parameterized by Perdew and Zunger (CA-PZ).<sup>54,55</sup> A  $k$ -point separation of  $2\pi \times 0.04 \text{ \AA}^{-1}$  was assigned to generate the  $k$ -point grid using the Monkhorst-Pack grid parameters.<sup>56</sup> Phonon dispersions were calculated using the Phonopy package<sup>57</sup> with the force constants calculated from VASP code.<sup>58</sup> Electronic band structures were further confirmed by the all-electron PAW method,<sup>59</sup> where  $2s^2 2p^2$  electrons were considered as the valence electrons of carbon atom, as implemented in the VASP code.<sup>58</sup> The Dirac cone is calculated around the Dirac point in a square of  $2\pi \times 0.018 \text{ \AA}^{-1}$  with  $60 \times 60$   $k$ -points. The fixed strain method was used to simulate the tensile strength.<sup>60–62</sup> In the aforementioned method, a fixed strain was applied step by step in the selected direction with the remaining structural parameters (*i.e.*, two lattice parameters and three angles) fully unconstrained until the stress tensors orthogonal to the applied stress were less than 0.02 GPa. Subsequently, a series of corresponding stresses were obtained to assess the tensile strength.

## Conclusions

We design a class of novel 3D  $sp^2$  covalently bonded carbons, named 3D GNR polymers. They are the energetically most stable  $sp^2$  carbons proposed thus far, approaching to the stability of graphite. Mechanically, they demonstrate the

unexpected combination of rubber-like ultra-stretchability, tensile-induced negative Poisson's ratio, high tensile strength along  $z$ -axis comparable to that of common ceramics, and high tensile strength along  $x$ - and  $y$ -axis comparable to those of graphene and graphite. Electronically, they show the variety of characteristics, such as graphene-like Dirac behaviour and graphite-like metallicity. The current design principle would stimulate the more effective synthesis of novel  $sp^2$  carbons with omnipotent properties.

## Conflicts of interest

There are no conflicts to declare.

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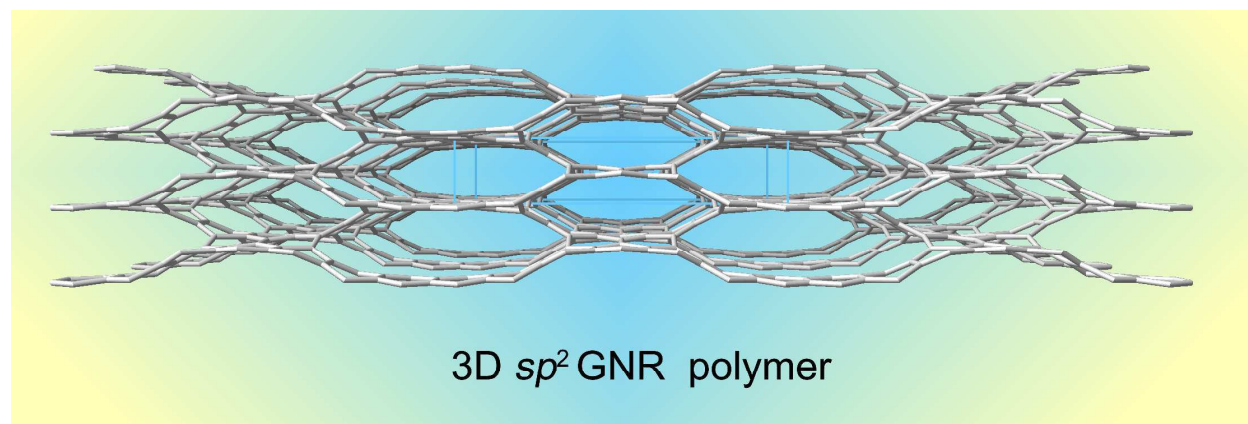
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## Table of Contents



Low-energy  $sp^2$ -carbons with metallicity and graphene-like Dirac cone, rubber-like ultra-stretchability, and negative Poisson's ratio, are theoretically designed from graphene nanoribbons.