Supporting Information

Spin-polarized *p*-block Antimony/Bismuth Single-atom Catalysts on Defect-free Rutile TiO_2(110) Substrate for High-efficient CO Oxidation

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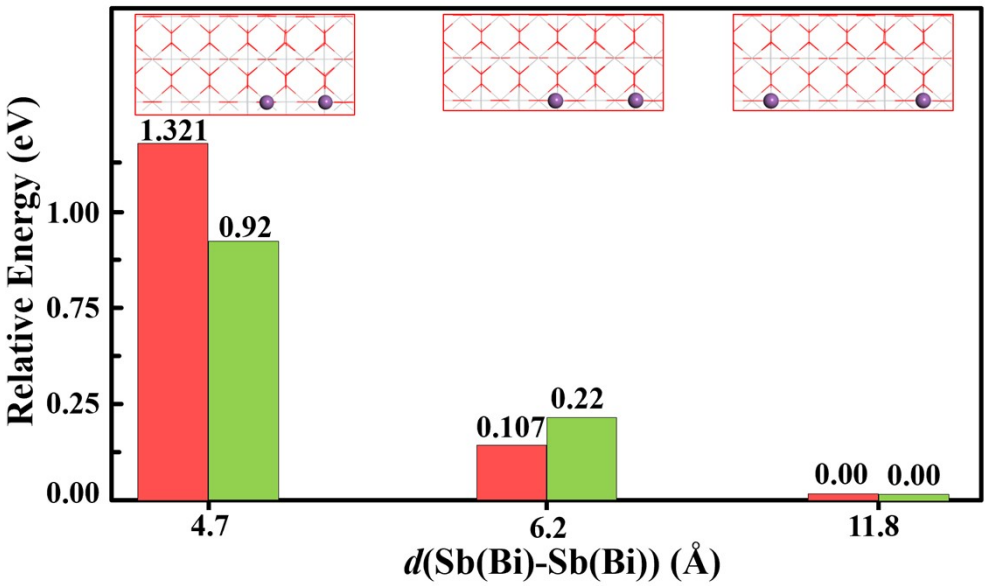

Figure S1. Pair interactions of two Sb(Bi) adatoms on the stoichiometric TiO_2(110). Energy profiles of two Sb or Bi adatoms on defect-free TiO_2(110) substrate, as a function of Sb(Bi)-Sb(Bi) distance *d*(Sb(Bi)-Sb(Bi)), the red and green bars correspond to the Sb and Bi cases, respectively.

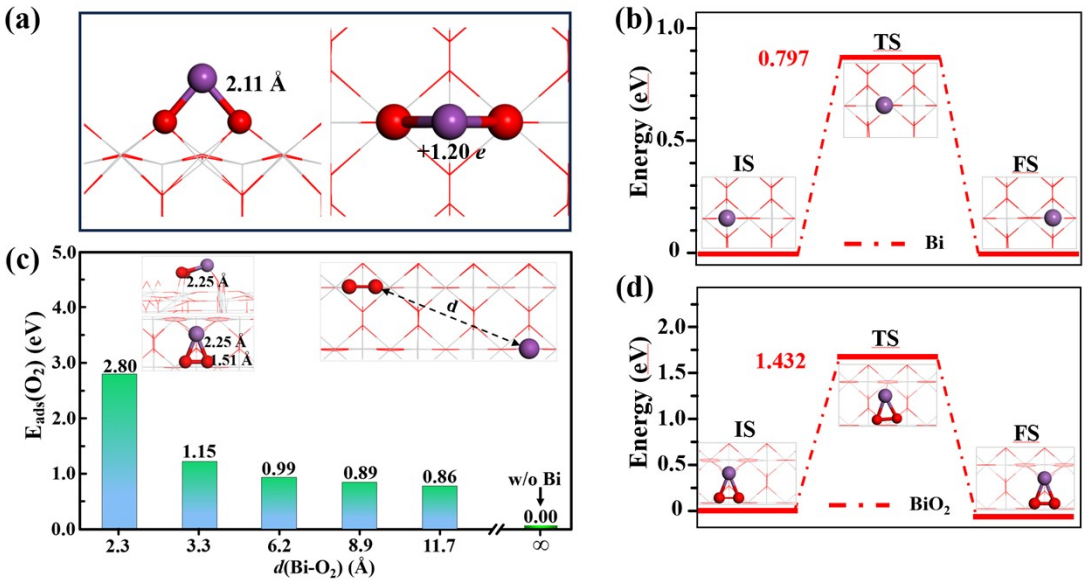

Figure S2. Geometric structures, thermodynamic and kinetic properties for Bi single atom and the Bi-O_2 unit with a molecular O_2 adsorb on the Bi reactive site on defect-free TiO_2(110). (**a**) Top and side view of the optimized most stable structure of Bi single atoms on defect-free rutile TiO_2(110) surface shown in ball and stick model. (**b**) Minimum energy path (MEP) for Bi diffusion along the oxygen bridging row. (**c**) Calculated relative adsorption energies of the O_2 molecule on the Bi/TiO_2(110) complex with different Bi-O_2 distance (d(Bi-O_2)) in c(8×2) supercell, the insert image on the left side refers to the side and top view of the most stable BiO_2 motif. (**d**) MEP for BiO_2 motif diffusion on TiO_2(110), the initial state, transition state and final state are labeled as IS, TS and FS, respectively.

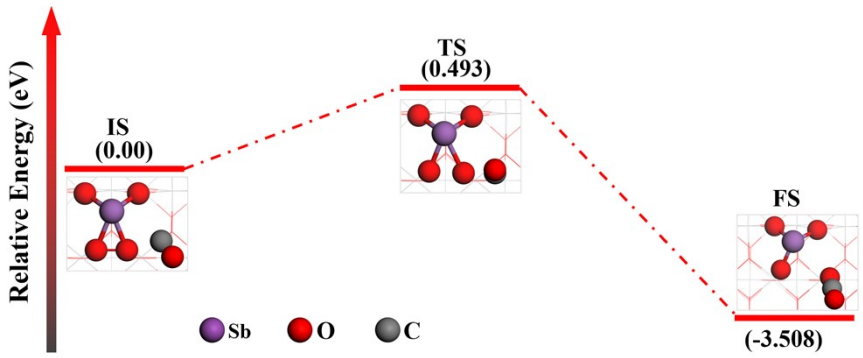

Figure S3. CO oxidation on the SbO_2 species stabilized on the defect-free TiO_2(110). The adsorbed O_2 molecule attacked by the incoming CO and release a CO_2 molecule.

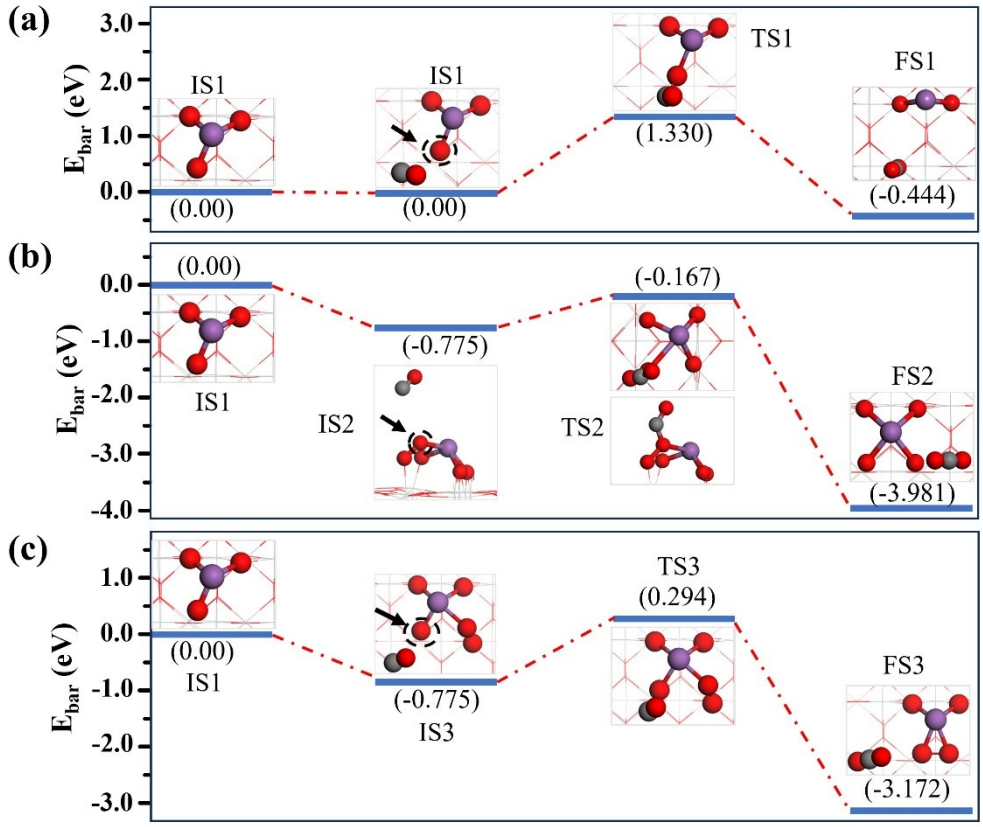

Figure S4. Possible MEP of CO oxidation on SbO_3 species on defect-free TiO_2(110) substrate. (**a**) CO attacking the remained O atom of SbO_3 species on the substrate. (**b**) CO oxidation by attacking the protruding O atom of the adsorbed O_2 in SbO_3-O_2 species. (**c**) CO attacking the remained O atom in SbO_3-O_2 species on defect-free TiO_2(110) substrate.

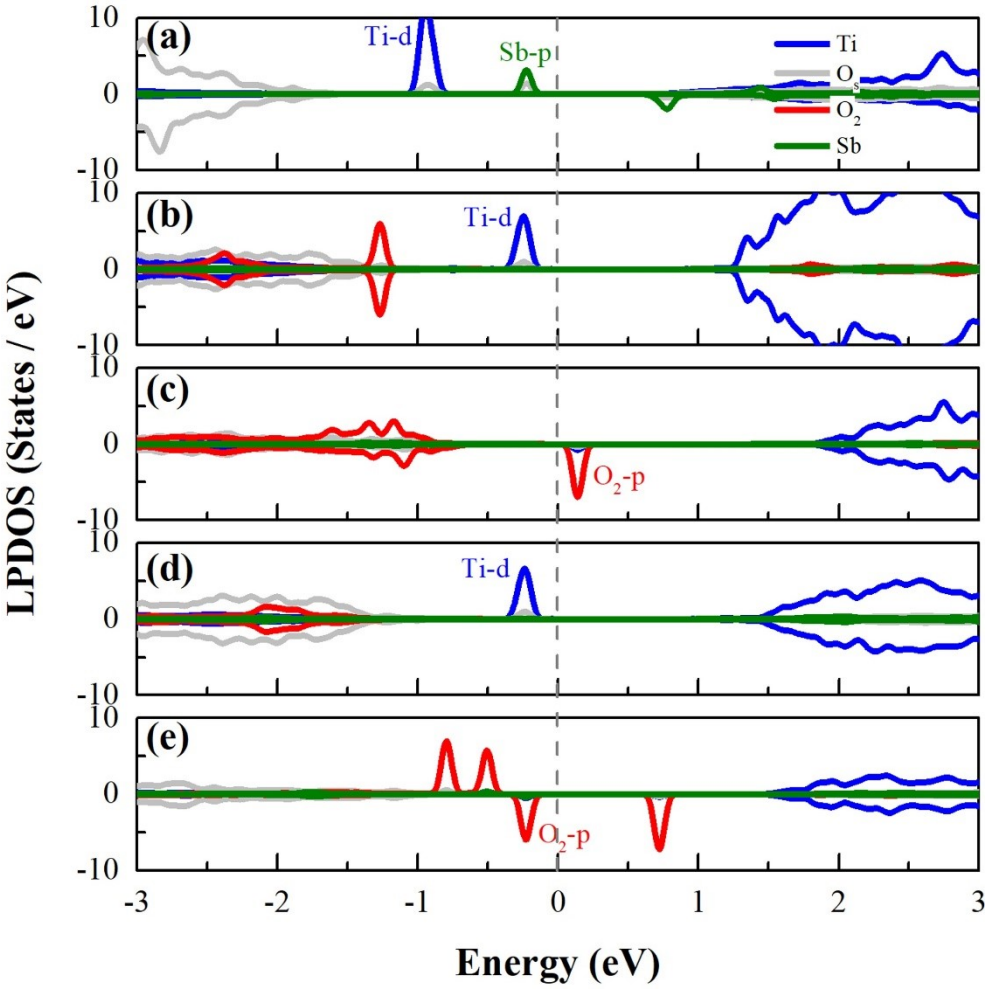

Figure S5. Local projected electronic density of states (LPDOS) analysis. (**a**) LPDOS of Sb/TiO_2(110). (**b**) LPDOS of SbO_2 species on TiO_2(110). (**c**) LPDOS of SbO_4 motif on TiO_2(110). (**d**) LPDOS of SbO_3 species on TiO_2(110). (**e**) LPDOS of SbO_3-O_2 species on TiO_2(110).

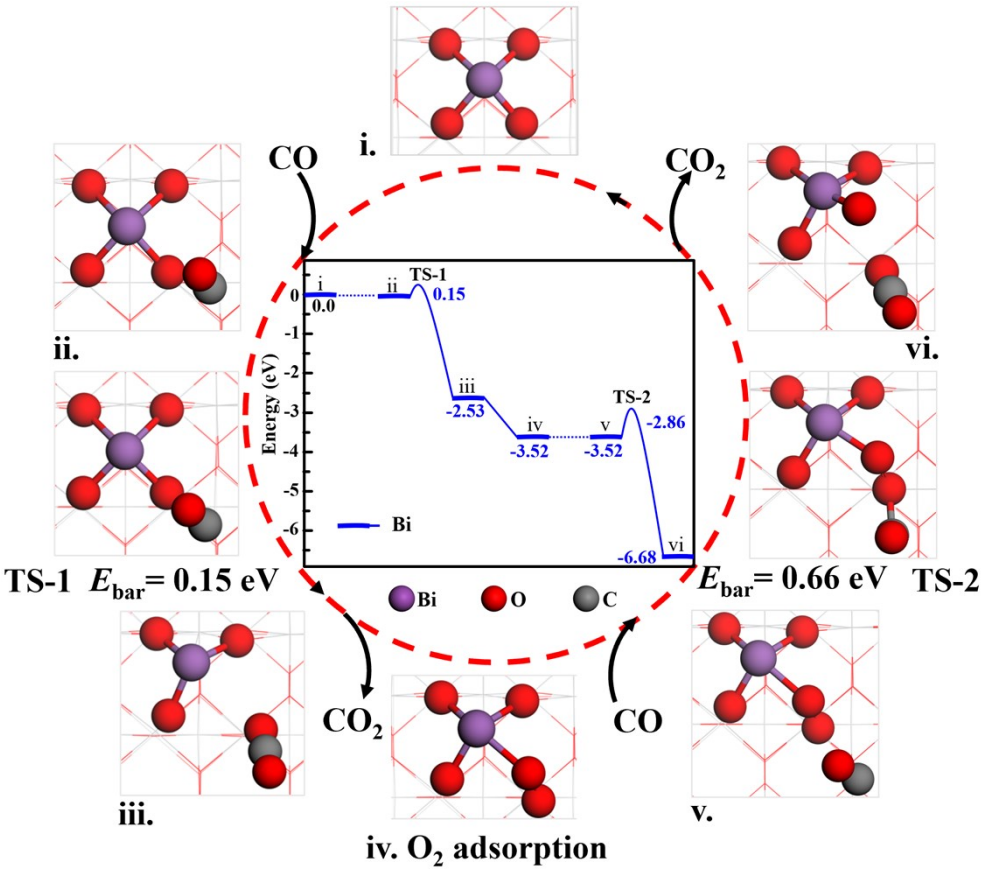

Figure S6. MEP for CO oxidation on the BiO_4 *p*-SACs stabilized on the defect-free TiO_2(110) substrate.

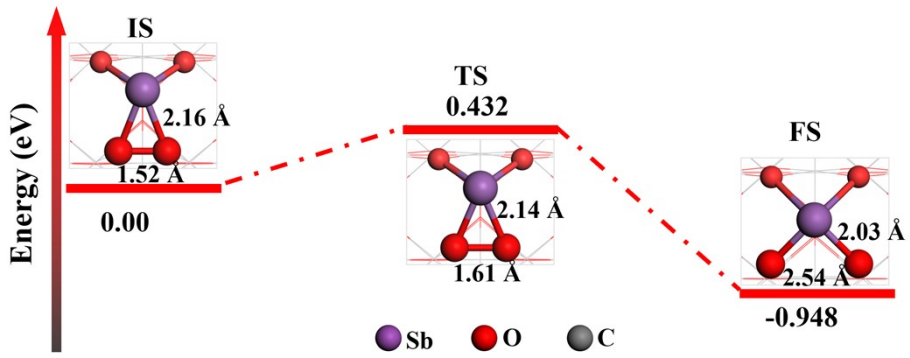

Figure S7. Schematic view of the MEP of O_2 dissociated of SbO_2 species on defect-free TiO_2(110) surface.

Here, the bond length change of O-O and Sb-O during the O_2 dissociation are displayed. Additionally, the optimized coordinates of the structures of O_2 dissociation on the Sb/TiO_2(110) complex.

The optimized coordinates of IS state are as below:

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The optimized coordinates of TS state are as below:

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         0.0000000000         13.1861276627          0.0000000000
         0.0000000000          0.0000000000         27.4730949402
   Ti     O    Sb
   64   130     1
Direct
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The optimized coordinates of FS state are as below:

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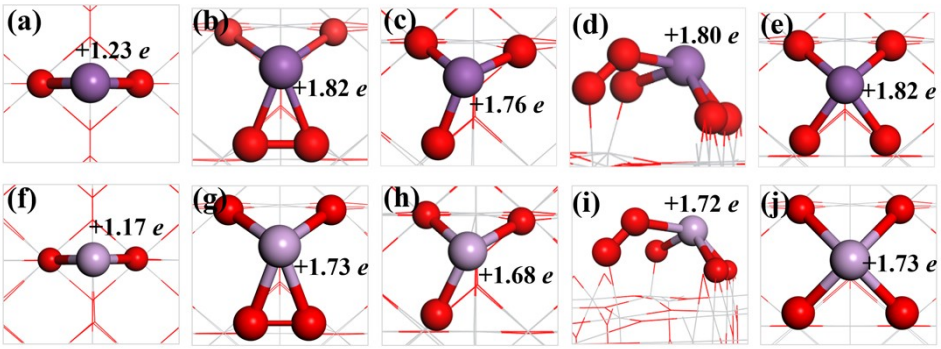

Figure S8. The oxidation state of Sb reactive site in (a) Sb_1, (b) SbO_2 motif, (c) SbO_3, (d) SbO_3-O_2, and SbO_4 species on TiO_2(110). (f)-(g) show the oxidation states of Bi reactive site in Bi_1, BiO_2, BiO_3, BiO_3-O_2, and BiO_4 species on TiO_2(110), respectively.

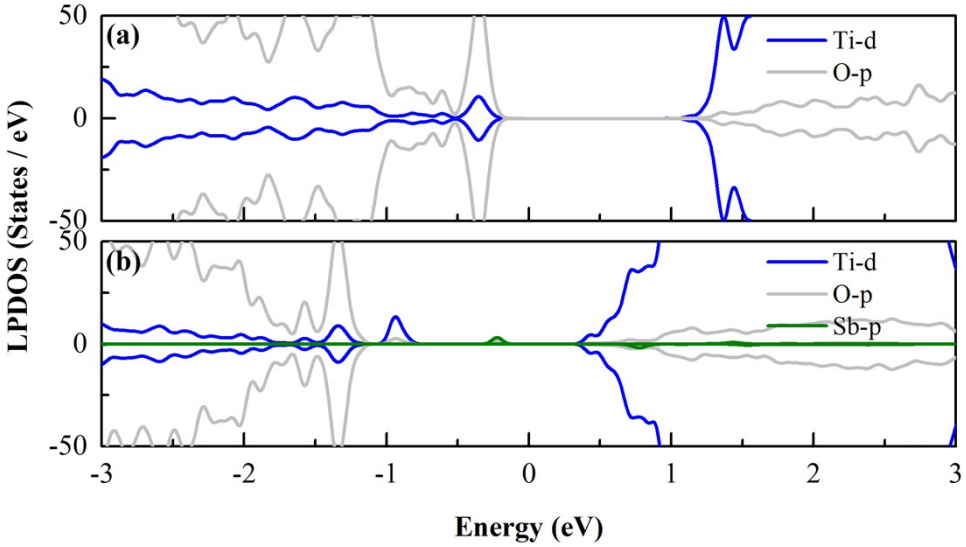

Figure S9. Local projected electronic density of states (LPDOS) analysis on (**a**) TiO_2(110). (**b**) Sb_1/TiO_2(110).

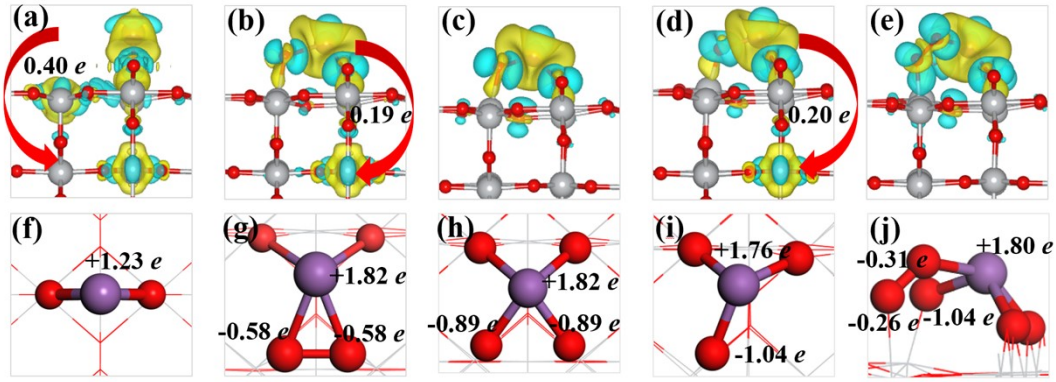

Fig. S10. Analysis of charge transfer between the SbOx system and TiO_2 (a)-(e) Side view of differential charge density of $Sb_1/TiO_2(110)$, SbO_2 motifs, SbO_4, SbO_3, and SbO_3-O_2 species on $TiO_2(110)$, respectively, with an isosurface value of 3×10^{-3} e/Å^3. Yellow and blue bubbles represent charge accumulation and depletion, respectively. (f)-(g) The oxidation state analysis including Sb reactive site and adsorbed O_2 in Sb_1, SbO_2 motif, SbO_4, SbO_3, and SbO_3-O_2 species on $TiO_2(110)$, respectively.

First, we note that, in $Sb_1/TiO_2(110)$ complex (see Fig. S10(a) and (f)), the Sb single atom donate about 1.23 |e| to the substrate, with about 0.4 |e| is accommodated by the nearby subsurface Ti (Ti_{sub}) atoms, as schematically donated by the arrow. As a consequence, there emerges a spin-polarized *d*-orbital state at about 0.95 eV below the Fermi level, see Fig. S5(a). In the optimized $SbO_2/TiO_2(110)$ complex (see Fig. S10(b) and (g)), the aforementioned Ti_{sub} atom donates about 0.21 |e| back to the adsorbed O_2 molecule, i.e., leaving 0.19 |e| maintained on the Ti_{sub}, as reflected by the significantly reduced spin-polarized LPDOS at around 0.24 eV below the Fermi level, see Fig. S5(b). For the case of SbO_4 shown in Fig. S10 (c) and (h), the two O atoms dissociated from the adsorbed O_2 molecule capture more electrons from the substrate, by about 0.62 |e|, with the Ti_{sub} atom donating the remained 0.19 |e|, correspondingly, there is already no LPDOS observed on the Ti_{sub} within the band gap, see Fig. S5(c).

For the case of SbO_3 species shown in Fig. S10(d) and (i), the left O atom is only charged by about 1.04 |e|, that is, relative to the case of SbO_4, about 0.74 |e| is back donated to the substrate, correspondingly, there emerge again a new LPDOS of the Ti_{sub} at around 0.24 eV below Fermi level, see Fig. S5(d).

Moreover, in the case of SbO_3-O_2 species on $TiO_2(110)$ (see Fig. S10 (e) and (j)), relative to the case of SbO_3, about 0.57 |*e*| is further transferred to the adsorbed O_2, mainly by the Ti_{sub}. As a consequence, the LPDOS of the Ti_{sub} within the band gap disappears, see Fig. S5(e).

Table. S1 The parameters of magnetic moments analysis for key steps of O_2 dissociation and CO oxidation on the Sb-*p*-SACs, the corresponding key step structures are also shown in (i)-(vii). The data include magnetic moments projected on different species, i.e., Sb, substrate Ti and O_{sub}, adsorbed O_2, and the CO molecule of the systems during the key cycle steps of O_2 activation and CO oxidation.

	Megnetic moments (μ_B)						
Steps	**i**	**ii**	**iii**	**iv**	**v**	**vi**	**vii**
Sb	0.00	0.00	-0.011	0.004	0.00	0.00	0.023
O_2	0.00	0.19	0.967	0.459	0.00	0.965	0.148
Ti	0.91	0.86	-0.017	-0.061	0.909	-0.017	0.005
C/O	\	\	\	0.147/0.043	\	\	0.515/0.295
O_{sub}	0.09	-0.05	0.061	0.408	0.091	0.048	0.014
Total	1.0	1.0	1.0	1.0	1.0	1.0	1.0