Supporting Information

Semiconducting SN_2 Monolayer with Three-Dimensional Auxetic Properties: A Global Minimum with Tetracoordinated Sulfurs

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[#] Equal contribution to this work.

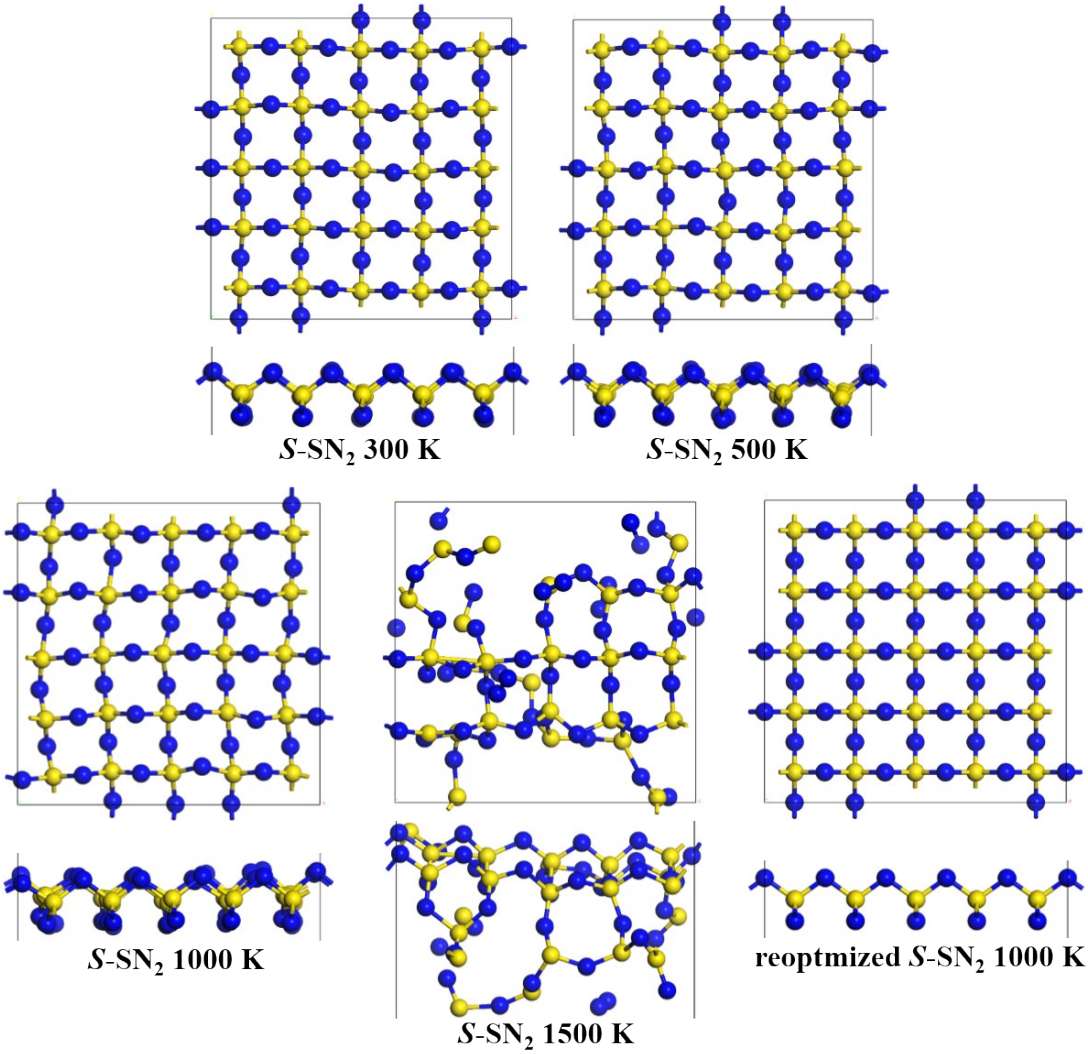

Fig. S1. The snapshots (top and side views) of the *S*-SN_2 monolayer after 10 ps FPMD simulations at 300 K, 500 K, 1000 K, and 1500 K, and the reoptimized structure of the final structure of *S*-SN_2 monolayer after 10 ps MD simulation at 1000 K.

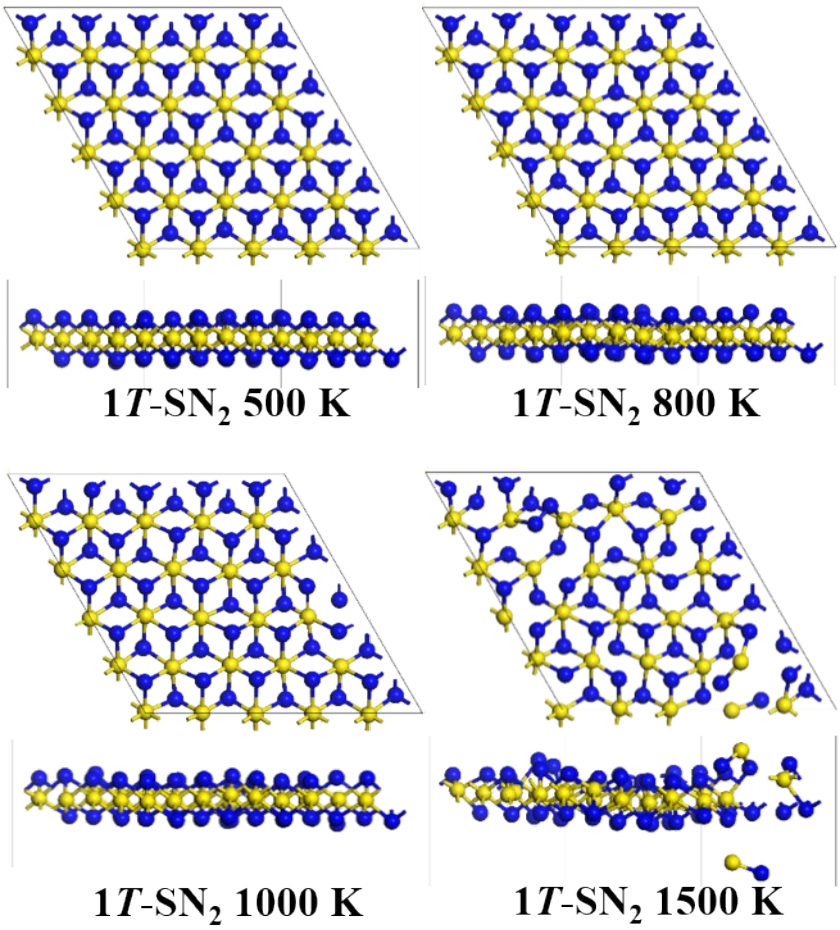

Fig. S2. The snapshots (top and side views) of the 1*T*-SN_2 monolayer after 10 ps FPMD simulations at 500 K, 800 K, 1000 K, and 1500 K.

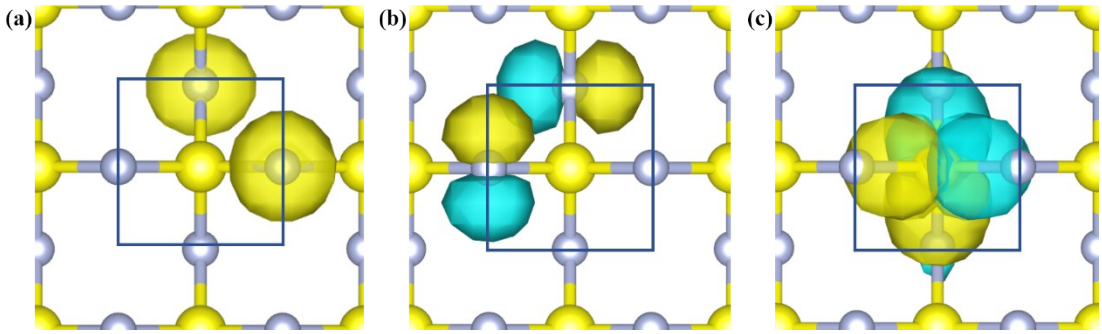

Fig. S3. The SSAdNDP chemical bonding pattern of the *S*-SN_2 unitcell (isovalue = 0.1 eÅ^{-3}). Totally eight bonding patterns are revealed, including (a) two *sp*-orbital lone-pairs on N atoms, with occupation numbers (ONs) as 1.82; (b) two *p*-orbital lone-pairs on N atoms, with ONs as 1.75; (c) four two-center-two-electron chemical bonds between N and S atoms, with ONs as 1.97.

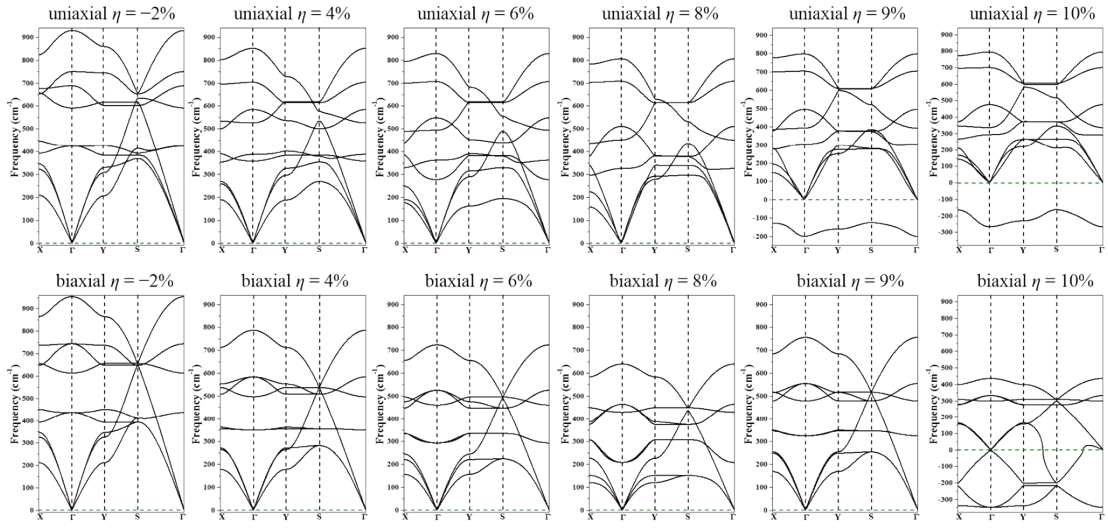

Fig. S4. The calculated phonon spectra of the *S*-SN_2 monolayer under uniaxial and biaxial strains.

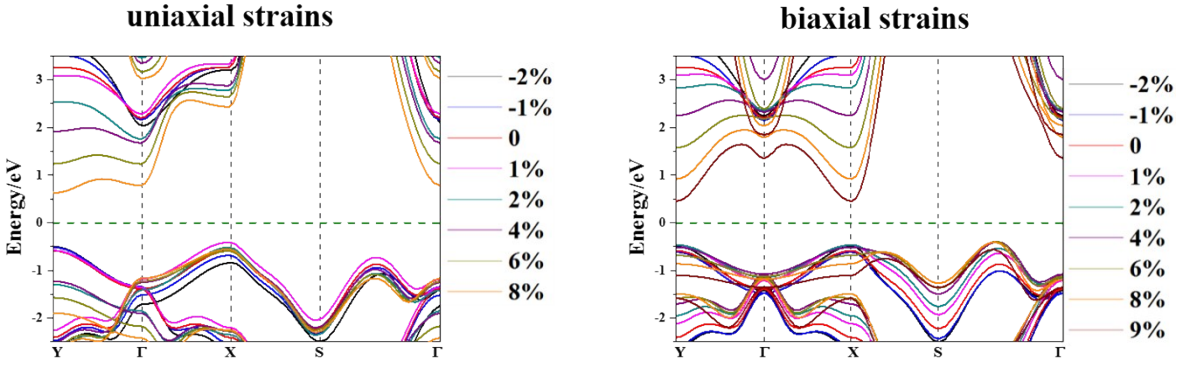

Fig. S5. The HSE06 band structures of the *S*-SN_2 monolayer under uniaxial and biaxial strains.

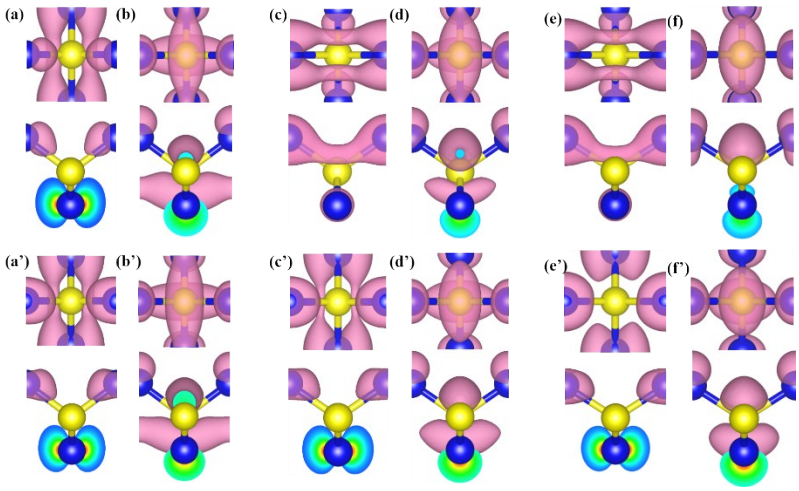

Fig. S6. The spatial distributions of wave functions of VBM and CBM from the top and side views (isovalue: 0.02 eÅ^{-3}) for the *S*-N_2S monolayer under uniaxial strain of –2% (a,b), 2% (c,d) and 6% (e,f), as well as biaxial strain of –2% (a',b'), 2% (c',d') and 6% (e',f').

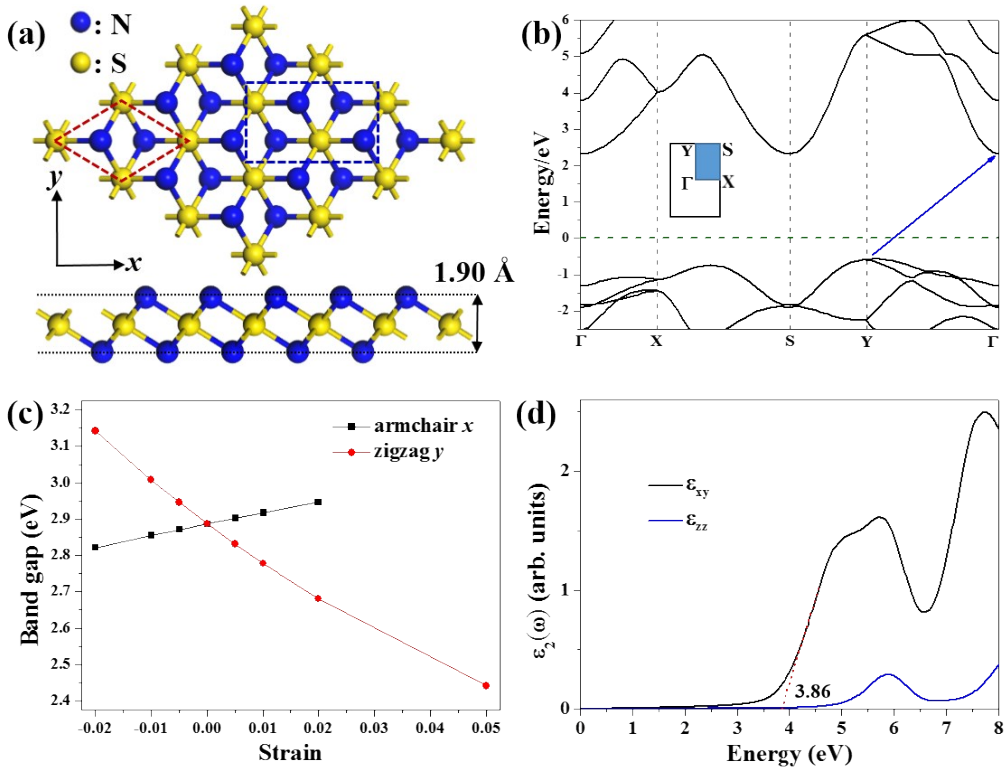

Fig. S7. 1*T*-SN_2 monolayer: (a) Structure from top and side views (a 3×3×1 supercell, the hexagonal unitcell and the orthogonal lattice are highlighte by the red dashed diamond and the blue dashed rectangle, respectively); (b) band structure (the green dashed line denotes the Fermi level); (c) the HSE06 band gap of 1T-SN_2 monolayer as a function of the external strains along the *x* (armchair) and *y* (zigzag) uniaxial directions; (d) the computed imaginary dielectric constants of the 1*T*-SN_2 monolayer. The red dashed line denotes an approximate linear fitting for estimating the band edge of the first adsorption peak.

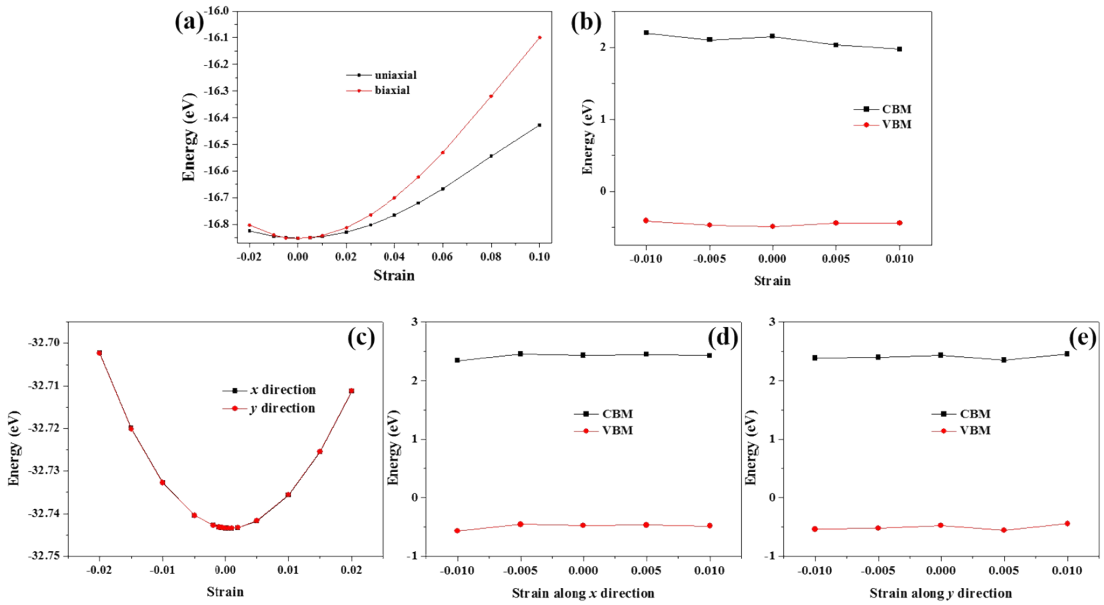

Fig. S8. The *S*-SN_2 monolayer (a,b): (a) The relationship between the total energy and uniaxial/biaxial strain of *S*-SN_2; (b) the HSE06 energy of VBM and CBM shift with respect to the lattice dilation and compression along *x* (*y*) direction. The 1*T*-SN_2 monolayer (c-e): The relationship between the total energy and strain along armchair (*x*) and zigzag (*y*) directions (c). The HSE06 energy of VBM and CBM shift with respect to the lattice dilation and compression along (d) armchair and (e) zigzag directions.

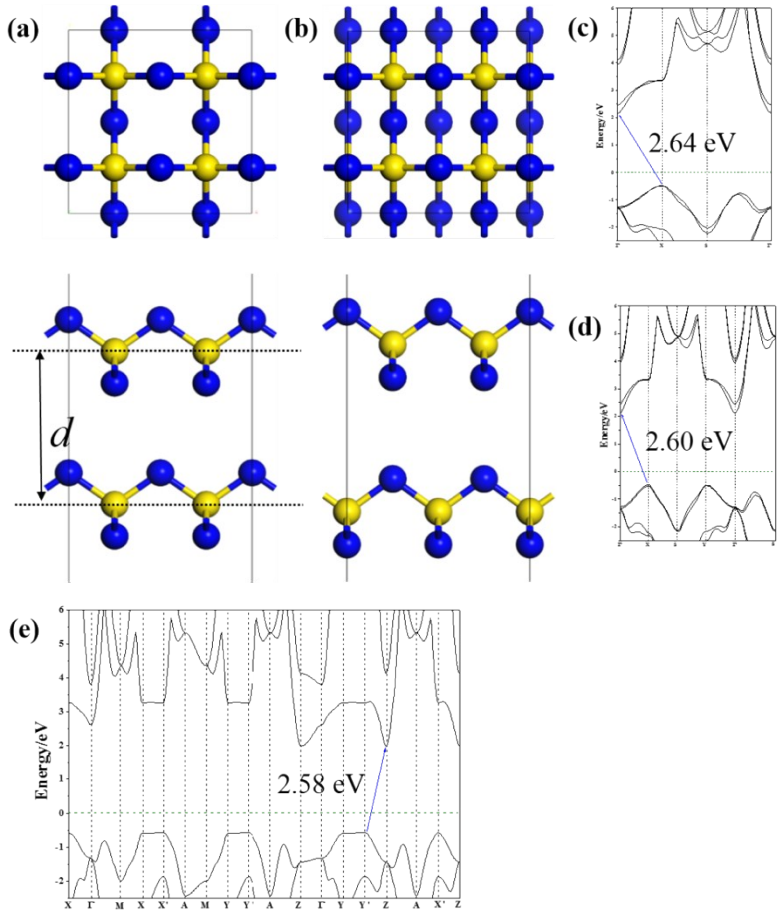

Fig. S9. The AA (a) and AB (b) stacking configurations for *S*-SN_2 bilayer from both the top and side views (a 2×2 supercell of the hexagonal lattice). Band structures of the *S*-SN_2 bilayer in AA (c) and AB (d) stacking configurations, as well as the bulk (e).

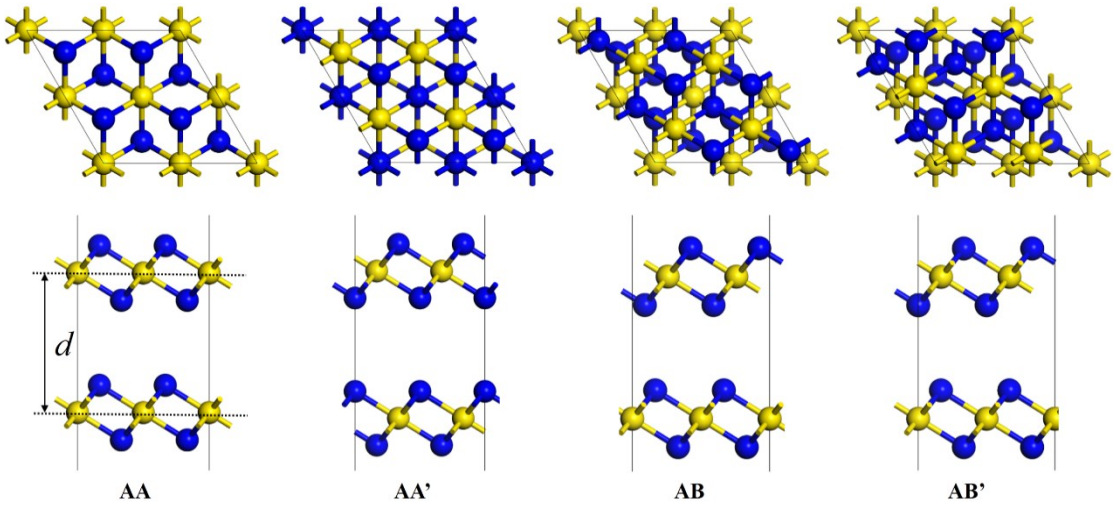

Fig. S10. Different stacking configurations for 1*T*-SN_2 bilayer from both the top and side views (a 2×2 supercell of the hexagonal lattice). The interlayer distance (*d*) was labeled in the AA stacking.

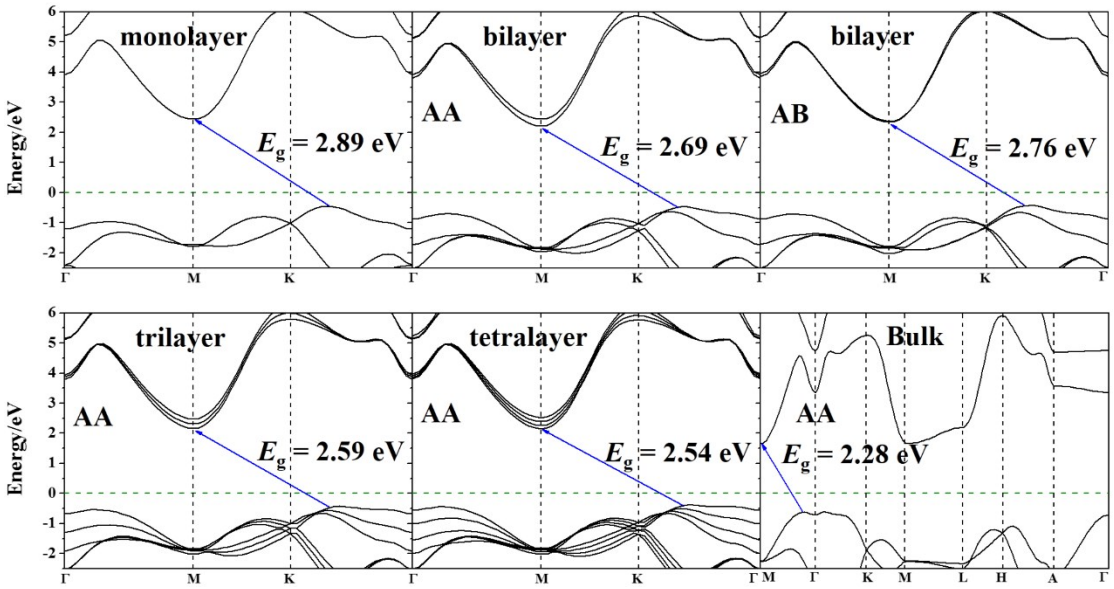

Fig. S11. Band structures of the few-layer and bulk SN_2 in 1*T* phase.

Table S1. The interlayer distance (*d*, in Å) and binding energy (E_b, in eV) of 1*T*-SN_2 bilayer in different stacking configurations and trilayer, tetralayer and bulk of AA stacking.[a]

		bilayer		
Stacking	**AA**	**AA'**	**AB**	**AB'**
d	2.95	2.97	2.97	3.07
E_b	0.28	0.28	0.29	0.28
		AA stacking		
	bilayer	**trilayer**	**tetralayer**	**bulk**
d	2.95	2.94	2.91/2.94	2.84
E_b	0.28	0.30	0.31	0.31

[a] The binding energy of trilayer, tetralayer and bulk in AA stacking was calculated by $E_b = (3 \times E_{monolayer} - E_{trilayer})/3$, $E_b = (4 \times E_{monolayer} - E_{tetralayer})/4$, and $E_b = E_{monolayer} - E_{bulk}$, respectively.