Supporting Information

Modulation of electronic properties from stacking orders and spin-orbit coupling for 3R-type MoS_2

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Fig. S1

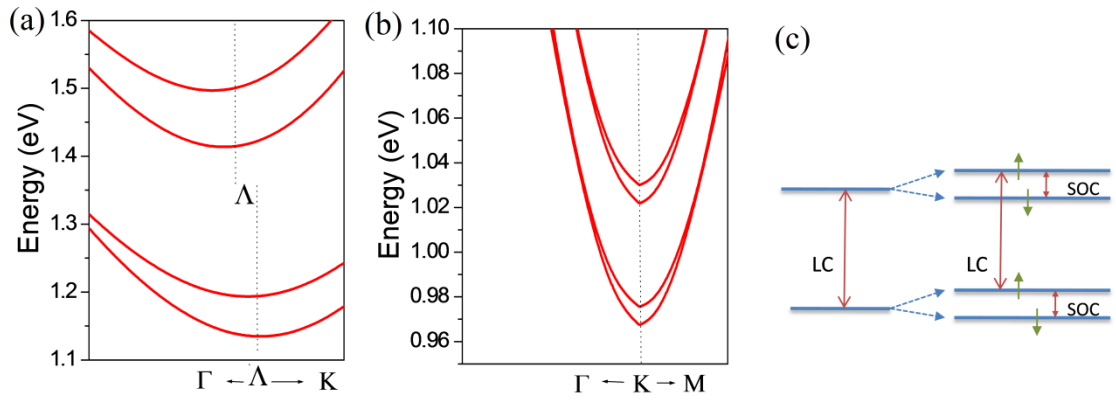

Fig. S1 Band structures of 2-layer MoS_2 with ab-stacking near the bottom of conduction band at Λ (a) and K point (b), and schematic of conduction band splitting at Λ and K point due to spin-orbit coupling and layer's coupling (c)

Fig. S2

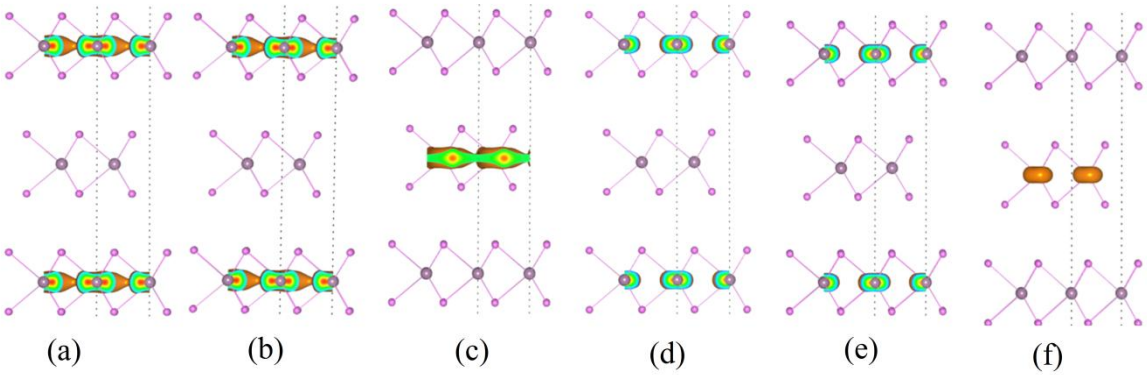

Fig. S2 Isosurface of band-decomposed charge density of six states of 3-layer MoS_2 with aba stacking order, at the top of valance band of K point (in Fig. 5a) including the states ~|1+3↑⟩-1(a), ~|1+3↑⟩-2(b), ~|2↑⟩(c), ~|1+3↓⟩-1(d), ~|1+3↓⟩-2(e) and ~|2↓⟩ (f).

The spin-up states ~|1+3↑⟩-1and ~|1+3↑⟩-2 are almost degenerate. The spin-up states ~|1+3↓⟩-1 and ~|1+3↓⟩-2 are almost degenerate. This may due to the being of mirror symmetry of aba stacking.

Fig. S3

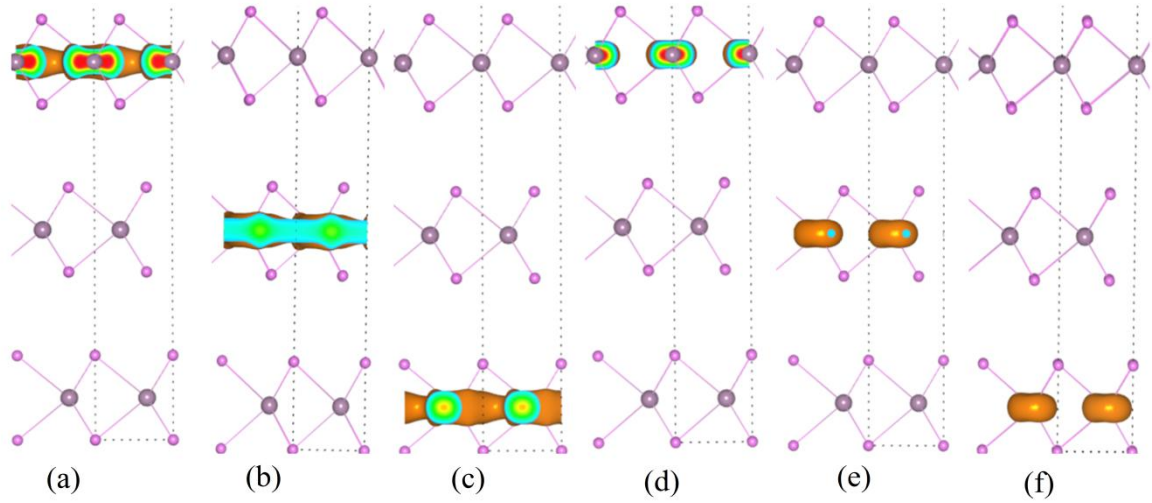

Fig. S3 Isosurface of band-decomposed charge density of six states of 3-layer MoS_2 with aba stacking order, at the top of valance band of K point (in Fig. 5a) including the states ~|1↑⟩ (a), ~|2↑⟩ (b), ~|3↑⟩ (c), ~|1↓⟩ (d), ~|2↓⟩ (e) and ~|3↓⟩ (f).

Fig. S4

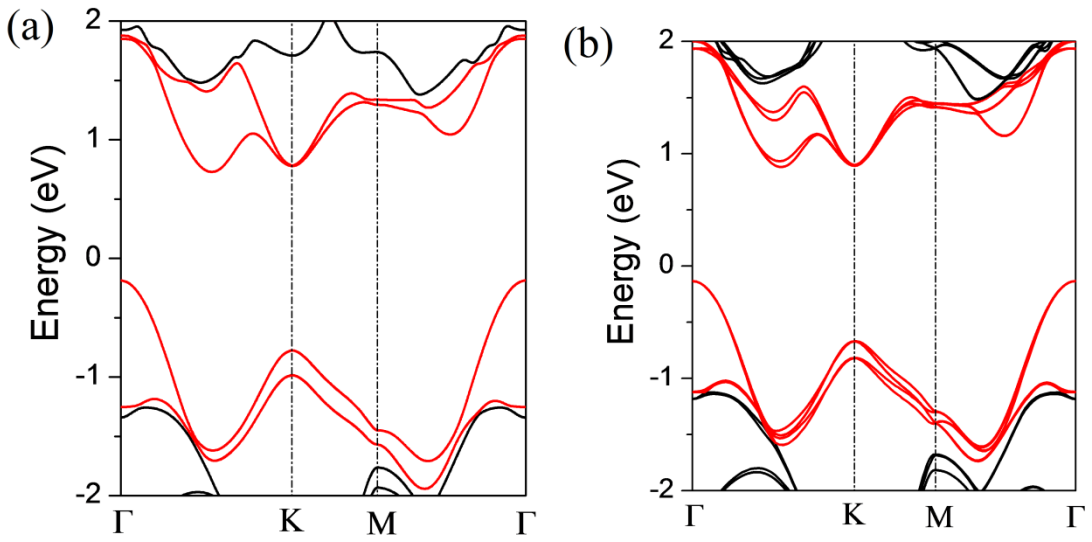

Fig. S4 Band structures of bulk 2H-MoS_2 (a) and 3R-MoS_2 (b) with spin-orbit coupling.

The band splitting of 2H-MoS_2 at CB-K is 208 meV and that of 3R-MoS_2 at CB-K is 149 meV.

Model Hamiltonian

The model Hamiltonian for tree-layer MoS_2

$$H(k)=\begin{pmatrix} E_0(k) & M_1(k) & M_2(k) \\ M_1^*(k) & E_0(k) & M_1(k) \\ M_2^*(k) & M_1^*(k) & E_0(k) \end{pmatrix}$$

The model Hamiltonian for four-layer MoS_2

$$H(k)=\begin{pmatrix} E_0(k) & M_1(k) & M_2(k) & M_3(k) \\ M_1^*(k) & E_0(k) & M_1(k) & M_2(k) \\ M_2^*(k) & M_1^*(k) & E_0(k) & M_1(k) \\ M_3^*(k) & M_2^*(k) & M_1^*(k) & E_0(k) \end{pmatrix}$$

The model Hamiltonian is used to analyze the splitting of band splitting near band gap and understand the layer's coupling. $M_1(k)$, $M_2(k)$ and $M_3(k)$ represent the coupling parameters of nearest-neighbor, second near-neighbor and third near-neighbor layer-coupling with same k point and same energy level , respectively.

Table S1. Band splitting values of the top of valance bands at Γ and K points (VB-Γ and VB-K) and the bottom of conduction bands at Λ and K points (CB-Λ and CB-K) for multi-layer 3R-type MoS_2 including 2L-ab, 3L-aba, 3L-abc, 4L-abab and 4L-abca with the different layers and stacking orders, calculated by DFT and fitted by model Hamiltonian (TM). Note that Δ_1, Δ_2 and Δ_3 represent the splitting values between the nearest-neighbor energy levels and Δ is for total splitting value.

Stacking way	VB-Γ(eV)		CB-Λ(eV)		CB-K(10^{-2} eV)		VB-K(10^{-2} eV)	
2L-ab	DFT	TM	DFT	TM	DFT	TM	DFT	TM
Δ	0.6389	0.6389	0.3058	0.3058	5.43	5.43	6.11	6.11
3L-aba								
Δ_1	0.2732	0.2757	0.2699	0.2698	5.5370	5.5340	0.7900	0.7920
Δ_2	0.5324	0.5307	0.1377	0.1378	0.1100	0.1100	6.0420	6.0420
Δ	0.8057	0.8604	0.4076	0.4076	5.6470	5.6440	6.8320	6.8340
3L-abc								
Δ_1	0.3052	0.3058	0.2278	0.2266	3.6910	3.6950	5.4900	5.4930
Δ_2	0.5228	0.5218	0.1926	0.1936	5.3490	5.3450	4.2960	4.2930
Δ	0.8281	0.8276	0.4204	0.4202	9.0400	9.0400	9.7860	9.7860
4L-abab								
Δ_1	0.1707	0.1708	0.1572	0.1580	0.9750	0.9750	0.8110	0.8040
Δ_2	0.3067	0.3066	0.2001	0.2006	4.2560	4.2220	5.1840	5.1760
Δ_3	0.4214	0.4204	0.1017	0.1004	0.7360	0.7750	1.1500	1.1640
Δ	0.8988	0.8978	0.4591	0.4590	5.9670	5.9720	7.1450	7.1440
4L-abca								
Δ_1	0.1810	0.1809	0.1700	0.1698	4.0870	4.0730	5.6170	5.6640
Δ_2	0.3037	0.3030	0.1798	0.1808	4.4640	4.4090	4.4890	4.4760
Δ_3	0.4317	0.4319	0.1357	0.1357	5.4900	5.5470	4.6540	4.6480
Δ	0.9164	0.9159	0.4855	0.4862	14.0410	14.0290	14.7600	14.7880

It is obvious that the values of band splitting from model Hamiltonian are consistent with that from DFT.