Supplementary material

Experimental and theoretical investigation of the tuning of electronic structure in SnO_2 via Co doping for enhanced styrene epoxidation catalysis

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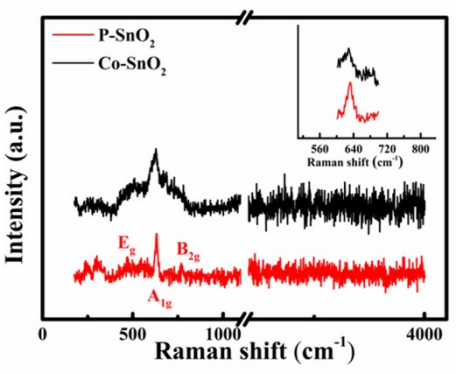

Fig. S1. Raman spectra of the samples.

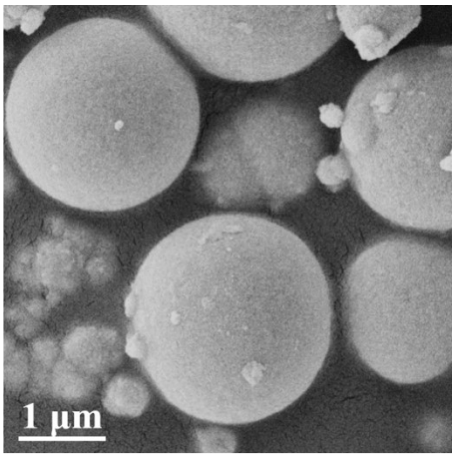

Fig. S2. SEM image of the P-SnO_2.

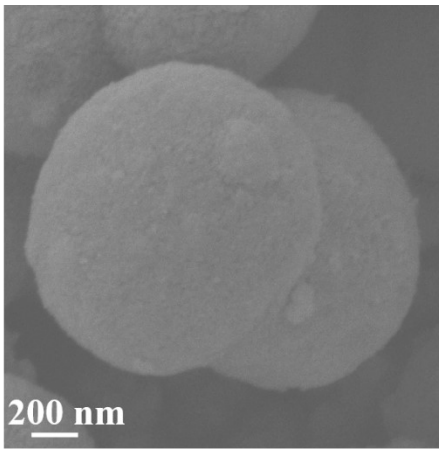

Fig. S3. SEM image of the Co-SnO_2.

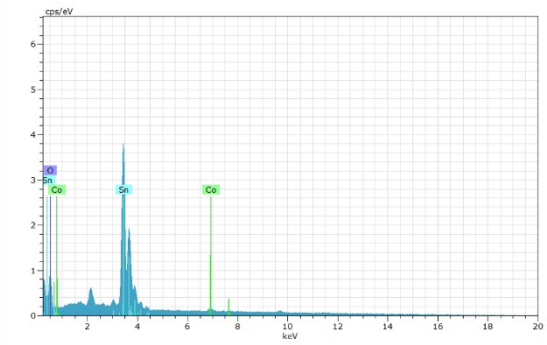

Fig. S4. EDS analysis of the elemental content in the Co-SnO_2.

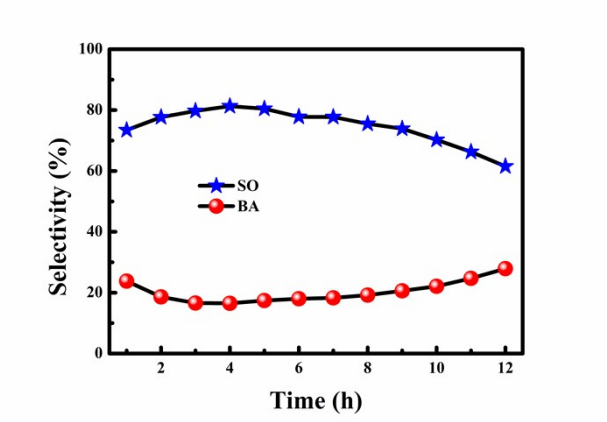

Fig. S5. The selectivity of SO and BA (benzaldehyde) in the SER reaction catalyzed by the Co-SnO_2. Reaction conditions: 0.1 g of Co-SnO_2, 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, 80 °C, 12 h.

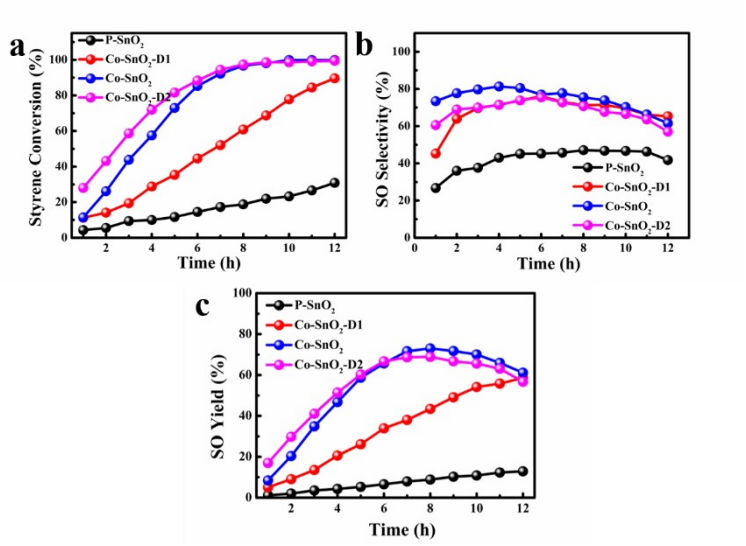

Fig. S6. Evaluation of the SER performance catalyzed by the Co doped SnO_2 catalysts with different Co doping contents. Co-SnO_2-D1, Co-SnO_2 and Co-SnO_2-D2 are the catalysts with Co doping content of 1.0 wt.%, 2.0 wt.% and 3.0 wt.%, respectively. Reaction conditions: 0.1 g of catalyst, 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, 80 °C, 12 h.

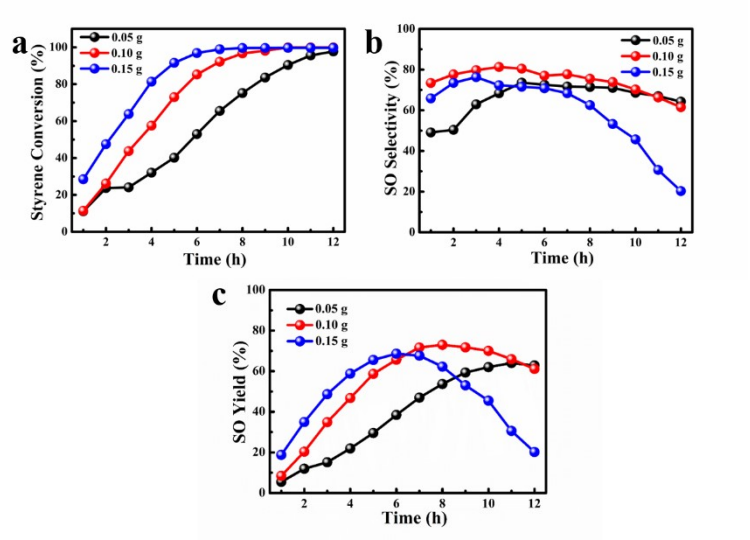

Fig. S7. Evaluation of the SER performance catalyzed by the Co-SnO_2 with different catalyst dosages. Reaction conditions: 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, 80 °C, 12 h.

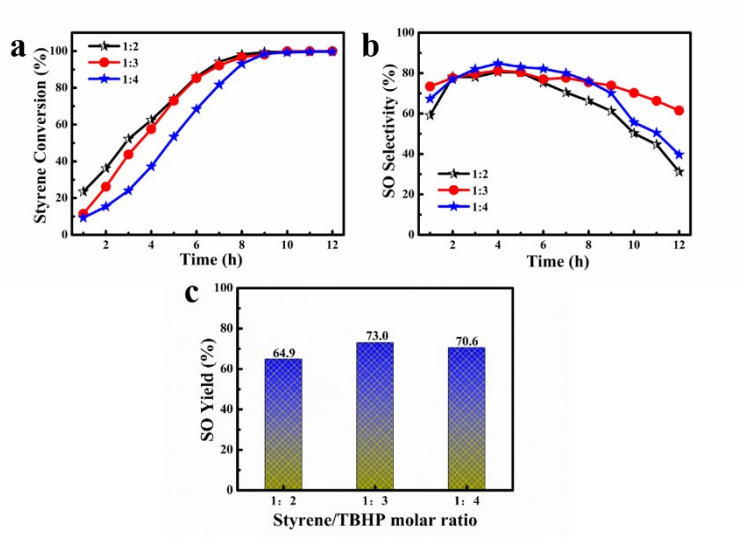

Fig. S8. Evaluation of the SER performance catalyzed by the Co-SnO_2 with different styrene/TBHP molar ratios. Reaction conditions: 0.1 g of catalyst, 15 mmol of styrene, 0.7 mol of acetonitrile, 80 °C, 12 h.

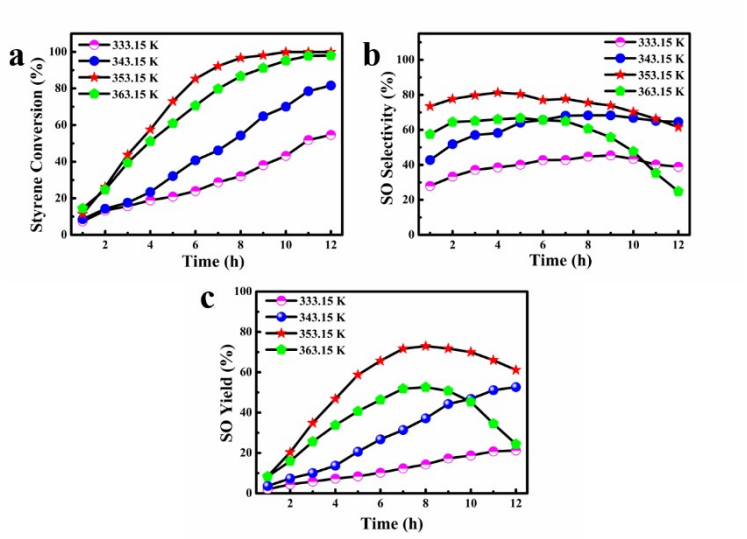

Fig. S9. Evaluation of the SER performance catalyzed by the Co-SnO_2 with different reaction temperatures. Reaction conditions: 0.1 g of catalyst, 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, 12 h.

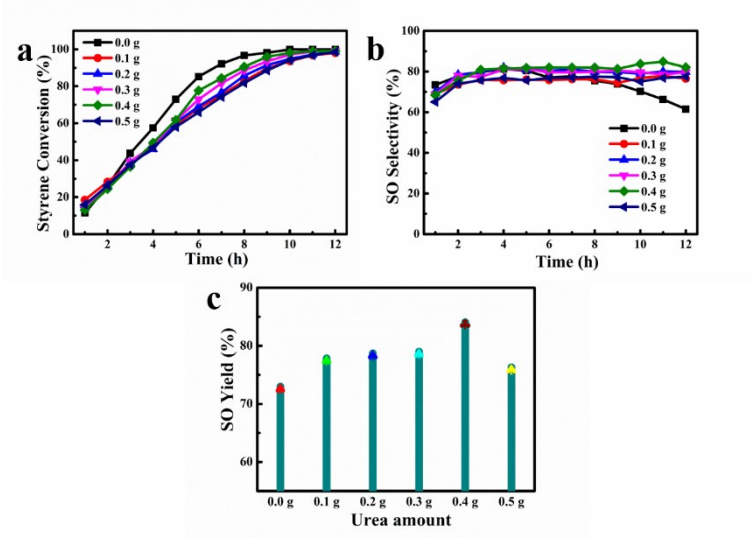

Fig. S10. Evaluation of the SER performance catalyzed by the Co-SnO_2 with the involvement of different amount of urea. Reaction conditions: 0.1 g of catalyst, 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, different amount of urea, 80 °C, 12 h.

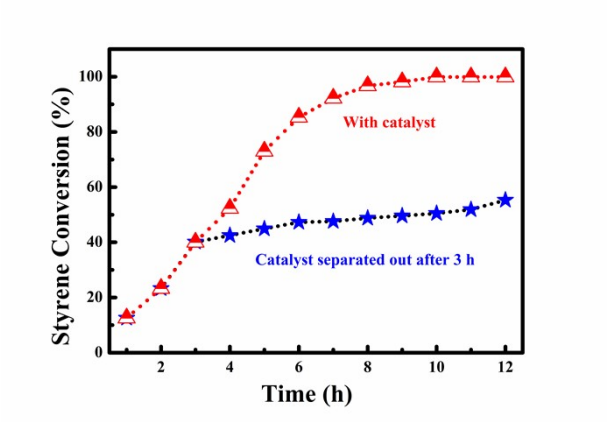

Fig. S11. The hot filtrate test of the Co-SnO_2 in the SER. Reaction conditions: 0.1 g of catalyst, 15 mmol of styrene, 0.7 mol of acetonitrile, 45 mmol of TBHP, 80 °C, 12 h.

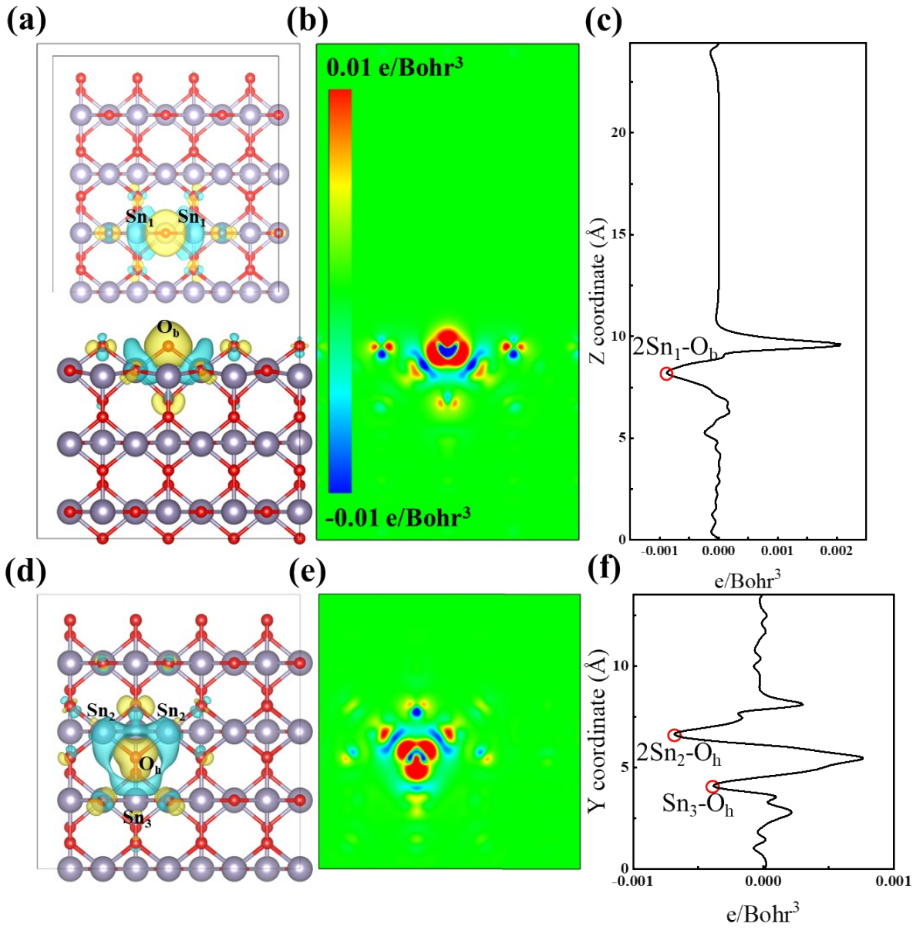

Fig. S12. The Charge Density Difference (CDD) (a, d), the corresponding 2D slices (b, e) and the distribution of CDD along the Z direction (c, f) of SnO_2 (110) surface with and without the O_b/O_h atom (i.e. without and with the OV_{bridge}/OV_{hollow}). The silver and red balls represents Sn and O atoms, respectively. In (a, d), the cyan area indicates the decrease of electron density, and the yellow indicates the increase of electron density. In the corresponding diagrams (b-c & e-f), the negative value means electrons transfer out, and the positive value means electrons capture.

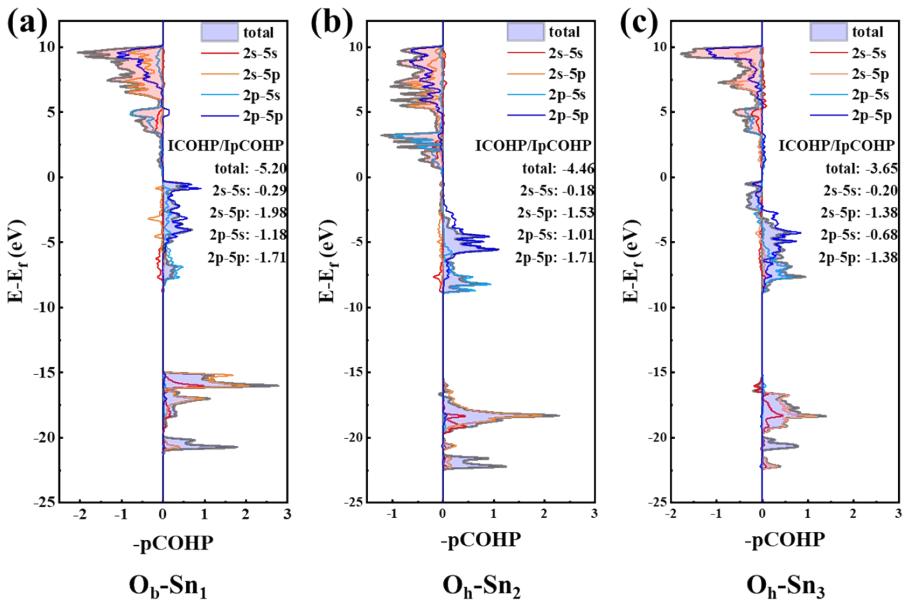

Fig. S13. The Crystal Orbital Hamilton Populations (COHP) and the integration of COHP (ICOHP) for the bonds of (a) O_b-Sn_1, (b) O_h-Sn_2 and (c) O_h-Sn_3 on SnO_2 (110) surface.

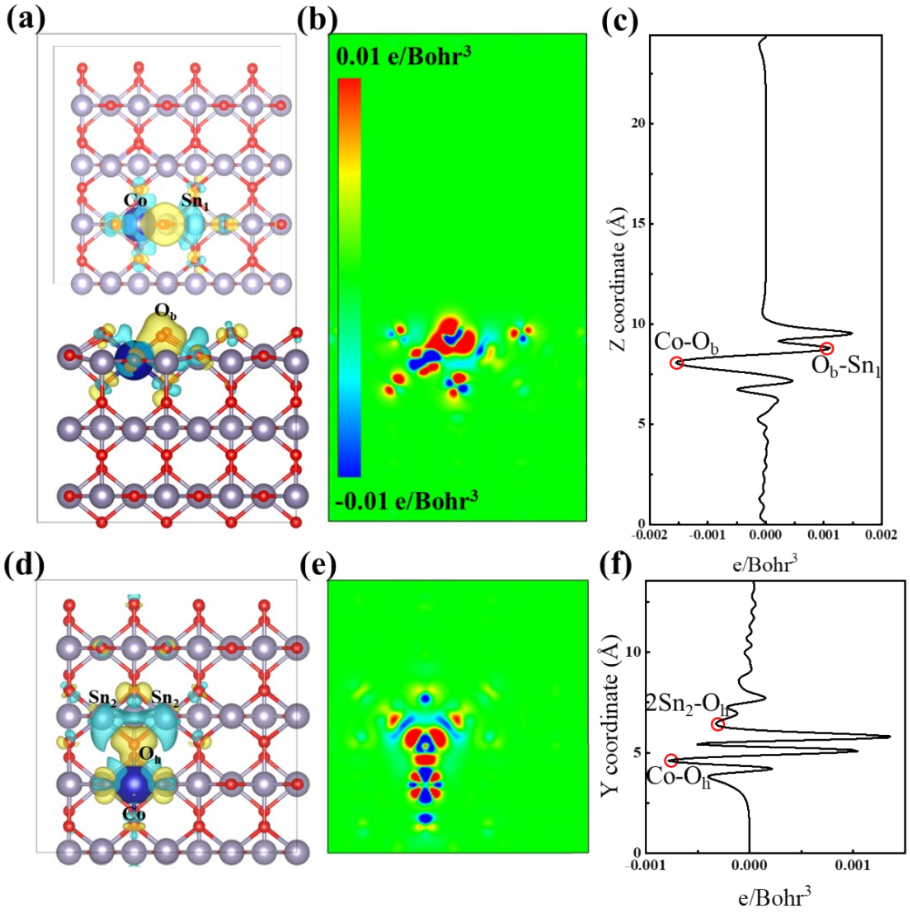

Fig. S14. The Charge Density Difference (CDD) (a, d), the corresponding 2D slices (b, e) and the distribution of CDD along the Z direction (c, f) of Co_{-1}-SnO_2 (110) surface with and without the O_b/O_h atom (i.e. without and with the OV_{bridge}/OV_{hollow}). The silver, blue and red balls represents Sn, Co and O atoms, respectively.

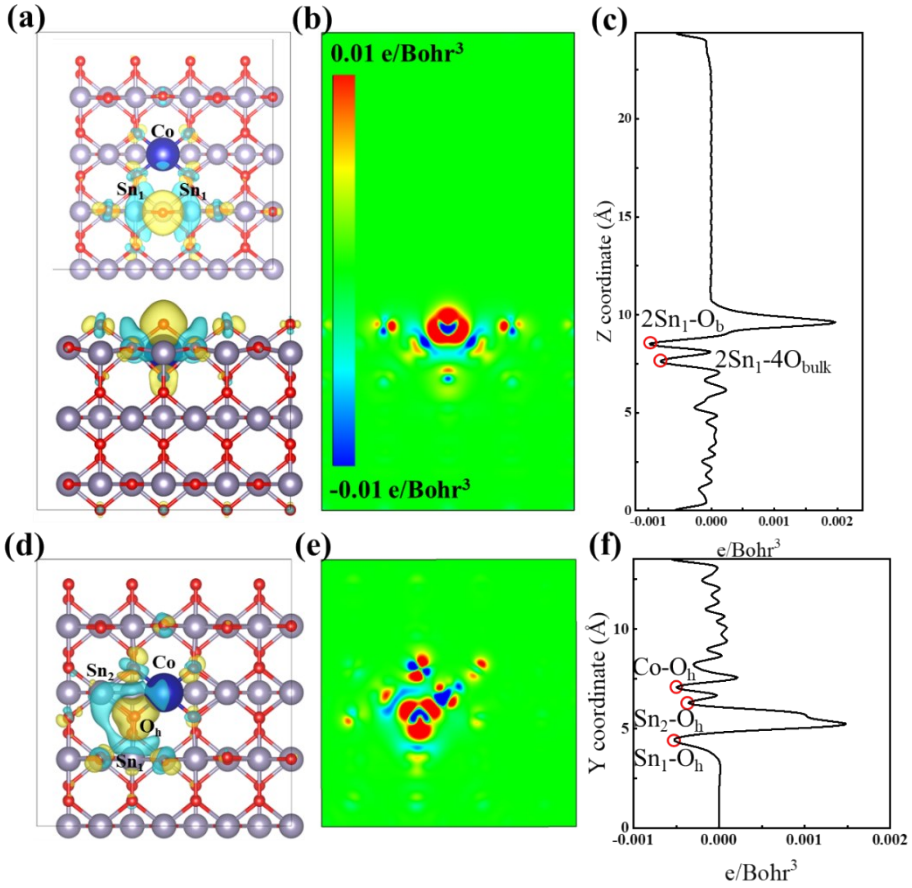

Fig. S15. The Charge Density Difference (CDD) (a, d), the corresponding 2D slices (b, e) and the distribution of CDD along the Z direction (e, f) of Co_{-2}-SnO_2 (110) surface with and without the O_b/O_h atom (i.e. without and with the OV_{bridge}/OV_{hollow}). The silver, blue and red balls represents Sn, Co and O atoms, respectively.

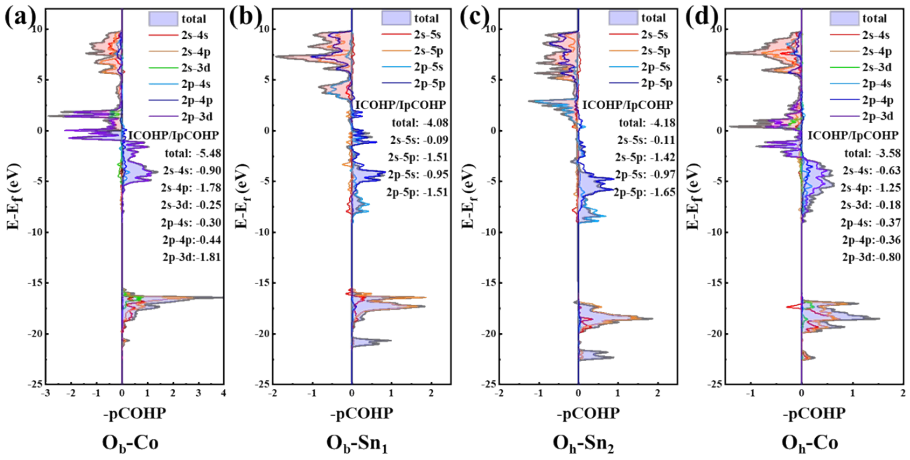

Fig. S16. The Crystal Orbital Hamilton Populations (COHP) and the integration of COHP (ICOHP) for the bonds of (a) O_b-Co, (b) O_b-Sn_1, (c) O_h-Sn_2 and (d) O_h-Co on Co_{-1}-SnO_2 (110) surface.

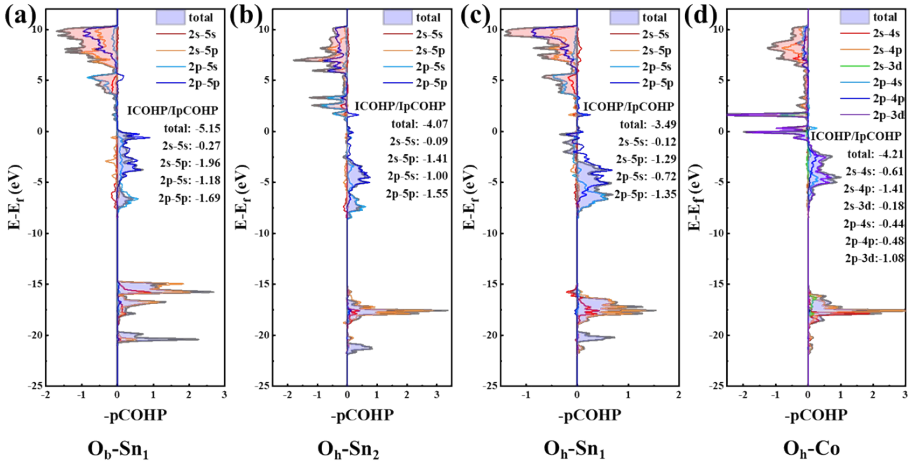

Fig. S17. The Crystal Orbital Hamilton Populations (COHP) and the integration of COHP (ICOHP) for the bonds of (a) O_b-Sn_1, (b) O_h-Sn_2, (c) O_h-Sn_1 and (d) O_h-Co on Co_{-2}-SnO_2 (110) surface.

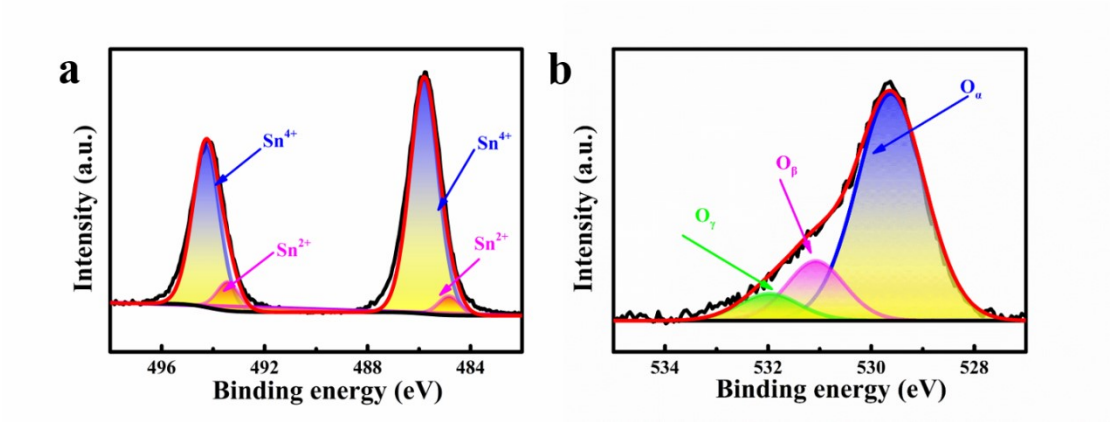

Fig. S18. XPS detection results for the TBHP treated Co-SnO_2 (TT-Co-SnO_2): high-resolution XPS Sn 3d (a) and O 1s (b) spectra. For the treatment, 0.1 g of Co-SnO_2 was dispersed in 45 mmol of TBHP, followed by treating at 80 °C for 12 h. After that, the catalyst was collected by centrifugation and washed with ethanol for several times and dried at 60 °C for 12 h. The obtained TT-Co-SnO_2 catalyst was then characterized by the XPS test.