

Tailored Synthesis of the Narrowest Zigzag Graphene Nanoribbon Structure by Compressing the Lithium Acetylide under High Temperature

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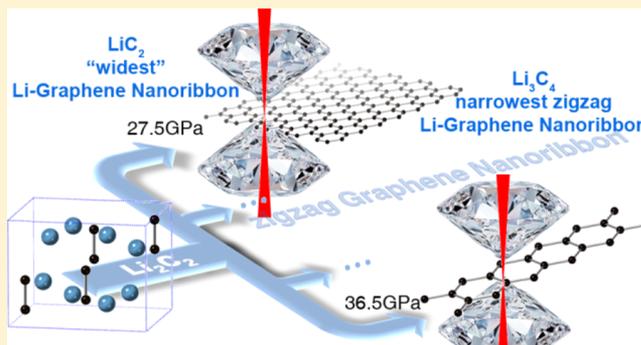
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Supporting Information

ABSTRACT: Scientists are searching for the goal-directed methods to synthesize graphene nanoribbons (GNRs) with a particular edge type and width, which determines their electronic transport properties. A series of Li zigzag GNRs (ZGNRs) with different widths were predicted under high pressure with a stoichiometric ratio of $\text{Li}_{n+1}\text{C}_{2n}$, which indicates a route to prepare ultranarrow GNRs. Here, with thermodynamics and ab initio Gibbs free-energy calculations by quasi-harmonic approximation, we investigated the phase stabilities of the Li GNR compounds under high pressure and high temperature. We have also identified Li graphenide LiC_2 ($n = \infty$) and Li polyacetylide Li_3C_4 ($n = 2$) experimentally at the predicted pressure and temperature conditions using in situ X-ray diffraction, which can be recognized as the two end members of $\text{Li}_{n+1}\text{C}_{2n}$ with the widest and narrowest ZGNR structures. High temperature and the temperature gradient increased the degree of polymerization and facilitated the formation of wider GNR or carbon slices. This suggests that by controlling temperature and pressure, we may get ultranarrow Li ZGNRs composed of a limited number of parallel carbon chains, such as 3- or 4-zigzag GNR, which is ready to be protonated or functionalized to form atomically ordered ZGNRs.



INTRODUCTION

Graphene nanoribbons (GNRs), defined as strips of graphene, exhibit exceptional electronic, optical, and magnetic properties.^{1–3} The quantum confinement nature of GNRs offers tunable band gaps, which can be modified by the width and edge structure (zigzag, armchair, or mixed).^{4,5} Among the GNRs, the ultranarrow GNRs, constructed by several parallel carbon chains, have band gaps comparable to typical semiconductors and have potential applications in high-performance field-effect transistors.^{6–9} Currently, the ultranarrow GNRs can only be controllably synthesized by “bottom-up” chemical methods, instead of “top-down” methods such as cutting and unzipping the graphite or carbon nanotubes.^{10–12} The “bottom-up” approach can control and modify the width and edge structure at the atomic scale, and the typical reaction is an aryl–aryl coupling, followed by cyclodehydrogenation.¹³ However, such reactions are severely limited by the solubility of oligophenylene, as well as the reactivity and regioselectivity.^{14–17} Only appropriate precursors

can scalably react to produce GNRs and their products are typically armchair GNRs or coved zigzag GNRs (ZGNRs), as reviewed in the literature.^{18,19} For ideal ZGNRs, there are very few examples, including the 6-ZGNR constructed by six zigzag chains²⁰ and 2-ZGNR (polyacenes).^{21–23} As the narrowest ZGNR, polyacene is even more difficult to be synthesized, and the longest pure polyacene is heptacene ([7]ac).²¹ Even if including those stabilized by the matrix or surface, the longest polyacene has only 11 hexagonal rings (undecacene, [11]ac).²⁴ Because the electronic properties of ultranarrow ZGNRs are significantly affected by the edge states, precise synthesis with clean, easily modified, and designed edges is of great interest, and the synthesis techniques still need to be developed.

Carbide is recognized as an important precursor to synthesize novel carbon allotropes, such as graphene, nano-

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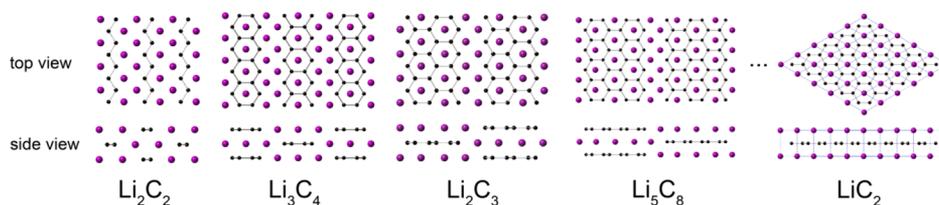


Figure 1. Predicted crystal structures of $\text{Li}_{n+1}\text{C}_{2n}$ ($n = 1, 2, \dots$). The black and purple spheres represent the carbon and lithium atoms, respectively.

tubes, and nanodiamonds.²⁵ Inspired by several successful synthesized silicon and germanium allotropes from the metal silicide or germanide,²⁶ pure novel carbon allotropes can be expected after leaching the metal atoms from specific metal carbides. Theoretically, carbon atoms in metal carbides can form a chain, ribbon, graphene sheet, and three-dimensional structure under high pressure.^{27–30} Among these, several lithium ZGNRs were predicted, such as Li_2C_2 (ribbon, *Cmcm*), Li_3C_4 , and Li_2C_3 (Li_4C_6).²⁹ These compounds have a common structural feature, that is, carbon ribbon constructed by antiphase parallel zigzag chains. On this basis, a broad range of compounds which have a general formula $\text{Li}_{n+1}\text{C}_{2n}$ ($n = 1, 2, \dots$) can be proposed (Figure 1). For example, Li_2C_2 (chain), Li_3C_4 , and Li_2C_3 contain 1, 2, and 3 chains, respectively (Figure 1). These ZGNRs are stacked perpendicularly to their planes, with Li sandwiched between two six-membered rings of neighboring ribbons and between the two half-rings on the edges (Figure 1).

Thus, following this rule, we can expect zigzag ribbon structures with any width, from a chain ($n = 1$) to sheet ($n = \infty$), which in principle have infinite length and identical edges. In our previous study, some polycarbide anions were identified when compressing Li_2C_2 into an amorphous state under room temperature.³¹ To obtain the predicted crystalline samples with regular ZGNRs, multidimensional pressure–temperature–composition space needs to be explored theoretically in advance. So far, all theoretical high-pressure investigations have been conducted at zero temperature, ignoring the temperature effects.^{27–30} Actually, the temperature not only determines the TS term where T is the temperature and S is the entropy in Gibbs energy but also affects volumes (V) and energies (E), that is, E , TS , and PV (P represents the pressure) terms are coupled, which can affect the phase stability and chemical reactions. Here, we employed quasi-harmonic approximation (QHA) theoretical calculations and high-pressure high-temperature (HPHT) experiments to reveal the phase transition tendency of the Li–C system under high temperature and high pressure. Several successful examples show the correction and universality of QHA for the HPHT situation.^{32–34} The lithium graphenide LiC_2 and lithium polyacene Li_3C_4 (ZGNRs $n = \infty$ and 2, respectively) were predicted under HPHT and then confirmed by in situ X-ray diffraction (XRD). Our research indicates that HPHT synthesis is an effective method to construct an ultranarrow GNR structure with defined edges and widths.

■ COMPUTATIONAL AND EXPERIMENTAL METHODS

Structure relaxations were performed using density functional theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) functional³⁵ in the framework of the all-electron projector augmented wave (PAW) method,³⁶ as implemented in the VASP code.³⁷ We used a plane-wave kinetic energy cutoff of

700 eV, and the Brillouin zone was sampled with a resolution of $2\pi \times 0.03 \text{ \AA}^{-1}$, which showed excellent convergence of the energy differences, stress tensors, and structural parameters.

The variable compound evolutionary algorithm USPEX,³⁸ used here for predicting new stable structures, searches for the lowest-enthalpy structures at a given pressure. Structure relaxations were performed using DFT within the PBE functional in the framework of the all-electron PAW method, as implemented in the VASP code. The first generation of structures was created randomly. All structures were relaxed at constant pressure and 0 K, and the enthalpy was used as fitness. The energetically worst structures (40%) were discarded and a new generation was created, 30% randomly and 70% from the lowest-enthalpy structures through heredity, lattice mutation, and transmutation. For the QHA calculation, phonon calculations were performed for all promising structures using the PHONOPY code.³⁹ The super cells of $3 \times 3 \times 3$, $2 \times 2 \times 2$, $2 \times 2 \times 4$, $2 \times 2 \times 2$, $1 \times 3 \times 4$, $3 \times 3 \times 2$, $2 \times 3 \times 1$, and $4 \times 4 \times 3$ are used for C, Li_2C_2 , Li_2C_3 , Li_2C , Li_3C_4 , Li_4C_3 , Li_5C_8 , and LiC_2 , respectively. Each structure is checked to have no imaginary phonon frequencies from 15 to 40 GPa. For each structure, phonons were computed at 31 different volumes to get the equilibrium volume and predict the Gibbs free energy. The Raman frequencies of the lithium carbides were calculated by vasp_raman pyvr at 27 GPa.⁴⁰

The Li_2C_2 sample was synthesized from the stoichiometric mixture of the Li metal and graphite powder, which was sealed inside a tantalum tube in a glovebox. The tube was then sealed inside an evacuated quartz tube and heated at 800 °C for 12 h. Phase analysis was performed by powder XRD on a Bruker D8 ADVANCE diffractometer (Cu $K\alpha$ radiation), and no significant impurities were detected (Figure S1). In situ HPHT XRD experiments were carried out at the 16-ID-B beamline at the Advanced Photon Source (APS), Argonne National Laboratory. A diamond anvil cell (DAC) with a diamond culet size of 300 μm in diameter was used to apply pressure. Tungsten gaskets were preindented to a thickness of 30 μm , and the center holes with 180 μm diameters were drilled to act as the sample chamber. Li_2C_2 powder was loaded in a glovebox, and Ar was loaded to improve thermal insulation and quasi-hydrostatic pressure conditions. Ruby fluorescence was used for pressure calibration.⁴¹ After Ar was loaded, the sample was checked using Raman spectroscopy and was proved to be Li_2C_2 .³¹ Then, it was compressed to 27.5 GPa for the HPHT experiments. Another DAC was prepared by using the above-described method and was compressed to 36.5 GPa for the HPHT experiments. To generate high temperatures, the samples were heated on both sides using an infrared laser. The temperature from each side was estimated by collecting the emitted thermal radiation, correcting for the optical system response and fitting the spectral data to Planck's equation. The temperatures used were recorded from the upstream side of the DAC. The X-ray patterns were collected during laser

heating using a CCD detector calibrated with a CeO_2 standard sample. The wavelength of the incident X-ray was 0.4066 Å. The preliminary data were reduced using the Dioptas program,⁴² and the background of the XRD patterns was subtracted. After the in situ XRD experiment, Raman spectra were measured at room temperature without changing the pressure. The wavelength of the incident laser is 488 nm.

RESULTS AND DISCUSSION

First, we used USPEX³⁸ to predict the thermodynamically stable Li–C phases and obtain the convex hull at 0 K under 27.5 and 36.5 GPa, respectively (Figure 2a,b), which is

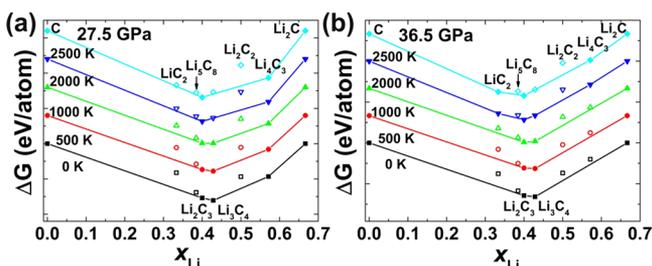


Figure 2. Convex hull of the Li–C system at (a) 27.5 and (b) 36.5 GPa at different temperatures, which are shifted by 0.08 eV/atom. The solid symbols represent thermal stable phases, that is, on the convex hull line. The open symbols represent metastable phases. The x_{Li} represents the atomic concentration of lithium in the compound Li_mC_n , which is defined as $x_{\text{Li}} = m/m + n$.

consistent with the literature.²⁹ Li_2C_3 and Li_3C_4 are predicted to be stable at 27.5 and 36.5 GPa, respectively, at 0 K, and Li_4C_3 is stable at 27.5 GPa. Their crystal structures and phonon spectra are also presented in Table S1 and Figure S2, respectively, with no imaginary frequency discovered. Then, we used the QHA method to study the Gibbs free energies of all candidate phases including C, LiC_2 , Li_2C_3 , Li_3C_4 , Li_2C_2 , Li_4C_3 , and $\text{Li}_6\text{C}_3(\text{Li}_2\text{C})$, to evaluate their thermodynamic stabilities at HPHT. As shown in Figure 2, both the convex hulls at 27.5 and 36.5 GPa vary significantly from 0 to 2500 K. With increasing temperature, LiC_2 becomes more stable, whereas Li_3C_4 is less stable.

On the basis of Gibbs free energies calculated under HPHT, we summarize the phase diagram of the carbon-rich phases, LiC_2 , Li_3C_4 , and Li_2C_3 , in Figure 3. Li_2C_3 is predicted to be stable in the whole investigated area. LiC_2 becomes thermodynamically stable at HPHT. The transition temperature to LiC_2 is 2334 K at 29 GPa and decreases to 1410 K at 40 GPa. Li_3C_4 (Li polyacene) will decompose at high temperature. The decomposition temperature is 1516 K at 20 GPa and linearly increases to 2665 K at 40 GPa.

Thus, the two decomposition lines of LiC_2 and Li_3C_4 divide the phase diagram into four zones. At low temperature (zone IV), Li_3C_4 is stable and LiC_2 is decomposed, which is consistent with previous theoretical calculations.²⁹ At low pressure and high temperature (zone II), both Li_3C_4 and LiC_2 decompose. Under high pressure and intermediate temperature, Li_3C_4 and LiC_2 coexist (zone III). The last zone (zone I) is for intermediate pressure and high temperature, where Li_3C_4 decomposes and LiC_2 is stable. The QHA calculations suggest that high temperature promotes polymerization and stabilizes wider GNR or carbon slices.

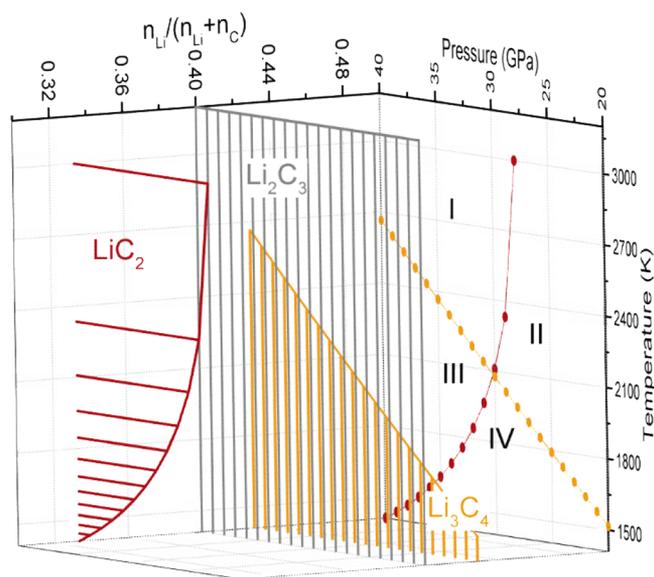


Figure 3. Calculated phase diagram of LiC_2 , Li_2C_3 , and Li_3C_4 by QHA. The red, gray, and orange shadings represent the thermodynamic stable P – T regions of LiC_2 , Li_2C_3 , and Li_3C_4 , respectively. The decomposition lines of LiC_2 and Li_3C_4 are projected on the P – T plane (red and orange line). The orange line represents the decomposition line of $6\text{Li}_3\text{C}_4 = 7\text{Li}_2\text{C}_3 + \text{Li}_4\text{C}_3$, whereas the red line represents the decomposition line of $2\text{LiC}_2 = \text{Li}_2\text{C}_3 + \text{C}$. In zones I and III, LiC_2 is stable, and in zones III and IV, Li_3C_4 is stable.

This phenomenon results from the structural features of these Li GNRs. For Li_3C_4 , carbon atoms are connected along the ribbon by C–C covalent bonds. In the other two directions perpendicular to the ribbon, the atoms are connected by the ionic interactions between the GNR and Li cations. For comparison, LiC_2 (Li graphenide) has a 2D covalent-bond sheet and ionic interaction between Li and the graphene sheet in the third direction.⁴³ Compared to ionic bonds, covalent bonds are harder to stretch with temperature, so LiC_2 has a smaller thermal expansion coefficient and a smaller volume increase at high temperature and becomes energetically favored under high pressure.

To confirm these predicted structures, we conducted in situ HPHT XRD experiments. Crystalline powder Li_2C_2 was compressed to 27.5 and 36.5 GPa, respectively, at room temperature and heated up (Figure 4a,b). As shown in Figure 4a, at 27.5 GPa and room temperature, most of Li_2C_2 transforms to the amorphous state, and only some residues are left (the blue arrows in Figure 4a). Most of the XRD peaks were ascribed to Ar and Li_2O (black and red arrows in Figure 4a). When heated up, several new peaks arose (represented by the asterisks) and indicated the formation of crystalline phase(s). By comparing the diffraction patterns collected under high temperature, we selected a pattern (1696 K) with sharp diffraction peaks and minor impurities. These diffraction peaks were indexed with a hexagonal $P6/mmm$ lattice, $a = b = 2.49193(13)$ Å and $c = 3.3823(2)$ Å. By performing a series of crystallographic analysis, the crystallized phase was determined as Li graphenide (LiC_2 , Figure 1), and the Rietveld refinement plot is shown in Figure 5a.

At 36.5 GPa, Li_2C_2 also experienced a similar process. New peaks (indicated by the asterisks in Figure 4b) gradually emerged above 1400 K and became stable when heated up to above 1800 K, which indicates a thermodynamic equilibrium.

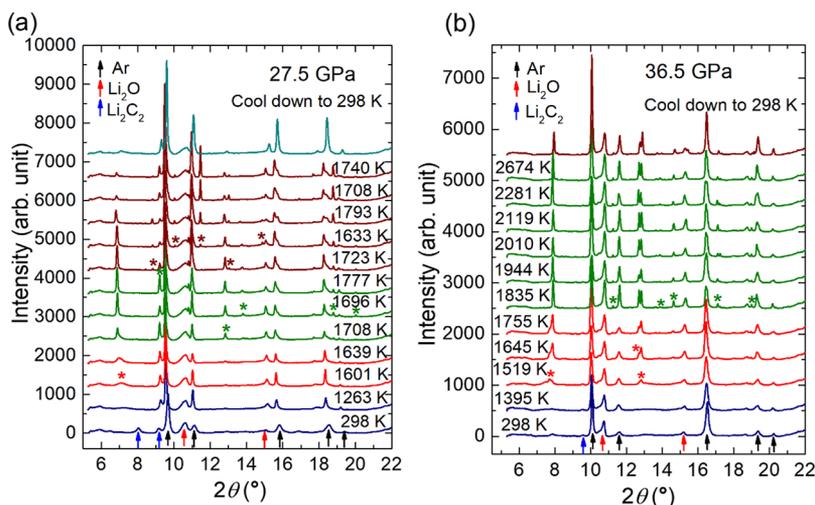


Figure 4. Selected in situ XRD patterns of Li_2C_2 under (a) 27.5 and (b) 36.5 GPa at high temperature. The wavelength of the incident X-ray is 0.4066 Å. The patterns are sequentially stacked up with increasing time and power. The asterisks (*) represent the new peaks. Ar is the pressure-transmitting medium, and Li_2O is the impurity introduced while loading Li_2C_2 into DAC.

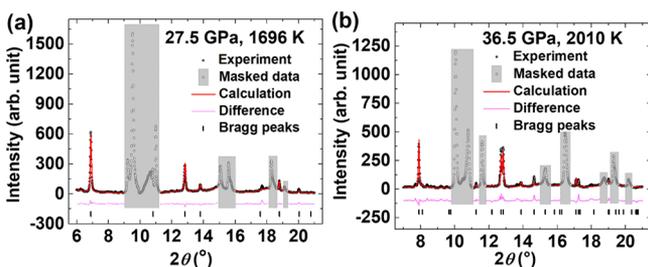


Figure 5. Rietveld refinement plots of (a) Li_2C_2 and (b) Li_3C_4 under 27.5 GPa, 1696 K and 36.5 GPa, 2010 K, respectively. The wavelength of the incident X-ray is 0.4066 Å. The peaks coming from Ar and Li_2O were masked.

After cooling down, the peaks are maintained, indicating that the new phase is stable at room temperature. By comparing the diffraction patterns to those of the predicted phases, we found that the predicted Li_3C_4 (*Immm*) phase fits the XRD pattern (36.5 GPa and 2010 K) very well.²⁹ The Rietveld refinement results are shown in Figure 5b, and the lattice parameters are $a = 11.4944$ Å, $b = 3.0525$ Å, and $c = 2.464$ Å. As shown in Figure 6a, the carbon atoms in Li_3C_4 polymerize into polyacene, the nanoribbon with two zigzag chains, which is referred to as the first-order structural unit. The Li cations are closely fitted between the (half) six-membered rings of neighboring ribbons, connecting the ribbons together and forming a second-order structural unit (the purple region in Figure 6a), which is neutral in charge. These Li cations form rectangular lattices as shown in the dashed line in Figure 6a. When the second-order structural units are stacked, the Li cations between the (half) six-membered rings are against the centers of the neighboring Li rectangles, that is, the negatively

charged secondary carbon is located on the edge of GNR. Actually, this Li–C (1.957 Å) distance is even shorter than the nearest Li–Li distance (2.301 Å) between the neighboring second-order units (Figure 6a), which is likely to result from significant electrostatic attraction and hence stabilizes the whole crystal.

Nominally, the C atom in Li_3C_4 has an oxidation state of 3/4 supposing Li keeps +1. Theoretical calculation shows that the carbon atoms on the edge and in the middle have Bader charges of -0.76 and -0.45 , respectively, whereas the Li atoms have Bader charges of $+0.81$. Li_3C_4 is predicted to be metallic with a conductive charged GNR, as shown in Figure 6b. The nonintegral oxidation state of carbon suggests an important rule under high pressure: effective stacking becomes more important compared to a traditional stoichiometry/integral oxidation state.

A metastable Li_2C_2 polyacene GNR phase was also predicted, as shown in Figure 7.²⁹ It has a similar second-order structural unit with Li_3C_4 , but with another layer of Li between them (indicated by the dashed circles in Figure 7), which may be responsible for the instability. Its fragment was identified when compressed under room temperature.³¹ By comparing the structural similarities of this Li_2C_2 and Li_3C_4 , we propose the following reaction process: C_2^{2-} in Li_2C_2 tends to polymerize under external pressure and forms ZGNR fragments in amorphous Li_2C_2 at room temperature. When heated up, the fragments start to connect to form ZGNRs, 1/4 of Li is excluded, and the Li GNRs are crystallized in the most energetically preferred structure, Li_3C_4 .

It is worth noting that the predicted Li_2C_3 was not observed in our experiment. From thermodynamic rules, when Li_3C_4 is thermodynamically stable, Li_2C_3 should not appear in the

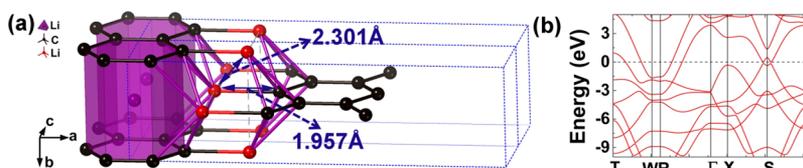


Figure 6. (a) Crystal and (b) band structure of Li_3C_4 .

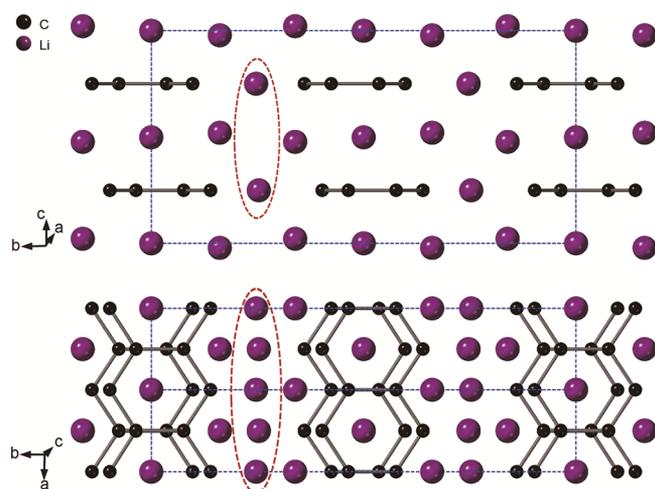


Figure 7. Crystal structure of Li_2C_2 - $Cmcm$ -ribbon phase.²⁹

sample with $\text{Li}/\text{C} = 1:1$. However, at 27.5 GPa, we observed LiC_2 , whose composition deviates even further away from 1:1. This is most likely due to compositional segregation. A significant amount of Li atoms may migrate outside the laser irradiation (and hence incident X-ray beam), and the composition left is carbon-rich. The possible reason of migration may include temperature and pressure gradient, which is still under investigation.

We also characterized the samples using Raman spectroscopy. The sample under 27.5 GPa does not show obvious features but high background (Figure 8). The sample under

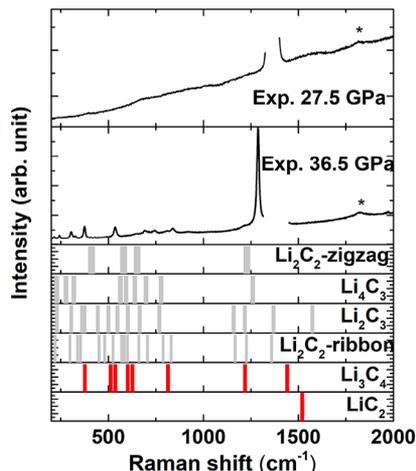


Figure 8. Raman spectra of the heated Li_2C_2 samples (LiC_2 and Li_3C_4) under high pressure. The Raman peak of the diamond is masked, and the peaks marked by asterisks are from the anvils.

36.5 GPa shows a series of peaks below 1300 cm^{-1} , with the strongest peak at $\sim 1288\text{ cm}^{-1}$. We calculated the Raman spectra of several lithium carbides and selected those with peaks in the range of $1200\text{--}1350\text{ cm}^{-1}$ for comparison. Most of these carbides are polycarbides with ribbon (Li_2C_2 ribbon, Li_3C_4 , Li_2C_3 , and LiC_2) or chain structures (Li_2C_2 zigzag, Li_4C_3), and this peak most likely indicates the ribbon structure. Among them, Li_3C_4 is the best candidate, though other phases cannot be excluded. This supports our discovery using in situ XRD. For LiC_2 , only one peak at 1520 cm^{-1} is predicted, and it

is not surprising that it was not observed because LiC_2 is metallic.

In the current experiment, we tested two P - T points and observed the two members of $\text{Li}_{n+1}\text{C}_{2n}$ with $n = 2$ and ∞ . We can expect more Li ZGNRs with various widths, by testing more points between 27.5 and 36.5 GPa and between 300 and 2200 K and by controlling the ratio of Li and carbon, temperature gradient, time, rate of heating, and so on. On one hand, the ZGNRs in $\text{Li}_{n+1}\text{C}_{2n}$ have identical edges. When lithium is removed, pure ultranarrow ZGNRs would be obtained. On the other hand, these Li GNRs have negative charges on the ribbons, which suggests that they are very good nucleophilic reagents and very easy to react with protic solvents including water and alcohol or other reagents with a positive charge. This will be a useful method to obtain a neutral ZGNR with controlled atomic width and will also be a method to synthesize functionalized GNRs.

In conclusion, we have theoretically predicted and experimentally synthesized two phases containing ZGNR structures, graphene compounds LiC_2 and polyacene Li_3C_4 by subjecting Li_2C_2 under HPHT conditions using the technique of laser-heated DAC. Their crystal structures under HPHT have been determined as closely packed ZGNR and Li^+ , in agreement with ab initio Gibbs free-energy calculation by QHA. On the basis of the calculation, several Li ZGNRs with a stoichiometric ratio of $\text{Li}_{n+1}\text{C}_{2n}$ have also been investigated, which are the intermediate phases between lithium polyacene Li_3C_4 and lithium graphenide LiC_2 . It is expected that with precise control of temperature and pressure, we can obtain lithium ZGNRs with an expected width, which will shed light on the “bottom-up” synthesis of ZGNRs with atomic ordering and a controlled width.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04081.

XRD pattern of synthesized Li_2C_2 raw material; phonon spectrum of Li_2C_3 and Li_3C_4 at 30 GPa; and crystal structures of the optimized Li_2C_2 , Li_3C_4 , and Li_2C_3 phases (PDF)

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X.D. and L.W. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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