Supplementary Information

Facilitating Room-Temperature Oxygen Ion Migration via Co-O Bond Activation in Cobaltite Films

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This file includes:

Figure (S1. to S15)

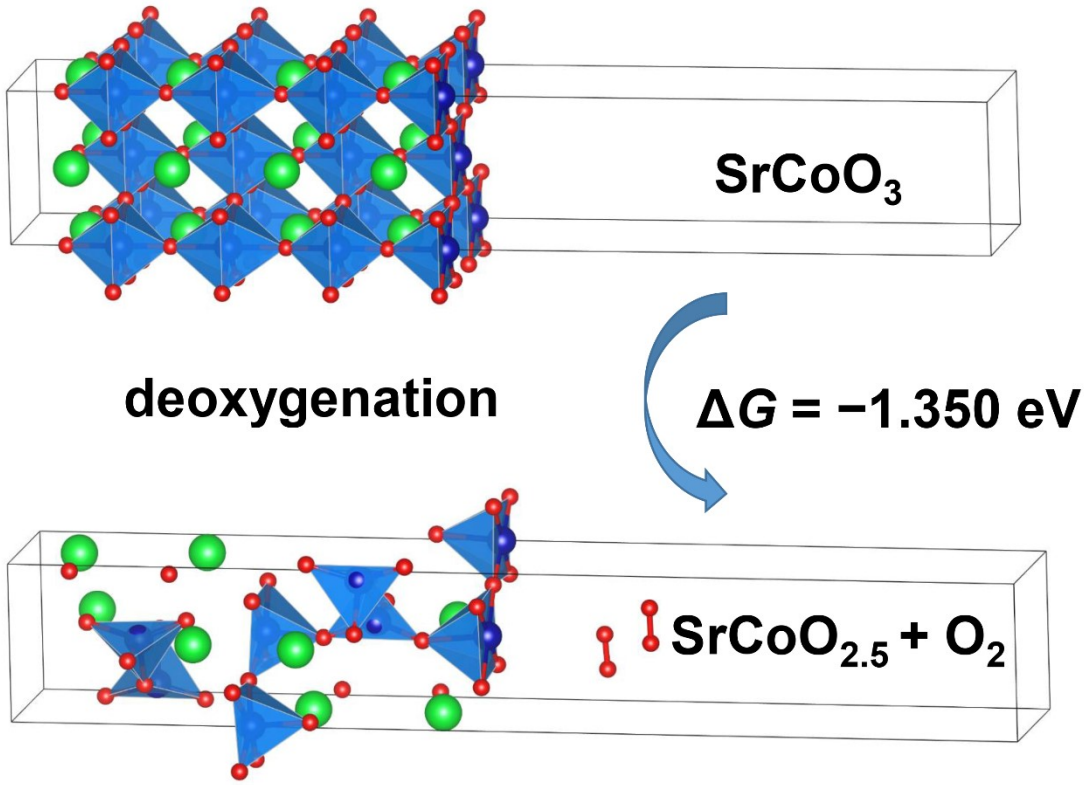

Fig. S1 Free energy decrease from P-SCO to B-SCO as a driving force of topotactic phase reduction.

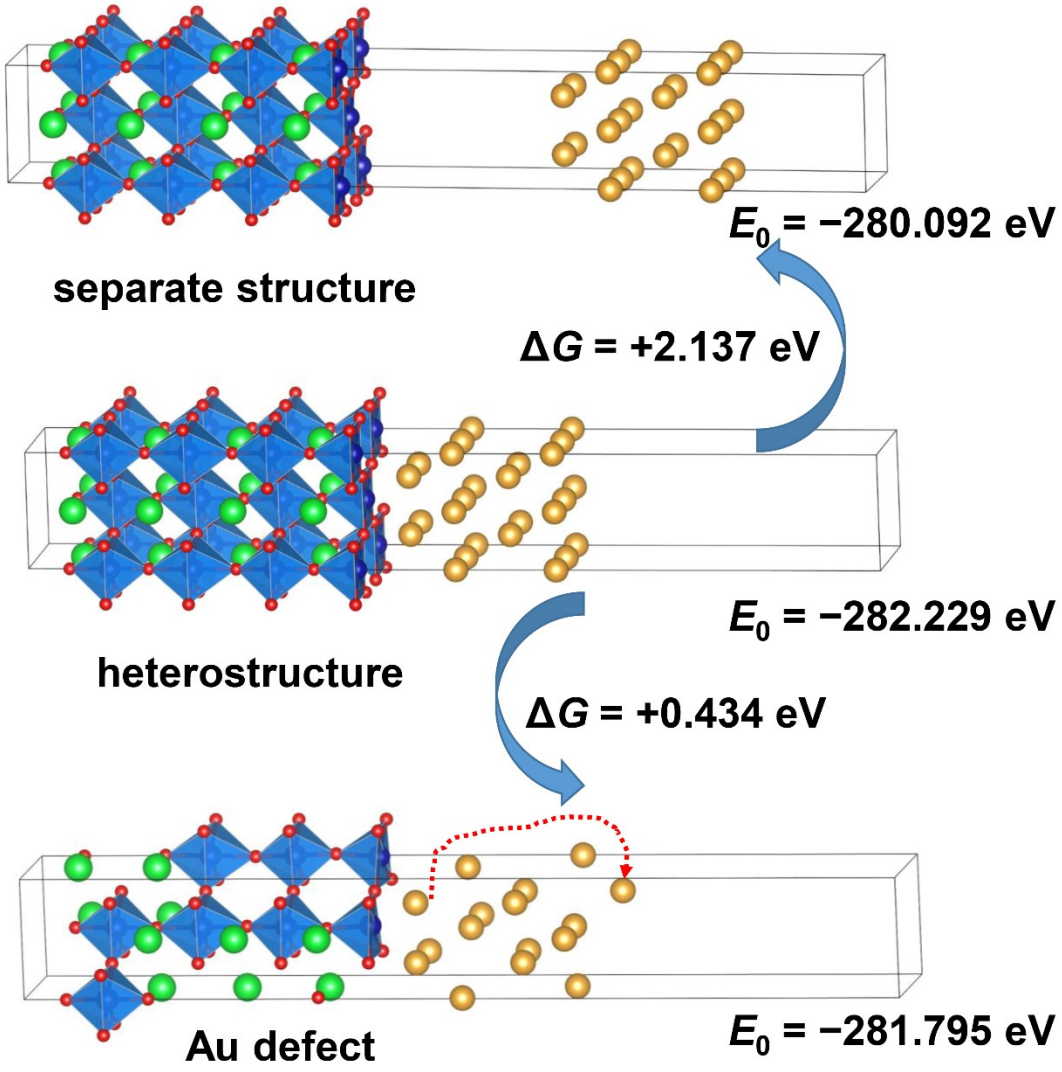

Fig. S2 Energy difference between SCO/Au heterostructure, separate structure, and structure with interfacial Au defect to calculate the Au-O bond energy and interface energy.

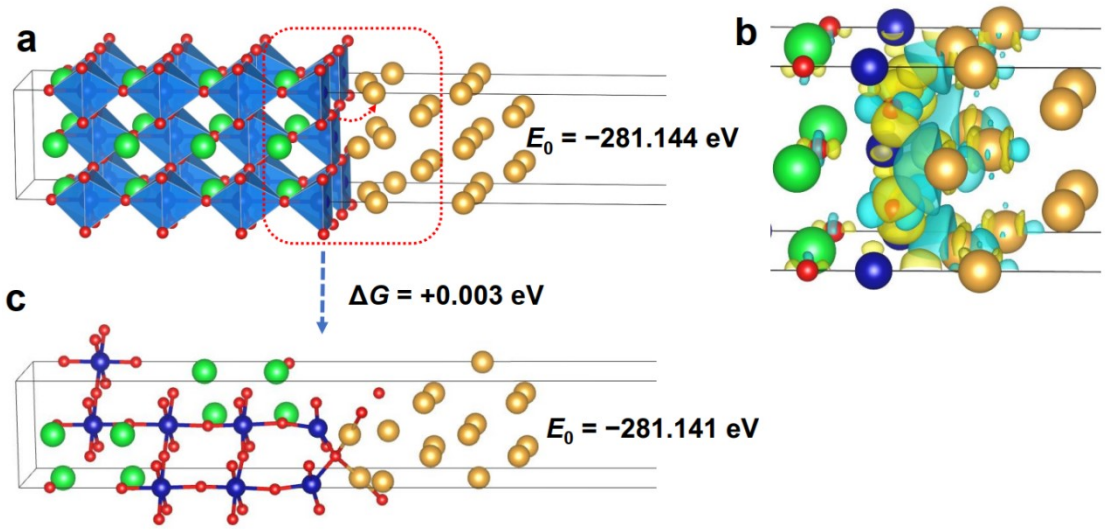

Fig. S3 $SrCoO_3$/Au heterostructure model without direct Au-O bonding at the interface. a optimized $SrCoO_3$/Au heterostructure. **b** differential charge density at the interface of **a**, showing the electron transfer from Au to CoO layer. **c** optimized structures from initial model in which an interfacial O oxygen atom move to the interstice of Au layer as noted by red arrows in **a**. Small deoxygenation barrier (0.003 eV) obtained in **d** demonstrates the activation effect of $SrCoO_3$.

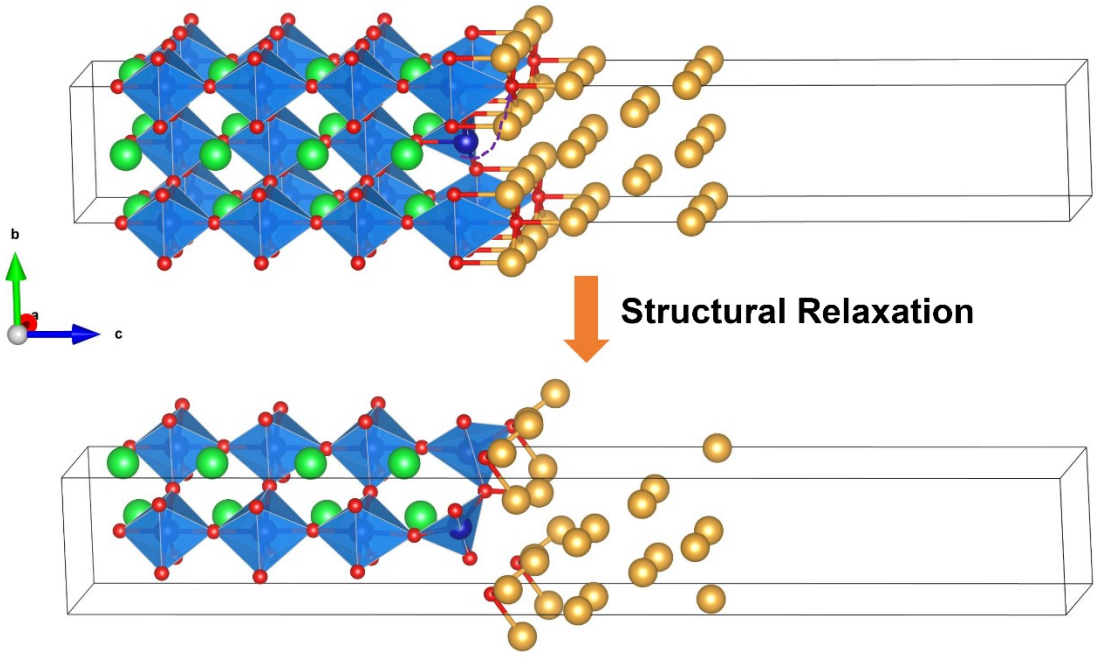

Fig. S4 Initial and optimized structure of $SrCoO_3$/Au where an oxygen atom moves from CoO layer to the interstice of interfacial Au atoms.

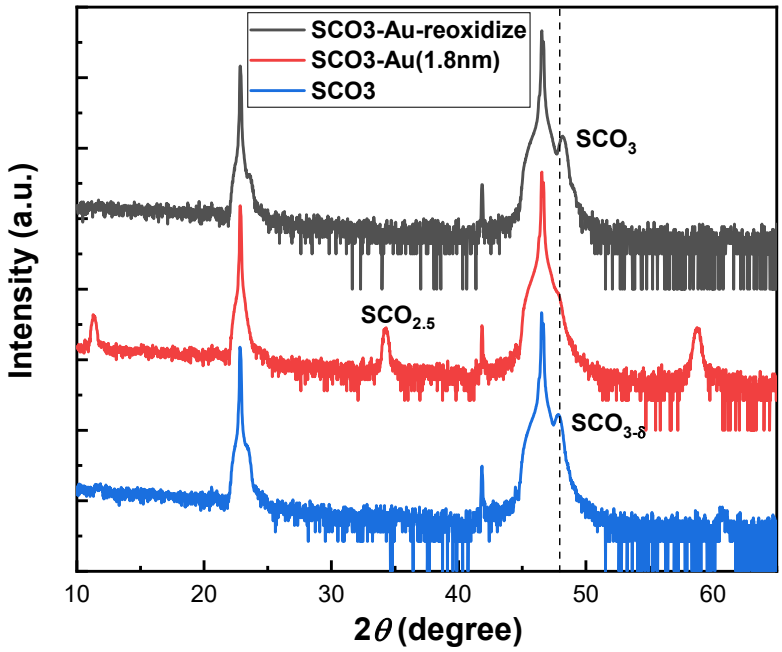

Fig. S5 reversible transition from B-SCO to P-SCO by wet-chemical oxidation by 3% NaClO solution for 5 min.

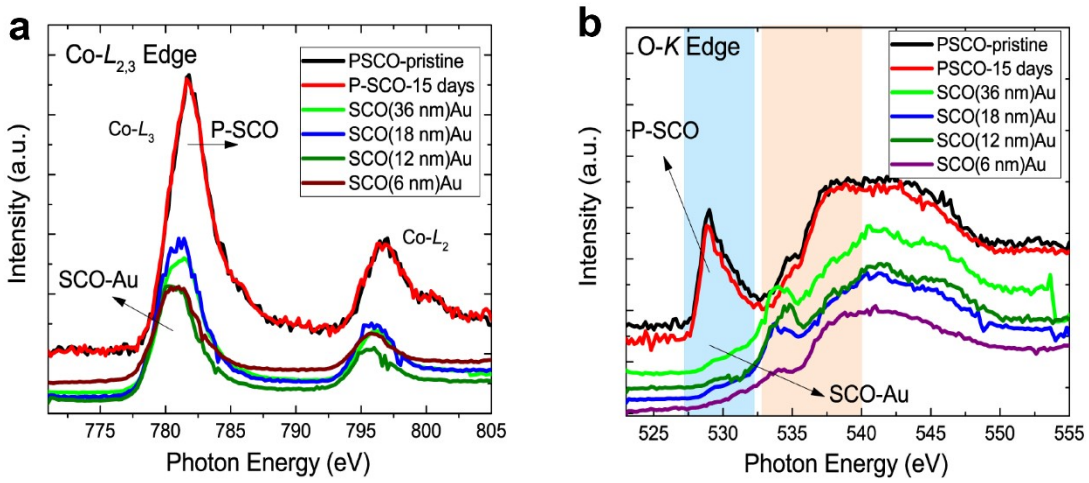

Fig. S6 a Co-*L* edge and **b** O-*K* edge XAS spectra of SCO/Au samples with different SCO thicknesses (6, 12, 18, 36 nm).

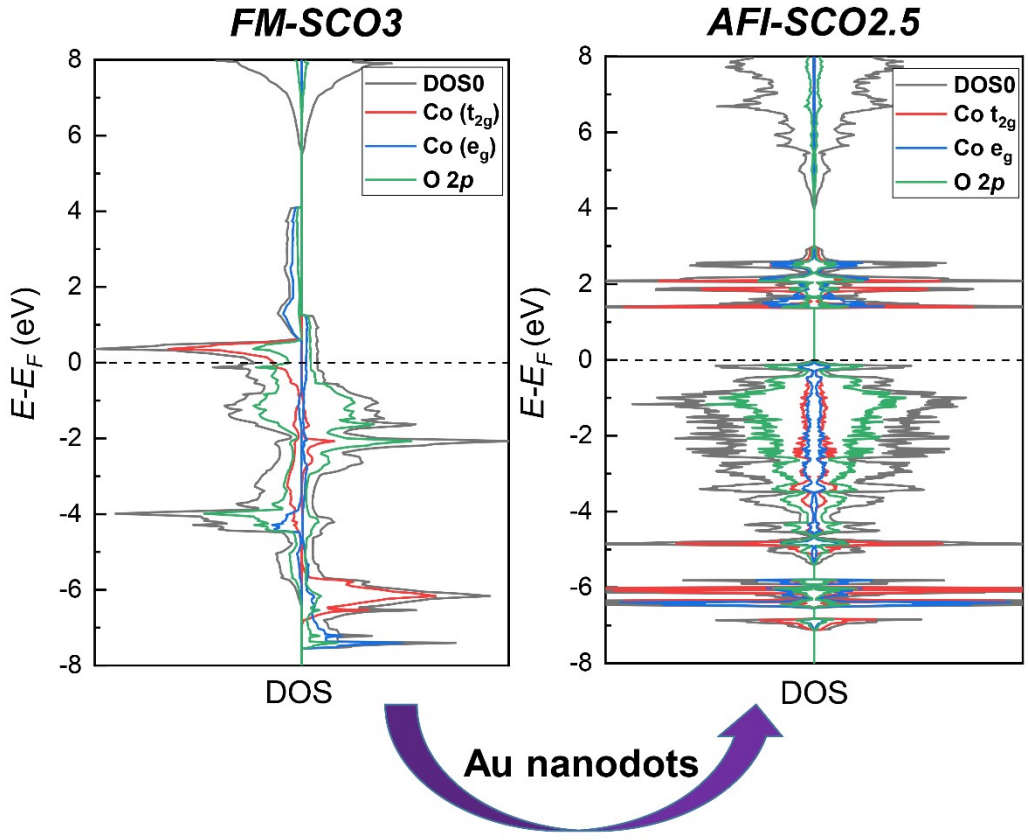

Fig. S7 calculated electronic structure (DOS) of P-SCO (ferromagnetic metal) and B-SCO (antiferromagnetic insulator) from DFT+*U* methods.

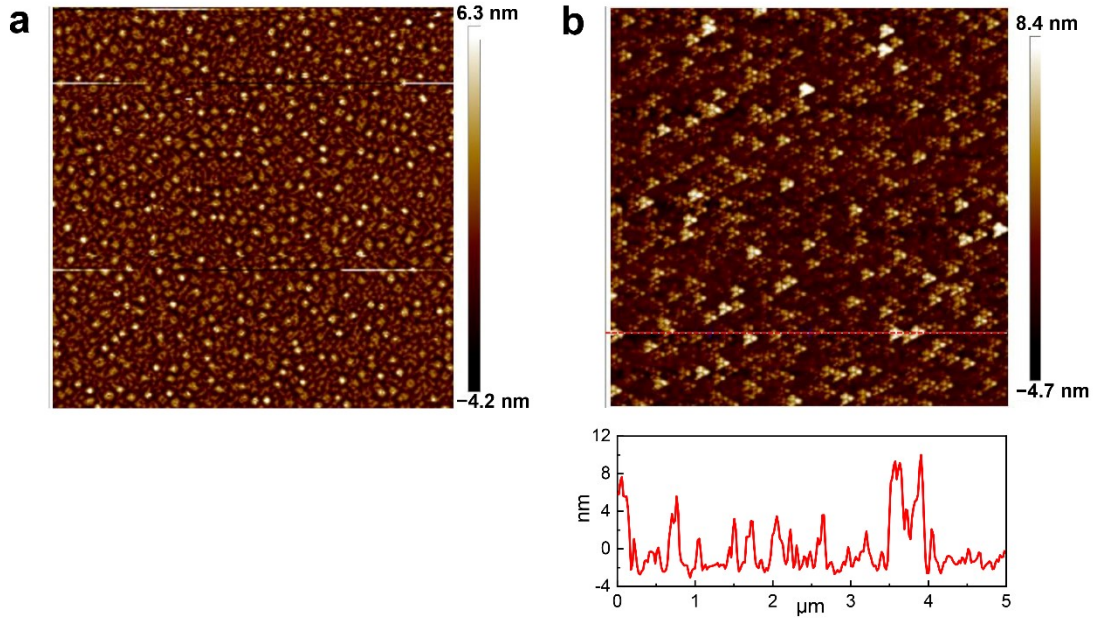

Fig. S8 AFM images before (**a**) and after (**b**) Au decoration in relatively rough P-SCO surface. Section-height analysis is given below morphology pictures to display surface fluctuation caused by Au nanodots.

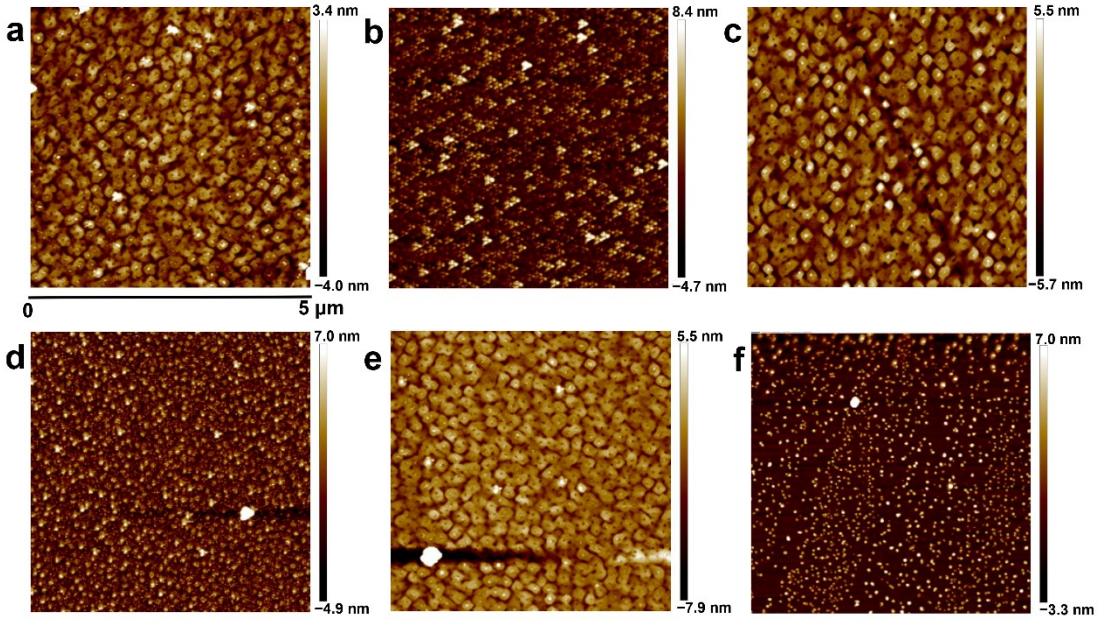

Fig. S9 Influence of Au deposition rates on surface morphology of SCO/Au films. **a** 0.1 Å/s. **b** 0.2 Å/s. **c** 0.3 Å/s. **d** 0.3 Å/s (heating at 160 ℃ for 1 hour). **e** 0.5 Å/s. **f** control sample (Au deposited on STO substrate at 0.2 Å/s).

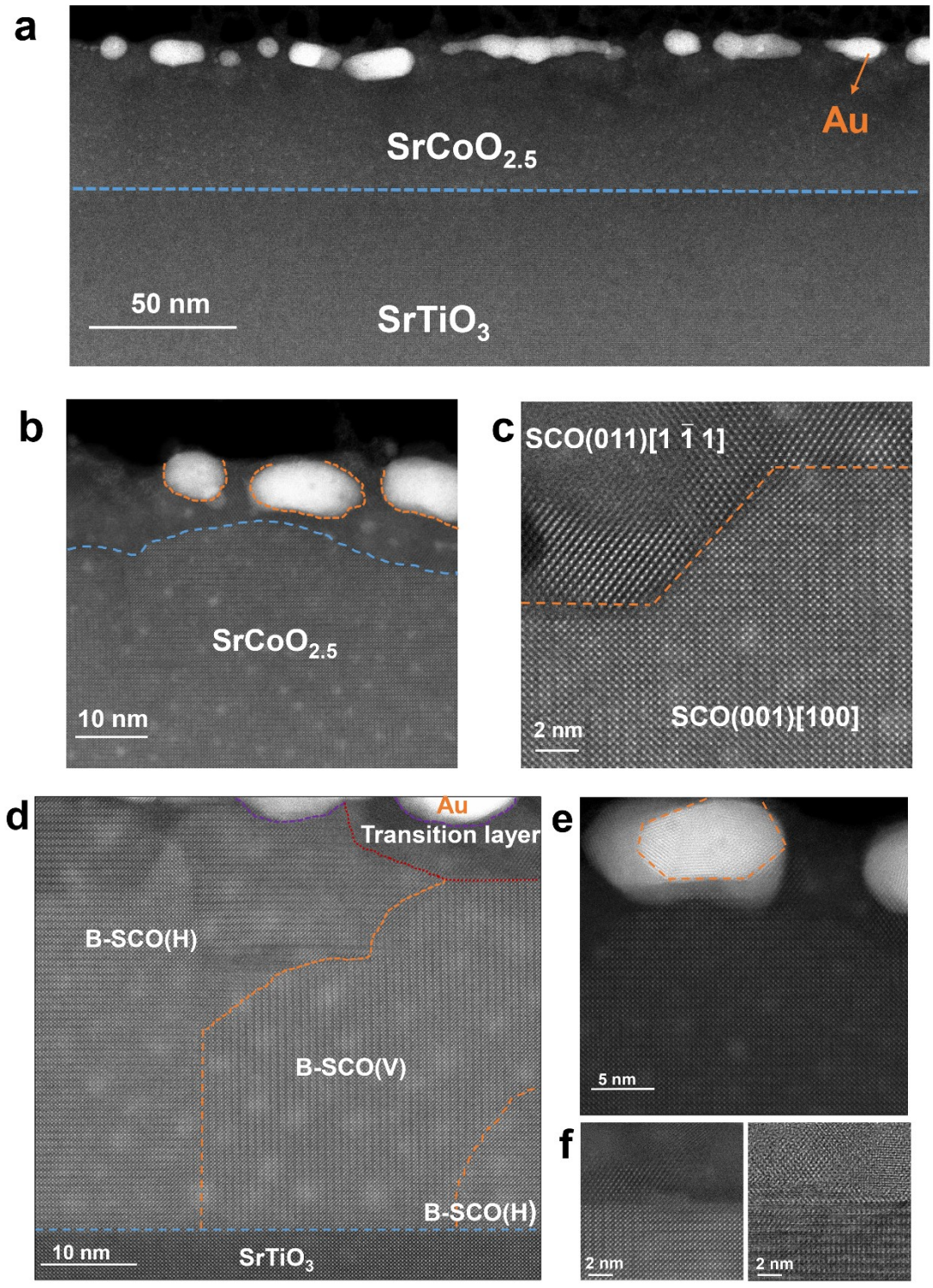

Fig. S10 Supplementary HADDF-STEM images of SCO/Au system. a size and distribution of Au nanodots in a large scope. **b** encapsulation of Au nanodots by SCO matrix. **c** sharp interface between normally oriented SCO and irregularly oriented SCO. **d** coexistence of B-SCO phases with horizontal and vertical oxygen vacancy channels,

STO substrate, transition layer and Au nanodots in this scope together. **e** crystalline Au particle supported by SCO. **f** dark field (left) and bright field (right) images of SCO with different orientations.

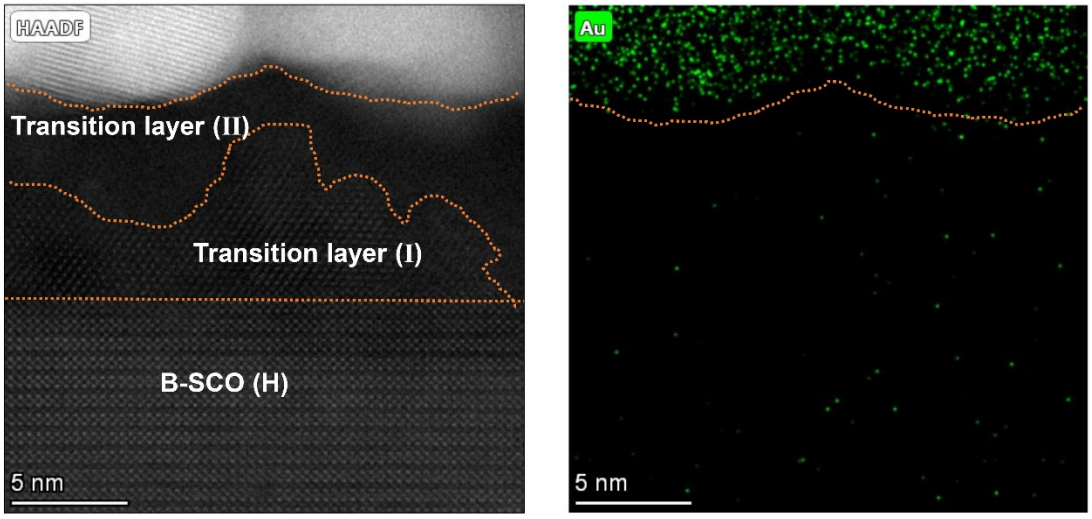

Fig. S11 EDS mapping of interfacial region of SCO/Au film.

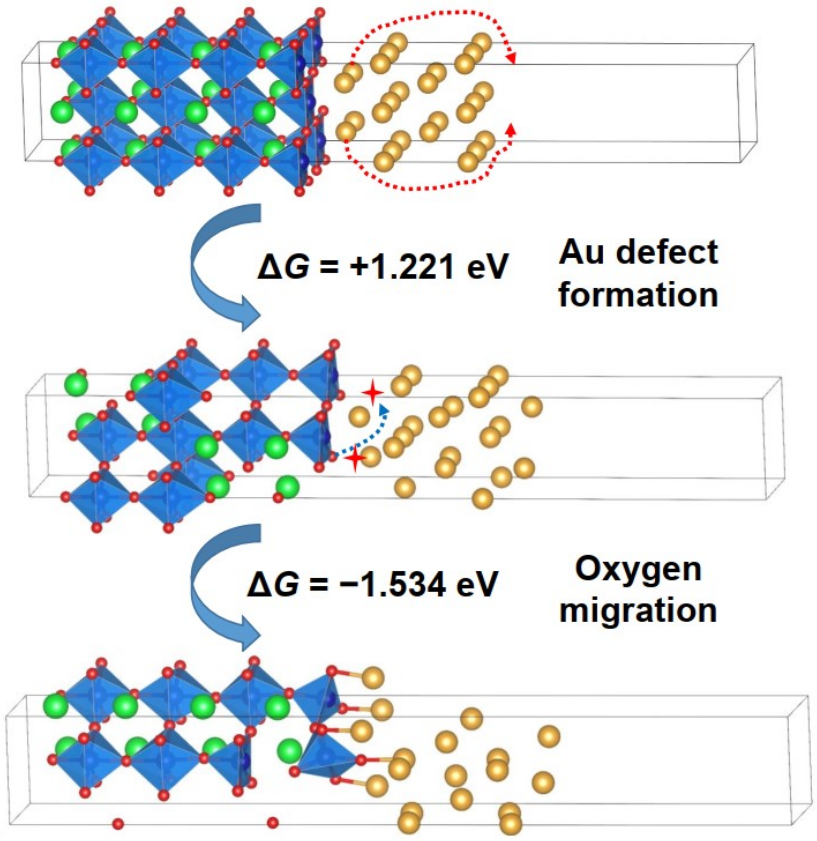

Fig. S12 Interface with high-density Au defects and its influence on oxygen migration.

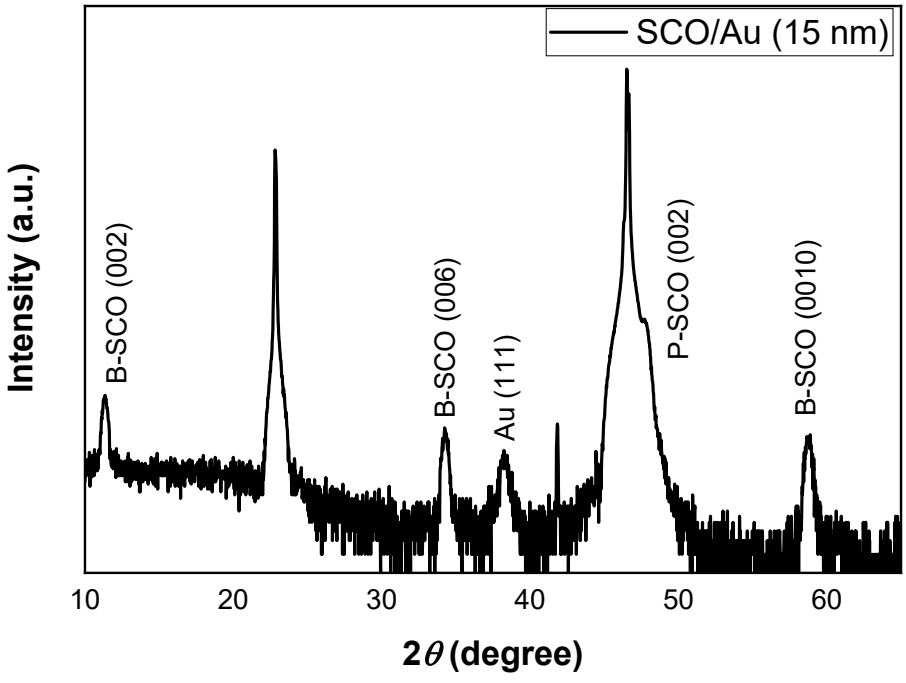

Fig. S13 Topotactic phase transition in SCO/Au film where Au film thickness is 15 nm.

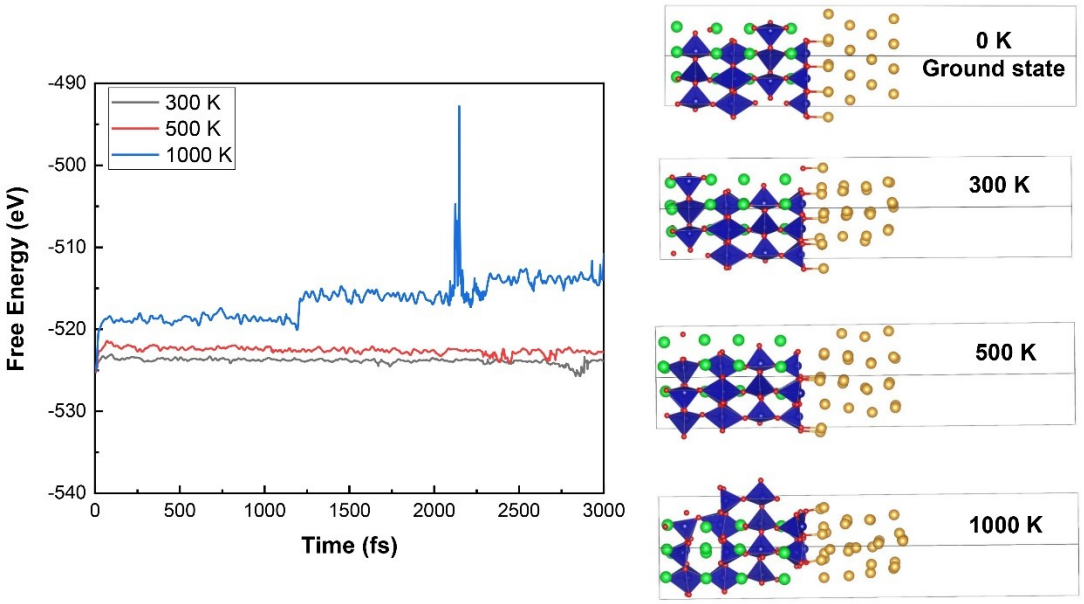

Fig. S14 *Ab-initio* molecular dynamics of $SrCoO_{2.5}$/Au system. Free energy variation (**left**) and final structures (**right**) at 300 K, 500 K and 1000 K. At 300 K and 500 K, the energy and structure of heterostructure keep stable. At 1000 K, $SrCoO_{2.5}$/Au heterostructure is metastable.

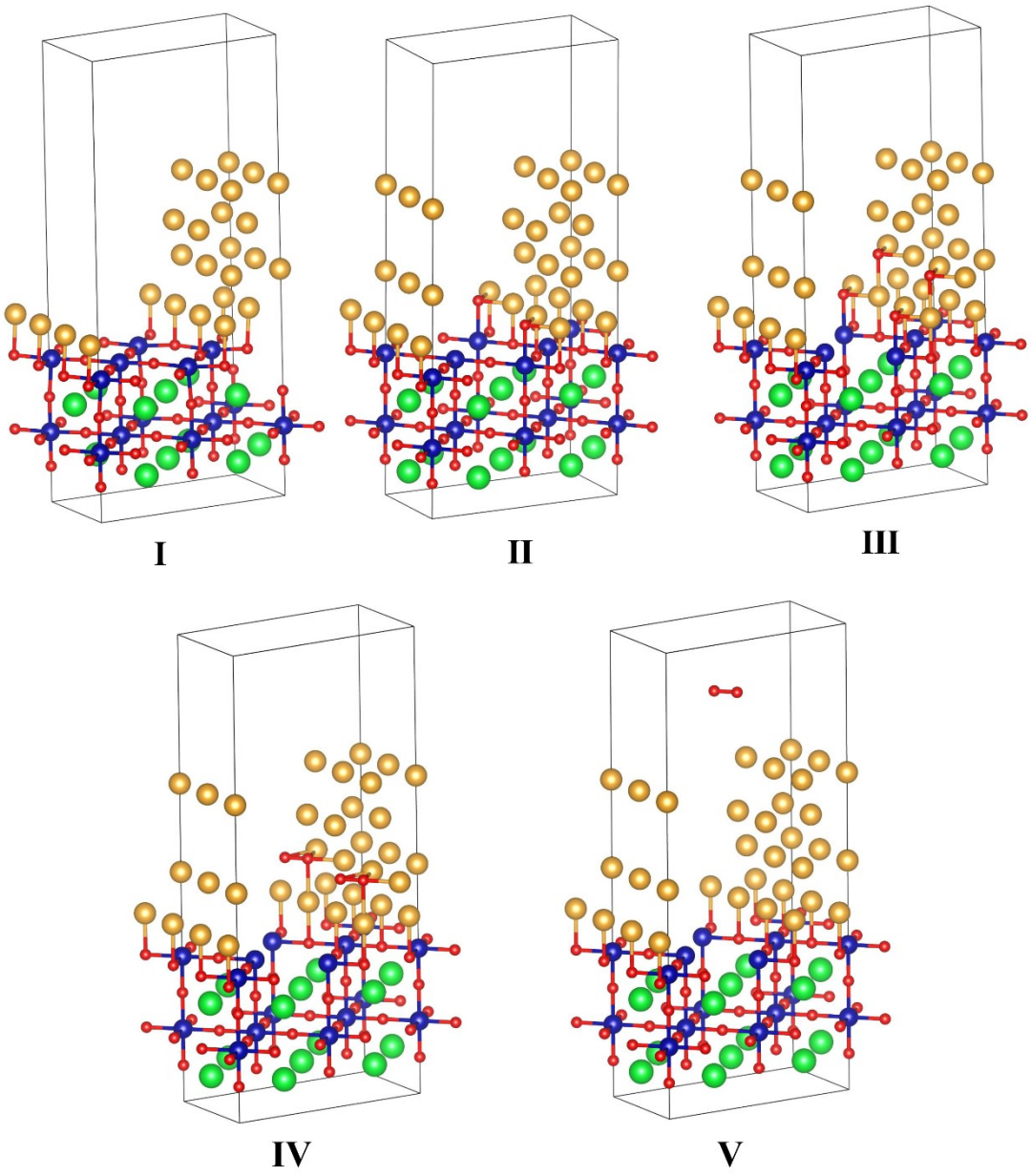

Fig. S15 Cluster models (initial structure before structure relaxation) in DFT calculations for verify the Au-assisted deoxygenation pathway. I no oxygen migration out of SCO, **II** an oxygen atom moving from SCO surface to Au cluster, **III** two oxygen atoms moving out of SCO and adsorbed on Au cluster, **IV** oxygen atoms combining into O_2 molecule. **V** O_2 molecule desorption from SCO/Au system.