Electronic Supporting Information

Discovery of a high-pressure phase of rutile-like CoO_2 and its potential as a cathode material

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The formulae to calculate bulk moduli (B), shear moduli (G), Young's modulus (E) and Possion's ratio (v) in orthorhombic phase are taken from Ref[1]. In the following, subscript V denotes the Voigt bound, R denotes the Reuss bound, and H denotes the Hill average which is the arithmetic average of Voigt and Reuss bounds. It is known that the Voigt bound is obtained by the average polycrystalline moduli based on an assumption of uniform strain throughout a poly-crystal, which is the upper limit of the actual effective moduli. However, the Reuss bound is obtained by assuming a uniform stress and is the lower limit of the actual effective moduli[2].

$$B_v=(1/9)[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]$$

$$G_v=(1/15)[C_{11}+C_{22}+C_{33}+3(C_{44}+C_{55}+C_{66})-(C_{12}+C_{13}+C_{23})]$$

$$B_r=\Delta[C11(C_{22}+C_{33}-2C_{23})+C_{22}(C_{33}-2C_{13})-2C_{33}C_{12}+C_{12}(2C_{23}-C_{12})+C_{13}(2C_{12}-C_{13})+C_{23}(2C_{13}-C_{23})]^{-1}$$

$$G_r=15\{4[C_{11}(C_{22}+C_{33}+C_{23})+C_{22}(C_{33}+C_{13})+C_{33}C_{12}-C_{12}(C_{23}+C_{12})-C_{13}(C_{12}+C_{13})-$$

$$C_{23}(C_{13}+C_{23})]/\Delta+3[(1/C_{44})+(1/C_{55})+()1/C_{66}]\}^{-1}$$

Young's modulus E and Possion's ratio v are obtained by using following formulae

$$E=9BG/(3B+G)$$

$$v=(3B-2G)/(6B+2G)$$

The results are shown in Table 1 in the text.

Table S1. Lattice parameters of rutile-like CoO_2 after removing pressure.

Symmetry	a (Å)	b (Å)	c (Å)	α=β=γ(°)
Pnnm	4.41	4.10	2.85	90
Atom	*x*	*y*	*z*	site
Co	0.00	0.00	1.00	2a
O	0.84	0.77	0.50	4g

Table S2. Elastic stiff constants (GPa) C_{ij} of rutile-like CoO_2 after removing pressure.

System	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
CoO2	368.9	184.7	402.4	120.2	138.3	206.9	191.9	153.4	52.1

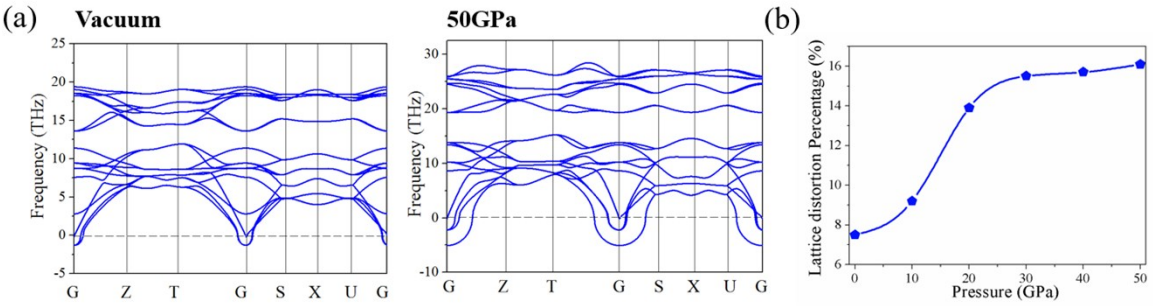

Figure S1. (a) Phonon spectra of standard-rutile CoO_2 at vacuum and 50GPa. (b) Pressure dependence of the lattice distortion for rutile-like CoO_2.

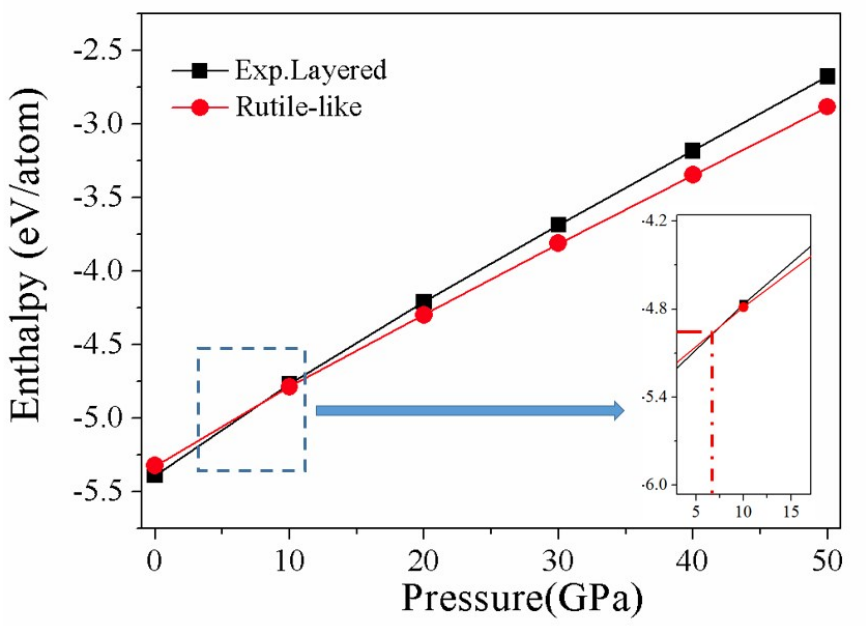

Figure S2. Pressure dependence of enthalpy of the predicted structure compared with the layered structure.

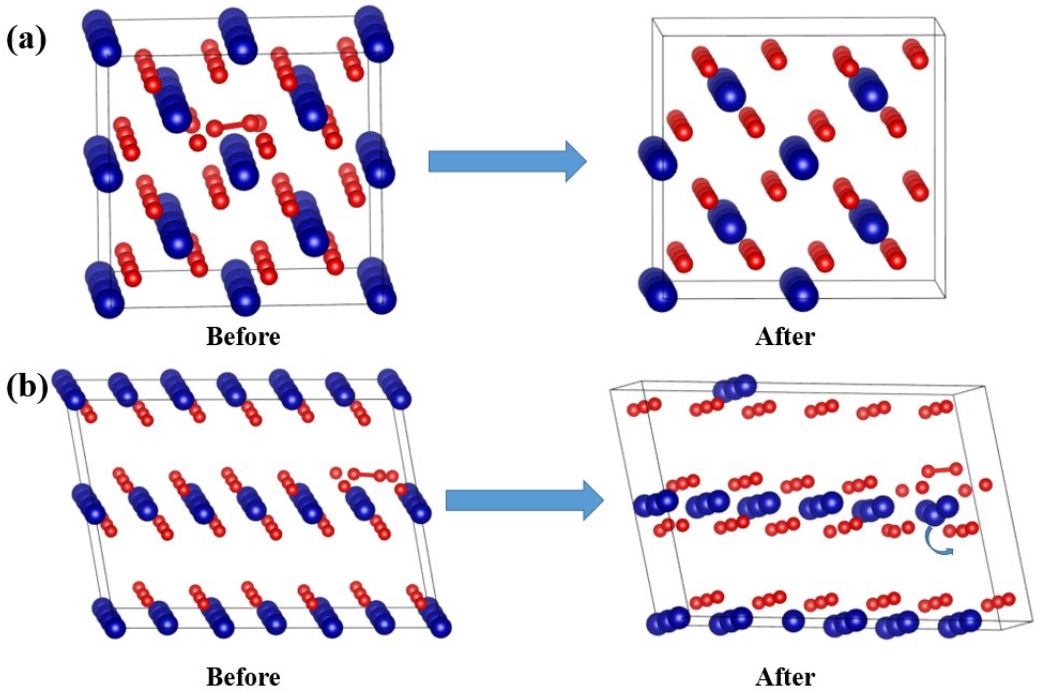

Figure S3. DFT optimized structural changes of oxygen dimer in (a) rutile-like, (b) layered CoO_2. The arrow marks the direction of atomic displacement. Red and blue represent O and Co, respectively.

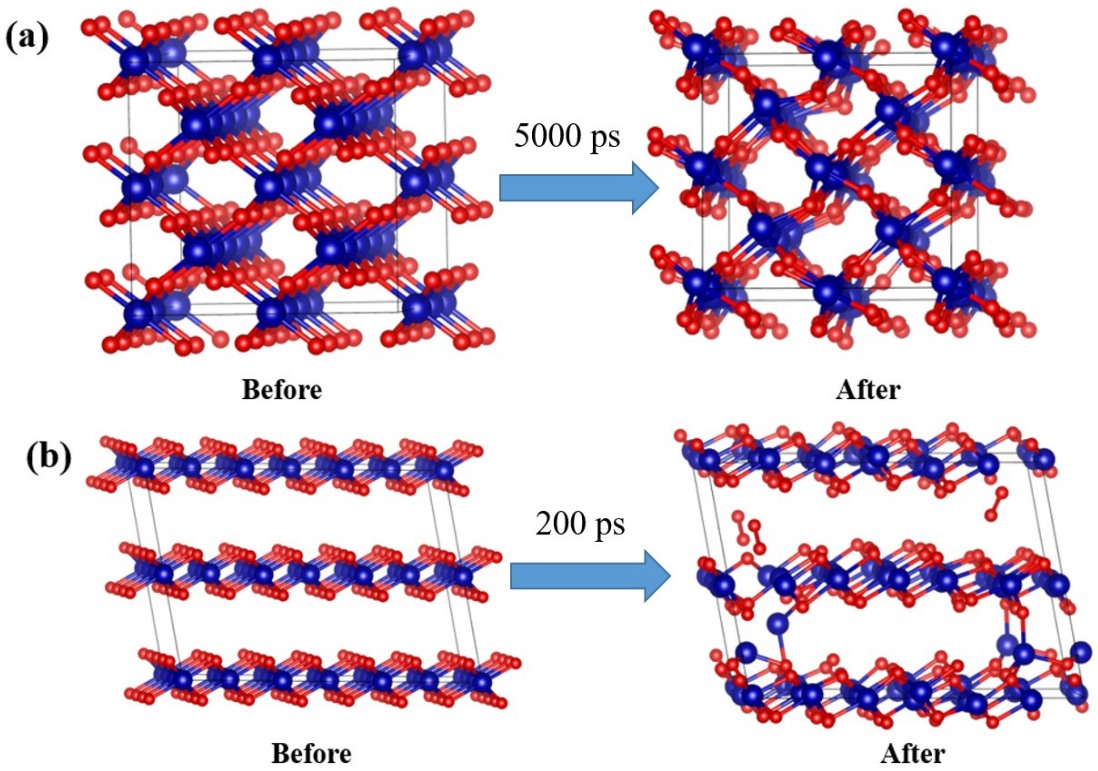

Figure S4. The initial and final structural diagrams of (a) rutile-like, (b) layered CoO_2 obtained by MD simulation at 1500K.

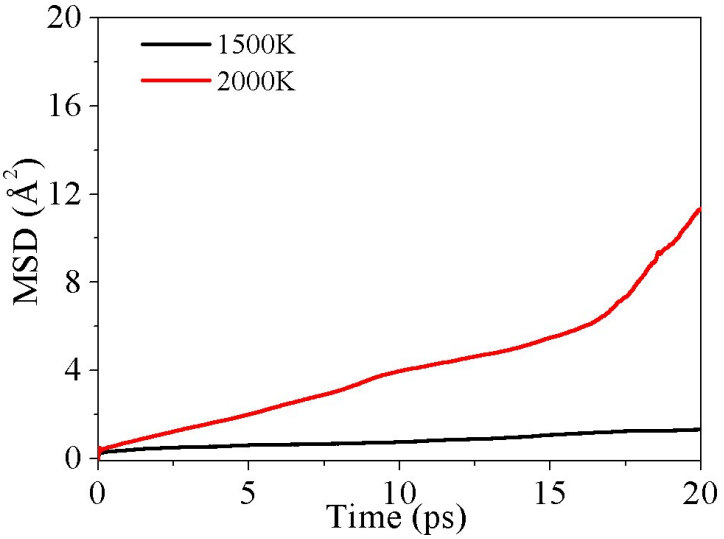

Figure S5. MSD_{Li} as a function of simulation time at different temperatures in 3×3×4 supercell of layered-structure $LiCoO_2$ used in the molecular dynamics (MD) simulation.

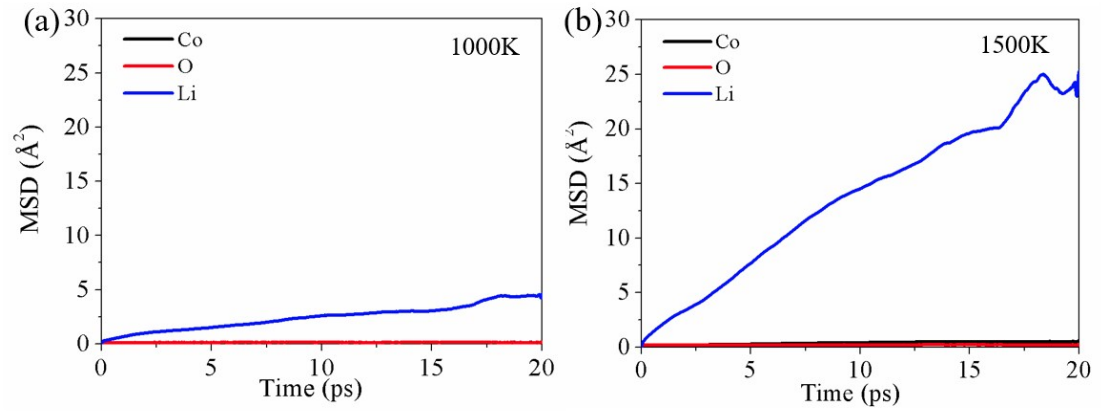

Figure S6. MSD of Li, O, Co as a function of simulation time at (a) 1000K and (b) 1500K in 2×2×4 supercell of rutile-like $Li_{0.5}CoO_2$ used in the molecular dynamics (MD) simulation.

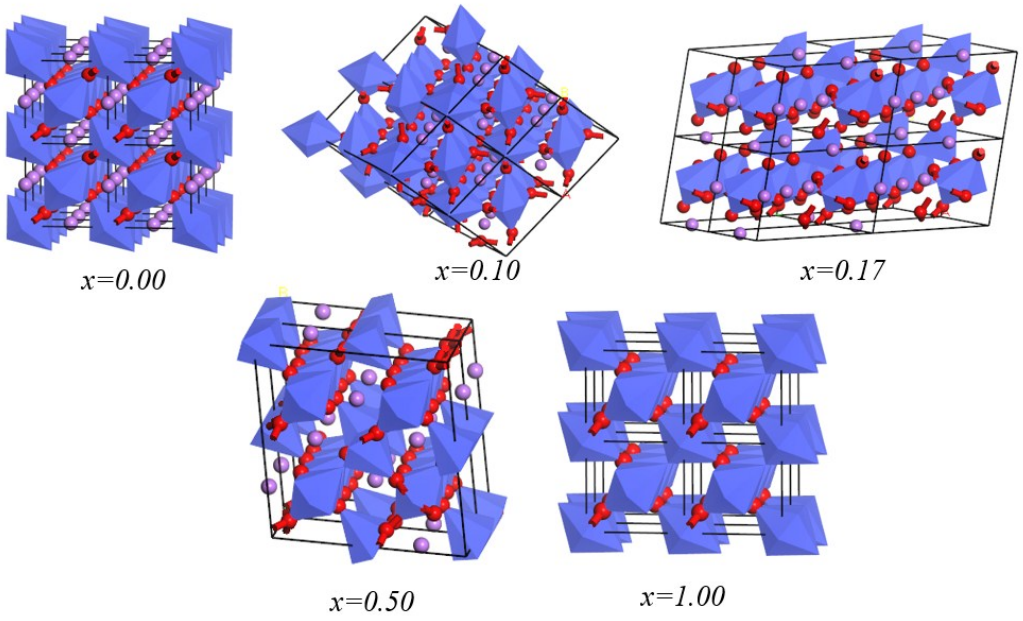

Figure S7. Configurations of lithiated/delithiated and three stable intermediate phases for rutile-like $Li_{1-x}CoO_2$.

1. Watt, J. P., Hashin - Shtrikman bounds on the effective elastic moduli of polycrystals with orthorhombic symmetry. *Journal of Applied Physics* **1980,** 51, (3), 1520-1524.

2. Wu, Z. J.; Zhao, E. J.; Xiang, H. P.; Hao, X. F.; Liu, X. J.; Meng, J., Publisher's Note: Crystal structures and elastic properties of superhard IrN[sub 2] and IrN[sub 3] from first principles [Phys. Rev. B 76, 054115 (2007)]. *Physical Review B* **2007,** 76, (5), -.