Auxetic Tetrahex Carbon with Ultrahigh Strength and a Direct Band Gap

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Tetrahex carbon is a recently predicted two-dimensional (2D) carbon allotrope that is composed of tetragonal and hexagonal rings. Unlike flat graphene, this new 2D carbon structure is buckled and possesses a direct band gap of approximately 2.6 eV and a high carrier mobility of approximately $10^4$ cm$^2$/V s with anisotropic features. In this work, we employ first-principles density-functional theory calculations to explore the mechanical properties of tetrahex C under uniaxial tensile strain. We find that tetrahex C demonstrates ultrahigh ideal strength, outperforming both graphene and pentagraphene. It shows superior ductility and sustains uniaxial tensile strain up to 20% (16%) until phonon instability occurs and the corresponding maximal strength is 38.3 N/m (37.8 N/m) in the zigzag (armchair) direction. It shows an intrinsically negative Poisson ratio. This exotic in-plane Poisson ratio takes place when the axial strain reaches a threshold value of 7% (5%) in the zigzag (armchair) direction. We also find that tetrahex C maintains a direct band gap of 2.64 eV at the center of the Brillouin zone. This direct-gap feature remains intact upon strain application, with no direct-indirect gap transition. The ultrahigh ideal strength, the negative Poisson ratio, and the integrity of the direct gap under strain in tetrahex C suggest that it may have potential applications in nanomechanics and nanoelectronics.

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I. INTRODUCTION

The successful fabrication of two-dimensional (2D) materials such as graphene [1–3], transition-metal dichalcogenides (TMDs) [4–7], and phosphorene [8,9] triggers tremendous interest with regard to materials research in 2D structures. Graphene has been considered as a promising material for many advanced applications in future electronics [1–3]. However, the intrinsically zero band gap in graphene limits its application in electronic devices. Many other 2D allotropes of carbon have been proposed, for example, $S$ graphene [10], $T$ graphene [11], various phases of carbon sheets [12,13], and $\alpha$, $\beta$, and $\delta$ graphynes [14,15]. Pentagraphene [16] composed of only carbon pentagons was theoretically predicted a few years ago and has drawn plenty of research attention due to its unique mechanical and electronic properties, such as its high strength and quasidirect band gap. Based on pentagraphene, Ram and Mizuseki [17] applied the Stone-Wales transformation [18] to generate a new 2D carbon allotrope that consists of tetragonal and hexagonal rings. This new structure, tetrahex C, shows slightly lower energy than pentagraphene, implying a larger chance of its being fabricated in reality. Exceptionally, it shows a direct band gap of 2.6 eV with a high electron mobility of approximately $10^4$ cm$^2$/V s [17]. It has also been reported that one-dimensional nanoribbons generated from this 2D tetrahex-C sheet have remarkable electronic and magnetic properties, depending on the chirality, width, and edge reconstruction [19].

The carbon family, such as diamond, graphene, and carbon nanotubes, has a reputation for excellent mechanical properties in terms of extraordinary strength and enormous Young’s modulus. It is of interest to evaluate the mechanical properties in this new tetrahex-C structure. We find that this material exhibits an ultrahigh ideal strength, outperforming both graphene and pentagaphrene. Remarkably, it also demonstrates an intrinsically negative Poisson ratio.

Monolayer semiconducting TMDs ($MX_2$; $M = Mo, W$ and $X = S, Se, Te$) and phosphorene possess a significant advantage over graphene in that they exhibit a direct band gap that is appropriate for applications in optoelectronic devices. However, these materials experience direct-to-indirect band-gap transition upon strain application. For example, 2D MoS$_2$ and WS$_2$ undergo direct-to-indirect band-gap transition with a moderate uniaxial strain of approximately 2% [20–22]. MoSe$_2$ and WSe$_2$ sustain slightly higher strain up to approximately 6%, until the indirect-gap transition [21]. Phosphorene experiences direct-to-indirect band-gap transition at 8% axial strain.
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We find that tetrahex C retains the integrity of its direct gap within the entire range of strain application up to 20% (16%) in the zigzag (armchair) direction.

II. COMPUTATIONAL METHODS

The first-principles density-functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP) with projector-augmented wave (PAW) potentials. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is chosen for general electronic structure calculations and geometry relaxation. The hybrid Heyd-Scuseria-Ernzerhof (HSE)06 method is used to calculate electronic band structures. Since the exchange-correlation functional in the HSE method uses a mixing parameter to incorporate Hartree-Fock (HF) exact exchange and the PBE functional, it yields a better prediction on the band gap of semiconductors. In this study, the fraction of the HF exchange is set to be the default value of 0.25.

The wave functions of the valence electrons are described using the plane-wave basis set. The reciprocal space is meshed using the Monkhorst-Pack method. A kinetic energy cutoff of 900 eV for the basis set and a $15 \times 13 \times 1$ mesh for the reciprocal space are chosen in the geometry-relaxation and force-field calculations. The energy-convergence criterion for electronic iterations is set to be $10^{-6}$ eV and the force is converged within 0.001 eV/A, with an energy criterion of $10^{-5}$ eV for geometric optimization of the unit cell. A kinetic energy cutoff of 500 eV for the plane-wave basis set is used for the HSE band-structure calculations. In the band structure, $11k$ points are collected along each high-symmetry line in the reciprocal space. The $z$ vector of the unit cell is set to be 20 Å to ensure that sufficient vacuum space is included in the calculations to minimize the interaction between the system and its replicas from the periodic boundary condition. The phonon frequencies are calculated using a supercell approach in the PHONOPY code, with the forces computed using VASP.

The initial structure of tetrahex C is constructed according to Ref. [17]. Unlike flat graphene, this 2D carbon network is buckled and composed of tetragonal and hexagonal rings as shown in Fig. 1. The unit cell contains 12 carbon atoms, which are either $sp^2$ or $sp^3$ hybridized at a ratio of 2:1. The $sp^3$-hybridized carbon is sandwiched between two layers of $sp^2$-bonded atoms.

Starting with the fully relaxed tetrahex-C structure, uniaxial tensile strain up to 40% at an increment of 1% is applied in either the $x$ (zigzag) or the $y$ (armchair) direction to explore its strain-stress relation and determine the ideal strength (the highest strength of a crystal at 0 K) and the critical strain (at which the ideal strength is reached) [23]. The tensile strain is defined as

$$\varepsilon = \frac{a - a_0}{a_0} \quad (1)$$

where $a$ and $a_0$ are the lattice constants of the strained and the relaxed structure, respectively. With strain applied in one direction, the lattice constant in the transverse direction is fully relaxed through minimization of the total energy to ensure no stress in the transverse direction. According to Eq. (1), the response strain in the transverse direction can be also calculated.

The Poisson ratio is defined as

$$v = \frac{\varepsilon_{\text{transverse}}}{\varepsilon_{\text{axial}}}, \quad v_{xy} = -\frac{\varepsilon_y}{\varepsilon_x}, \quad v_{yx} = -\frac{\varepsilon_x}{\varepsilon_y}, \quad (2)$$

where $\varepsilon_{\text{axial}}$ and $\varepsilon_{\text{transverse}}$ are the applied axial strain and its response strain in the transverse direction, respectively. In order to depict the nonlinear lattice response for finite strain, the Poisson ratio is usually calculated using the finite-difference method, as [35–37]

$$v = -\frac{d \varepsilon_{\text{transverse}}}{d \varepsilon_{\text{axial}}}. \quad (3)$$

FIG. 1. (a),(b) Snapshots of buckled tetrahex C. The dashed rectangle represents a conventional cell. The $sp^2$- and $sp^3$-hybridized carbon atoms are in black and orange, respectively. (c) The schematics of the uniaxial strain in the zigzag (top) and armchair (bottom) directions, respectively.
In our numerical calculations, the Poisson ratio is computed using the central finite-difference method, as [36]

\[ v_{xy} = -\frac{\epsilon_x^{j+1} - \epsilon_y^{j-1}}{\epsilon_x^{j+1} - \epsilon_x^{j-1}}, \quad v_{yx} = -\frac{\epsilon_y^{j+1} - \epsilon_y^{j-1}}{\epsilon_y^{j+1} - \epsilon_y^{j-1}}, \]

where the integer \( j \) represents the strain increment number.

The strain-stress relation is calculated using the method described in Refs. [38,39], which has been designed for three-dimensional material. For a 2D system, the stress calculated from the DFT has to be adjusted, since the DFT-reported stress is largely underestimated due to the averaging force over vacuum space. To avoid this, in this work the stress adopts the force per unit length in units of N/m.

III. RESULTS AND DISCUSSION

A. Structural and mechanical properties

The lattice constants of the relaxed tetrahex C in our calculations are \( a = 4.531 \, \text{Å} \), \( b = 6.102 \, \text{Å} \), and buckling thickness \( d = 1.163 \, \text{Å} \), which are in very good agreement with the literature [17]. Two distinct bond lengths, three bond angles, and the buckling thickness are denoted in Fig. 1(a). We obtain \( r_1 = 1.534 \, \text{Å}, r_2 = 1.338 \, \text{Å}, \alpha = 112.2^\circ, \beta = 123.9^\circ, \) and \( \gamma = 95.2^\circ \). As shown in Fig. 1, two neighboring hexagonal rings along the \( x \) axis are not coplanar; the dihedral angle, denoted as \( \phi_{1234} \), is determined by the neighboring atoms 1-2-3-4, and our calculated \( \phi_{1234} = 125.6^\circ \). The dihedral angle between two neighboring hexagonal and tetragonal shapes, \( \phi_{2345} = 137.4^\circ \).

Uniaxial tensile strain is applied to tetrahex C with increments of 1% up to 40%. The obtained strain-stress relation is presented in Fig. 2(a). The material is torn apart with 40% (33%) strain loaded in the \( x \) (\( y \)) direction. The material is more ductile along the \( x \) (zigzag) axis compared to the \( y \) (armchair) direction. To check the stability of tetrahex C under uniaxial tensile strain, the phonon spectrum of the strained structure is calculated. We find that phonon instability occurs near the center of the Brillouin zone, when the strain goes beyond 20% (16%) in the \( x \) (\( y \)) direction. This leads to the ideal strength of tetrahex C being 38.3 N/m and 37.8 N/m in the \( x \) and \( y \) directions, respectively. This ultrahigh strength outperforms that of pentagraphene, which shows 23.5 N/m strength with 18% uniaxial strain in both the zigzag and armchair directions [40]. It is comparable to that of graphene, i.e., 36.7 N/m (40.4 N/m) in the zigzag (armchair) direction, with phonon instability occurring at a strain of 19.4% (26.6%) [34]. We recalculate the strain-stress relation of graphene using the exact same parameters in this work and obtain an ideal strength of 34.4 N/m (38.0 N/m) in the zigzag (armchair) direction. To further test the robustness of our results as predicted from the PBE functional, we use two additional functionals, PBESol [41] and DFT-D3 [42], both of which provide an improved description of the solids. These two functionals predict the same strain-stress relation as presented in Fig. 2(a).

The response strain in the transverse direction and the Poisson ratio in tetrahex C are presented in Fig. 2(b). Tetrahex C shows an intrinsically in-plane negative Poisson ratio when the strain goes beyond a threshold value, which is 7% (5%) in the \( x \) (\( y \)) direction. It is found that the Poisson ratio is in the range of \(-0.081\) to \(+0.043\) for uniaxial strain up to 20% in the zigzag direction. Similarly, the value is between \(-0.127\) and \(+0.036\) when strain up to 16% is applied in the armchair direction. The Poisson ratio clearly demonstrates the anisotropic features of tetrahex C.

To explore the mechanism of the intrinsically negative Poisson ratio, we investigate the variation of the structural...
geometries and electronic band structures with respect to the strain. The structure geometries of relaxed and strained tetrahex C are compared and the structural change is presented in Fig. 3 as evidence of a macroscopic view. The electronic level view, i.e., the band-structure variation with the strain, is presented in Sec. B.

The bond lengths $r_1, r_2$, the buckling thickness $d$, and the bond angles $\alpha, \beta, \gamma$ are denoted in Fig. 1. $\phi_{1234}$ is the dihedral angle of two neighboring hexagonal rings along the $x$ axis and $\phi_{2345}$ is the dihedral angle of neighboring tetragonal and hexagonal rings. The vertical axis in Fig. 3 gives the change of each quantity relative to its original value in the relaxed tetrahex C. From Fig. 3(a), it is clear that when the structure is under uniaxial strain in the zigzag direction, the leading extension factors are the bond length $r_1$ in Fig. 3(a) and bond angle $\gamma$ in Fig. 3(c), both of which show an 11% increase (for the case of $\varepsilon_x = 20\%$) compared to the relaxed structure. Note that the bond length $r_1$ involving a given $sp^3$ atom forms the four sides of the tetragonal shape and that they are all tilted from the $x$ axis with an apparent $y$ projection. Under the uniaxial strain applied in the $x$ direction, the expansion in $r_1$ necessarily results in the extension of lattice constant along the $y$ axis, leading to the negative Poisson ratio. On the other hand, for the case of strain in the armchair direction in Fig. 3(b), the primary change comes from the squeezing of the buckling thickness (13.5% down for the case of $\varepsilon_y = 16\%$), the lengthening of the bond lengths $r_2$ (8.2% increase) and $r_1$ (6% increase) as shown in Fig. 3(b), and the decrease of the bond angle $\alpha$ (down 10.9%) in Fig. 3(d). The squeezing of the buckling thickness $d$ and the lengthening of $r_1$ combined together act as the primary factors for the negative Poisson ratio.

To obtain other mechanical properties, including the elastic stiffness constants and moduli, the energy surface of tetrahex C is scanned in the small strain range $-0.6\% < \varepsilon_{xx} < +0.6\%$, $-0.6\% < \varepsilon_{yy} < +0.6\%$, and $-0.6\% < \varepsilon_{xy} < +0.6\%$. The strain energy is calculated as

$$E_s = E(\varepsilon) - E_0,$$

FIG. 3. The structural change of tetrahex C under uniaxial strain applied in the (a),(c),(e) zigzag and (b),(d),(f) armchair directions. (a),(b) The bond lengths, buckling thickness, (c),(d) bond angles, and (e),(f) dihedral angles are denoted in Fig. 1(a). The vertical axis represents the change relative to their original values in the relaxed structure.
where $E(\varepsilon)$ and $E_0$ are the total energies of the strained and relaxed systems, respectively. The obtained strain energy is then fitted using the following equation:

$$E_\varepsilon = a_1 \varepsilon_{xx}^2 + a_2 \varepsilon_{yy}^2 + a_3 \varepsilon_{xx} \varepsilon_{yy} + a_4 \varepsilon_{xy}^2. \quad (6)$$

The coefficients $a_i$ in Eq. (6) can be determined and the elastic stiffness constants can be calculated as

$$C_{ij} = \frac{1}{A_0} \frac{\partial E_\varepsilon}{\partial \varepsilon_{ij}}, \quad (7)$$

where $i,j = xx, yy$, or $xy$ and $A_0$ is the area of the simulation cell in the $x$-$y$ plane. The Young’s and shear moduli for a 2D system can be derived as a function of $a_i$ [23,43]:

$$E_x = \frac{4a_1a_2 - a_3^2}{2a_2A_0}, \quad E_y = \frac{4a_1a_2 - a_3^2}{2a_1A_0}, \quad G_{xy} = \frac{2a_4}{A_0}. \quad (8)$$

Our calculated elastic constants in tetrahex C are $C_{11} = 289$ N/m, $C_{12} = 15$ N/m, $C_{22} = 282$ N/m, and $C_{33} = 125$ N/m, which are in agreement with the literature [17]. The Young’s moduli are $E_x = 288$ N/m and $E_y = 281$ N/m in the zigzag and armchair directions, respectively, and the calculated shear modulus is $G_{xy} = 125$ N/m.

The Young’s and shear moduli along an arbitrary direction can be obtained as follows [23]:

$$\frac{1}{E_\psi} = S_{11} \cos^4 \psi + (2S_{12} + S_{66}) \cos^2 \psi \sin^2 \psi + S_{22} \sin^4 \psi, \quad (9)$$

$$\frac{1}{G_\psi} = S_{33}(\sin^4 \psi + \cos^4 \psi) + 4 \left( S_{11} - 2S_{12} + S_{22} - \frac{1}{2} S_{33} \right) \cos^2 \psi \sin^2 \psi, \quad (10)$$

where $\psi \in [0, 2\pi]$ is the angle of an arbitrary direction from the $+x$ axis and $E_\psi$ and $G_\psi$ are the Young’s and shear moduli along that direction, respectively. The $S_i$ are elastic compliance constants, which are correlated with the elastic stiffness constants:

$$S_{11} = \frac{C_{22}}{C_{11}C_{22} - C_{12}^2}, \quad S_{22} = \frac{C_{11}}{C_{11}C_{22} - C_{12}^2},$$

$$S_{12} = -\frac{C_{12}}{C_{11}C_{22} - C_{12}^2}, \quad S_{33} = \frac{1}{C_{33}}. \quad (11)$$

The direction dependence of the Young’s and shear moduli is presented in Fig. 4. The maximal Young’s modulus is along the $x$ (zigzag) direction, with a value of 288 N/m, whereas the minimal, 273 N/m is along the [11] direction. The average Young’s modulus over all directions is 279 N/m. However, it is the opposite for the shear modulus. The maximal and minimal shear moduli are along the [11] (135 N/m) and the $x$ ($y$) direction (125 N/m), respectively.

B. Electronic properties

Tetrahex C possesses a direct band gap at the center of the Brillouin zone [17]. Our calculations confirm this and the band structure is presented in Fig. 5(a), based on the hybrid HSE functional. Our calculated HSE band gap is 2.64 eV, close to the value of 2.63 eV reported in Ref. [17]. Under uniaxial tensile strain in the zigzag direction, the conduction-band minimum (CBM, i.e., state C) decreases, while the valence-band maximum (VBM, i.e., state B) increases with the strain, as shown in Figs. 5(a)–5(c), resulting in a band-gap reduction. The direct-gap feature at $\Gamma$ remains intact under uniaxial strain in the zigzag direction up to 20% (beyond 20%, the phonon spectrum suggests instability of the structure). On the other hand, under axial strain in the armchair direction, the band gap remains direct (or quasidirect) at $\Gamma$ until the strain reaches 16%, where phonon instability occurs.

A detailed analysis of the energy variation with strain for the states A-E (labeled in Fig. 5)—since they are near the edges of the conduction and valance bands, we refer them the near-edge states) reveals that the CBM remains at state C and VBM stays at state B under strain in the zigzag direction up to 20%. However, energy-state crossover takes place for the strain applied in the armchair direction. For example, at $\varepsilon_y = 12\%$ (16%), as shown in Figs. 5(e) and

FIG. 4. The directional dependence of the Young’s (blue dashed line) and shear (black solid line) moduli in tetrahex C.

FIG. 5. The band structure is presented in Fig. 5(a), based on the hybrid HSE functional. Our calculated HSE band gap is 2.64 eV, close to the value of 2.63 eV reported in Ref. [17]. Under uniaxial tensile strain in the zigzag direction, the conduction-band minimum (CBM, i.e., state C) decreases, while the valence-band maximum (VBM, i.e., state B) increases with the strain, as shown in Figs. 5(a)–5(c), resulting in a band-gap reduction. The direct-gap feature at $\Gamma$ remains intact under uniaxial strain in the zigzag direction up to 20% (beyond 20%, the phonon spectrum suggests instability of the structure). On the other hand, under axial strain in the armchair direction, the band gap remains direct (or quasidirect) at $\Gamma$ until the strain reaches 16%, where phonon instability occurs.
5(f), the CBM and VBM are no longer their original states C and B, respectively. Instead, state D (A) becomes the CBM (VBM). The energy of state D decreases rapidly with strain and has a lower value than that of state C at $\varepsilon_y = 12\%$ (16%). A similar situation occurs in the valence bands. The energy of state A increases with strain and exceeds that of state B, thus representing the VBM.

We also note that at $\varepsilon_y = 4\%$ (8%), the VBM shifts away slightly from $\Gamma$ toward X and the energy difference between the VBM and the $\Gamma$ point is only 0.03 eV (0.05 eV), leading to a quasirectangular band gap for tetrahex C in the strain range of 4%-9%. These results are consistent with those of Ref. [17], in which the band gap remains direct up to 16.4% of biaxial strain.

The HSE-predicted band gap as a function of the uniaxial strain in tetrahex C is presented in Fig. 6(a). We also test the general trends in Fig. 6(a) using other three density functionals, PBE [29], PBEsol [41], and DFT-D3 [42]. They all predict a similar trend as presented in Fig. 6(a), except that these three functionals report an underestimated band gap compared to that of the HSE method [30,31]. Unlike the straight decrease of the gap with strain in the $x$ direction, strain in the $y$ direction shows a rich tunability of the gap. To understand this behavior, we further plot the energy variation with strain of the near-edge states A-E in Figs. 6(b)–6(d). Figure 6(b) shows the CBM (state C) and VBM (state B) energy with strain $\varepsilon_x$. Both demonstrate relatively linear variation, which results in a reduction of the band gap with $\varepsilon_x$. However, for strain in the $y$ direction, as shown in Fig. 6(c), the VBM experiences an interesting shift from the original state B to state E (at approximately 5.4%) and then to state A (at approximately 9%) and the CBM moves from state C to state D at $\varepsilon_y = 10.6\%$.

The different energy-variation patterns of the states in Figs. 6(c) and 6(d) are related to their specific orbitals and bonding/antibonding characteristics. Figure 7 presents the electron-density contour plots of the near-edge states A–E. The wave-function character of each state is examined by projecting the wave function onto $s$, $p$, and $d$-orbitals at each ionic site. It is found that state A is contributed by $p_x$ orbitals, while all other states are dominated by $p_z$ orbitals. Examining the dominant $spd$ orbitals along with the phase factors of the wave function, one can determine the state’s bonding and antibonding characteristics along a specific direction. When strain is applied in that specific direction, the energy variation with strain of the state obeys the pattern schematically illustrated in Fig. 7(f) [44,45]. These schematics are derived from the Heitler-London exchange-energy model [46], in which the energies of the bonding and antibonding states are primarily different in terms of the exchange-correlation energy of electrons. The exchange-correlation energy is contributed from either nonclassical electron-electron (positive) or electron-ion interaction (negative), with the latter dominant for orbitals with nonlocalized electron density. Therefore, with an applied tensile strain and an increase of the bond lengths, the energy of the bonding states increases while that of the antibonding state decreases [44,45].
FIG. 6. (a) The HSE band gap as a function of the uniaxial strain, (b) the CBM and VBM energy variation with strain in the zigzag direction, together with the energy variation of (c) valence-band states A, B, and E, and (d) conduction-band states C and D under uniaxial strain in the armchair direction. For valence bands, the state B and E energy crossover occurs at 5.4% strain, the state A and E crossover at 9%, and the state A and B crossover at 7%. For conduction bands, the state C and D energy crossover occurs at 10.6% strain.

From Fig. 7, states A and E possess bonding orbitals along the y axis; therefore, their energies increase with strain. State D shows an antibonding nature along the y axis and its energy decreases with strain. State B, contributed by the 84% $p_z$ and 16% $p_y$ orbitals, shows a mixed nature, with a weak $p_z$ bonding and a strong $p_y$ antibonding character along the bond length $r_2$. The overall trend of its energy variation follows the antibonding pattern. State C is also a mixture, with 76% $p_z$, 19% $p_y$, and 5% $s$ orbitals, in which weak $p_z$ antibonding and strong $p_y$ bonding characteristics along the bond length $r_2$ result in an overall bonding behavior.

IV. SUMMARY

We conduct first-principles DFT calculations to investigate the mechanical and electronic properties of tetrahex C under uniaxial tensile strain along the zigzag and armchair directions, respectively. Tetrahex C shows ultrahigh strength, which outperforms both graphene and pentagraphene. It shows superior ductility and retains phonon stability with uniaxial tensile strain up to 20% (16%) in the zigzag (armchair) direction. This 2D carbon also demonstrates a tunable intrinsically negative Poisson ratio when the axial strain is beyond a threshold value of 7% (5%) in the zigzag (armchair) direction. This auxetic property is retained over a large strain range of 10%–20% (5%–16%) in the zigzag (armchair) direction. Tetrahex C has a direct band gap of 2.64 eV (HSE gap) at Γ. This direct-gap feature remains intact over the entire range of axial-strain application up to 20% (16%) in the zigzag (armchair) direction, until phonon instability occurs. The band gap is tunable in the range 1.68–2.97 eV with uniaxial strain. The ultrahigh strength, the negative Poisson ratio, and the direct band gap in tetrahex C imply potential applications in nanomechanics and nanoelectronics.

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