Supplementary Information for:

A New 3D Dirac Nodal-line Semimetallic Graphene Monolith for Lithium Ion Battery Anode Material

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SI Text

Text S1 The relationship between the band crossing point and time reversal and space inversion symmetries.

Neglecting the weak spin-orbit coupling, the band crossing point in HAGM-42 is fourfold degenerate, which is protected by the coexistence of time reversal and space inversion symmetries. If the required symmetry constraints are broken, the degeneracy will be destroyed and a band gap may open up. To verify this, we artificially break the time reversal and space inversion symmetries of HAGM-42, and calculate the corresponding electronic band structures. The time reversal symmetry is broken by doping HAGM-42 with Mn atoms as a magnetic impurity (see Fig. S4a). The resulting band structures, plotted in Fig. S4b, show that the spin up and down bands are split and the pristine four-fold degenerate band crossing point is decomposed to two two-fold degenerate points. In contrast, when the dopant is replaced with a nonmagnetic element like Li, the four-fold degenerate point still remains, as shown in Fig. S4c. To break the space inversion symmetry, we make a small movement for some atoms in HAGM-42, as shown in Fig. S5a, and calculate its electronic band structure. The results in Fig. S5b clearly show that a gap is opened up because of the breakage of space inversion.
symmetry.

**SI Table**

**Table S1**  Lattice parameters (a, b and c, in Å) for HZGM-42, diamond, and graphite calculated using different exchange-correction functionals.

<table>
<thead>
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<th>Methods</th>
<th>HZGM-42</th>
<th>Diamond</th>
<th>Graphite</th>
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<tr>
<td>PBE</td>
<td>a</td>
<td>16.82</td>
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<tr>
<td></td>
<td>b</td>
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<td>PBE-D2</td>
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**SI Figures**

**Fig. S1** Calculated total energy versus volume per atom for HZGM-42, graphite, diamond, T6, bct-C$_4$, IGN, bco-C$_{16}$, and Hex-C$_{18}$. 
Fig. S2 Total potential energy fluctuation during AIMD simulation at 1200 K of HZGM-42. The inset shows the atomic configurations (1×1×4 supercell for HZGM-42) at the end of AIMD simulations at 1200 K.

Fig. S3 (a) Band structure of HAGM-42 along the high symmetric path Γ/2→A. (b) and (c) Charge densities of P1 and P2 states, respectively. The isosurface value is 0.005 e/Å$^3$. 
Fig. S4 (a) Structure of Mn-doped HAGM-42. (b) and (c) Electronic band structures of Mn- and Li-doped HAGM-42, respectively.
**Fig. S5** (a) Illustration of atomic movement in HAGM-42, and (b) the resulting electronic band structure.

**Fig. S6** Electronic band structure of HZGM-42 calculated by using the HSE06 functional.
**Fig. S7** (a) Top and (b) side views of the optimized structure of HZGM-42 with a mono-vacancy at the sp$^3$ carbon site. A $1 \times 1 \times 4$ supercell is used.

**Fig. S8** (a) Three symmetry-inequivalent migration paths of Li diffusion considered along the z-direction around the mono-vacancy at the sp$^3$ carbon site. (b)-(d) Diffusion energy barrier profiles of the three diffusion paths displayed in (a).
**Fig. S9** (a) Top and (b) side views of the full Li-intercalated configuration of HZGM-42. The green, light blue and purple spheres represent lithium ion, $sp^2$-, and $sp^3$-hybridized carbon atoms, respectively.

**Fig. S10** Total potential energy fluctuation during AIMD simulation at 1200 K of HZGM-66. The inset shows the atomic configurations ($1\times1\times4$ supercell for HZGM-66) at the end of AIMD simulations at 1200 K.
Two elemental building motifs of HZGM phases, i.e. (a) the graphene nanoribbons with tunable width, and (b) the linkers composed of $sp^3$-hybridized carbon atoms. $N(1+2n)$ donates the width of the zigzag graphene nanoribbons. (c) Top and side views of HZGM-66 with $N = 3$. (d) Phonon band structure, (e) electronic band structure calculated by DFT-GGA/PBE (blue dashed lines) and the HSE06 hybrid functional (red solid lines), and (f) the orientation-dependent stress-strain relationships of HZGM-66.
**Fig. S12** (a) Top and side views of the possible Li absorption sites for HZGM-66. (b) Binding energies of the four configurations in (a). Configuration Li_{III} changes to Li_{II} after full geometry optimization. (c) Considered migration paths of Li diffusion and the corresponding diffusion energy barrier profiles.

**Fig. S13** (a) Top and (b) side views of the full Li-intercalated configuration of HZGM-66.