Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

The thermodynamics and electronic structures of P-doped spinel Co_3O_4

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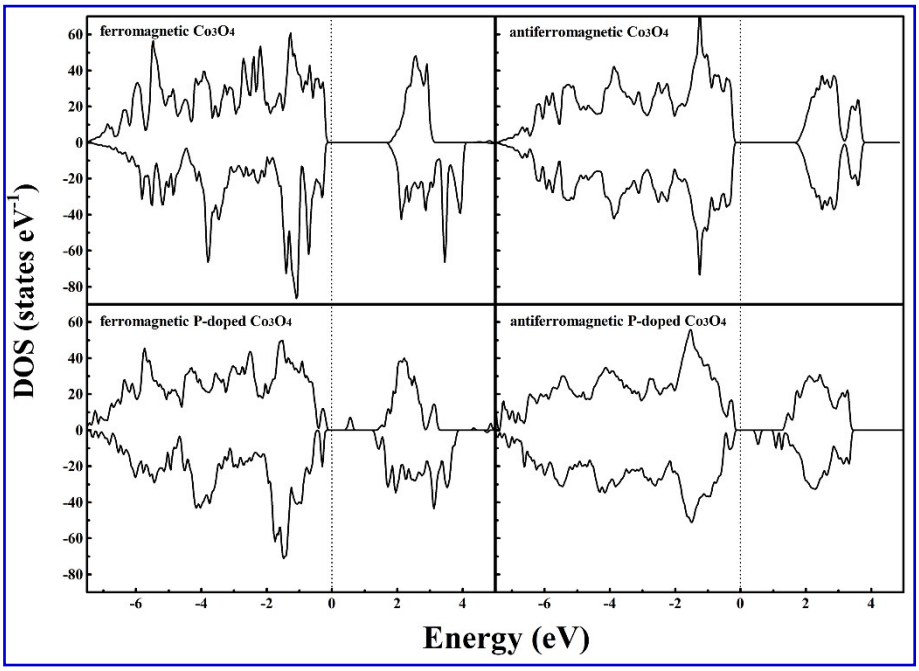

Fig. S1. The DOS of intrinsic and P-doped (O) Co_3O_4 with different magnetic configuration. The Fermi level (E_f) is set to be 0 eV.

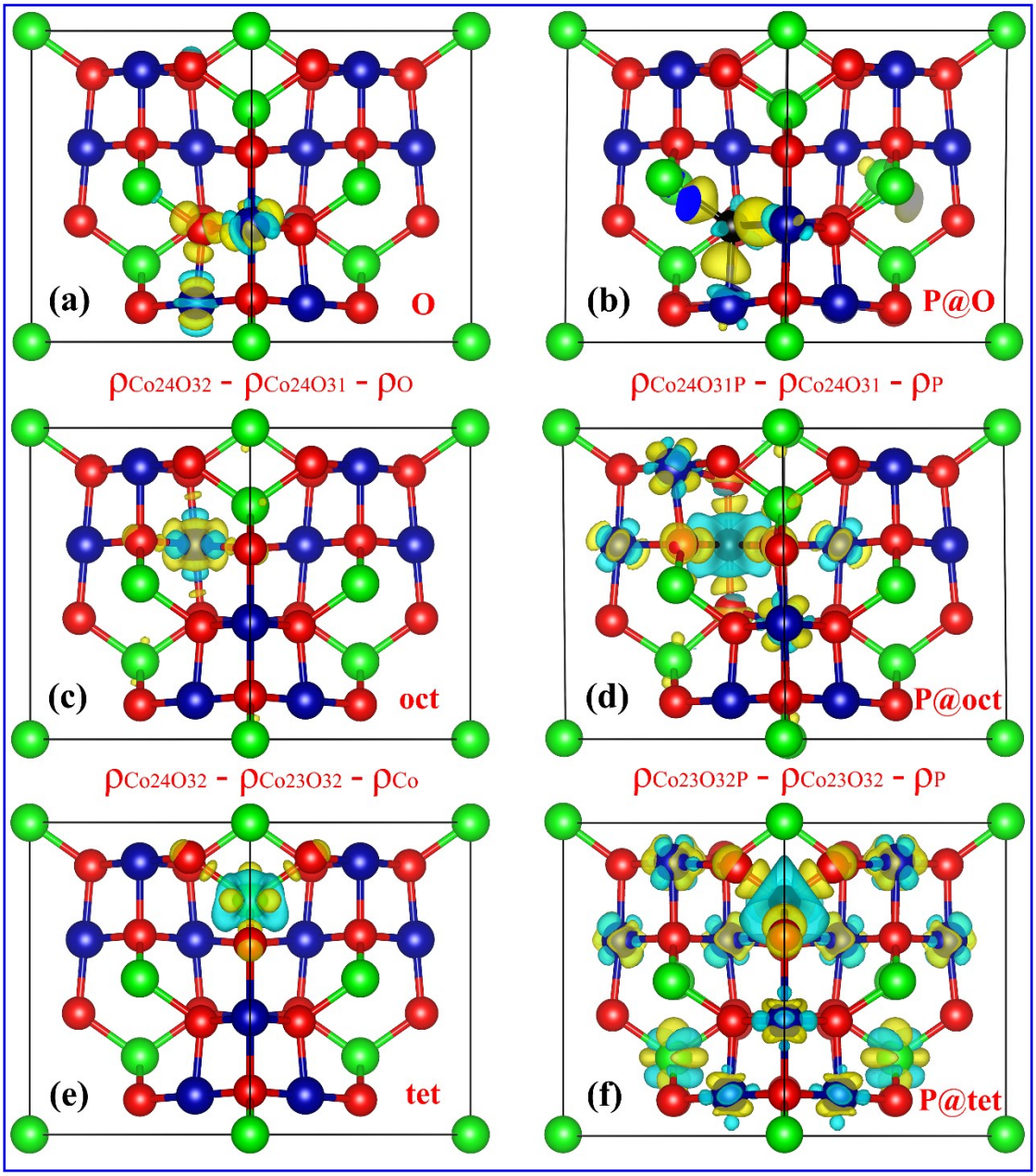

Fig. S2. The calculated charge density difference of intrinsic (a, c, e) and P-doped (b, d, f) Co_3O_4, the yellow and sky-blue represent negative charge and positive charge accumulation, respectively. The isosurface values are set to be 0.015 and 0.01 electron/Å^3 for intrinsic and P-doped Co_3O_4.

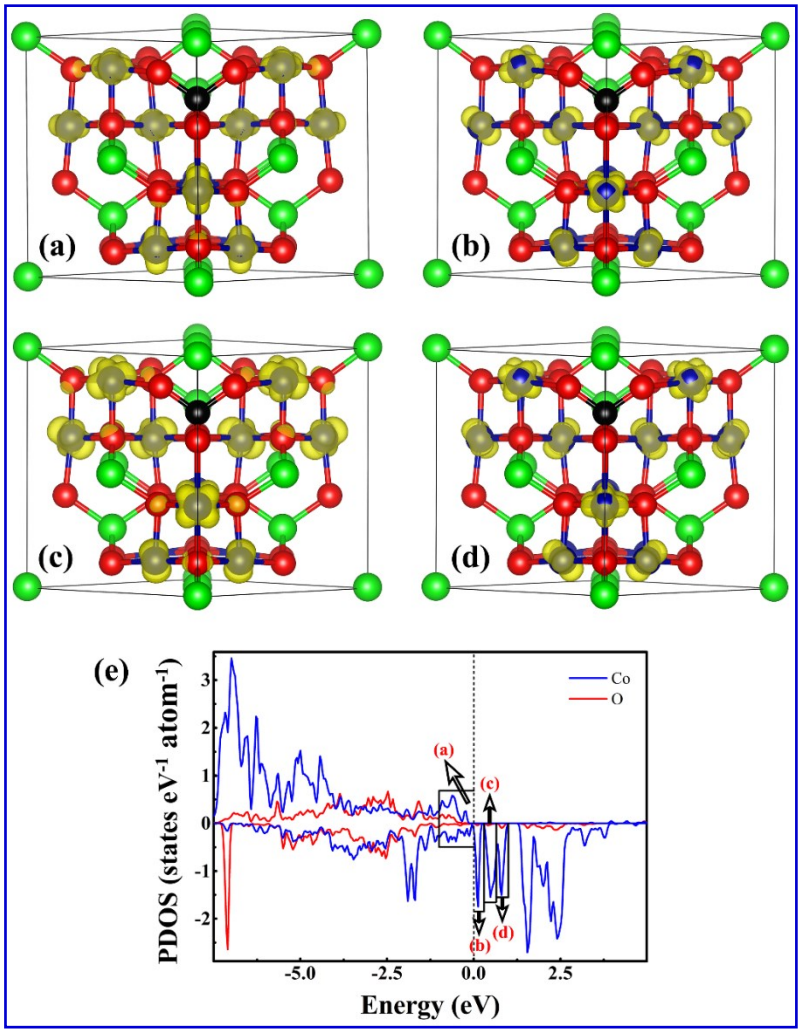

Fig. S3. **(a), (b), (c)** and **(d)** are the decomposed charge density of P doping at Co_{tet} in the energy range of (E_f-1.0 eV, E_f), (E_f, E_f+0.3 eV), (E_f+0.3 eV, E_f+0.7 eV) and (E_f+0.7 eV, E_f+1.0 eV), respectively. **(e)** presents the atomic PDOS of the Co_{oct} and O atoms closest to the doped P atom. The blue, green, red and black spheres denote the octahedral Co, tetrahedral Co, O and P atoms, respectively. The charge density contours are in transparent yellow and the isosurface values are set to be 0.009 electron/$Å^3$.

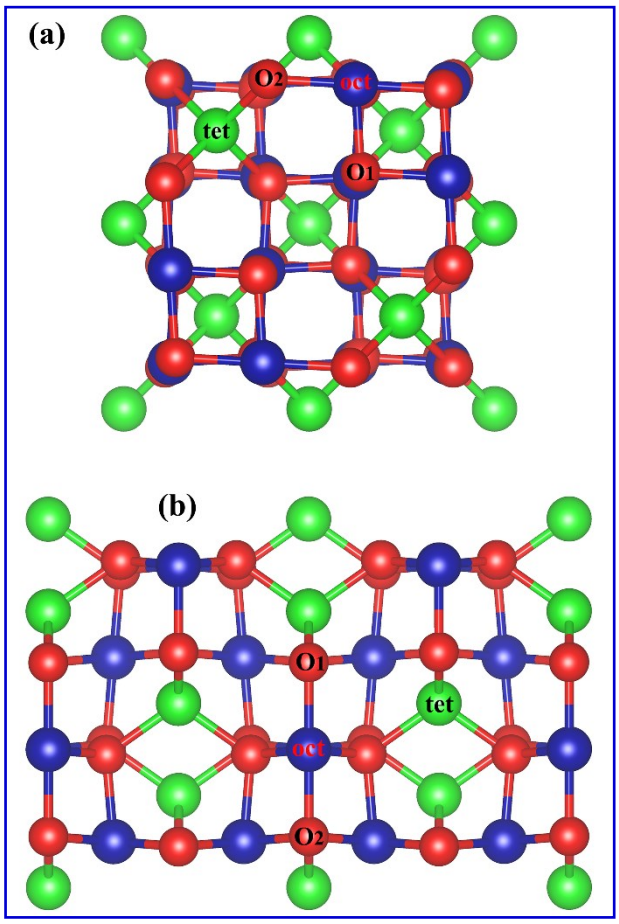

Fig. S4. **(a)** and **(b)** are top views of the atomic structures of the (100)-B and (110)-B slab models, respectively.

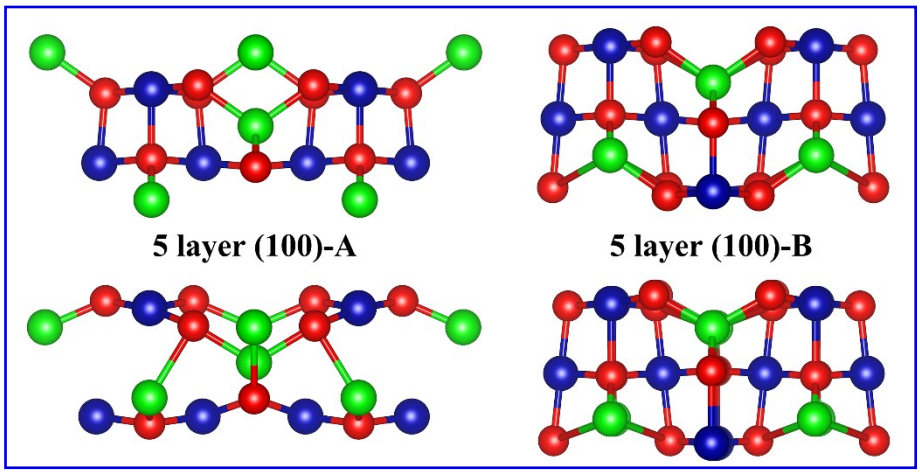

Fig. S5. The side view of the atomic structure of the 5-layer surface models before (up) and after (down) optimization.

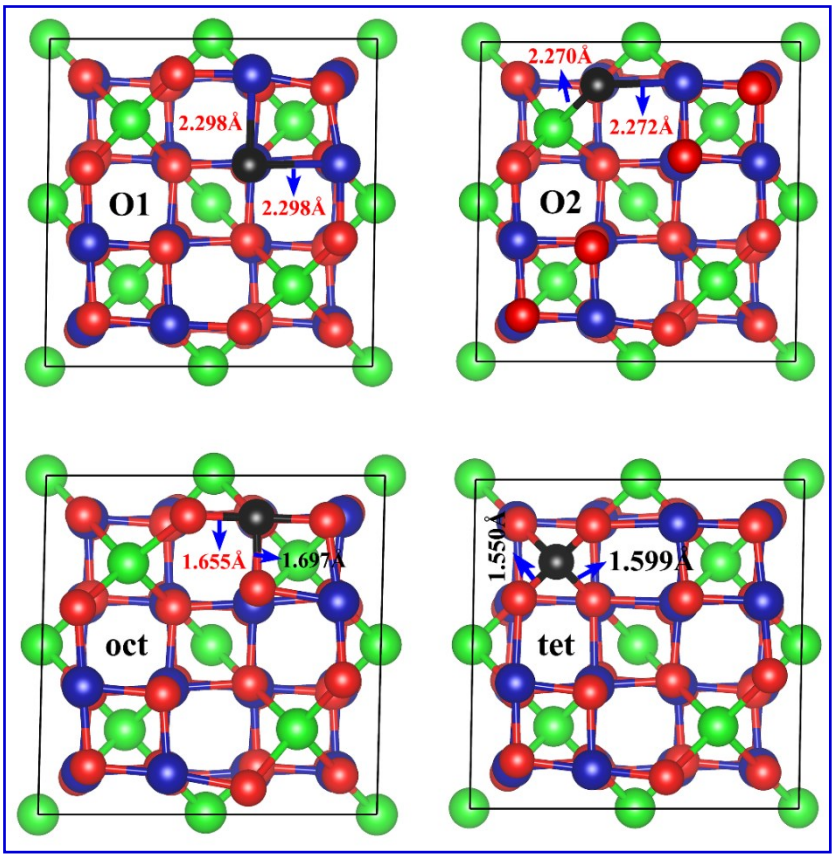

Fig. S6. The top views of the atomic structures of the 9-layer (100)-B slab model after P doping at different sites.

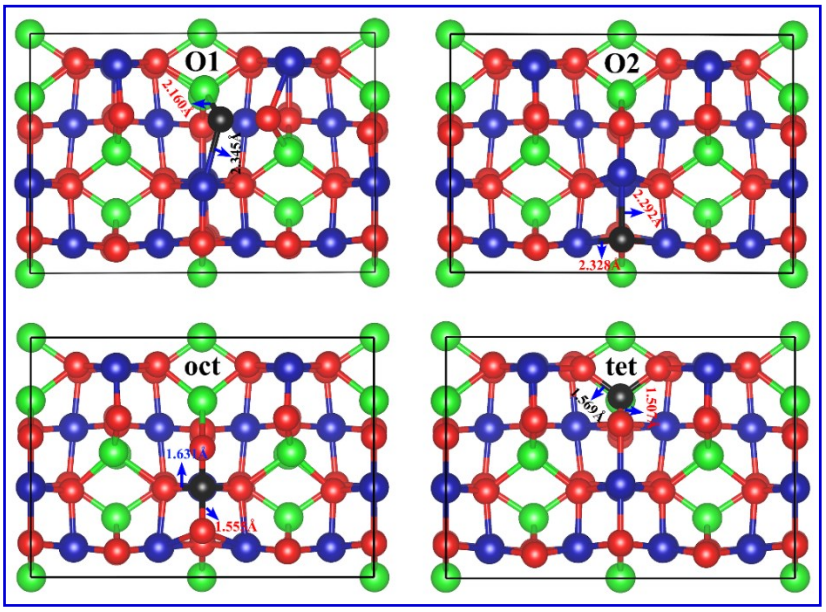

Fig. S7. The top views of the atomic structures of the 7-layer (110)-B slab model after P doping at different sites.

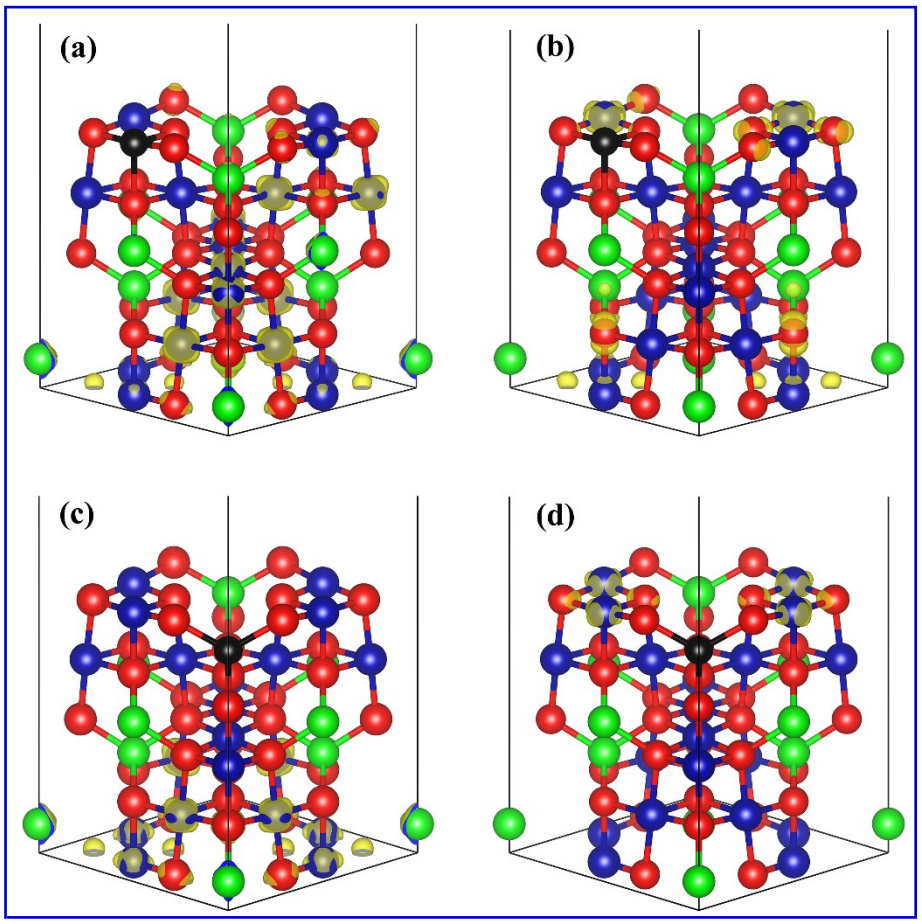

Fig. S8. **(a)** and **(b)** are the decomposed charge density of P doping at 100-B Co_{oct} in the energy range of (E_f-1.0 eV, E_f) and (E_f, E_f+1.0 eV). **(c)** and **(d)** are the decomposed charge density of P doping at 100-B Co_{tet} in the energy range of (E_f-1.0 eV, E_f) and (E_f, E_f+1.0 eV). The blue, green, red and black spheres denote the octahedral Co, tetrahedral Co, O and P atoms, respectively. The charge density contours are in transparent yellow, and the isosurface values are set to be 0.1, 0.01, 0.09 and 0.04 electron/Å^3 for **(a)**, **(b), (c)** and **(d)**, respectively.

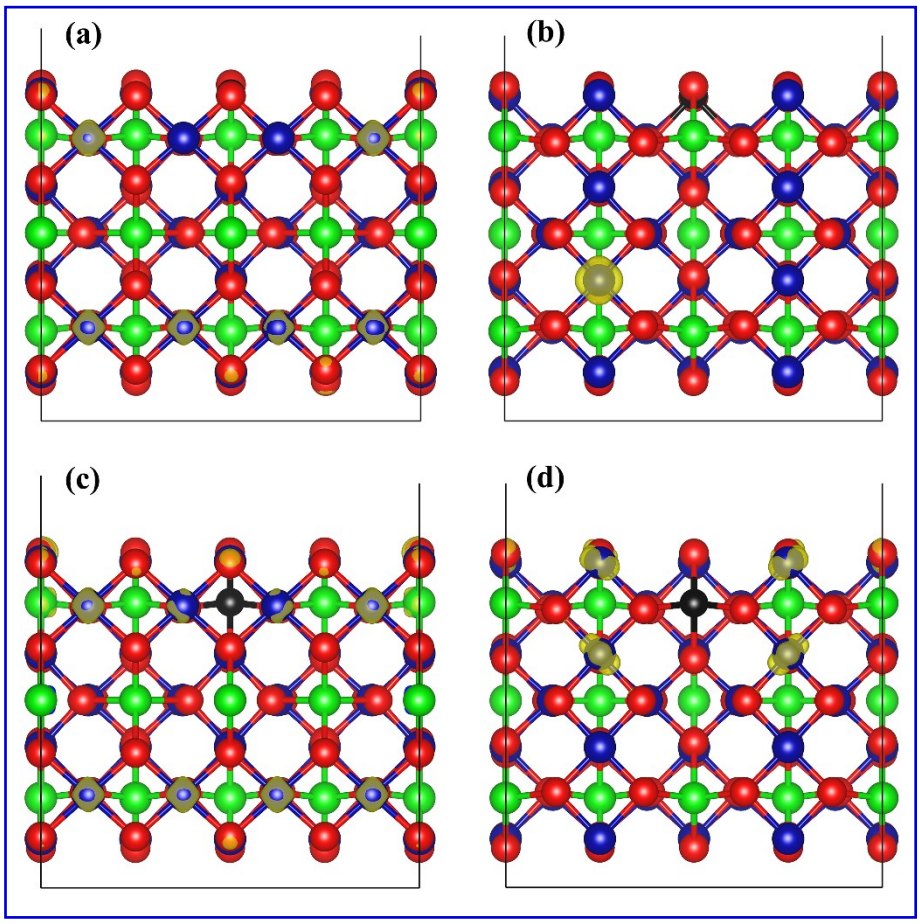

Fig. S9. **(a)** and **(b)** are the decomposed charge density of P doping at 110-B Co_{oct} in the energy range of (E_f-1.0 eV, E_f) and (E_f, E_f+1.0 eV). **(c)** and **(d)** are the decomposed charge density of P doping at 110-B Co_{tet} in the energy range of (E_f-1.0 eV, E_f) and (E_f, E_f+1.0 eV). The blue, green, red and black spheres denote the octahedral Co, tetrahedral Co, O and P atoms, respectively. The charge density contours are in transparent yellow, and the isosurface values are set to be 0.13, 0.05, 0.12 and 0.03 electron/Å^3 for **(a)**, **(b), (c)** and **(d)**, respectively.