

SUPPORTING INFORMATION

Hidden Symmetry-Broken Phase of MoS₂ Revealed as A Superior Photovoltaic Material

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Table S1. Crystallographic Data of 1T_d and 1H' phases.

Notation	Space group	Lattice parameters (Å, degree)	Atomic coordinates
1T _d	P31m	a = 5.611 c=35.844 γ = 120	Mo:3c (0.614 0.614 0.447)
			S: 3c (0.684 0.000 0.403)
1H'	P2/c	a = 3.096 c = 7.261 b=17.999 β = 128.19	S: 2b (0.667 0.333 0.493)
			S: 1a (0.000 0.000 0.480) unique axis c
			Mo: 2f (0.50 0.48 0.25)
			S: 4g (0.34 0.41 0.50) unique axis b

Table S2. The calculated atomic vibrations for the different modes of 1T_d and 1H phases. The irreducible representation for zone center phonons in 1T_d is $\Gamma = 6A_1 + 7E$.

	Mode	$\omega(\text{cm}^{-1})$	Exp ^a	Active
1H	E_{2g}^1	378.0	384.2	I+R
	A_{1g}	400.4	404.9	R
	A_{2g}	461.2	-	I
1T _d		180.2	-	I+R
		236.5	-	I+R
		276.4	-	I+R
	E	300.9	-	I+R
		318.0	-	I+R
		347.7	-	I+R
		405.5	-	I+R
		35.9	-	I+R
		193.6	-	I+R
	A_1	250.8	-	I+R
	309.8	-	I+R	
	397.6	-	I+R	
	468.4	-	I+R	

^aHong, L. et al. From bulk to monolayer MoS₂: evolution of Raman scattering. *Adv. Funct. Mater.* 22(7), 1385-1390 (2012)

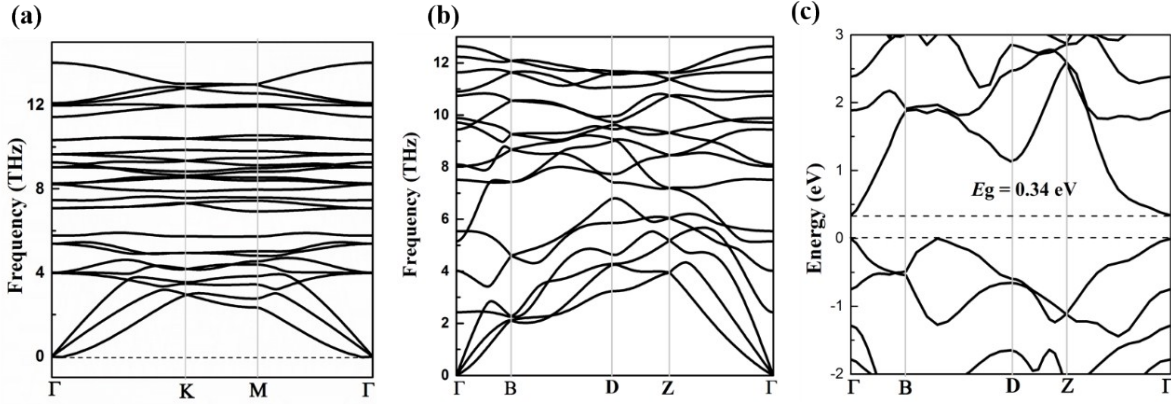


Figure S1. The phonon dispersions for (a) 1T_d and (b) 1H'. (c) Band structure of 1H' at HSE06 level of theory.

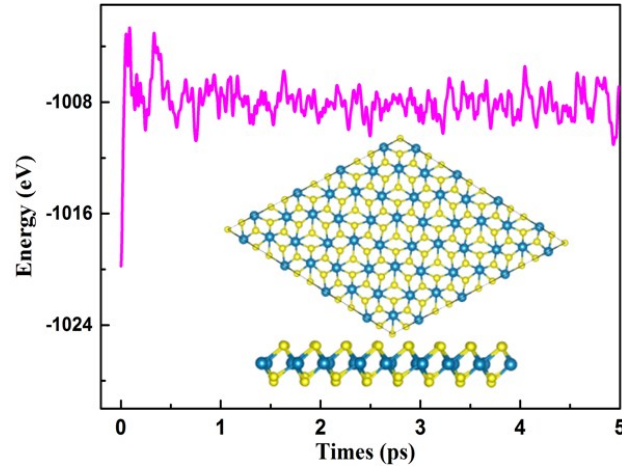


Figure S2. The fluctuation of potential energy of 1T_d phase (144 atoms/cell) as a function of AIMD simulation steps at 600 K. No structural destruction is found after 5ps simulations. The inset is the snapshot of the structure at the end of 5ps simulation.

Further analysis on the orbital levels of 1T_d-MoS₂

The electronic structure of TMDs strongly depends on the coordination environment of the transition metal and its d-electron count. The distorted octahedral coordination of transition metal (D_{3d}) form degenerate two orbitals of a_1 and $2e$, corresponding to one-fold d_{z^2} orbital and four-fold degenerated $d_{x^2-y^2}$, d_{xy} , d_{xz} , and d_{yz} orbitals. The diverse electronic properties of TMDs with 1T_d structure arise from the progressive filling of the non-bonding d bands for MoS₂, PdS₂ and SnS₂. When the orbitals are partially filled, as in the case of 1T_d-PdS₂, TMDs exhibit metallic conductivity. When the orbitals are fully occupied, such as in 1T_d-MoS₂ and 1T_d-SnS₂. Specially, once Mo is substituted by Pd, d^2 electron count changes to d^4 ; therefore, one-fold a_1 orbital is fully filled and two

doubly degenerated e orbitals are partially filled, leading to the metallic behavior of 1T_d-PdS₂. For 1T_d-SnS₂, 10 d electrons can completely fill five d orbitals; thus, resulting in its semiconducting character.

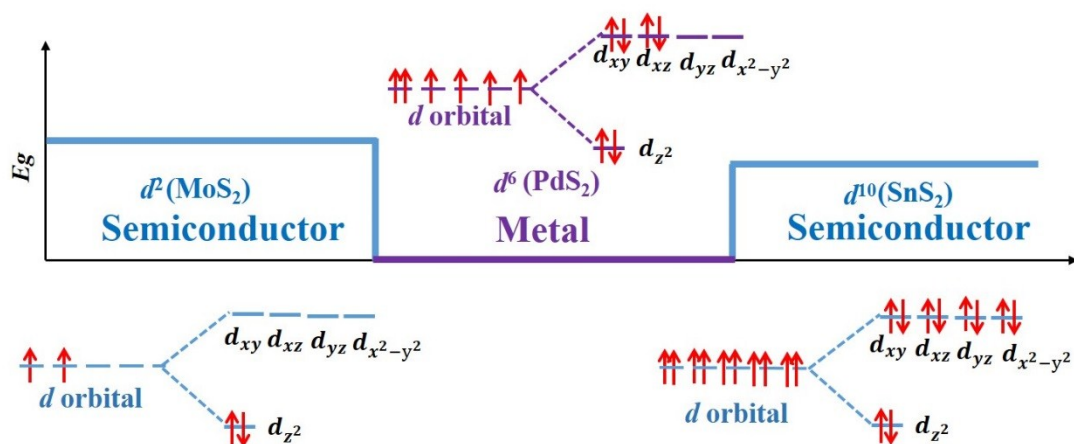


Figure S3. Schematic diagrams of the orbital levels of MoS₂, PdS₂ and SnS₂ in 1T_d phase.

Stacking configurations of tri-layers 1T_d phase

The geometric and electronic properties of tri-layers 1T_d phase with three different stacking configurations, namely AAA, AAB, and ABA, respectively, are similar. The computed total energies suggest that these three different stacking configurations are essentially isoenergetic.

Furthermore, AAA, AAB and ABA stacking configurations are all direct band gap semiconductors, and their gap values are 0.69 eV, 0.72 eV and 0.74 eV, respectively. Due to the very weak interlayer vdW interactions, stacking patterns have little effect on total energies and electronic properties. Thus, AAA stacking configuration is adopted in text.

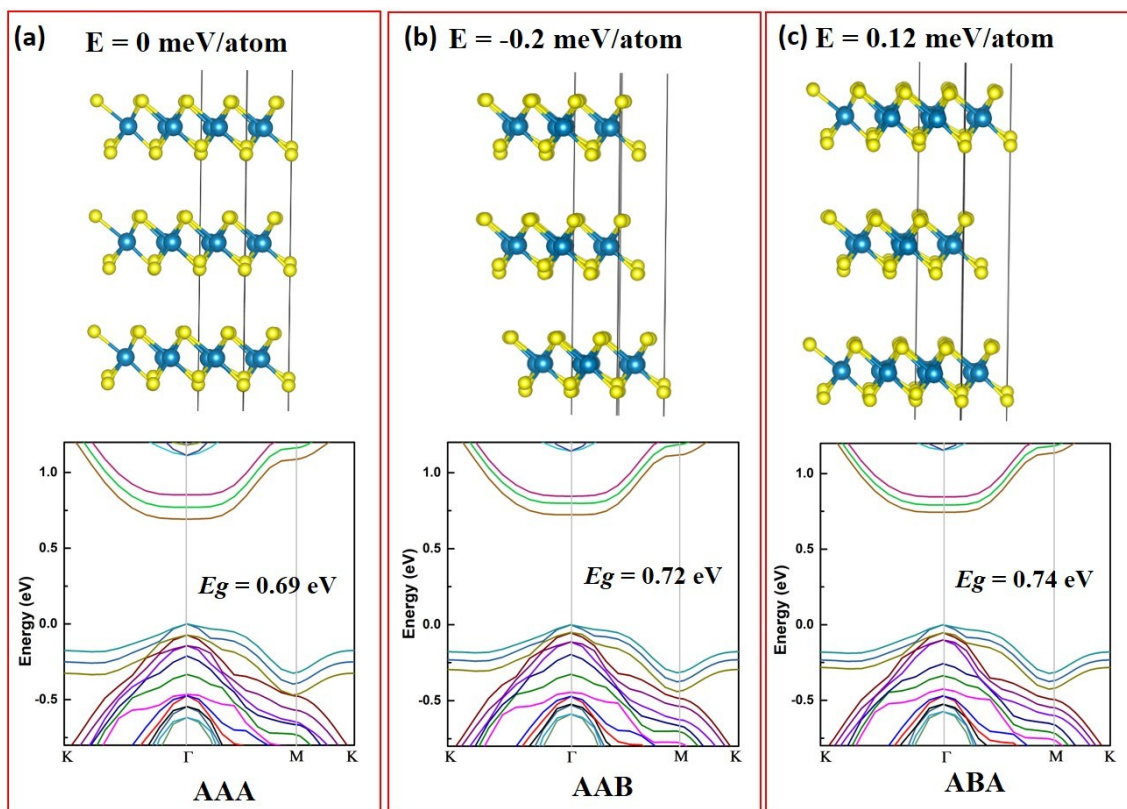


Figure S4. The optimized geometric structures, total energies with respect to that of AAA stacking pattern, and the band structures using PBE functional of tri-layers with three stacking patterns: (a) AAA, (b) AAB, and (c) ABA.

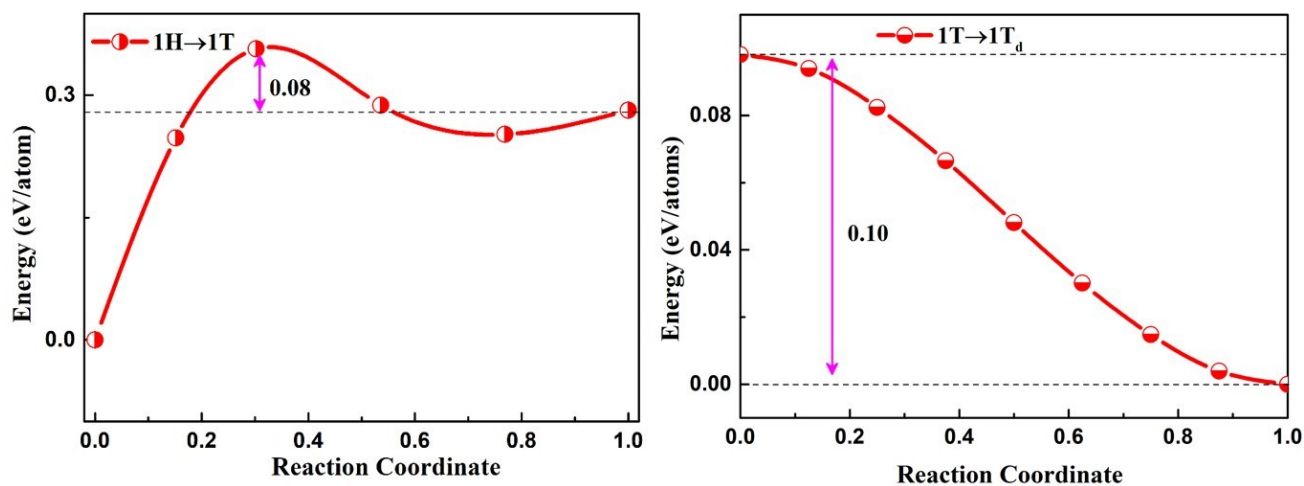


Figure S5. Different images on minimum energy path from 1H to 1T and 1T to 1T_d phases, respectively.

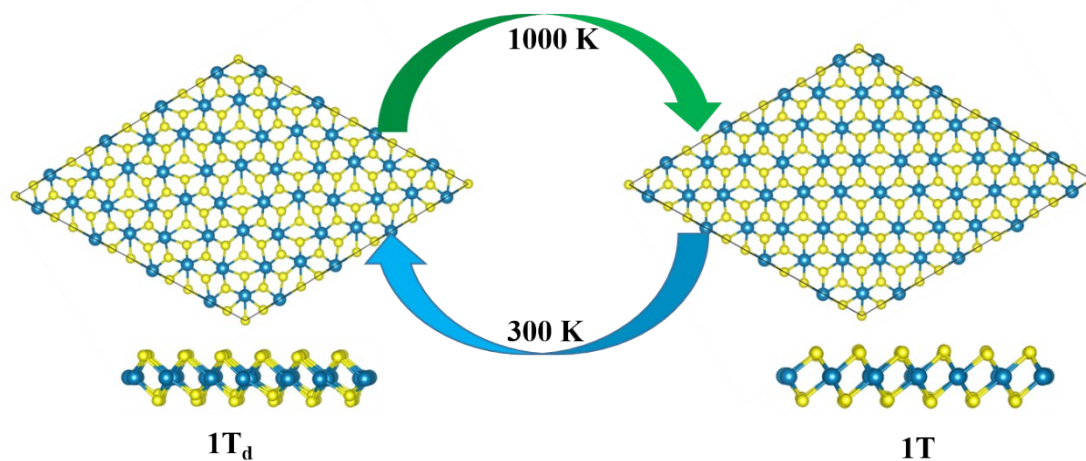


Figure S6. AIMD simulations of the temperature-induced phase transition between 1T_d phase and 1T phase.

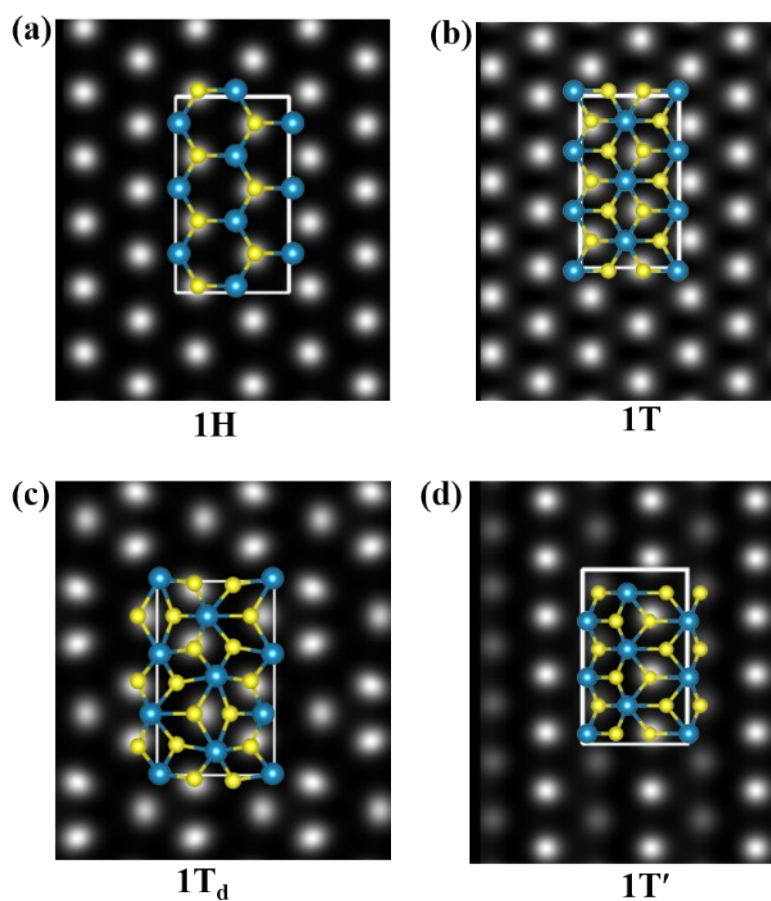


Figure S7. The simulated occupied state STM images at a bias of -0.5 V for the 1H phase (a), 1T phase (b), 1T_d phase (c) and 1T' phase (d) of MoS₂.

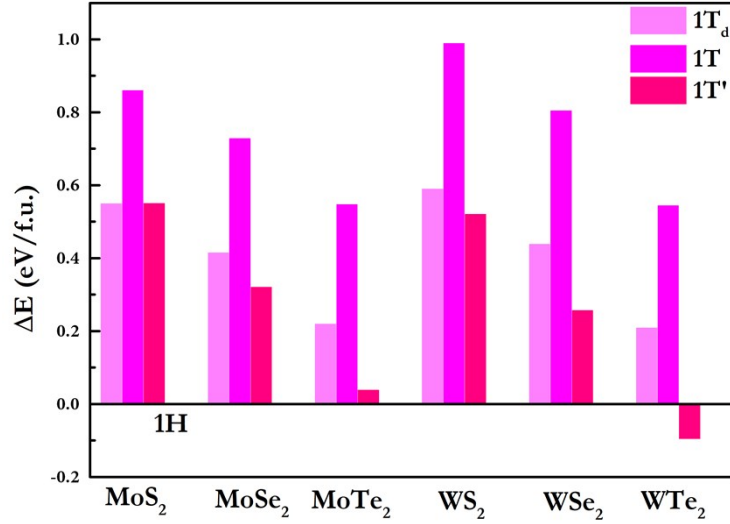


Figure S8. The total energies of 1T_d, 1T- and 1T'-phases relative to the 1H phase for MX₂ monolayers.

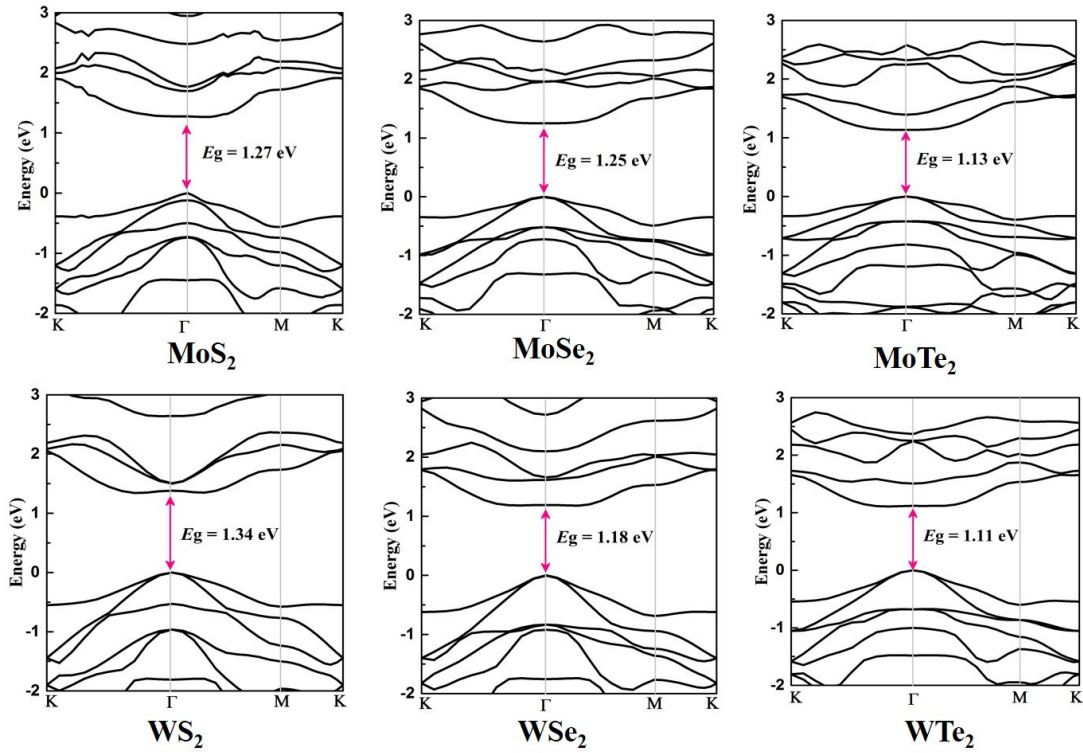


Figure S9. The band structures of 1T_d phase for various MX₂ monolayers at HSE06 level of theory.

Calculation methods for spectroscopic limited maximum efficiency (SLME): The maximum solar cell efficiency is simulated through calculating spectroscopic limited maximum efficiency (SLME) based on the improved Shockley-Queisser model. The SLME of a material takes into account the band gap size, the band gap type (direct versus indirect), and the optical absorption spectrum, all of which can be obtained from reliable first principles calculations. The calculation of radiative and non-radiative recombination current is based on detailed balance theory using the

energy difference between the minimum band gap and direct-allowed gap as the input. The simulation is performed under the standard AM1.5G solar spectrum at room temperature.