"Supporting Information"

Mechanistic Insight into Sodium Intercalation Dynamics and Dual-Functional Electrocatalysis in 2D-FeS_2

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1. Supplementary methods

1.1 Sulfur reduction reaction pathways

The detailed pathways are described in Eqs. (1)-(6).[1, 2]

$$S_8 + 2(Na^+ + e^-) + * \rightarrow * Na_2S_8 \quad (S1)$$

$$* Na_2S_8 + 4(Na^+ + e^-) + * \rightarrow 2Na_2S + * Na_2S_6 \quad (S2)$$

$$* Na_2S_6 + 4(Na^+ + e^-) + * \rightarrow * Na_2S_4 + 2Na_2S \quad (S3)$$

$$* Na_2S_4 + 4(Na^+ + e^-) + * \rightarrow 2Na_2S + * Na_2S_2 \quad (S4)$$

$$* Na_2S_2 + 2(Na^+ + e^-) + * \rightarrow * Na_2S + Na_2S \quad (S5)$$

$$* Na_2S \rightarrow * + Na_2S \quad (S6)$$

where * is for 2D-Na_xFeS_2 (x = 0, 1.5 and 2). $* Na_2S_8$, $* Na_2S_6$, $* Na_2S_4$, $* Na_2S_2$ and $* Na_2S$ indicate that Na_2S_8, Na_2S_6, Na_2S_4, Na_2S_2 and Na_2S are adsorbed on 2D-Na_xFeS_2 surface, respectively.

1.2 Calculation details for Gibbs free energy

The * is for the active site of 2D-Na_xFeS_2 (x = 0, 1.5 and 2). The *Na_2S_n ($0 \leq n \leq 8$) represented the intermediate species adsorbed on the active sites. Gibbs free energy is obtained from the following formula. ΔG is for each reaction step.

$$\Delta G = \Delta E_{\mathrm{DFT}} + \Delta \mathrm{ZPE} - T\Delta S \quad (S7)$$

ΔE_{DFT} is the total energy calculated by DFT, ΔZPE represents zero energy, $T\Delta S$ represents entropy contribution. ΔZPE and $T\Delta S$ are obtained by calculating the rotational frequency of the adsorbed molecules (NaPSs), and the temperature is set as 298.15 K. In Gibbs free energy calculation, SCF conversion and max force are set to 450 eV and 1.0 x 10^{-7} eV. Gramma point of Brillouin 3×3×1 was applied to calculate the frequency.

2. Supplementary figures

Figure S1. Adsorption structures for Na^+ on the top (a), hollow (b) and Fe (c) sites of 2D-FeS_2 surface

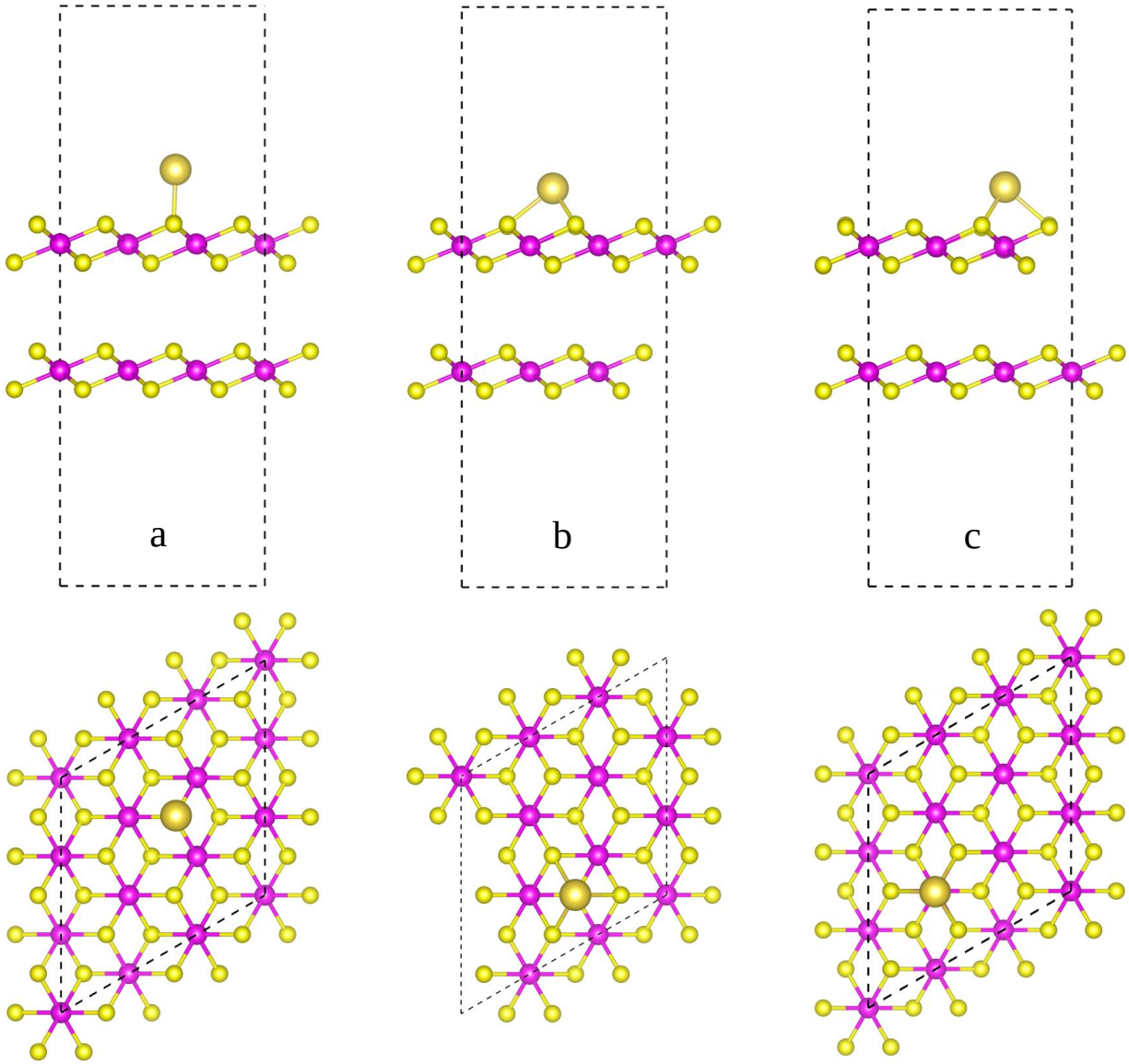


Figure S2. Structures for 2D-$Na_{0.17}FeS_2$-1 (a), 2D-$Na_{0.17}FeS_2$-2 (b) and 2D-$Na_{0.17}FeS_2$-3 (c)

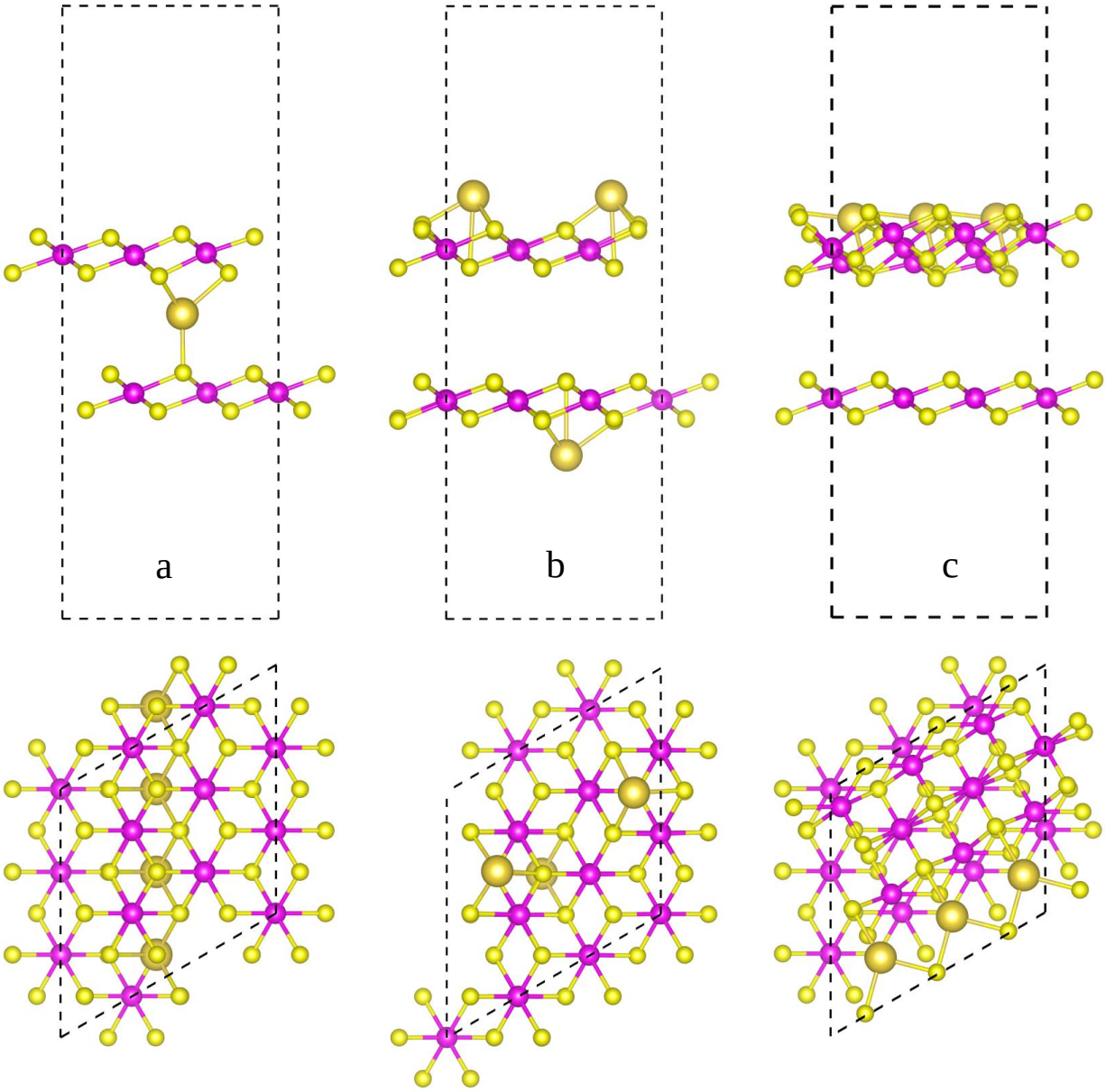


Figure S3. Structures for 2D-$Na_{0.33}FeS_2$-1 (a), 2D-$Na_{0.33}FeS_2$-2 (b) and 2D-$Na_{0.33}FeS_2$-3 (c)

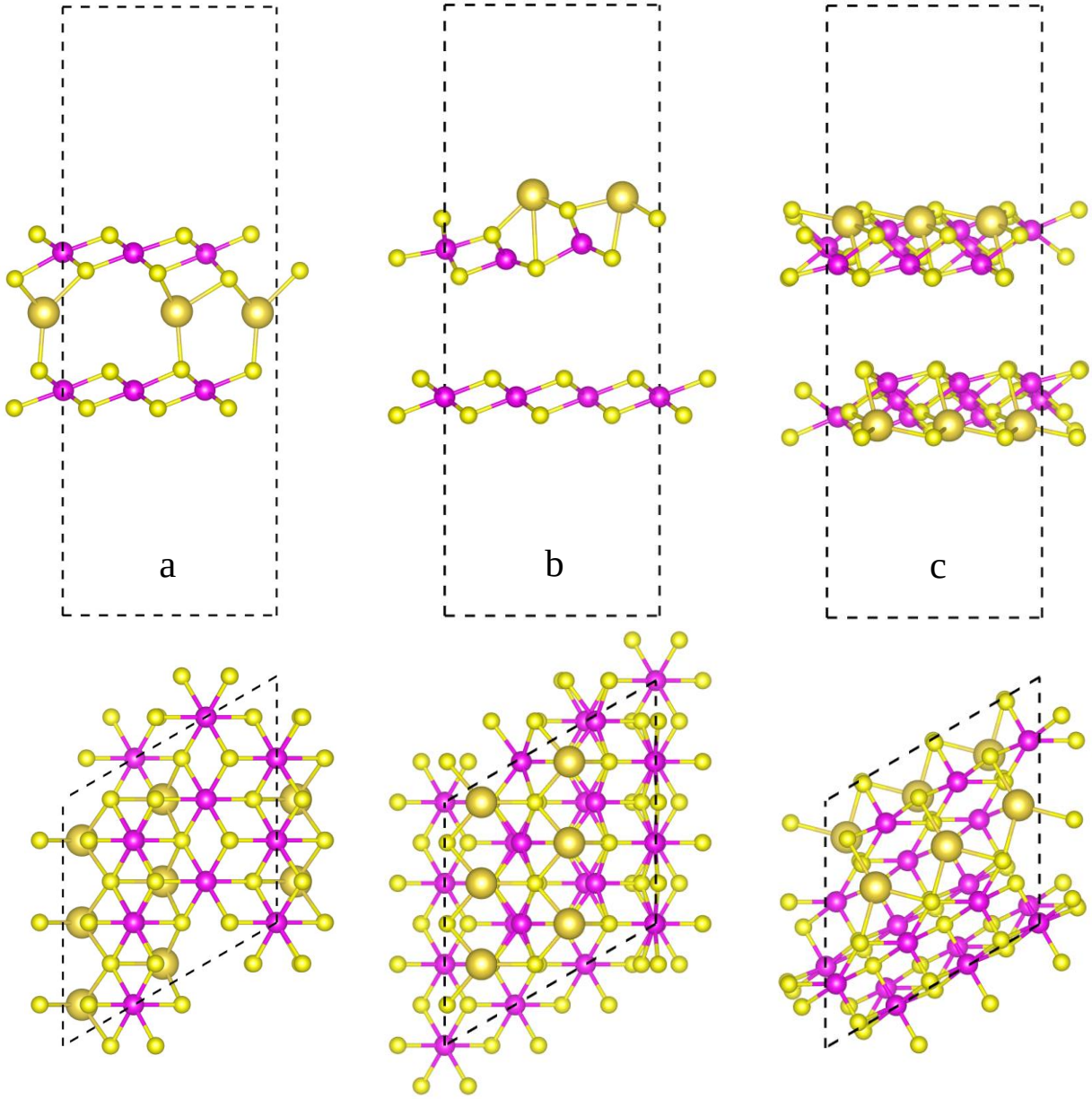


Figure S4. Structures for 2D-$Na_{0.5}FeS_2$-1 (a) and 2D-$Na_{0.5}FeS_2$-2 (b)

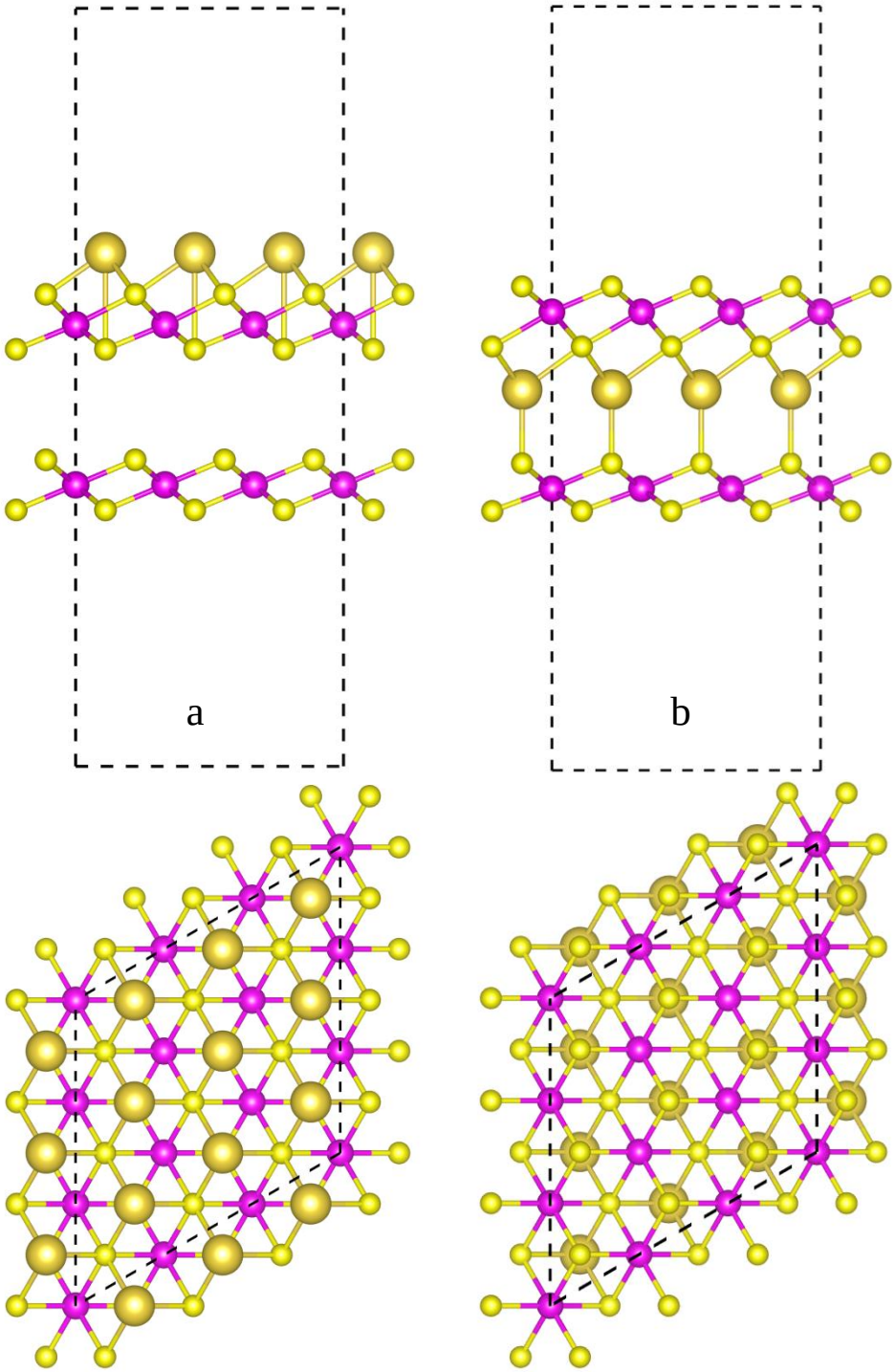


Figure S5. Structures for 2D-$Na_{0.67}FeS_2$-1 (a), 2D-$Na_{0.67}FeS_2$-2 (b) and 2D-$Na_{0.67}FeS_2$-3 (c)

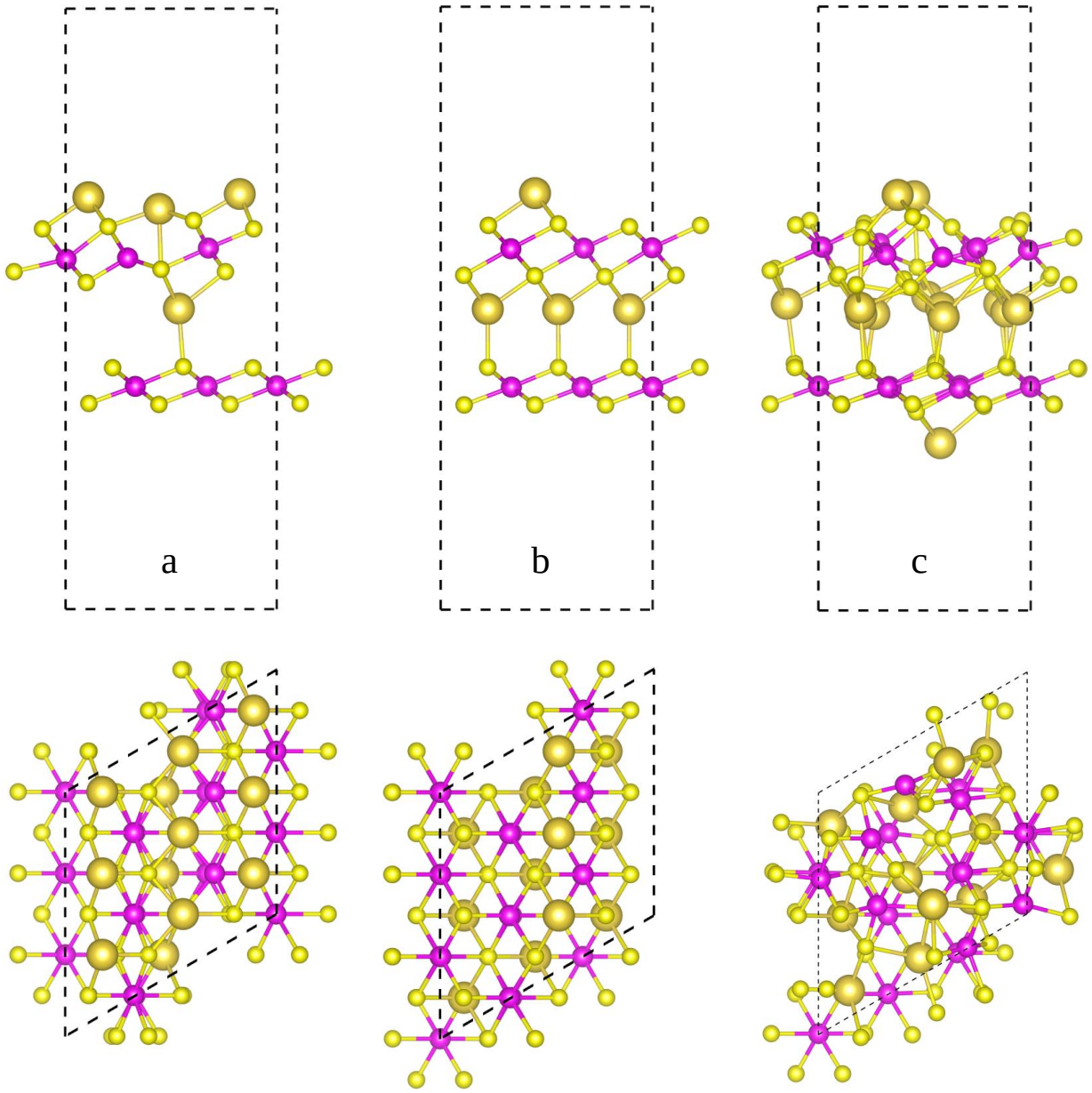


Figure S6. Structures for 2D-$Na_{0.83}FeS_2$-1 (a), 2D-$Na_{0.83}FeS_2$-2 (b) and 2D-$Na_{0.83}FeS_2$-3 (c)

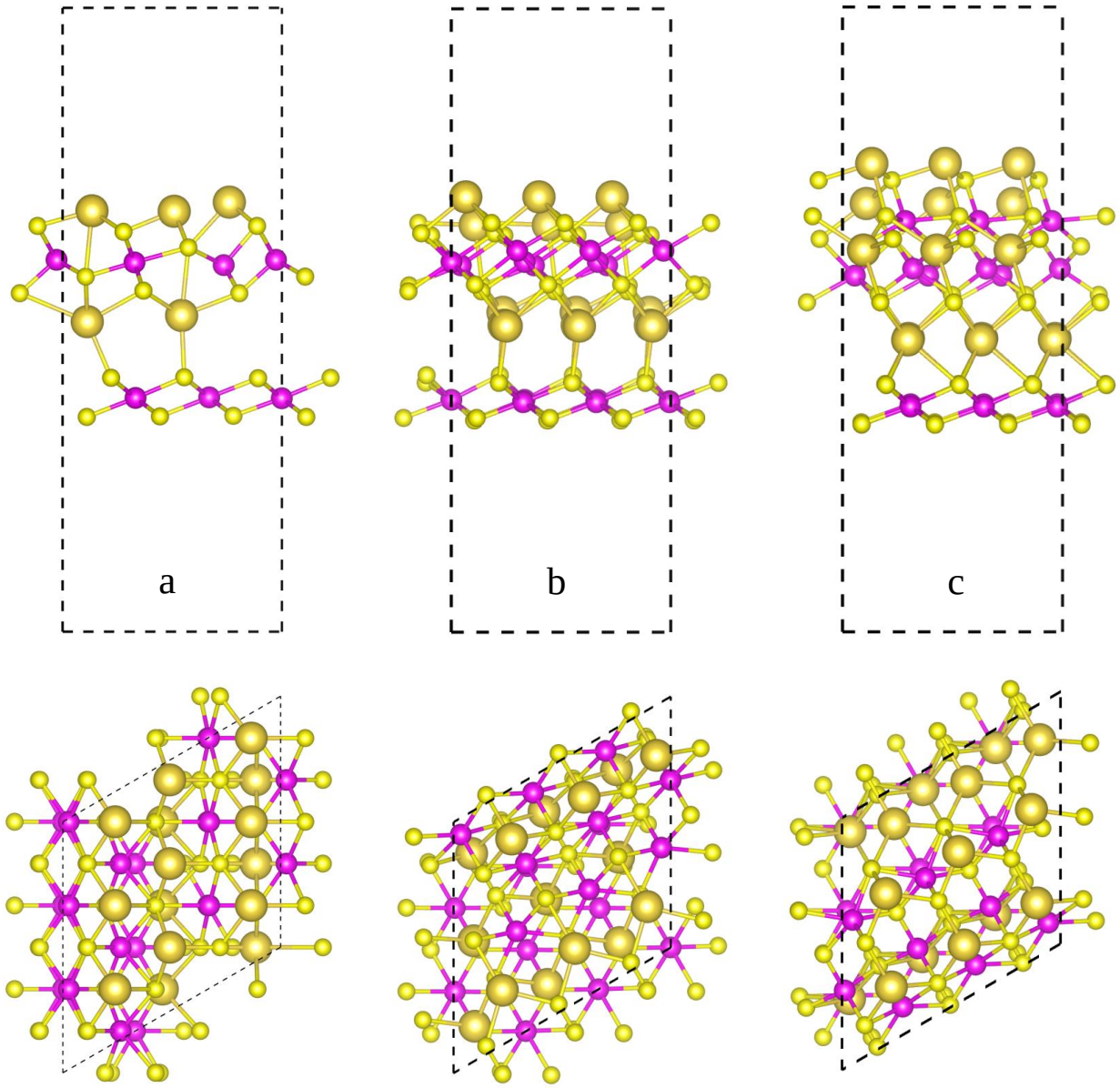


Figure S7. Structures for 2D-$NaFeS_2$-1 (a), 2D-$NaFeS_2$-2 (b), 2D-$NaFeS_2$-3 (c) and 2D-$NaFeS_2$-4 (d)

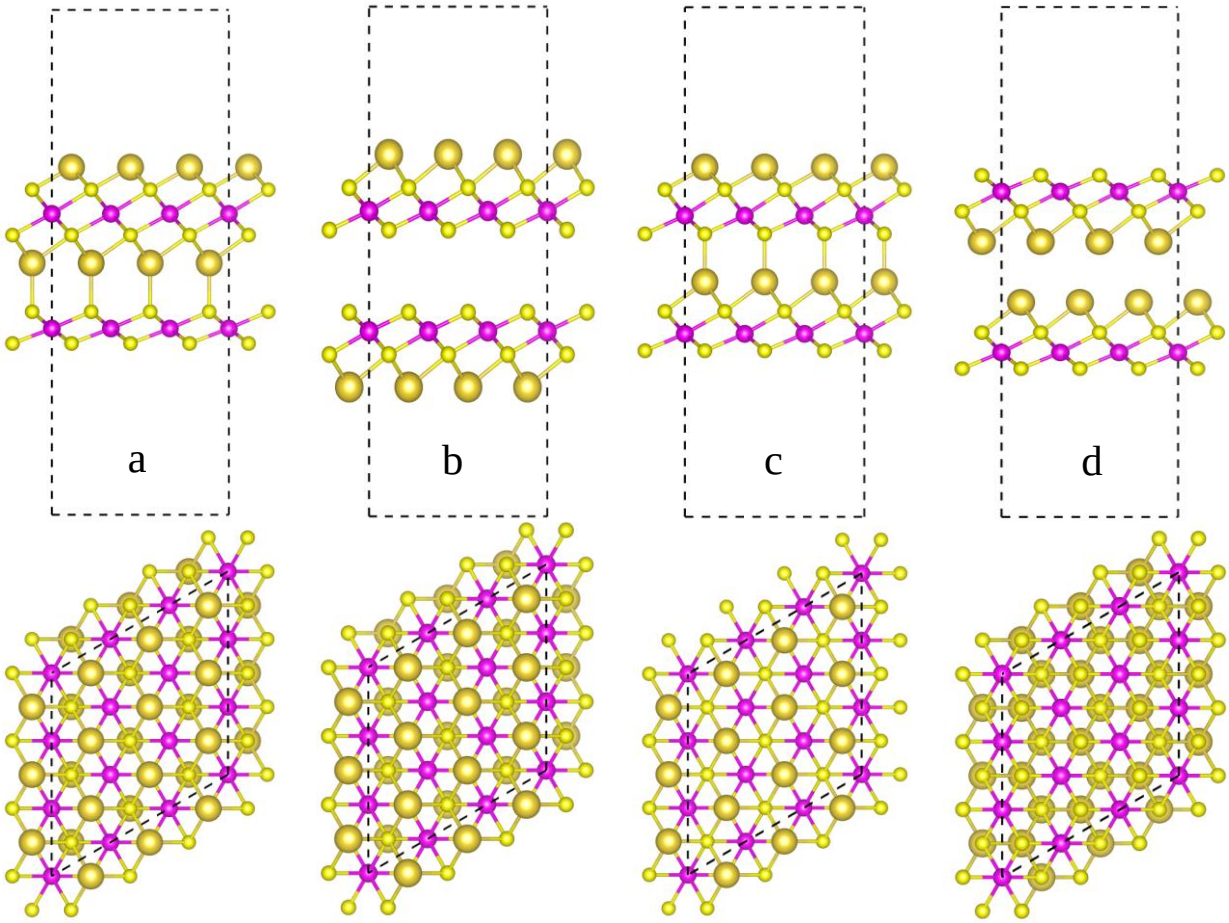


Figure S8. Structures for 2D-$Na_{1.17}FeS_2$-1 (a), 2D-$Na_{1.17}FeS_2$-2 (b) and 2D-$Na_{1.17}FeS_2$-3 (c)

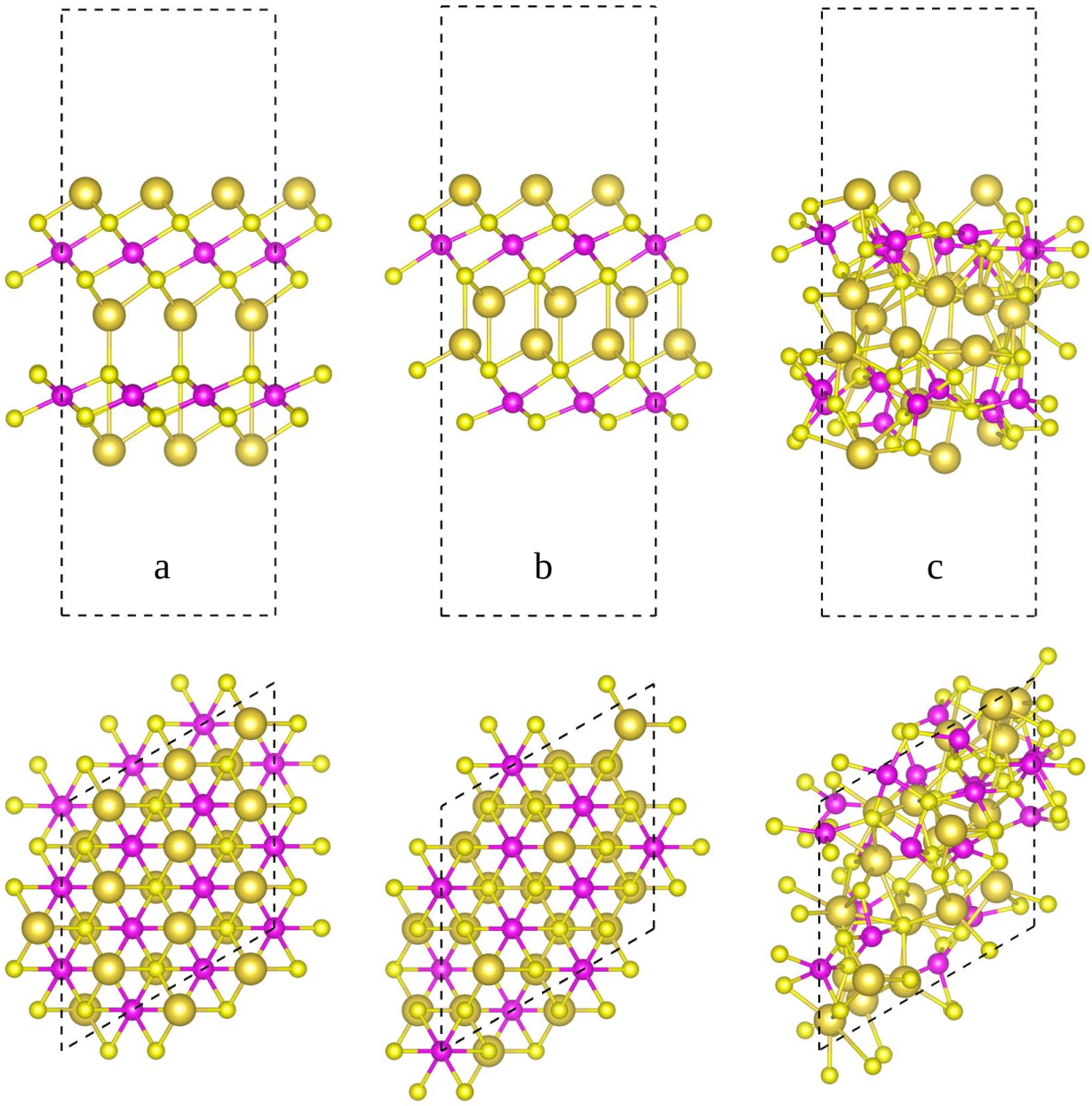


Figure S9. Structures for 2D-$Na_{1.33}FeS_2$-1 (a), 2D-$Na_{1.33}FeS_2$-2 (b), 2D-$Na_{1.33}FeS_2$-3 (c) and 2D-$Na_{1.33}FeS_2$-4 (d)

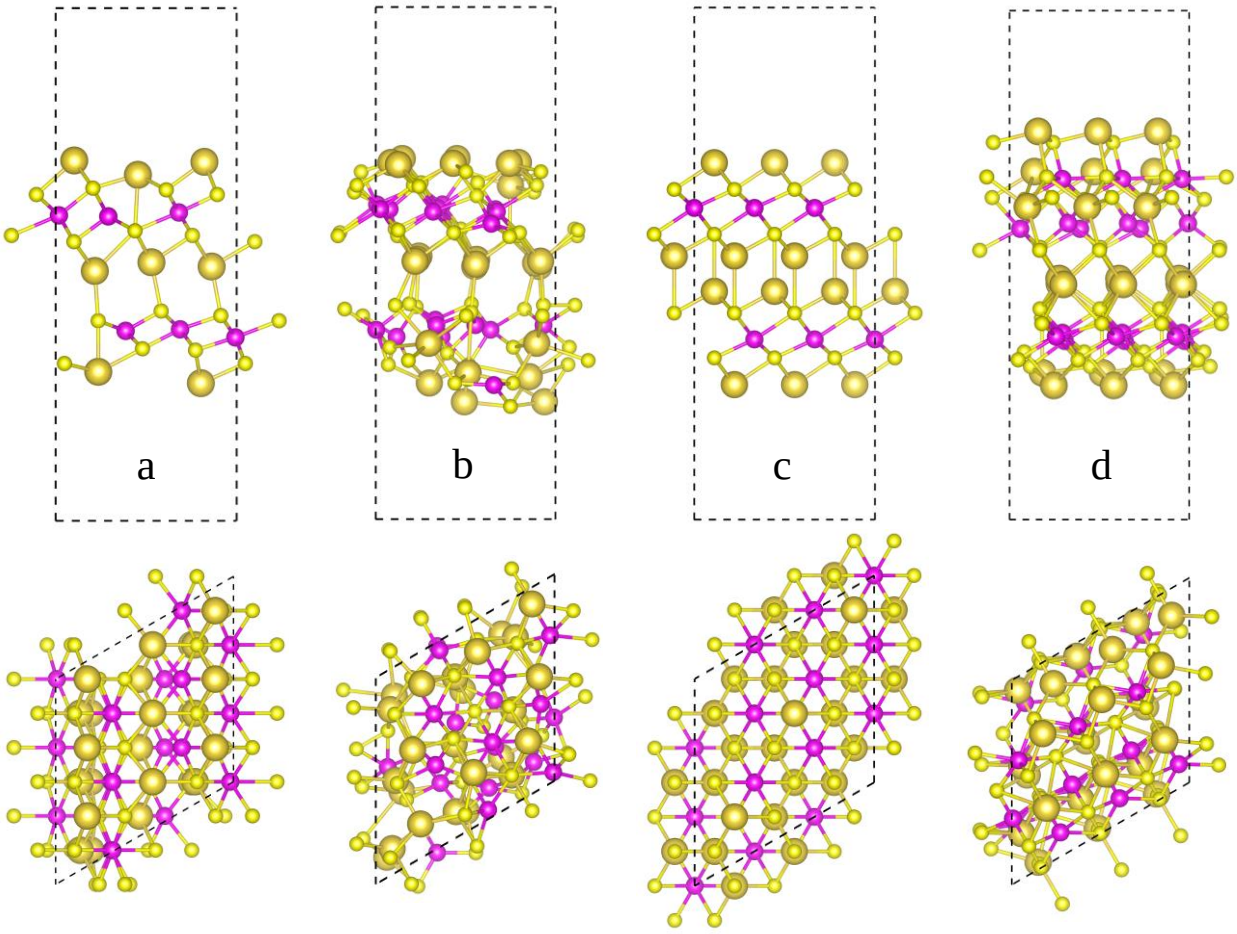


Figure S10. Structures for 2D-$Na_{1.5}FeS_2$-1 (a), 2D-$Na_{1.5}FeS_2$-2 (b) and 2D-$Na_{1.5}FeS_2$-3 (c)

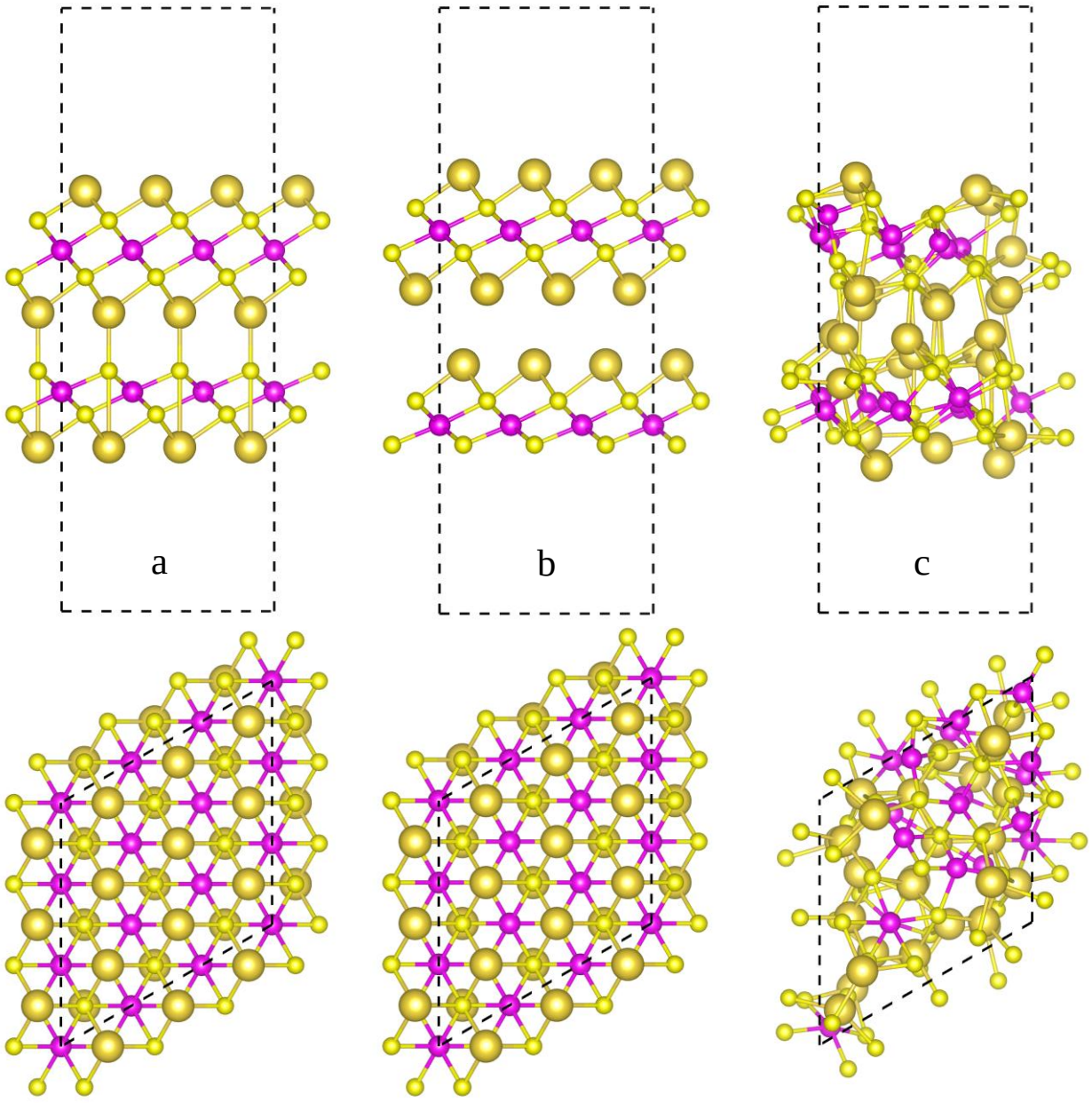


Figure S11. Structures for 2D-$Na_{1.67}FeS_2$-1 (a) and 2D-$Na_{1.67}FeS_2$-2 (b)

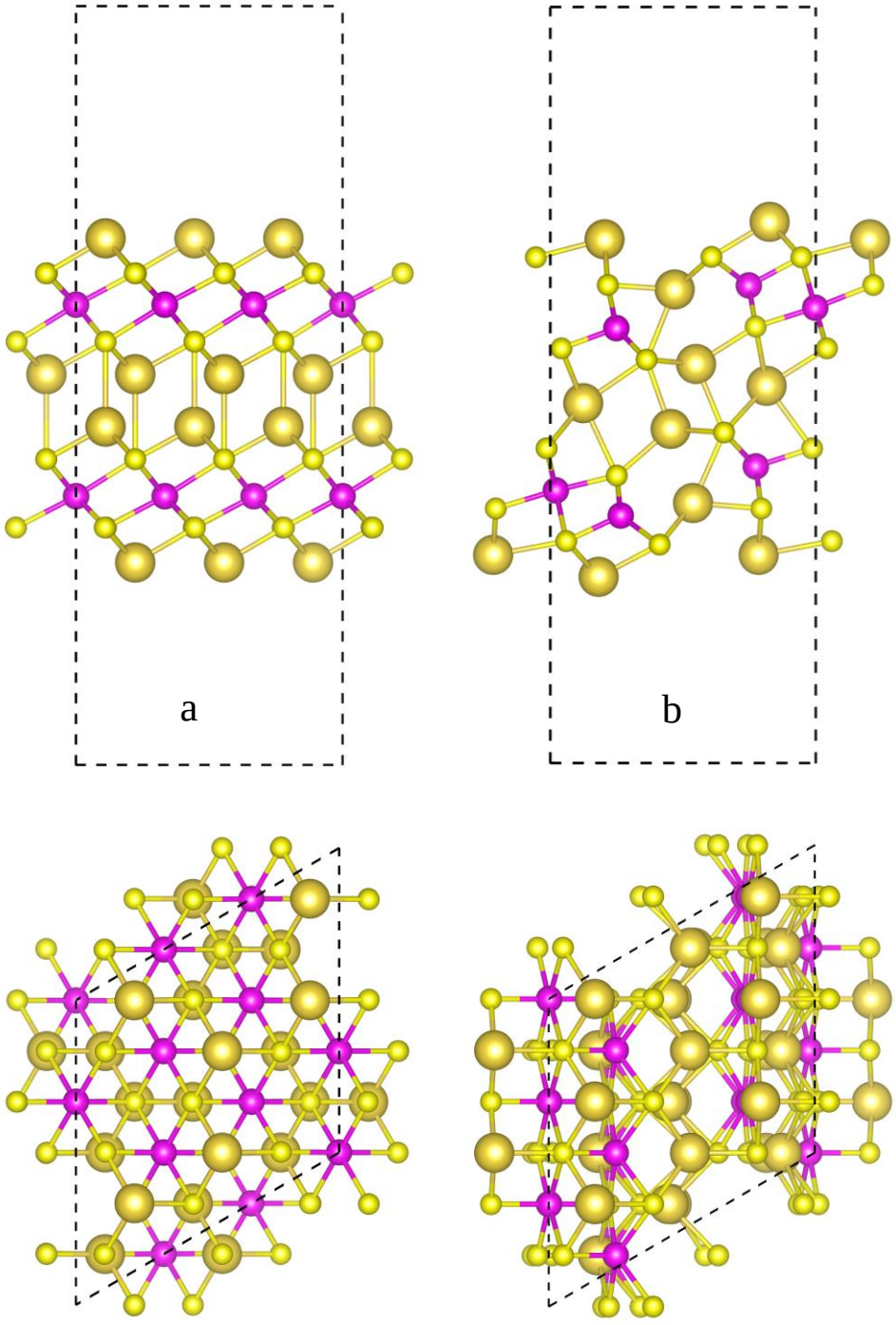


Figure S12. Structures for 2D-$Na_{1.83}FeS_2$-1 (a) and 2D-$Na_{1.83}FeS_2$-2 (b)

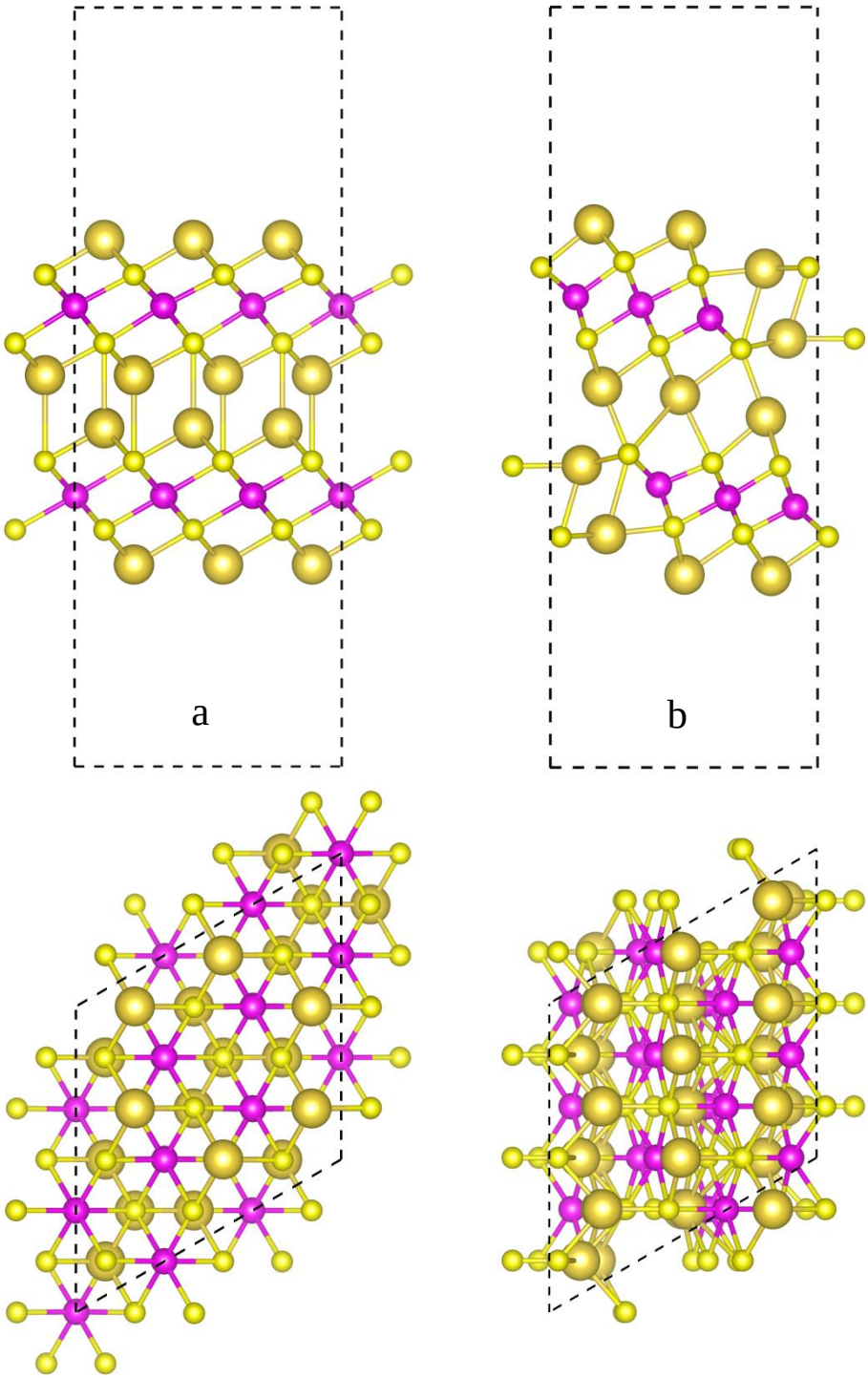


Figure S13. Structure of 2D-Na_2FeS_2

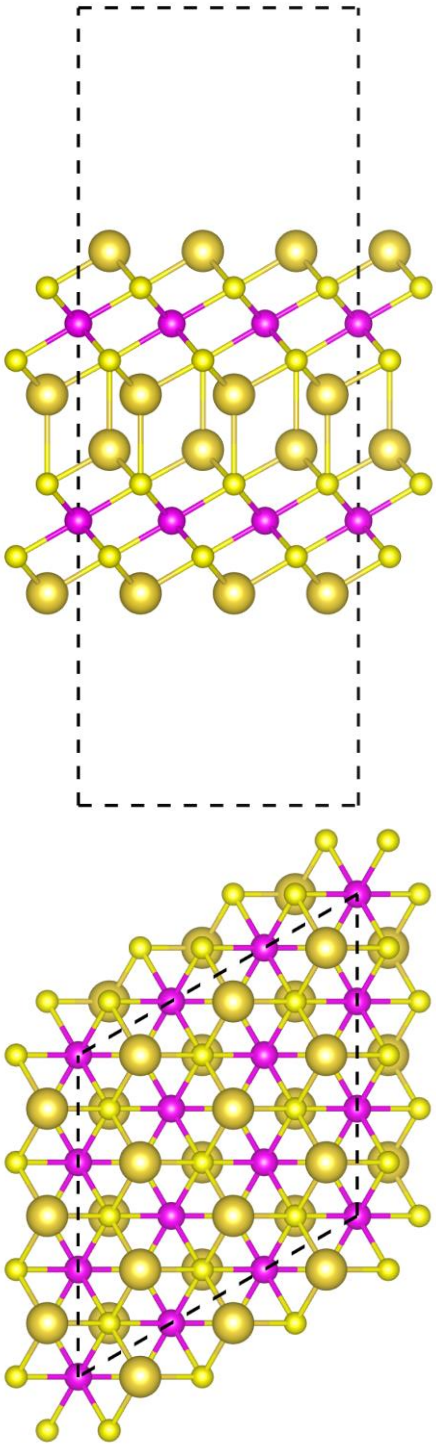


Figure S14. Na^+ diffusion path on 2D-FeS_2 (a), 2D-$Na_{0.17}FeS_2$ (b), 2D-$Na_{0.33}FeS_2$ (c), 2D-$Na_{0.67}FeS_2$ (d), 2D-$Na_{1.17}FeS_2$ (e), 2D-$Na_{1.5}FeS_2$ (f) and 2D-Na_2FeS_2 (g) surfaces.

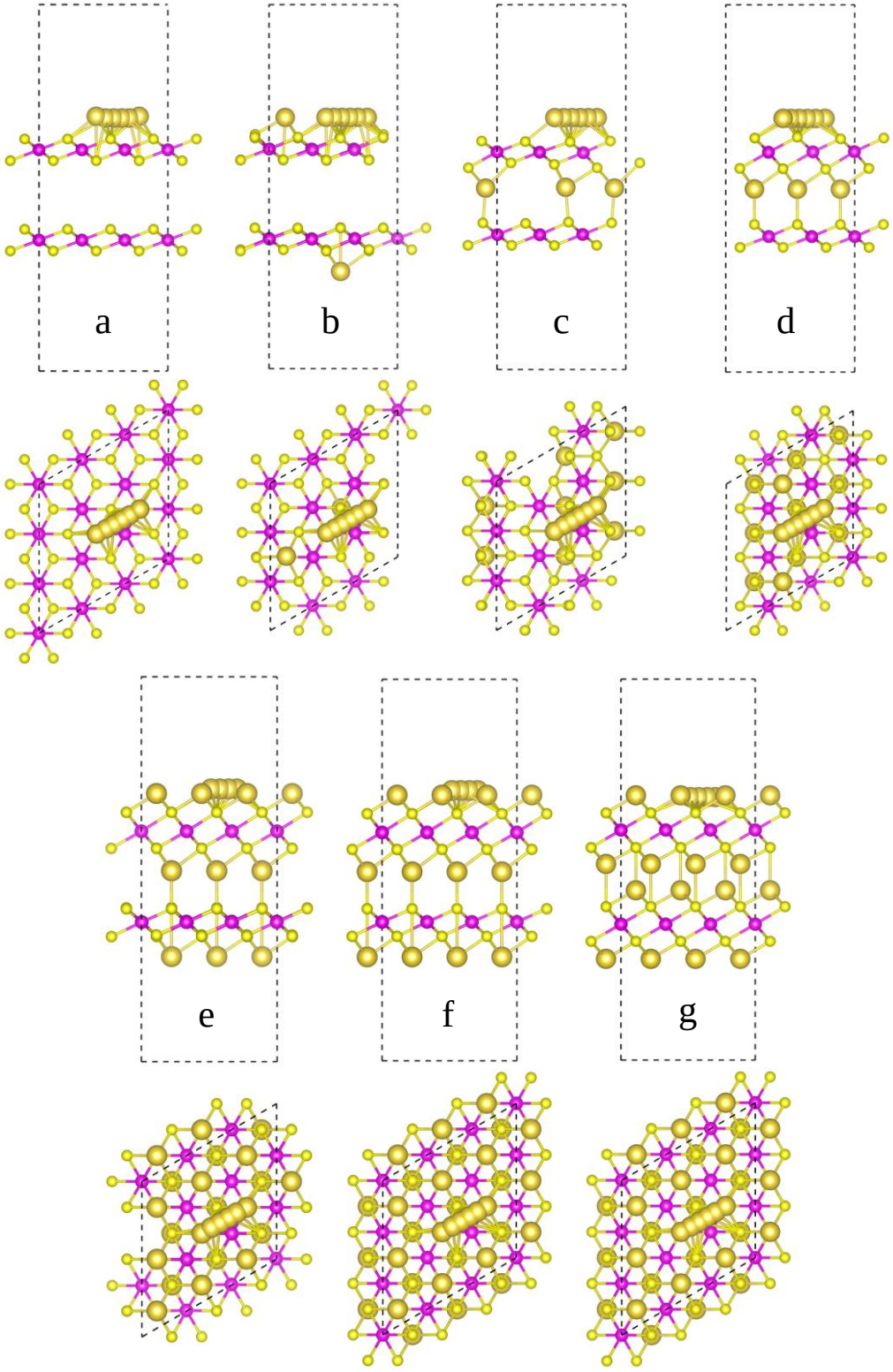


Figure S15. Adsorption structures of S_8 (a), Na_2S_8 (b), Na_2S_6 (c), Na_2S_4 (d), Na_2S_2 (e) and Na_2S (f) on 2D-FeS_2 surface

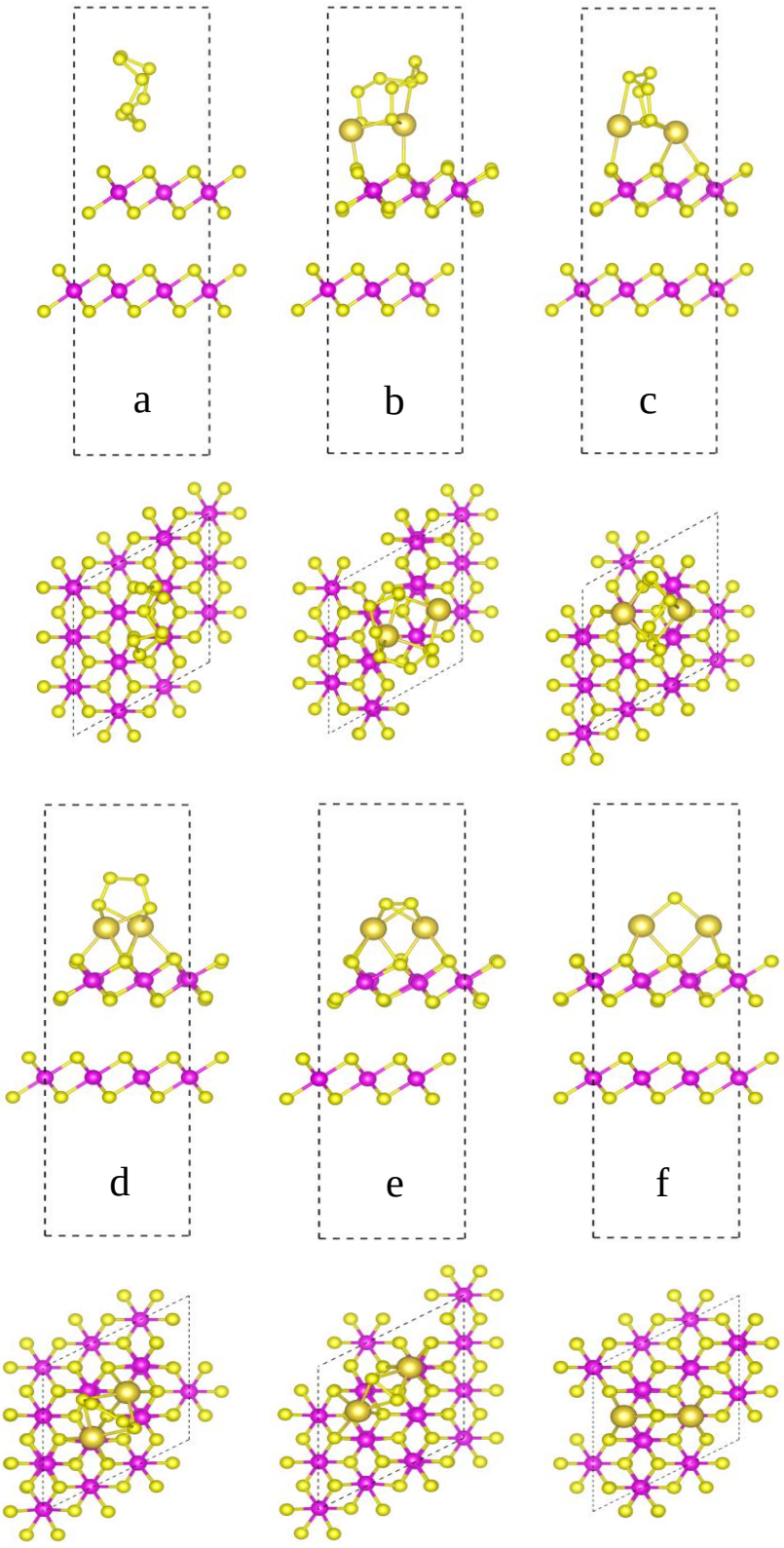


Figure S16. Adsorption **s**tructures of S_8 (a), Na_2S_8 (b), Na_2S_6 (c), Na_2S_4 (d), Na_2S_2 (e), and Na_2S (f) on 2D-$Na_{1.5}FeS_2$ surface

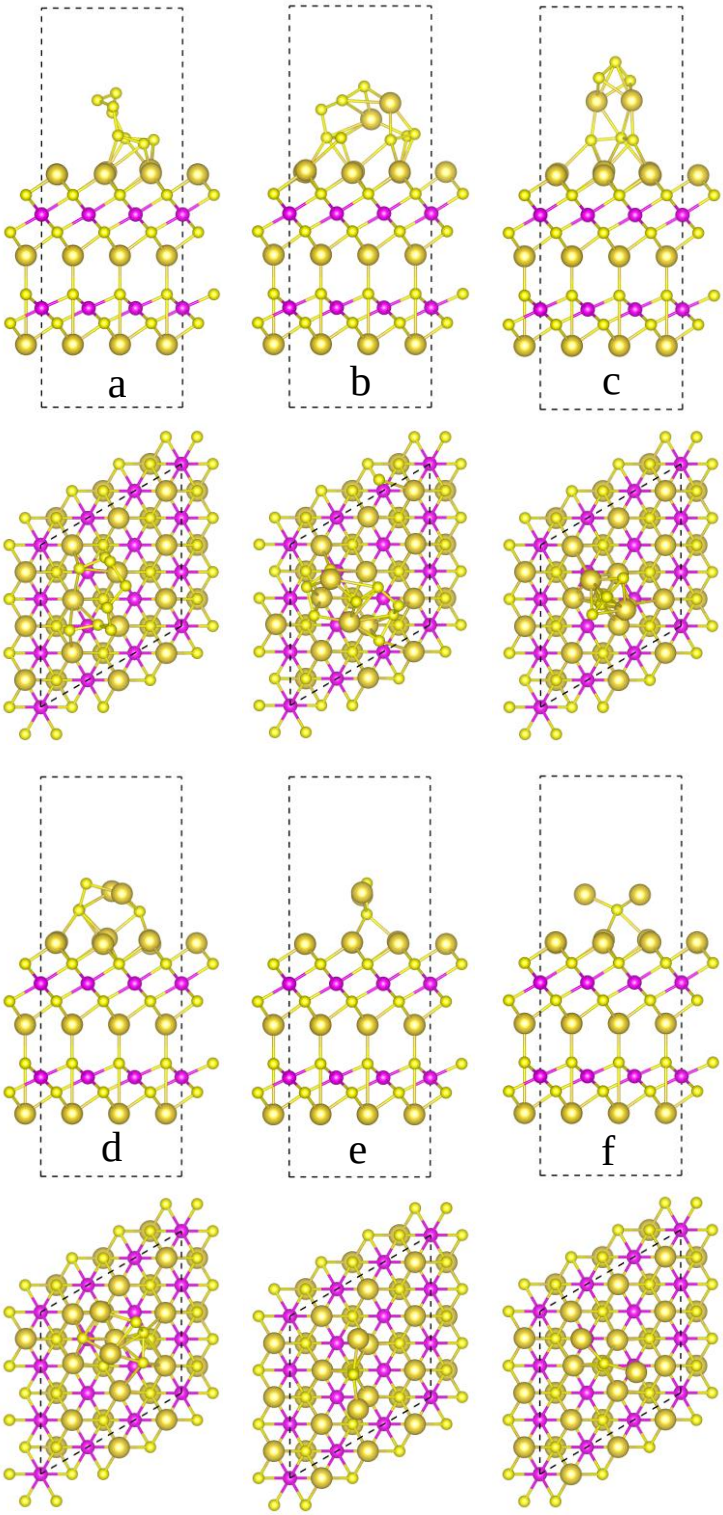


Figure S17. Adsorption **s**tructures of S_8 (a), Na_2S_8 (b), Na_2S_6 (c), Na_2S_4 (d), Na_2S_2 (e), and Na_2S (f) on 2D-Na_2FeS_2 surface

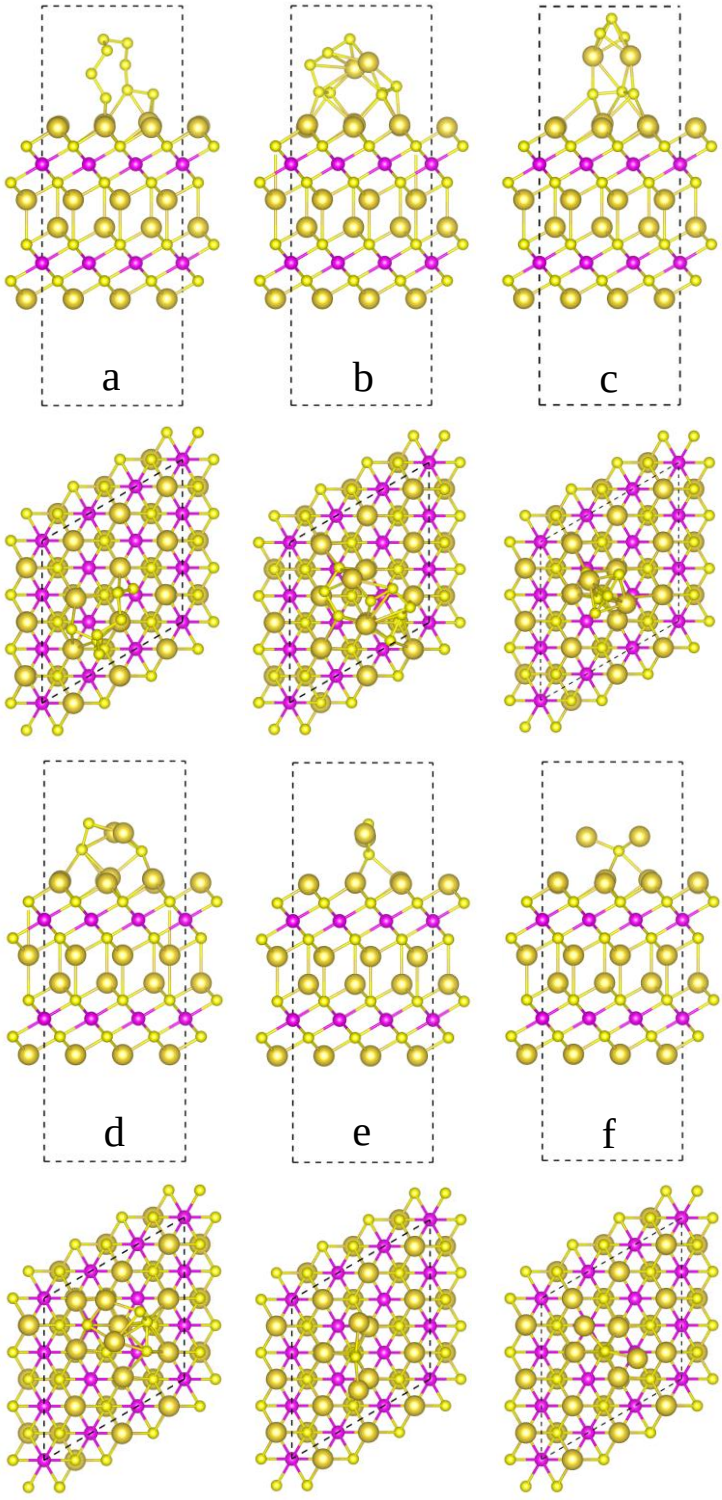
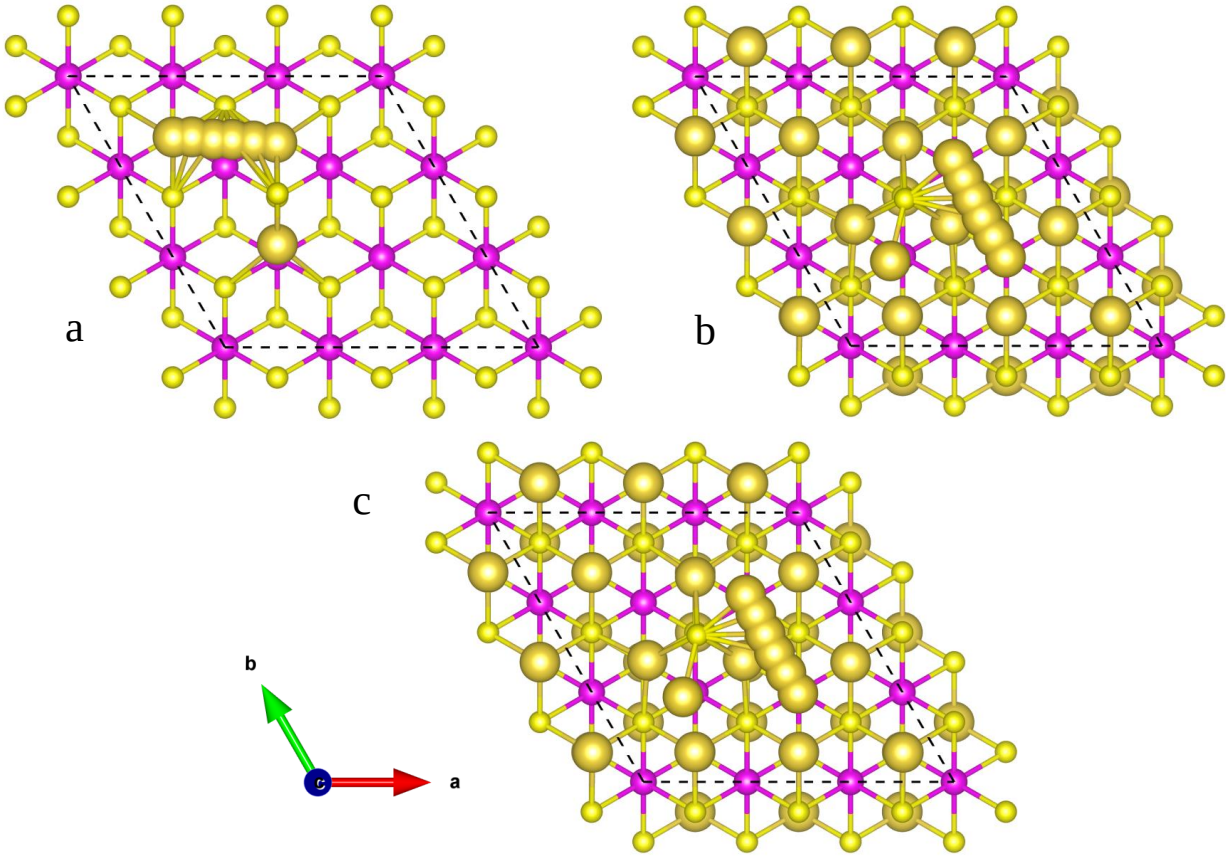


Figure S18. Decomposition paths for Na_2S on 2D-FeS_2 (a), 2D-$Na_{1.5}FeS_2$ (b) and 2D-Na_2FeS_2 (c) surfaces



References

1. L. Zhao, Y. Tao, Y. Zhang, Y. Lei, W. H. Lai, S. Chou, H. K. Liu, S. X. Dou and Y. X. Wang, *Adv. Mater.*, 2024, **36**, 2402337.
2. Y. J. Lei, H. W. Liu, Z. Yang, L. F. Zhao, W. H. Lai, M. Chen, H. Liu, S. Dou and Y. X. Wang, *Adv. Funct. Mater.*, 2023, **33**, 2212600.