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Supplemental Material – Insight into structural and electrochemical properties of interface between Na_6SOI_2 solid electrolyte and metallic Na anode

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Structural Modeling

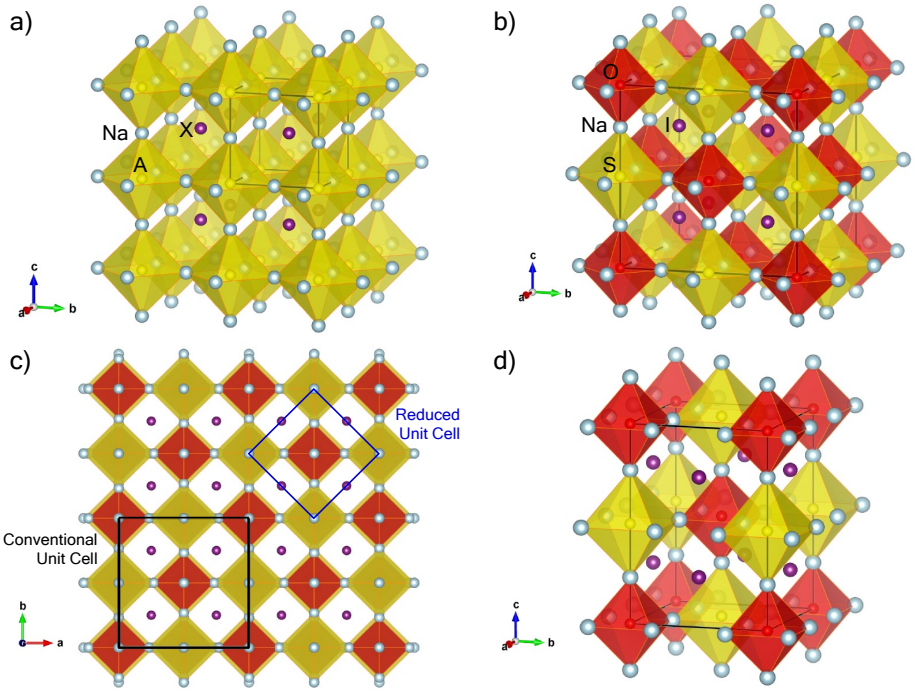

Figure S1. Polyhedral crystal structures of (a) Na-rich anti-perovskite (NaRAP) with general formula of Na_3AX, (b) Na-rich double anti-perovskite (NaRDAP) Na_6SOI_2, (c) Top-view of Na_6SOI_2 conventional and reduced unit cells and (d) Na_6SOI_2 reduced unit cell

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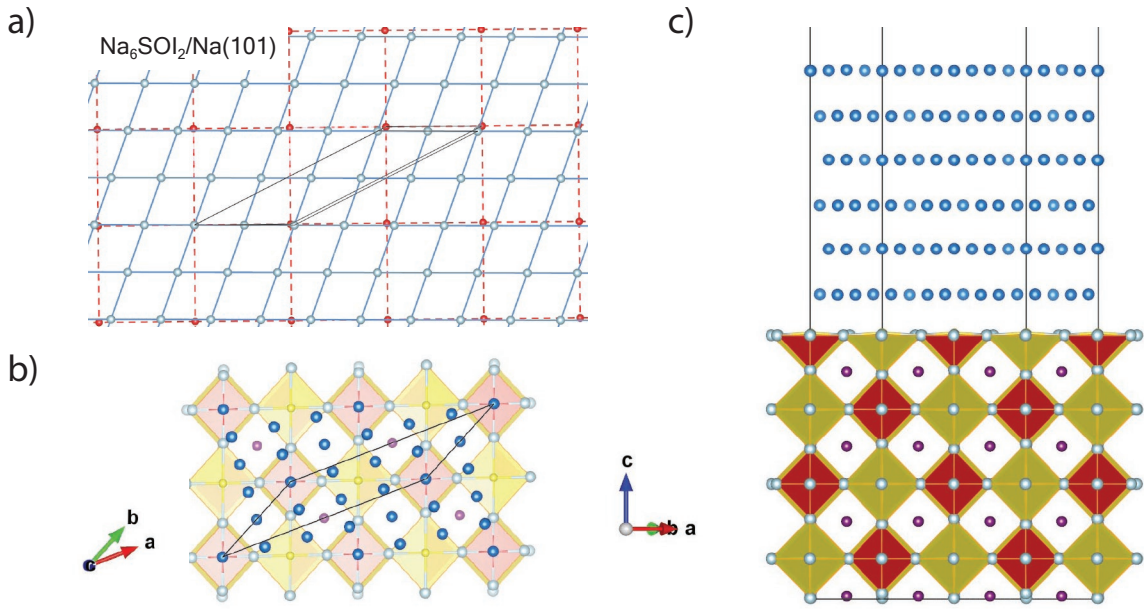

Figure S2. (a) Bravais lattices of Na_6SOI_2 and Na(001) surfaces showing the coincidence lattice model with minor mismatch. (b) Polyhedral top-view and (c) side-view of [NSO]/Na(001) interface model.

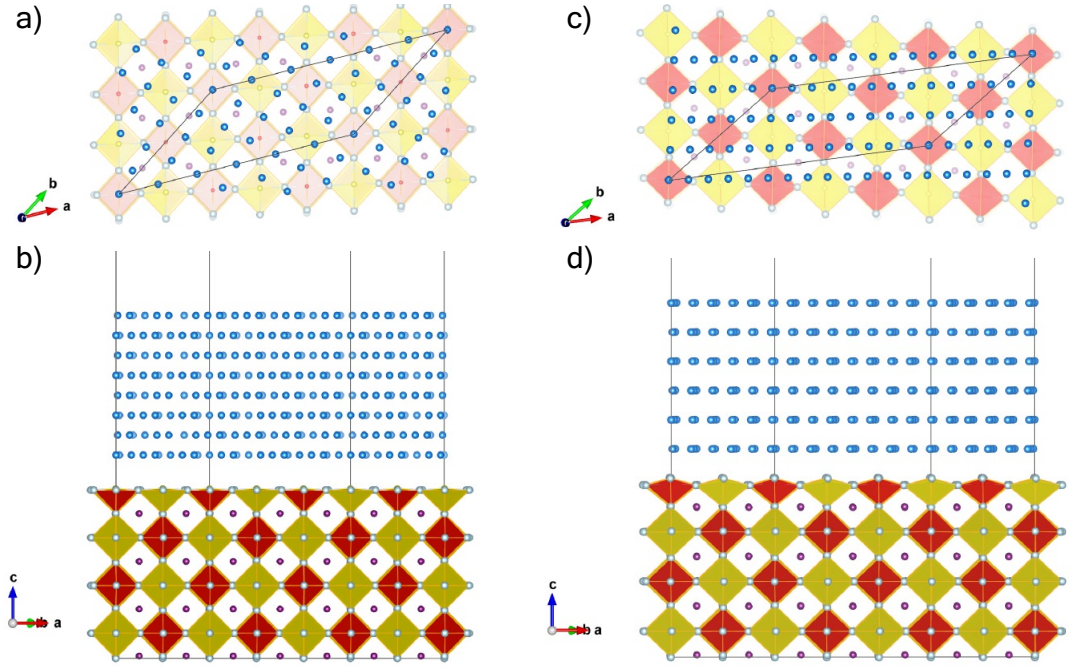

Figure S3. Polyhedral structures of interface models for SIESTA simulation – [NSO]/Na(001) : (a) top-view and (b) side-view, and [NSO]/Na(101) : (c) top-view and (d) side-view.

Structural Properties

Table S1. Lattice constants of the reduced unit cell of Na_6SOI_2 in bulk phase calculated by several codes - VASP, QE and SIESTA. Calculation results of this work are compared with those of Ref.[a] obtained from calculation by VASP(PBE).

Code(XC-func.)	$a = b$(Å)	c(Å)	$\alpha = \beta = \gamma$(°)	V(Å^3)	$r_{a,b}$(%)	r_c(%)	r_V(%)
VASP (PBE)[a]	**7.04**	**9.96**	**90.00**	**493.60**	–	–	–
QE (PBE-sol)	7.00	9.90	90.00	484.58	−0.59	−0.65	−1.83
QE (PBE)	7.09	10.03	90.00	504.82	0.76	0.74	2.27
SIESTA (PBE)	7.17	10.15	90.00	522.18	1.90	1.87	5.79

[a] Y. Yu, Z. Wang and G. Shao, J. Mater. Chem. A, 2018, 6, 19843-19852

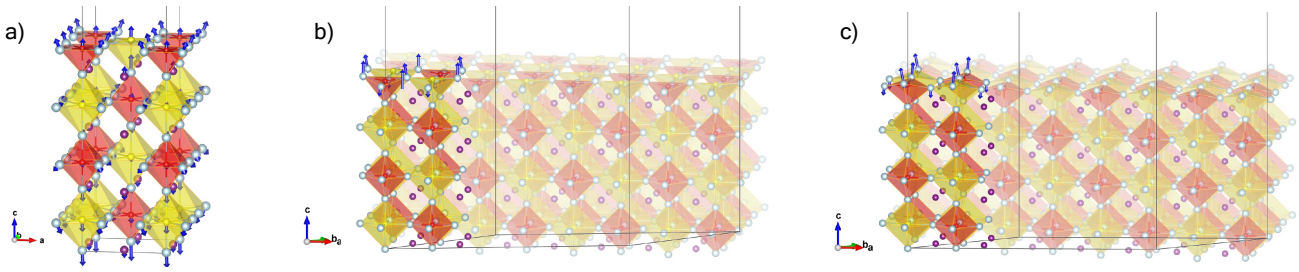

Figure S4. Structural optimization results by SIESTA calculations. (a) Polyhedral view of optimized structural models for (a) Na_6SOI_2 surface model, and the strained ones of coincidence lattice with (b) Na(001) surface and (c) Na(101) surface. Blue arrows denote the displacement of the atoms.

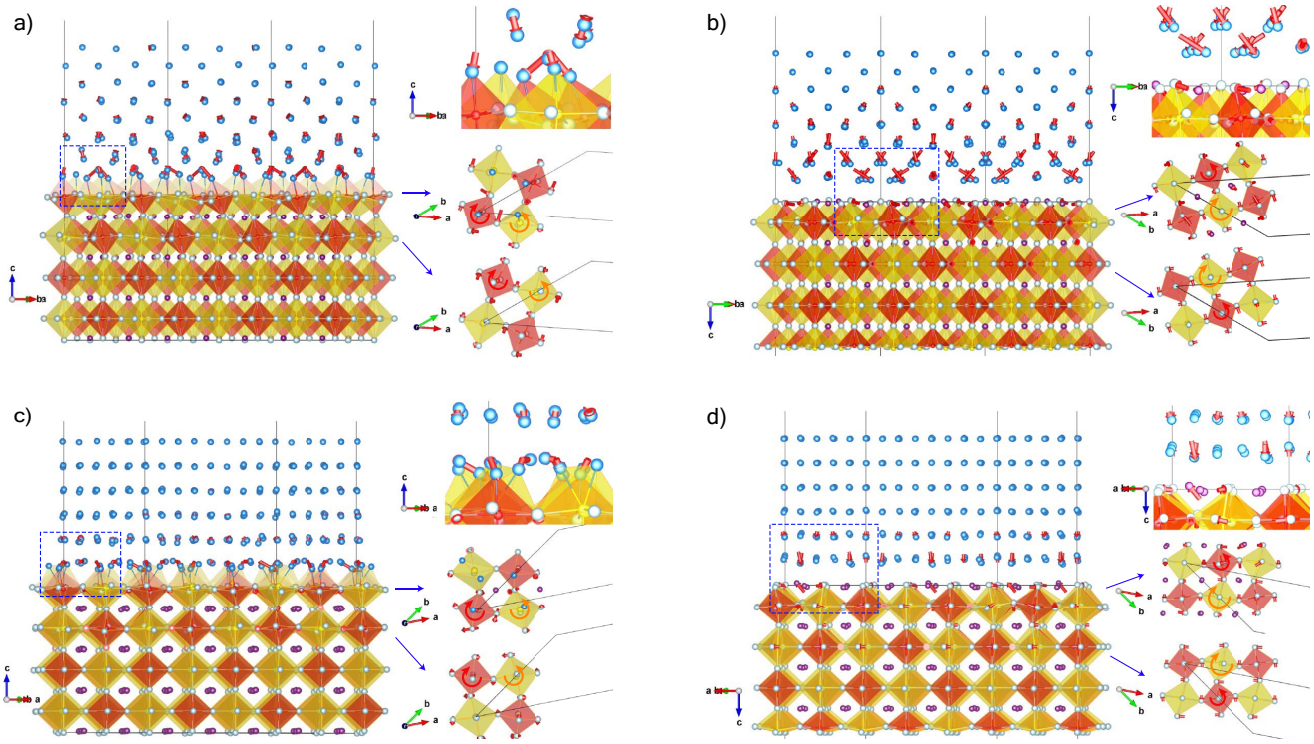

Figure S5. Structural optimization results by SIESTA calculations for interface models – (a) [NSO]/Na(001), (b) [NI]/Na(001), (c) [NSO]/Na(101), and (d) [NI]/Na(101). Red arrows denote the displacement of the atoms, while orange and red arrows depict the rotation of S- and O-centered polyhedra, respectively.

Ion Migration

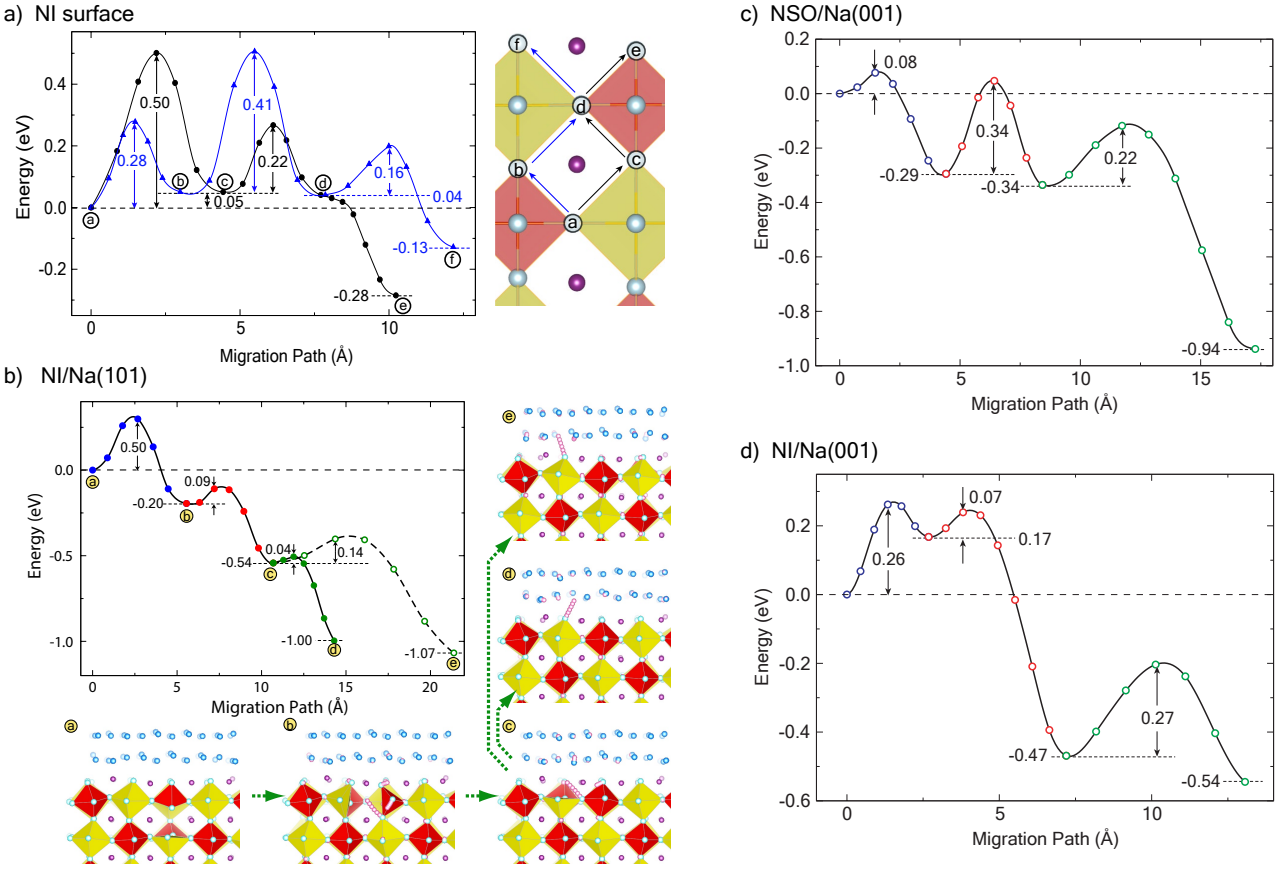

Figure S6. Energy profiles for V_{Na} migration near (a) NI surface termination, (b) NI/Na(101), (c) NSO/Na(001) and (d) NI/Na(001) interfaces. The migration paths are indicated in the right panel of (a) and the snapshots of V_{Na} migration in (b) NI/Na(101) interface model are shown in the surrounding where the light pink balls illustrate the migration paths of Na.

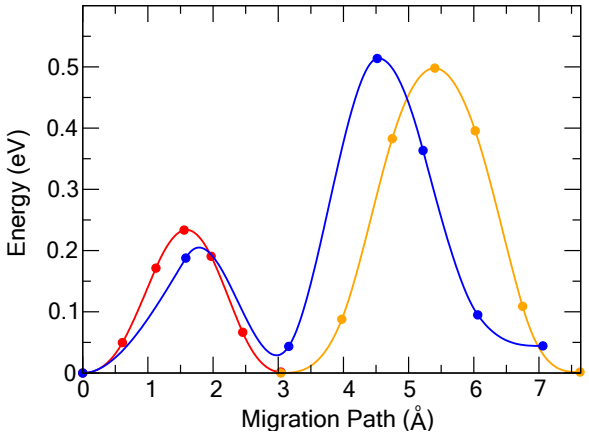

Figure S7. Migration energy profiles of V_{Na} for concurrent migration scheme (blue curve) and sequential migration scheme (red and orange curves).

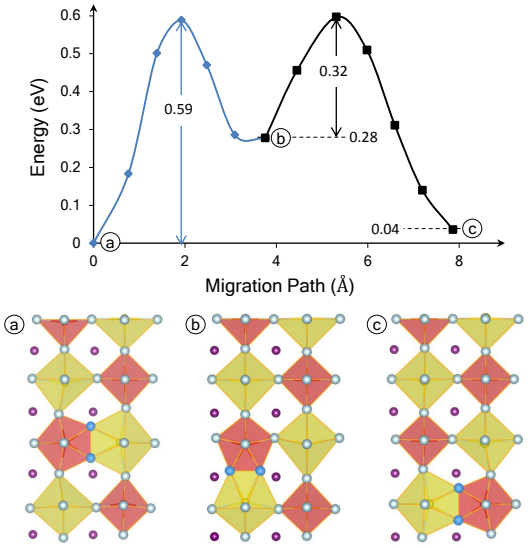

Figure S8. Migration energy profiles of Na_i for rotational scheme and the snapshots of migration.

Electronic Structures

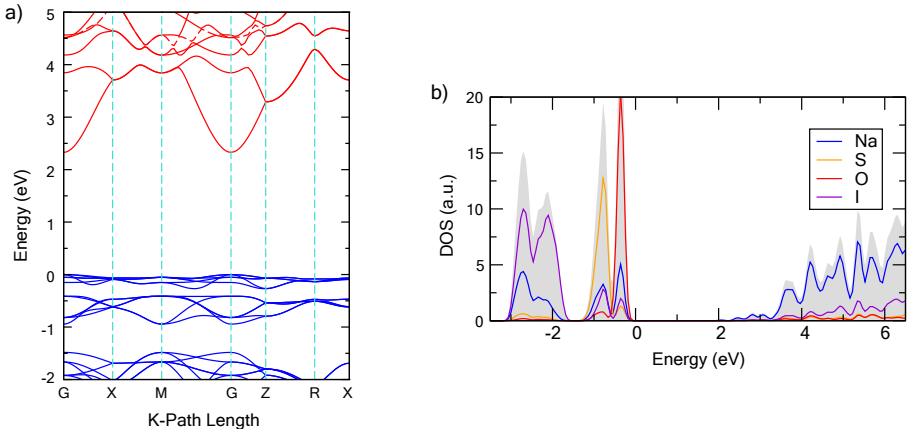

Figure S9. Electronic structures of Na_6SOI_2 in bulk phase; (a) band structure and (b) atom-resolved PDOS.

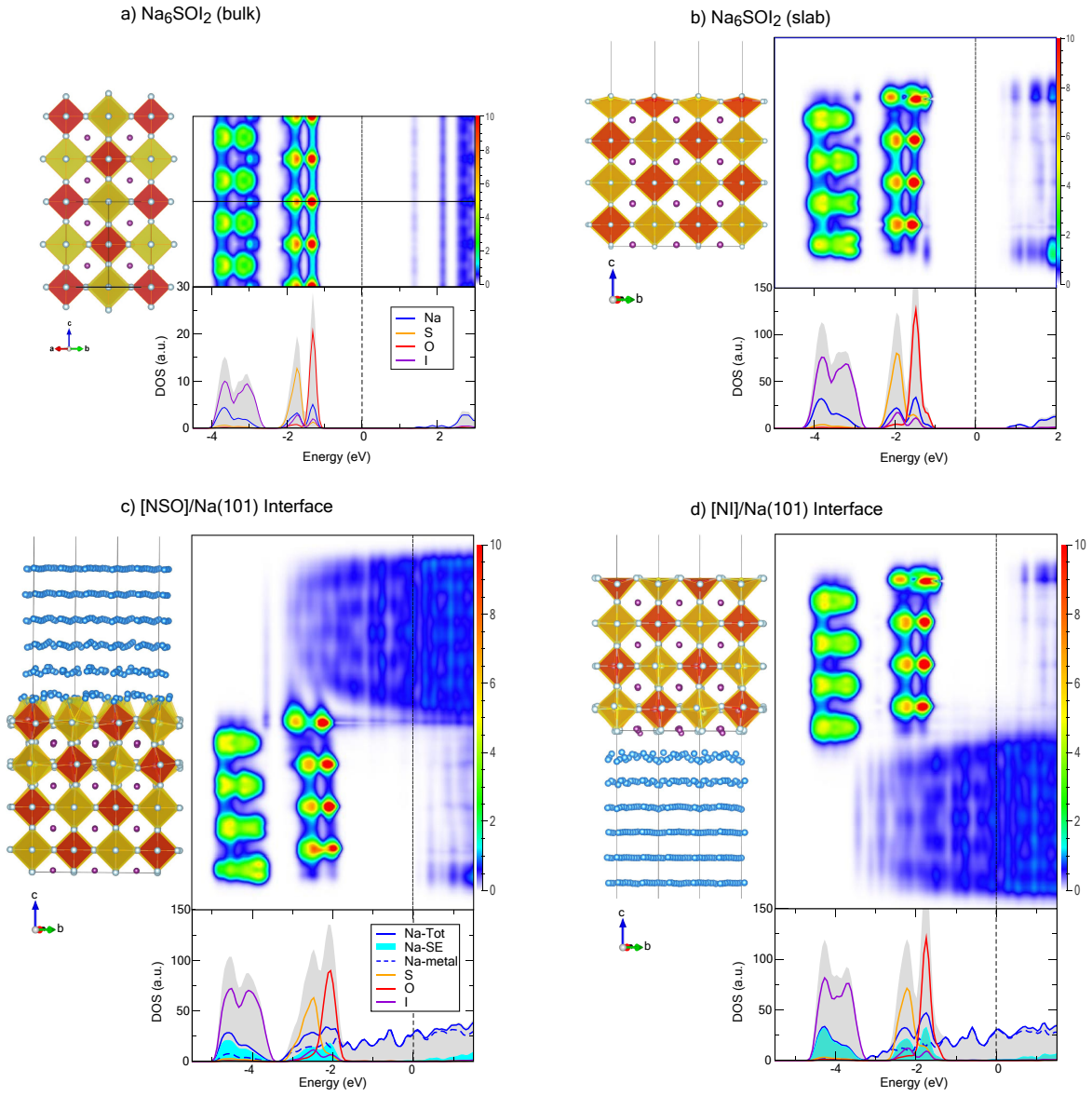

Figure S10. Atom-resolved PDOS and LDOS along $c-$direction integrated over $a-b$ plane; (a) Na_6SOI_2 in bulk phase (b) Na_6SOI_2 surface model, (c) [NSO]/Na(101) interface model, and (d) [NI]/Na(001) interface model. Vertical ($c-$direction) and horizontal (energy) axes of the LDOS graphs are shared by the structural model in the left and PDOS graph at the bottom, and the Fermi level is fixed as 0 eV.