Electronic supplementary information

Computational Prediction of Electronic Structure and Optical Properties of Graphene-Like β-CuN_3

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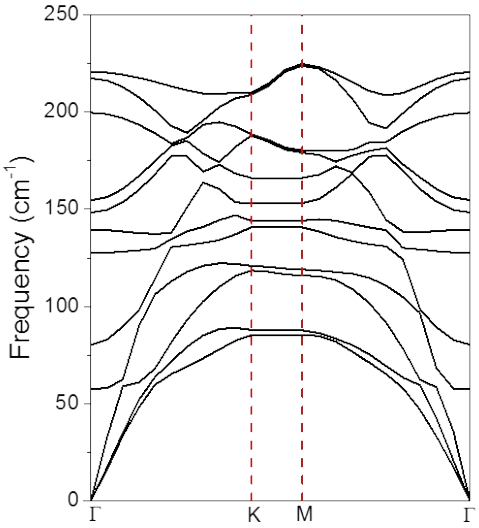

Fig. S1 Phonon dispersion spectrum of β-CuN_3 monolayer. The fractional coordinates of high-symmetry points: Γ (0, 0, 0), K (0.5, 0, 0) and M (0.5, 0.5, 0).

The standard free energy of CuN_3 is calculated based on the following equations:

$$\Delta G_f^\circ = G_{CuN_3(s)}^\circ - G_{Cu(s)}^\circ - 3/2 G_{N_2(g)}^\circ \quad (1)$$

$$G_{CuN_3(s)}^\circ = E_{f[CuN_3(s)]} + E_{zpe[CuN_3(s)]} - T\Delta S_{CuN_3(s)}(T) \quad (2)$$

$$G_{Cu(s)}^\circ = E_{f[Cu(s)]} + E_{zpe[Cu(s)]} - T\Delta S_{Cu(s)}(T) \quad (3)$$

$$G_{N_2(g)}^\circ = E_{f[N_2(g)]} + E_{zpe[N_2(g)]} - T\Delta S_{N_2(g)}(T) \quad (4)$$

The following equation can be obtained from (1), (2), (3) and (4).

$$\Delta G_f^\circ = E_{f[CuN_3(s) - Cu(s) - 3/2N_2(g)]} + E_{zpe[CuN_3(s) - Cu(s) - 3/2N_2(g)]} - T\Delta S_{[CuN_3(s) - Cu(s) - 3/2N_2(g)]}(T) \quad (5)$$

Moreover, the entropy changes of $CuN_3(s)$ and Cu(s) can be neglected, thus equation (5) can be written as:

$$\Delta G_f^\circ = \Delta E_f + \Delta E_{zpe} - 3/2 T\Delta S(T) \quad (6)$$

where ΔE_f is the formation energy of β-CuN_3, ΔE_{zpe} is the zero point energy correction and ΔS is the entropy of N_2 under standard conditions (T = 298 K). The entropy of N_2 at standard condition (298 K) is taken from NIST database, which is 191.61 $J \cdot mol^{-1} \cdot k^{-1}$, thus the calculated entropy change for N_2 is 0.59 eV at 298 K. As a result, the calculated formation enthalpy for β-CuN_3 bulk and monolayer are 0.45 and 0.57 eV/atom, respectively, while he calculated Gibbs free energy for β-CuN_3 bulk and monolayer are 0.74 and 0.84 eV/atom, respectively.

The standard free energy of $Cu(N_3)_2$ is calculated based on the following equations:

$$\Delta G_f^\circ = G_{Cu(N_3)_2(s)}^\circ - G_{Cu(s)}^\circ - 3 G_{N_2(g)}^\circ \quad (7)$$

$$G_{Cu(N_3)_2(s)}^\circ = E_{f[Cu(N_3)_2(s)]} + E_{zpe[Cu(N_3)_2(s)]} - T\Delta S_{Cu(N_3)_2(s)}(T) \quad (8)$$

$$G_{Cu(s)}^\circ = E_{f[Cu(s)]} + E_{zpe[Cu(s)]} - T\Delta S_{Cu(s)}(T) \quad (9)$$

$$G_{N_2(g)}^\circ = E_{f[N_2(g)]} + E_{zpe[N_2(g)]} - T\Delta S_{N_2(g)}(T) \quad (10)$$

The following equation can be obtained from (7), (8), (9) and (10).

$$\Delta G_f^\circ = E_{f[Cu(N_3)_2(s) - Cu(s) - 3/2N_2(g)]} + E_{zpe[Cu(N_3)_2(s) - Cu(s) - 3/2N_2(g)]} - T\Delta S_{[Cu(N_3)_2(s) - Cu(s) - 3N_2(g)]}(T) \quad (11)$$

Moreover, the entropy changes of $Cu(N_3)_2(s)$ and Cu(s) can be neglected, thus equation (11) can be written as:

$$\Delta G_f^\circ = \Delta E_f + \Delta E_{zpe} - 3T\Delta S(T) \quad (12)$$

where ΔE_f is the formation energy of $Cu(N_3)_2$, ΔE_{zpe} is the zero point energy correction and ΔS is the entropy of N_2 under standard conditions (T = 298 K). The calculated Gibbs free energy for $Cu(N_3)_2$ is 0.90 eV/atom.

Table S1 Lattice parameters *a* (Å), *b* (Å), length of Cu-N bond (Å) and N-N bond (Å), interlayer distance D_{in} (Å), the exfoliation energy E_{ex} (J/m^2) and the band gap calculated by HSE06 for β-CuN_3 bulk, monolayer, bilayer, trilayer and tetralayer, respectively.

system	*a* (Å)	*b* (Å)	Cu-N (Å)	N-N (Å)	D_{in} (Å)	E_{ex} (J/m^2)	Band gap (eV)
bulk	3.29	10.70	1.86/1.98	1.16/1.21	2.70	\	2.23
monolayer	3.34	10.59	1.85/1.98	1.17/1.21	\	0.41	2.39
bilayer	3.28	10.66	1.85/1.98	1.17/1.21	2.62	0.43	2.05
trilayer	3.28	10.67	1.86/1.98	1.16/1.21	2.69	0.44	2.00
tetralayer	3.28	10.68	1.86/1.98	1.17/1.21	2.69	0.44	2.00

Table S2 The relative Z-axis coordinates (Å) of the outer layer atoms for bilayer, trilayer and tetralayer β-CuN_3. N_1, N_2 and N_3 represent the position of bonding with two Cu atoms, the center of N_3 and bonding with one Cu atom, respectively.

system	Cu	N_1	N_2	N_3
bilayer	0	5.1×10^{-2}	3.3×10^{-2}	1.1×10^{-2}
trilayer	0	4.3×10^{-2}	3.4×10^{-2}	2.3×10^{-2}
tetralayer	0	4.1×10^{-2}	3.1×10^{-2}	1.9×10^{-2}

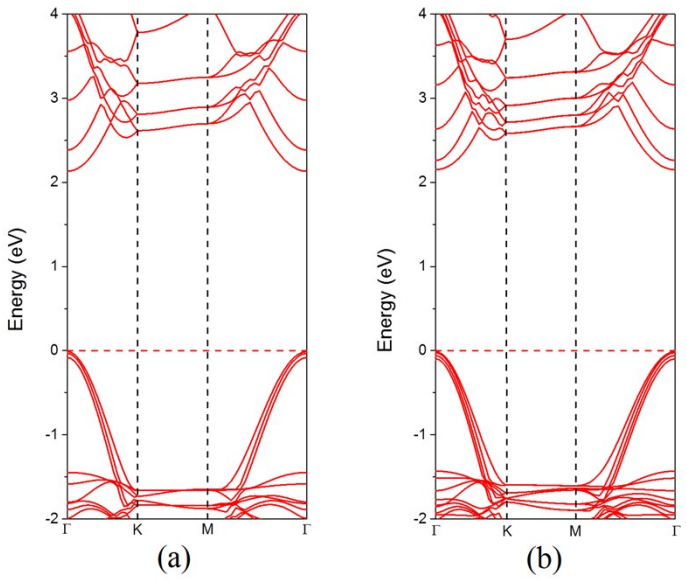

Fig. S2 Band structures near Fermi level calculated with HSE06 functional for flat (a) trilayer and (b) tetralayer β-CuN_3.

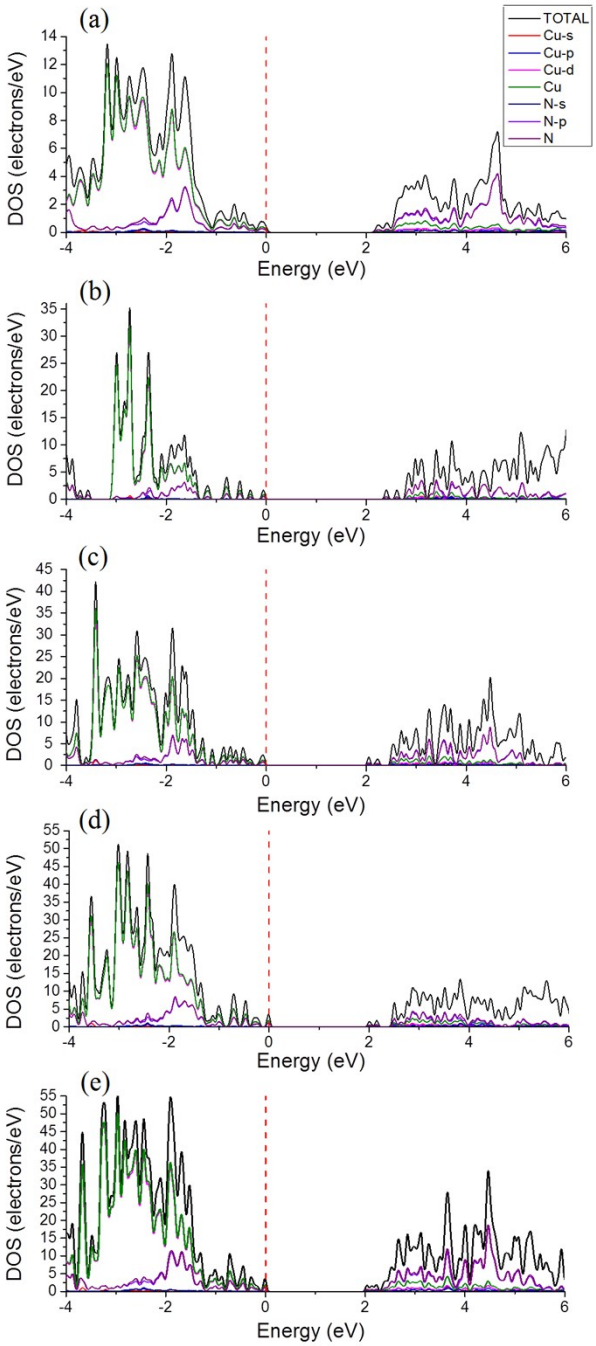

Fig. S3. Density of states of (a) bulk, (b) monolayer, (c) bilayer, (d) trilayer and (e) tetralayer β-CuN_3. Fermi level is set to zero and denoted by a red dash.

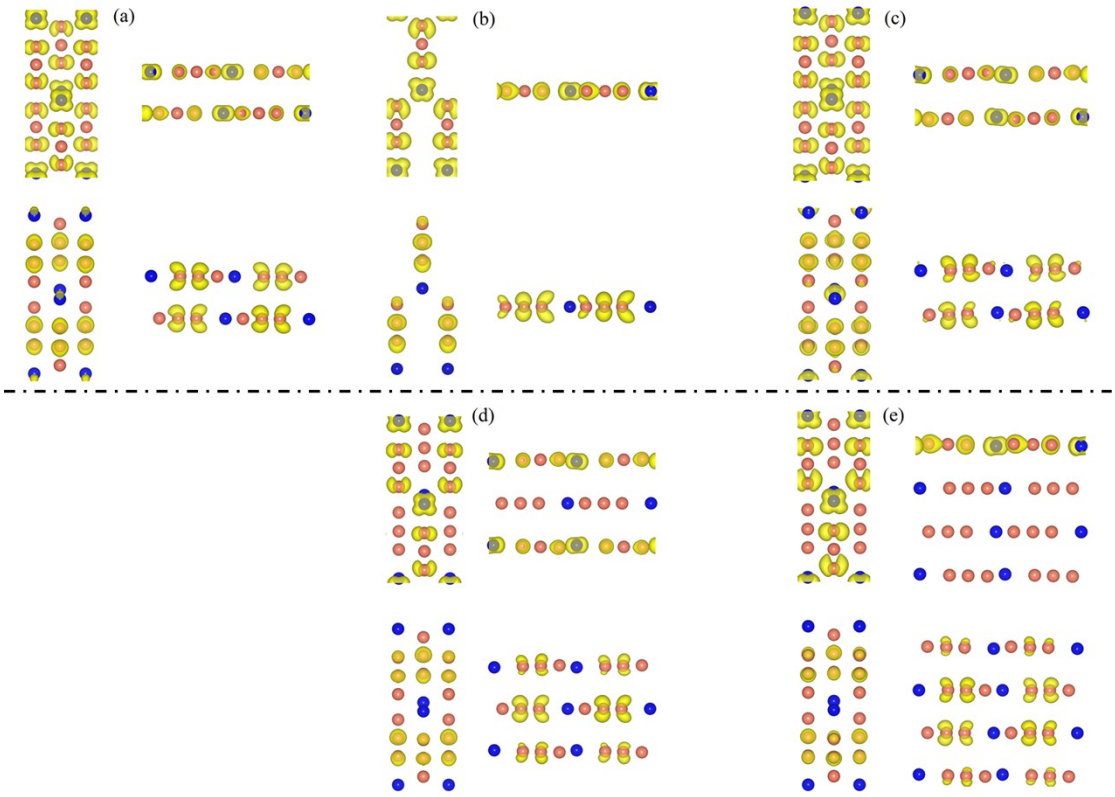

Fig. S4 Spatial structure of wave functions for β-CuN_3 using an isosurface of 0.005 e $Å^{-3}$. The top and side view of VBM and CBM for (a) bulk structure, (b) monolayer, (c) bilayer, (d) trilayer and (e) tetralayer.

Table S3 Calculated charge transfer c.t. (e) for β-CuN_3. N_1, N_2 and N_3 represent the position of bonding with two Cu atoms, the center of N_3 and bonding with one Cu atom, respectively. For trilayer and tetralayer, Cu and Cu' represent the position of the outer layer and the inner layer, respectively, the same as N.

	atom	c.t.	atom	c.t.	atom	c.t.	atom	c.t.
bulk	Cu	-0.71	N_1	0.22	N_2	0.46	N_3	0.03
monolayer	Cu	-0.66	N_1	0.23	N_2	0.32	N_3	0.11
bilayer	Cu	-0.67	N_1	0.35	N_2	0.18	N_3	0.12
trilayer	Cu	-0.67	N_1	0.34	N_2	0.20	N_3	0.13
	Cu'	-0.66	N_1'	0.35	N_2'	0.21	N_3'	0.10
tetralayer	Cu	-0.67	N_1	0.34	N_2	0.20	N_3	0.13
	Cu'	-0.65	N_1'	0.33	N_2'	0.21	N_3'	0.11

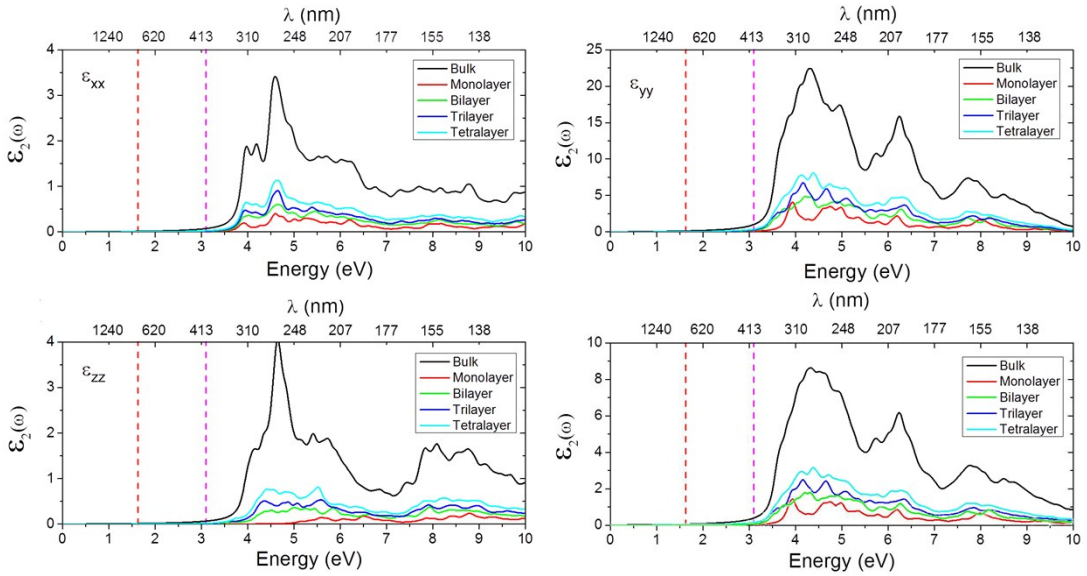

Fig. S5 Imaginary parts $\varepsilon_2(\omega)$ of dielectric function for β-CuN_3. (a) x direction; (b) y direction; (c) z direction; (d) the average of x, y and z directions. The area between the red and the purple lines represents the visible range. The directions are the same as those shown in Fig. 1.

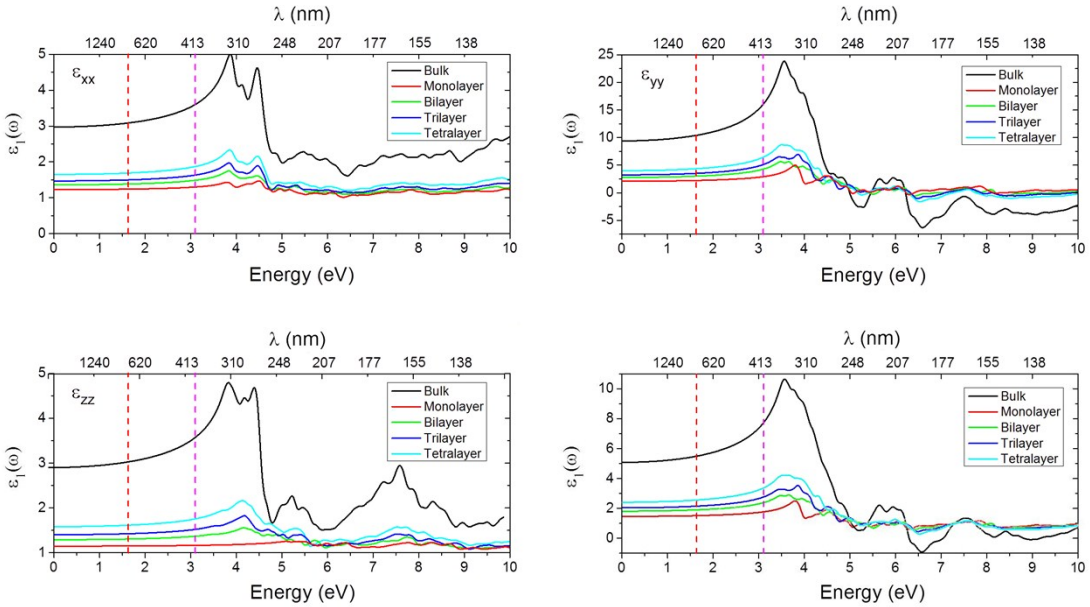

Fig. S6 Real parts $\varepsilon_1(\omega)$ of dielectric function for β-CuN_3. (a) x direction; (b) y direction; (c) z direction; (d) the average of x, y and z directions. The area between the red and the purple lines represents the visible range. The direction as shown in Fig. 1.

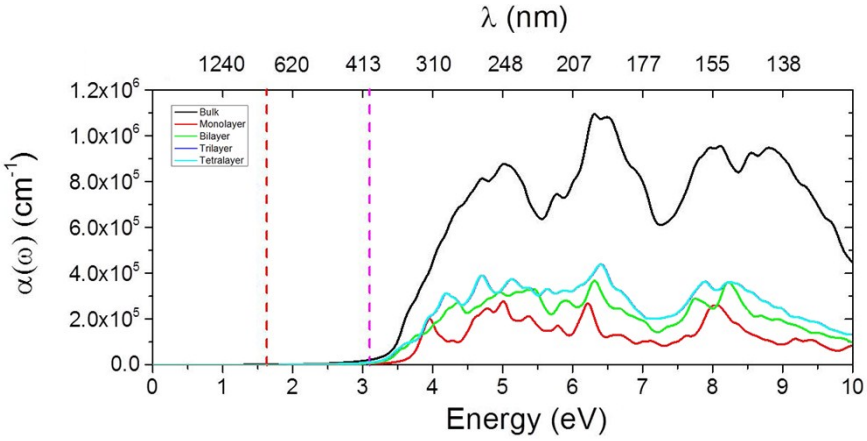

Fig. S7 Optical absorption coefficient α(ω) for β-CuN_3.