

Supporting Information

Ideal two-dimensional nodal-ring semimetal in tetragonal borophene oxide

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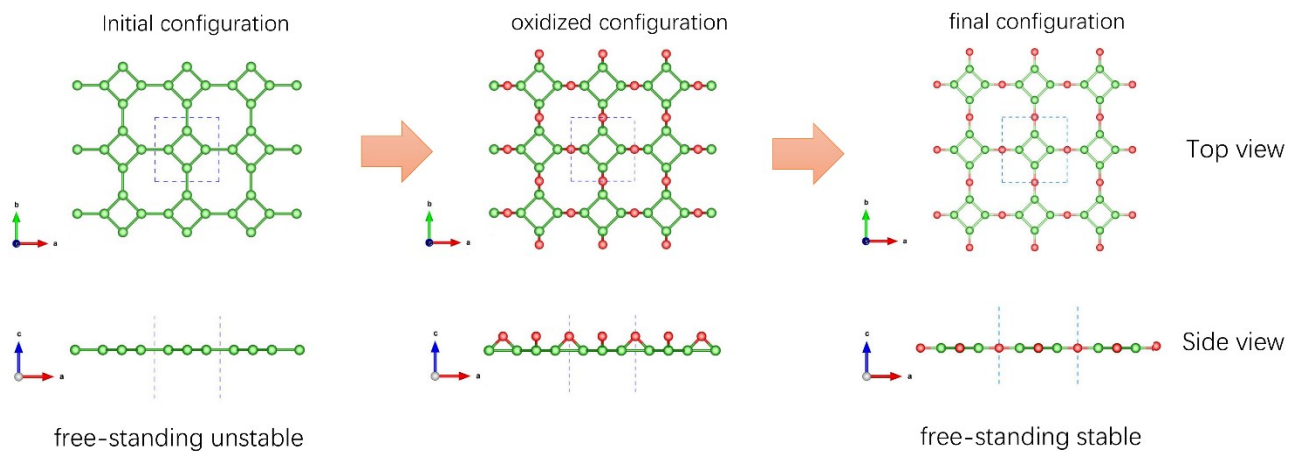


Figure S1. The procedure to acquire T-borophene oxide, *i.e.* t-B₂O, from T-borophene.

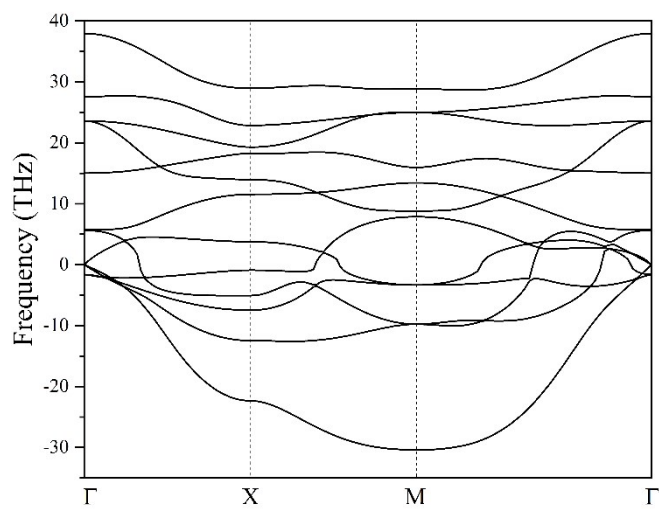


Figure S2. The phonon dispersion of free-standing T-borophene.

Supporting note: the discussion of formation energy and the realizability of t-B₂O on metal substrates

we calculated the formation energy of t-B₂O with formula
$$\Delta E = \frac{E(B_xO_y) - xE(B) - yE(O)}{x + y}$$
, where $E(B_xO_y)$ is the total energy of the material B_xO_y , and $E(B)$ and $E(O)$ are the energies per atom in the solid boron α -B₁₂ and oxygen molecule respectively. In combination with the value of ΔE in B₂O₃, which is the most stable bulk boron oxide in Material Project¹, we construct a simple energy convex hull for boron oxide (see Figure S3).

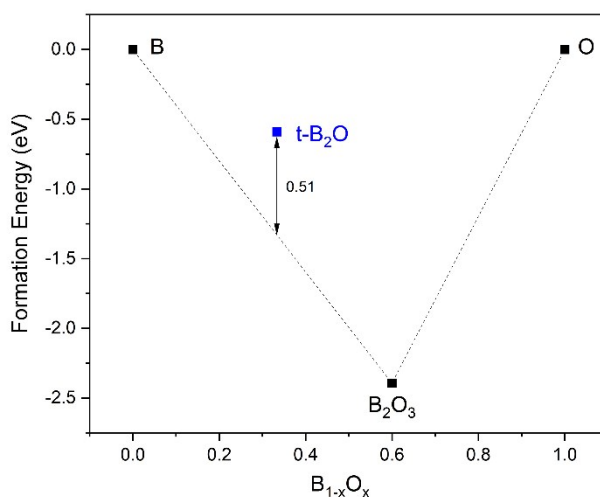


Figure S3. Convex hull for B_{1-x}O_x. The convex hull as defined by the bulk phases is represented by the black dashed lines. The blue square denotes the formation energy of t-B₂O.

Despite for a material to be thermodynamically stable requires that ΔE be negative not only relative to its pure elemental phases but relative to all other competing phases, *i.e.* its energy must be below the convex hull. However, this rule in general, but for 2D materials in particular, cannot be directly applied as a criterion for stability and realizability. The most important reasons for this are: (i) the intrinsic uncertainty on the DFT energies stemming from the approximate xc -functional in that the

accuracy of the PBE functional for the formation energy is only around 0.2 eV per atom on average²; (ii) substrate interactions or other external effects that can stabilize the monolayer, which can be exemplified by lots of 2D materials have been fabricated on different substrates³, such as silicene can be grown on the silver substrate despite its formation energy is 0.66 eV higher than its ground state bulk silicon⁴ or hexagonal borophene has been realized on Aluminum surface⁵ albeit it has high energy and shows huge imaginary frequencies in its phonon dispersion; (iii) kinetic barriers that separate the monolayer from other lower energy phases, as manifested by many metastable 2D graphene allotropes (*e.g.* graphyne family) have been experimentally reported even their formation energy are much higher than that of graphene⁶⁻⁸.

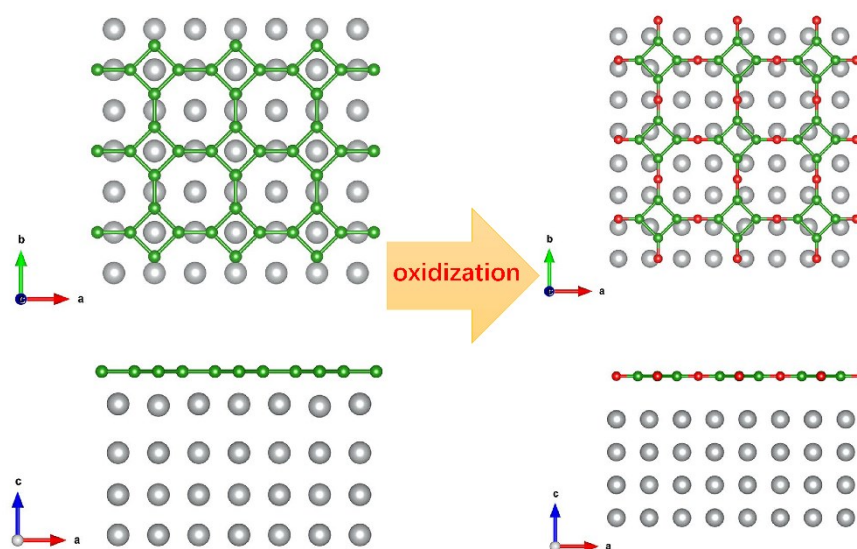


Figure S4. The route to prepare t-B₂O through oxidizing the T-borophene

Substrates, most of the time, play non-negligible roles in stabilizations and fabrications of 2D materials. Up to now, a great deal of 2D materials have been realized on different kinds of substrates, such as silicene/borophene on Ag (111) surface^{5, 9-11}, CuSe on Cu (111)¹², stanene on Bi₂Te₃(111)¹³ or InSb (111)¹⁴, just name a few. Although there are many factors to affect the growth of 2D materials on substrates and it is also not easy to choose a proper substrate to fabricate an ideal 2D material, but

some prerequisites still are considered at first, such as a 2D material usually tends to form more uniform sheets on a symmetry matched surface with small lattice mismatch¹⁵. Based on these considerations, here we attempt to propose a route to realize t-B₂O. We notice that T-borophene has square lattice symmetry with optimized lattice constant $a = 4.023 \text{ \AA}$ and many metals have cubic unit cells with lattice constants very close to that of T-borophene, for example, $a = 4.086/4.049/4.078 \text{ \AA}$ for Ag/Al/Au. Therefore, T-borophene can be initially grown on the (001) surface of those metals, e.g. Ag(001), then t-B₂O can be obtained through oxidizing as-prepared T-borophene (see Figure S4).

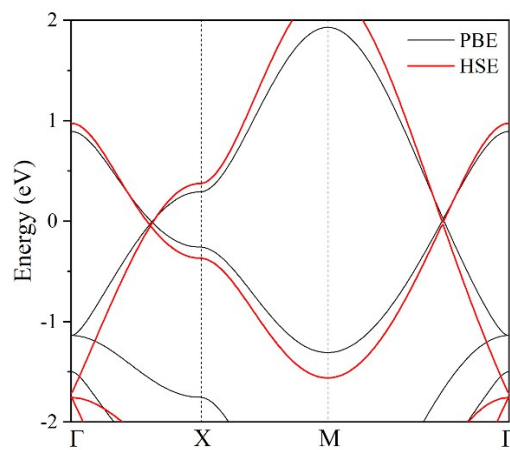


Figure S5. The band structures of t-B₂O at PBE and HSE levels. The comparison between HSE and PBE results didn't show any qualitative change, just the energy window of the nodal-loop has been shifted slightly.

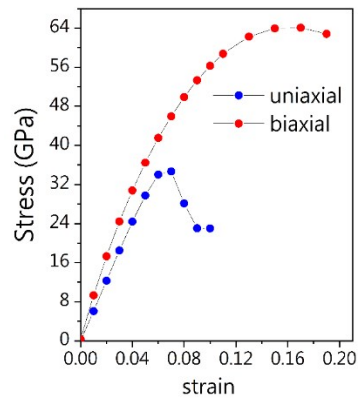


Figure S6. The strain-stress relationship of t-B₂O under uniaxial and biaxial strains.

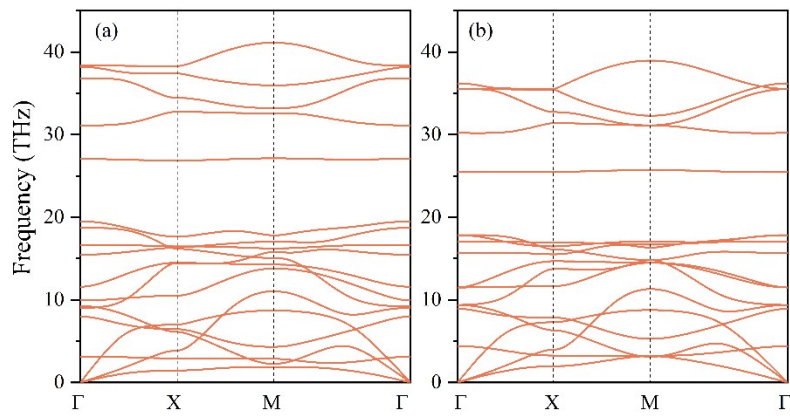


Figure S7. The calculated phonon spectra of t-B₂O under uniaxial 2% and biaxial 2% strains.

Supporting References:

1. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials*, 2013, **1**, 011002.
2. M. Pandey and K. W. Jacobsen. Heats of formation of solids with error estimation: The mBEEF functional with and without fitted reference energies. *Phys. Rev. B*, 2015, **91**, 235201.
3. G. Li, Y. Y. Zhang, H. Guo, L. Huang, H. Lu, X. Lin, Y. L. Wang, S. Du and H. J. Gao. Epitaxial growth and physical properties of 2D materials beyond graphene: from monatomic materials to binary compounds. *Chem Soc Rev*, 2018, **47**, 6073-6100.
4. J. Zhao, H. Liu, Z. Yu, R. Quhe, S. Zhou, Y. Wang, C. C. Liu, H. Zhong, N. Han, J. Lu, Y. Yao and K. Wu. Rise of silicene: A competitive 2D material. *Prog. Mater. Sci.*, 2016, **83**, 24-151.
5. W. Li, L. Kong, C. Chen, J. Gou, S. Sheng, W. Zhang, H. Li, L. Chen, P. Cheng and K. Wu. Experimental realization of honeycomb borophene. *Sci. Bull.*, 2018, **63**, 282-286.
6. H. Yu, Y. Xue and Y. Li. Graphdiyne and its Assembly Architectures: Synthesis, Functionalization, and Applications. *Adv. Mater.*, 2019, **31**, e1803101.
7. X. Gao, H. Liu, D. Wang and J. Zhang. Graphdiyne: synthesis, properties, and applications. *Chem. Soc. Rev.*, 2019, **48**, 908-936.
8. C. Huang, Y. Li, N. Wang, Y. Xue, Z. Zuo, H. Liu and Y. Li. Progress in Research into 2D Graphdiyne-Based Materials. *Chem. Rev.*, 2018, **118**, 7744-7803.
9. C.-L. Lin, R. Arafune, K. Kawahara, M. Kanno, N. Tsukahara, E. Minamitani, Y. Kim, M. Kawai and N. Takagi. Substrate-Induced Symmetry Breaking in Silicene. *Phys. Rev. Lett.*, 2013, **110**.
10. A. Curcella, R. Bernard, Y. Borenstein, A. Resta, M. Lazzeri and G. Prévot. Determining the atomic structure of the (4×4) silicene layer on Ag(111) by combined grazing-incidence x-ray diffraction measurements and first-principles calculations. *Phys. Rev. B*, 2016, **94**, 165438.
11. B. Kiraly, X. Liu, L. Wang, Z. Zhang, A. J. Mannix, B. L. Fisher, B. I. Yakobson, M. C. Hersam and N. P. Guisinger. Borophene Synthesis on Au(111). *ACS Nano*, 2019, **13**, 3816-3822.
12. L. Gao, J. T. Sun, J. C. Lu, H. Li, K. Qian, S. Zhang, Y. Y. Zhang, T. Qian, H. Ding, X. Lin, S. Du and H. J. Gao. Epitaxial Growth of Honeycomb Monolayer CuSe with Dirac Nodal Line Fermions. *Adv. Mater.*, 2018, **30**, 1707055.
13. F. F. Zhu, W. J. Chen, Y. Xu, C. L. Gao, D. D. Guan, C. H. Liu, D. Qian, S. C. Zhang and J. F. Jia. Epitaxial growth of two-dimensional stanene. *Nat. Mater.*, 2015, **14**, 1020-1025.

14. C.-Z. Xu, Y.-H. Chan, P. Chen, X. Wang, D. Flötotto, J. A. Hlevyack, G. Bian, S.-K. Mo, M.-Y. Chou and T.-C. Chiang. Gapped electronic structure of epitaxial stanene on InSb(111). *Phys. Rev. B*, 2018, **97**, 035122.
15. J. P. Xian-Li Zhang, Xin Jin, Yan-Fang Zhang, Jia-Tao Sun, Yu-Yang Zhang, and S. Du. Database Construction for Two-Dimensional Material-Substrate Interfaces. *Chin. Phys. Lett.*, 2021, **38**, 66801.