Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

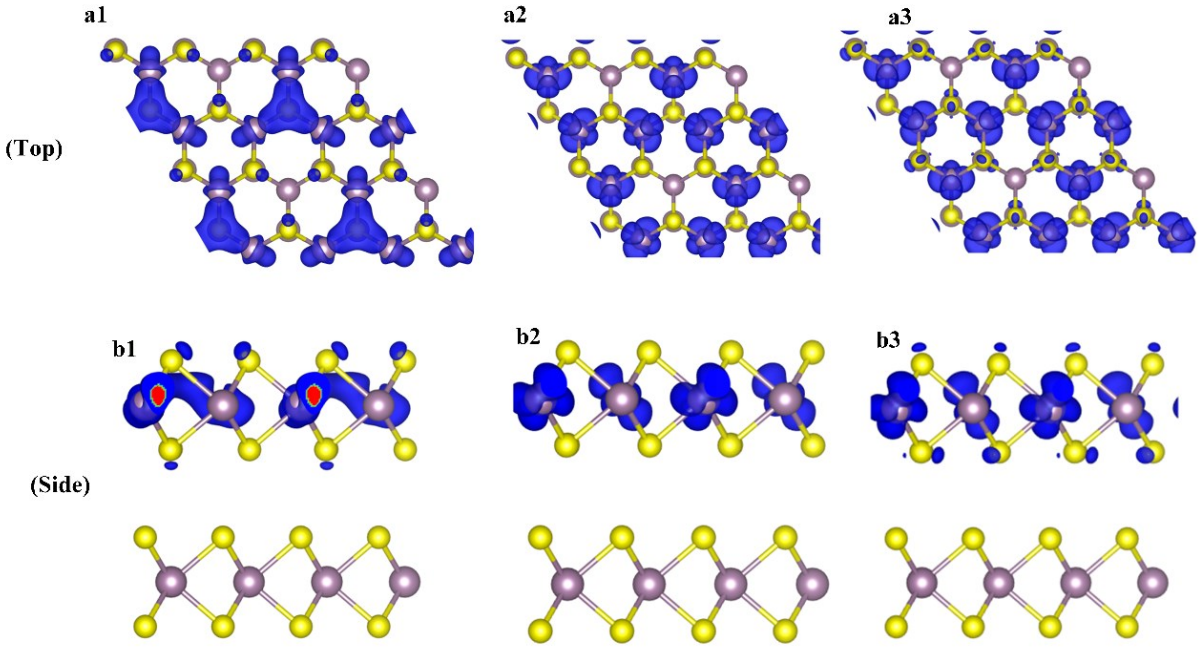

Figure S1. The Kohn–Sham orbitals corresponding to the new states (red curves in Figure 1b) (a1, a2, a3 are top view and b1, b2, b3 are side view) and the images from left to right represent for the states from bottom to top in Figure 1b, respectively.

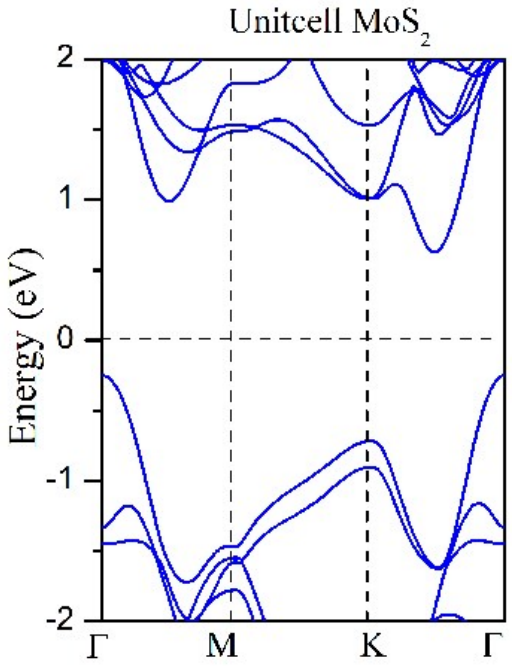

Figure S2 The band structure by DFT calculation using 1×1 unit cell

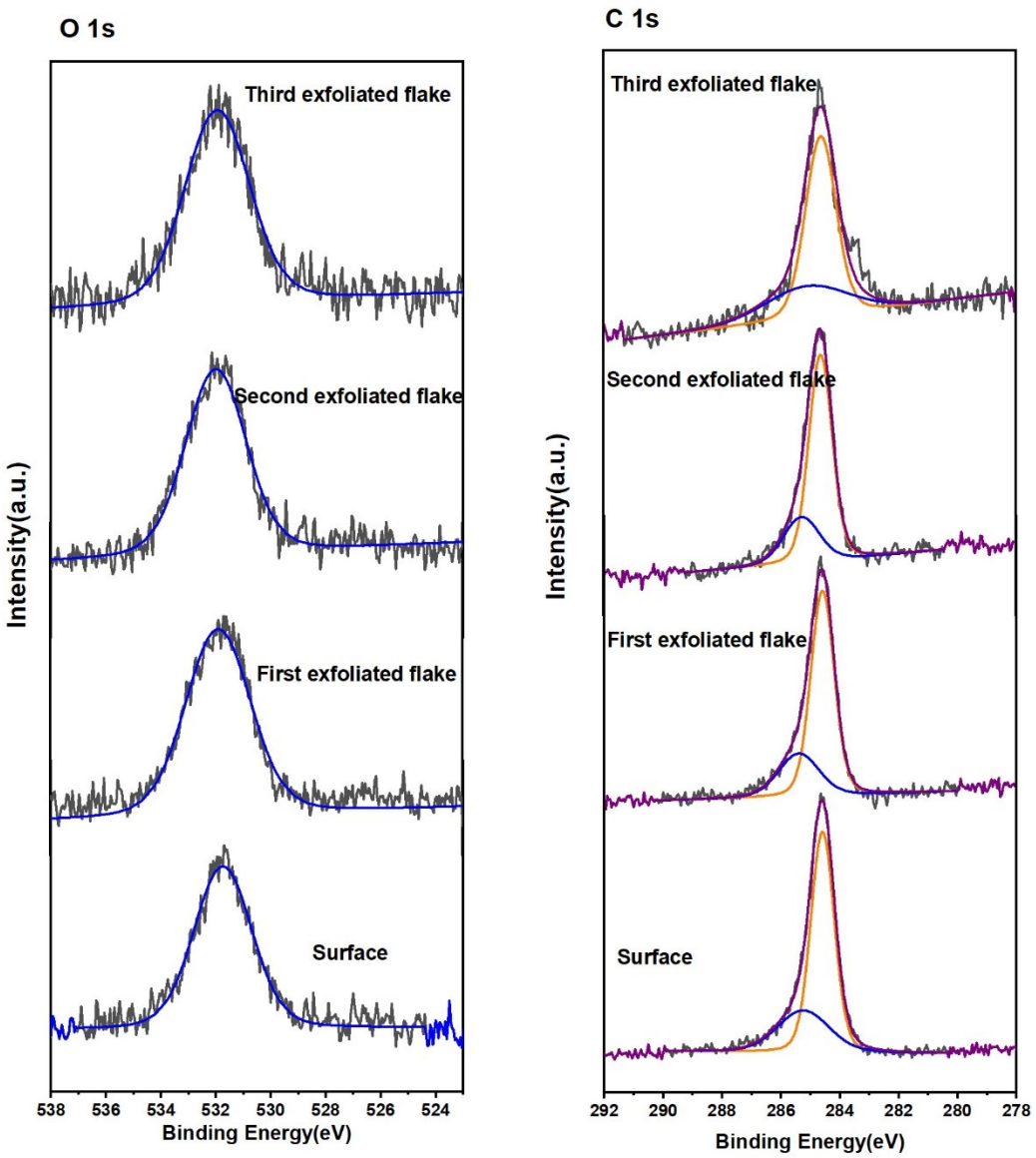

Figure S3. C1s and O 1s XPS spectra of MoS_2 crystal annealed in vacuum at 1000 ^{o}C for 100 h.

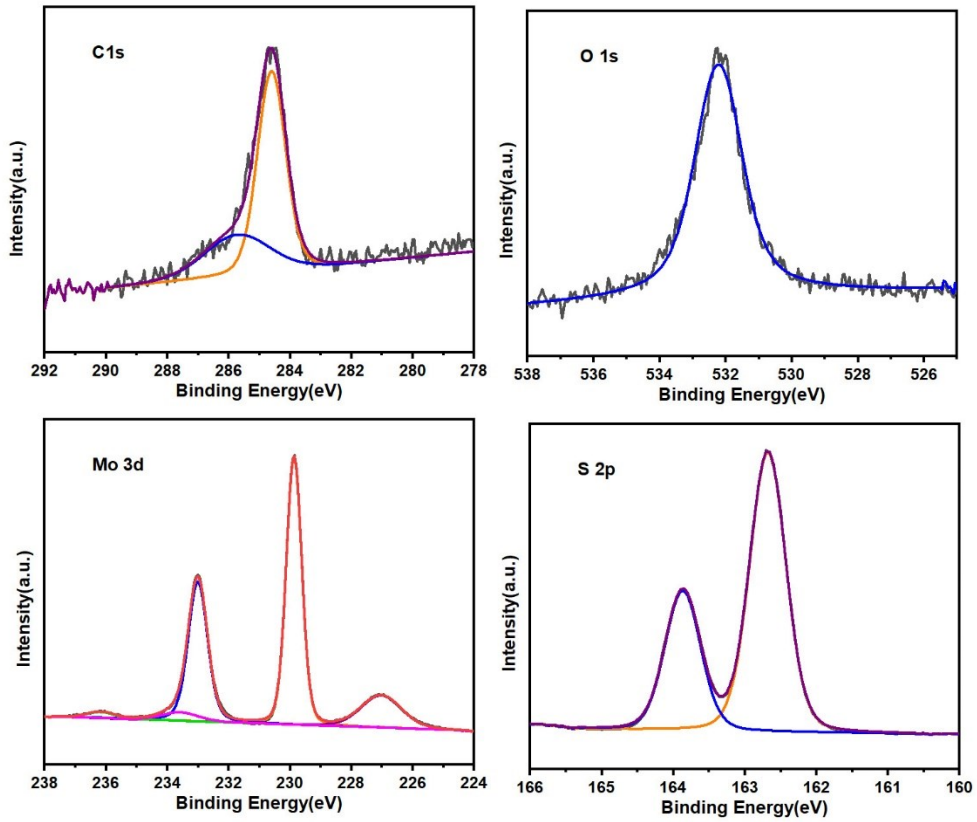

Figure S4. XPS spectra of as-grown MoS_2 crystal

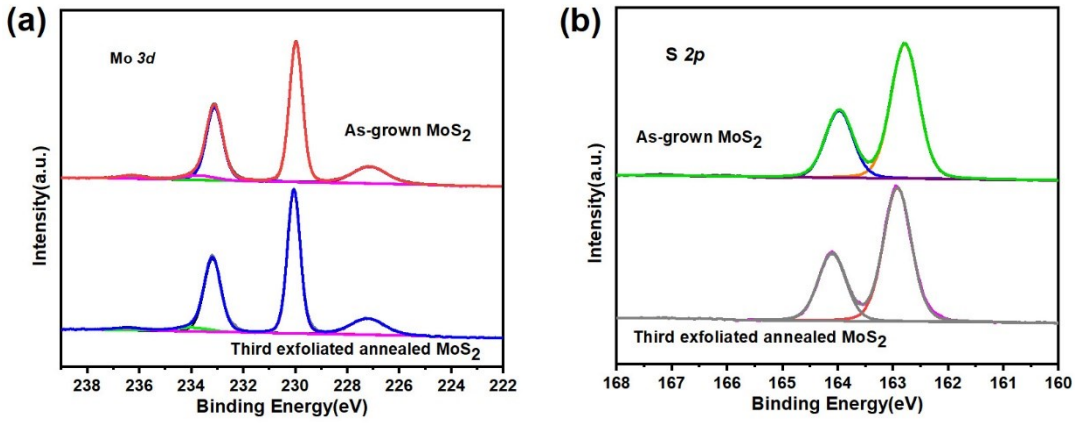

Figure S5. Mo *3d* (a) and S *2p* (b) XPS spectra of as-grown and annealed MoS_2 crystal

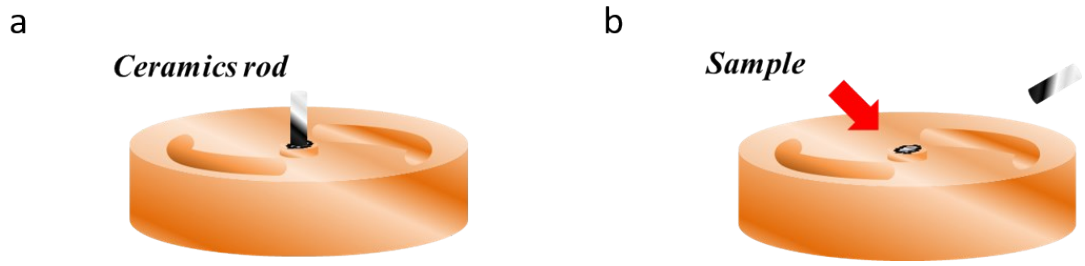

Figure S6. Schematic exfoliation of sample for ARPES

The annealed MoS_2 crystal was glued on the sample holder by silver paste, then the rod was glued on the top of MoS_2, as shown in Figure S6(a). The surface of the crystal was peeled off in-situ with the rod, then the MoS_2 with a clean and smooth surface was left on the sample holder. After that, we did the first exfoliation in the analysis chamber with base pressure 9×10^{-11} Torr before ARPES measurement, as shown in Figure S6(b). Then, the same MoS_2 sample was cleaved again for the second measurement. That second exfoliation reaches the inside layers of the crystal, which can be considered as as-grown crystal with few sulfur vacancies. All the exfoliations were operated in the vacuum system.

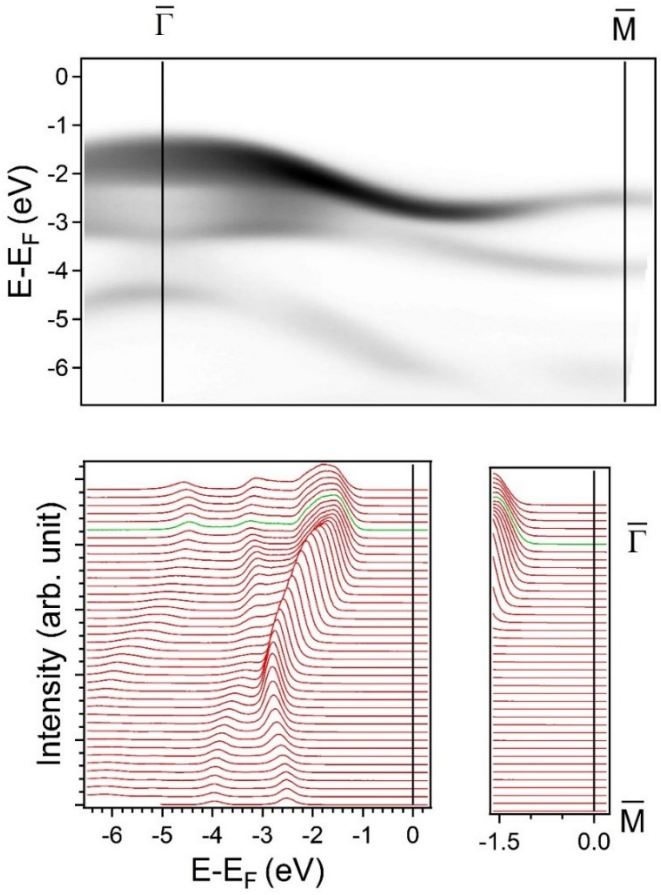

Figure S7. ARPES electronic structure (top) and energy distribution curves (bottom) of as-grown MoS_2 crystal