Electronic Supplementary Information

Surface-dependent band structure variations and bond-level deviations of Cu_2O

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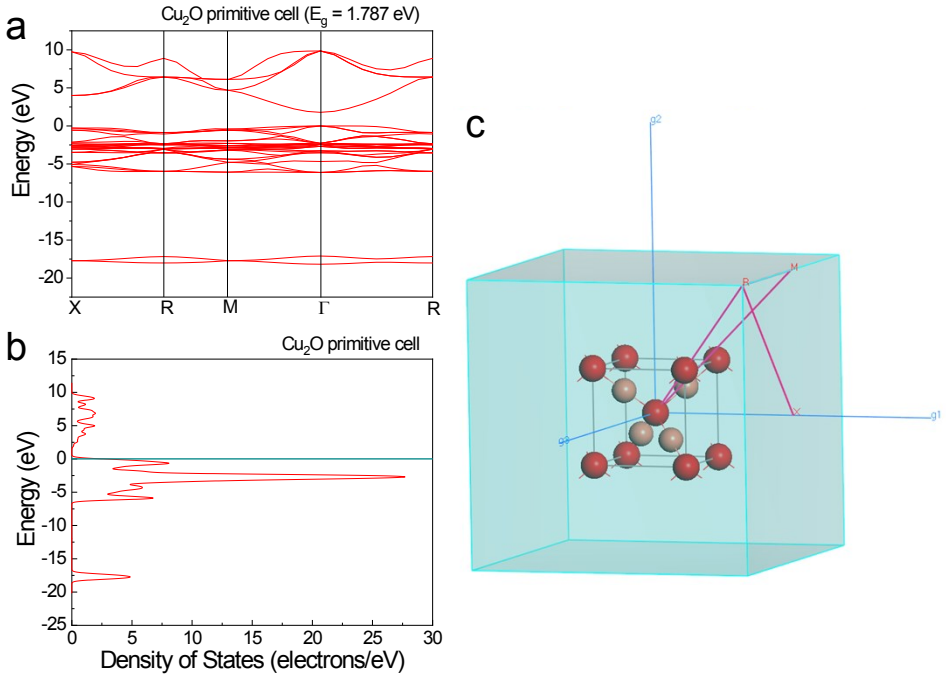

Fig. S1 (a) Band structure and (b) DOS diagram of the Cu_2O primitive cell. (c) Cu_2O primitive cell with Brillouin zone. Pink spheres are O atoms and red spheres are Cu atoms.

Table S1 Enthalpy variations using different starting points to calculate band structures of 1 layer of Cu_2O (111) plane from a 3 × 3 × 3 supercell.

Cu_2O 3x3x3 1 layer	Enthalpy (eV)
Slab starts at 0	-6775.50
Slab starts at 0.167	-6757.08
Slab starts at 0.25	-6757.08
Slab starts at 0.333	-6775.50
Slab starts at 0.5	-6757.08
Slab starts at 0.583	-6757.08
Slab starts at 0.667	-6775.50
Slab starts at 0.883	-6757.09
Slab starts at 0.917	-6757.09

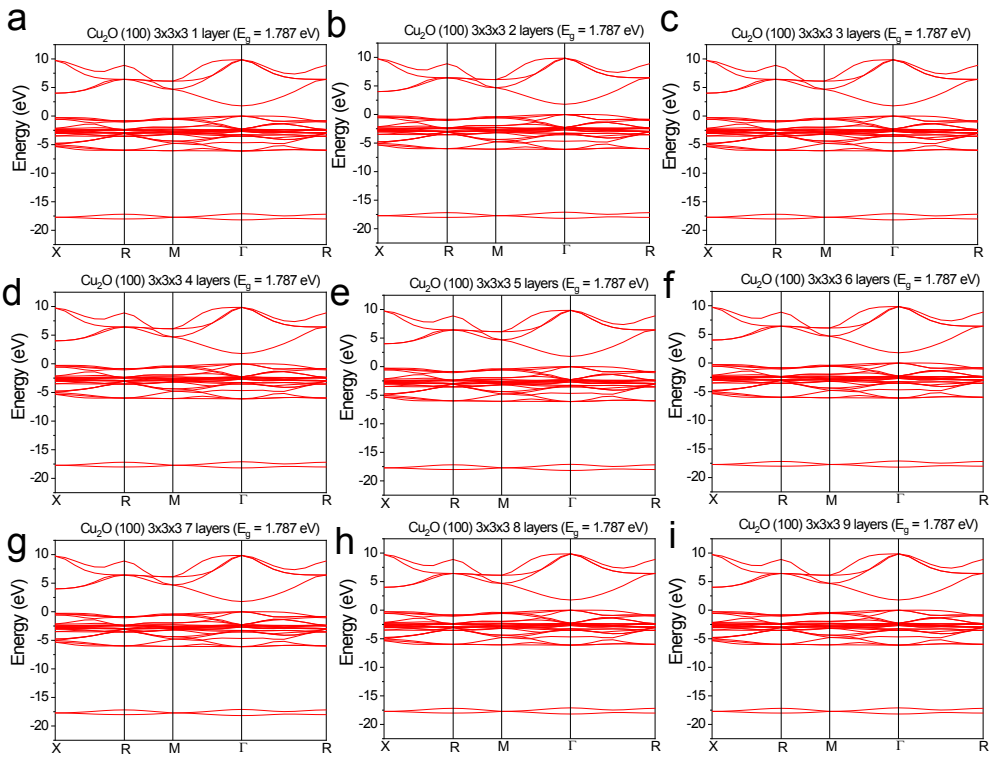

Fig. S2 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (100) planes obtained using slabs from a 3 × 3 × 3 Cu_2O supercell.

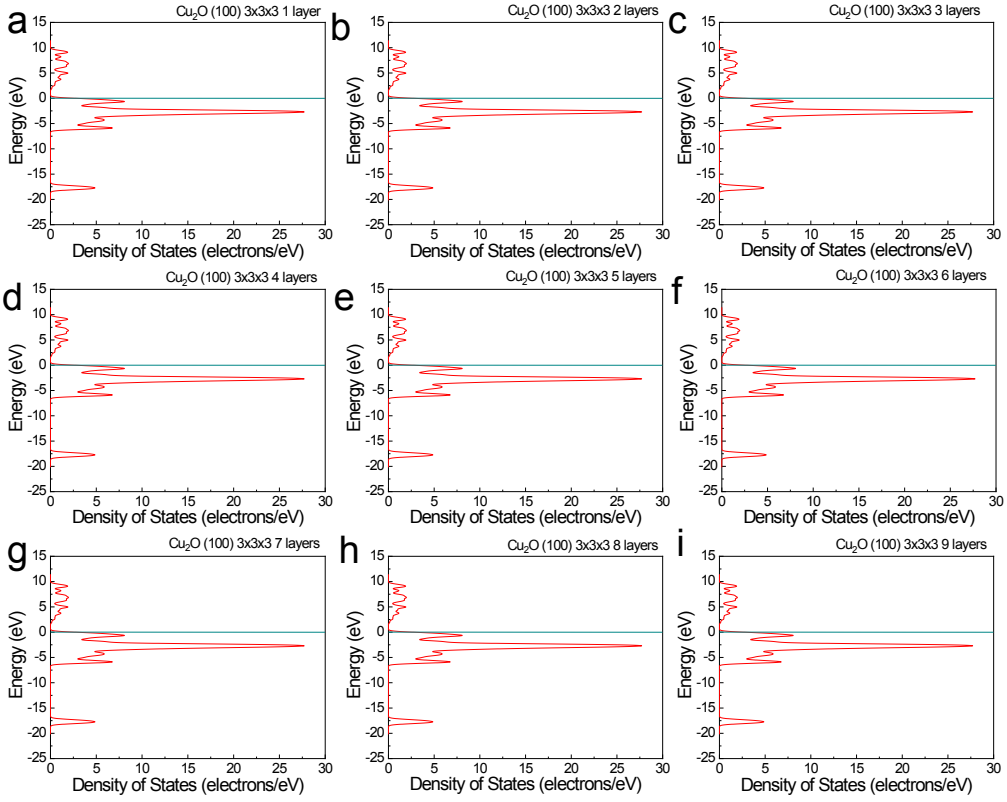

Fig. S3 DOS diagrams of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (100) planes obtained using slabs from a 3 × 3 × 3 Cu_2O supercell.

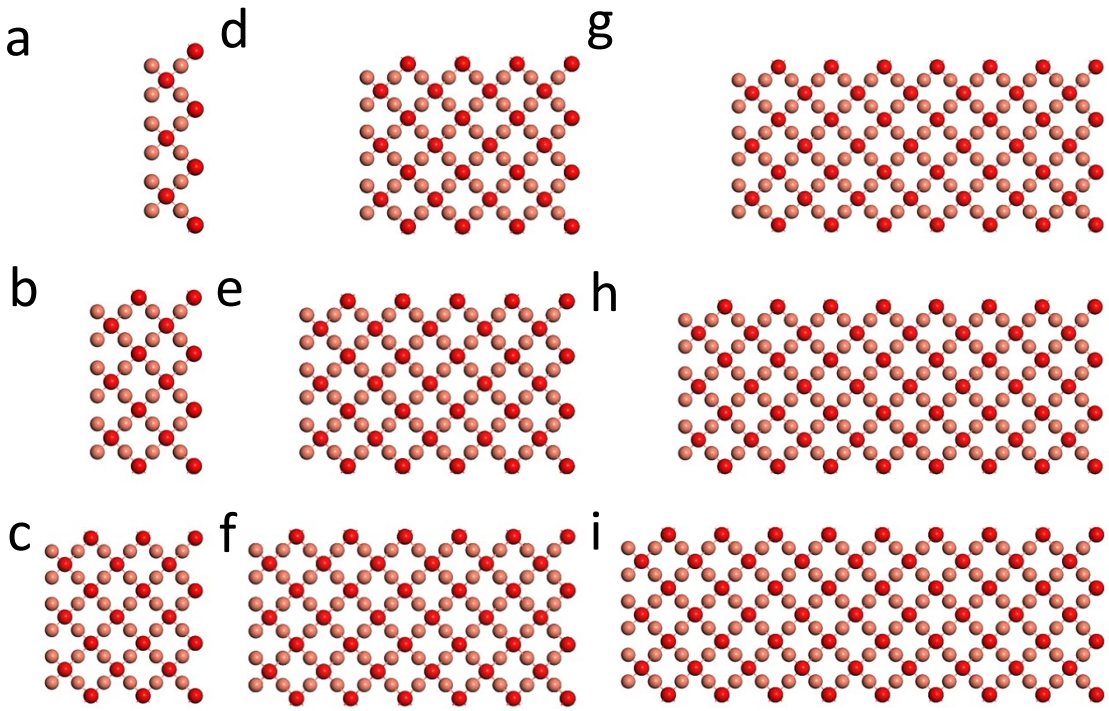

Fig. S4 Slab structures of 1–9 layers of Cu_2O (100) planes.

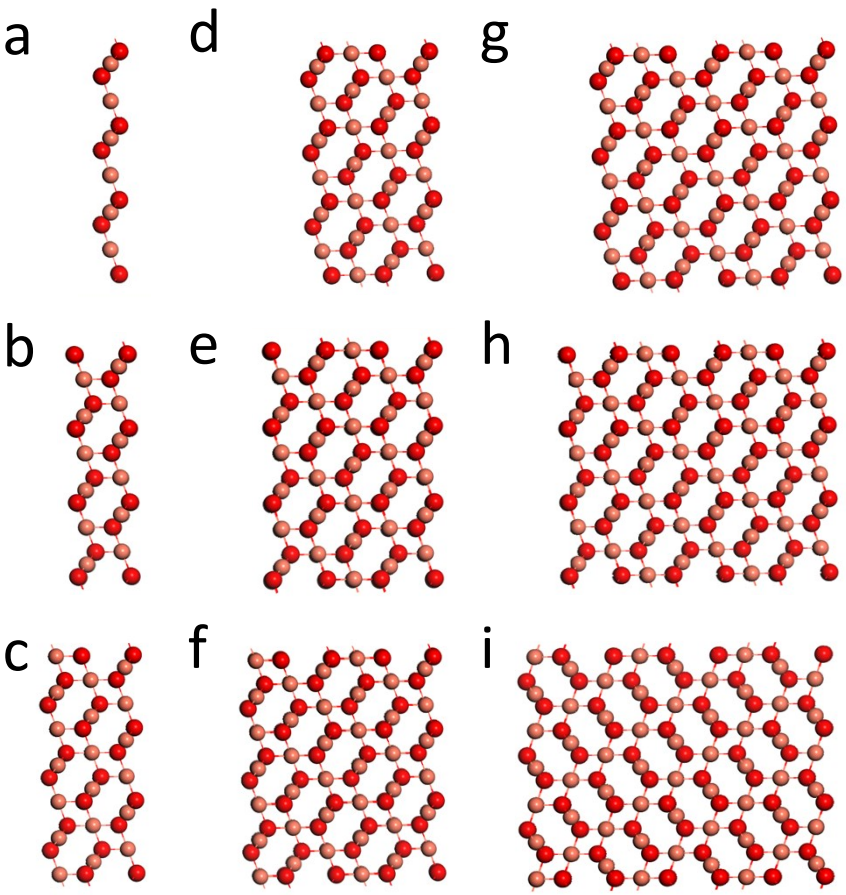

Fig. S5 Slab structures of 1–9 layers of Cu_2O (111) planes.

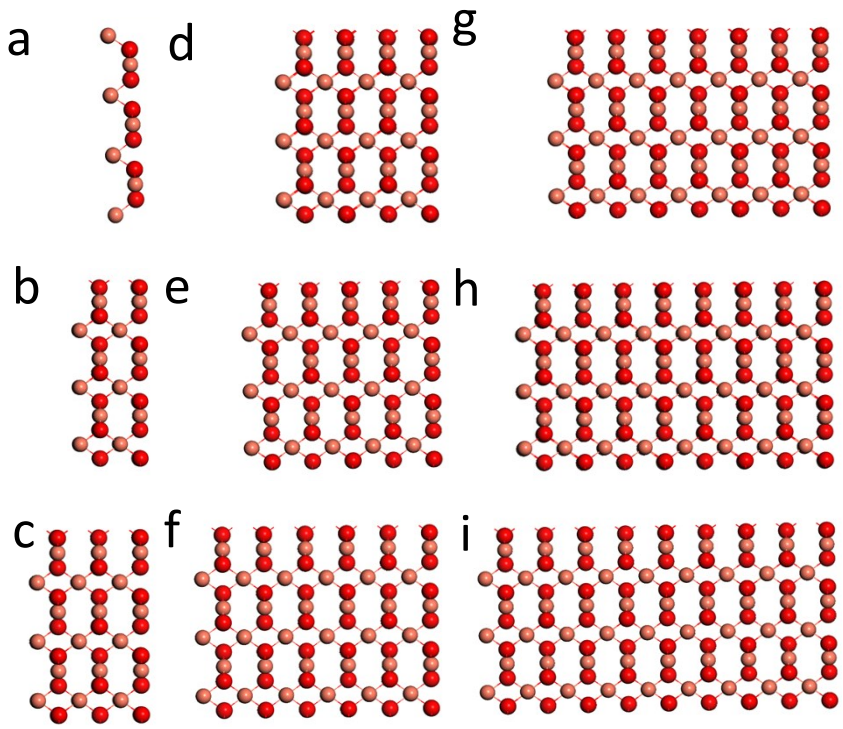

Fig. S6 Slab structures of 1–9 layers of Cu_2O (110) planes.

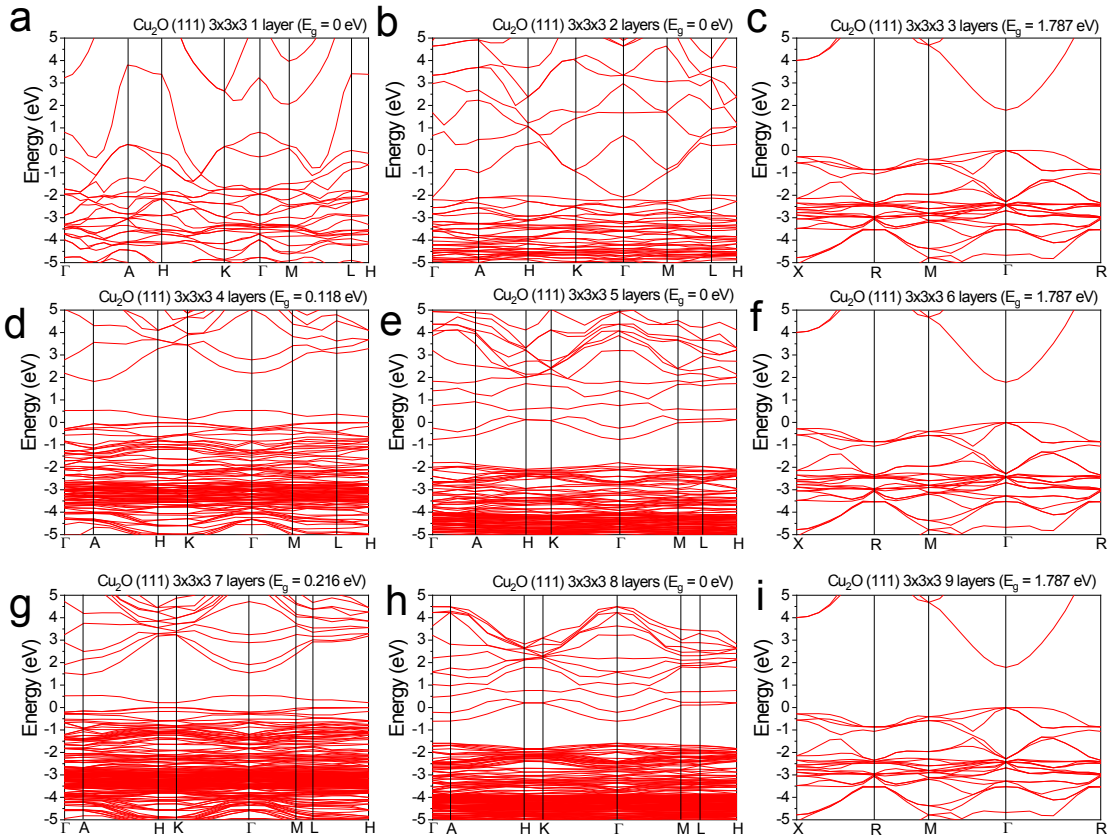

Fig. S7 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 3 × 3 × 3 Cu_2O supercell.

Only an energy range of 5 to –5 eV is shown.

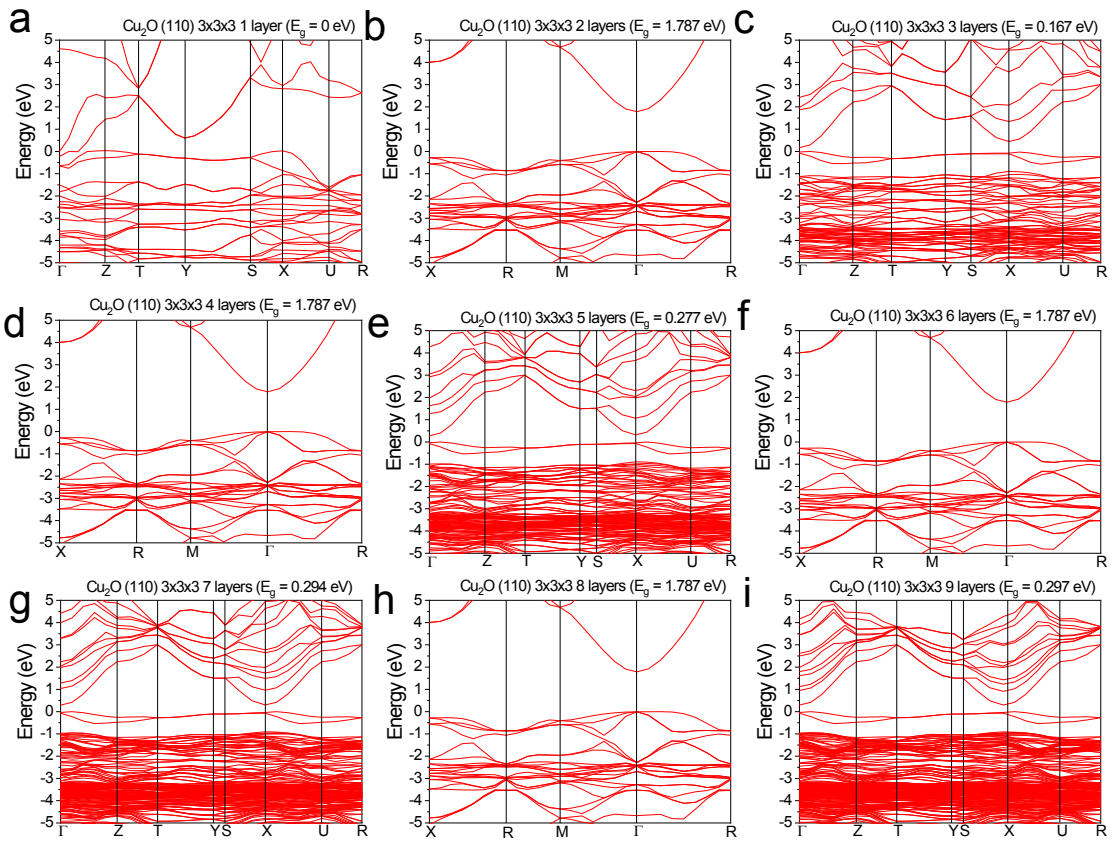

Fig. S8 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (110) planes obtained using slabs from a 3 × 3 × 3 Cu_2O supercell. Only an energy range of 5 to –5 eV is shown.

Table S2 Band gap variation with respect to the number of plane layers.

Band gap (eV)	1 layer	2 layers	3 layers	4 layers	5 layers	6 layers	7 layers	8 layers	9 layers
(111) slab from 5x5x5 supercell	0	0	1.787	0.118	0	1.787	0.216	0	1.787
(111) slab from 4x4x4 supercell	0	0	1.787	0.118	0	1.787	0.216	0	1.787
(111) slab from 3x3x3 supercell	0	0	1.787	0.118	0	1.787	0.216	0	1.787
(111) slab from 2x2x2 supercell	0	0	1.787	0.118	0	1.787	0.216	0	1.787
(111) slab from 1x1x1 supercell	0	0	1.787	0.118	0	1.787	0.216	0	1.787
(110) slab from 3x3x3 supercell	0	1.787	0.167	1.787	0.277	1.787	0.294	1.787	0.297
(100) slab from 3x3x3 supercell	1.787	1.787	1.787	1.787	1.787	1.787	1.787	1.787	1.787

Table S3 Cu_2O layer thicknesses vs. the number of plane layers.

Cu_2O layer thickness (Å)	1 layer	2 layers	3 layers	4 layers	5 layers	6 layers	7 layers	8 layers	9 layers
(111)	2.46	4.92	7.38	9.84	12.3	14.76	17.22	19.68	22.14
(110)	3.02	6.04	9.06	12.08	15.10	18.12	21.14	24.16	27.18
(100)	4.27	8.54	12.81	17.08	21.35	25.62	29.89	34.16	38.43

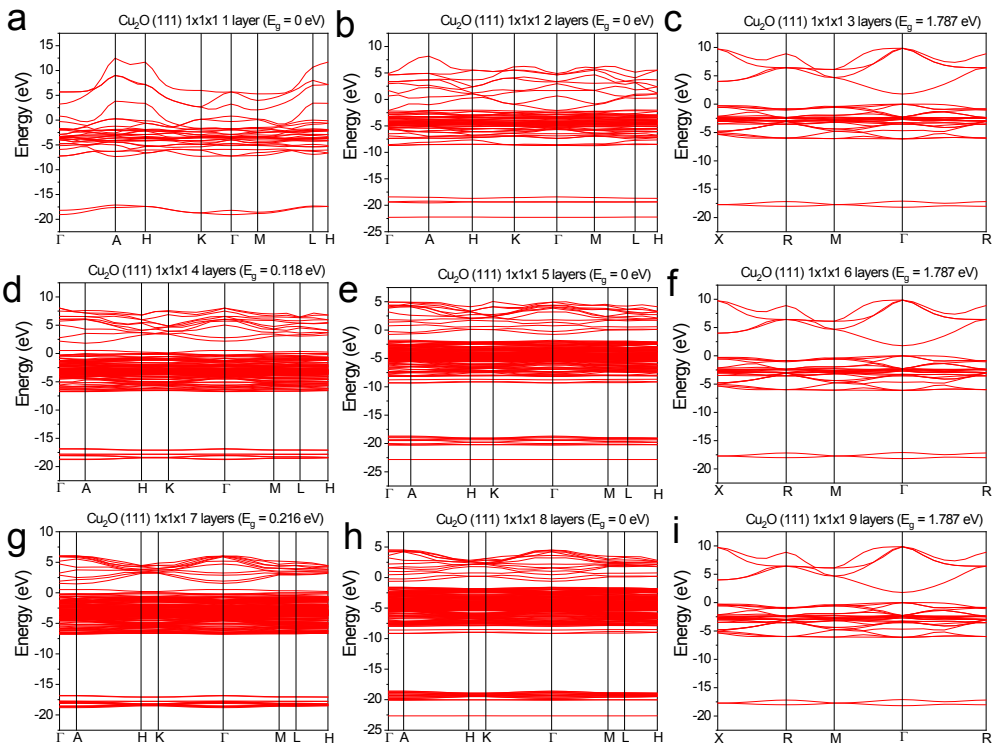

Fig. S9 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 1 × 1 × 1 Cu_2O supercell.

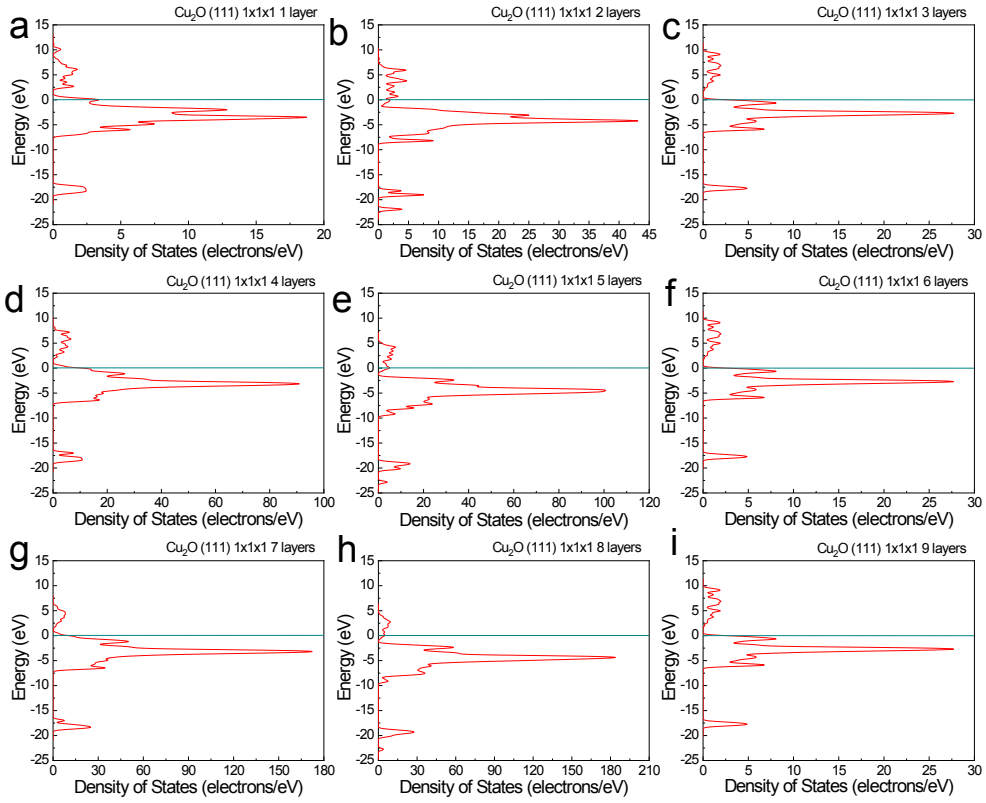

Fig. S10 DOS diagrams of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 1 × 1 × 1 Cu_2O supercell.

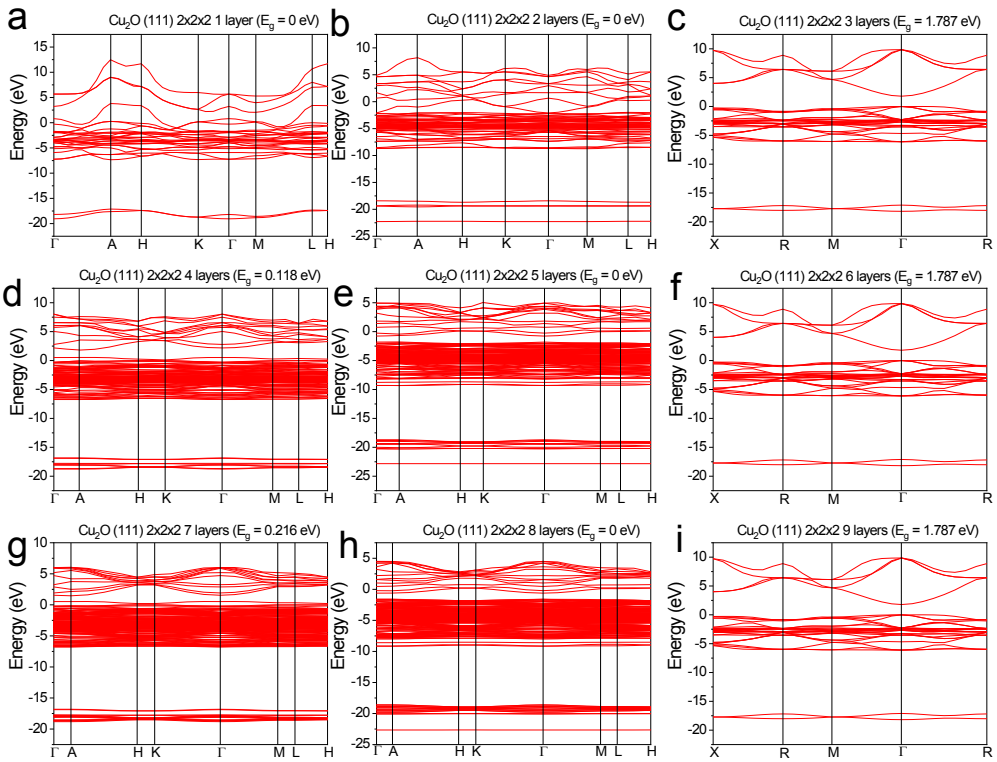

Fig. S11 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 2 × 2 × 2 Cu_2O supercell.

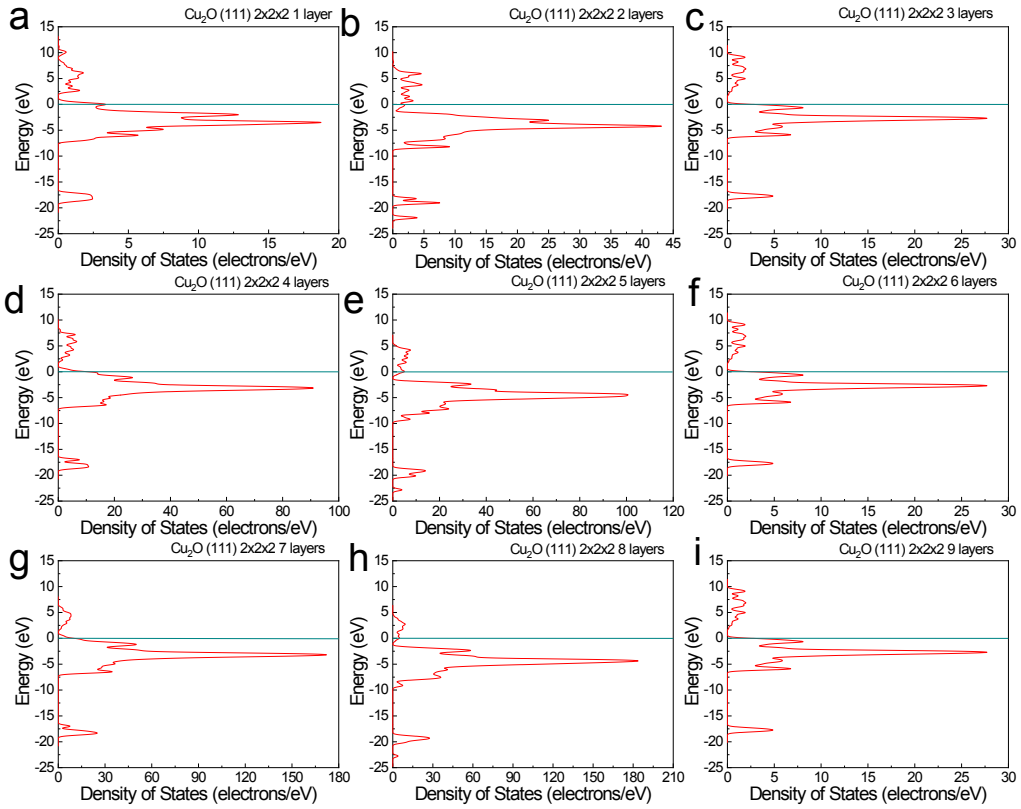

Fig. S12 DOS diagrams of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 2 × 2 × 2 Cu_2O supercell.

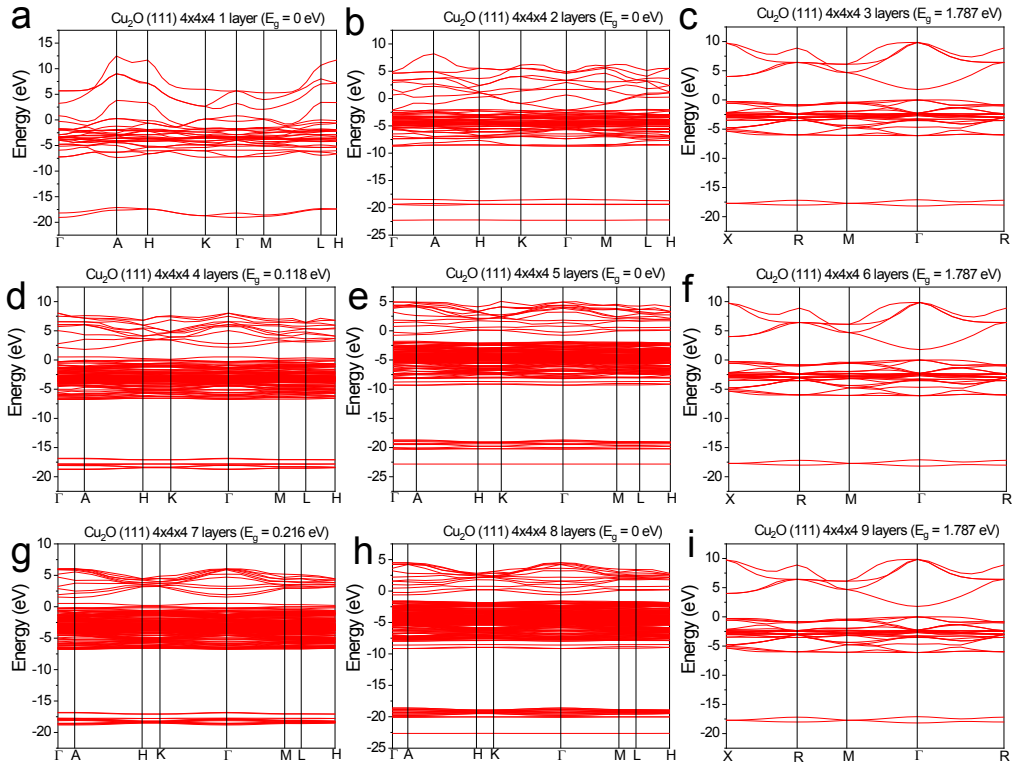

Fig. S13 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 4 × 4 × 4 Cu_2O supercell.

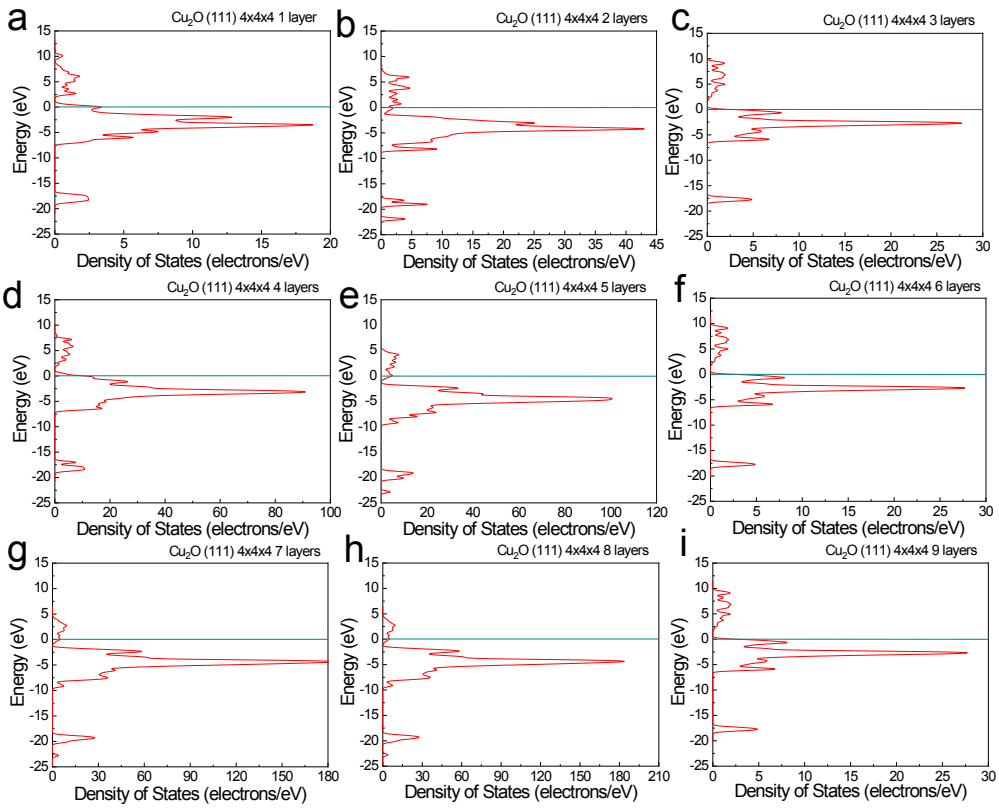

Fig. S14 DOS diagrams of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 4 × 4 × 4 Cu_2O supercell.

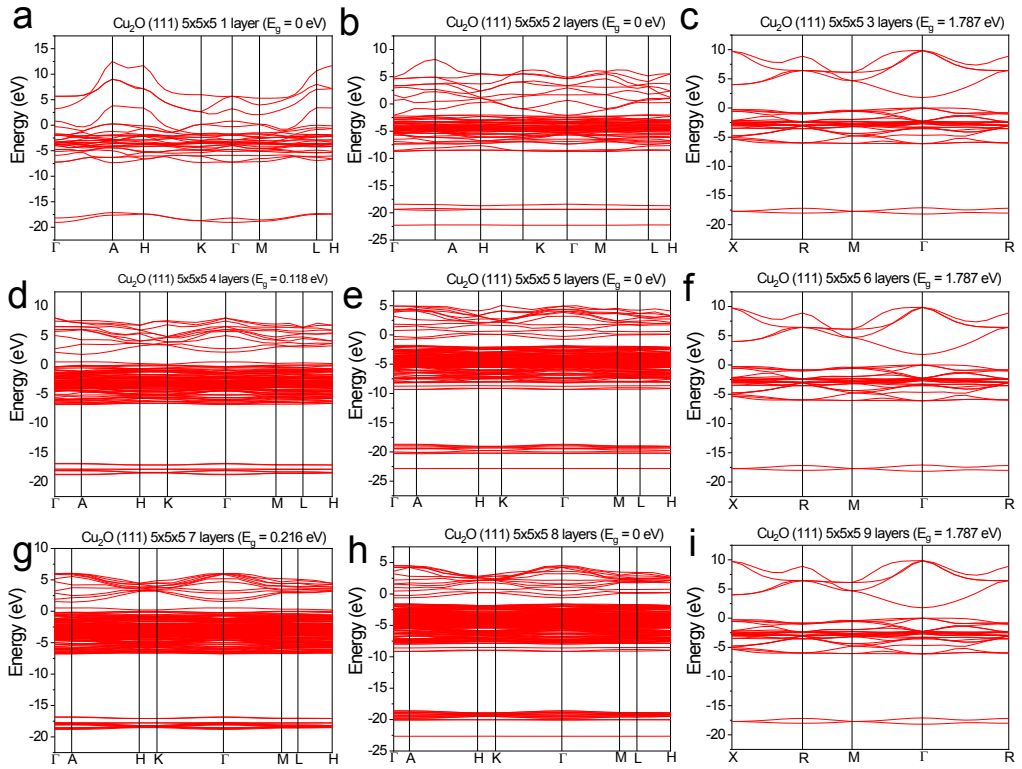

Fig. S15 Band structures of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 5 × 5 × 5 Cu_2O supercell.

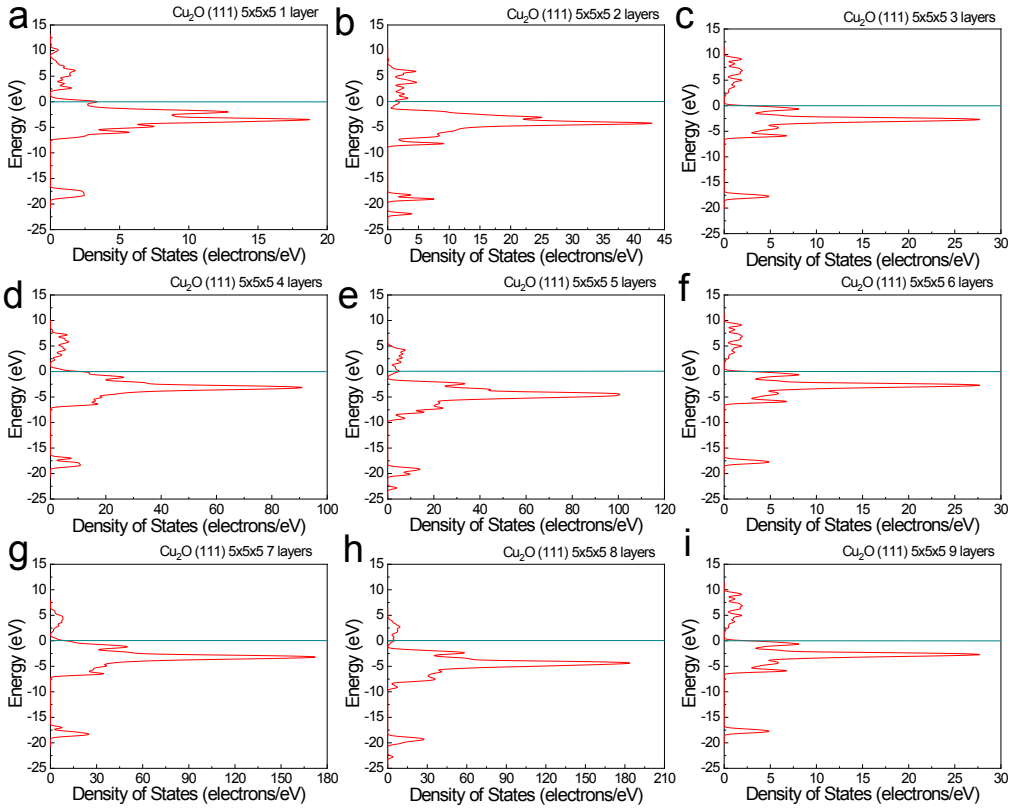

Fig. S16 DOS diagrams of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9 layers of Cu_2O (111) planes obtained using slabs from a 5 × 5 × 5 Cu_2O supercell.

Table S4 Average Cu–O bond length variation with respect to the number of plane layers.

Cu-O average bond length (Å)	1 layer	2 layers	3 layers	4 layers	5 layers	6 layers	7 layers	8 layers	9 layers
(111) slab from 5 x 5 x 5 super cell	1.88	1.88	1.85	1.84	1.86	1.85	1.85	1.86	1.85
(111) slab from 4 x 4 x 4 super cell	1.88	1.88	1.85	1.84	1.86	1.85	1.85	1.86	1.85
(111) slab from 3 x 3 x 3 super cell	1.88	1.88	1.85	1.84	1.86	1.85	1.85	1.86	1.85
(111) slab from 2 x 2 x 2 super cell	1.88	1.88	1.85	1.84	1.86	1.85	1.85	1.86	1.85
(111) slab from 1 x 1 x 1 super cell	1.88	1.88	1.85	1.84	1.86	1.85	1.85	1.86	1.85
(110) slab from 3 x 3 x 3 super cell	1.93	1.85	1.87	1.85	1.87	1.85	1.87	1.85	1.86
(100) slab from 3 x 3 x 3 super cell	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85

Table S5 Cu–O bond distortion percentages with respect to the number of plane layers.

Cu–O bond distortion (%)	1 layer	2 layers	3 layers	4 layers	5 layers	6 layers	7 layers	8 layers	9 layers
(111) Slab from 5x5x5 super cell	1.684	1.828	0	–0.278	0.700	0	0.018	0.485	0
(111) Slab from 4x4x4 super cell	1.684	1.830	0	–0.277	0.606	0	0.019	0.451	0
(111) Slab from 3x3x3super cell	1.683	1.828	0	–0.279	0.445	0	0.023	0.394	0
(111) Slab from 2x2x2 super cell	1.684	1.836	0	–0.279	0.716	0	0.023	0.479	0
(111) Slab from 1x1x1 super cell	1.684	1.829	0	–0.278	0.652	0	0.019	0.440	0
(110) Slab from 3x3x3super cell	4.276	0	1.059	0	1.353	0	0.973	0	0.697
(100) Slab from 3x3x3super cell	0	0	0	0	0	0	0	0	0

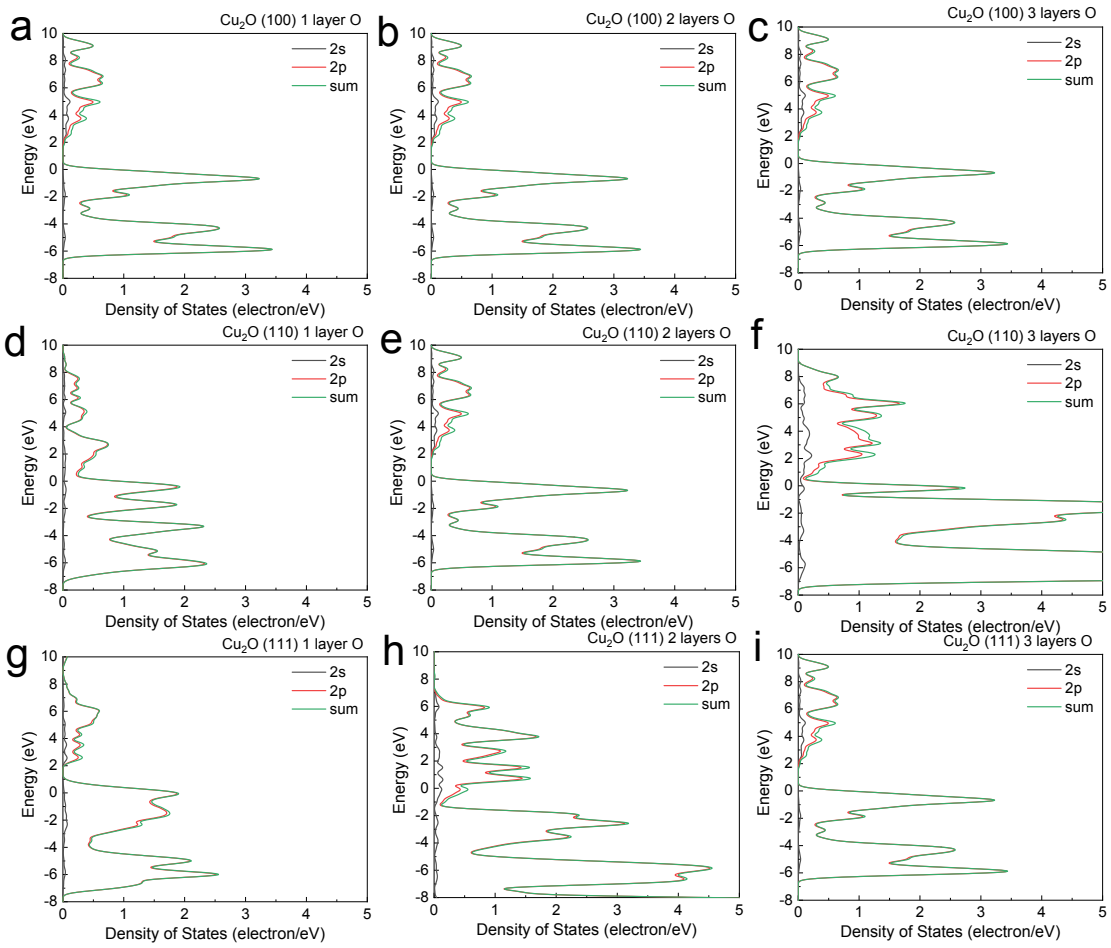

Fig. S17 Partial DOS diagrams of 1–3 layers of Cu_2O (a–c) (100), (d–e) (110), and (g–i) (111) planes showing the contributions by the frontier orbitals of oxygen atoms.