Electronic supplementary information

Theoretical insights into surface-phase transition and ion competition during alkali ion intercalation on the Cu_4Se_4 nanosheet

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Table S1 presents the structural parameter of monolayer, bilayer, trilayer, four-layer and bulk CuSe crystal. The vibrational frequencies of the Cu_4Se_4 nanosheet is given in Table S2. The geometric structures and cohesive energies of monolayer, bilayer, trilayer and four-layer CuSe nanosheet are plotted in Figures S1-S4, respectively.

All possible configurations of two, four, six, eight, ten, twelve, fourteen, sixteen sodium atoms adsorbed on the Cu_4Se_4 nanosheet are shown in Figures S5-S12, respectively, and those for potassium atoms are given in Figures S13-S20.

Figures S21-S25 are the geometric structures and adsorption energy of protons on the Cu_4Se_4 nanosheet with different intercalated proton number, where the adsorption energy of protons, E_H, is defined as

$$E_H = \left(E_{H_n(Cu_4Se_4)_9} - E_{(Cu_4Se_4)_9} - nE_{H_2} / 2 \right) / n \quad \text{(S1)}$$

where $E_{H_n(Cu_4Se_4)_9}$, $E_{(Cu_4Se_4)_9}$, and E_{H_2} are energies of the proton intercalated system, Cu_4Se_4 nanosheet and a hydrogen molecule in the gas phase.

Table S1 Crystal lattice constants (a, c), bond lengths ($l_{Ch1\text{-}Cu1}$, $l_{Ch2\text{-}Cu2}$, $l_{Ch1\text{-}Cu2}$, and $l_{Ch2\text{-}Ch2}$) and cohesive energies (E_{coh}) of CuSe bulk crystals and nano-layers

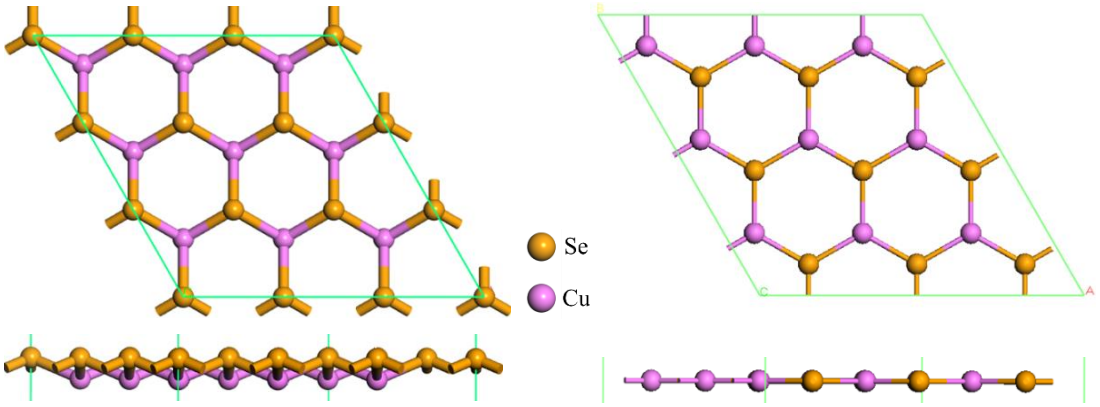
Materials	a, c (Å)	$l_{Se1\text{-}Cu1}$(Å)	$l_{Se2\text{-}Cu2}$(Å)	$l_{Se1\text{-}Cu2}$(Å)	$l_{Se2\text{-}Se2}$(Å)	E_{coh} (eV/atom)
Monolayer						
CuSe-a	3.756, 30.0	2.308				-2.948
CuSe-b	3.977, 30.0	2.295/2.303				-2.945
Bilayer						
Cu_2Se_2-a	4.059, 30.0		2.345		2.651	-3.144
Cu_2Se_2-b	3.690, 30.0	2.375	2.404	2.542		-3.248
Trilayer						
Cu_3Se_3-a	4.005, 30.0	2.315/2.363	2.435	2.429	2.507	-3.312
Cu_3Se_3-b	3.889, 30.0	2.360	2.364/2.376	2.455/2.485		-3.217
Tetralayer						
Cu_4Se_4-a	3.912, 30.0	2.346	2.412	2.453	2.425	-3.387
Cu_4Se_4-b	3.928, 30.0	2.433	2.271/2.379	2.332	2.542	-3.331
			2.386	2.456		
Bulk cystal						
CuSe(c)	3.994, 17.215	2.306	2.394	2.445	2.426	-3.442
CuSe(c,exp)	3.938, 17.250	2.274	2.391	2.451	2.386	

Table S2 Vibrational modes and frequencies of the Cu_4Se_4 nanosheet.

mode	Au_amu	cm^{-1}	meV	THz
1	0.005516	28.4	3.52	0.850
2	0.005588	28.7	3.56	0.861
3	0.012463	64.1	7.94	1.921
4	0.014540	74.7	9.27	2.241
5	0.015304	78.7	9.75	2.358
6	0.015718	80.8	10.02	2.422
7	0.015856	81.5	10.11	2.444
8	0.021733	111.7	13.85	3.349
9	0.024770	127.3	15.79	3.817
10	0.028402	146.0	18.10	4.377
11	0.035131	180.6	22.39	5.414
12	0.035147	180.7	22.40	5.417
13	0.040520	208.3	25.83	6.245
14	0.041926	215.5	26.72	6.461
15	0.042104	216.4	26.83	6.489
16	0.042763	219.8	27.26	6.590
17	0.042844	220.2	27.31	6.603
18	0.043175	221.9	27.52	6.654
19	0.046571	239.4	29.68	7.177
20	0.051162	263.0	32.61	7.884
21	0.051443	264.4	32.79	7.928

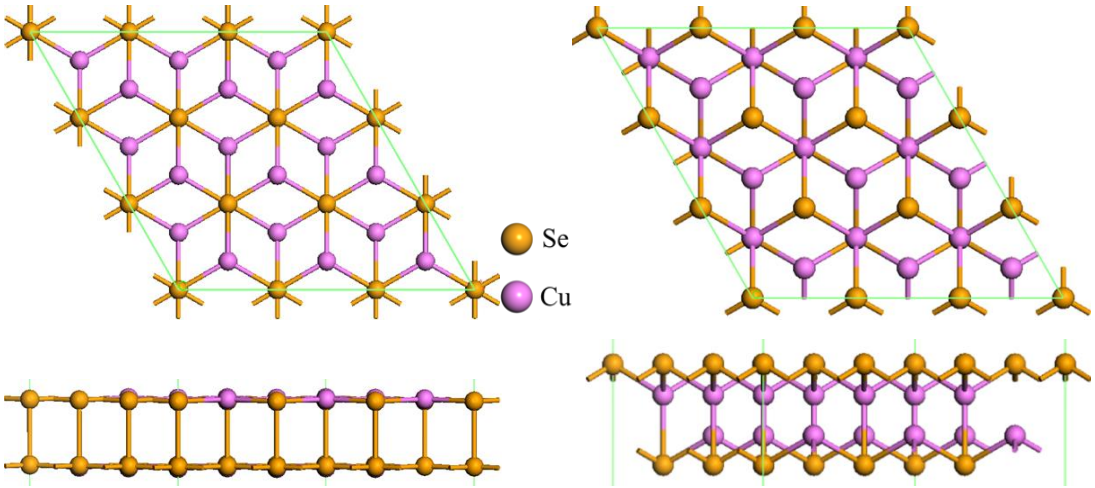
Table S3 Calculted lattice parameters for pristine and Na/K intercalted Cu_4Se_4 crystals

Crystal	Space group	*a* / Å	*b* / Å	*c* / Å
Cu_4Se_4	*P6₃/mmc*	3.898	3.898	24.151
$NaCu_4Se_4$	*P6₃/mmc*	4.029	4.029	24.819
KCu_4Se_4	*P6₃/mmc*	4.042	4.042	26.639



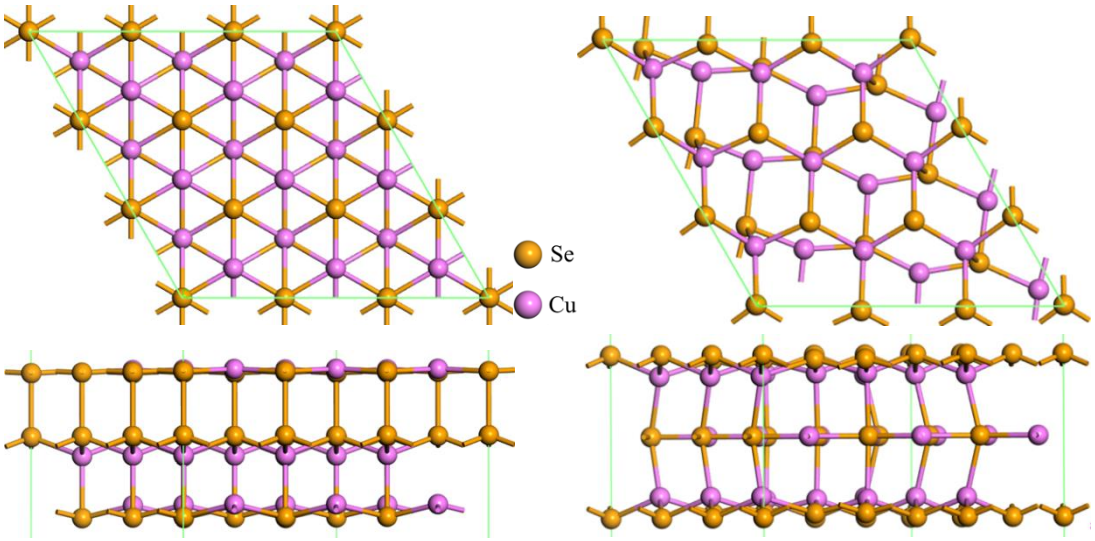
(a) *a* =11.266 Å E_{coh} = -2.948 eV/atom (b) *a* =11.930Å E_{coh} = -2.945 eV/atom

Fig. S1 Top and front views, lattice constants and cohesive energies of 3×3×1 CuSe monolayers



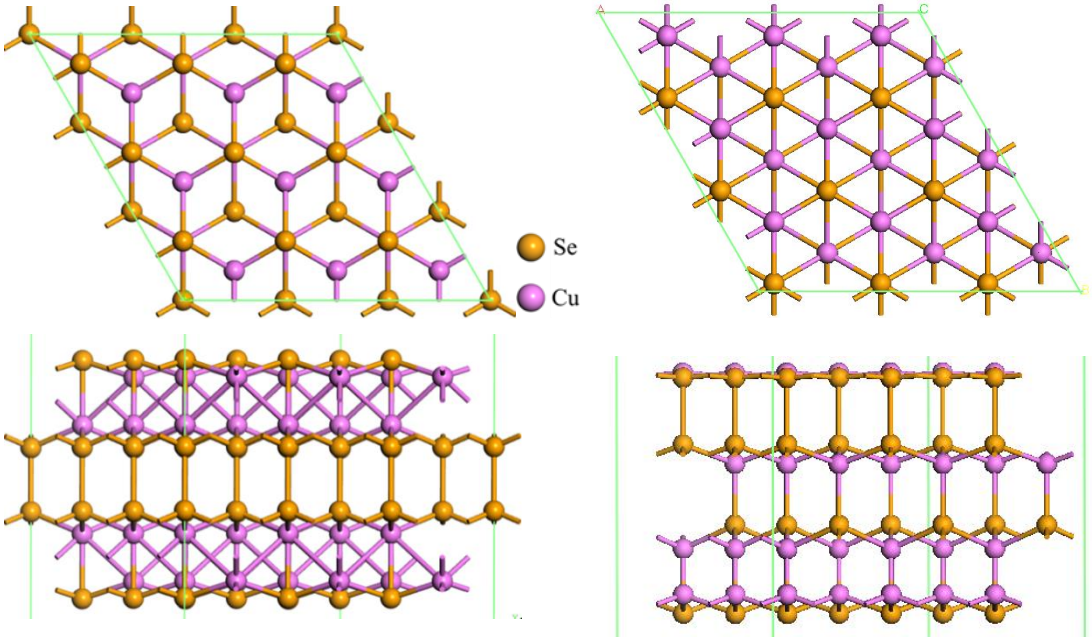
(a) *a* =12.177Å E_{coh} = -3.144 eV/atom (b) *a* =11.071Å E_{coh} = -3.248 eV/atom

Fig. S2 Top and front views, lattice constants and cohesive energies of 3×3×1 Cu_2Se_2 sheets



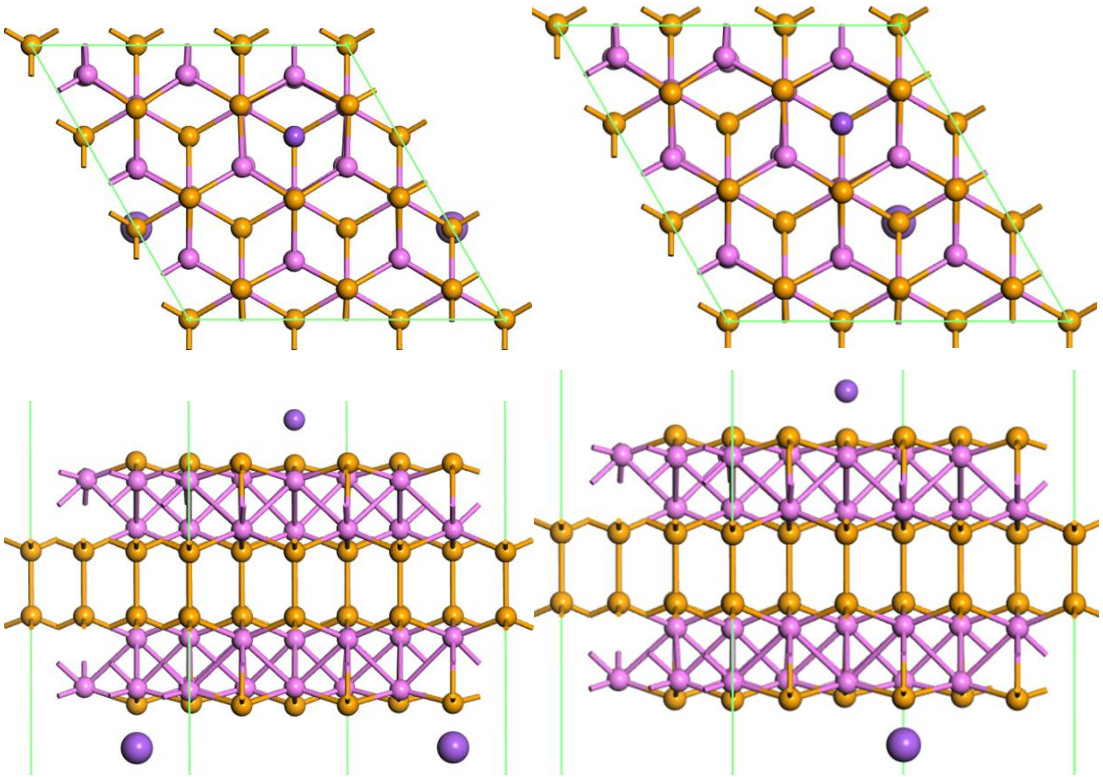
(a) a =12.015 Å E_{coh} = -3.312 eV/atom (b) a = 11.666 Å E_{coh} = -3.217 eV/atom

Fig. S3 Top and front views, lattice constants and cohesive energies of 3×3×1 Cu_3Se_3 sheets

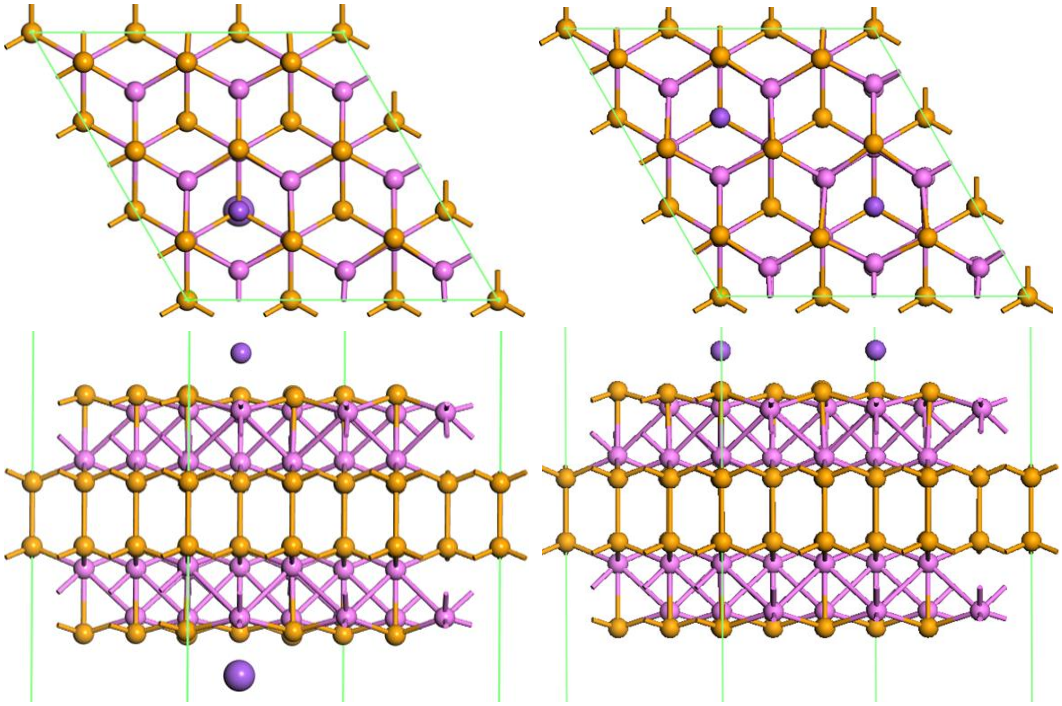


(a) a =11.736 Å E_{coh} = -3.387 eV/atom (b) a =11.785 Å E_{coh} = -3.331 eV/atom

Fig. S4 Top and front views, lattice constants and cohesive energies of 3×3×1 Cu_4Se_4 sheets

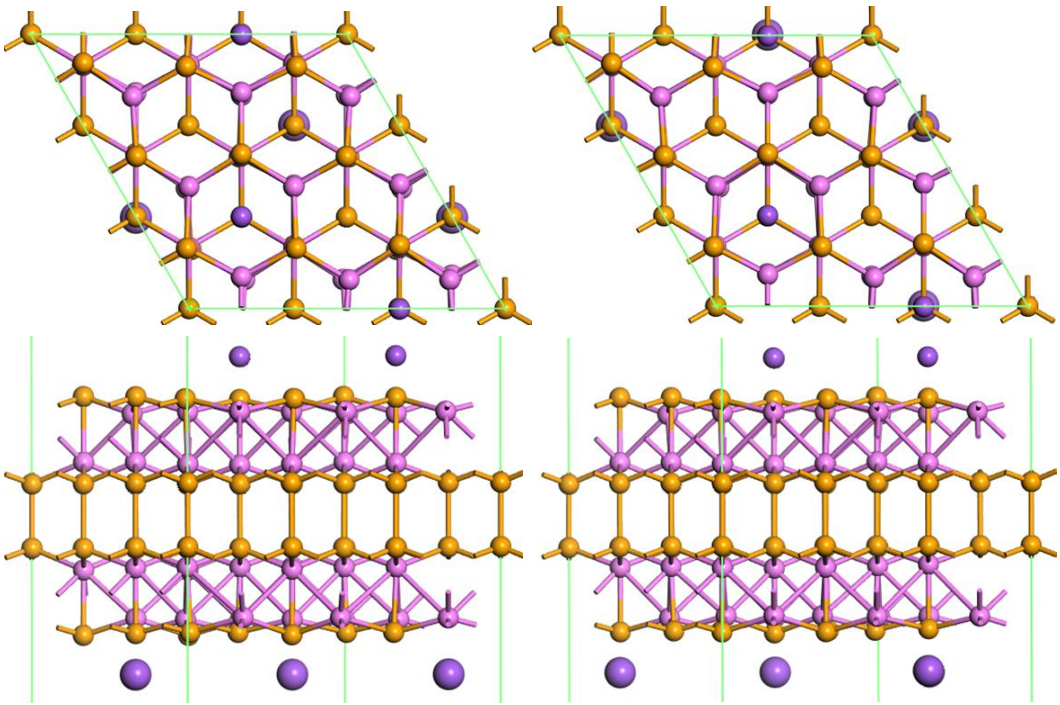


(a) a =11.801 Å ΔE_f=-0.1481 eV (b) a =11.801 Å ΔE_f = -0.1482 eV

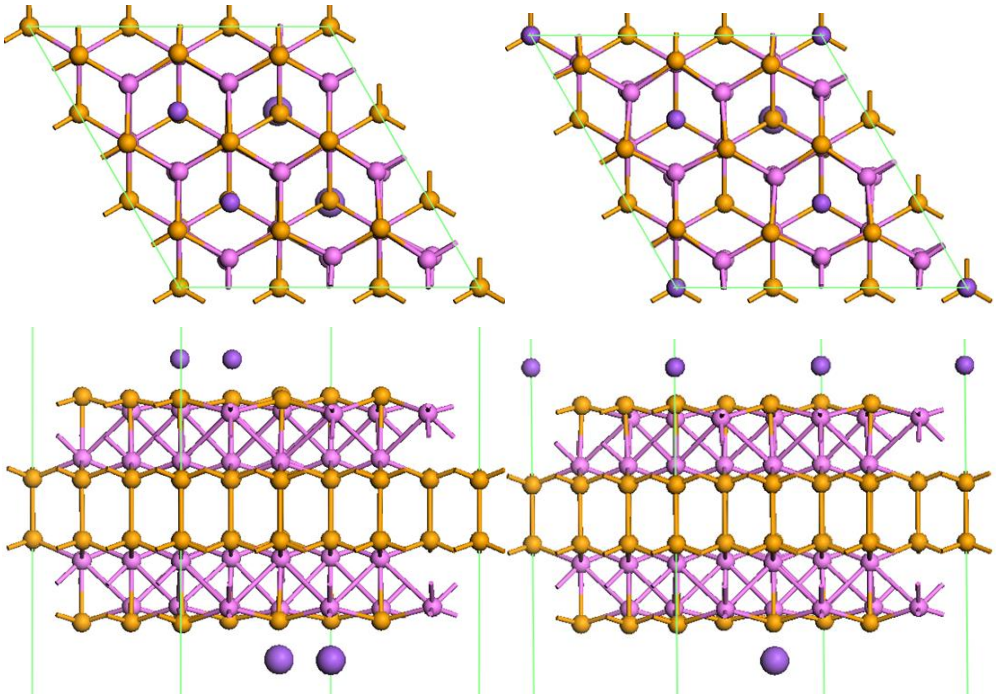


(c) a = 11.800 Å ΔE_f = -0.1479 eV (d) a = 11.796 Å ΔE_f = -0.1324 eV

Fig. S5 Top and front views of two sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell.

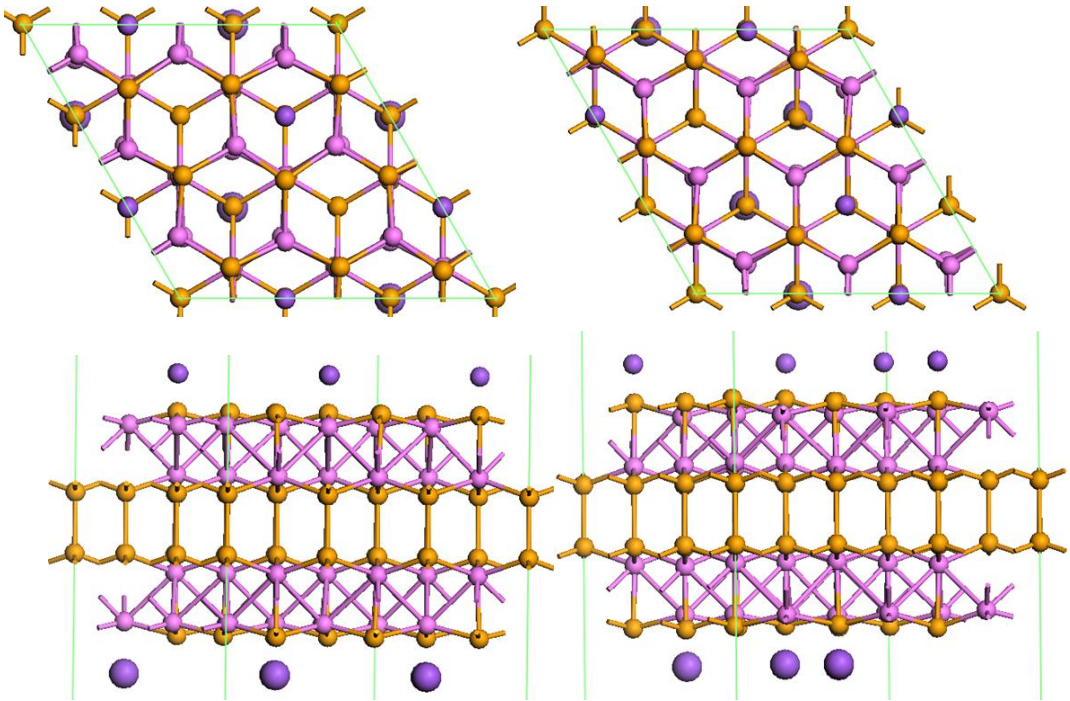


(a) a = 11.874 Å ΔE_f = -0.2575 eV (b) a = 11.874 Å ΔE_f = -0.2573 eV

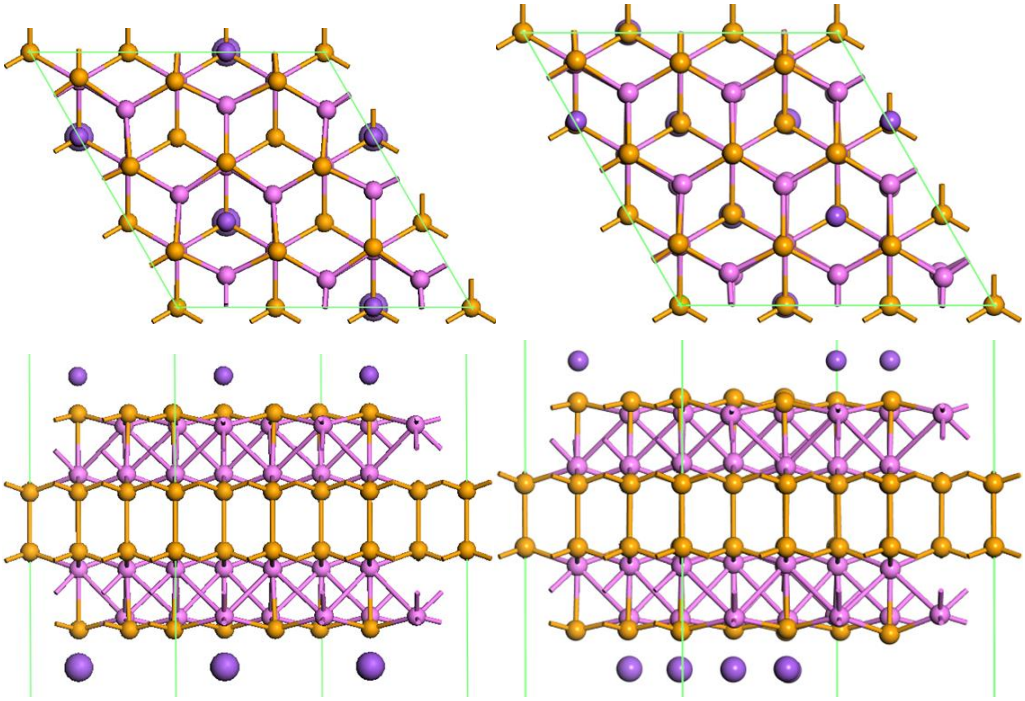


(c) a =11.883 Å ΔE_f = -0.2240 eV (d) a = 11.872 Å ΔE_f = -0.2439 eV

Fig. S6 Top and front views of four sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

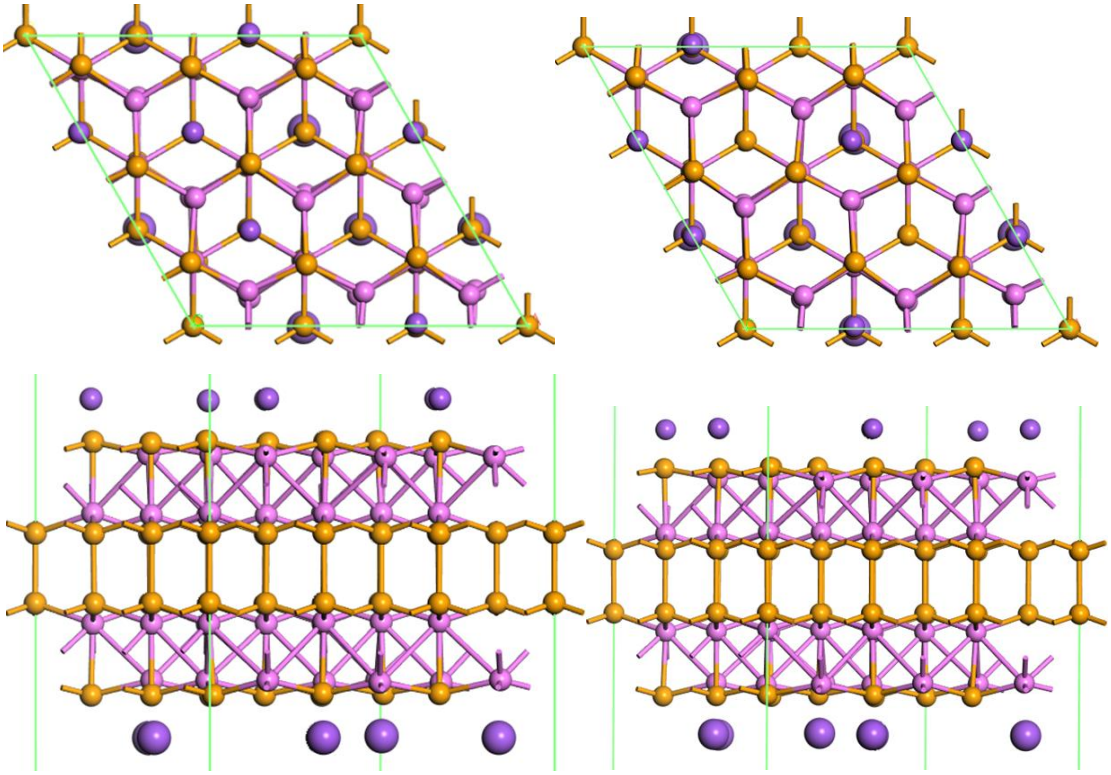


(a) a = 11.955 Å ΔE_f = -0.3366 eV (b) a = 11.967 Å ΔE_f = -0.2776 eV

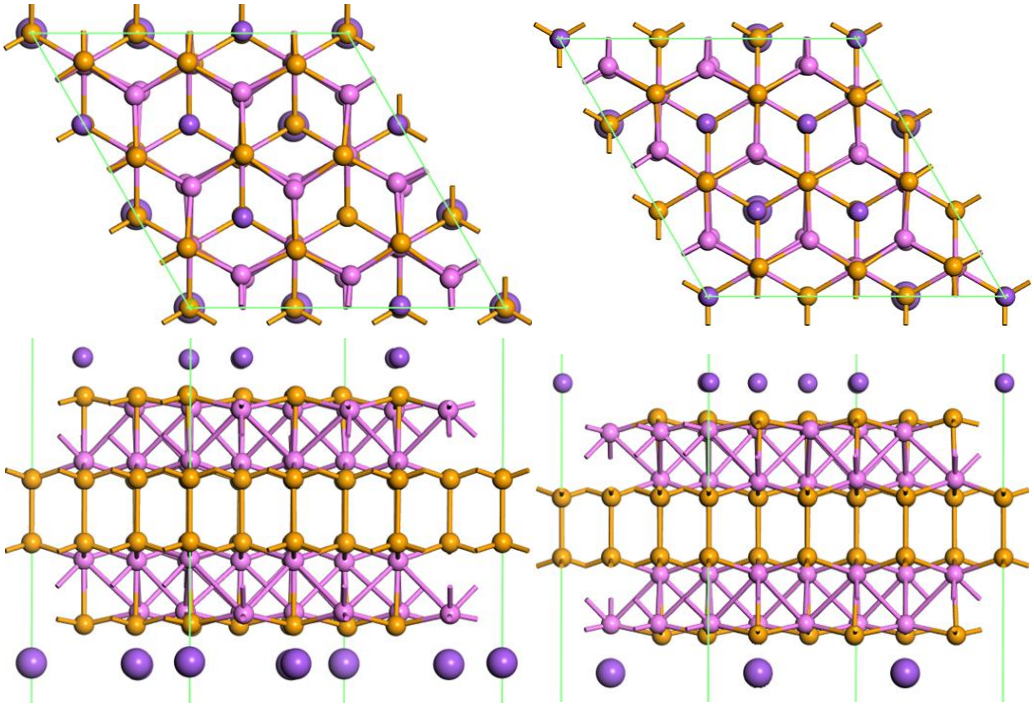


(c) a = 11.950 Å ΔE_f = -0.3363 eV (d) a = 11.971 Å ΔE_f = -0.2363 eV

Fig. S7 Top and front views of six sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

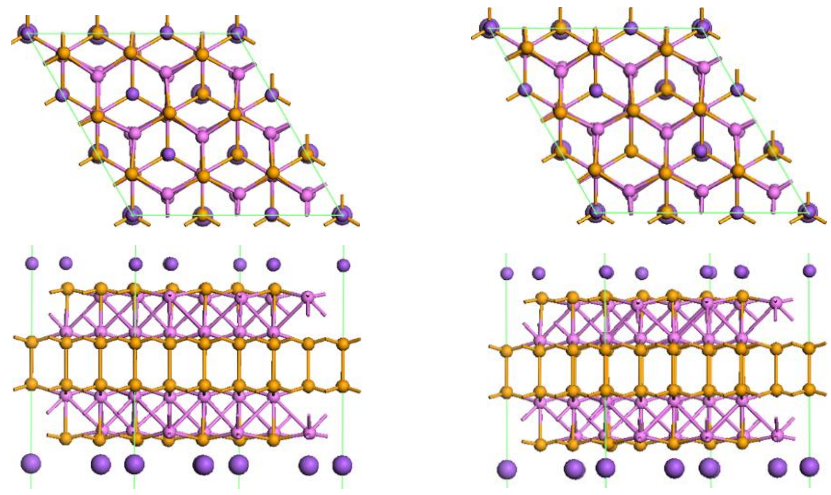


(a) a = 12.040 Å ΔE_f = -0.3125 eV (b) a = 12.038 Å ΔE_f = -0.3124 eV

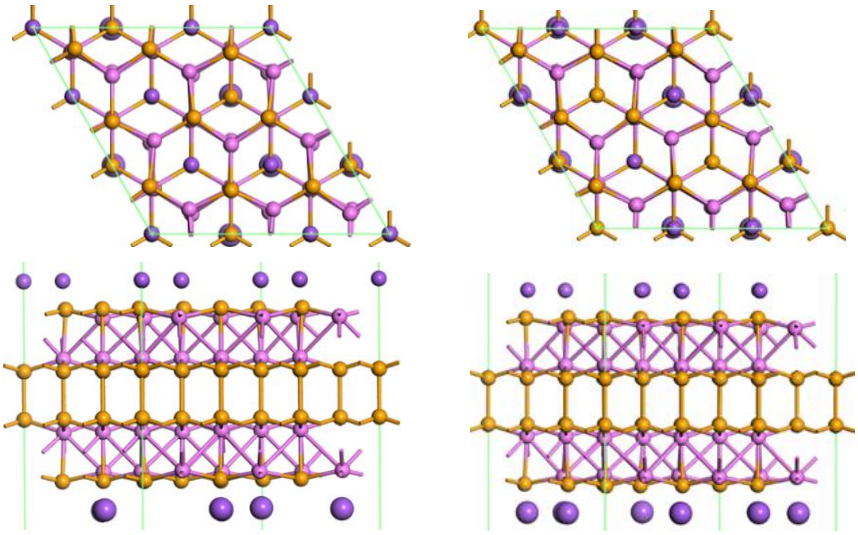


(c) a = 12.037 Å ΔE_f = -0.3125 eV (d) a = 12.045 Å ΔE_f = -0.2925 eV

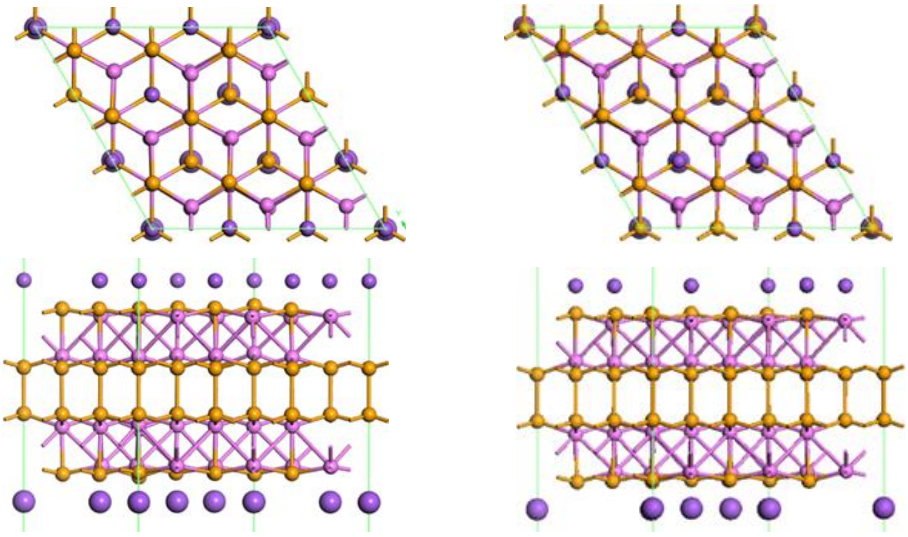
Fig. S8 Top and front views of eight sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.



(a) a = 12.117Å ΔE_f = -0.3125 eV (b) a = 12.115 Å ΔE_f = -0.2843 eV

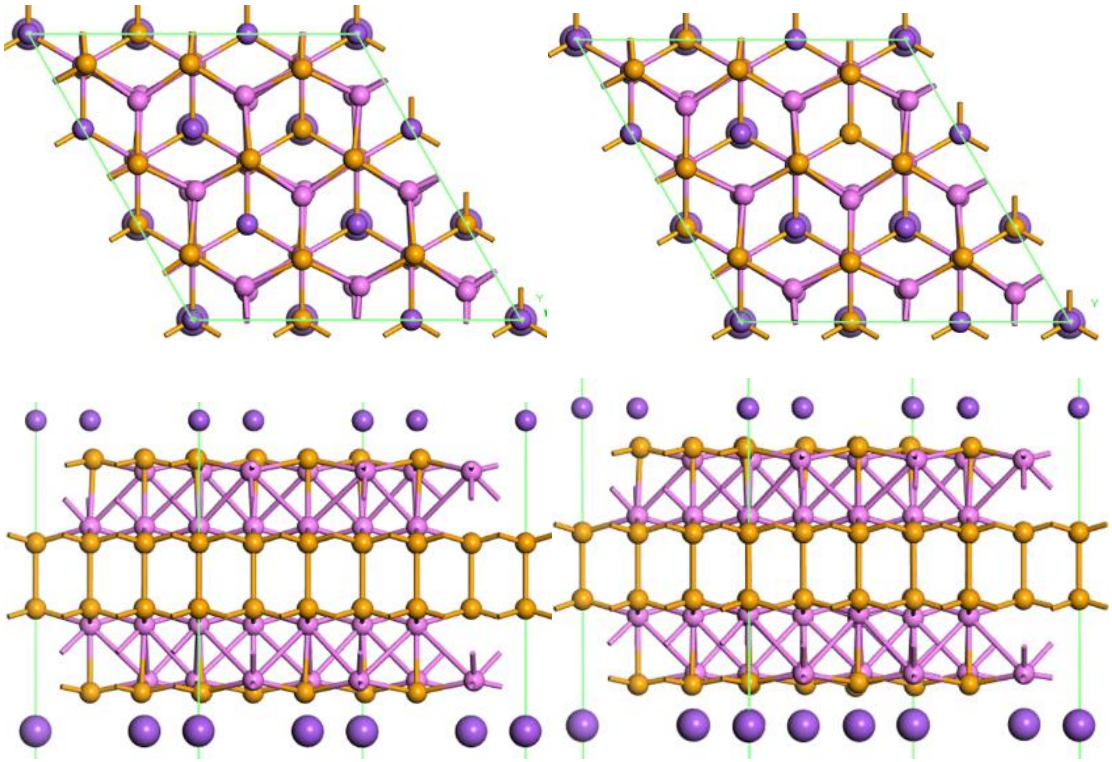


(c) a = 12.116 Å ΔE_f = -0.2788 eV (d) a = 12.114 Å ΔE_f = -0.2842 eV

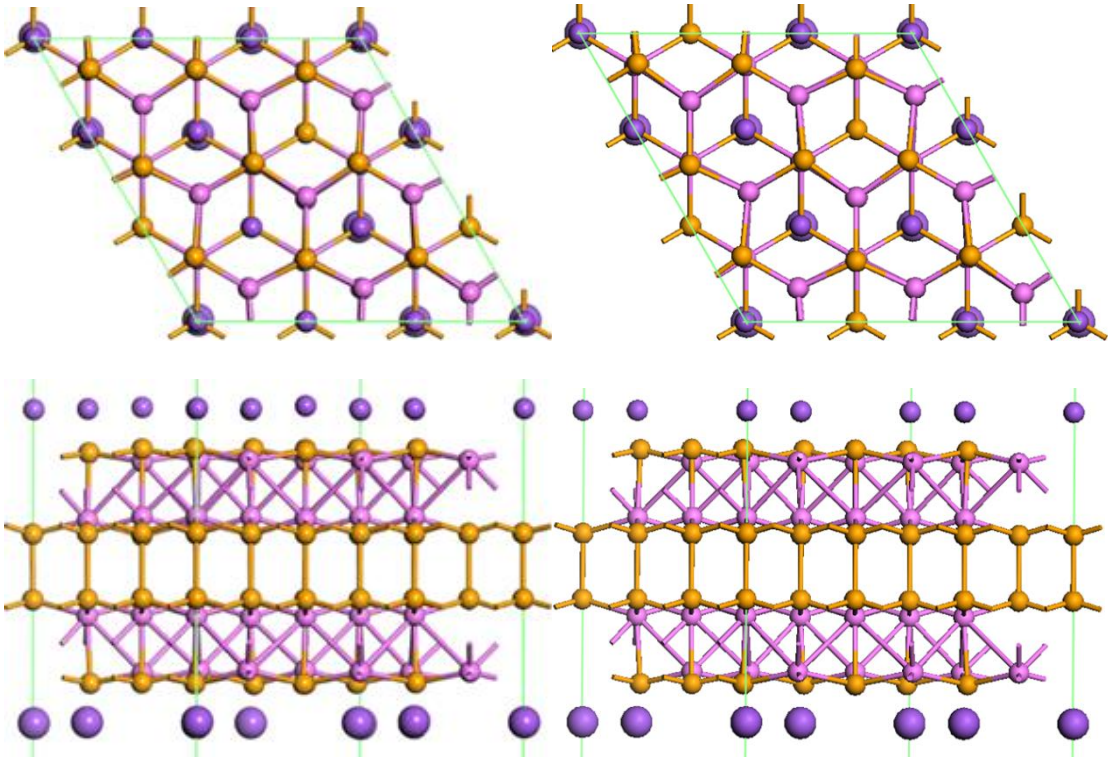


(e) a = 12.128 Å ΔE_f = -0.2283 eV (f) a = 12.127Å ΔE_f = -0.2574 eV

Fig. S9 Top and front views of ten sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

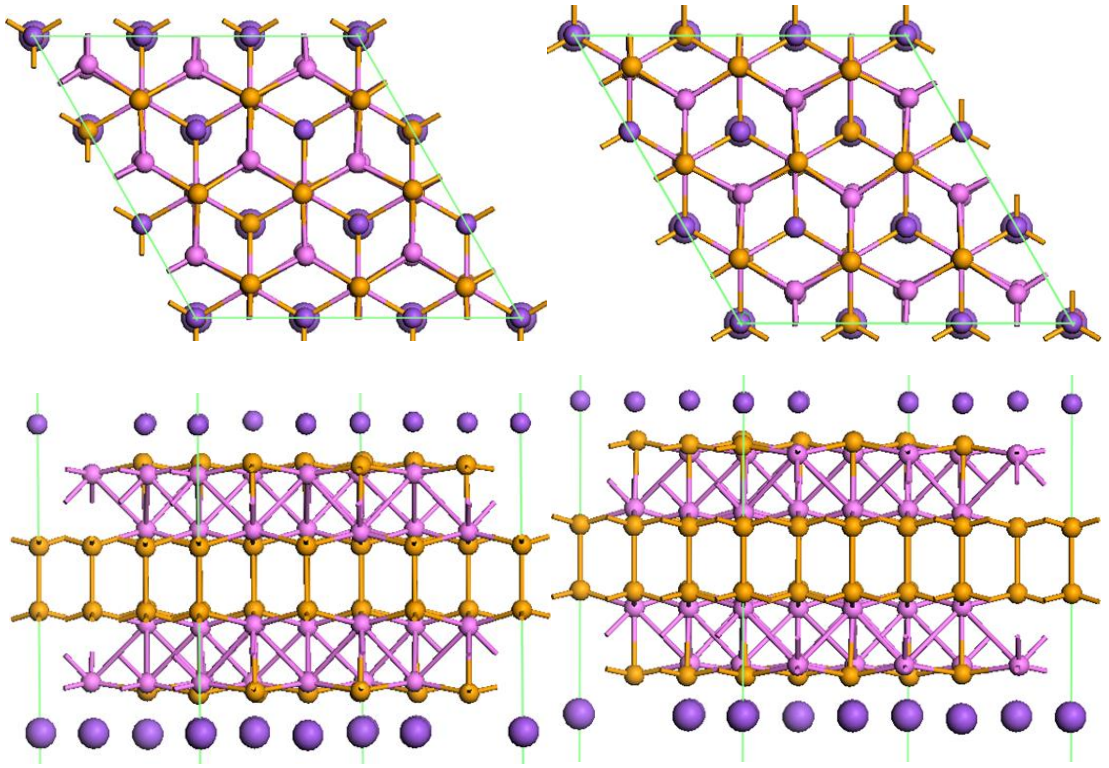


(a) a = 12.187 Å ΔE_f = -0.2516 eV (b) a = 12.180 Å ΔE_f = -0.2285 eV

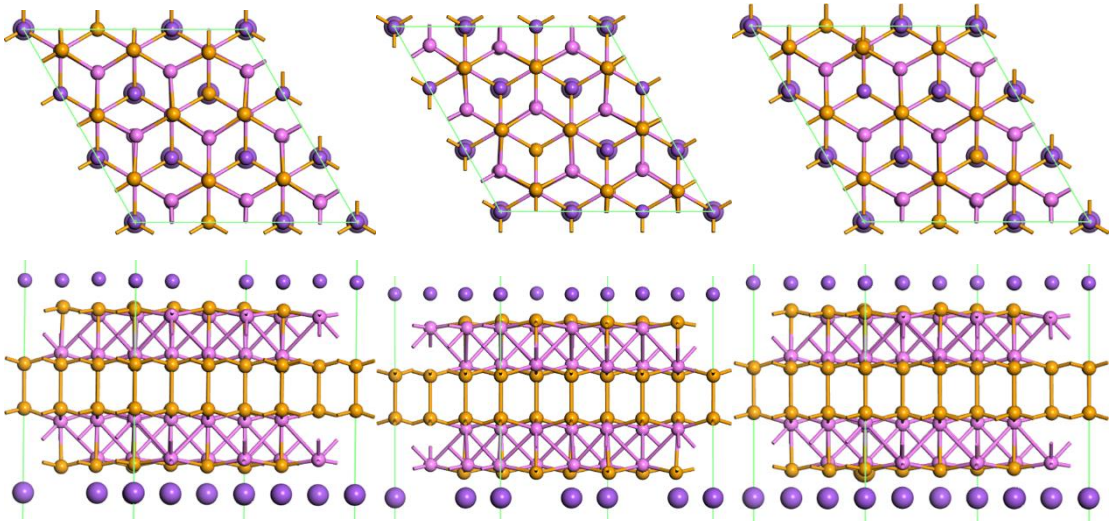


(c) a = 12.166Å ΔE_f = -0.2199 eV (d) a = 12.181 Å ΔE_f = -0.2514 eV

Fig. S10 Top and front views of twelve sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

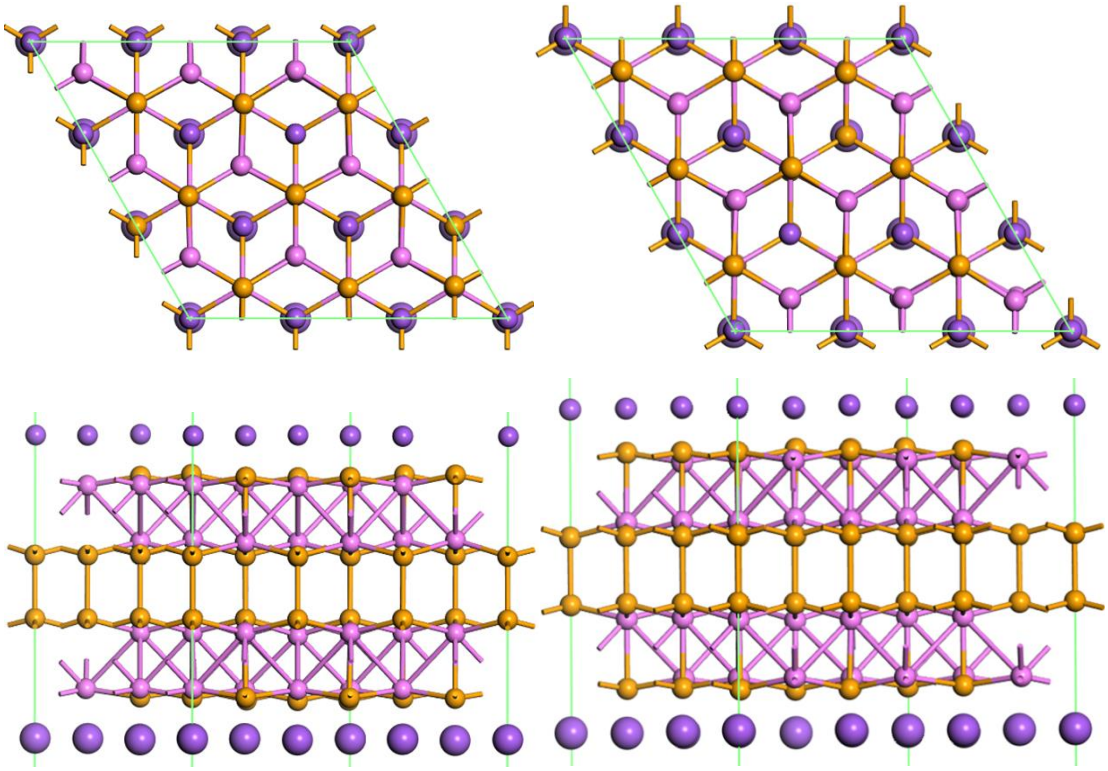


(a) a = 12.230 Å ΔE_f = -0.1605 eV (b) a = 12.225 Å ΔE_f = -0.1606 eV

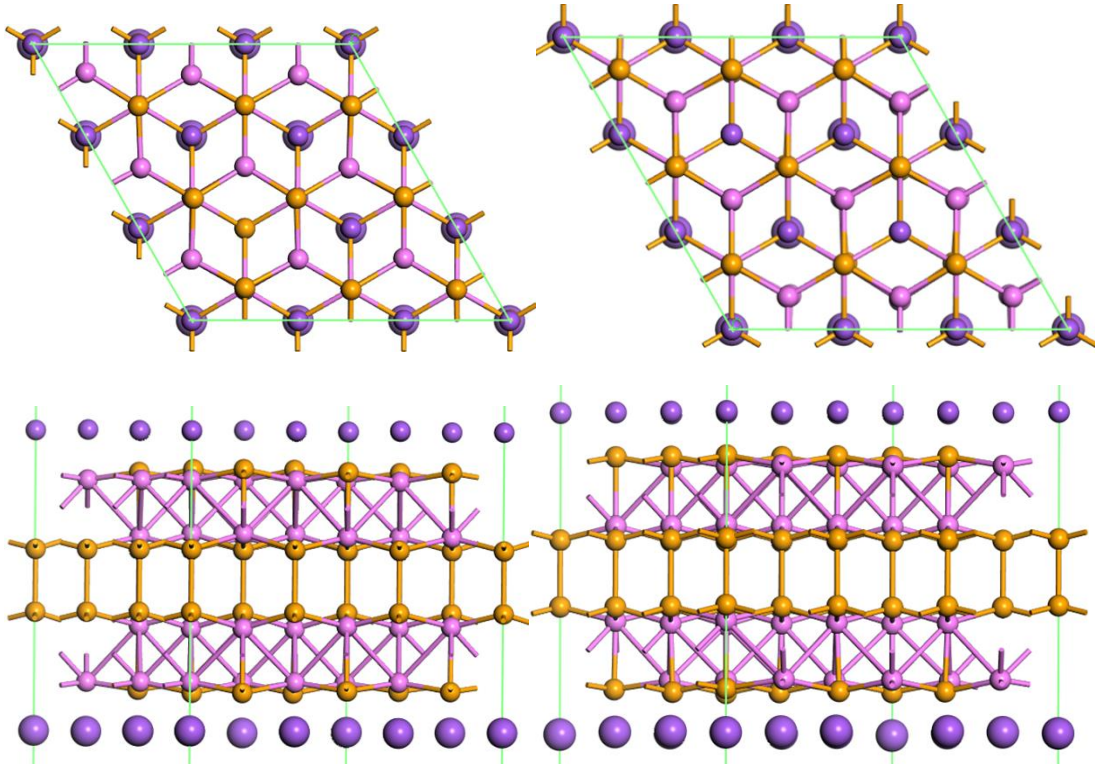


(c) a = 12.223 Å ΔE_f = -0.1495 eV (d) a = 12.217 Å ΔE_f = -0.1660 eV (e) a = 12.221 Å ΔE_f = -0.1384 eV

Fig. S11 Top and front views of fourteen sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

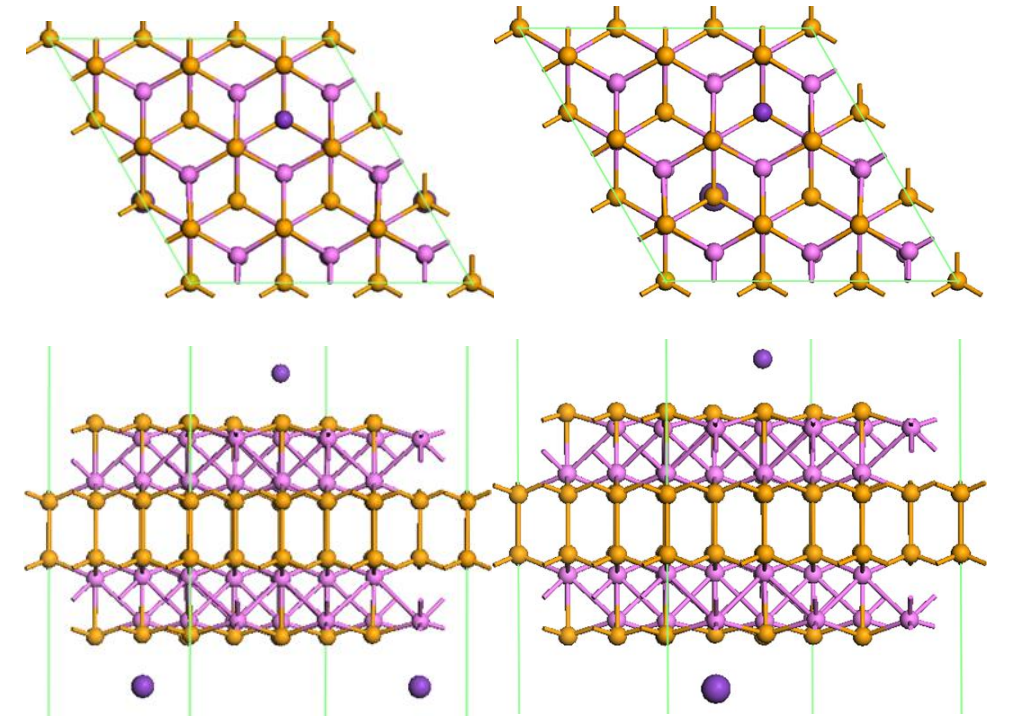


(a) a = 12.250 Å ΔE_f = -0.0780 eV (b) a = 12.249 Å ΔE_f = -0.0777 eV

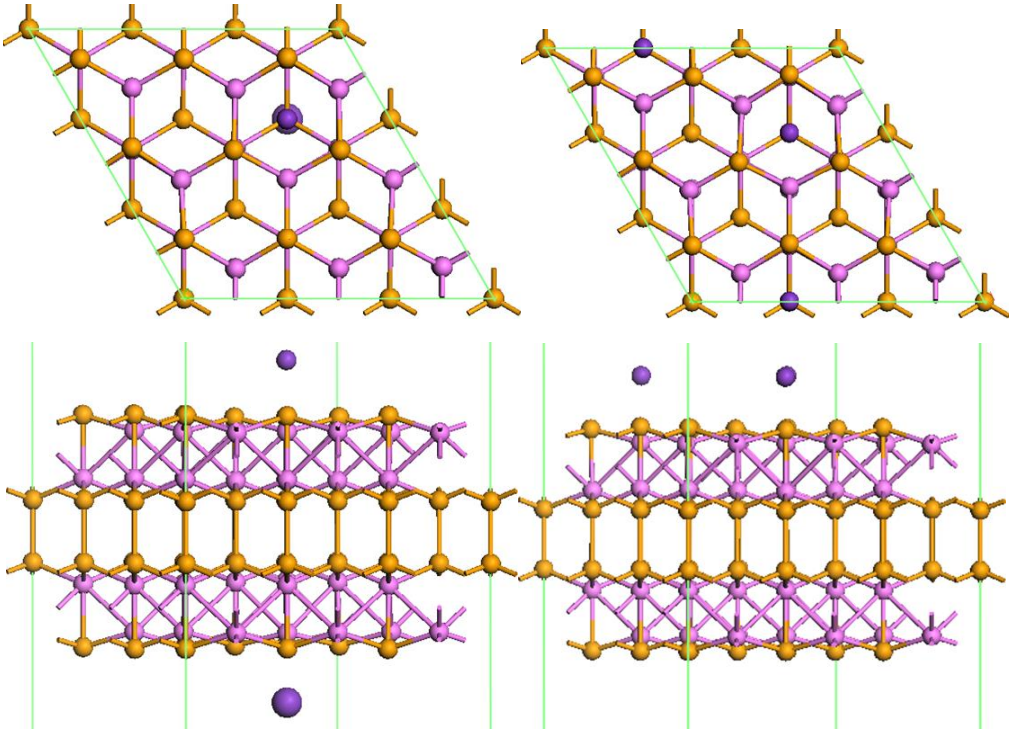


(c) a = 12.248 Å ΔE_f = -0.0775 eV (d) a = 12.246 Å ΔE_f = -0.0813 eV

Fig. S12 Top and front views of sixteen sodium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S5.

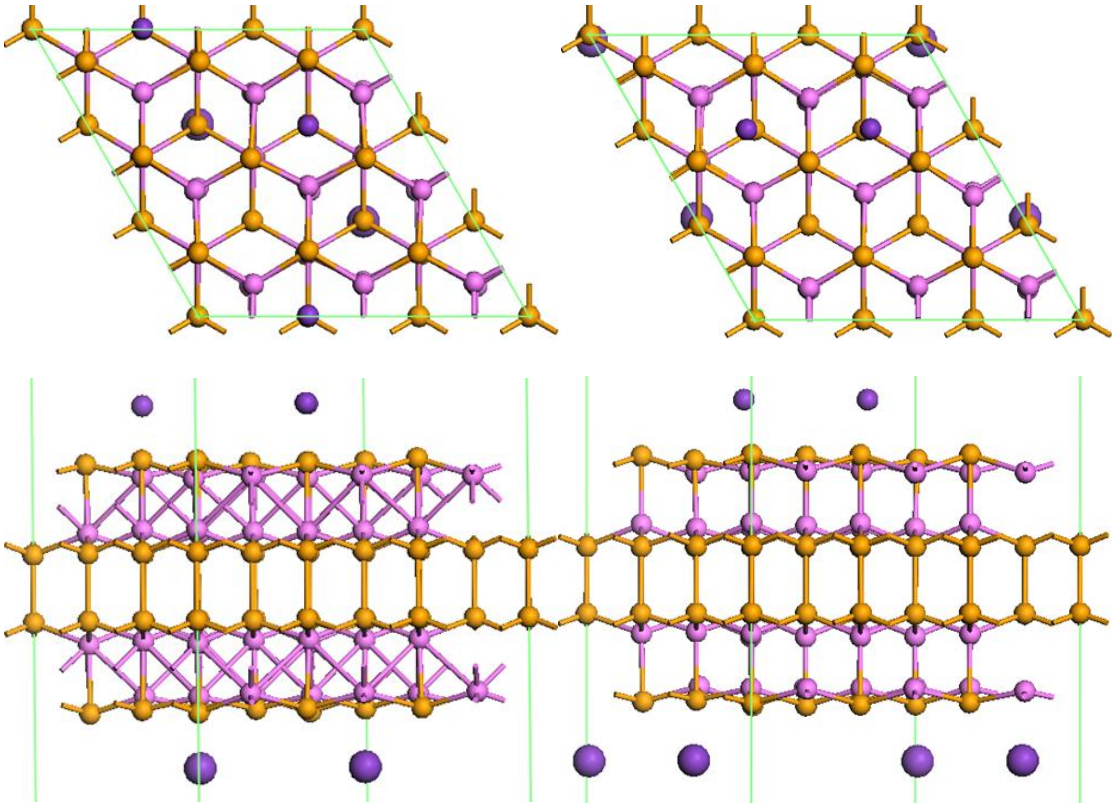


(a) a = 11.781 Å ΔE_f = -0.23484 eV (b) a = 11.801 Å ΔE_f = -0.23637 eV

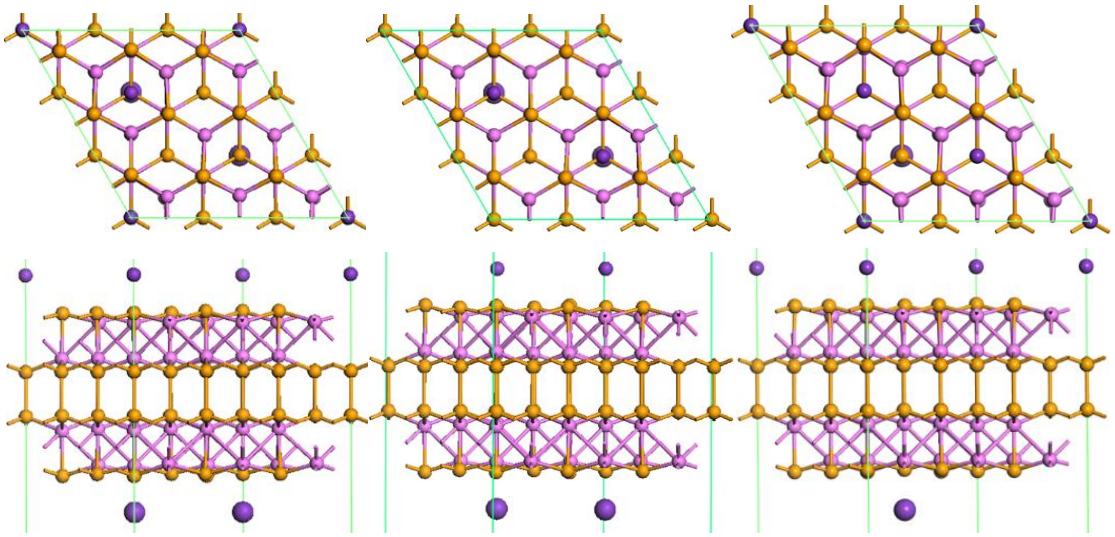


(c) a = 11.804 Å ΔE_f = -0.23642 eV (d) a = 11.805 Å ΔE_f = -0.20327 eV

Fig. S13 Top and front views of two potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell.

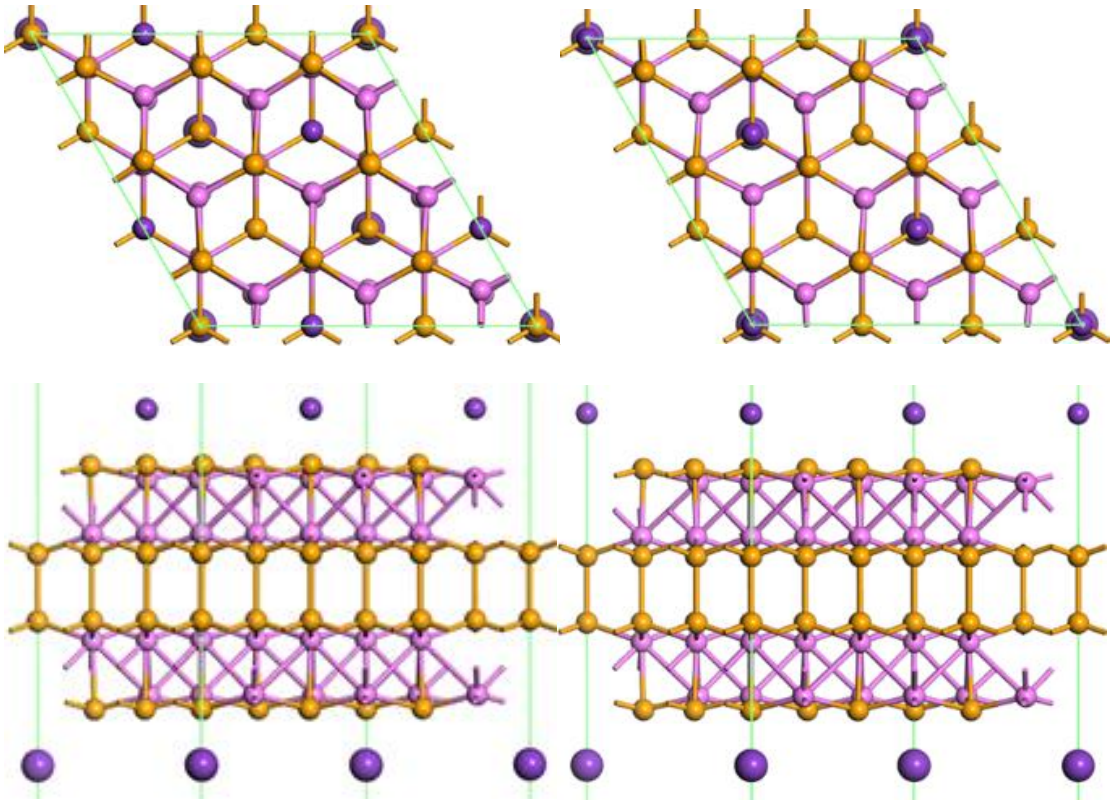


(a) a = 11.878 Å ΔE_f = -0.37770 eV (b) a = 11.886 Å ΔE_f = -0.3347 eV

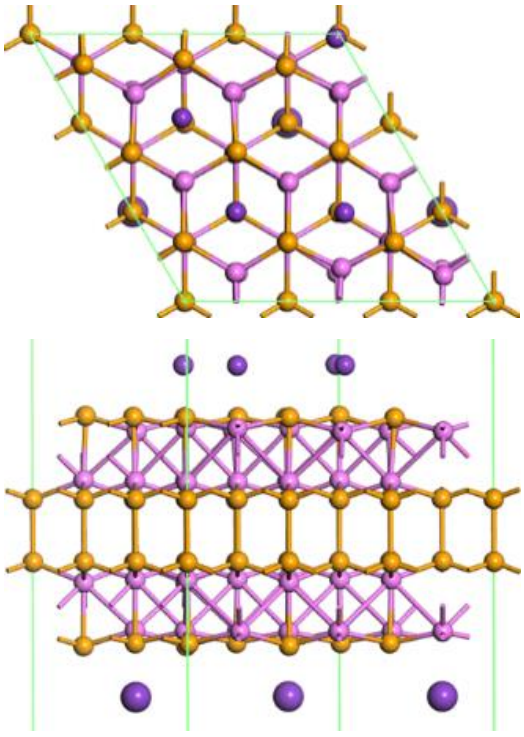


(c) a = 11.879 Å ΔE_f = -0.37773 eV (d) a = 11.877 Å ΔE_f =-0.37802 eV (e) a = 11.879 Å ΔE_f = -0.35256 eV

Fig. S14 Top and front views of four potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.

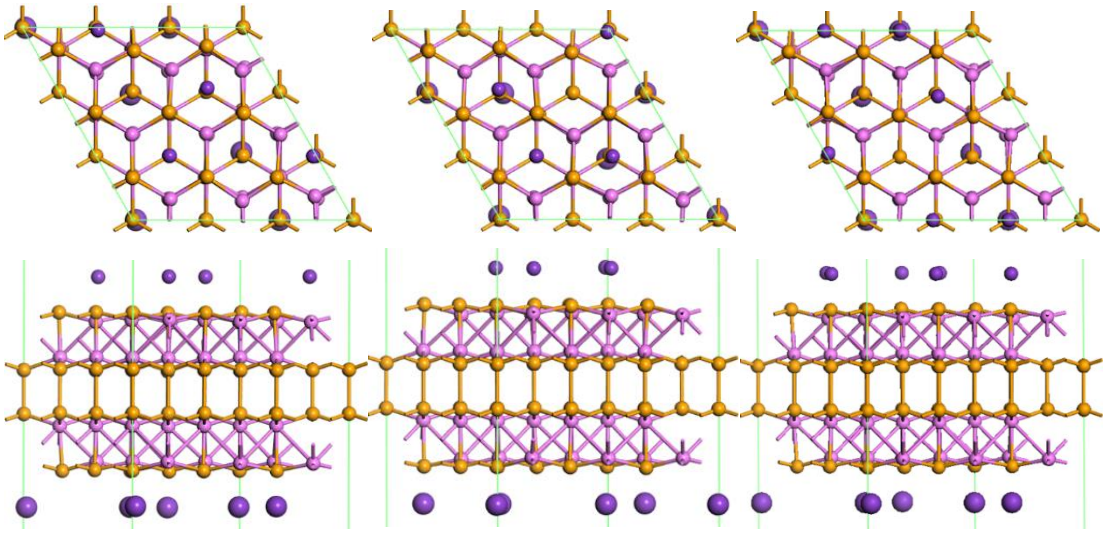


(a) a = 11.962 Å ΔE_f = -0.4535 eV (b) a = 11.958 Å ΔE_f = -0.4534 eV

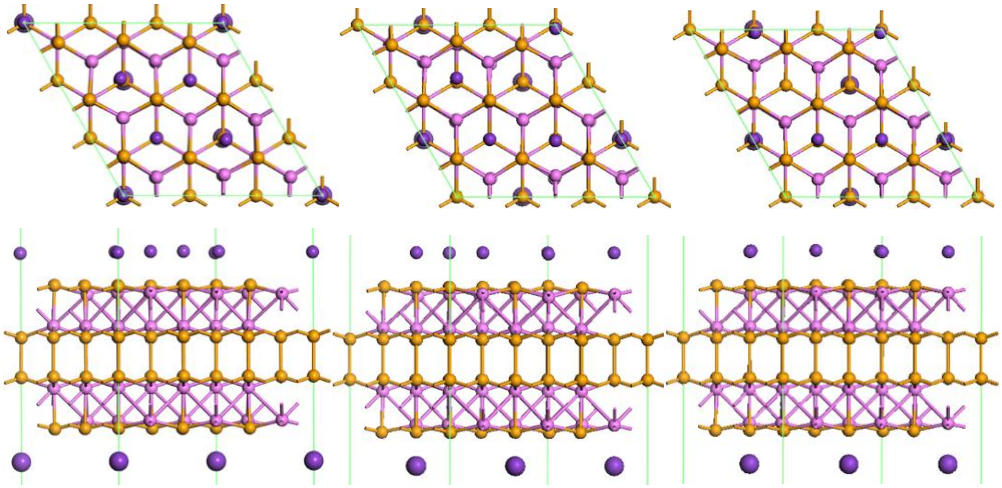


(c) a = 11.969 Å ΔE_f = -0.3735 eV

Fig. S15 Top and front views of six potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.

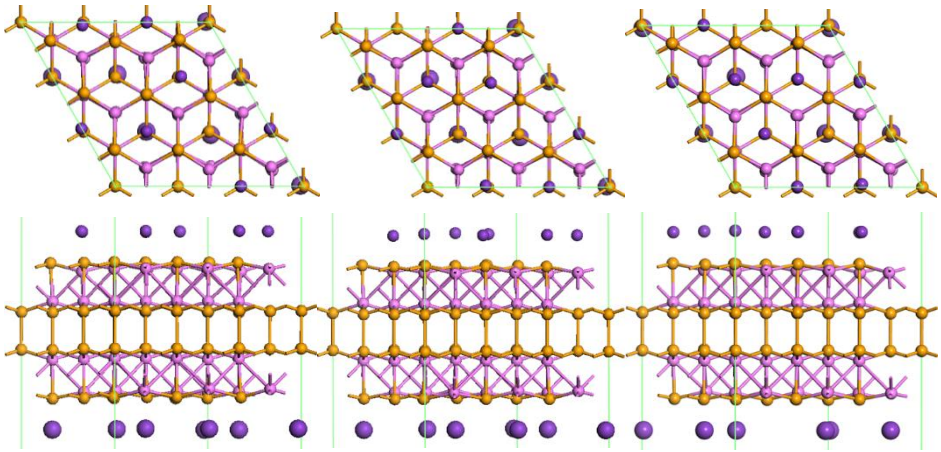


(a) a = 12.046 Å ΔE_f = -0.36854 eV (b) a = 12.047 Å ΔE_f = -0.36863 eV (c) a = 12.045 Å ΔE_f = -0.36795 eV



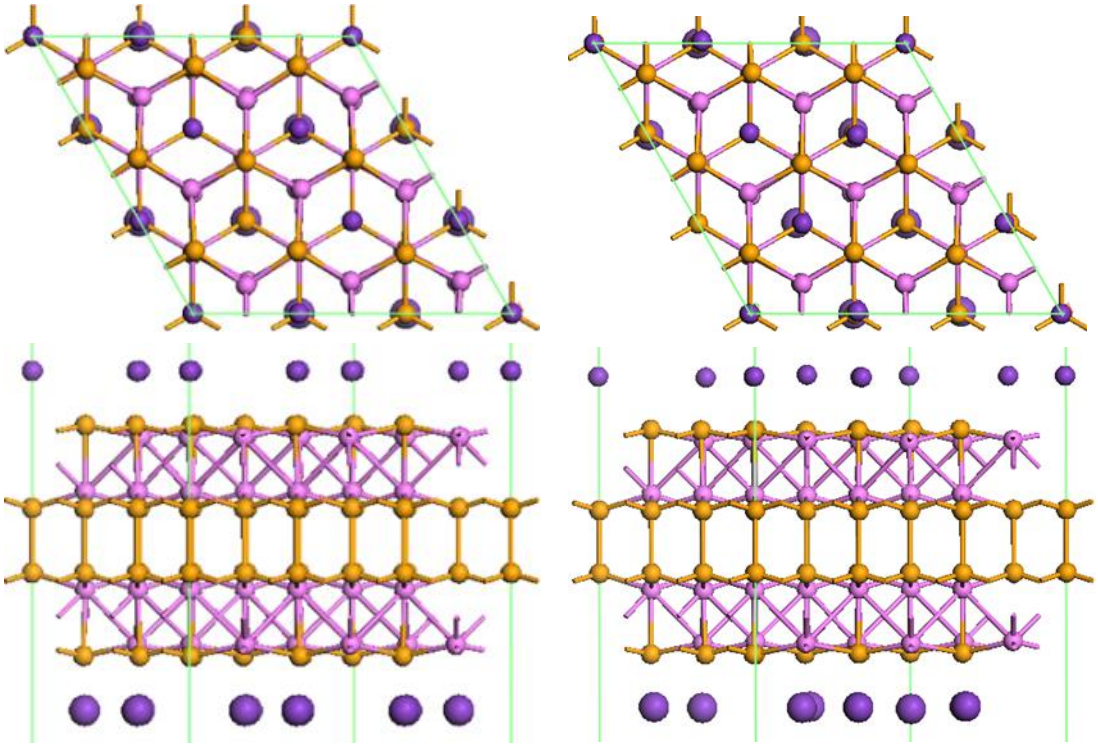
(d) a = 12.028 Å ΔE_f = -0.36685 eV (e) a = 12.030 Å ΔE_f = -0.36704 eV (f) a = 12.030 Å ΔE_f = -0.35623 eV

Fig. S16 Top and front views of eight potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.

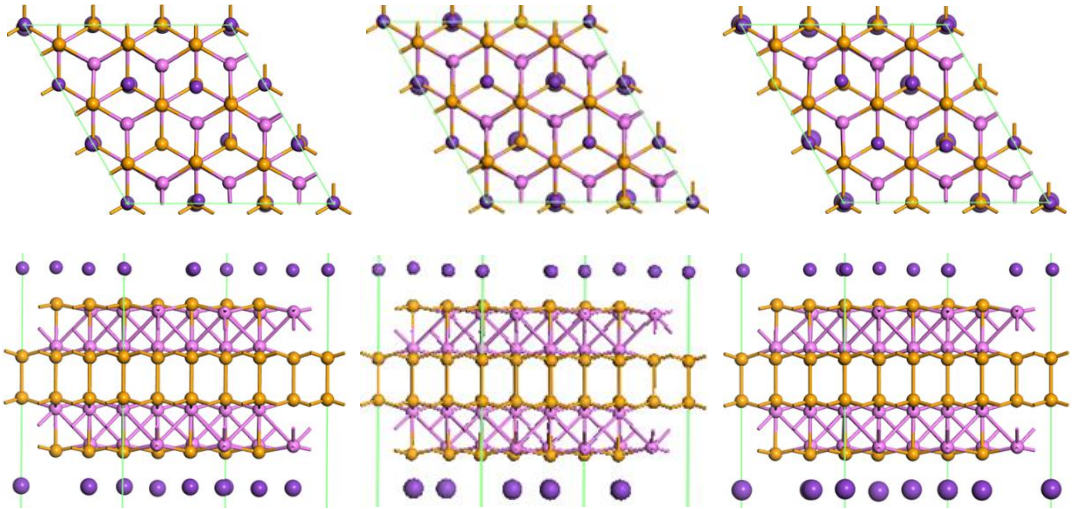


(a) a = 12.095 Å ΔE_f = -0.28456 eV (b) a = 12.089 Å ΔE_f = -0.28642 eV (c) a = 12.085 Å ΔE_f = -0.29383 eV

Fig. S17 Top and front views of ten potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.

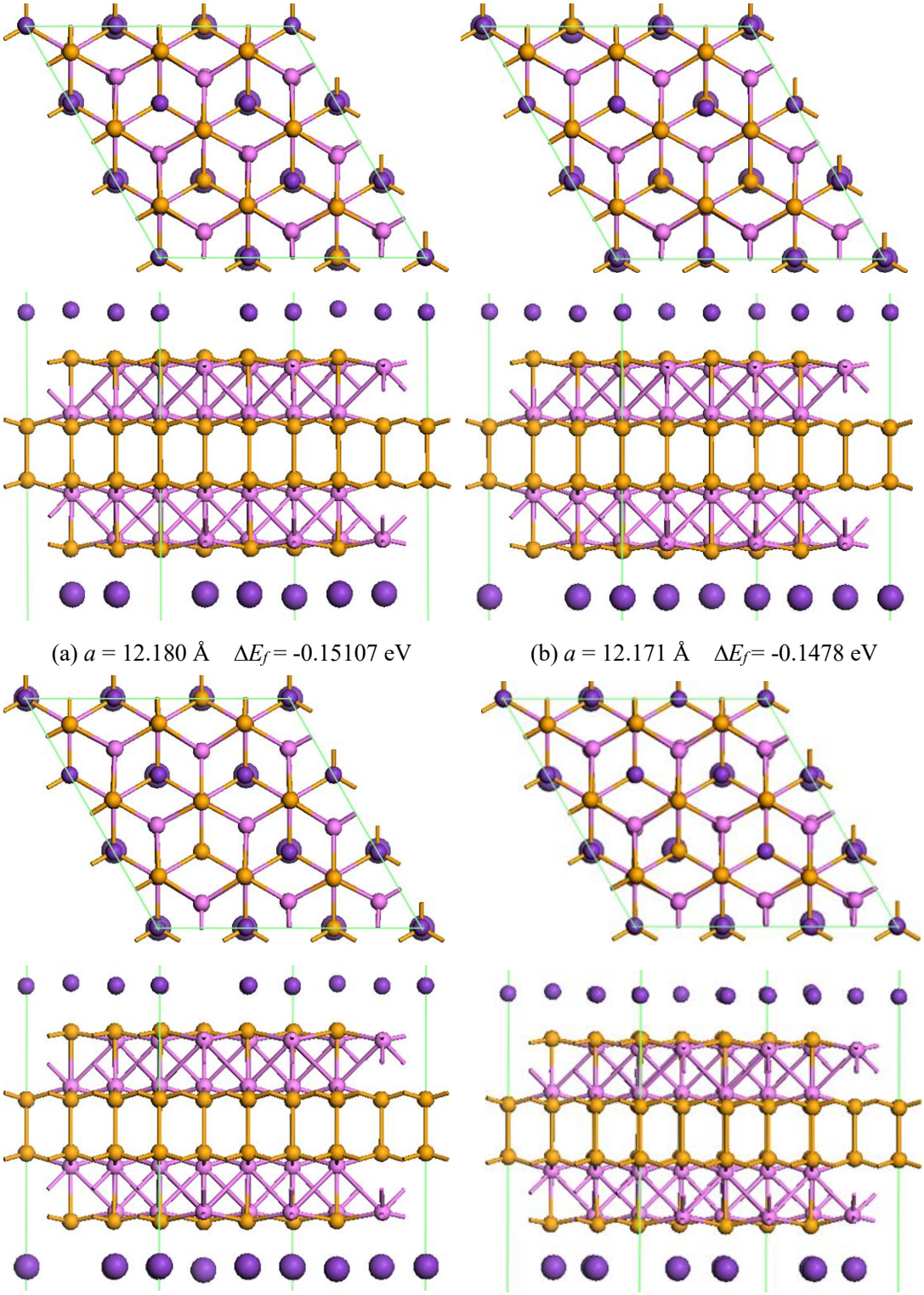


(a) a = 12.132 Å ΔE_f = -0.20388 eV (b) a = 12.128 Å ΔE_f = -0.21875 eV



(c) a = 12.128 Å ΔE_f = -0.21896 eV (d) a = 12.136 Å ΔE_f = -0.2175 eV (e) a = 12.129 Å ΔE_f = -0.21902 eV

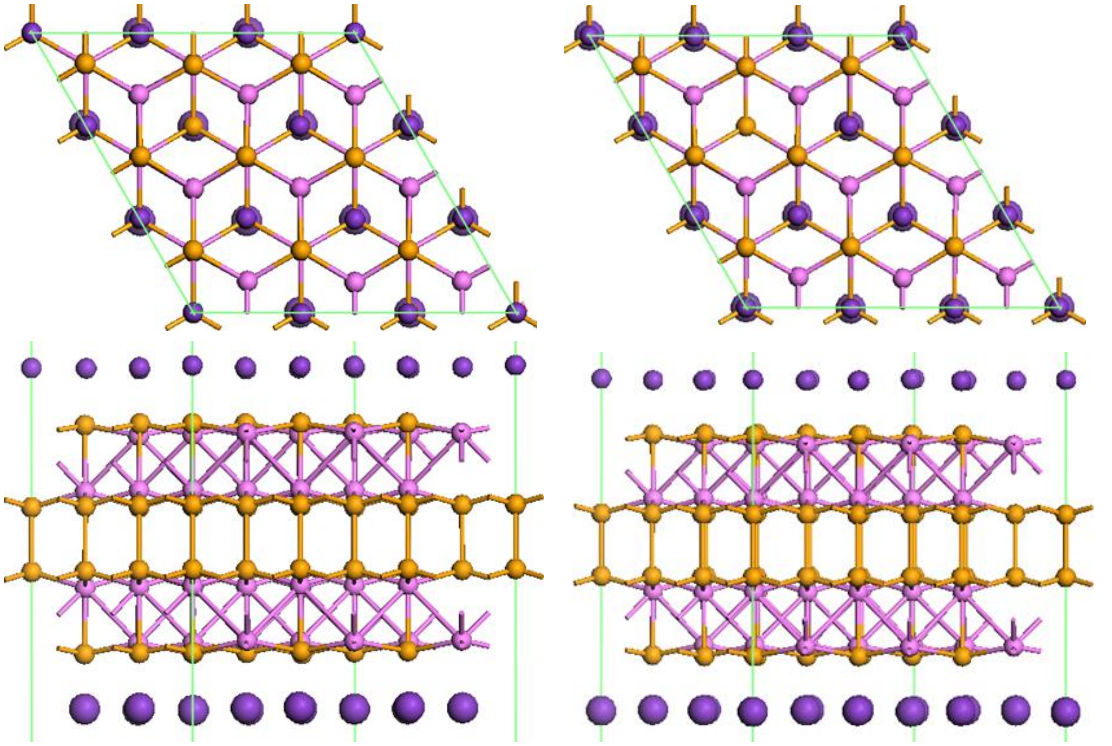
Fig. S18 Top and front views of twelve potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.



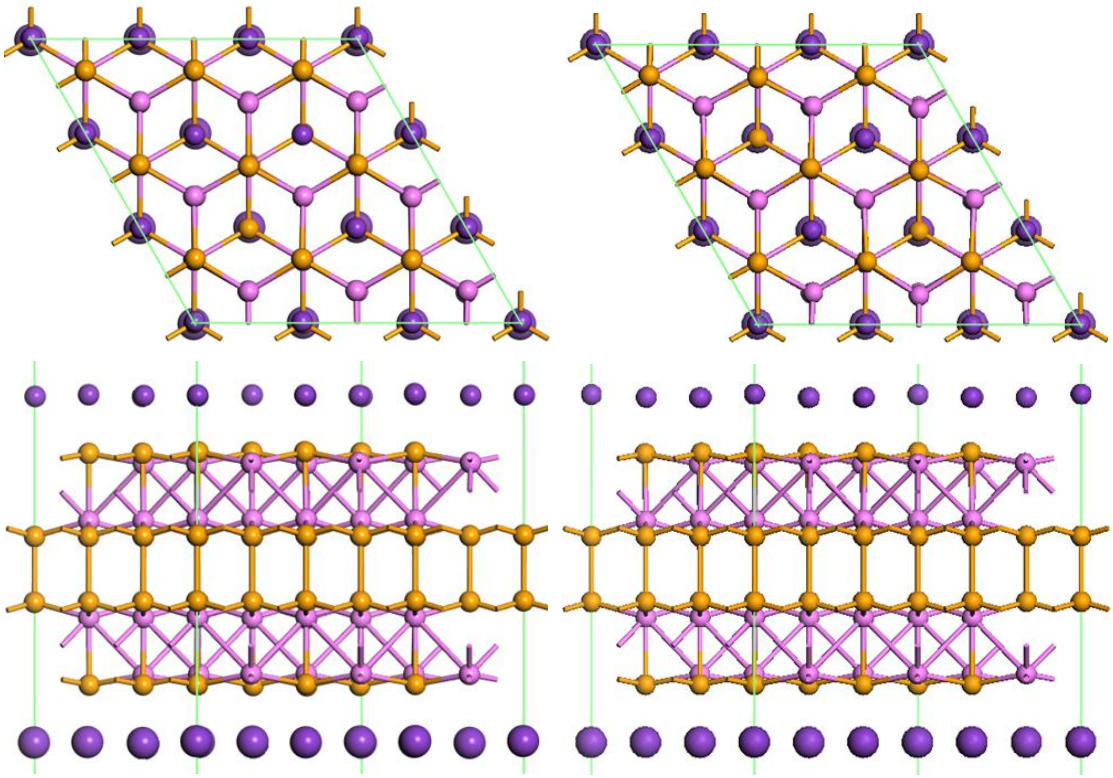
(a) a = 12.180 Å ΔE_f = -0.15107 eV (b) a = 12.171 Å ΔE_f = -0.1478 eV

(c) a = 12.177 Å ΔE_f = -0.15111 eV (d) a = 12.179 Å ΔE_f = -0.14165 eV

Fig. S19 Top and front views of fourteen potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.



(a) a = 12.215 Å ΔE_f = -0.07706 eV (b) a = 12.214 Å ΔE_f = -0.07688 eV



(c) a = 12.216 Å ΔE_f = -0.07704 eV (d) a = 12.215 Å ΔE_f = -0.07512 eV

Fig. S20 Top and front views of sixteen potassium atoms adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S13.

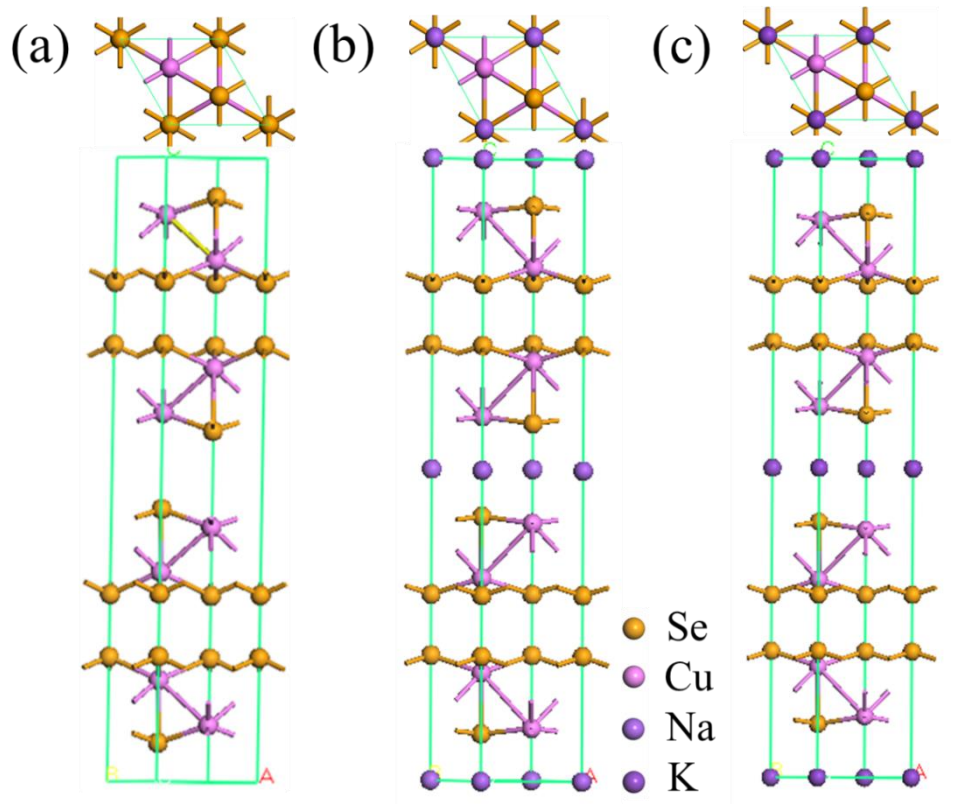
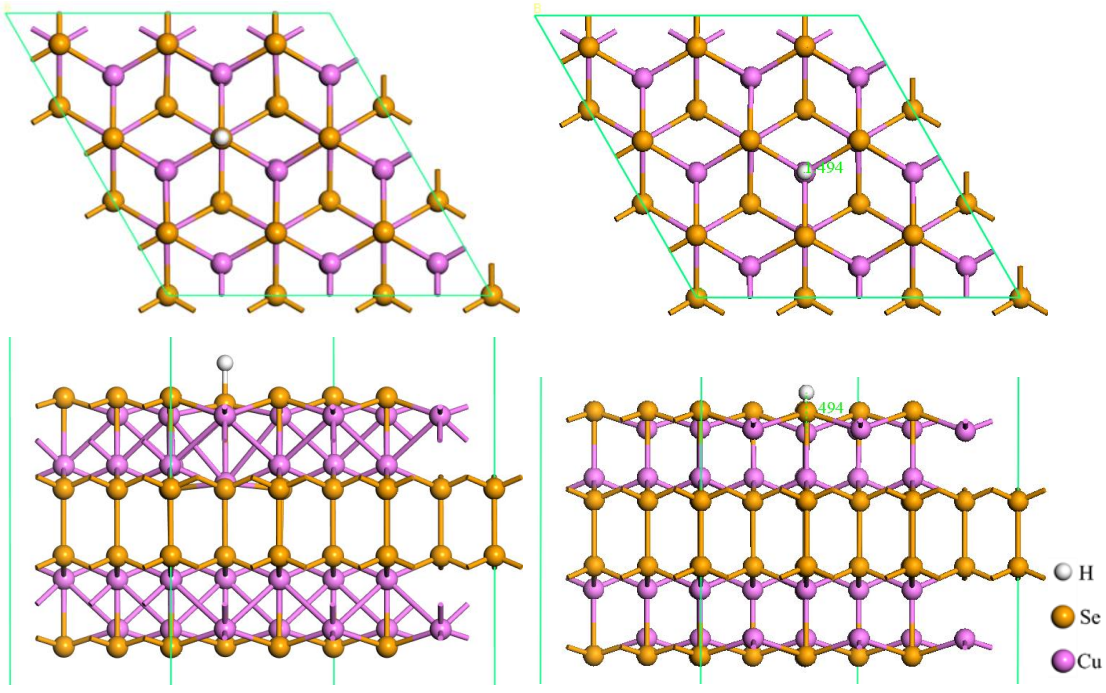
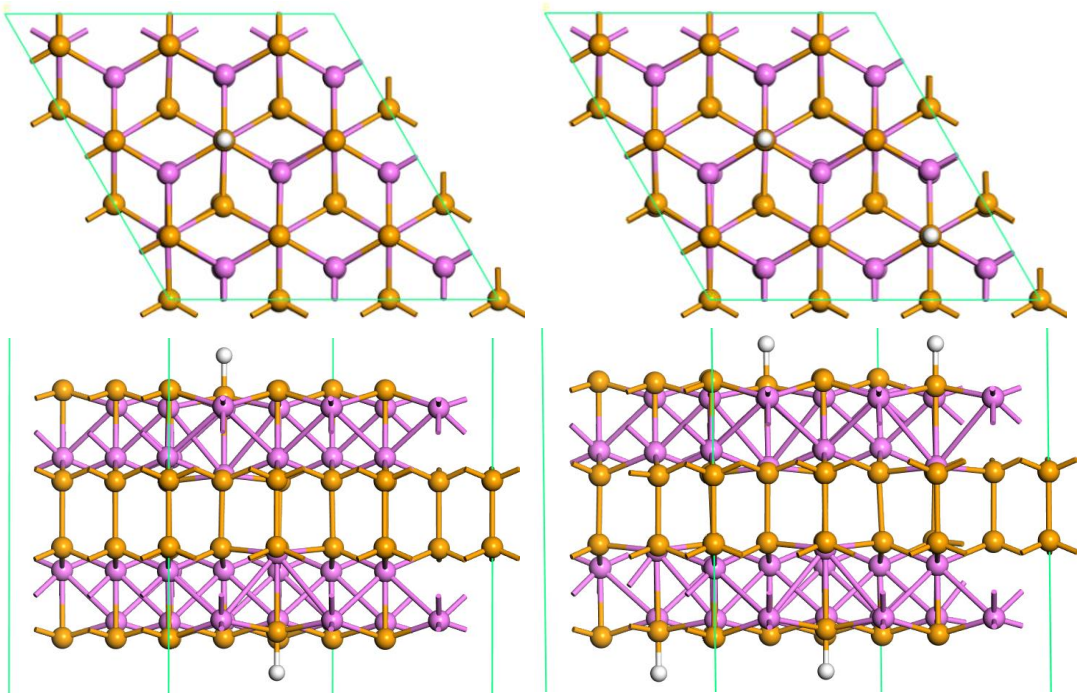


Fig. S21 Top and front views of geometric structures of (a) Cu_4Se_4, (b) $NaCu_4Se_4$ and (c) KCu_4Se_4 crystals.



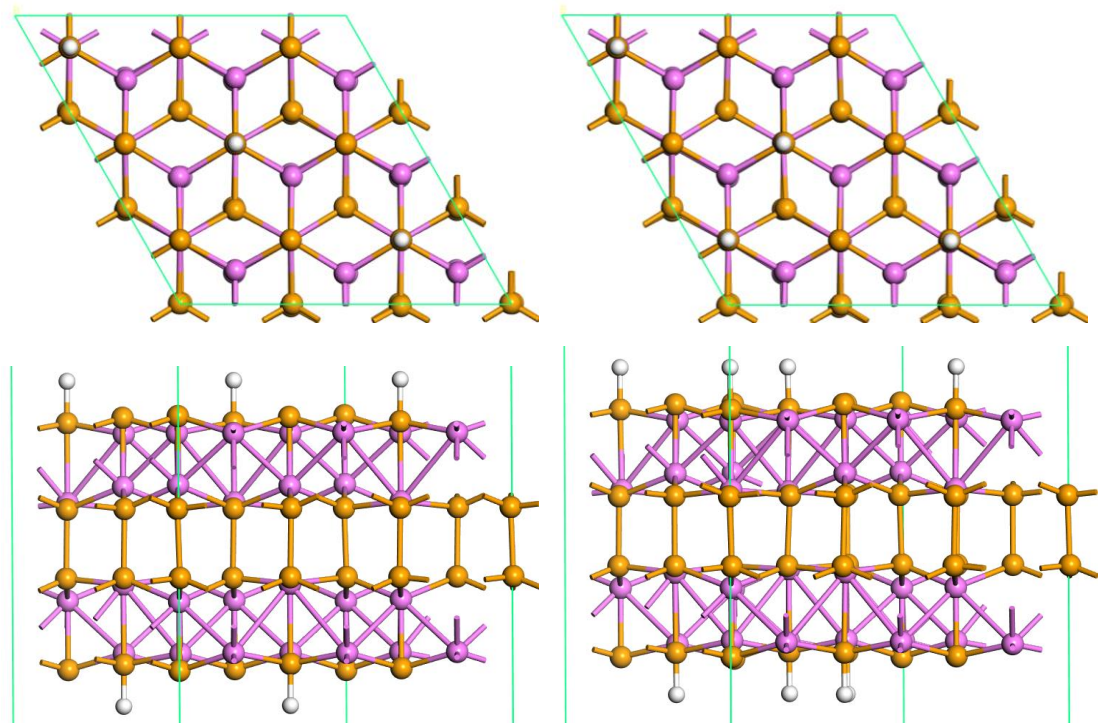
(a) a = 11.761 Å, E_H = 0.439 eV (b) a = 11.744 Å, E_H = 1.009 eV

Fig. S22 Top and front views of a proton adsorbed on the 3×3×1 Cu_4Se_4 supercell: (a) adsorbed on top of S atom and (b) on top of Cu atom.

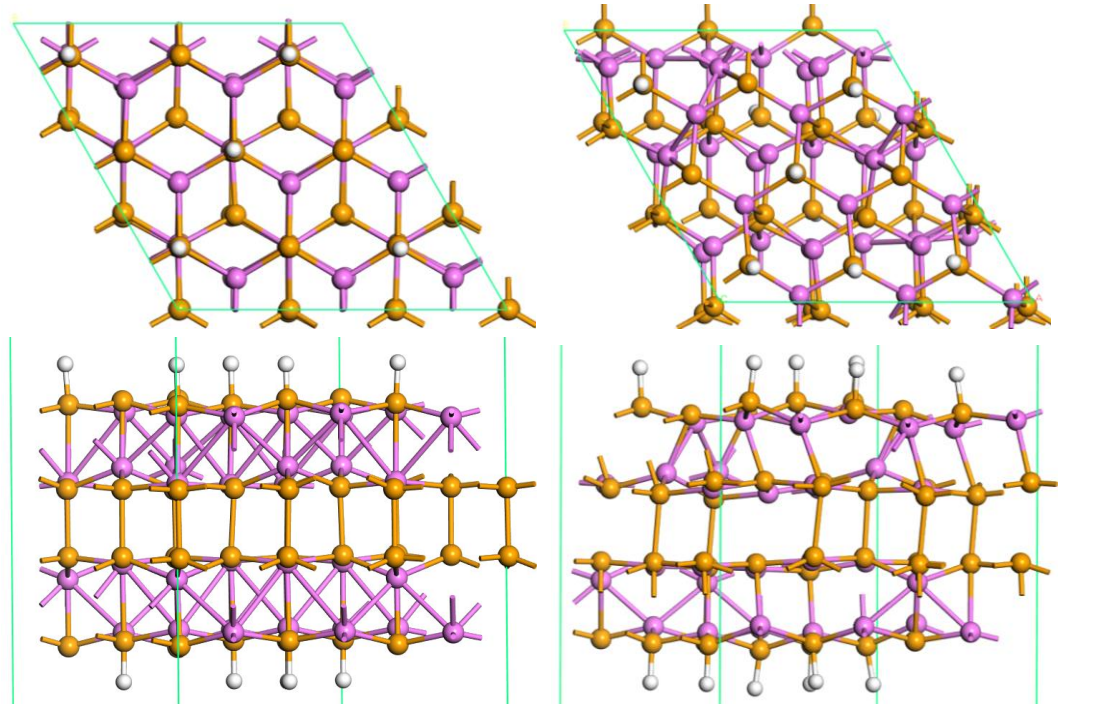


(a) $H_2(Cu_4Se_4)_9$, a = 11.802 Å, E_H = 0.435 eV (b) $H_4(Cu_4Se_4)_9$, a = 11.861 Å, E_H = 0.438 eV

Fig. S23 Top and front views of (a) two and (b) four protons adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S22.

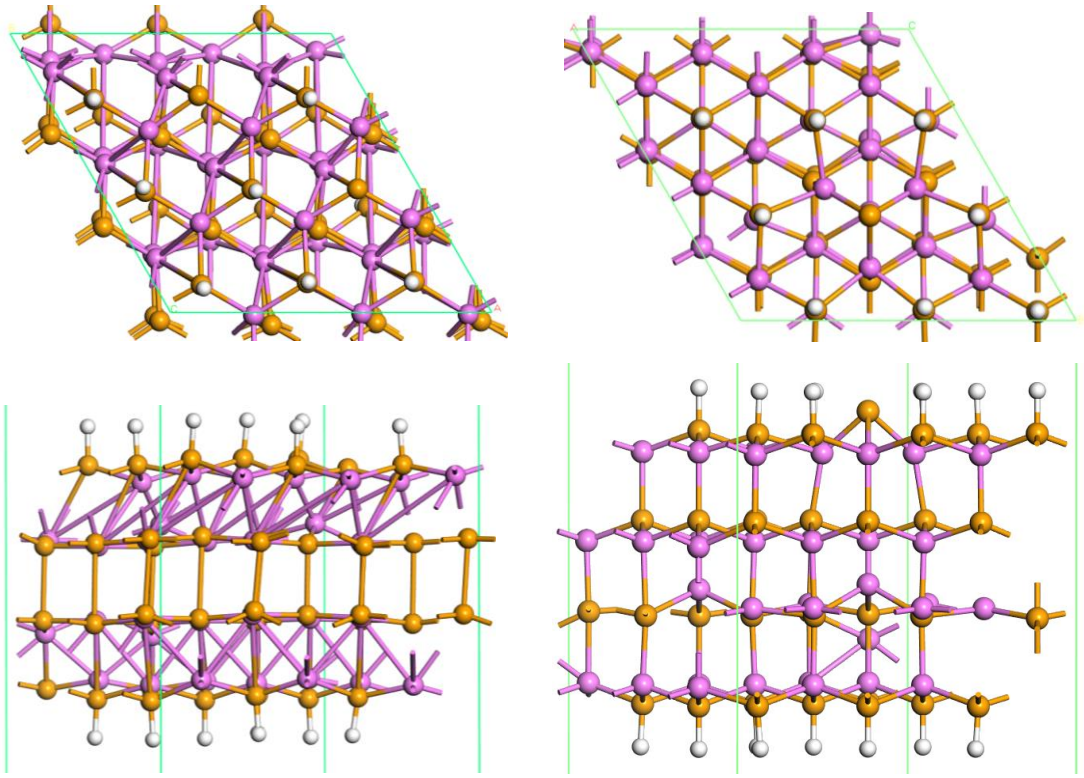


(a) $H_6(Cu_4Se_4)_9$, a = 11.919 Å, E_H = 0.445 eV (b) $H_8(Cu_4Se_4)_9$, a = 11.998 Å, E_H = 0.482 eV



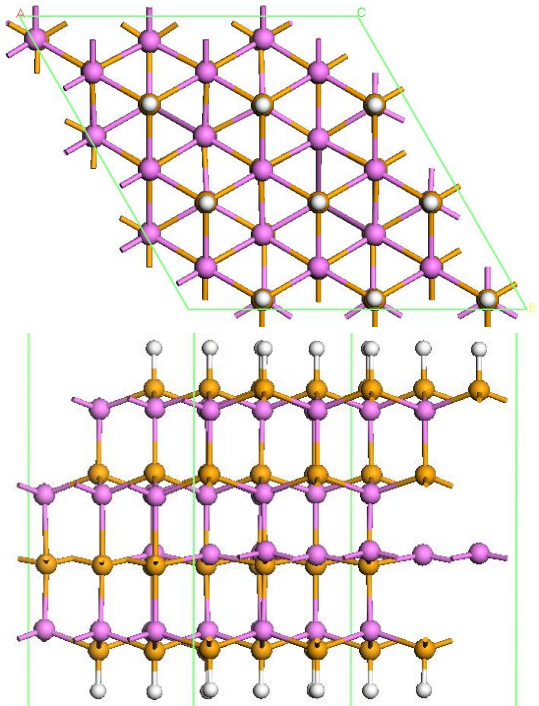
(c) $H_{10}(Cu_4Se_4)_9$, a = 12.064 Å, E_H = 0.518 eV (d) $H_{12}(Cu_4Se_4)_9$, a = 12.071 Å, E_H = 0.484 eV

Fig. S24 Top and front views of (a) six, (b) eight, (c) ten and (d) twelve protons adsorbed on the 3 ×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S22.



(a) $H_{14}(Cu_4Se_4)_9$, a = 12.245 Å, E_H = 0.457 eV (b) $H_{16}(Cu_4Se_4)_9$, a = 11.791 Å, E_H = 0.184 eV

Fig. S25 Top and front views of (a) fourteen and (b) sixteen protons adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S22.



a = 11.815 Å, E_H = 0.143 eV

Fig. S26 Top and front views of eighteen protons adsorbed on the 3×3×1 Cu_4Se_4 supercell. The atoms for which balls in different colors stand are the same as in Fig. S22.