2D carbon sheets with negative Gaussian curvature assembled from pentagonal carbon nanoflakes

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Buckled Cario pattern

Fig. S1 Flat Cario pattern.

In Fig. S1, we show the 2D flat Cario pattern, within it the four-fold symmetry requires all pentagons must have 90° inner angles. When we have inner angle, α, larger than 90°, then the 2D space is not sufficient to accommodate these pentagons with 4α > 360° when put them together. As a result, a buckled 2D pattern is expected, and this is the reason why our CG₅₆₈ allotropes are highly curved.

Phonon spectra from empirical potential
To obtain phonon spectra, we need to first calculate harmonic interatomic force constants (IFCs). In our case, the structures are pretty large with hundreds of atoms per unit cell. Hence, we choose to calculate IFCs based on Tersoff empirical potential as complements to first principle results in Fig. 3b. Since all carbon atoms in CG568 structures share similar bonding features as graphene, with slight deviation from perfect $sp^2$ hybridization, we believe Tersoff potential, which is optimized to better reproduce the acoustic phonon frequencies and group velocities of graphene, could properly describe the bonding in our structures. Then the harmonic IFCs are calculated by finite displacement method in conjunction to LAMMPS package, and the phonon spectra are calculated by diagonalizing the dynamical matrix constructed from IFCs obtained. The results for three new carbon allotropes are presented in Fig. S2. It is clear that no imaginary phonon modes are observed for all three structures in the entire Brillouin zone.

**Tiny dip of acoustic phonon branch near $\Gamma$**

According to classical mechanics, a 2D material would have one particular transverse acoustic branch with quadratic dispersion near the $\Gamma$ point, which is pretty sensitive to numerical accuracy. Even for some stable 2D materials, acoustic modes with negative frequencies of small magnitude can appear due to numerical inaccuracies. Especially in our case, where cell size is pretty large and Brillouin zone is rather small, those phonon modes of tiny negative frequencies in Fig. 3 are actually of very small wave vector $k$ (very long wave length). In fact, such tiny dip of acoustic phonon branch near $\Gamma$ has been observed in other systems.$^{1-5}$

**Molecular Dynamics simulations**

![Figure S2: Phonon spectra of CG568-80, CG568-180 and CG568-320 calculated from Tersoff empirical potential.](image)
Fig. S3 Fluctuation of potential energy. (a) NVT FPMD simulation (1×1×1 unitcell), the inset is snapshot of structure at the end of simulation. (b) NVT MD based on Tersoff empirical potential (CG568-80: 5×5×1 supercell; CG568-180: 4×4×1 supercell; CG568-320: 3×3×1 supercell).

To understand the dynamical stability of our new carbon sheets, we carried out molecular dynamics (MD) simulations. In Fig. S3(a), we plot the fluctuation of potential energy of CG568-80 during FPMD simulations using VASP at alleviated temperature (1000 K) up to 10 ps. Clearly, the structure maintains its stability at the end of simulation.

Due to high computational cost, we can afford only the FPMD simulation of CG568-80 using its unit cell (~ 10 ps). Therefore, we launched MD calculations based on Tersoff empirical potential using LAMMPS with thousands of atoms as complements. In Fig. S3(b), we can see only random fluctuations of total potential energy around constant values demonstrating the stability of three structures at least at the empirical potential level.

Bond-length/angle and bond-length/angle variation distribution
Fig. S4 C-C bond-length $\angle$CCC bond-angle distribution in three allotropes.

Fig. S5 Bond-length and bond-angle variation distribution (each bond and angle is given an index number). Red line: magnitude of $\overline{\epsilon}$ and $\overline{\sigma}$; Red dash line: magnitude of $\sqrt{\epsilon^2}$ and $\sqrt{\sigma^2}$. 
$\overline{\epsilon} = \frac{1}{N} \sum_{i} |\epsilon_i|$, $\overline{\sigma} = \frac{1}{N} \sum_{i} |\sigma_i|$, $\sqrt{\epsilon^2} = \frac{1}{N} \sum_{i} \epsilon_i^2$, $\sqrt{\sigma^2} = \frac{1}{N} \sum_{i} \sigma_i^2$. $\epsilon_i$, $\sigma_i$: $i$-th bond-length variation; $\epsilon_i$, $\sigma_i$: $i$-th bond-angle variation, $N$ is the total number of bonds or angles.
**Effective Mass**

**Table S1** The locations of CBM and VBM in k-space.

<table>
<thead>
<tr>
<th>Allotropes</th>
<th>VBM</th>
<th>CBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG$_{568}$-80</td>
<td>(0.396, 0.0)</td>
<td>(0.208, 0.208)</td>
</tr>
<tr>
<td>CG$_{568}$-180</td>
<td>(0.0, 0.0)</td>
<td>(0.176, 0.176)</td>
</tr>
<tr>
<td>CG$_{568}$-320</td>
<td>(0.461, 0.0)</td>
<td>(0.346, 0.346)</td>
</tr>
</tbody>
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**Deformation potential constants**
Fig. S7 Band edge position shifts of VBM and CBM of under lattice dilation or compression of CG$_{568}$-80 (a), CG$_{568}$-180 (b) and CG$_{568}$-320 (c). $\Delta l$ refers to variation of lattice size, whereas $l_0$ refers to equilibrium lattice constant.

References